



Advanced Technologies in Wastewater Treatment

Pulp and Paper Industry

Edited by

Mohammad Reza Rahimpour

Angelo Basile

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ADVANCED TECHNOLOGIES IN WASTEWATER TREATMENT

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Pulp and Paper Industry

Edited by

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Preface

The paper and pulp industry (PPI) ranks among the world's most influential industrial sectors, significantly impacting the global economy, with an output value of USD 580 billion in 2020. Though water constitutes less than 10% of the final product, it serves as a critical medium throughout the production stages, requiring substantial freshwater input—ranging from 10 to 40 cubic meters per ton of paper, depending on product type and facility age. Consequently, the wastewater generated in this process poses a considerable environmental pollution risk.

PPI has long been recognized as one of the most polluting industries due to its massive wastewater output (from 6 to 200 mL/tonne), including high levels of biological and chemical oxygen demand, colorants, suspended solids, and various additives (e.g., acids, fillers, starches, and alkalis). Communities and ecosystems surrounding these facilities are especially vulnerable to related health risks. The industry's environmental impact is increasingly visible, from soil contamination to declining air and water quality, emphasizing the urgent need for waste management solutions.

Currently, the PPI ranks as the sixth-most polluting global industry and is the third-largest producer of effluents by volume, trailing only the primary metals and chemicals industries. Sustainable management and effective treatment of PPI wastewater can reduce environmental pollution and provide economic benefits, driving green and sustainable industry practices.

This book presents a comprehensive exploration of both established and innovative methods in Pulp and Paper (P&P) wastewater treatment, offering insights into future research directions. It covers physical processes, such as sedimentation and froth flotation, and delves into physiochemical methods like activated carbon filtration and chemical precipitation, along with biological techniques including aerobic and anaerobic treatments. Advanced and emerging techniques, such as ozonation, photocatalysis, advanced oxidation processes (AOPs), electrolysis, and microbial fuel cells (MFCs), are examined in dedicated chapters. Finally, this book discusses the industry's challenges, economic considerations, and future prospects for PPI wastewater management.

This volume serves as a valuable resource for R&D professionals interested in the latest technological advancements in P&P wastewater treatment, as well as academic researchers and postgraduate students in the field.

Below is a summary of the book's chapters:

Chapter 1 examines the characteristics of PPI wastewater, as well as methods for pollutant recovery and reuse. Over the years, numerous strategies for water recirculation and chemical and energy recovery have been developed to reduce effluent volume and pollution.

Chapter 2 addresses the environmental and human health impacts of PPI waste. Ranked among the most energy-intensive industries, PPI generates vast amounts of solid, liquid, and gaseous waste, threatening aquatic habitats, food chains, and public health. This chapter highlights the major pollutants and associated environmental and health risks, advocating for strict adherence to environmental standards and regulatory frameworks.

Chapter 3 examines the release, handling, and treatment challenges of PPI wastewater. Process optimization and wastewater treatment are important for reducing effluent pollution. Key strategies include diversifying feedstock, updating technologies, and recirculating water, with the goal of achieving near-zero discharge. For older facilities and new closed-cycle mills, innovative wastewater treatment technologies are essential.

Chapter 4 explores the influence of operating parameters on wastewater treatment, emphasizing the significance of hybrid treatment technologies. This chapter focuses on recent advancements in P&P wastewater treatment over the past decade and aims to guide future research in this area to produce more comparable and practical results.

Chapter 5 reviews physical methods, particularly membrane-based techniques, for treating P&P wastewater. It highlights how these methods enable water reuse by physically removing impurities through external pressure and semipermeable membranes. While effective, these systems face challenges like membrane fouling due to adsorption and surface polarization.

Chapter 6 provides a detailed overview of physicochemical treatment methods, including coagulation, flocculation, sedimentation, filtration, advanced oxidation, and electrochemical techniques. Hybrid systems that combine physicochemical and biological methods are also discussed.

Chapter 7 examines the use of membrane technology in the PPI, highlighting pressure-driven processes like microfiltration, ultrafiltration, nanofiltration, and reverse osmosis for wastewater

reclamation. It also addresses emerging methods, such as electro-dialysis and membrane distillation, with a focus on expanding applications in this water-intensive sector.

Chapter 8 focuses on biological treatment methods, including microbial technologies involving bacteria, fungi, algae, and enzymes, as well as hybrid approaches that combine biological and physicochemical processes. These sustainable techniques offer significant environmental benefits, though further research is needed to address the current challenges.

Chapter 9 examines the role of photocatalysis in PPI wastewater treatment, highlighting advanced oxidation technologies that offer high efficiency and sustainability.

Chapter 10 discusses the ozonation method, covering recent advances in ozone-based treatment of PPI wastewater. Ozone's unique properties make it valuable for treating both drinking water and industrial effluents, although economic and environmental factors must be considered.

Chapter 11 provides a thorough review of AOPs, including ozonation, hydroxyl radical-based, sulfate radical-based, photochemical, electrochemical, and ultrasonic methods. This chapter highlights recent research and future directions for AOPs to enhance efficiency and sustainability in PPI wastewater treatment.

Chapter 12 describes the application of MFCs in PPI wastewater treatment. MFCs use microbial activity to degrade organic matter, generating electricity while producing minimal sludge, offering an eco-friendly approach to wastewater treatment.

Chapter 13 examines the use of agricultural and bio-based materials, such as biosorbents, biomembranes, and bioflocculants, in PPI wastewater treatment. These sustainable materials present numerous advantages, including improved pollutant removal and reduced environmental impact.

Finally, the editors extend their heartfelt gratitude to the authors for their invaluable contributions to this volume, and to the Elsevier team for their unwavering support and guidance throughout the publication process.

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Introduction to pulp and paper industries

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Pulp and paper industry wastewaters and pollutants: characteristics, recovery, and utilization

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1.1 Introduction

The pulp and paper sector plays a crucial role in the global economy. Global consumption of paper has been estimated at around 417 million tons in 2021 and is expected to reach 476 million tons by 2032. This expected growth may be related to the increase in global investment in pulp and paper machinery, which rose from \$520.88 billion to \$554.93 billion between 2021 and 2022 (Saleem et al., 2023). China concentrated 30% of world production in 2021, emerging as the world's largest paper producer (Dai et al., 2023). In 2022 total paper and board production in Europe reached 32% production, while that of Canada--United States was 25% (UNECE and FAO, 2023).

The pulp and paper industry is the sixth-most polluting industry in the world (Sharma et al., 2022). Approximately 40% of the trees felled for industrial purposes are used to produce paper. The fourth-largest greenhouse gas manufacturing sector in the United States is pulp and paper. Paper accounts for approximately 26% of municipal solid waste in landfills, despite being recyclable, and generates methane as a result of its decomposition or carbon dioxide when burned or composted. The pulp and paper industry is also considered to be one of the five most energy-intensive industries in the world. It consumed 6% of global industrial energy (Kong et al., 2020).

The production of 1 ton of paper requires 5 to 150 m³ of water, and the process generates at least 4 and 125 m³ of effluent (Kumar et al., 2024). Pulp and paper mills are the third-largest producers of effluents in terms of quantity, after the primary metals and chemical industries. The quantity and characteristics of the final pulp and paper effluents depend on the scale of production, the raw materials used, the requirements of the paper and pulp products produced, variations in operating conditions and production rates, design realized in recovery systems, and technology adopted at the wastewater treatment plant (Saleem et al., 2023).

Different chemical species are used during washing, pulping, and bleaching processes, so the waste stream of pulp and paper mills contains a large number of pollutants such as organic compounds, solid particles, and heavy metals (Liu et al., 2024). These toxic chemical contaminants can cause cancer, diabetes, hyperactivity, reproductive failures, allergies, immune system conditions, and respiratory distress due to irritation of mucous membranes (Singh et al., 2022).

This chapter presents the main pulp and paper production processes with attention to wastewater production to analyze their characterization. The aim is to understand wastewater recovery systems and their use.

1.2 Main processes for paper manufacture

Processes in paper manufacturing can be divided into three main stages: pulp making, pulp processing, and paper production (Heminway, 1995). Pulp can be produced from virgin fiber and/or by repulping recovered paper. Virgin fiber can be obtained from the vegetative tissues of vascular plants. Wood contains about 50% water, and the solid fraction is typically composed of about 45% cellulose, 25% hemicelluloses, 25% lignin, and 5% other materials (Murray, 1992). Logs are cut to a manageable size and then debarked. Bark removal methods are mechanical or hydraulic. The wet debarking process uses large volumes of water. Depending on the moisture content of the bark, it must dry before burning, or it can burn directly to produce energy (European Commission, 2001; Smook, 1992).

Debarked logs are reduced to uniform-sized distribution of chips by chipping machines. Screened chips are digested into their fibrous components through chemical, mechanical, or a combination of chemical and mechanical means (Shah, 2020). In mechanical pulping, fibers are separated by mechanical shear forces without removing lignin, while in chemical pulping, lignin is dissolved from wood using chemicals (Harrison et al., 2023). Chemical pulping usually involves cooking wood chips in aqueous chemical solutions

at high temperatures and pressures. There are two main types of chemical pulping currently used: (1) kraft pulping and (2) sulfite pulping (Heminway, 1995).

The pulp, composed of separated and purified fibers, can be bleached to improve brightness and processed into a form suitable for papermaking equipment. At the paper manufacturing stage the pulp can be combined with different additives and then dehydrated into a wire conveyor. After pressing the sheet enters a steam drying section in a multistage drying machine, where paper fibers begin to bond together as steam-heated rollers compress the sheets (Bajpai, 2016; Smook, 1992).

1.2.1 Mechanical pulping

In mechanical pulping, mechanical energy is applied to the wood matrix, causing the bonds between the fibers to break. In this way the wood fibers are separated from each other and are released. Unlike chemical pulping, in this technique, it is desirable to preserve part of the lignin because it improves the yield with acceptable strength properties and brightness (Bajpai, 2016).

Mechanical pulping has higher yield (between 94% and 97%) and requires less energy and chemicals than chemical pulping (Harrison et al., 2023). Additionally, it generates heat during the grinding process, which can be used to produce steam or electricity for the mill. However, the pulp obtained by mechanical processes has lower brightness and strength than chemical pulping, and it is prone to yellowing and deterioration over time due to the oxidation of lignin by light and air (Heminway, 1995).

Any mechanical pulping process involves a wood storage site with wastewater collection system, rotating stone grinders, a screening and cleaning installation, a thickening stage with disc filters or thickening drums, and storage towers or tanks. The initial defibration takes place in the grinders, where wood is warmed, and the presence of enough water softens lignin bonds and releases fibers (Smook, 1992).

There are three main types of mechanical pulping processes (Sixta, 2006). Groundwood (GW) process produces a pulp with low strength and brightness, but it has high yield. To improve the pulp quality, process modifications to the traditional procedures have been applied. In thermomechanical (TMP) processes, heat and steam are used to soften the wood before grinding it. As a result, TMP pulp has higher brightness and strength than in GW process. The last technique is the chemi-thermomechanical (CTMP) process, which combines mechanical and chemical treatments. Sodium sulfite is used to partially dissolve the lignin before grinding wood chips. The pulp obtained has the highest strength and brightness among all mechanical pulps.

1.2.2 Chemical pulping: the kraft process

The most usual form of chemical pulping is kraft pulping, which comprises 80% of the total chemical pulping industry. It is also called sulfate pulping because sodium sulfate is added as a makeup chemical to compensate for chemical losses (Smook, 1992). The kraft pulp has a low yield (about 45%–50%) but high strength and brightness.

The kraft process uses a 10% solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), called white liquor, as active cooking chemicals. The white liquor is mixed with the wood chips in a reactor vessel or digester at 155°C–175°C, and lignin is dissolved from cellulose and hemicellulose fibers. As a result of the high content of hydroxide the pH value at the start of a cook is between 13 and 14. Hydroxide (OH^-) and hydrosulfide (HS^-) anions are formed and crack the aromatic ether bonds within the lignin structure and release thioglignin oligomers (Shah, 2020). Digester systems may be batch or continuous systems. Most kraft pulping is done in batch digesters, although recently, continuous digesters are being installed more commonly (Cheremisinoff, 2009).

The output of cooking consists of a pulp containing wood fibers and black liquor, a liquid that contains the dissolved lignin solids in a solution of reacted and unreacted pulping chemicals. The black liquor is removed from the pulp in a washing stage, commonly rotary vacuum washers, rotary pressure washers, and horizontal belt filters. The pulp is screened with pressure screens or centricleaners, and it may also be thickened by removing a portion of the water (Sixta, 2006; Sjöström & Alén, 1999).

Delignification can be further continued by oxygen in one or two stages in alkaline conditions after cooking. Magnesium sulfate is added to preserve the strength of the pulp. The organic material dissolved during these stages can be recovered by the chemical recovery system (European Commission, 2001).

1.2.3 Chemical pulping: sulfite process and other techniques

The sulfite process is based on the use of acid solutions of sulfurous acid and bisulfite ions to extract lignin. A bisulfite of sodium, magnesium, calcium, or ammonium is used to buffer the cooking solution (Cheremisinoff, 2009). The predominant furnish employed is softwood of only nonresinous species (Heminway, 1995). A sulfite pulp mill usually includes the production unit's wood room, digester house, washroom, screening room, and bleach plant. The pulp obtained has a higher yield (about 50%–55%) but lower brightness and strength than kraft pulp.

The cooking process occurs under high pressure and high temperature in either continuous or batch digesters. This is associated with the high flexibility of the process because a series of batch pressure vessels can be operated according to different cooking programs. After the cooking process the pulp is washed and screened, and so the spent liquor or weak liquor is obtained. This can be discarded, incinerated, or sent to an energy and chemicals recovery plant (Shah, 2020; Sixta, 2006).

Another alternative chemical process, one of the first ones, is the soda process, which employs only sodium hydroxide as the primary cooking agent. The soda process has limited use for easily pulped materials like straws and some hardwoods. The pulp has a low yield (about 35%–40%) and low strength and brightness, but it is easy to bleach and can be used for specialty papers (Smook, 1992).

The last pulping process described is the most common type of semichemical pulp: the neutral-sulfite semichemical pulp. The process combination has a high yield, and the furnish can be used without debarking (Bajpai, 2016). Wood chips are cooked in a neutral solution of sodium sulfite and sodium carbonate (Cheremisinoff, 2009). Sulfite ions react with lignin, and sodium bicarbonate acts as a buffer, in such a way that only a portion of the lignin is removed during the cook. The spent liquor can be recovered involving similar steps to the sulfite process (Bajpai, 2008). The pulping process is completed by mechanical disintegration.

1.2.4 Bleaching stages

Bleaching is defined as any process that chemically alters pulp to increase its brightness (Heminway, 1995). The objective of bleaching is to obtain the required pulp quality with respect to brightness, brightness stability, cleanness, and strength.

To achieve the desired brightness in chemical pulp, lignin and some carbohydrates are structurally modified, oxidized, degraded, or chlorinated. For these purposes, chemicals such as chlorine dioxide, sodium hydroxide, elemental chlorine, oxygen, ozone, and peroxide are widely used. Due to its high chlorine content, bleach plants tend to discharge effluent to external treatment. Metal ions must be removed by using metal chelating agents like EDTA or diethylenetriaminepentaacetic acid, or acid washing (European Commission, 2001). In recent years, some mills have completely eliminated the use of bleaching chemicals containing chlorine by combining oxygen delignification with an ozone stage and/or a peroxide stage (Sousa et al., 2023).

Traditional bleach plants consist of three to five stages of chemical bleaching and water washing, where different chemicals are added and mixed with the pulp. Bleaching stages generally

alternate between alkaline and acid conditions. Acid stages increase the whiteness of the pulp, and alkaline stages dissolve the lignin at high temperature. Washing stages remove the lignin and reaction products from the pulp (Sixta, 2006; Smook, 1992).

Mechanical pulps are bleached differently than chemical pulps due to its high lignin content. Bleaching of mechanical pulps consists of changing the chromophoric groups of lignin polymers into a colorless form. Alkaline hydrogen peroxide is the most commonly used bleaching agent for mechanical pulp, and the temperature is lower than in chemical pulp bleaching. Another reagent used to bleach mechanical pulps is sodium dithionite (Bajpai, 2016; Cheremisinoff, 2009).

1.2.5 Recovered paper processing

The most common furnishings are wood and secondary fibers. Secondary fibers are constituted by preconsumer fibers (e.g., mill waste fibers) and postconsumer fibers (sources are diverse, e.g., newsprint and corrugated boxes). They must be processed to remove ink and impurities and defiber, depending on the destination of the products. Generally, recovered paper processing can be split into two main categories: processes with exclusively mechanical cleaning and processes with mechanical cleaning and deinking comprising products (Sixta, 2006). In both cases, recovered paper is treated with hot water and pulped with agitation to disintegrate into fibers. The mechanical cleaning operations are based on the differences in physical properties between fibers and impurities, such as density, size, and weight particles. Ink removal implies a chemical pretreatment in flotation cells when the brightness paper is important. The other stages of the process—washing, bleaching, and paper processing—are conducted as described before (Han et al., 2021).

1.3 Main waste streams in the papermaking industry

Pulp and paper industry wastewater is constituted by different organic and inorganic compounds which are generated during the stages previously described. The volume of wastewater load discharged from the mill is closely linked with the volume of water used (Rizwan et al., 2022). The water consumption varies considerably between different mills in a range of 15 to 100 m³/ton (European Commission, 2001). These values can be reduced by increasing internal water recirculation and reuse in the mill, as discussed in Sections 1.4 and 1.5.

Bleaching is the most crucial point of discharge of pollutants to water in a pulp mill due to the large volume and the presence of chlorinated compounds. Pulping stage wastewaters are also relevant because of the high content of oxygen-consuming organic substances. Other stages where effluents are generated are the wood handling, screening, dewatering, and chemical recovery (Lacorte et al., 2003). Table 1.1 summarizes the characteristics of each waste stream.

Pollutants present in wastewaters are mainly oxygen-consuming organic compounds, which are measured as chemical oxygen demand (COD) and biochemical oxygen demand (BOD). The wastewater contains a variety of toxic organic compounds which affect the properties of an aquatic ecosystem (Karrasch et al., 2006). Emissions of colored substances decrease the water transparency and affect the life of aquatic species, and emissions of nutrients such as nitrogen and phosphorus have a negative impact due to eutrophication (Harrison et al., 2023). Additionally, various constituents of pulp paper mill wastewater may accumulate in the fish and affect its reproductive organs (Haq et al., 2017).

The effluent generated during the papermaking processes is a complex mixture of hundreds of organic compounds. Lignin, tannins, terpenes, waxes, resin acids, fatty acids, alcohols, and phytosterols are present with a high content of suspended solids. These organic substances are degraded and form new compounds such as surfactants, phenols, furans, dioxins, and others (Chandra & Abhishek, 2011; Chandra & Singh, 2012; Shah, 2020). Chlorinated compounds are also present, and they are degraded to adsorbable organic halides (AOXs) like chlorinated resin acids, chlorinated hydrocarbons, and chlorophenol, which are well-known toxic chemical compounds. Thus effluents discharged from papermaking processes are heavily loaded with organic matter containing 200 organics and 700 kinds of inorganic compounds (Ali & Sreekrishnan, 2001; Savant et al., 2006).

Individual metals were also detected in pulp and paper production wastewater. They are extracted from the wood and may be present in the effluents at low concentration. It has been reported the presence of lead, iron, chromium, copper, cadmium, and zinc (Rizwan et al., 2022; Singh et al., 2022).

1.3.1 Wastewater from debarking and wood handling

The raw material preparation generates a low volume of effluent because it involves mainly mechanical processes. The water is used in wood handling, debarking, and chip washing (Singh et al., 2022).

Table 1.1 Major sources of wastewater in a pulp and paper mill and their main characteristics.

Stage of papermaking	Source of generation	Pollution intensity	Effluent characteristics
Wood handling	Raw material washing and debarking	Small volume and minimal pollution	Solids, BOD, and color
Pulping	Washing of pulp	Pollutants are highly concentrated	High BOD, COD, TSS, and heat
Screening	Pressure screens or centricleaners	Large volume with high concentration	High suspended solids (fibers, grit, and sand)
Bleaching	Washing and cleaning of pulp	Large volume and toxic, mutagenic, and carcinogenic characteristics	High BOD, COD, TSS, and pH with poisonous chloro-organic chemicals
Paper machine	Filtrates and dewatering	Variable volume and low toxicity	High TSS and low BOD and COD
Chemical recovery	Condensates from evaporators	Variable volume	Low BOD, COD, and color

Notes: Compilation based on data from [Ince et al. \(2011\)](#), [Heminway \(1995\)](#), [Singh et al. \(2022\)](#), and [Lacorte et al. \(2003\)](#). *BOD*, Biochemical oxygen demand; *COD*, chemical oxygen demand; *TSS*, total suspended solids.

These stages of paper mills produce muddy wastewater, whose dark color is caused by the excessive amount of tannins (Salmi, 2020). The debarking occurs because of the friction created from the rotating drum action (Bajpai, 2018). In wet drum barkers the drum is divided into two zones: the early solid steel portion, where water is added, and the remaining portion, which has slots to allow the removed bark to fall out. In the other case, dry debarking, the entire drum length has slots so the bark can be fired directly to obtain energy, and the water can be recycled (Sixta, 2006).

Table 1.2 presents data collected on effluent production. The major source of wastewater is the washing and screening of chips, whereas the effluent, which contains higher pollution loads, is produced in the debarking. It can be observed that BOD, COD, and phosphorus loads are more than two times lower in dry debarking compared to wet debarking.

1.3.2 Kraft black liquor waste streams

Water consumption in kraft pulping is estimated in a range of 40 to 60 m³/ADt of pulp (dry weight). Kraft black liquor contains varying amounts of organic compounds derived from all wood constituents and inorganic compounds coming from white liquor. Main organic substances are lignin (~30% dry weight) and aliphatic carboxylic acids (~30% dry weight) (Chandra et al., 2011; Pokhrel & Viraraghavan, 2004). High-molecular-weight lignin predominates, and among the carboxylic acids, formic and acetic acids can be highlighted (Sjöström & Alén, 1999).

With respect to inorganic substances, sodium carbonate, sodium sulfide, sodium sulfate, sodium sulfide, and sodium hydroxide are the compounds present in the highest concentration. Small amounts of K, Si, Ca, Fe, Al, Mg, Mn, and P are also present (Sjöström & Alén, 1999). Additionally, low concentrations of cadmium, chromium, copper, nickel, and zinc have been detected (Arivoli et al., 2015).

Table 1.3 summarizes the main physicochemical characteristics of black liquor. High pH value, COD, BOD, and total suspended solids (TSS) are highlighted (Rintala & Puhakka, 1994). Also, the low BOD:COD ratio indicates that black liquor has low biodegradability.

After cooking the pulp is washed, and the black liquor is sent to the chemical recovery system. High pulp washing efficiency improves the amount of chemicals recovered and minimizes the consumption of bleaching chemicals (Shah, 2020; Sousa et al., 2023). An important mill control parameter is the kappa number, which quantifies the delignification degree of the pulp. The lower the kappa number, the lower the lignin content of the pulp and the utilization of bleaching chemicals (Cabrera, 2017). Pulp cooking and

Table 1.2 Wastewater streams are produced in the debarking, washing, and screening stages, with their main physical–chemical characteristics.

Stage of raw material preparation	Volume (m ³ /t wood)	pH	Total solids (kg/t wood)	BOD (kg/t wood)	COD (kg/t wood)	P (g/t wood)	N (kg/t wood)
Wet debarking and pressing	0.75–2.5	4.7–6.2	1.0–1.6	1.13–3.25	5.0–7.5	6.25–8.75	0.4
Dry debarking and pressing	0.125–0.625	~5	–	0.13–0.50	0.25–2.5	2.5–5.0	0.3
Chip washing and screening	8–24	6.4–8.0	0.67–1.12	0.04–0.06	0.22–0.56	0.4–1.8	0.03

Notes: Compilation based on data from [Cabrera \(2017\)](#), [Leiviskä et al. \(2012\)](#), and [European Commission \(2001\)](#). *BOD*, Biochemical oxygen demand; *COD*, chemical oxygen demand.

Table 1.3 Main physicochemical characteristics of kraft black liquor.

Variable	Value
pH	8.6–9.0
Total solids (kg/m ³)	2–6
Dissolved solids (g/m ³)	350–450
BOD (kg/m ³)	4.9–5.3
COD (kg/m ³)	11.8–12.7
Lignin (mg/L)	650–670
Sulfates (mg/L)	1700–1800
Phenols (mg/L)	30–50

Notes: Compilation based on data from [Shah \(2020\)](#), [Sjöström and Alén \(1999\)](#), [Chandra et al. \(2011\)](#), [Pokhrel and Viraraghavan \(2004\)](#), and [Rintala and Puhakka \(1994\)](#). *BOD*, Biochemical oxygen demand; *COD*, chemical oxygen demand.

pulp washing are key points to decrease the kappa number. Whereas black liquor is sent to the chemical recovery system, as discussed in [Section 1.4](#), the recovery of bleaching effluents is more difficult. In conclusion the higher the kappa number of the pulp, the higher the wastewater production of the mill.

1.3.3 Sulfite pulping process and other techniques waste streams

Typical sulfite spent liquors differ from kraft black liquor in many aspects. Water consumption in sulfite pulping is estimated in a range of 40 to 100 m³/ADt of pulp (dry weight). When calcium bisulfite is used to buffer the cooking solution, the water consumption is higher than when magnesium bisulfite is used ([Rintala & Puhakka, 1994](#)).

Organic compounds present in spent sulfite liquor can be classified into lignosulfonates, carbohydrates, aldonic acids, acetic acid, extractives, and others. High-molecular-weight lignosulfonates form the main organic fraction of these liquors, and they produce sulfonated lignin-derived monomers and dimers as degradation products ([Luthe, 1990](#)). Carbohydrates are mainly monosaccharides such as mannose, xylose, galactose, and glucose, which are formed by polysaccharide degradation as well as aldonic and acetic acids ([Sjostrom, 1993](#)). Among the extractives, p-cymene is highlighted, though other fatty acids, fatty alcohols, and sterols have been detected ([Pearl & McCoy, 1961](#)).

With respect to inorganic compounds the active species in the sulfite process are sulfur dioxide, hydrogen sulfite, and sulfite, and sodium is the predominant cation (Al-Rudainy et al., 2017). Thiosulfates and polythionates are harmful components generated during sulfite pulping (Sjostrom et al., 1963).

Table 1.4 summarizes the main physicochemical characteristics of spent sulfite liquor. A wide range of pH values and very high oxygen-consuming organic compounds content are highlighted.

On the contrary, at the end of the soda pulping stage, a dark brown wastewater stream is generated. It has lignin and its degradation products, resins, hemicelluloses, phenols, and acids (Hermosilla et al., 2015). High COD, BOD, and TSS may be highlighted (Pokhrel & Viraraghavan, 2004).

1.3.4 Mechanical pulping process waste streams

Mechanical pulping processes are characterized by their high yield linked to the stability of cellulose and lignin. On the contrary, different compounds (e.g., proteins, resin and fatty acids, hemicelluloses, and inorganic substances) are dispersed or dissolved in the process water. In Table 1.5, it can be observed that the TMP pulping process involves greater effluent volume than the others, due to the steam used for impregnation and preheating of the wood chips (Mboowa, 2021).

The addition of sodium sulfite in CTMP increases the extraction capacity of the process due to the liquor penetration (Bajpai, 2018). Therefore this pulping process produces effluents with high BOD, COD, suspended solids, and amounts of phosphorus and nitrogen (Murray, 1992). The GW process preserves more of the lignin, which is reflected in the low BOD of the wastewater.

Table 1.4 Main physicochemical characteristics of spent sulfite liquor.

Variable	Value
pH	2–7
COD (kg/m ³)	> 100
TSS (g/m ³)	150–500
Dry solids (g/m ³)	120–220
Lignin (mg/L)	50–400
Carbohydrates (g/L)	270–500
Phenols (g/L)	1.5–5.1
Acetic acid (g/L)	1–11

Notes: Compilation based on data from Guo and Olsson (2014), He and Chen (2020), Pereira et al. (2013), and Sjostrom (1993). COD, Chemical oxygen demand; TSS, total suspended solids.

Table 1.5 Wastewater streams produced in the different pulping processes with their main physical–chemical characteristics.

Pulping process	Volume (m³/ADt pulp)	Suspended solids (kg/ADt pulp)	BOD (kg/ADt pulp)	COD (kg/ADt pulp)	P (kg/ADt pulp)	N (kg/ADt pulp)
Groundwood	10–15	–	8.5–10	15–32	20–25	80–100
Thermomechanical process	10–30	10–40	13–22	40–80	30–40	100–130
Chemi-thermomechanical process	10–15	20–50	17–30	60–120	35–45	110–140

Notes: Compilation based on data from [Cabrera \(2017\)](#), [European Commision \(2001\)](#), and [Rintala and Puhakka \(1994\)](#). *BOD*, Biochemical oxygen demand; *COD*, chemical oxygen demand.

1.3.5 Waste streams from the bleach plant

In a pulp mill the bleach plant is the most important point of discharge of wastewater streams. Their content and quantity depend on a series of considerations: the wood species, the washing losses, the degree of delignification achieved upstream, the bleaching steps chosen and their order (hence bleaching chemicals used), the final brightness of the bleached pulp to be reached, and the degree of closure of the bleach plant (Harrison et al., 2023). Table 1.6 summarizes the ranges of wastewater generation volumes and physicochemical parameters reported in the literature for the three major pulping processes.

Brightening mechanical pulps is realized with reducing agents, for example, dithionite, or oxidants, such as hydrogen peroxide, often in a single-stage process or, in some cases, in a two-stage process (Bajpai, 2018). The alkaline peroxide step significantly increases the organic pollutant content of the waste stream (Caldeira et al., 2021). The pH of the effluent can be acidic due to the presence of resinous acids and fatty acids in the wood extracts, which are dissolved during the bleach process.

Bleaching chemical pulps is accomplished using chlorine-based chemicals. As a result the effluent generated is dark brown in color due to the presence of chromophoric polymeric lignin derivatives (Bajpai, 2013). In addition, it contains a large number of toxic chlorinated organic compounds, including chlorophenols, extractable organic halides (EOXs), AOXs, a small proportion of extremely toxic DDT, furans, polychlorinated biphenyls (PCBs), and polychlorinated dibenzodioxins (Heminway, 1995). Their amount varies with types of wood, kappa number of the pulp, bleaching sequence design, and operation conditions chosen. About 80% of the organically bound chlorine can be considered high-molecular-weight persistent chlorinated lignin material (molecular weight > 1000), which is the major contributor to chronic toxicity (Shah, 2020). The other part corresponds to the relatively low molecular weight material and constitutes a current with potential danger due to its ability to cross cell membranes and its tendency to bioaccumulate.

To reduce the chlorine species production, different alternative processes have been developed. Among them, elemental chlorine-free (ECF) and totally chlorine-free (TCF) processes can be highlighted (Cheremisinoff, 2009; Deshmukh et al., 2009).

1.3.6 Condensates from cooking and evaporation

The vapors from digesters and the evaporation plant generate condensates. A total of 8–10 m³/ADt of total condensates are formed. Generally, about 40% of condensates are low contaminated, 40% are medium, and 20% are heavily polluted. Heavy polluted condensates have a COD concentration of 10–20 kg/m³, whereas weaker

Table 1.6 Wastewater streams produced in pulp bleaching, which come from different pulping processes, with their main physical–chemical characteristics.

Bleach process	Volume (m³/ADt pulp)	pH	Suspended solids (kg/ADt pulp)	BOD (kg/ADt pulp)	COD (kg/ADt pulp)	P (kg/ADt pulp)	N (kg/ADt pulp)	AOX (kg/ADt pulp)
Mechanical pulp	10–80	4–8	10–50	2–10	50–180	–	–	–
Kraft pulp	60–100	2.2–5	10–40	5–40	70–140	0.04–0.09	0.08–0.23	1.2–5
Sulfite pulp	150–180	4–6	20–60	18	120–180	0.1	0.3	1.8–3.6

Notes: Compilation based on data from [Rintala and Puhakka \(1994\)](#), [Bajpai \(2018\)](#), [Pokhrel and Viraraghavan \(2004\)](#), [World Bank \(1980\)](#), [Cabrera \(2017\)](#), [Bajpai \(2013\)](#), [Caldeira et al. \(2021\)](#), [Deshmukh et al. \(2009\)](#), [Ribeiro et al. \(2020\)](#), and [Källqvist et al. \(1989\)](#). *AOX*, Adsorbable organic halide; *BOD*, biochemical oxygen demand; *COD*, chemical oxygen demand.

condensates are formed with COD ranging from 0.5 to 2 kg/m³ (Cabrera, 2017; Dufresne et al., 2001). The COD load in condensates is normally much higher at sulfite pulp mills compared to kraft mills, as stripping is not a normal practice (Heminway, 1995).

Almost 50% of COD is methanol, and another important percentage is explained by ethanol, organic acids, and organic sulfur compounds content. Phenols and terpenes content has also been reported in condensates (Hayes et al., 2022; Silva et al., 2009). Inorganic content is low, mainly due to inorganic sulfur content and ammonia. Organic sulfur compounds include methyl mercaptan, dimethyl sulfide, and diethyl disulfide, while inorganic sulfur compounds include sulfites, sulfates, and hydrogen sulfide. Sodium, calcium, magnesium, and potassium are the main cations present in condensates. Additionally, other metals have also been reported, mainly iron and aluminum (Blackwell et al., 1979; Dufresne et al., 2001).

The evaporator operation variations have generated highly variable compositions observed for the contaminated condensates. Table 1.7 summarizes the main physicochemical characteristics of condensates from pulp and paper production.

1.4 Classical chemical and energy recovery systems

There are mature, widely known, and effective technologies for recovering energy and recycling chemicals from the pulping

Table 1.7 Main physicochemical characteristics of pulp and paper production condensates.

Variable	Value
pH	7–10
COD (kg/m ³)	2–15
BOD (kg/m ³)	1–10
TSS (mg/L)	20–100
Dissolved solids (mg/L)	100–700
Methanol (kg/m ³)	1–10
Total sulfur (mg/L)	70–400
Total Kjeldahl nitrogen (mg/L)	20–90
Acetate (mg/L)	10–80
Phenols (mg/L)	15–45

Notes: Compilation based on data from Hayes et al. (2022), Dufresne et al. (2001), Blackwell et al. (1979), and Silva et al. (2009). *BOD*, Biochemical oxygen demand; *COD*, chemical oxygen demand; *TSS*, total suspended solids.

industry. They include recovery boilers where usable heat is produced and other stages for regenerating the cooking chemicals (Tran, 2020). Kraft pulping mills have high closed processes and high degree of chemical and energy recovery. Sulfite pulping mills have different energy recovery systems and chemical recovery stages for sodium- and magnesium-based processes (Ahmad & Pant, 2018; Bajpai, 2008). Total effluents from sulfite pulp mills are higher than the one from kraft pulp mills due to less closed processes, and magnesium-based mills have difficulty in recycling water from associated stages where sodium hydroxide is used to control the pH. Finally, there are energy recovery technologies for mechanical pulping mills, in which heat may be used for heating water streams or for generating steam (Smook, 1992). The residual bark from debarking and material removed from chip screening can be burned in an additional solid fuel boiler with heat recovery (Tran, 2020).

A large number of pulp and paper mills do not recycle bleach plant wastewater to the chemical recovery system due to the high dilution of the chemicals to be recycled and the corrosive nature of chloride (Harrison et al., 2023). Additionally, all recovery processes face significant challenges with respect to air emissions, effluent discharge, and the need for improved energy recovery and utilization (Heminway, 1995; Shah, 2020).

1.4.1 Recovery system in a kraft pulp mill

The chemical and energy recovery system of a kraft pulp mill consists of three circuits linked to each other: the alkali circuit, the calcium circuit, and the condensates circuit (Fig. 1.1). The alkali circuit starts when the wood chips are cooked with the white liquor at the digester. After cooking, black liquor is sent to washing devices where a pulp stream and a weak black liquor stream are obtained. Then, the pulp stream continues as discussed in Section 1.2.2, and black liquor is sent to the evaporation plant. Weak black liquor has a dissolved solids content which has to be increased before the liquor can be burned. Dry solid content increases in the evaporation plant, and sodium sulfate is added to concentrated black liquor to compensate for chemical losses. Then, the liquor is burned in the recovery boiler, where energy is recovered from the flue gases for steam or electricity generation. Sodium and sulfur remain in a suitable form to regenerate, and water is added to form the green liquor, a mixture of sodium carbonate and sodium sulfide. Green liquor is mixed with calcium oxide in the causticizing stage to regenerate the sodium hydroxide, and calcium is removed in the separation stage. Finally, the white liquor with sodium hydroxide

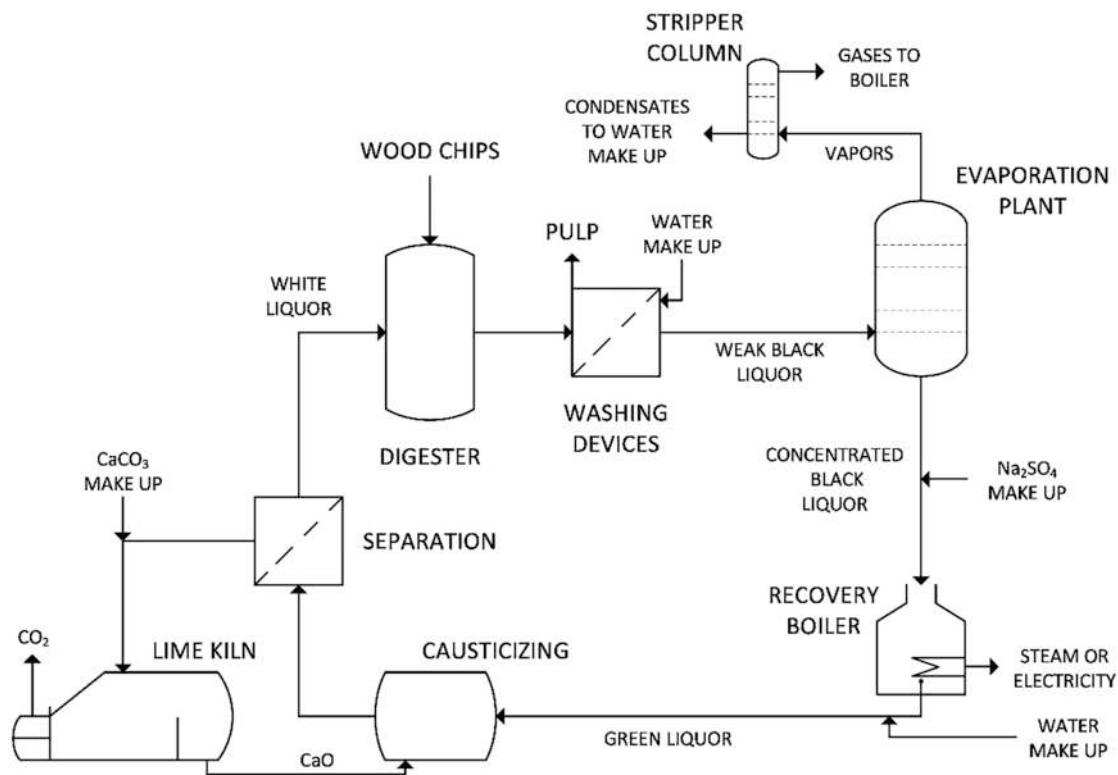


Figure 1.1 Recovery circuits of chemicals and energy for a kraft mill. Own elaboration based on Ahmad & Pant (2018), Heminway (1995) and Cheremisinoff (2009).

and sodium sulfide is sent to the digester (Ahmad & Pant, 2018; Cheremisinoff, 2009; Heminway, 1995).

The calcium circuit consists of the causticizing and separation stages and the lime kiln. After calcium separation, calcium carbonate is added, and the mixture is sent to the lime kiln, where calcium oxide is regenerated (Ahmad & Pant, 2018; Blackwell et al., 1979).

The condensate circuit starts in the evaporation plant with the steam stream. Condensates from the black liquor evaporators are treated in a stripper column that is normally integrated with the evaporation plant (Blackwell et al., 1979). After stripping, it is possible to reuse the condensates as makeup water for green liquor or in washing unbleached pulp (Kumar et al., 2022).

Although the kraft pulping process has a widely known chemical and energy recovery system, it is a big challenge to operate it at high efficiency. Mechanical and process problems can occur. Evaporators often experience problems with foaming, tube corrosion, and liquor side fouling. Fouling of heat transfer tubes and plugging of flue gas

passages are frequent problems of recovery boilers, as well as tube corrosion, damage, or cracking. Lime kilns can experience low thermal efficiency with high fuel consumption and poor lime quality. Overliming and poor mud settling and washing are frequent problems of causticizing stage, which implies low liquor causticizing efficiency (De Almeida & Park, 2009; Tran, 2020).

The traditional kraft pulping recovery system has important environmental challenges. One of the key environmental challenges is control of air emissions. Particulate, reduced sulfur gases, sulfur dioxide, and nitrogen oxides are the historically main concerns. However, other gases such as chlorine, ammonium, carbon monoxide, methanol, and other volatile organic compounds have attracted attention recently (Kumar et al., 2022).

1.4.2 Recovery system in a sulfite pulp mill

Due to the variety of cooking liquor bases used, sulfite pulping mills present numerous schemes for heat and/or chemical recovery. In calcium-based systems and ammonium-based systems, heat can be recovered by combusting the spent liquor, but there is not a practical chemical recovery system (Cheremisinoff, 2009). The base chemical can only be recovered from magnesium- and sodium-based processes (Heminway, 1995).

The chemical recovery of magnesium-based liquors may reach a degree of liquor recovery of 97% (European Commission, 2001). Once cooking is finished, the mixture passes through a washing stage where a pulp stream and a weak red liquor stream are formed. Red liquor recovery process starts with its concentration in an evaporation plant and burning in a specially designed recovery boiler (Bajpai, 2008; Casimiro et al., 2022). Unlike the kraft chemical recovery process, no smelt is produced. The chemicals are swept with the flue gases in the form of magnesium dioxide ash and sulfur dioxide gas. A first separation stage removes the magnesium ash, and a gas/liquid contactor extracts the sulfur dioxide. The separation stage may be based on cyclonic collectors or electrofilters, whereas the gas/liquid contactor is usually a system of multistage venturi scrubbers. A magnesium hydroxide solution formed by slaking of magnesium oxide ash is used as scrubbing liquid in the contactor. Thus the magnesium bisulfite liquor is regenerated; then, it is clarified and reinforced with sulfur dioxide (Bhattacharya et al., 2005; Smook, 1992). A flowchart of a typical chemical and energy recovery system for a sulfite pulping process is presented in Fig. 1.2

The chemical recovery of sodium-based liquors starts with an evaporation plant and a kraft-type recovery boiler where green liquor containing sodium sulfite and sodium carbonate is produced

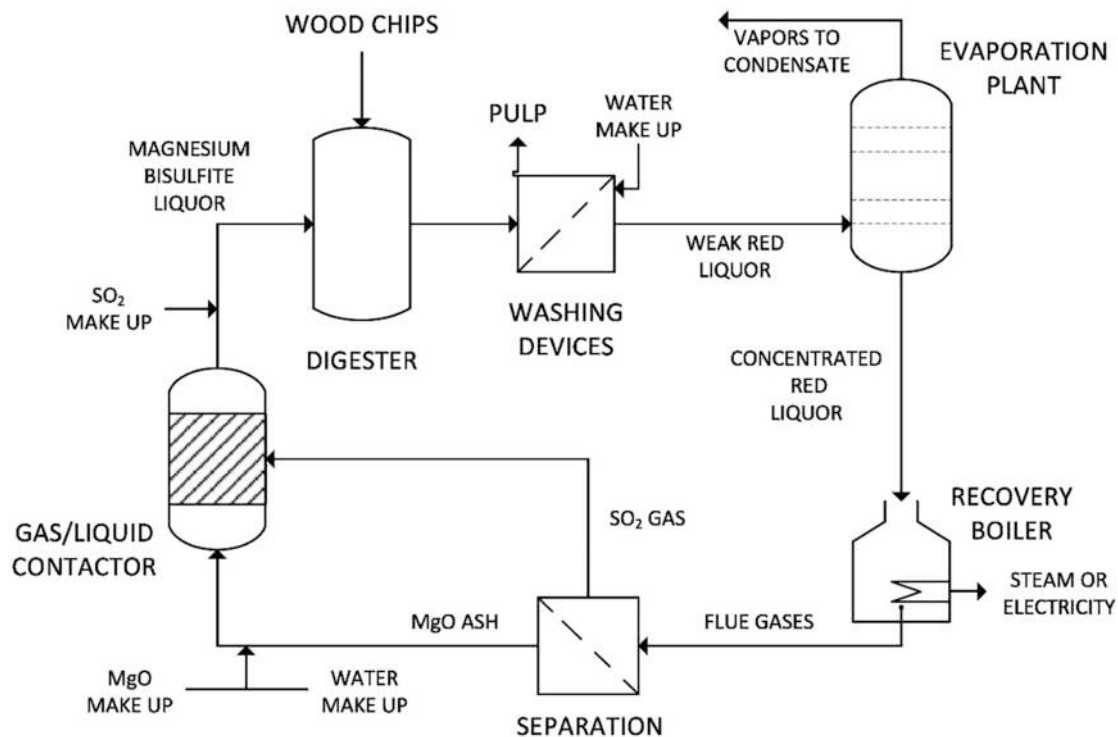


Figure 1.2 Recovery circuit of chemicals and energy for a magnesium-based sulfite pulping mill. Own elaboration based on Bajpai (2008), Cheremisinoff (2009), Heminway (1995), and Smook (1992).

(Heminway, 1995). To convert the smelt chemicals into a regenerated cooking liquor, different methods have been developed. The Rauma process consists of a decarbonating tower where the green liquor reacts with carbon dioxide, a decomposer to produce sodium sulfite, and a reaction step with SO_2 to finally regenerate the sodium bisulfite. The Tampella process consists of a partial carbonization step, a steam stripper step to produce sodium carbonate and hydrogen sulfide, a hydrogen sulfide burning step to produce sulfur oxide, and an absorption step to regenerate the sodium bisulfite (Bajpai, 2008; Smook, 1992). Other sodium-based mills sell the recovery boiler smelt to kraft mills to produce green liquor (Cheremisinoff, 2009).

1.4.3 Recovery system in a mechanical pulp mill

The greatest potential for energy recovery from mechanical pulping is limited to that part of the process carried out under pressure, which makes the production of stronger mechanical pulps

from pressurized systems economically attractive. At least 65% of the energy required in pressurized GW pulping and 75% of the energy required in TMP or CTMP pulping can be recovered (Cropp, 1991).

TMP and CTMP processes occur at high temperatures. Thus it is quite feasible to recover a large portion of the energy in a form that is useful in other sections of the mill, which can reduce the energy cost from 35% to 40%. The heat recovery potential for mechanical pulping processes is normally classified into low and high pressure, depending on whether the pulping process pressure exceeds 25 psig (Bajpai, 2016; Smook, 1992). Low-pressure recovery heat can be used for heat process water, heat grinder shower water, or heat boiler feedwater makeup. High-pressure energy recovery is not only about producing hot water but also about generating clean steam. For those purposes a special heat exchanger called a reboiler is used, which utilizes heat from the condensing exhaust steam to generate fresh steam. Recovered steam can be used for paper drying, though its pressure is normally low, and it may need to be boosted to a higher pressure. Maximum heat recovery can be obtained by using pressurized refining in all stages, and its end use will depend on the mill's configuration (Cropp, 1991; Heminway, 1995).

The suitability of a specific water fraction for reuse and the level of contaminants that are allowed to accumulate in the process determine the degree of recirculating water within a mechanical pulping process. However, in integrated mills, paper machine white water covers most of the process water needs. Typically, water loops are separated by thickening steps (European Commission, 2001; Smook, 1992).

1.5 Recent wastewater recovery processes

Diverse emerging technologies have been developed in recent years for raw material pretreatment, drying, and alternative chemical and energetic recovery processes (Kong et al., 2016). Additionally, recovery of lignin, hemicellulose, and other byproducts from cooking liquors and wastewaters has become a usual research topic. Marson et al. (2023) concluded that the use of kraft liquor as a chemical feedstock has better environmental performance and reduced impacts than its use as an energy source. Other studies have also been published about gasification of the residual bark from debarking and the material removed from chip screening (Garcia et al., 2023; Pio et al., 2020).

1.5.1 Alternative chemical and energetic recovery processes

The development of new kraft black liquor recovery methods involves gasification technologies, alternative causticization

processes, or combinations of these two groups. Black liquor gasification (BLG) is an emergent technology which can be an alternative to using a recovery boiler, described in [Section 1.4.2](#), to produce electricity, chemicals, or fuels ([Domingos et al., 2023](#); [Naqvi et al., 2010](#)).

BLG is based on the partial oxidation of concentrated black liquor (> 60% solids) to form inorganic compounds and synthesis gas (syngas). Integrated gasification and combined cycle operation ([Fig. 1.3](#)) may increase recovery energy efficiency by 10% and may generate two to three times more electricity in the cellulose plant ([Pio et al., 2020](#)). Also, the syngas can be used as a raw material to produce chemicals of interest in biorefineries ([Kong et al., 2016](#)).

The different BLG processes can be categorized into low- and high-temperature gasification, depending on whether working above or below the melting temperature range (650°C–800°C) of the pulp chemicals used ([Bajpai, 2008](#)). The low-temperature gasification produces an improved sodium and sulfur separation and requires fewer restrictions for materials of construction. However, the syngas produced may contain higher quantities of tars, which contaminate downstream operations and turbines of the gasifier ([Naqvi et al., 2010](#); [Pio et al., 2020](#)).

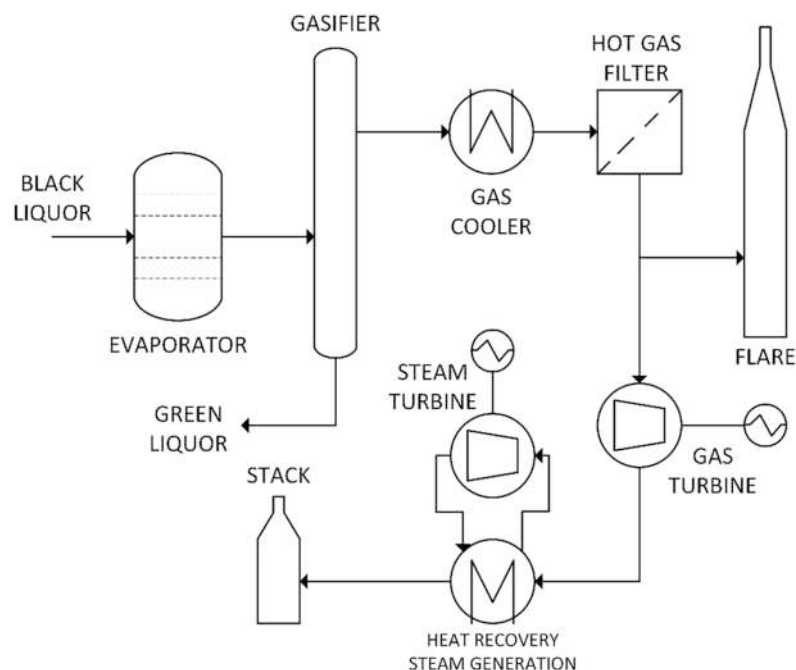


Figure 1.3 Integrated gasification and combined cycle diagram. Own elaboration based on [Bajpai \(2008\)](#) and [Tran \(2020\)](#).

Alternative causticization processes can be classified into direct causticization and autocausticization processes. In both cases an oxide is used as causticizing agent. If the oxide is water soluble, it is called autocausticization. In case the oxide is insoluble in alkaline solutions and precipitates, such as titanium oxide, manganese oxide, and iron oxide, the process is considered direct causticization. The main disadvantages are that the price of these metal oxides can be high, and it is necessary to develop a viable option to separate dregs from recycled metal oxides (Bajpai, 2018).

Proposed oxides for autocausticization in the literature are silicon dioxide, phosphorus oxide, aluminum oxide, and boric oxide. The most promising ones for the kraft pulp mill are borates. Autocausticizing allows higher caustic production without increasing lime demand and can even eliminate lime demand (Bajpai, 2016). When sodium borates are added to the kraft liquor in a lower quantity than the stoichiometric relation, a portion of the sodium carbonate is causticized in the recovery boiler, and the other portion is recausticized in a conventional plant with a reduced quantity of lime.

1.5.2 Emerging bleaching technologies

Efforts to achieve new developments for the bleaching process focus on reducing the pollutant load of the effluent, replacing the chemicals used, and reducing the consumption of fresh water by treating the water used to recirculate it. To reduce the content of AOXs in bleaching effluents, ECF processes were promoted that replace chlorine with chlorine dioxide as a delignifying chemical. Less pulp is expected to be obtained per ton of wood fibers because the use of more bleaching/washing steps results in greater fiber loss (Bajpai, 2018). The challenge in this type of process is to design a more efficient sequence of bleaching and washing steps and recover effluent flows for recirculation, with treatments to remove sodium chloride that causes corrosion problems (Hintz & Lawal, 2018).

With the same objective, completely chlorine-free processes (TCF) have been developed. They include oxygen-based chemicals such as ozone, hydrogen peroxide, oxygen molecules, and peroxoacids, and enzyme systems, which involve the application of xylanases and laccases. The ozone bleaching is an effective step to reduce the amount of some chlorophenolic compounds. Although it is limited due to carbohydrate degradation, an undesired reaction produced by the formation of superoxide and hydroxyl radicals (Sharma et al., 2020). On the contrary, hydrogen peroxide has become a bleaching agent often used as an additive for alkaline

extraction steps and applied in combination with other bleaching stages, both in ECF and TCF processes (Hintz & Lawal, 2018).

Attractive technologies in exploration involve enzymatic processes in pulp bleaching. Two principal strategies have been developed: hemicellulases (particularly xylanases) and ligninases (or laccases). The extracted xylanase enzyme can be used as a pretreatment to remove lignin from the raw pulp, which is then treated with other bleaching chemicals (Hintz & Lawal, 2018). Furthermore, laccase enzymes directly attack lignin, oxidize it, and make it soluble to the extraction step (Atalla et al., 2004). Both enzymatic treatments are investigated to improve their effectiveness and reduce costs, also because they require specific pH and temperature conditions (Singh et al., 2019).

Additionally, it is considered that the use of peracetic acid before ECF bleaching may give the advantage of reduced water utilization, chlorine dioxide demand, and effluent volume. This chemical is the strongest candidate to bleach the pulp with high brightness and limited degradation to carbohydrate content. Another alternative to reduce the use of water in pulp bleaching units is proposed through modifications to the operating system of the factory. In some cases a semicounter-current pulp washing system is implemented, where fresh water is only used to clean the pulp after the last bleaching stage. In other situations the use of fresh water to wash the bleached pulp can be completely replaced by water from the pulp drying machine (Sousa et al., 2023).

1.5.3 Recovery of lignin and hemicellulose

Lignin can be recovered from cooking liquor for later fuel or material applications. The acidification of the liquor lowers the solubility of the lignin and allows its separation by filtration and washing (Ahmad & Pant, 2018; Yiamsawas et al., 2023). The acidification may be done by using the carbon dioxide emitted from internal boilers, which helps in reducing greenhouse gas emissions. There are at least three commercialized processes for lignin recovery using carbon dioxide in the form of carbonic acid as an acidifying agent (Chen, 2005). The LignoBoost process consists of two acidification steps comprising precipitation and filtering, while the LignoForce process includes a preoxidation step that avoids the need for two filtration stages. The latest method is the Sequential Liquid-Lignin Recovery and Purification (SLRP), in which the carbon dioxide is added to the liquor under pressure and high temperature (Argyropoulos et al., 2023). Flowcharts of these three commercialized processes for lignin recovery are presented in Fig. 1.4.

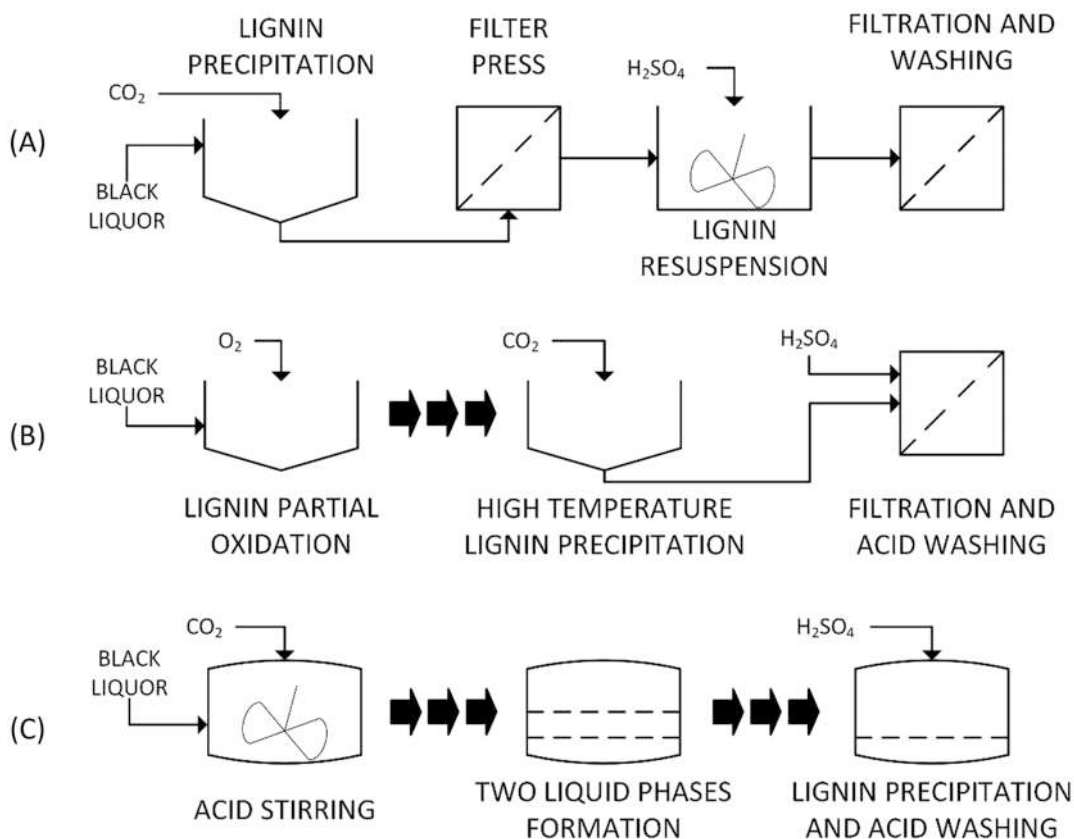


Figure 1.4 Flowcharts of commercialized processes for lignin recovery: (A) LignoBoost®, (B) LignoForce®, and (C) sequential liquid-lignin recovery and purification. Own elaboration based on [Argyropoulos et al. \(2023\)](#) and [Chen \(2005\)](#).

Precipitated kraft lignin is usually used as fuel in the lime kiln. Novel approaches for converting lignin into useful products are its gasification or its coprocessing with fossil feedstocks in a refinery. Lignin refining operations may include hydrothermal liquefaction to produce oils and esterification and hydroprocessing of esterified lignin to produce long-chain carboxylic acids ([Abdelaziz & Hultberg, 2020](#); [Prakash et al., 2021](#)). Recently, material applications of kraft lignin have been developed. Polyurethanes, phenol-formaldehyde, and epoxy resins are lignin-based thermosets, while lignin-based thermoplastics and carbon fibers can also be produced ([Argyropoulos et al., 2023](#); [Wang et al., 2016](#)).

Another process used for concentration or separation of lignin is membrane filtration of black liquor. Membranes of variable cutoff can be used, offering fractions starting from black liquor. The main advantage of membrane techniques is that they do not need to

adjust the pH or temperature (Jönsson, 2016). The membranes may be of either ceramic or polymeric type (Argyropoulos et al., 2023).

Hemicellulose is another byproduct of chemical pulping, which can be used in packing, textile, paper, electronic, food, and other applications (Jönsson, 2016). It can be removed from the liquor by membrane technologies with the lignin. Then, hemicelluloses can be isolated by ultrafiltration before precipitation of lignin (Wallmo et al., 2009). Xylan is the most important compound obtained from hemicellulose isolation. It is extracted using ultrafiltration with subsequent ethanol precipitation. Reverse osmosis is also an effective method for isolating hemicelluloses (Roy et al., 2023).

1.5.4 Recovery of other byproducts of interest

Emerging technologies have been developed for recovering other byproducts from cooking liquors and wastewater of the pulp and paper industry.

Tall oil is a byproduct from kraft pulping mills. Resin acids and fatty acids are liberated from black liquor by the addition of sulfuric acid, which forms crude tall oil. Rosin, fatty acids, and resins are obtained by the distillation of the tall oil. Fatty acids are used in alkyd resin production, whereas rosin is mainly used in the sizing of paper and as an adhesive (Ahmad & Pant, 2018; Churchill et al., 2024).

Xylooligosaccharides can be obtained from bleach kraft pulp and are emerging prebiotics with several benefits for health. Recent studies reported the production of xylooligosaccharides by acid hydrolysis using the alkaline filtrate of the bleached kraft pulp (Henriques et al., 2021). Additionally, valuable sugars were obtained from hemicellulose-rich side streams of a TMP pulping plant in Sweden. Green technology and commercially available acidic heterogeneous catalysts were used (Méndez et al., 2023).

Wastewater streams and solid wastes may also be a source of cellulose fibers. Silva et al. (2008) characterized the unbleached screen rejects, the bleaching effluent, and the eucalyptus bark from a kraft pulp mill to valorize them. They concluded that these streams can be potential raw material in fiber-based applications. Evtyugin et al. (2023) developed a new method for isolating β -sitosterol from the bleaching effluent of sulfite pulp mills. This phytosterol has wide potential in food, cosmeceutical, and biomedical applications.

Finally, a novel pulp mill wastewater recovery process has been developed for carbon dioxide and sulfur oxide capture from the boiler flue gases. It consists of metal ion separation, sulfur oxide capture using calcium hydroxide, and carbon dioxide capture using potassium perchlorate. Thus sulfur and carbon remain available for future use (Lee et al., 2022).

1.6 Conclusions and future trends

The pulp and paper industry is the sixth-most polluting industry in the world and the third-largest producer of effluents in terms of quantity. Its wastewaters are generated during the various stages of each particular mill and are characterized by having high oxygen-consuming organic compound content and a large number of toxic chlorinated organic substances.

The pulp and paper production process can be described in three stages: pulp making, pulp processing, and paper production. Different techniques exist to manufacture the pulp, which have been modified to improve the performance of this stage, simultaneously to reduce the effluents generated using closed energy and chemical recovery systems. Pulp processing generates large amounts of wastewater, containing a large number of toxic chlorinated organic compounds. In recent years, efforts have been concentrated on modify the bleaching agents used and on developing processes that do not contain chlorinated species in effluents, such as ECF and TCF processes.

Advanced technologies have been developed to address the common operating problems. Superconcentrators achieving more than 80% solid content with less fouling are starting to be used in the evaporation step. Recovery boilers begin to have large firing capacity, high steam temperature and pressure, high solids firing, and air systems with low nitrogen oxide emissions (Tran, 2020). Pressurized filters for green and white liquors, online FTIR liquor analyzers, and online lime mud solids analyzers started to be included in the kraft calcium circuit. However, many common operating problems still exist. They include the scaling of evaporators, the fouling, plugging, corrosion, emissions, and low steam production in recovery boilers, high kiln fuel consumption, poor green liquor filterability, poor causticizing efficiency, and poor mud settling in lime kiln and recausticizing stages (Bajpai, 2018).

The advanced technologies have helped alleviate many problems, but they have also created new challenges. These problems are usually related to elements that do not participate in the pulping process. Main sources of these elements are wood, makeup lime, makeup water, additives, and corrosion products. Chloride and potassium accumulate in the liquor cycle due to the high solubility of their compounds and have adverse effects on fouling and corrosion in recovery boilers (Agnihotri & Horváth, 2024; Odunlami et al., 2023).

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List of acronyms

ADt	Air dry ton
AOX	Adsorbable organic halide
BLG	Black liquor gasification
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CTMP	Chemi-thermomechanical
DTPA	Diethylenetriaminepentaacetic acid
ECF	Elemental chlorine-free
EDTA	Ethylenediaminetetraacetic acid
EOX	Extractable organic halide
FTIR	Fourier transform infrared spectroscopy
GW	Groundwood
IGCC	Integrated gasification and combined cycle
NSSC	Neutral-sulfite semichemical
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxin
SLRP	Sequential Liquid-Lignin Recovery and Purification
TCF	Totally chlorine-free
TMP	Thermomechanical
TSS	Total suspended solids

List of symbols

pH Potential of hydrogen

References

- Abdelaziz, O. Y., & Hulteberg, C. P. (2020). Lignin depolymerization under continuous-flow conditions: Highlights of recent developments. *ChemSusChem*, 13(17), 4382–4384. <https://doi.org/10.1002/cssc.202001225>.
- Agnihotri, S., & Horváth, S. (2024). I. Integrated products biorefinery options within the swedish pulp and paper industry: Current status. *Sustainable Chemistry for the Environment*, 100128.
- Ahmad, E., & Pant, K. K. (2018). Lignin conversion: A key to the concept of lignocellulosic biomass-based integrated biorefinery. In *Waste biorefinery: Potential and perspectives*. India: Elsevier, 409–444. <http://doi.org/10.1016/B978-0-444-63992-9.00014-8>, <http://www.sciencedirect.com/science/book/9780444639929>.
- Al-Rudainy, B., Galbe, M., & Wallberg, O. (2017). Influence of prefiltration on membrane performance during isolation of lignin-carbohydrate complexes from spent sulfite liquor. *Separation and Purification Technology*, 187, 380–388.

- Ali, M., & Sreekrishnan, T. R. (2001). Aquatic toxicity from pulp and paper mill effluents: A review. *Advances in Environmental Research*, 5(2), 175–196. [https://doi.org/10.1016/S1093-0191\(00\)00055-1](https://doi.org/10.1016/S1093-0191(00)00055-1), <http://elsevier.com/locate/aer>.
- Argyropoulos, D. D. S., Crestini, C., Dahlstrand, C., Furusjö, E., Gioia, C., Jedvert, K., Henriksson, G., Hultberg, C., Lawoko, M., Pierrou, C., Samec, J. S. M., Subbotina, E., Wallmo, H., & Wimby, M. (2023). Kraft lignin: A valuable, sustainable resource, opportunities and challenges. *ChemSusChem*, 16(23). <https://doi.org/10.1002/cssc.202300492>.
- Arivoli, A., Mohanraj, R., & Seenivasan, R. (2015). Application of vertical flow constructed wetland in treatment of heavy metals from pulp and paper industry wastewater. *Environmental Science and Pollution Research*, 22, 13336–13343.
- Atalla, R. H., Reiner, R. S., Houtman, C. J., & Springer, E. L. (2004). *PULPING | New technology in pulping and bleaching*. Elsevier BV, 918–924. <http://doi.org/10.1016/b0-12-145160-7/00141-1>.
- Bajpai, P. (2008). *Chemical recovery in pulp and papermaking*. Pira International Ltd.
- Bajpai, P. (2013). Bleach plant effluents from the pulp and paper industry. In *SpringerBriefs in applied sciences and technology*. Springer International Publishing. <http://doi.org/10.1007/978-3-319-00545-4>.
- Bajpai, P. (2016). Pulp and paper industry. In *Energy conservation*. Elsevier.
- Bajpai, P. (2018). *Biermann's handbook of pulp and paper: Raw material and pulp making* (3rd). India: Elsevier, 1–647. <http://doi.org/10.1016/C2017-0-00513-X>, <https://www.sciencedirect.com/book/9780128142400>.
- Bhattacharya, P. K., Todi, R. K., Tiwari, M., Bhattacharjee, C., Bhattacharjee, S., & Datta, S. (2005). Studies on ultrafiltration of spent sulfite liquor using various membranes for the recovery of lignosulphonates. *Desalination*, 174(3), 287–297. <https://doi.org/10.1016/j.desal.2004.09.017>.
- Blackwell, B. R., MacKay, W. B., Murry, F. E., & Oldham, W. K. (1979). Review of kraft foul condensates. Sources, quantities, chemical composition, and environmental effects. *TAPPI*, 62(10), 33–40.
- Cabrera, M. N. (2017). *Pulp mill wastewater: Characteristics and treatment*. InTech. <http://doi.org/10.5772/67537>.
- Caldeira, D. D., Silva, C. C., Ávila, M., Menezes, J. V., & Zanuncio, A. V. (2021). A case study on the treatment and recycling of the effluent generated from a thermo-mechanical pulp mill in Brazil after the installation of a new bleaching process. *Science of the Total Environment*, 763.
- Casimiro, F. M., Costa, C. A. E., Vega-Aguilar, C., & Rodrigues, A. E. (2022). Hardwood and softwood lignins from sulfite liquors: Structural characterization and valorization through depolymerization. *International Journal of Biological Macromolecules*, 215, 272–279. <https://doi.org/10.1016/j.ijbiomac.2022.06.067>.
- Chandra, R., & Abhishek, A. (2011). Bacterial decolorization of black liquor in axenic and mixed condition and characterization of metabolites. *Biodegradation*, 22(3), 603–611. <https://doi.org/10.1007/s10532-010-9433-1>.
- Chandra, R., Abhishek, A., & Sankhwar, M. (2011). Bacterial decolorization and detoxification of black liquor from rayon grade pulp manufacturing paper industry and detection of their metabolic products. *Bioresource Technology*, 102(11), 6429–6436.
- Chandra, R., & Singh, R. (2012). Decolourisation and detoxification of rayon grade pulp paper mill effluent by mixed bacterial culture isolated from pulp paper mill effluent polluted site. *Biochemical Engineering Journal*, 61, 49–58. <https://doi.org/10.1016/j.bej.2011.12.004>.
- Chen, K. (2005). Industrial scale lignin recovery from pulping liquors. *Natural polyphenols from wood tannin and lignin—An industrial perspective* (pp. 123–145). Elsevier.

- Cheremisinoff, N. (2009). *Handbook of Pollution Prevention and Cleaner Production*. William Andrew, 2.
- Churchill, J. G. B., Borugadda, V. B., & Dalai, A. K. (2024). A review on the production and application of tall oil with a focus on sustainable fuels. *Renewable and Sustainable Energy Reviews*, 191, 114098.
- Cropp, H. V. (1991). Efficient use of recovered energy is a key mechanical pulping goal. *Pulp and Paper*, 65(4), 162–164.
- Dai, M., Sun, M., Chen, B., Xie, H., Zhang, D., Han, Z., Yang, L., & Wang, Y. (2023). Advancing sustainability in China's pulp and paper industry requires coordinated raw material supply and waste paper management. *Resources, Conservation and Recycling*, 198, 107162. <https://doi.org/10.1016/j.resconrec.2023.107162>.
- De Almeida, G. M., & Park, S. W. (2009). Ash deposits monitoring in a convective heat transfer section of a kraft recovery boiler. *Computer Aided Chemical Engineering*, 27, 1467–1472. [https://doi.org/10.1016/S1570-7946\(09\)70635-2](https://doi.org/10.1016/S1570-7946(09)70635-2), http://www.elsevier.com/wps/find/bookdescription.cws_home/BS_CCE/description#description.
- Deshmukh, N. S., Lapsiya, K. L., Savant, D. V., Chiplonkar, S. A., Yeole, T. Y., Dhakephalkar, P. K., & Ranade, D. R. (2009). Upflow anaerobic filter for the degradation of adsorbable organic halides (AOX) from bleach composite wastewater of pulp and paper industry. *Chemosphere*, 75(9), 1179–1185. <https://doi.org/10.1016/j.chemosphere.2009.02.042>.
- Domingos, M. E. G. R., Flórez-Orrego, D., dos Santos, M. T., de Oliveira Junior, S., & Maréchal, F. (2023). Process modeling and integration of hydrogen and synthetic natural gas production in a kraft pulp mill via black liquor gasification. *Renewable Energy*, 219, 119396. <https://doi.org/10.1016/j.renene.2023.119396>.
- Dufresne, R., Liard, A., & Blum, M. (2001). Anaerobic treatment of condensates: Trial at a kraft pulp and paper mill. *Water Environment Research*, 73(1), 103–109.
- European Commission. (2001). *Reference document on best available techniques in the pulp and paper industry. Integrated pollution prevention and control*.
- Evtugin, D. D., Prates, A., Domingues, M. R., Casal, S., & Evtuguin, D. V. (2023). New method for isolating β -sitosterol from bleaching effluent of sulphite pulp mill. *Food and Bioproducts Processing*, 140, 151–159. <https://doi.org/10.1016/j.fbp.2023.05.007>, http://www.elsevier.com/wps/find/journaldescription.cws_home/713883/description#description.
- Garcia, L., Cordoba, M., Dosso, L., Nardi, F., Vera, C., Quiroga, M., Busto, M., & Badano, J. (2023). Catalytic gasification and reforming of residual biomass in a bench scale system with low cost catalysts. *ChemPlusChem*, 88(12), e202300376. <https://doi.org/10.1002/cplu.202300376>.
- Guo, Z., & Olsson, L. (2014). Characterization and fermentation of side streams from sulfite pulping. *Process Biochemistry*, 49(8), 1231–1237. <https://doi.org/10.1016/j.procbio.2014.05.002>, www.elsevier.com/inca/publications/store/4/2/2/8/5/7.
- Han, N., Zhang, J., Hoang, M., Gray, S., & Xie, Z. (2021). A review of process and wastewater reuse in the recycled paper industry. *Environmental Technology & Innovation*, 24, 101860. <https://doi.org/10.1016/j.eti.2021.101860>.
- Haq, I., Kumar, S., Raj, A., Lohani, M., & Satyanarayana, G. N. V. (2017). Genotoxicity assessment of pulp and paper mill effluent before and after bacterial degradation using *Allium cepa* test. *Chemosphere*, 169, 642–650. <https://doi.org/10.1016/j.chemosphere.2016.11.101>.
- Harrison, S., Rumjeet, S., Mostert, L., Wessels, C., Rini, S., Manenzhe, T., Zulu, N., & Kotsiopoulos, T. (2023). *The pulp and paper wastewater biorefinery. potential for concomitant value recovery and wastewater treatment*.

- Hayes, A., Nesbø, C., Edwards, E. A., & Jenson, E. (2022). Anaerobic digestion of kraft pulp mill foul condensate under thermophilic and mesophilic conditions. *Environmental Engineering Science*, 39(6), 573–583.
- He, Q., & Chen, H. (2020). Increased efficiency of butanol production from spent sulfite liquor by removal of fermentation inhibitors. *Journal of Cleaner Production*, 263, 121356. <https://doi.org/10.1016/j.jclepro.2020.121356>.
- Heminway (1995). *Profile of the Pulp and Paper Industry*.
- Henriques, P., Martinho, M., Serrano, M., Brites, S., & Alves, A. (2021). Xylooligosaccharides production by acid hydrolysis of an alkaline extraction filtrate from Eucalyptus globulus bleached kraft pulp. *Industrial Crops and Products*, 159.
- Hermosilla, D., Merayo, N., Gascó, A., & Blanco, Á. (2015). The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: A review. *Environmental Science and Pollution Research*, 22(1), 168–191. <https://doi.org/10.1007/s11356-014-3516-1>.
- Hintz, H., & Lawal, S. (2018). Paper: Pulping and bleaching. *Reference Module in Materials Science and Materials Engineering*.
- Ince, B. K., Cetecioglu, Z., & Ince, O. (2011). Pollution prevention in the pulp and paper industries. *Environmental Management in Practice*, (5), 224–246.
- Jönsson, A. S. (2016). Membranes for lignin and hemicellulose recovery in pulp mills. In *Membrane technologies for biorefining*. Sweden: Elsevier Inc, 105–133. <http://doi.org/10.1016/B978-0-08-100451-7.00005-0>, <http://www.sciencedirect.com/science/book/9780081004517>.
- Källqvist, T., Carlberg, G., & Kringstad, A. (1989). Ecotoxicological characterization of industrial wastewater—Sulfite pulp mill with bleaching. *Ecotoxicology and Environmental Safety*, 18(3), 321–336.
- Karrasch, B., Parra, O., Cid, H., Mehrens, M., Pacheco, P., Urrutia, R., Valdovinos, C., & Zaror, C. (2006). Effects of pulp and paper mill effluents on the microplankton and microbial self-purification capabilities of the Biobío River, Chile. *Science of the Total Environment*, 359(1–3), 194–208.
- Kong, L., Hasanbeigi, A., & Price, L. (2016). Assessment of emerging energy-efficiency technologies for the pulp and paper industry: A technical review. *Journal of Cleaner Production*, 122, 5–28.
- Kong, L., Zhao, J., Li, J., Lou, R., & Zhang, Y. (2020). Evaluating energy efficiency improvement of pulp and paper production: Case study from factory level. *Journal of Cleaner Production*, 277, 124018. <https://doi.org/10.1016/j.jclepro.2020.124018>.
- Kumar, A., Singh, A. K., Bilal, M., Prasad, S., Rameshwari, K. R. T., & Chandra, R. (2022). Paper and pulp mill wastewater: Characterization, microbial-mediated degradation, and challenges. In *Nanotechnology in paper and wood engineering: Fundamentals, challenges and applications*. India: Elsevier, 371–387. <http://doi.org/10.1016/B978-0-323-85835-9.00011-8>, <https://www.sciencedirect.com/book/9780323858359>.
- Kumar, R., Maurya, A., & Raj, A. (2024). Exploring the potential of bacterial consortium for the treatment of paper mill effluent treatment through various treatment strategies and evaluation of their toxicity. *Journal of Water Process Engineering*, 60, 105135.
- Lacorte, S., Latorre, A., Barceló, D., Rigol, A., Malmqvist, A., & Welander, T. (2003). Organic compounds in paper-mill process waters and effluents. *TrAC - Trends in Analytical Chemistry*, 22(10), 725–737. [https://doi.org/10.1016/S0165-9936\(03\)01009-4](https://doi.org/10.1016/S0165-9936(03)01009-4), www.elsevier.com/locate/trac.
- Lee, H., Lim, J., Cho, H., & Kim, J. (2022). Novel pulp mill wastewater recovery process for CO₂ and SO_x utilization. *Journal of Cleaner Production*, 371, 133298. <https://doi.org/10.1016/j.jclepro.2022.133298>.

- Leiviskä, T., Sarpola, A., & Tanskanen, J. (2012). Removal of lipophilic extractives from debarking wastewater by adsorption on kaolin or enhanced coagulation with chitosan and kaolin. *Applied Clay Science*, 61, 22–28.
- Liu, Z., Zhao, L., Lu, S., Hou, X., Hou, D., & Ma, J. (2024). Porous ceramsite catalytic ozonation for the treatment of pulp and paper mill wastewater in a continuous-flow reactor. *Chemical Engineering Science*, 288, 119855. <https://doi.org/10.1016/j.ces.2024.119855>.
- Luthe, C. E. (1990). Isolation and characterization of lignosulphonates from an ultra high yield neutral sulphite pulping effluent. *Holzforschung*, 44(2), 107–112. <https://doi.org/10.1515/hfsg.1990.44.2.107>.
- Marson, A., Samec, J., & Manzardo, A. (2023). Consequential life cycle assessment of kraft lignin recovery with chemical recycling. *Science of the Total Environment*, 882, 163660.
- Mboowa, D. (2021). A review of the traditional pulping methods and the recent improvements in the pulping processes. *Biomass Conversion and Biorefinery*, 14, 1–12.
- Méndez, F., Orozco, F., & Grénman, G. M. (2023). Techno-economic evaluation of obtaining valuable rare sugars from thermo-mechanical pulping side streams utilizing the latest technology. *Chemical Engineering Journal*, 455(2).
- Murray, W. (1992). *Pulp and paper: The reduction of toxic effluents*. Library of Parliament.
- Naqvi, M., Yan, J., & Dahlquist, E. (2010). Black liquor gasification integrated in pulp and paper mills: A critical review. *Bioresource Technology*, 101(21), 8001–8015.
- Odulami, O. A., Amoo, T. E., Adisa, H. A., Elehinfafe, F. B., & Oladimeji, T. E. (2023). Application of mass transfer in the pulp and paper Industry – Overview, processing, challenges, and prospects. *Results in Engineering*, 20, 101498. <https://doi.org/10.1016/j.rineng.2023.101498>.
- Pearl, I. A., & McCoy, P. F. (1961). Studies on the chemistry of aspen wood. VIII. An investigation of the neutral extractives of commercial aspen spent sulfite liquor. *Journal of Organic Chemistry*, 26(2), 550–552. <https://doi.org/10.1021/jo01061a063>.
- Pereira, S. R., Portugal-Nunes, D. J., Evtuguin, D. V., Serafim, L. S., & Xavier, A. M. R. B. (2013). Advances in ethanol production from hardwood spent sulphite liquors. *Process Biochemistry*, 48(2), 272–282. <https://doi.org/10.1016/j.procbio.2012.12.004>.
- Pio, D. T., Tarelho, L. A. C., & Pinto, P. C. R. (2020). Gasification-based biorefinery integration in the pulp and paper industry: A critical review. *Renewable and Sustainable Energy Reviews*, 133, 110210.
- Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater—A review. *Science of The Total Environment*, 333(1–3), 37–58. <https://doi.org/10.1016/j.scitotenv.2004.05.017>.
- Prakash, D. G., Gopinath, K. P., Vinatha, V., Shreya, S., Sivaramakrishnan, R., & Lan Chi, N. T. (2021). Enhanced production of hydrocarbons from lignin isolated from sugarcane bagasse using formic acid induced supercritical ethanol liquefaction followed by hydrodeoxygenation. *Chemosphere*, 285, 131491. <https://doi.org/10.1016/j.chemosphere.2021.131491>.
- Ribeiro, J. P., Marques, C. C., Portugal, I., & Nunes, M. I. (2020). Fenton processes for AOX removal from a kraft pulp bleaching industrial wastewater: Optimisation of operating conditions and cost assessment. *Journal of Environmental Chemical Engineering*, 8(4), 104032. <https://doi.org/10.1016/j.jece.2020.104032>.
- Rintala, J. A., & Puhakka, J. A. (1994). Anaerobic treatment in pulp- and paper-mill waste management: A review. *Bioresource Technology*, 47(1), 1–18. [https://doi.org/10.1016/0960-8524\(94\)90022-1](https://doi.org/10.1016/0960-8524(94)90022-1).

- Rizwan, K., Rasheed, T., Bilal, M., & Iqbal, H. M. N. (2022). Pulp and paper industry-based pollutants, and their adverse impacts. In *Nanotechnology in paper and wood engineering: Fundamentals, challenges and applications*. Pakistan: Elsevier, 143–160. <http://doi.org/10.1016/B978-0-323-85835-9.00005-2>, <https://www.sciencedirect.com/book/9780323858359>.
- Roy, Y., Top, R. W., de Vos, W. M., & Schuur, B. (2023). Organic solvent reverse osmosis (OSRO) for the recovery of hemicellulosic derivatives after wood-pulping with a deep eutectic solvent. *Chemical Engineering Science*, 267, 118367. <https://doi.org/10.1016/j.ces.2022.118367>.
- Saleem, A., Ali, S., & Liaquat, I. (2023). Methanol production from the pulp mills and paper industry. In *Reference module in chemistry, molecular sciences and chemical engineering*. Elsevier.
- Salmi, P. (2020). *Membrane filtration of debarking plant wastewater*.
- Savant, D. V., Abdul-Rahman, R., & Ranade, D. R. (2006). Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater. *Bioresource Technology*, 97(9), 1092–1104.
- Shah, M. P. (2020). *Microbial bioremediation & biodegradation*. India: Springer Singapore, 1–550. <http://doi.org/10.1007/978-981-15-1812-6>.
- Sharma, N., Bhardwaj, N., & Singh, R. (2020). Environmental issues of pulp bleaching and prospects of peracetic acid pulp bleaching: A review. *Journal of Cleaner Production*, 256, 120338.
- Sharma, P., Iqbal, H., & Chandra, R. (2022). Evaluation of pollution parameters and toxic elements in wastewater of pulp and paper industries in India: A case study. *Case Studies in Chemical and Environmental Engineering*, 5, 100163.
- Silva, F., Nadais, H., Prates, A., Arroja, L., & Capela, I. (2009). Modelling of anaerobic treatment of evaporator condensate (EC) from a sulphite pulp mill using the IWA anaerobic digestion model no. 1 (ADM1). *Chemical Engineering Journal*, 148(2–3), 319–326. <https://doi.org/10.1016/j.cej.2008.09.002>.
- Silva, M. C., Lopes, O. R., Colodette, J. L., Porto, A. O., Rieumont, J., Chaussy, D., Belgacem, M. N., & Silva, G. G. (2008). Characterization of three non-product materials from a bleached eucalyptus kraft pulp mill, in view of valorising them as a source of cellulose fibres. *Industrial Crops and Products*, 27(3), 288–295. <https://doi.org/10.1016/j.indcrop.2007.11.005>.
- Singh, A. K., Kumar, A., & Chandra, R. (2022). Environmental pollutants of paper industry wastewater and their toxic effects on human health and ecosystem. *Bioresource Technology Reports*, 20, 101250.
- Singh, G., Kaur, S., Khatri, M., & Arya, S. K. (2019). Biobleaching for pulp and paper industry in India: Emerging enzyme technology. *Biocatalysis and Agricultural Biotechnology*, 17, 558–565. <https://doi.org/10.1016/j.bcab.2019.01.019>.
- Sixta, H. (2006). *Handbook of pulp*. WILEY-VCH Verlag GmbH & Co.
- Sjostrom, E. (1993). *Wood chemistry. Fundamentals and applications*. Academic Press.
- Sjöström, E., & Alén, R. (1999). *Analytical methods in wood chemistry, pulping and papermaking*. Berlin Heidelberg: Springer-Verlag.
- Sjostrom, E., Haglund, P., & Janson, J. (1963). Changes in cooking liquor composition during sulfite pulping. *Svensk Papperstidn*, 65, 855–869.
- Smook, G. (1992). *Handbook for pulp and paper technologists* (2nd). TAPPI PRESS.
- Sousa, A. M., Pinto, I. S. S., Machado, L., Gando-Ferreira, L., & Quina, M. J. (2023). Sustainability of kraft pulp mills: Bleaching technologies and sequences with reduced water use. *Journal of Industrial and Engineering Chemistry*, 125, 58–70. <https://doi.org/10.1016/j.jiec.2023.05.033>.
- Tran, H. (2020). *Kraft recovery boilers* (3rd). TAPPI Press.

- UNECE and FAO. (2023). Data Brief 2023: Pulp, paper and paperboard. United Nations Economic Commission for Europe and United Nations and the Food and Agriculture Organization of the United Nations.
- Wallmo, H., Theliander, H., Jönsson, A. S., Wallberg, O., & Lindgren, K. (2009). The influence of hemicelluloses during the precipitation of lignin in kraft black liquor. *Nordic Pulp and Paper Research Journal*, 24(2), 165–171. <https://doi.org/10.3183/npprj-2009-24-02-p165-171>, <https://www.degruyter.com/view/j/npprj?rskey=Gbxn1W&rskey=Gbxn1W>.
- Wang, C., Kelley, S., & Venditti, R. (2016). Lignin-based thermoplastic materials. *ChemSusChem*, 9(8), 770–783.
- World Bank. Environmental considerations in the pulp and paper industry (1980). Beak Consultants Limited, Vancouver, Canada.
- Yiamsawas, D., Watcharin, K., & Pongprayoon, T. (2023). Enhanced performance of lignin recovery with a carbon dioxide acidification method. *ACS Omega*, 8, 7438–7447.

Environmental effects and human health challenges of pulp and paper industry wastes

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2.1 Introduction

The pulp and paper sector is a vital component of global manufacturing, contributing significantly to the manufacture of key materials used in many facets of our everyday life. This industry stands as one of the most significant consumers of water and energy globally (Cetecioglu and Ince, 2011). In ranked fifth among all the energy-intensive industries as it accounts for approximately 4% of the world overall energy consumption. Moreover, it also generates a large amount of waste during its different processes. Around 500 million tons of paper and related products are generated annually, emitting 100 million kilograms of toxic pollutants. Asia Pulp & Paper, International Paper, Oji Paper, Sappi, Stora Enso, Nippon Paper, and Orchids Paper Products are the leading players in the global pulp and paper production. The pulp and paper sector is growing significantly each year. With a combined share of more than 50% of global paper manufacture the United States, China, and Japan are the primary countries responsible for paper production (Fig. 2.1).

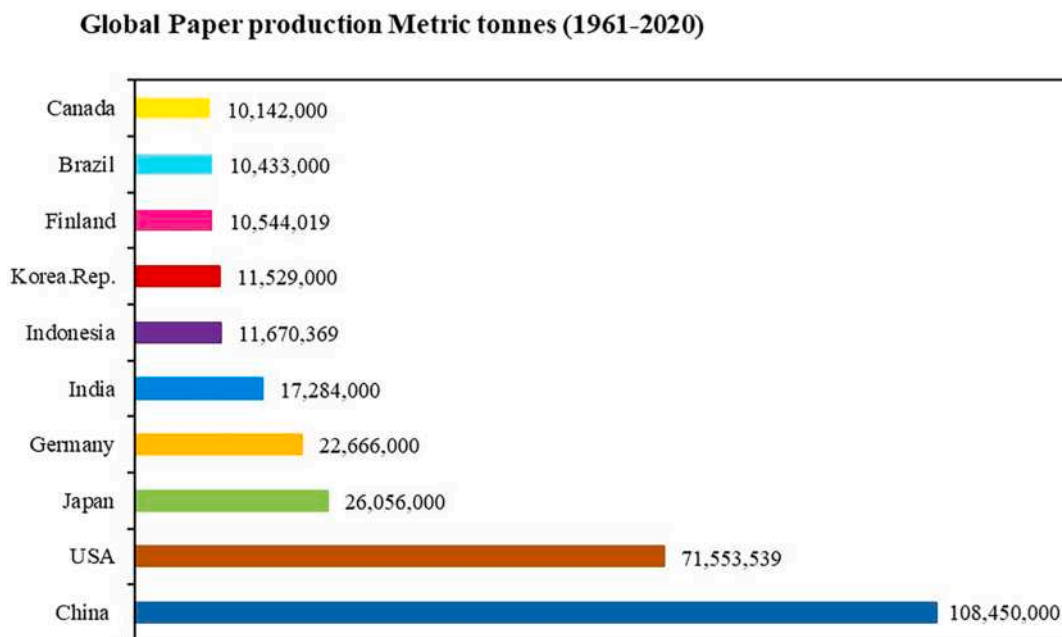


Figure 2.1 Global paper production in metric tons in different countries from the years 1961–2020.

A large number of paper production plants are located in Germany, Brazil, Finland, Canada, and Sweden.

Global paper output is projected to steadily increase, with an anticipated annual growth rate of 1.1% that is predicted to persist until 2030. The European Union is forecasted to undergo a little uptick in its growth rate, reaching an annual rate of 1.5%. The paper and pulp industry (PPI), an established sector, presently manufactures approximately 400 million tons (Mt) of paper annually. The projected estimate for 2050 is 900 million metric tons, with a predominant concentration in Asia. Global paper production has consistently increased, resulting in a commensurate annual increase in paper consumption. The worldwide mean paper consumption is at 55 kg per individual year. Nevertheless, a more intricate examination of per capita paper usage unveils a more nuanced narrative. The manufacturing of pulp and paper entails complex procedures that include wood and fiber pulping, bleaching, papermaking, and several supplementary operations.

The pulp and paper industry, although a significant sector in every country worldwide, not only promotes to the gross domestic product (GDP) but also unexpectedly leads to environmental damage and health concerns. The pulp and paper industry (PPI)

consumes a lot of energy and resources, poses a significant negative impact of the environment, and causes serious health hazards throughout the 20th century. Various communities and ecosystems, which lie in the vicinity of these operations, are more prone to health risks. Environmental impacts, including contamination of soil and poor air and water quality, are growing more widely, which highlights the need for a thorough evaluation of waste management techniques.

This chapter thoroughly explained the effect of pollutants from the pulp and paper industry on the environment, as well as health implications. Various kinds of effluents (solid, liquid, and gaseous) produced during different manufacturing processes of pulp and paper are discussed. These pollutants directly incorporate into the soil, affect the local quality of air and water, damage the aquatic life, food crops, and ultimately contribute to food chain contamination, causing serious human diseases. The story transitions its attention to the health challenges encountered by people, notably scrutinizing the occupational hazards confronted by workers in several sectors and the health ailments experienced by communities living in close proximity to industrial mills. The emphasis is placed on the exposure to harmful and poisonous substances. The chapter explores legislative frameworks, technology solutions, and best practices, while also showcasing case studies that highlight health and environmental challenges.

2.2 Pulp and paper production processes

The term “paper” originates from the plant papyrus, utilized by the Egyptians to create the earliest rudimentary writing medium in existence. In 105 AD, Tsai-Lun of China utilized mulberry and bamboo barks to create the initial genuine papermaking technique. Paper is a continuous network of material formed by the interweaving of mineral, vegetable, animal, or synthetic fibers, either alone or in combination with other substances, resulting in the entanglement of the fibers.

2.2.1 Raw material used in the industry

The quality of paper is significantly influenced by the choice of raw materials, as variations in fiber length and pulp content can have a profound impact. Most paper in modern society is made from cellulose fibers obtained from coniferous trees, particularly spruce and pine, which are predominantly found in the northern temperate regions of North America and Europe. The wood cell wall is primarily composed of cellulose, hemicellulose, and lignin.



Figure 2.2 Different kinds of raw materials used in pulp and paper industry (PPI).

Cellulose provides fibrous properties due to its straight, elongated, and aligned fibers. Hemicelluloses are crucial for pulp soaking and forming linkages during the beating process. Lignin acts as a natural adhesive in wood cells but does not form fibers. Wood is the main and traditional source of paper, including both softwood and hardwood types. Softwoods such as pine and spruce are favored because their long fibers improve the strength of the paper. Pulpwood, consisting of either logs or wood chips, acts as the fundamental material for the pulping procedure, which disintegrates wood into fibers that are appropriate for the creation of paper. The industry is progressively adopting sustainability practices by integrating recycled paper derived from both postconsumer and preconsumer sources. In addition to wood, several alternative materials such as cottonseed hair, flax, leaves, sunflower stalk, bamboo, bagasse (a by-product of sugarcane processing), cotton, hemp, and even papyrus in certain places are used as raw materials. Fig. 2.2 shows different types of raw materials and their average percentage employed for the production of paper. This multifaceted strategy exemplifies the industry endeavors to achieve a harmonious equilibrium between resource use and environmental concerns, as well as to investigate novel materials for the production of paper.

2.2.2 Key stages in pulp and paper manufacturing

The pulp and paper production process has five primary stages: pulping, bleaching, beating and refining, paper manufacture, and final treatment (Fig. 2.3). Raw material preparation occurs before the pulping process. It can be referred to as the preliminary phase of paper production. Here are the main stages in pulp and paper manufacturing:

- 1. Raw material preparation:** Wood logs are introduced into rotating drums during the process of raw material preparation, with the purpose of removing the bark (Bajpai, 2015).
- 2. Pulping:** Isolating wood fibers by mechanical, chemical, or thermal treatments or by combining these techniques is the process known as pulping. While mechanical grinding physically breaks down and separates the fibers, chemical pulping uses chemical substances for softening the lignin. Most commonly the pulping is carried out when both strategies (chemical and mechanical) are being exploited together.

Paper manufacturing process



Figure 2.3 Key stages involved in the paper manufacturing process.

3. **Bleaching of pulp:** Bleaching pulp can be done in two common ways: oxidative bleaching and chlorination. Utilizing oxidative bleach to break down and dissolve lignin while improving the pulp purity and whiteness is known as oxidative bleaching. Commonly used bleaching chemicals include hypochlorite, Cl_2 , and ClO_2 . Bleaching pulp primarily with oxidative bleaching is still the practice used nowadays.
4. **Pulp beating and refining:** The process of beating and refining pulp involves mechanical treatment of chemical pulps in the presence of water, which serves to enhance fiber properties. The purpose of the beating is to enhance the durability of the resulting paper. The refining process, akin to the beating process, is employed to enhance the physical characteristics of the final sheet.
5. **Papermaking:** The production of paper mainly utilizes three methods: the Fourdrinier machine, the cylinder machine, and twin wire formers. During paper formation the fibrous material, which is approximately 99% water, passes through rollers or wire mesh to remove water and form the paper web (Bajpai, 2015).
6. **Final treatment:** The final processing techniques for the produced paper, tailored to the industry or packaging requirements, include calendering, supercalendering, sizing, laminating, impregnating, or saturating. Calendering involves applying pressure to realign surface fibers, resulting in a smoother paper surface. Paper treated with calendering is known to have a machine finish. Supercalendering is similar to calendering but involves the addition of moisture and the application of higher pressure. Sizing involves applying substances like starch, casein, or alum to the paper to enhance its appearance, barrier properties, and strength.

2.3 Types of wastes generated

The waste generated by the pulp and paper sector is classified into various categories, including pulping rejects, bleaching rejects, washing rejects, primary sludge, and secondary sludge. The aforementioned waste products have the ability to contaminate the atmosphere, land, and marine resources. Lignocellulosic waste consists of several inorganic and organic pollutant compounds that are generated as a by-product of the pulp bleaching operation and wood digestion process (Pokhrel & Viraraghavan, 2004). Most of the effluents are generated through the pulping process and are then followed by either bleaching or washing (Fig. 2.4). Wood residues, pulping chemicals, and sludge are classified as solid waste, whereas

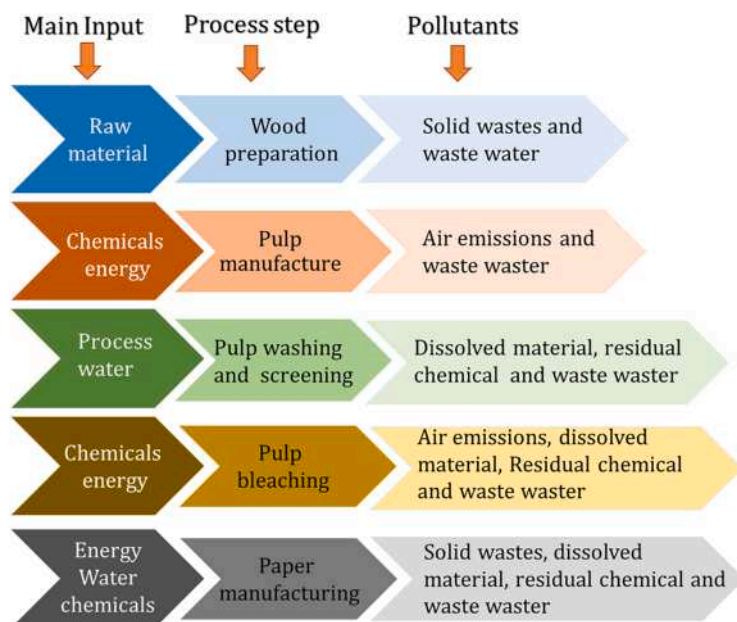


Figure 2.4 Effluents generated from pulp and paper industry.

liquid waste refers to the effluents generated from washing, bleaching, and pulping operations. Greenhouse gases (GHGs) are a type of gaseous waste, while liquid waste consists of wastewater generated by pulping, bleaching, papermaking, and cleaning operations. The primary categories of waste produced in pulp and paper plants are succinctly outlined here:

2.3.1 Wastes generated from the pulp mills

The waste materials generated by the pulp mills consist mostly of undesired components such as sand, bark, and wood remnants that arise from the treatment of wood and are not appropriate for the production of paper. These discarded materials usually have a relatively low amount of water, considerable heat values, and can be easily separated from water. As a result, they are typically burned in the bark boiler of the mill to efficiently recover energy. In addition to these rejects, other residual products (inorganic sludge) that are removed from the chemical recovery process include lime mud, dregs, and green liquor sludge. After undergoing dewatering and drying procedures, these sludges are often discarded in landfills.

Pulp mills produce wastewater treatment sludge, which comes from two sources: primary sludge and biological sludge produced in

the second clarifier. These mixtures of sludges are commonly combined, treated with a polymer, and then dehydrated together to obtain a solid material with a moisture content ranging from 25% to 40%. Furthermore, there exists chemical flocculation sludge, which is a result of water treatment. This sludge is distinguished by its elevated concentration of inorganic substances and water. Usually, this thick, muddy substance is taken to designated areas for waste disposal because of its specific makeup and qualities.

2.3.2 Wastes generated from paper mills

The waste management procedures pertaining to recovered paper encompass various essential elements. Initially, the rejects obtained from recycled paper comprise contaminants such as fibers, staples, metals, sand, glass, plastics, and different components of paper. These waste materials have high heating properties and a low moisture content, may be easily separated from water, and are usually either burned or disposed off in landfills (Monte et al., 2009). Deinking sludge is a by-product that consists of short fibers, coatings, fillers, ink particles, and deinking chemicals. Despite its low calorific value, this sludge is frequently repurposed in other sectors or sent to incineration. The primary sludge, which is produced during the clearing of process water, consists primarily of small particles and substances used to fill gaps or voids. Accordingly, the waste can be incorporated back into the board industry process, burned, disposed off, or combined with deinking or secondary sludge, depending on the desired quality of the end product. The secondary or biological sludge generated during wastewater treatment is either reused in the board industry or subjected to processes such as thickening, dewatering, incineration, or landfill disposal. Because heavy, fibrous, or inorganic components are eliminated in the primary clarifier, secondary sludge volumes are lower than those of primary sludge.

2.4 Environmental impact of wastes from pulp and paper industries

The papermaking process is intricate and carries significant environmental consequences. It entails vast water and natural resource (wood) consumption, while simultaneously releasing diverse forms of solid, liquid, and gaseous waste into the environment (Fig. 2.5).

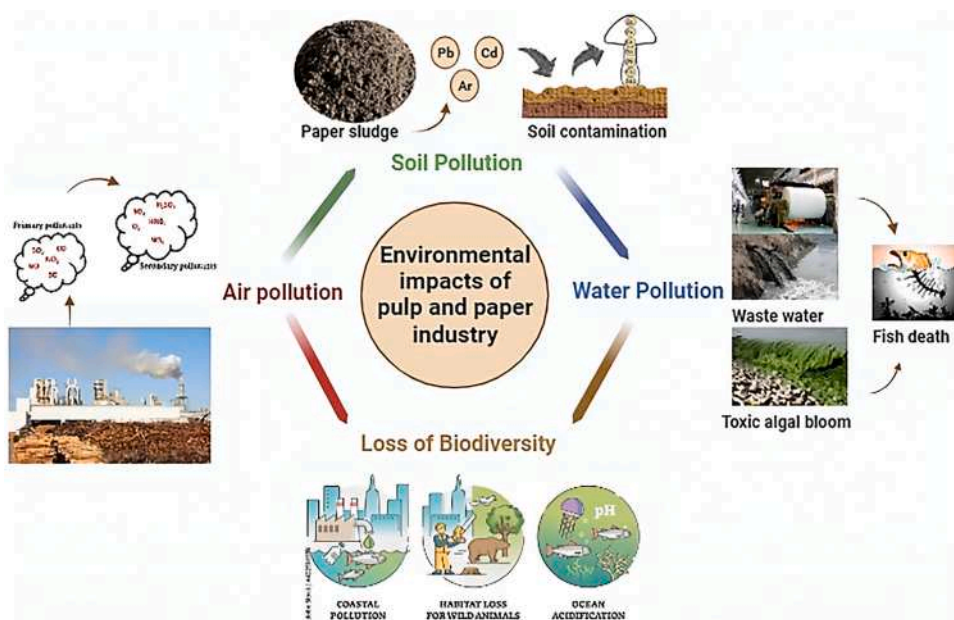


Figure 2.5 Different kinds of pollution caused by pulp and paper industry and their effect on the environment.

2.4.1 Soil contamination from solid waste disposal

The pulp and paper industry land disposal techniques, such as the utilization of sludge and waste materials on soil, can lead to soil contamination. The sludge contains remnants of chemicals, heavy metals, and organic materials, which present difficulties for soil quality and agricultural production. The solid waste materials originating from pulp and paper industries predominantly consist of treatment sludges, lime mud, lime slaker grits, green liquor dregs, boiler and furnace ash, scrubber sludges, and residuals from wood processing. Wastewater treatment sludges are of particular environmental concern due to their inclusion of chlorinated compounds. With the exception of boiler and furnace ash the solid waste generated by pulp and paper mills is largely organic in nature. Elements such as magnesium, sodium chloride, and sulfur, which are prevalent in pulp mill wastewater, have the potential to disrupt nutrient balance in crops, elevate soil salinity, and degrade soil structure, ultimately leading to reduced crop productivity over time. Each year, the pulp and paper industry produces more than one hundred thousand dry tons of solid waste, presenting a major challenge in managing substantial volumes of wastewater. This wastewater comprises dissolved solids such as sodium and calcium chlorides and sulfates, along with varying levels of suspended

organic substances. Typically alkaline, these effluents pose high chemical and biological oxygen demands. Paper mill effluents also contain toxic trace elements that can accumulate excessively in soils, posing severe risks to human health and animals through the food chain. Untreated industrial effluents harbor high concentrations of heavy metals, disrupting soil quality by increasing soil pH, altering soil color and texture, upsetting the balance of macro- and micro nutrients, inhibiting soil microbial activities, disrupting natural cycles, decreasing germination percentage, hindering seedling growth, increasing organic load, and depleting soil oxygen supply.

2.4.2 Effect of effluents on water quality and aquatic life

Various pulping processes require different quantities of water, and all of these processes are highly water-intensive. The quality of wastewater produced during pulping and bleaching varies significantly due to differences in processes and chemical compositions. About 200 m³ of water are utilized per ton of pulp produced, with a significant portion being highly polluted, particularly the wastewater generated from the chemical pulping process. Among the different stages of the process, wood preparation, pulping, pulp washing, screening, washing, bleaching, paper machine, and coating operations stand out as the most significant sources of water pollution. Wastewaters originating from the pulping stage mainly consist of wood debris, soluble wood materials, and certain chemicals from the chemical pulping process. In contrast the wastewater from the bleaching process exhibits distinct qualities. While these wastewaters may not possess higher strength than pulping process wastewater, they do contain toxic components.

The untreated wastewater originating from pulp and paper mills is commonly released into waterways, leading to detrimental effects on water quality. This discharge results in the water acquiring a discernible brown hue that can be observed from considerable distances. Moreover, the effluents contain elevated levels of biological and chemical oxygen demands (BOD and COD), as well as lignin compounds and their derivatives. In their undiluted form, these effluents pose toxicity to aquatic organisms and demonstrate pronounced mutagenic properties. Additionally, certain compounds within the effluents resist biodegradation and have the potential to accumulate within the aquatic food chain.

Research has revealed diverse reactions within downstream fish communities residing near bleached kraft pulp mills. These reactions encompass postponed sexual maturation, diminished gonad dimensions, modifications in fish reproductive patterns, and a

decrease in secondary sexual attributes. A notable concern arising from pulp and paper mills is the spread of sewage fungus in the rivers that receive their discharges. The dense coloration and elevated turbidity resulting from suspended particles can induce water cloudiness and the coating of river or lake bottoms, with extensive covering potentially instigating anaerobic decomposition underneath, thereby discharging hydrogen sulfide into aquatic ecosystems. This darkness and covering can also diminish photosynthetic activity in aquatic plants, initiating a chain of adverse effects on the aquatic ecosystem, ultimately affecting the growth of primary, secondary, and tertiary consumers. Consequently, it is imperative to eliminate color and toxicity from these effluents before they are discharged into surface waters.

2.4.3 Air emission from pulp and paper and impact on local air quality

Pulp and paper mills are notorious for being significant emitters of air pollution, posing considerable environmental challenges. In the pulp and paper industry, air pollution mainly arises from the production of various volatile sulfur compounds during the sulfite pulping process. This includes the release of odorous gases such as hydrogen sulfide, methyl mercaptan, and dimethyl sulfide, which originate from reduced sulfur compounds. Additionally, sulfur and nitrogen oxide particulates are emitted from various processing units, including digesters, multiple-effect evaporators, and recovery plants (Gupta et al., 2019).

Pollutants emitted from pulp and paper mills frequently consist of intricate mixtures of inorganic metallic and nonmetallic waste products. Manganese, chromium, iron, and cadmium are among the metals released from paper mills; nonmetallic elements include mostly sodium, calcium, magnesium, sulfate, and compounds based on chlorine. The bleaching, washing, and pulping processes are the sources of these contaminants. Among other factors the content of paper effluent and the existence of inorganic nonmetallic components determine the toxicity levels of heavy metals (Chandra et al., 2018). The harmful effluents generated during the pulp and paper manufacturing process not only release GHGs but also contribute to acid rain, ultimately exacerbating climate change by fueling global warming (Bajpai, 2015).

2.4.4 Biodiversity loss

The profound impact of industrialization and aggressive economic development on biodiversity has led to a gradual, and in some cases, rapid extinction of species and the depletion of green cover. This has

resulted in significant global environmental degradation. Paper mills play a crucial role in industrial growth and economic development, with Pakistan boasting a total of 163 Paper mills in Pakistan. The majority of these paper mills rely on forest-based raw materials such as bamboo and forest wood, exerting a direct influence on ecology and biodiversity through the extensive consumption of forest products and the simultaneous release of substantial amounts of toxic waste into the environment (Gupta et al., 2019). Globally, vast expanses of untouched forests are being cut down to produce paper pulp, contributing to the troubling trend of deforestation. The paper industry plays a significant role in releasing harmful chemicals into water and air, posing a threat to ecosystems. The substantial discharge negatively impacts the water quality in receiving wetlands, endangering aquatic life, plankton diversity, and the fundamental components of the food chain, including endangered species. This, in turn, contributes to issues such as ozone layer depletion, acid rain, global warming, and respiratory problems. The papermaking process generates a considerable amount of solid waste, a significant portion of which is often disposed of on cropland or in suburban areas. This disposal method raises concerns about potential contaminants in the soil and runoff into nearby water bodies. As growth and development take precedence, it is essential for industries to prioritize biodiversity to establish sustainable practices. Biodiversity conservation plays a vital role in supporting livelihoods and improving socioeconomic conditions. To expedite sustainable development, industries must willingly engage in environmental protection and adopt a sustainable approach to utilizing natural resources. To achieve a balance between the demands of forest-based resources, their regeneration, environmental maintenance, and biodiversity conservation a comprehensive work plan is essential. Paper mills must establish robust research and development facilities to explore sustainable resource practices and explore alternatives to forest-based materials in paper manufacturing. It is crucial to upgrade existing technologies to effectively combat environmental pollution. Mills should also take precautions in the operation of effluent treatment mechanisms to reduce the toxicity of released effluents, conducting periodic examinations to assess the pollution load. Sampling for analysis should occur at the point of release or at the inlet. The aeration system in the effluent treatment plant should be maintained in optimal condition. If treated effluent is used for irrigation, it is imperative to ensure the addition of appropriate nutrients to support crop growth.

2.5 Negative impacts on human well-being

Throughout the process of creating paper either from pulp or materials that have been recycled, a variety of extracts are incorporated to enhance the final product properties. Numerous chemical additives are employed in different stages such as bleaching, digestion, pulping, and ultimate handling, including sizing, calendaring, and changing. These additives have the potential to engage with food substances, leading to potential negative health effects in humans (Fig. 2.6). The overall movement, which refers to the transfer of every element derived from the packaging material to the nutrition, is a critical consideration. Specific migration, on the contrary, pertains to the migration of a particular substance. According to the European Union guidelines (2002/72), the maximum permissible migration from packaging material to food is set at 60 mg/kg. For small containers under 500 mL, flexible films, and nonfillable items, this limit is reduced to 10 mg/dm². Several studies have investigated the migration of inorganic hydrocarbon wax from waxed paper to food surfaces. These studies found that wax migration increases with higher temperatures. In the outer layer of bread samples the mineral hydrocarbon wax content reached up to 50 mg/kg. For toffee products, levels ranged from 110 to 1300 mg/kg, while wrapped

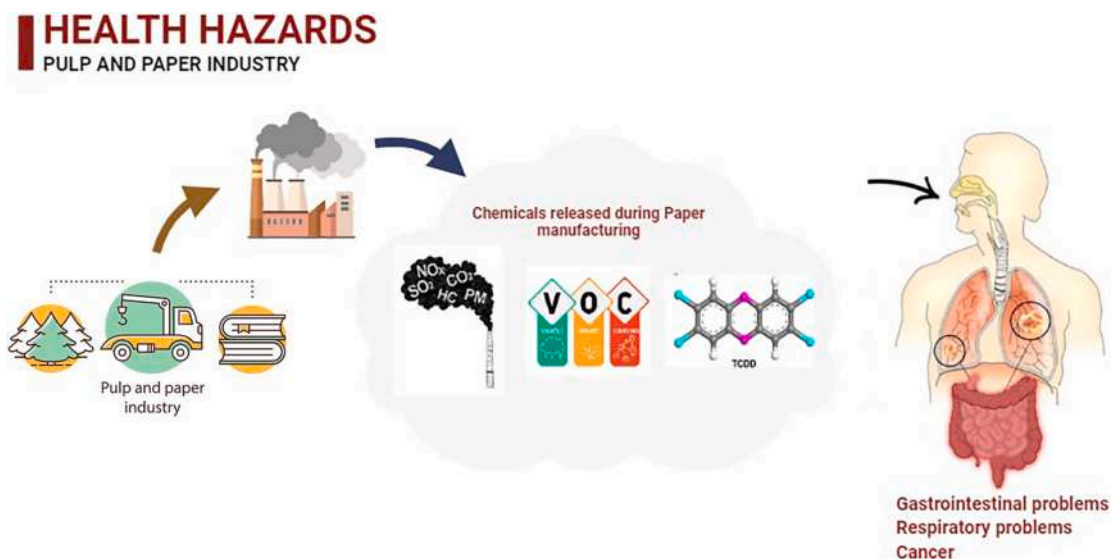


Figure 2.6 Human health hazards from pulp and paper industry.

sweets showed wax content between 12 and 1300 mg/kg on the product surface (Castle et al., 1993; Castle et al., 1994).

Polyfluorinated surfactants (PFS) are widely utilized to provide water and oil resistance to paper and paperboard products. These surfactants, especially those with a molecular weight over 3600 g/mol, along with their degradation products, are toxic and can disrupt endocrine function. Alarming, PFS have been detected in a variety of food items packaged in paper bags or cardboard boxes, including microwavable popcorn, burger boxes, rye bread mix, coffee, noodles, chocolate cake, and curry chicken with jasmine rice (Trie et al., 2011). Bisphenol A and its structural analog Bisphenol S are used as pigment developers in thermal receipt paper. These compounds are frequently found on food packaging and containers in large-scale retail food outlets (Pivnenko et al., 2018). Bisphenol A is known to cause endocrine disruption, leading to its proposed ban from usage in thermal paper starting in 2020. Promoting paper recycling is a key aspect of addressing sustainability and environmental concerns. Despite these efforts, there have been concerns about food containers made from recycled paper and paperboard being a significant contributor to the migration of mineral oil into foodstuffs. Within a few weeks, food items become infiltrated with hydrocarbons that consist of up to 20 carbon atoms (n-C20), while those with 20–28 carbon atoms (n-C20–28) do so at low rate. The primary source of mineral oil has been identified as the inks in printed recycled board, which contain mineral oil levels ranging from 300 to 1000 mg/kg (less than n-C28). However, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) has set a maximum daily intake limit for < n-C28 at 0.01 mg/kg body weight (Biedermann & Grob 2010). The migration of organic pollutants from recycled paperboard is influenced by the volatility of the substances and the composition of the recycled paper. The extent of migration is also directly related to the fat content of the food (Triantafyllou et al., 2007).

2.6 Food chain contamination

The waste produced through the pulp and paperboard factories has a direct or indirect influence on the agricultural and fisheries-related food chain. The discharge of wastewater into surface water bodies renders them inhospitable for the proliferation of microbes, plankton, and small fish, consequently hindering the development of greater fish intended for the marketplace. Additionally, mutagens found in the wastewater have been identified in zooplankton, roaches, and seals near the outlets of the pulp and paper industry (Stepanova et al., 2000). The bioassays utilizing plant-derived

materials employing *Allium cepa* and *Tradescantia* sp also verify the genotoxic impact of wastewater (Bhat et al., 2019). Waste discharged by the pulp industry alters the typical microbial compositions in surface water, with bacterial groups like *Fusibacter* and *Desulfo-bulbus* serving as indicators of pollution. Moreover, the buildup of harmful substances like polyhydroxybutyrates and persistent organic pollutants renders these waters toxic to secondary and tertiary consumers, leading to diverse health issues (Fig. 2.7) (Guo et al., 2016). A research investigation conducted in Assam, India, revealed elevated levels of cadmium and chromium pollution attributed to the release of effluents from paper mills (Borah et al., 2018). The irrigation with water contaminated by heavy metals results in phytotoxicity in plants, posing a threat to human health when consumed and causing severe health issues (Muchuweti et al., 2006). Therefore both primary producers and later individuals in the food hierarchy experience adverse effects, impacting the overall functioning of the ecosystem (Vashi et al., 2018). The overall danger of pulp and paper discarded in the tested soil microorganisms was significant in terms of toxicity. The ethanol extracts from these wastes resulted in a reduction in the luminescence of *Vibrio fischeri*, indicating the toxic impact of the waste (Fraser et al., 2009).

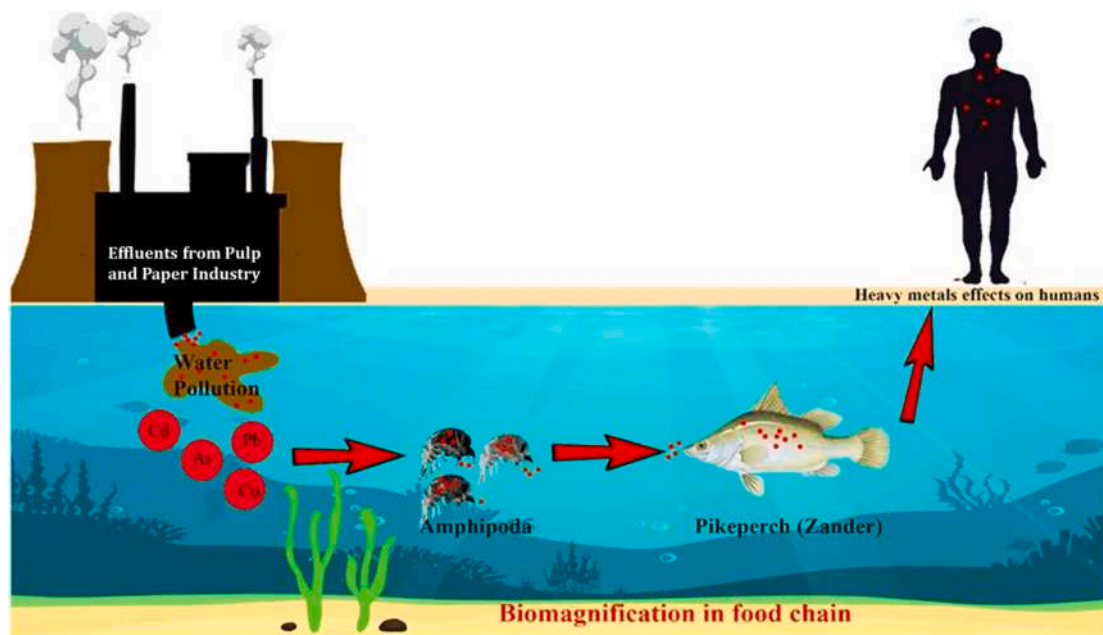


Figure 2.7 Food chain contamination due to pulp and paper industry ultimately affecting human health (Dehghani et al., 2022).

Furthermore, [Song et al. \(2018\)](#) conducted an analysis to examine the toxicological impact of fertilizers derived from waste liquor of pulping on soil-dwelling earthworms. The use of fertilizers resulted in elevated levels of reactive oxygen species and malondialdehyde, contributing to an increase in free radicals and antioxidant enzymes. This surge in oxidative stress caused DNA damage within 14 days of application, highlighting the detrimental impact of pollutants.

2.7 Mitigation strategies

Due to the substantial waste generated by the pulp and paper industry, there is a pressing requirement for strategies to address forthcoming challenges and ensure the safe disposal of waste materials. Owing to technological advancements, diverting waste to various industries for secondary utilization has become more feasible. The utilization of such waste not only enhances industry efficiency but also mitigates the environmental risks associated with waste. Refer to [Table 2.1](#) for a comprehensive summary of pollutants originating from the paper industry, their corresponding health hazards, and the corresponding treatment technologies.

2.7.1 Developing methods for treating wastewater

Various approaches have been employed to minimize both carbon-based and inert contaminants in pulp and paper wastewater. The oxidation process at an advanced level has proven effective in treating water across various sectors and solid waste from municipalities ([Cesaro et al., 2019](#)). The treatment of waste is notably influenced by ozonation and biological treatment ([Bajpai, 2017](#)). [Purkarová et al. \(2018\)](#) conducted black liquor gasification in 2018, achieving a carbon efficiency of 24%. Their findings suggested that the existence of lignin within the black liquor led to apparatus clogging. Despite this challenge the process resulted in the production of hydrogen sulfide, a highly toxic substance harmful to living organisms. Derived from steel mill waste, polymeric ferric aluminum sulfate chloride served as a composite coagulant alongside polyacrylamide, resulting in a substantial reduction of Chroma levels, standing at 71.2%, while COD is recorded at 65.3%. This approach demonstrated effectiveness at an industrial scale ([Yang et al., 2019](#)). Aerobic granulation proves to be an effective approach for treating wastewater with elevated levels of BOD and COD, offering advantages such as a reduced ecological impact, heightened tolerance to toxicity, and improved resilience to impact ([Morais et al., 2016](#)). Granular sludge with aerobic characteristics eliminates 54% of tannins and lignin extracted from wastewater ([Vashi et al., 2019](#)).

Table 2.1 Types of waste, their harmful effects, and sustainable applications of treatments of various waste types generated by the pulp and paper industry.

Sr. no.	Types of waste and their harmful effects	Treatment methods	Sustainable results	Bibliography
1.	Sludge Effects: Leaching of nutrients in the soil and the release of greenhouse gases like methane and nitrous oxide	Anaerobic digestion The application of mathematical modeling	Production of methane	Yang et al. (2019)
2.	Wastewater Effects: Respiratory dysfunction adversely affects the reproductive systems of both aquatic and terrestrial organisms	Coagulant containing polyacrylamide without organic components	Decrease in chemical oxygen demand and chromaticity	Vashi et al. (2018)
3.	Black liquor Effects: Respiratory irritation, skin and eye discomfort, allergic responses, and potential mutagenic effects	Membrane filtration system method Biological treatment method	Decreased output of evaporator burdens, phenolic compounds, dissolved solids, and a reduction in color pigments	Raj et al. (2018)
4.	Heavy metals Effects: Toxic effects on the nervous system, heart, kidneys, potential for causing cancer, and hindered growth	Sedimentation treatment Biological treatment	Diminished buildup of heavy metals such as cadmium (Cd), manganese (Mn), lead (Pb), and chromium (Cr)	Pokhrel and Viraraghavan (2004)
5.	Adsorbable organic halogens (AOX) Effects: Persistent respiratory issues, feelings of nausea, and persistent headaches	Application of oxygen-based bleaching	Diminished manufacturing of chlorinated organic compounds	Sarma (2014)

(Continued)

Table 2.1 (Continued)

Sr. no.	Types of waste and their harmful effects	Treatment methods	Sustainable results	Bibliography
6.	Biosludge Effects: Genotoxic and carcinogenic to aquatic fish, leading to the inhibition of egg production	Anaerobic digestion (including pyrolysis and incineration processes)	Decreased harm to aquatic life resulting from the elimination of both carcinogenic and noncarcinogenic substances	Fraser et al. (2009)
7.	Organic and inorganic pollutants Effects: Identified as endocrine-disrupting chemicals (EDCs), these substances are associated with symptoms such as dizziness, carcinogenic effects on fish, bronchitis-related lung damage, and mortality, among other concerns	Before initiating the breakdown of secondary treatment	Minimized gradual deterioration and buildup	Monte et al. (2009)
8.	Sedimented fiber Effects: Toxic and damaging effects on cells and genetic material	Anaerobic treatment method	Simple mitigation and the generation of methane	Song et al. (2018)

The microbial fuel cell represents a novel method for both wastewater treatment and energy generation. Some of the advantages include direct electrical energy generation, elimination of the need for ventilation, and versatile applications in both centralized and decentralized settings (Neto et al., 2018). The utilization of biosorbents for addressing wastewater in the pulp and paper industry is a burgeoning method to eliminate chromophoric compounds from the waste. The creation of absorbents using agroindustrial residues offers a cost-effective and straightforward approach to wastewater treatment (Kakkar et al., 2018). The efficient treatment of wastewater shows promise through the use of advanced oxidation processes. By optimizing the Fenton process with response surface methodology a significant reduction in COD levels was achieved, lowering them from 32,000 to 1920 mg/L (Kumar et al., 2019). The utilization of advanced oxidation processes resulted in a 94% reduction in COD. Additionally, electrocoagulation proved to be another effective technology for waste treatment, exhibiting removal efficiencies of 85.3% for ammonia, 98.5% for color, 83.4% for total suspended solids (TSS), and 79.5% for COD (Izadi et al., 2018).

2.7.2 Technologies for treating primary and secondary sludge

The environmental influence of pulp and paper mill sludge is noteworthy due to its organic and inorganic mechanisms. In a 2019 study conducted in Sweden by Mohammadi et al. (2019), the investigators engaged the process of decomposition without the presence of oxygen on sludge derived from pulp and paper mills. This study examines the combination of anaerobic absorption with incineration and the integration of incineration with pyrolysis (burning combined with pyrolysis) to evaluate and compare the results. Within the system of anaerobic digestion and pyrolysis the process resulted in the production of biochar, contributing to enhanced forest efficiency and the development that is environmentally responsible for ecosystems in countries grappling with substantial waste generation. Additionally, anaerobic digestion played a crucial role in extracting lignin from sludge in its modified form, making lignin accessible for degradation and conversion into valuable products (Khan & Ahring, 2019). Biogas generation through anaerobic digestion has been documented; however, achieving successful large-scale production remains a challenge (Lopes et al., 2018). Utilizing enzymes instead of chemicals in the bioleaching process is an alternative method for minimizing pollutants within the pulp and paper sector. Xylanase and laccase are commonly employed in the bioleaching of pulps derived from wood

and agricultural sources. The incorporation of enzymes results in reduced chlorine intake and improved quality of the product, particularly regarding luminosity and intensity (Kumar et al., 2019).

2.7.3 Utilization of computational tools in the process of selecting technology

Analyzing studies involving computation proves valuable in measuring the most appropriate technologies for a specific industry, aiding in the lessening of waste emissions by seeing industry infrastructure, raw materials, and processing techniques. Akhundzadeh and Shirazi (2017) have familiarized a practical 2-filter fuzzy decision-making method that enables the assessment and selection of technology. This method aids industries prevent future losses and contributes to environmental preservation. The use of metric based on Slack and the Malmquist-Luenberger (ML) index in China proves to be effective in assessing and managing environmental impact measures. The ML index, derived from the Malmquist index (M-index), gauges the productivity of decision-making units as a comprehensive factor over time. This index permits for the calculation of mechanical changes and efficiency adjustments in the presence of unfavorable outputs. Concurrently, the Slack-based measure considers adverse outputs, providing a comprehensive evaluation of eco-efficiency (Yu et al., 2016).

2.8 Emerging technologies of treatment

Following are the various emerging technologies for wastewater treatment within the pulp and paper industry. Each technology is designed to enhance the efficiency and effectiveness of wastewater management, contributing to sustainable practices and environmental conservation.

2.8.1 Biological treatment

Treatment of wastewater using biological processes aims to break down contaminants present in waste through the activity of microbes. These microbes make use of the pollutants as nutrients for their survival and reproduction. However, it is essential for the pollutants to be soluble in water and nontoxic to facilitate this degradation process (Bajpai, 2012).

2.8.2 Membrane technologies

Within the realm of the pulp and paper sector, membrane treatment plays a crucial role in optimizing loop closure, leading to a reduction in both fresh water intake and the need for extensive

wastewater treatment. Membrane processes serve various purposes, including enhancing product quality by minimizing pollution in loop water, facilitating the utilization of treated effluent in manufacturing processes, recovering precious elements like application of pigments to coat surfaces while minimizing environmental impact through enhanced quality of discharged water. Some mills have already implemented complete membrane filtration for effluents from the pulp and paper industry. Several years ago, a newsprint paper mill adopted nanofiltration treatment for its total effluent. The key advantage of nanofiltration lies in its ability to recover water for recirculation, allowing the use of clean water even under the most challenging circumstances of the paper mill.

2.8.3 Anaerobic treatment

Since the early 1980s, the widespread adoption of anaerobic technology for treating industrial effluents has been evident in the pulp and paper industry. Numerous installations, numbering in the hundreds, are effectively treating diverse wastes from various pulp and paper factories. The primary application of anaerobic treatment is observed in effluents generated by recycled paper mills, particularly in the production of containerboard. Additionally, wastewater from processes like pulping through mechanical means with peroxide bleaching, pulping process involving partial chemical treatment, and condensates from sulfite and kraft evaporators can be practiced anaerobic processing ([Bengtsson et al., 2008](#)).

2.8.4 Aerobic treatment

Aerobic microorganisms, relying on oxygen for metabolic activity, play a crucial role in effluent treatment. Aeration equipment designed for specific purposes introduces oxygen into the discharge in the form of air through the aerobic method. This method facilitates the total breakdown of organic components in paper mill wastewater. Plants that work aerobically demonstrate increased sturdiness and reduced vulnerability to variations in both parameters of both the effluent and the plant ([Barwal & Chaudhary, 2014](#)).

2.9 Conclusion and future trend

The industry of pulp and paper generates a significant volume of surplus per ton of paper make, leading to severe repercussions for both marine and terrestrial creatures. The wastewater poses healthiness risks ranging from skin discomfort to hereditary conditions. Despite regulatory efforts to promote sustainable environmental

practices, achieving compliance in the industrial sector remains a major task. Addressing this issue necessitates the adoption of latest technological developments to alleviate the burden on industries. Emerging methods such as formation through aerobic granulation and coagulant precipitation derived from steel mill waste offer affordable and eco-conscious substitutes. Recent developments in electrocoagulation and adsorbent-based wastewater treatment also show promise. Innovative approaches, such as electricity generation through microbial fuel cells and bioremediation using potential microbes, could serve as pivotal steps toward both energy production and waste disposal. However, relying solely on technology proves insufficient in favor of lasting progress. The integration of artificial intelligence databases and computer-based analysis can assist industries in identifying effective integration methods to reduce their environmental footprint. Leveraging computational tools can enhance efficiency in energy utilization and minimize the creation of waste utilizing suitable models within the pulp and paper sector at each processing stage. The ongoing development of more sophisticated models to integrate industry-based technology is imperative for sustainable progress.

Conflict of interest

The authors declare no conflict of interest regarding the publication of this chapter.

List of acronyms

AOX	Adsorbable organic halogens
BOD	Biological oxygen demand
COD	Chemical oxygen demand
EDCs	Endocrine-disrupting chemicals
GDP	Gross domestic product
GHGs	Greenhouse gasses
JECFA	Joint FAO/WHO Expert Committee on Food Additives
PFS	Polyfluorinated surfactants
PPI	Paper and pulp industry
TSS	Total suspended solids

References

- Akhundzadeh, M., & Shirazi, B. (2017). Technology selection and evaluation in Iran's pulp and paper industry using 2-filtered fuzzy decision making method. *Journal of Cleaner Production*, 142, 3028–3043.
- Bajpai, P. (2017). *Pulp and paper industry: Emerging waste water treatment technologies*. Elsevier.

- Bajpai, P. (2012). *Biotechnology for pulp and paper processing*. US: Springer. <https://doi.org/10.1007/978-1-4614-1409-4>.
- Bajpai, P. (2015). *Basic overview of pulp and paper manufacturing process*. Springer Science and Business Media LLC, 11–39. https://doi.org/10.1007/978-3-319-18744-0_2.
- Barwal, A., & Chaudhary, R. (2014). To study the performance of biocarriers in moving bed biofilm reactor (MBBR) technology and kinetics of biofilm for retrofitting the existing aerobic treatment systems: A review. *Reviews in Environmental Science and Bio/Technology*, 13(3), 285–299. <https://doi.org/10.1007/s11157-014-9333-7>.
- Bengtsson, S., Werker, A., Christensson, M., & Welander, T. (2008). Production of polyhydroxyalkanoates by activated sludge treating a paper mill wastewater. *Bioresource Technology*, 99(3), 509–516. <https://doi.org/10.1016/j.biortech.2007.01.020>.
- Bhat, S. A., Cui, G., Li, F., & Vig, A. P. (2019). Biomonitoring of genotoxicity of industrial wastes using plant bioassays. *Bioresource Technology Reports*, 6, 207–216. <https://doi.org/10.1016/j.biteb.2019.03.005>, <https://www.journals.elsevier.com/bioresource-technology-reports>.
- Borah, P., Singh, P., Rangan, L., Karak, T., & Mitra, S. (2018). Mobility, bioavailability and ecological risk assessment of cadmium and chromium in soils contaminated by paper mill wastes. *Groundwater for Sustainable Development*, 6, 189–199. <https://doi.org/10.1016/j.gsd.2018.01.002>.
- Castle, L., Kelly, M., & Gilbert, J. (1993). Migration of mineral hydrocarbons into foods. 2. Polystyrene, ABS, and waxed paperboard containers for dairy products. *Food Additives and Contaminants*, 10(2), 167–174. <https://doi.org/10.1080/02652039309374140>.
- Castle, L., Nichol, J., & Gilbert, J. (1994). Migration of mineral hydrocarbons into foods. 4. Waxed paper for packaging dry goods including bread, confectionery and for domestic use including microwave cooking. *Food Additives and Contaminants*, 11(1), 79–89. <https://doi.org/10.1080/02652039409374204>.
- Cesaro, A., Belgiorno, V., Siciliano, A., & Guida, M. (2019). The sustainable recovery of the organic fraction of municipal solid waste by integrated ozonation and anaerobic digestion. *Resources, Conservation and Recycling*, 141, 390–397. <https://doi.org/10.1016/j.resconrec.2018.10.034>.
- Chandra, R., Sharma, P., Yadav, S., & Tripathi, S. (2018). Biodegradation of endocrine-disrupting chemicals and residual organic pollutants of pulp and paper mill effluent by biostimulation. *Frontiers in Microbiology*, 9(MAY). <https://doi.org/10.3389/fmicb.2018.00960>, <https://www.frontiersin.org/articles/10.3389/fmicb.2018.00960/full>.
- Dehghani, A., Aminjan, A.R., & Dehghani, A. (2022). Trophic transfer, bioaccumulation, and health risk assessment of heavy metals in Aras River: Case study: Amphipoda–zander–human. *Environmental Science and Pollution Research*, 29(20), 30764–30773. <https://doi.org/10.1007/s11356-021-18036-7>.
- Fraser, D. S., O'Halloran, K., & van den Heuvel, M. R. (2009). Toxicity of pulp and paper solid organic waste constituents to soil organisms. *Chemosphere*, 74(5), 660–668. <https://doi.org/10.1016/j.chemosphere.2008.10.065>.
- Guo, J., Zhao, L., Lu, W., Jia, H., & Sun, Y. (2016). Bacterial communities in water and sediment shaped by paper mill pollution and indicated bacterial taxa in sediment in Daling River. *Ecological Indicators*, 60, 766–773. <https://doi.org/10.1016/j.ecolind.2015.08.028>.
- Gupta, G. K., Liu, H., & Shukla, P. (2019). Pulp and paper industry-based pollutants, their health hazards and environmental risks. *Current Opinion in Environmental Science & Health*, 12, 48–56.
- Izadi, A., Hosseini, M., Darzi, G. N., Bidhendi, G. N., & Shariati, F. P. (2018). Treatment of paper-recycling wastewater by electrocoagulation using aluminum and iron electrodes. *Journal of Environmental Health Science and Engineering*, 16(2), 257–264. <https://doi.org/10.1007/s40201-018-0314-6>.

- K., B., Cetecioglu, Z., & Ince, O. (2011). *Pollution prevention in the pulp and paper industries*. InTech. <https://doi.org/10.5772/23709>.
- Kakkar, S., Malik, A., & Gupta, S. (2018). Treatment of pulp and paper mill effluent using low cost adsorbents: An overview. *Journal of Applied and Natural Science*, 10(2), 695–704. <https://doi.org/10.31018/jans.v10i2.1769>.
- Khan, M. U., & Ahring, B. K. (2019). Lignin degradation under anaerobic digestion: Influence of lignin modifications – A review. *Biomass and Bioenergy*, 128. <https://doi.org/10.1016/j.biombioe.2019.105325>, <http://www.journals.elsevier.com/biomass-and-bioenergy/>.
- Kumar, V., Suraj, P., & Ghosh, P. (2019). Optimization of COD removal by advanced oxidation process through response surface methodology from pulp & paper industry wastewater. *Journal of Scientific and Industrial Research*, 78(6), 386–390. <http://nopr.niscair.res.in/handle/123456789/46>.
- Lopes, A. D. C. P., Silva, C. M., Rosa, A. P., & de Ávila Rodrigues, F. (2018). Biogas production from thermophilic anaerobic digestion of kraft pulp mill sludge. *Renewable Energy*, 124, 40–49.
- Mohammadi, A., Sandberg, M., Venkatesh, G., Eskandari, S., Dalgaard, T., Joseph, S., & Granström, K. (2019). Environmental performance of end-of-life handling alternatives for paper-and-pulp-mill sludge: Using digestate as a source of energy or for biochar production. *Energy*, 182, 594–605. <https://doi.org/10.1016/j.energy.2019.06.065>.
- Monte, M. C., Fuente, E., Blanco, A., & Negro, C. (2009). Waste management from pulp and paper production in the European Union. *Waste Management*, 29(1), 293–308. <https://doi.org/10.1016/j.wasman.2008.02.002>.
- Morais, I. L. H., Silva, C. M., & Borges, C. P. (2016). Aerobic granular sludge to treat paper mill effluent: Organic matter removal and sludge filterability. *Desalination and Water Treatment*, 57(18), 8119–8126. <https://doi.org/10.1080/19443994.2015.1022803>, <http://www.tandfonline.com/toc/tdwt20/current>.
- Muchuweti, M., Birkett, J. W., Chinyanga, E., Zvauya, R., Scrimshaw, M. D., & Lester, J. N. (2006). Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health. *Agriculture, Ecosystems & Environment*, 112(1), 41–48. <https://doi.org/10.1016/j.agee.2005.04.028>.
- Neto, S. A., Reginatto, V., & De Andrade, A. R. (2018). Microbial fuel cells and wastewater treatment. In *Electrochemical water and wastewater treatment*. Brazil: Elsevier, 305–331. <http://www.sciencedirect.com/science/book/9780128131602>, <https://doi.org/10.1016/B978-0-12-813160-2.00012-2>.
- Pivnenko, K., Laner, D., & Astrup, T. F. (2018). Dynamics of bisphenol A (BPA) and bisphenol S (BPS) in the European paper cycle: Need for concern? *Resources, Conservation and Recycling*, 133, 278–287. <https://doi.org/10.1016/j.resconrec.2018.01.021>, www.elsevier.com/locate/resconrec.
- Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater—A review. *Science of The Total Environment*, 333(1–3), 37–58. <https://doi.org/10.1016/j.scitotenv.2004.05.017>.
- Purkarová, E., Ciahotný, K., Šváb, M., Skoblia, S., & Beňo, Z. (2018). Supercritical water gasification of wastes from the paper industry. *The Journal of Supercritical Fluids*, 135, 130–136.
- Raj, A., Kumar, S., Singh, S. K., & Prakash, J. (2018). Production and purification of xylanase from alkaliphilic *Bacillus licheniformis* and its pretreatment of eucalyptus kraft pulp. *Biocatalysis and Agricultural Biotechnology*, 15, 199–209. <https://doi.org/10.1016/j.bcab.2018.06.018>, <http://www.journals.elsevier.com/biocatalysis-and-agricultural-biotechnology/>.

- Sarma, B. K. (2014). Impact of paper industry on environment: A case study of the Nagaon paper mill. In *2014 International conference on trends in economics, humanities and management (ICTEHM'14)*, 72–76.
- Song, P., Ping, L., Gao, J., Li, X., Zhu, M., & Wang, J. (2018). Ecotoxicological effects of fertilizers made from pulping waste liquor on earthworm *Eisenia fetida*. *Ecotoxicology and Environmental Safety*, 166, 237–241. <https://doi.org/10.1016/j.ecoenv.2018.09.092>.
- Stepanova, L. I., Lindström-Seppä, P., Hänninen, O. O. P., Kotelevtsev, S. V., Glaser, V. M., Novikov, C. N., & Beim, A. M. (2000). Lake Baikal: Biomonitoring of pulp and paper mill waste water. *Aquatic Ecosystem Health & Management*, 3(2), 259–269. <https://doi.org/10.1080/14634980008657024>.
- Triantafyllou, V., Akridademertzi, K., & Demertzis, P. (2007). A study on the migration of organic pollutants from recycled paperboard packaging materials to solid food matrices. *Food Chemistry*, 101(4), 1759–1768. <https://doi.org/10.1016/j.foodchem.2006.02.023>.
- Vashi, H., Iorhemen, O. T., & Tay, J. H. (2018). Degradation of industrial tannin and lignin from pulp mill effluent by aerobic granular sludge technology. *Journal of Water Process Engineering*, 26, 38–45. <https://doi.org/10.1016/j.jwpe.2018.09.002>.
- Vashi, H., Iorhemen, O. T., & Tay, J. H. (2019). Extensive studies on the treatment of pulp mill wastewater using aerobic granular sludge (AGS) technology. *Chemical Engineering Journal*, 359, 1175–1194. <https://doi.org/10.1016/j.cej.2018.11.060>.
- Yang, S., Li, W., Zhang, H., Wen, Y., & Ni, Y. (2019). Treatment of paper mill wastewater using a composite inorganic coagulant prepared from steel mill waste pickling liquor. *Separation and Purification Technology*, 209, 238–245. <https://doi.org/10.1016/j.seppur.2018.07.049>.
- Yu, C., Shi, L., Wang, Y., Chang, Y., & Cheng, B. (2016). The eco-efficiency of pulp and paper industry in China: An assessment based on slacks-based measure and Malmquist–Luenberger index. *Journal of Cleaner Production*, 127, 511–521. <https://doi.org/10.1016/j.jclepro.2016.03.153>.

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Release, handling, and treatment challenges of wastewaters from pulp and paper industries

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3.1 Introduction

The Confederation of European Paper Industries (CEPI) represents nearly 480 pulp and paper (P&P) and board manufacturing facilities in the European Union. Its associates range from small to multi-national enterprises from 18 countries. CEPI provides key statistics that give insight into the performance and relevance of the P&P industry in terms of world production, but data is primarily related to the European Union. As reported by CEPI, from 2020 to 2022 (CEPI (2021), CEPI (2023)), the worldwide average production was 181.5 million tonnes of pulp, and 418 million tonnes of paper and board.¹ For the considered period, three regions (Asia, Europe, and North America) were responsible on average for 81.3% of the pulp and 92.5% of the paper and board production, with the distribution in Table 3.1.

Even in the face of increasing communication and information transfer by computer, the paper industry is not losing importance in the market, and its growth is expected to continue.² However, this huge P&P industry encounters persistent and complex challenges in terms of sustainable systems. The challenges lie in the introduction of eco-friendly raw materials and updated technologies for P&P manufacturing, the integration of energy- and water-saving practices, the optimization of ongoing treatment processes, and the control of environmental pollution. The goal in resolving these issues is to find solutions that prompt sustainable operations, environmental protection, and regulatory compliance. In this chapter, the focus is on the problems of wastewater release, handling, and treatment.

¹ It is worth to say that the paper and board produced in 2020 has not been considered to estimate the average world production because that year it has been unusually reduced.

² For understanding of the P&P industry terminology, a glossary and a list of acronyms are given at the end of the chapter.

Table 3.1 Distribution of world pulp and paper and board production in 2020–22 (CEPI, 2021, 2023).

Worldwide production →	Pulp production. Million tonnes			Paper and board production. Million tonnes		
	2020	2021	2022	2020	2021	2022
	178.7	183.0	182.7	90.6	412.5	423.4
Production by Region ↓	Pulp production (%)			Paper and board production (%)		
	2020	2021	2022	2020	2021	2022
1. Asia	23.2	23.0	24.5	47.3	47.5	48.2
2. CEPI	20.2	20.7	20.3	21.4	21.7	21.4
Other countries in Europe	5.4	4.9	4.9	4.6	4.3	4.5
3. Latin America	16.8	16.0	17.0	5.5	5.4	5.5
4. North America	32.3	33.2	31.3	19.2	19.1	18.4
5. Rest of the world	2.1	2.2	2.0	2.0	2.0	2.0

The P&P mill facilities discharge significant amounts of effluents that can only enter a "waterbody," a liquid stream, or reservoirs if treated first. The effluents from the mills have large biochemical oxygen demand (BOD), chemical oxygen demand (COD), and a solid black-brown color. It is not unusual for heavy metals, adsorbable organic halogens (AOX), and other toxic content to be present in the effluents. How the treated or untreated effluents impact the environment has been investigated with controversial outcomes. In any event, records of damage to aquatic life and multiple ecosystems exist. From this perspective, increasingly stringent environmental regulations and discharge standards have been put into effect. Compliance with these regulations can be a demanding task in P&P mills, particularly for older facilities that need the most recent treatment technologies. The difficulty in discerning the markers and consequences of release in P&P plants is due to the fort heterogeneous characteristics of the wastewater originating in P&P mills. The effluent attributes depend on the type of feedstock, process technologies, and monitoring practices. They moreover rely on how wastewater is handled, whether the recirculation of effluents is rehearsed for recuperation, or what quantity of water is consumed in the various process stages. Ultimately, the quality of the mill effluent is firmly resolved by the choice of wastewater treatment strategies.

This chapter details the challenges outlined above. Its content is organized as follows. The second section, after the introduction, gives the reader elementary knowledge about P&P processing, including how it differs in raw materials and processes. It furthermore provides basic data about standard and advanced treatment strategies.

It has been acknowledged that P&P mills produce large volumes of wastewater with substantial variations in pollutant load and composition. The complex nature of the wastewater composition makes its handling and treatment more challenging. Thus the third section of this chapter first targets the effluent characterization in P&P mills. After that, water recycling and reuse achieved by closed-cycle operations and zero liquid discharge systems are introduced as advanced options to gain sustainability. This operating mode is discussed here as a practical and highly demanding process choice. Lowering water usage and effluent discharge is increasingly desirable for environmental care and the growth of industrial capacity. However, these systems are technologically demanding and require significant investment. Other valorization strategies are moreover discussed to overcome P&P global challenges, which have to do with generating energy and value-added products, as well as recovery of waste.

The fourth Section describes first how the core processes of P&P mills operate—raw material handling, pulping, bleaching, and papermaking—and explains the challenges of handling wastewater effluents due to deficiencies in the equipment or processes' performance particularly at the Kraft process. The value of process monitoring and the control schemes at different management levels are alike briefly placed under review.

Ultimately, the fifth Section of this Chapter copes with wastewater treatment. Relevant challenges relative to this subject are the following:

Accomplishing high treatment efficiency for removing a wide range of pollutants from wastewater can be difficult. In this context, effluent treatment often needs a combination of physical, chemical, and biological processes, which can be problematic and costly to operate and maintain. Moreover, advanced wastewater treatment is mandatory to remove specific pollutants. At the same time, new technologies increase the complexity and cost of wastewater treatments. Sludge is the last solid waste from wastewater treatment; managing sludge in an eco-friendly, sustainable, and cost-effective manner is significantly complicated. It is a matter of reviewing the solutions to this problem. In other respects, wastewater treatment processes can be energy-intensive, particularly those involving advanced technologies for treatment. Augmented energy consumption adds to the operational costs and ecological issues. It is a question of finding a trade-off between cost and benefits. The development of hybrid strategies for treatments is one of the main challenges to improve the existing technologies.

3.2 Overview of pulp and paper industry

The best available techniques (BAT) Reference Document for the Production of Pulp, Paper and Board (Suhr et al., 2015) defines the paper as:

“A sheet of cellulose fibres with a number of added constituents, when necessary, to affect the quality of the sheet and its fitness for the intended end use.”

Paper is a product offered in the market with commercial forms as varied as its uses. The simple aforementioned definition provides information on the material that is processed to obtain it, and on how it is given specific characteristics that make it useful.

Shortening, paper can be obtained from various raw materials, but the wood from which the pulp (essentially cellulose) is derived is the primary resource. The transformation stages are numerous and incorporate several chemicals and other constituents with different natures. In addition, water consumption in many of the processing stages is very large. At the end of the process, it becomes a waste effluent with a significant amount of undesired organic and inorganic matter.

The introduction to the topic of wastewaters in the P&P industry begins with basic data and notions on resources, inputs, processing stages, and types of products in the P&P industry, which give insights into the nature of the mills effluents. The introductory knowledge furthermore includes distinguishing the principal types of treatment strategies. The whole information is intended to support giving a lecture to the subject of wastewater treatment challenges.

3.2.1 Inputs to P&P mill facilities

Inputs to P&P mills are wood, recycled paper, water, thermal energy in the form of heat and steam, electrical energy, and chemical additives.

Pulp is currently produced from wood. CEPI (2023) reports the use of raw hardwood and softwood materials. In the European Union, in 2022, 25.4% of wood consumption was hardwood, while 74.6% was softwood. The hardwood species include birch, eucalyptus, beech, and aspen, but about 1.5% of the consumed hardwood feedstock are other species. The softwood species comprise pine, spruce, and other species.

Paper can likewise be produced from fibers other than wood. There is a growing trend towards using nonwood plant fibers in the P&P industry. The causes are their renewable nature, suitability to be used as alternatives to hardwood and softwood, and their versatility for producing various paper grades. The nonwood fiber

material is crucial in regions with limited forest resources. These resources include agricultural residues, industrial crops, and plants. More specific, some fiber sources are grasses or Gramineae, cereal straws, corn stalks, bamboo, bagasse, and fibers of bast, seed hull, or leaf. The quality of papermaking raw materials can be significantly improved to be processed in the P&P mills. Other nonwood fibers are flax, hemp, jute, kenaf, cotton, sisal, and abaca ([Abd El-Sayed et al., 2020](#); [Liu et al., 2018](#)). Nonwood fibers demonstrate excellent physical and optical properties. Although they constitute a small portion of global paper and paperboard raw materials, some developing countries derive approximately 60% of their cellulose fiber from nonwood materials.

The recycled material is an additional input in P&P plants. It is composed of fibers and unusual materials. The P&P mills generate significant quantities of non-hazardous solid waste, mainly sludge containing fibers, fillers, and other materials removed during wastewater treatment. Certain types of sludge with high fiber content and suitable physical properties can be reused as raw materials in the paper and board production. The suitability for reuse sludges depends on their fiber content, quality, and physicochemical properties. The strategies for recycling the residual materials within the P&P industry support the “zero waste” challenge. Recycling promotes likewise sustainability, reduces landfills, and mitigates the impacts of incineration ([Simão et al., 2018](#); [Ochoa De Alda, 2008](#)).

[CEPI \(2023\)](#) moreover registers that, in practice, the primary energy furnishing in European P&P mills grouped by this European Confederation originates from gas, fuel oil, coal, other fossil fuels, biomass, and, in a lower proportion, from other sources. The primary source in the European mills is biomass, followed by gas.

A challenge in P&P industry is to use new raw materials for paper production. The issues associated with using nonwood plant fibers in P&P industry are centered on the material processing forms as in papermaking, including collection, transportation, storage, handling, washing, and bleaching. Other issues of nonwood fiber and recycled material incorporation in P&P manufacturing are linked to investigating the factors influencing the strength, adhesion, and water filtration properties of nonwood fiber pulps, as well as their impact on paper properties.

3.2.2 Types of products in the paper industry

The Forest Products Annual Market Review, 2022–23 ([UNECE/FAO, 2023](#)) reports key statistics that give insights into the market of forest products in North America, Europe, Eastern Europe, Caucasus and Central Asian subregion. The records distinguish the classes of

products for the end-user. The data ranges from primary handled products to value-added products. The classification of paper and board product includes graphic papers, sanitary and household papers, packing materials, and other paper and paperboard. These products derive from wood pulp, pulp from fibers other than wood, and from recovered pulp. If recovered paper feeds the process, secondary products are manufactured, which include composite paper and paperboard, special coated and pulp products, carbon and copying papers, household and sanitary paper, packing, carton, boxes, and similar products, other articles of paper and paperboard.

UNECE/FAO (2023) gives a detailed description of each product. The product guide specifies the usage, manufacturing form, sizing, characteristics such as paper grammage, and quality features. Sometimes, manufacture processes are specified too.

3.2.3 The classification of pulping methods in the P&P industry

The wood constituents are cellulose, hemicellulose, and lignin. The wood composition is about 50% water, 45% solid fraction, 25% cellulose, 25% hemicellulose, 25% lignin, and 5% other organic and inorganic materials (Suhr et al., 2015). For lignocellulosic material, the constitution ranges widely: 35%–95% cellulose, 2%–50% hemicellulose, and 3%–31% lignin. Then, pulping is the process of converting lignocellulosic materials into pulp by physical, chemical, or biological means. Making pulp uses mainly wood, but other lignocellulosic materials can also produce paper.

The pulp is the product delivered as a mixture of wood or other lignocellulosic material mixed with water, forming a mass thereupon transformed into paper. Technological advances have been made to produce pulp in several ways—the pulp properties change following the pulp production method. Fig. 3.1 shows the classification of pulping methods. Four broad groups include mechanical, chemical, semichemical, and biological pulping. A comprehensive description of them is reported by Mboowa (2021); Kumar et al. (2020); Reid (1991); and Suhr et al. (2015).

Fig. 3.2 lists the various methods of pulping within the category of sulfite chemical pulping.

Mechanical pulping is a pulping method by grinding wood into fibers. This approach involves shear forces to aid in separating the fibers while the lignin content remains with the fibers. The yield is high in quantity of pulp but results in lower strength. The process retains both lignin and cellulose fibers. Because of their long fiber length, pulps obtained from softwoods improve mechanical strength.

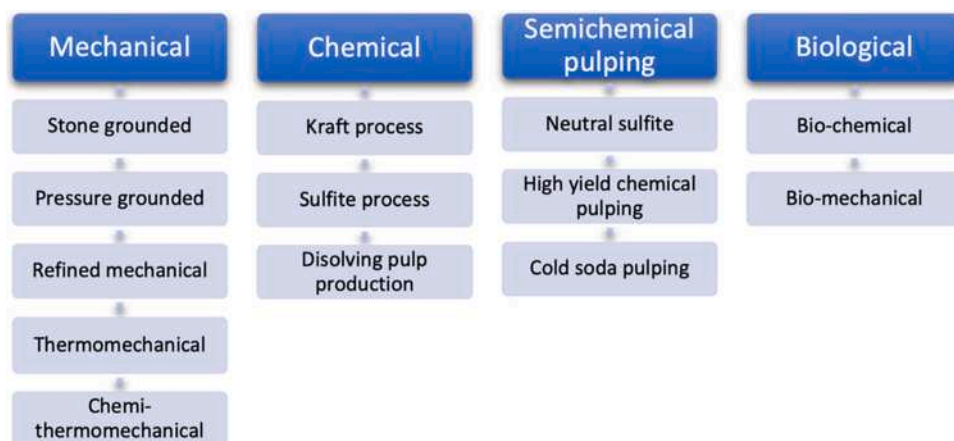


Figure 3.1 Pulping methods.

Source: Condensed from [Mboowa \(2021\)](#) and [Suhr et al. \(2015\)](#).

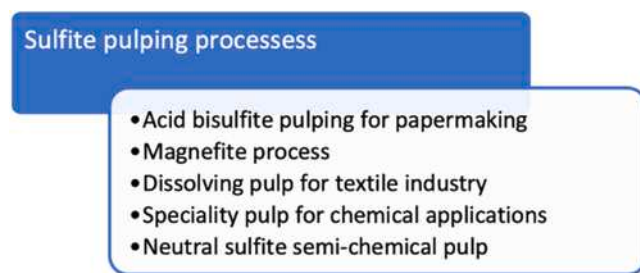


Figure 3.2 Sulfite pulping processes ([Suhr et al., 2015](#)).

Chemical pulping uses chemical substances to dissolve lignin and release fibers. Chemical pulping methods, including Kraft and sulfite processes, can produce superior quality pulp, albeit at the expense of reduced yield. In the Kraft pulping, pulp is obtained by cooking wood chips in a pressure vessel, using NaOH. In the sulfite pulping, pulp is obtained by cooking wood chips in a pressure vessel, using bisulfite liquor.

Semichemical pulping is a method that combines either chemical or mechanical processes, striking a balance between yield and quality. This pulping method involves partial digestion with chemicals.

Integrating biotechnology into pulping by fungal pretreatments to wood chips enhances the pulping process.

Biological pulping is an environmentally friendly alternative that leverages organisms to treat wood chips prior to mechanical pulping. Biopulping removes lignin and hemicelluloses in wood

and increases cellulose content through selective delignification by white-rot fungi (WRF). The prevailing lignin-degrading strains are *Ceriporiopsis subvermispota*, *Trametes versicolor*, and *Phanerochaete chrysosporium*. The pretreatment of wood chips with fungi facilitates fiber separation, decreases energy and chemical consumption during subsequent pulping stages, and offers the potential for improved paper properties. It increases pulp tensile and burst strength and brightness. Other potential benefits of biopulping are improved pulp yield and viscosity.

According to the BAT Reference Document for the Production of Pulp, Paper and Board (Suhr et al., 2015), in the industrial practice, there are five main categories of P&P mills in operation, which regroup facilities following the pulping methods:

- Kraft pulp mills.
- Sulfite pulp mills.
- Mechanical and chemimechanical mills.
- Paper recycling mills.
- Non-integrated mills, including special mills. This group furthermore comprises the papermaking process of mills integrating kraft, sulfite, chemithermomechanical pulp, and chemimechanical mills.

The Kraft process or sulfate process is the most practiced pulping method, accounting for closely 80% of the world production of pulp. From now on, the description of paper manufacturing processes is limited to the Kraft process.

3.2.4 Main P&P manufacture processes

P&P overall process consist of four elementary stages: raw material handling, pulping, bleaching and papermaking. Fig. 3.3 outlines the P&P processing, starting with the feedstock type description. The complete process integrates the widely used Kraft pulping. Thorough theoretical frameworks are provided in the lectures of Mboowa (2021); Singh and Chandra (2019); Suhr et al. (2015); Thompson et al. (2001); Bajpai and Bajpai (1992).

Wood handling engages all procedures to prepare and store raw wood material from the mill gate to the pulping process. In this stage, water is used to spray the wood to avoid the wood drying and darkening. Softwoods and hardwoods are received in the plant yard as logs or chips. The debarking of this material is made with a drum. Then, the bark is removed in a rotating drum. The preferred way is dry debarking, compared to wet systems. In the dry debarking, a low quantity of water is used to wash the log. Afterward, the recirculated water has low pollutant content, and the bark burns quickly. Dry

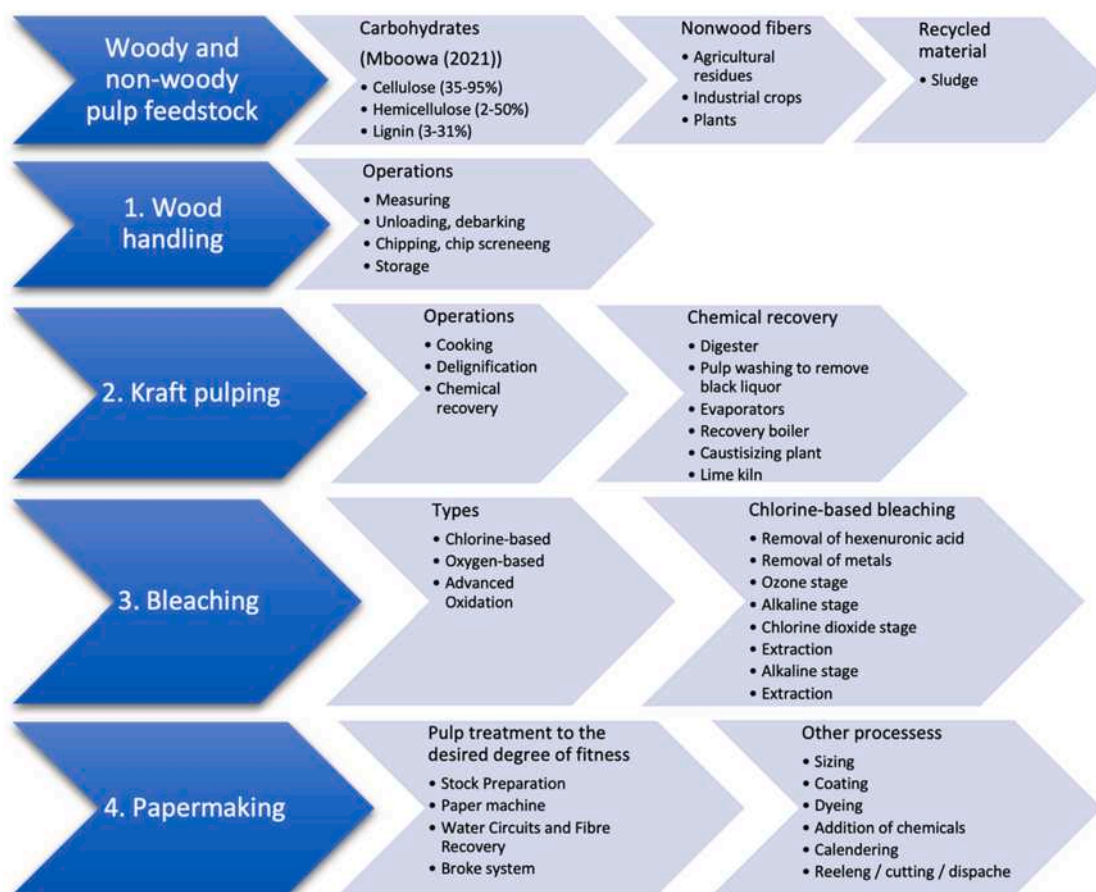


Figure 3.3 P&P overall process. Classification and main characteristics of different stages (Mboowa, 2021; Singh & Chandra, 2019; Suhr et al., 2015; Thompson et al., 2001; Bajpai & Bajpai, 1992).

debarking yields low BOD and COD effluent and some material toxic to aquatic life. The logs become chips to aid in fast and uniform water and chemical infiltration. A proper chip size distribution controls the pulping efficiency and the quality of the pulp. The chip material is stored in piles inside the mill. Some issues with the stock are degradation and reduction in chip quality. The solution to these problems should additionally strongly affect pulping efficiency.

The wood chips are then cooked in the so-called Kraft process. This chemical pulping undergoes degradation and solubilization of lignin. The wood chips are treated in a solution of sodium sulfide Na_2S and Sodium hydroxide, known as lye or caustic soda NaOH to achieve this process. The operating conditions are reported to be at elevated temperature and pressure. Among other reactions, partial

depolymerization of the lignin occurs. The reaction predominantly forms phenolic hydroxyl groups that remove the lignin and hemicellulose in the alkaline liquor. The preserved cellulose fibers are further processed in the papermaking operations.

The chemical recovery unit is a part of the Kraft process. The waste material is a liquid black liquor stream. [Fig. 3.3](#) lists the kraft primary operations and the black liquor recovery sequence. The recovery boiler produces a green liquor, further reduced by a causticizing reaction. The green liquor reacts with lime (CaO) in the reactor to convert the Sodium carbonate Na_2CO_3 to NaOH . The yielded NaOH and lime mud (CaCO_3) are separated. The solid part of the product is burnt in a lime kiln. The molten smelt enters a dissolving tank to form green liquor. The causticized green liquor becomes the “white liquor,” composed mainly of NaOH and Na_2S , used for cooking. So, the white liquor returns to the digester to be reused in pulping.

Most of the Kraft pulp undergoes bleaching before papermaking. The residual lignin causes a brown color. Thus it is degraded and dissolved in a series of bleaching steps. The standard bleaching process is the CEDED sequence composed by C, D, E chemical treatments for high brightness in the bleaching stage. This acronym denotes the succession of treatments as the chlorine, alkali extraction, chlorine dioxide treatment, alkali extraction, and chlorine dioxide treatment. The bleaching operations are then followed by a washing step to release undesired chemicals. The effluents from bleaching are among the most polluting and toxic in the P&P mills.

Papermaking deals with paper and board manufacturing. Papermaking in integrated pulp mills is complex due to the broad assortment of paper products and process configurations in the P&P mills. After papermaking, stock preparation is needed to convert the raw material into a furnished form as the load to the paper machine. The prepared stock is a blend of diluted pulps and chemicals that follow processing on the paper machine. Here, the paper acquires the specified properties.

The plant undergoes water recirculation. A primary water circuit is formed by a water flow rich in fibers, fines, and filler. It is recycled for stock dilution. The secondary water circuit contains water exceeding from sections of sheet-forming, suction, press water, and cleaning water. This water can be treated by sedimentation, flotation, or filtration. The tertiary water circuit contains more than the secondary circuit and other processes. Chemomechanical or biological treatment plants treat this water. In the end, the broke system returns the paper fiber, providing uniformity and quality to the material entering the paper machine. There are intermediate steps, but the ones described here constitute the base process.

3.2.5 Main P&P wastewater treatment technologies

Two compelling industrial practices are currently applied to reduce effluent loads in the P&P mills. The first approach entails process optimization with different operational goals. The second one is implementing wastewater treatments. The treatment approaches are categorized into primary, secondary, and tertiary methods. Fig. 3.4 shows the standard methods for each category (Dagar et al., 2022).

Primary treatments essentially eliminate organic material in the form of suspended solids (SS). Biological treatments use batch reactors fed with microorganisms to break down organic materials, dissolved and fine colloidal matter in wastewater. In aerobic treatments, bacteria, algae, fungus, protozoa, rotifers, and other organisms transform biodegradable matter into CO_2 and H_2O in the

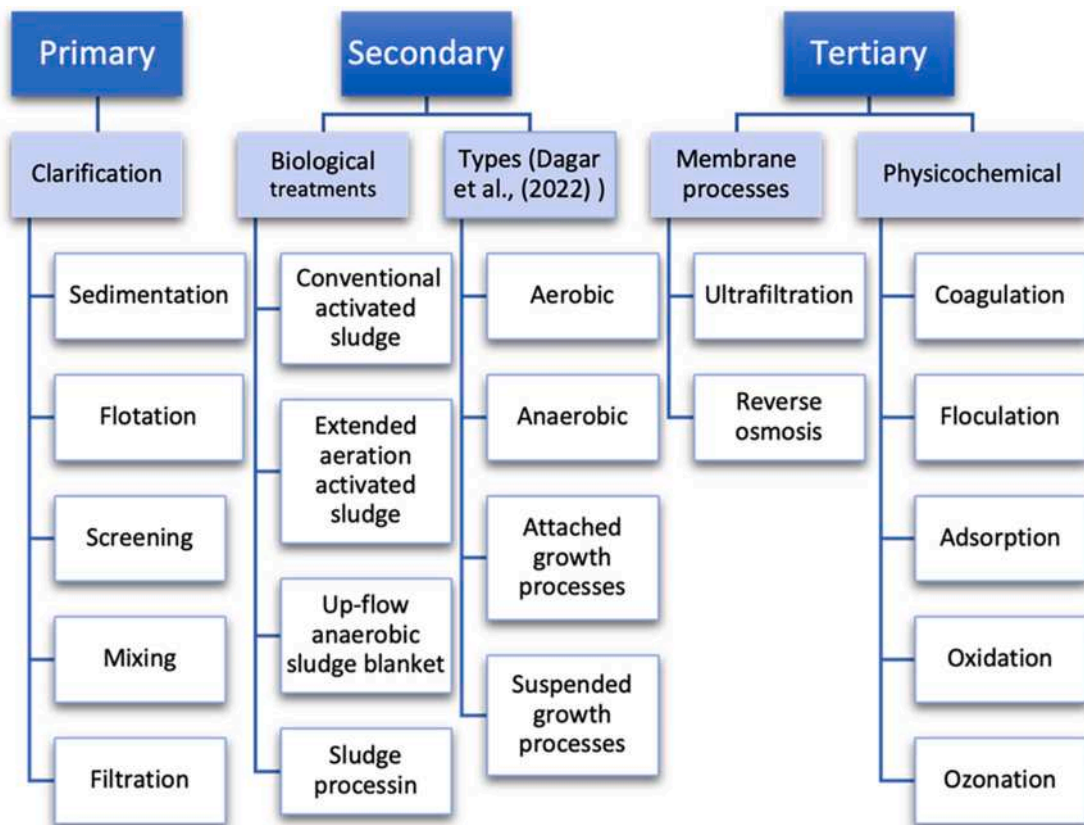


Figure 3.4 Standard wastewater treatments in the P&P industry (Mainardis et al., 2024; Buyukkamaci & Koken, 2010; Sharma et al., 2014; Kamali & Khodaparast, 2015; Thompson et al., 2001).

presence of O_2 . In anaerobic treatments, anaerobic microbes convert organic substrates into CO_2 , CH_4 , and H_2O in the absence of O_2 . The activated sludge process (ASP) and up-flow anaerobic sludge blanket are in widespread use as a biological treatment. The process is carried out in a perfect mixed aeration tank connected to a clarifier. Suspended growth systems are, for example, activated sludge, aerated lagoons, and aerobic digestion. In these systems, waste and microorganisms are combined, whereas oxygen is diffused. The microorganisms are congregated into flocs and settled in the clarifier, whereas part of the sludge is returned to the aeration tank. Otherwise, attached-growth systems have fixed or moving support media. Microorganisms stand and grow on the media (Dagar et al., 2022; Ebrahimi & Najafpour, 2016).

The sequence of chemical coagulation and flocculation followed by sedimentation is a tertiary treatment extensively used to remove SS. Other tertiary treatments are suitable for biologically resistant material. Among others, the following are available, adsorption, membrane filtration, and advanced oxidation. Adsorption with activated carbon has proved to be effective for color. The membrane processes reduce BOD, COD, total dissolved solids (TDS), total suspended solids (TSS), AOX, and color from P&P effluents. The membrane-based techniques include microfiltration, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) (Mainardis et al., 2024; Buyukkamaci & Koken, 2010).

The wastewater content in P&P mills is heterogeneous, which means that its content may vary greatly, as do the toxicity and hazardous levels. Wastewater can contain refractory organic harmful contaminants for which only advanced treatment potentially encounters the release criteria. Refractory pollutants in wastewaters include chlorolignin, chlorophenols, chlorocatechols, chloroguaiacol, cyanide, furan, dioxins, different organic compounds, and heavy metals, like nickel (Ni), zinc (Zn), chromium (Cr), iron (Fe), lead (Pb), arsenic (As) (Wang et al., 2022). Advanced oxidation processes (AOPs) have been reported as effective for wastewater treatment of these effluents resistant to degradation. Fig. 3.5 regroups the main advanced wastewater treatments reported in the literature, their development level ranges from laboratory to industrial practice. The review reported by Kumar et al. (2023) offers a thorough assessment of the performance and challenges of standard and emerging treatment approaches in paper mill wastewater.

Advanced oxidations lead to “total mineralization” by changing recalcitrant or refractory compounds into inorganic substances, such as CO_2 and H_2O_2 , or “partial mineralization” by converting these compounds into more biodegradable materials (Covinich et al., 2014). Advanced oxidation methods use $^{\bullet}OH$ and $SO_4^{\bullet -}$ radicals

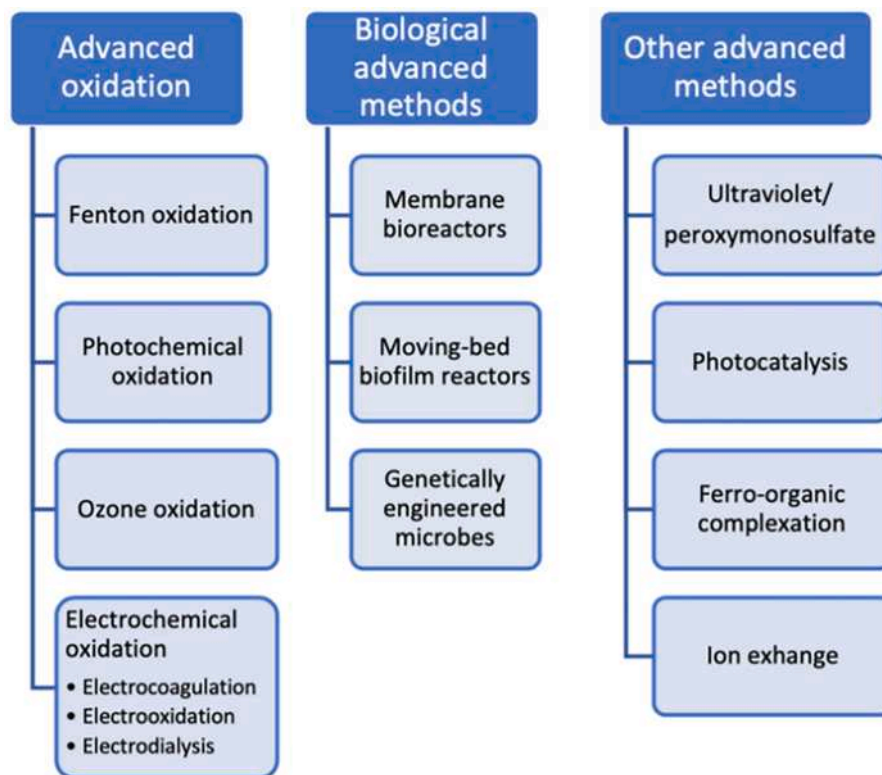


Figure 3.5 Advanced wastewater treatment methods (Wang et al., 2022).

to degrade most of organic matter. The most common oxidants to produce these radicals are peroxymonosulfate (PMS) and hydrogen peroxide (H_2O_2). Ultraviolet (UV) radiation, transition metals and other energy forms activate these two oxidants to easily produce radicals and prevent excessive sludge formation (Wang et al., 2022; Covinich et al., 2014).

Biological remediation advanced methods use bioreactors. Membrane Bioreactors (MBR) combines an ASP and a physical separation using a membrane. Compared to conventional activated sludge, the MBRs are more efficient for liquid-biosolids separation, produce less sludge and lower footprint, but the fouling is the most critical issue. Moving-bed biofilm reactors (MBBR) use plastic carriers immersed in aeration tanks to form biofilms as a media to attract and break down organic matter. These reactors present lower membrane fouling, and production of sludges compared to active sludge and conventional membrane reactors. Moreover, Biotechnology contributes to the development and design of advanced genetically

modified microbes that degrade pollutants. These genetically modified microbes are more powerful than their natural counterparts and have enhanced abilities to break down a wide range of pollutants (Kumar et al., 2023). Some microbial bioreactors used in bioremediation are slurry phase, partitioning, stirred tank, packed bed, airlift, biofilters, and MBR (Tekere, 2019). Challenges in the field of wastewater treatment rely on difficulty to mitigate pollution, toxicity, and harmfulness condition due to the highly heterogeneous characteristics of P&P mills. The solution can be to a certain degree specific. However, all-inclusive wastewater solutions can be designed by developing hybrid treatment schemes.

3.3 Pollutants release challenges from the P&P industry

With a view to pick out the challenges in releasing the effluents of P&P mills, the review below underlines the highly diversified composition of wastewater from this industry. The characteristics of the wastewater are described, and the type of process from which it originates is placed. Then, an overview of common pollutants in the P&P plant aids in contrasting the most toxic stages in P&P production. The measures to characterize the physicochemical and biological properties of effluents in the P&P mills are listed as part of the quality control techniques. The defies in releasing P&P effluents and minimizing environmental impacts are acknowledged from a general viewpoint. In this context, some strategies for valorizing and reducing P&P waste are presented in the end of this section.

3.3.1 Characterization of wastewater in P&P mills

The standard raw material in P&P mills is wood. Secondary materials are non woody biomass, and recycled papers. The input materials have certainly different characteristics. In processing this feedstock into fibers, the mills wash away wastewater rich in wood residues and soluble wood material that is difficult to degrade. This feedstock, which is composed of carbohydrates, mainly causes COD in P&P mill effluents that give a rather low toxicity. Eugenol, a degradation product from lignin depolymerization, and tannins released from wood are likewise toxic compounds present in the effluents of mills. Other wood-derived compounds, such as resin acids, produce more severe toxicity. The wood compounds are released into the effluents during washing, dewatering, and screening. The chemical composition of wastewater in P&P mills changes vastly from one plant to another. While the effluents are

always highly concentrated, their composition falls on a wide range of COD since many classes of substrates can be the basis for manufacture. Softwood, hardwood species, and recycled paper are some examples. The variation in the wastewater composition occurs moreover due to the broad class of pulping and papermaking processes that can be conducted. These steps are configured following the fiber material and the class of end-product. Among the P&P mills stages, the most polluting ones are wood conditioning, pulping, pulp washing, screening, paper machine, bleaching, papermaking, and coating (Hubbe et al., 2016). Pulping causes heavy-duty sewage, mainly by chemical wood pulping, whereas bleaching yields the most toxic pollutants due to the chlorine used for pulp brightening (Pokhrel & Viraraghavan, 2004). Existent in the effluents, too, are unsaturated fatty acids, which are less toxic than resin acids.

3.3.1.1 *The P&P effluents composition*

The effluents of P&P mills are mixtures highly concentrated in organic matter and inorganic compounds, which give rise to challenges in dealing with degradability. These wastes are mainly alkaline, and their compositions vary wildly from one industry to another. They have high CODs and BODs and contain toxic materials. The matter is in the form of dissolved solids, suspended material, or traces. The types of pollutants found in wastewater from the P&P and paper industry belong to the following groups of species (Lindholm-Lehto et al., 2015):

Organic pollutants: There is always lignin and its derivatives in P&P effluents. Furthermore, typically present among the organic material are chlorinated organic compounds, resin acids, fatty acids, sterols, and extractives. These compounds originate from wood debarking, pulp washing, and bleaching.

Extractives: These substances are lipophilic and can be extracted using organic solvents. Wood extractives consist of terpenes, phenolic compounds, aliphatic carboxylic acids, and alcohols. If they are soluble in water, they are considered wood resin or pitch. Examples of extractives include free fatty or resin acids, betulinol, waxes, fatty alcohols, esters, sterols, glycerides, and ketones. The content and composition of wood extractives depend upon different aspects, such as wood species, age, growth conditions, environment, and others.

Toxic compounds: Chlorinated phenolics and lignin derivatives are particularly notable for their toxic properties.

Biocides: These are substances that control microbial growth but can be harmful to aquatic life.

Dioxins and furans: These byproducts of chlorine bleaching are known for their toxicity and persistence in the environment.

Heavy metals: Wastewater from the P&P industry contains different types of heavy metals that may surpass the admissible content. Some of the encountered metals are Cd (Cadmium), Ba (Barium), and Cu (Cuprum) (Aprianti et al., 2018).

Table 3.2 gives details about the material forming part of the P&P mills effluents, differentiating the process stage from which the pollutant matter originates.

3.3.1.2 Color origin in the P&P effluents

Wastewater becomes colored because of bacterial decomposition and the presence of suspended and colloidal material. In P&P wastewater, color diverge greatly from light to dark brown, or black. Lignin and derived compounds are the primary color sources. The color results of the lignin degradation, causing the existence of chlorinated organic compounds. This degradation occurs in stages such as pulping, bleaching and extraction of alkali (Shokunbi & Omenka, 2022). In the mill's effluents, lignin is present as sodium lignite and lignin sulfonic acid. Other organic compounds equally responsible for effluent color are resinous and phenolic compounds, wood biomass extractives, resins, synthetic dyes, tannins, and their decomposition derivatives (Singh & Tripathi, 2020). Under anaerobic toxic conditions, sulfides such as ferrous sulfide and hydrogen sulfide, as well as divalent metal irons, the dark color of effluents is more striking.

The effluents from wood debarking are extremely colored because of the high-level of lignin and its derivatives, as well as the presence of tannins. During the pulping process, lignin becomes thio- and alkaline lignin, whereas lignosulfates are formed during sulfite processes. Lignin and its byproducts produce disagreeable smell and reduce photosynthesis (Lindholm-Lehto et al., 2015).

3.3.1.3 Toxicity and environment impact of effluents from P&P mills. Causes and effects

The toxicity of P&P wastewater effluents reveals their grade of harmfulness. Assessment and reports of the toxicity of the wastewater flow of P&P mills are scarce due to the difficulty of tracking the mixed toxic effects of pollutants on aquatic life and the impact on the environment. Wood consumption as feedstock in the P&P industry affects biodiversity survival and causes climate change. Furthermore, producing one ton of paper requires nearly 190–200 m³ of water. At the same time, organic and inorganic pollutants are generated during pulp digestion and bleaching if untreated wastewater streams are released into aquatic ecosystems. In countries like India, infectious diseases have been reported.

Table 3.2 Characteristics and composition of main effluents in pulp and paper (P&P) mills.

Processes / sources of effluents	Characteristics of effluents	Compounds	References
Wood preparation, debarking, and handling.	Wood residues. The major source of pollution in this stage is the debarking plant.	Lignin and its derivatives, suspended solids (SS), biochemical oxygen demand (BOD), dirt, grit, fibers, color, resin acids, fatty acids, bark, sand, chlorinated organic compounds, dissolved organics, sterols, and extractives.	Lindholm-Lehto et al. (2015) Suhr et al. (2015) Sharma et al. (2014) Badar and Farooqi (2012) Pokhrel and Viraraghavan (2004) Wang et al. (2004)
Pulping. Digester.	Black liquor in Kraft process contains cooking chemicals.	Spillage of fibers, chemical oxygen demand (COD), BOD, resin acids, wood extractives, fatty acids, color, adsorbable organic halogens (AOX), reduced sulfur components, chlorides, acids, volatile organic compounds (VOC) like terpenes and diterpene alcohols, tannins, alkaloids wax fats, alcohols, phenols, and acetone, chloroform. Bark ash that contains calcium carbonate (CaCO_3) which turns to carbon oxide (CaO), and potassium salts. Wood debris and soluble wood materials, lignin, carbohydrates, and extractives. Chemicals in the Kraft process include sodium hydroxide and sodium sulfide. Toxic sodium lignosulfonates derived from lignin, highly toxic and recalcitrant dibenzo-p-dioxin and dibenzofuran. Toxic juveniles.	Singh and Tripathi (2020) Sharma et al. (2014) Wang et al. (2004) Michniewicz et al. (2000)
Pulping. Pulp screening, thickening, and cleaning	White waters.	SS, BOD, COD, high pH, color.	Singh and Tripathi (2020) Badar and Farooqi (2012)

(Continued)

Table 3.2 (Continued)

Processes / sources of effluents	Characteristics of effluents	Compounds	References
Bleaching	Chlorinated organic compounds are recalcitrant and toxic to aquatic life. Many are likewise genotoxic.	Fibers, COD, carbohydrate, lignin, color, AOX, inorganic chlorinated compounds including chlorate (ClO_3^-), dioxins, furans, organic halogens, Phenolic compounds classified in chlorinated phenols (from monochlorinated compounds to polychlorinated), guaiacols, catechols and vanillins, VOCs including acetone, methylene chloride, transition metals, chelating agents, and dioxins carbon disulfide, chloroform, chloromethane, trichloroethane. Some agents are chlorine dioxide, oxygen, ozone, and hydrogen peroxide.	Kumar et al. (2021) Singh and Tripathi (2020) Bajpai (2015) Sharma et al. (2014) Pokhrel and Viraraghavan (2004)
Papermaking	Discoloration if dyes produce colored paper.	Particulate waste, organic compounds, inorganic dyes, COD, acetone, cellulose “fines” and other additives.	Sharma et al. (2014) Thompson et al. (2001)
De-ink process by flotation, washing and screening	Soluble compounds	Starch, ink residues, Spillage of fibers.	Thompson et al. (2001) Suhr et al. (2015)
Papermaking		Particulate matter, organic compounds, dyes, COD, acetone.	
General P&P mills effluents		Concentrations of Na^+ , K^+ , Ca^{+2} , Mg^{+2} , Cl^- , NO_2 , bicarbonates, Mn, coliform Bacteria.	Singh and Tripathi (2020) Pokhrel & Viraraghavan (2004)
	Toxic, mutagenic, harmful for biological system	Phytosterols.	
	Toxic compounds	SS, Aldehydes, ketones, amines, cyanide, metallic pollutants, plasticizer, alkalis, oils, greases, dyes, biocides, nonbiodegradable substances, radioactive matter, and thermal impurities.	Singh and Tripathi (2020)

Generally, the land is irrigated with wastewater because the decomposition of the organic material degrades and detoxifies the bacterial matter in the soil. Research on this topic concerns wastewater toxicity from P&P mills on agricultural lands. The wastewater boosts nitrogen, phosphorus, potassium, and nutrients in soils. Conversely, some pollutants negatively impact the texture and pH of fertile soils. After crops are irrigated with P&P mill wastewater, the concentration of Nitrogen N, Phosphorus P, Potassium K, and Sodium Na in the soil grows compared to this content after well-water soil irrigation. It is necessary to analyze the effect of wastewater on cropland because soil pollution and health problems can arise with industrial wastewater. Plants can continuously absorb undesired molecules that eventually cannot stop. Thus the pollution content intensifies inside the plant. Wastewater irrigation is at fault for the toxicity affecting the crop quality and lowering soil fertility, quality, and yielding capacity. It has been reported that seed germinations can be damaged due to the raised concentration of soluble salts and heavy metals from irrigation wastewater. Otherwise, the impact on human health can be significant alike. Unsafe levels of heavy metals in the soil may cause kidney or liver disease. Toxic chemicals in the wastewater streams, like chlorophenols, hexadecane, and octadecane, cause cancer (Singh et al., 2022).

The content of low-molecular-weight (LMW) compounds is seen as the primary cause of toxicity in P&P effluents. The LMW compounds give rise to mutagenicity, caused by their hydrophobicity and facility to infiltrate cell membranes (Lindholm-Lehto et al., 2015). The LMW materials accumulate in live organisms with a broad toxicity potential. Conversely, the high-molecular-weight (HMW) compounds are inactive from a biological standpoint and have slight toxicity potential.

The AOX are normally found in P&P mills effluents. It has been reported that most of the AOXs (70%–80%) are HMW species. However, the small rest of the AOXs with LMW have an increased toxic potential, are bioaccumulative, persistent, and contain chloro-olignin that can harm certain aquatic organisms. Besides, their slow degradation connects with elevated COD. This kind of AOXs yields carcinogenicity, mutagenicity, or acute toxicity. On this account, the high toxicity of AOXs in P&P effluents compels the establishment of restrictive criteria in the case of industrial release. In particular, bound norms prevent the discharge of these compounds per ton of pulp. Conversely, the HMW fraction of AOX is not severe but still can affect submarine organisms.

After that, hydrophobic toxic compounds are mainly adsorbed by the suspended particulate matter (SPM), which retains short-living

and persistent pollutants. Its accumulation acts in aquatic organisms with the attack of toxic compounds. Aquatic creatures can consume SPM and thus stock pollutants in their organism.

Likewise, in P&P effluents, the macromolecular species with molecular weights over 1000 are toxic. These types of species stem from the pulping process. Within this class, chlorolignosulfonic acids are released in sulfite pulp mills, whereas chlorothiolignins are found in kraft mill effluents. Then, the organosulfur and tetrachlorinated dimethyl sulfone content is quite lower in P&P mills effluents.

3.3.1.4 Essential physicochemical properties always present in the P&P effluents

3.3.1.4.1 Biological oxygen demand

measure of the amount of oxygen consumed by microorganisms, such as bacteria, during the oxidizing of organic matter (Dagar et al., 2022; Shokunbi & Omenka, 2022; Kumar & Puri, 2012). In the P&P industry, a high BOD reveals a marked content of organic matter involving wood fibers and chemicals. The excess of organic matter can lead to oxygen depletion in bodies of water, which poses a threat to aquatic life.

3.3.1.4.2 Chemical oxygen demand

measure of the oxygen needed to oxidize organic and inorganic compounds in water. It is a faster method than BOD and is widely used in the P&P industry to estimate the level of pollutants in wastewater.

3.3.1.4.3 Total solids

It is a measure of the content of solids and determines the transparency of water. The presence of solids affects the photosynthesis.

3.3.1.4.4 Total suspended solids

It is a measure of the content of un-dissolved suspended materials. Moreover, the presence of SS affects the photosynthesis.

3.3.1.4.5 Total dissolved solids

It is a measure of the content of organic, inorganic matter, and other species dissolved in water. It is likewise defined in terms of the content of cations and anions in wastewater.

3.3.1.4.6 Turbidity

The water used in a P&P mill undergoes anaerobic processes that boost algae growth, which gives rise to turbidity. The turbidity is the opacity or cloudiness of the water that retains suspended solid matter. A nephelometer measures it. With a light source and photoelectric detectors, this instrument measures the light reflected off the particles induced by the cloudiness in a wastewater sample. Turbidity is a measure that determine the quality of water.

3.3.1.4.7 pH

determines the acidic or basic nature of a solution. This measure is determined in terms of the concentration of the hydrogen ion $[H^+]$ activity in the solution. It is defined as:

$$pH = -\log(H^+) \quad (3.1)$$

A value between 6 and 9 is safe for aquatic life.

3.3.1.4.8 Hardness

This characteristic is produced by the content of calcium and magnesium and is calculated by the sum of the concentration of these compounds. The hardness determines the ability of water to precipitate soap.

3.3.1.4.9 Alkalinity

It is used to analyze color and measure the content of carbonate, bicarbonate, and hydroxide. Alkalinity is caused by the content of basic salts, such as sodium and potassium.

3.3.1.5 *Physicochemical characterization tests of wastewater effluent. Standard procedures*

The physicochemical analyses for P&P effluents help monitor pollutants in the plant. To know the effluent composition aids in predicting the environmental impact in the case of effluent release. To mention a few examples, the characterization helps to evaluate wastewater treatments efficacy and potential pollution remediation methods. Table 3.3 shows different physicochemical analyses that are appropriate for characterization tasks.

The information shown retains the objectives of different types of studies and standard measurement techniques or standard permissible limits for parameters typically followed in the P&P industry.

Table 3.3 Physicochemical measurements for effluent characterization.

Physicochemical characterization measurements	Study	Standards	Effluent / waterbody	References
pH, color, temperature, turbidity, Total Alkalinity (TA), total hardness (TH), chemical oxygen demand (COD), total suspended solids (TSS), total solids (TS) and total dissolved solids (TDS).	Evaluation of the efficacy of an effluent treatment with sand bed filters and adsorption method.	Standard measurement procedures by American Public Health Association (APHA). Industrial effluent discharge limit World Health Organization (WHO) and Indian Standards Institute (ISI). WHO and ISI standards.	Pulp effluent (black liquor), before and after treatment.	Shokunbi and Omenka (2022)
Color, odor, pH, COD, temperature, turbidity, TH, TA, TDS, TS, TSS.	Purification of black liquor with sand bed filters and adsorption with activated carbon.		Pulp effluent (black liquor),	Shokunbi and Omenka (2022)
BOD, COD, TP, TN, turbidity, TS, TDS. TSS, electrical conductivity, pH, Na, K, TH, Ca, Mg, Cl ⁻ , TA CO ₃ ⁻² , HCO ₃ , chloride, sulfate, Fe, Cu, Zn.	Physicochemical Characterization to study the pollution of the Upper Awash River in Ethiopia.	Standard measurement procedures by APHA. Permissible limits of WHO and EEPA standards.	Raw and treated effluents	Jebessa and Wondemagegnehu (2018)

3.3.1.6 Standards methods for physicochemical and biological characterization of effluents and guidelines for parameter limits in water quality

With respect to regulatory practices and guides for wastewater analysis, the American Public Health Association (APHA) provides standard methods for the analyses and measurement of physical and chemical characteristics of Water and Wastewater. The analyses include numerous laboratory methods to quantify TDS, metals, Free and Total Chlorine, odor, total organic carbon (TOC), among others.

The Regulation on the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) prescribed by the European Chemical Agency dictates the industrial chemicals analysis and practices that promote innovation and safety and support the development of testing methods. A major objective is to address data gaps with respect to the properties and uses of industrial chemicals. There is an interest to generate safety data sheets, and other chemical safety information that guarantee good handling practices in the production chain. Then proper actions to release and distribute emissions within the environment. Another task is to identify the harmful chemicals and promoting substitute them with safer alternatives. REACH furthermore direct the chemicals evaluation practices (Foth & Hayes, 2008).

Several agencies additionally establish permissible limits for measurements that ensure treated wastewater quality. The ecological legislation is dictated and published by the World Health Organization standard limits (WHO) in the form of guidelines for the quality of drinking-water; the Central Pollution Control Board providing standard limits guidelines from the Ministry of Environment, Forest & Climate Change; the guidelines of the Indian Council of Medical Research; the Standard Methods for the Examination of Water and Wastewater of the APHA, with the collaboration of the American Water Works Association, and the Water Environment Federation; then Indian Standards Institute establishes standards for growth and efficiency preservation of industries. The aim is to promote the safely use of wastewater.

3.3.1.7 Methodologies for identification tests and toxicity determination

No single method provides a comprehensive approach to assess the level of P&P wastewater toxicity. The detection and analysis methods vary from mill to mill due to the absence of a standardized approach. The main techniques are as follows (Lindholm-Lehto et al., 2015):

3.3.1.7.1 Analytical methods

Chromatographic methods: The instrumental methods include gas chromatography or liquid chromatography coupled with flame ionization detectors, mass spectrometry, or tandem mass spectrometry. The combined tests effectively drive the qualitative and quantitative analysis of the vast organic and inorganic pollutants in P&P mills effluents.

Spectroscopic analytical methods: Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy are further instrumental methods that provide qualitative and quantitative analysis of effluents.

Other analytical methods: Gravimetric, titrimetric, and photometric methods are applied to measure the content of specific compounds within the effluents. The choice of a method depends on the specific needs of the analysis, in particular, the required sensitivity and specificity. The heterogeneous content of wastewater and the diverse range of toxicity need multiple analytical techniques to assess the environmental impact of P&P mill effluents comprehensively.

3.3.1.7.2 Biological assays

These tests are developed to examine aquatic toxicity. The information on toxicity levels assists in formulating environmental management measures. Biological assays are increasingly significant as they evaluate the cumulative impact of the complex mixtures in wastewater.

3.3.1.7.3 Bacterial and algal screening tests

This development leads to sensitive, rapid, and cost-effective alternatives to using new organisms. Bacterial and algal screening tests can effectively detect the presence of toxic substances, although they may not provide detailed insights into the causes of toxicity.

3.3.1.7.4 Conventional toxicity tests

These analyses permit the assessment of wastewater toxicity and may involve bacteria, algae, and higher organisms. Typical toxicity test organisms include *rainbow trout*, *salmon*, *Daphnia magna*, or *Vibrio fischeri* bacteria. The choice of test organism depends on the specific objectives of the toxicity assessment.

3.3.1.7.5 Mutagenicity tests

The analysis of the wastewater's mutagenicity is based on bioassays and analytical methods. Assessing mutagenicity permits

identifying genotoxics and understanding their potential hazard, even if it does not specify the exact toxicants or their properties.

A combination of tests involving sensitive microorganisms from different levels is necessary for a thorough assessment. Current trends in toxicity testing favor the utilization of living organisms, particularly lower-level organisms like bacteria, due to their lower costs and ethical considerations. These organisms respond well to the overall effects of toxicity, making them valuable indicators of environmental impact.

3.3.1.8 Release problems, challenges and potential solutions

The successful valorization and reduction of P&P waste faces challenges in terms of technological constraints, economic feasibility, regulatory constraints, and market approval for the derived products. However, there is a growing emphasis on sustainability and opportunities for innovation. On the one hand, valorizing waste in the P&P industry by transforming it into resources gives insights into the transition towards more sustainable and circular practices. On the other hand, minimizing wastes involves high level of recycling and reusing, which in turn, entails a significant technological effort.

3.3.1.9 Valorization and reduction of waste in P&P industry

In a widespread sense, valorization involves practices to make scientific expertise available and functional to the industry. In the P&P industry, it is achieved by recovering and transforming waste materials from the mills into valuable products. As a result, waste reduction, resource conservation, and economic gain can be expected. The valorization strategies align well with the circular economy and sustainability principles. In what follows, some strategies for valorizing paper and pulp waste are recapitulated. The practices lie in four fields of application:

- Recycle effluents partially or totally, with an emphasis on closed-cycle mill operation.
- Energy production.
- Material recovery and recycling.
- Production of value-added Products.

3.3.1.10 Closed-cycle mill operation

In the P&P industry, closed-cycle mills are highly integrated systems that reform how mills handle water, chemicals, and waste materials. Unlike the standard mode, this closed process aligns well with practical measures and trends to minimize water and chemical

consumption by maximizing recycling. The result is near-zero wastewater discharge. This mode likewise prevents the depletion of water resources. In the end, it enhances sustainability and offers an eco-friendlier paper production. References on these subjects are [Han et al. \(2021\)](#); [Tran and Vakkilainen \(2008\)](#); [Bajpai \(2015\)](#).

Water and chemical recycling primarily occur during pulping, bleaching, and papermaking. These valuable resources are recovered and treated within the process. These efforts reduce the plant's reliance on fresh water and minimize the release of solid waste and by-products. In fact, water and chemicals are recycled within the mill processes or used in other industries. The amount of water saved, and the degree of water recycling differ for each mill, based on the materials used and the products yield. It is important to maintain a balance between various process variables, such as water flow rates, pulp consistency, and physical, chemical, thermal, and microbiological properties. This is essential for optimizing water usage and minimizing the requirement for additional fresh water.

Additionally, these mills often capture and use the heat generated during manufacturing, which leads to further gains in energy efficiency and overall sustainability. This practice moreover reduces the carbon footprint of mills.

Closed-cycle operations focus on minimizing the generation of solid wastes and by-products. Waste management involves to either recycle by-products within the mill processes or utilize them in other industries, such as bioenergy feedstocks or raw materials.

Switching mills to closed-cycle operations is an operation entailing meaningful challenges and demands advanced treatment technologies and significant investment. Although the initial cost can be high, changes have long-term benefits. In successfully converting the plant, it is crucial to prioritize technology withdrawal and selective process modifications. Then, process optimization, treatment, and reusing practices are essential in completing plant conversion. Concessions include reduced operational costs due to savings on water and chemicals, lower waste treatment costs, and compliance with stringent environmental regulations.

Closed-cycle operation challenge in the P&P industry involve innovative wastewater treatments and optimized processes. Technologies for water recycling in the P&P industry are, for example, different pressure-driven membrane types, such as UF, NF, and RO. UF membranes are gaining attention for their ability to exclude some metals and complex any remaining metals during the clarification process. NF, with a slightly larger pore size than RO, is suitable for removing metals, color, and hard-to-degrade organic compounds. It is considered more suitable for large-scale operations due to its lower pressure and higher permeate flux. RO is highly

efficient in separating monovalent ions and is prominent in water reclamation through wastewater treatment and desalination. The closed-cycle mill operation needs to delve into novel membranes that can resist the demanding conditions of papermaking and the development of water management systems tailored to individual paper mills. Filtration and other membrane separation technologies are taken up again in [Section 3.5](#).

The importance of water management, real-time monitoring, and tailoring technologies to the unique chemistry of each paper mill is highlighted for ensuring effective water use. Conducting economic analyses helps to demonstrate the feasibility of closed-cycle operation technologies and highlight their environmental advantages.

3.3.1.11 Energy production from wastes of P&P mills

3.3.1.11.1 Biomass used as fuel

Waste biomass from P&P mills can be burned as fuel in biomass boilers. Potential materials to recover and burn are found in the black liquor from the Kraft process, wood residues from pulping, rejects from screening and cleaning processes during handling, pulping and paper recycle operations, sludge from water treatment, deinking of recycled papers, and other sludge sources. Wood wastes are sawdust, fallen bark, pins and fines from chip screening, waste from yard sources. Black liquor is the most abundant biomass in a kraft mill and has a high heating value. It contains close to 50% of wood matter. Wood wastes are the second most copious biomass fuel in a mill. Some materials have low heating values, in those cases, biomass can be combined with another fuel to enhance the heating value. Greenhouse gases emissions from biomass incineration are formed, mainly, carbon dioxide, CO₂, methane, CH₄ and nitrous oxide, N₂O. The first is generated in greater quantity than the other two ([Gavrilescu, 2008](#)).

3.3.1.11.2 Biogas production

Anaerobic digestion of organic waste streams, including sludge, can be processed to obtain biogas. This biofuel can be, in turn, be converted into heating energy or electricity. As an example, [Priadi et al. \(2014\)](#) reported an anaerobic digestion process to produce biogas for energy recovery from sludge produced in P&P mills, particularly, after primary and secondary treatments originated from different sources, along the lines of virgin wood fiber, recycled paper, and non-wood fibers. Anaerobic digestion is a typical form of biological sludge stabilization. The stabilization processes reduce the content of compounds easy to degrade, unstable and with a high-energy content, and then alleviate the pathogens content in the

sludge material. According to [Priadi et al. \(2014\)](#), the produced sludge in the P&P industry ranges from 0.3 to 1 m³ per ton of paper delivered. [Ochoa De Alda \(2008\)](#) states that dry sludge outcome of P&P mills corresponds to 4.3% of the produced paper, percentage that is augmented to 20%–40% for recycled paper manufacture. Following the study of [Hackett et al. \(1999\)](#), the P&P industry in United States and Canada before 2000 delivered close to 12.2 and 1.6 mt/year of primary and secondary sludge, respectively.

3.3.1.12 Waste material recovery and recycling

3.3.1.12.1 Fiber recovery

Fibers from P&P waste streams can be recycled back into the papermaking process. This practice should reduce the demand for virgin fiber and the use of natural resources. Ochoa de Alda, 2008 assessed the fiber content and quality of sludges from European mills, as well as its physicochemical properties, such as humidity, content of ash, harshness, drainability, and O₂ consumption. P&P mill primary sludge is mainly composed of wood fibers and papermaking fillers. In the cited paper, the studied sludge material was shown to vary widely in composition and properties, but two types were distinguished with low and high ash content. For this material, the alluded study revealed feasible to reuse at least 60% of the tested sludge material from the European mills. A closing remark of the research is that viability is high to recover and reuse fiber material in papermaking processes. Primary sludge has properties and composition comparable to recycled paper, especially in relation to the fiber, fillers and even contaminant content. A difference is that the water content in the sludge is lower than the contained in the recycled paper (two-thirds). Following the sludge grades, it can be recycled to obtain products of specific qualities. In Europe, there exist standard grades that classify recovered paper and board in five groups. The sludge to be processed depends on the type of final product. The higher-quality sludge has good strength features and need simple processing, it is used to produce printing, writing, and wrapping papers, and tissue. A second-quality sludge include brown sludges with high fiber content that need further processing stages like cleaning, bleaching in order to obtain brightness, for instance, to make newsprint or magazine paper, and tissue. Otherwise, without further processing, this second type of sludge can be raw material for corrugated board, boxboard, or certain tissues. The third-quality type of sludge can be used as feedstock for mills that operate with closed water cycles if the final product tolerates some contaminants, as it is the case for some packaging and construction papers.

The viability of processing the biomass from P&P mills to obtain high value-added biomaterials has been largely studied. In the P&P industry, significant efforts have been made to clarify black liquor from the mills by removing lignin, with lignin acid precipitation being the leading purification method. Lignin, a crucial raw material for carbon fibers, has been explored in several biomaterials (for details, see the work of [Haile et al., 2021](#)). *Carbon-based fibers*, considered high-performance composites with exceptional density and mechanical properties, are gaining traction in the industry. Their standard production is driven by polyacrylonitrile, which requires high carbon content. The carbon comes from fossil-based material and requires a complex and time-consuming spinning process. As an alternative, lignin is a potential precursor for carbon fiber production, provided it can undergo proper spinning and carbonization procedures. In P&P mills, the Kraft process leads to high volumes of lignin with a 60%–65% carbon composition. The usual process to deliver carbon fibers from lignin consists of melt spinning, thermo-stabilization over 200°C–350°C, and carbonization over 1000°C operations.

3.3.1.12.2 Fillers and coatings production

If minerals and other materials are recovered, these can be reused as fillers and coatings in P&P or other industries. The sludge formed in the deinking paper is a waste that retains chemicals that, if refreshed, can be used as colorants and fillers. Recycling this material is another form of waste valorization in P&P mills. These Recycled agents mainly consist of kaolin and calcium carbonate. Chemicals such as talc, calcium sulfate, and titanium oxide are further components of these agents. Moreover, chemicals can be zinc oxide, magnesium oxide, iron, copper, or chrome complexes for coating and coloration. [Tofani et al. \(2021\)](#) studied the feasibility of reusing fillers recycled from deinking paper sludge in newspaper manufacture. The sludge needs to be incinerated at 575°C. The obtained ashes follow a bleaching process. After this procedure, the agents preserve their molecular structure. Then, the physical and optical properties of the newspaper produced were likewise found to be appropriate, so the agents were validated as fillers. Their efficacy was comparable to that of purchasing and using fresh fillers, demonstrating the practicality and success of this waste valorization method.

3.3.1.12.3 Composting and soil amendments and land applications

Organic waste from P&P mills can be composted to produce soil amendments, including soil fertility enhancement. This practice

should enrich the soil for agriculture by the increase of soil organic matter, nutrients, and pH, and by enhancing in general the biological, physical, and chemical soils properties (Camberato et al., 2006). The decomposition of the P&P mill sludge is undertaken in two stages, a short step of fast decay preceding a slow decay over an extended period. Camberato et al. (2006) revised reports which specify that for deinking sludge, cellulose degradation is rather associated with the fast decay step, whereas lignin is better related to the slow decay. Hackett et al. (1999) proposed specific research for composting power boiler fly ash with sludge from wastewater treatment in the P&P mills. The final compost was obtained with a high content of nutrients, a mean C:N ratio of 43:1, and pH of 8.5. Furthermore, regulations concerning metals, polychlorinated biphenyls, chlorophenol and polycyclic aromatic hydrocarbons content were met.

3.3.1.13 Production of value-added products

3.3.1.13.1 Cellulose derivatives

Cellulose recovered from P&P waste can be processed into various derivatives, such as cellulose ethers, esters and grafting copolymers or recovered stock, such as fibers and films. The derived compounds have applications in food, pharmaceuticals, and other industries. The standard methods to regenerate materials based on cellulose need a large amount of energy and are highly pollutant. A specific implementation was reported by Xia et al. (2016). Their proposal was to convert waste newspapers into cellulose-based films. In this process, the challenge is to find a proper solvent to dissolve the cellulose. The solution was to use ionic liquids, which have better dissolving capacity than classical solvents, do not need pretreatment methods, and is easily recuperated.

3.3.1.13.2 Bioplastics

A technical approach is to convert cellulose and lignin from P&P wastes into biodegradable plastics. This practice is a sustainable choice for petroleum-based plastics. Jiang et al. (2020) have proposed a significant step toward sustainability in the P&P industry. The idea is to reinforce cellulose fiber by integrating lignin into this material through successive infiltration and mechanical hot-pressing operations. The resultant lignin-cellulose composite offers several environmental benefits, including biodegradability and UV-blocking performance. It likewise exhibits an isotropic tensile strength of 200 MPa and a significant wet strength of 50 MPa, making it a viable alternative to non-biodegradable plastics.

This research not only addresses the issue of waste valorization but also contributes to the replacement of non-biodegradable plastics, a pressing environmental concern in the P&P industry. This approach holds promise for a more sustainable future in the industry.

3.3.1.13.3 Activated carbon

The conversion of carbon-rich materials from waste streams into activated carbon is sustainable. The product gives a path to water and air purification and has various industrial uses. [Ramalingam et al. \(2024\)](#), thoroughly reviewed biomass and waste-derived materials for energy applications. The study focused on silica and ammonia and included activated carbon materials. Biomass-derived carbon has attractive properties such as its adaptable porosity and morphology, high stability, and exceptional electrical conductivity. It also exhibits low-cost and eco-friendly features. A source of this material is biomass waste. The cited review focuses on agricultural waste, but this conversion can be extended to wastes from P&P mills with equivalent composition. In the same sense, [Mostafa et al. \(2018\)](#) proposed a method to produce cellulose acetate biofiber using flax fibers and cotton linters. A catalyzed acetylation process using sulfuric acid yields the cellulose biopolymer. The resulting biopolymer is biodegradable. It has comparable resistance to polyethylene and polypropylene. It has been proven to replace non-biodegradable and petroleum-based materials effectively. A challenge is looking for different plasticizers that improve the physical and eco-friendly properties of biopolymers.

3.3.1.13.4 Lignin valorization. Production of bio-lignin from P&P wastewater to be used for lead removal

Recovering and converting lignin from pulp waste is sustainable. The converted lignin yields bio-based chemicals, materials, and fuels. A specific case is the recuperation of lignin from P&P mills and its application in adsorption processes for lead removal in wastewater.

[Khamdahsag et al. \(2023\)](#) proposed and discussed the extraction of lignin, a by-product of P&P mills, and its use to release lead from wastewater by driving adsorption processes. Two modes of lignin extraction are exceedingly feasible in creating lignin-based adsorbents: lignin precipitated by hydrochloric acid (LP) and lignin separated through the coagulation-flocculation process with iron (III) trimesate (LPF).

LPF contrasts with LP, exhibiting amorphous properties, increased surface area, and porous properties. It is worth noting that LPF contains iron oxide derived from the coagulation-flocculation process

using iron (III). These characteristics make LPF a promising material for removing lead (Pb) from polluted water, as it proved a significant decrease in Pb content of about 65% in just 60 minutes. In practice, it has been shown that batch adsorption followed the physisorption mechanism occurred spontaneously.

The quoted work has shown that LPF-based adsorbents in adsorption processes can mitigate Pb pollution in industrial effluents with up to 94.7% removal efficiency. As a concluding remark, this wastewater treatment can address environmental and public health concerns that lead to pollution relief in P&P plants.

The techniques for characterizing lignin give insights into its structure, composition, and thermal behavior, which are basic to evaluating its suitability and efficiency as an adsorbent for lead removal. The effective analysis techniques are:

The scanning electron microscope (SEM) makes it possible to scan the morphology of lignin. An outcome of SEM tests is that a mesoporous lignin structure favorable for adsorption has been observed.

The nitrogen adsorption-desorption technique evaluates the specific surface area and porosity of lignin. This test enables proof of good porosity and surface area traits after treatment.

Fourier transform infrared spectroscopy places functional groups in lignin. This test highlights the presence of hydroxyl, carbonyl, and guaiacyl groups.

X-ray fluorescence provides for elemental analysis. This test confirms whether the iron oxide content in lignin boosts after specific treatments.

Thermogravimetric analysis assess the thermal stability of lignin. This test then portrays the different decomposition stages of lignin.

3.3.1.13.5 Extraction of biochemicals

Biochemical compounds, such as enzymes, organic acids, and sugars, are recovered from P&P mill waste streams. They can then be used as base materials for the chemical, food, and pharmaceutical industries.

3.3.1.13.6 Use of bio-polymeric additives to replace conventional chemical additives

P&P mills are sources of massive amounts of polluting, hazardous, toxic wastewater. One of the origins of this effluent type is the significant quantity of chemicals handled in the various P&P processes. Mechanical beating or chemical additives are standard solutions to upgrade important paper attributes like strength,

softness, density, bright intensity, filler retaining, water and grease resistivity, and so forth. A strategy to detour the demand for toxic chemicals and weak methods in P&P mills is to adopt renewable and bio-based materials to improve the properties of the paper products (details are reported by [Basu et al. \(2021\)](#)). A proposal has pointed to handling more sustainable, versatile, and eco-friendly operations that replace conventional practices. The approach to enhancing the chemical-physical properties of paper is to introduce renewable biopolymers, including starch, cellulose, proteins from plants, biopolymers of microbial or animal origin, and gums. One must underline the applications of bio-based materials and their role in strengthening paper, retaining fillers, and providing water barrier properties.

Recommended literature on the subject includes the work of [Basu et al. \(2021\)](#). [Table 3.4](#) gathers some alternative bio-additives to be utilized in different stages of P&P processes. The information displayed is about the class and subclass of bio-additive, the non-wood source, the process where it is used, and which properties the additive enhances.

Some biopolymers that substitute chemical additives and their characteristics are as follows ([Basu et al., 2021](#)):

Cellulose and its derivatives are used to produce pulp and to enhance paper properties as additives. Cellulose is extracted from wood and other materials through mechanical and chemical pulping. Its derivatives, such as carboxymethyl cellulose, are chemically modified forms of cellulose that improve the strength, durability, and smoothness of paper. These derivatives are obtained by reacting cellulose with various chemicals, making them versatile additives in paper manufacturing.

Hemicellulose is another essential component used mainly during the pulping phase. It is a complex carbohydrate found in plant cell walls alongside cellulose. Hemicellulose is extracted from biomass, such as wood, straw, and agricultural residues, through different pulping processes. By acting as a binder or filler within the paper structure, hemicellulose can enhance the printability, strength, and flexibility of the paper.

Starch and its derivatives are primarily used as additives in the wet-end phase of paper production to improve paper strength and in the coating process to enhance surface properties like printability and smoothness. They derive from agricultural sources such as corn, wheat, rice, and potatoes. Starch is extracted by separating it from other plant components, such as proteins and fibers, through washing and centrifugation.

Chitosan is a strength additive that enhances the antimicrobial properties of paper. It is dosed during the wet-end phase to improve

Table 3.4 Bio-additives to enhance paper properties and reduce pollutants release in pulp and paper (P&P) industry (Basu et al., 2021; Tajik et al., 2021).

Bio-additive	Derivatives	Source/extraction	P&P process	Paper property enhancement
Cellulose	• Cationic cellulose. • Carboxymethyl cellulose (CMC). • Hydroxyethyl cellulose. • Nanocellulose. • Nano-Fibrillated Cellulose (NFC). • (b) Nano-Crystalline Cellulose (NCC). • Other cellulose derivatives.	• Primary component of plant cell walls, it is extracted from wood and other plant materials and/or recycled fibers. • Some derivatives are chemically modified forms of cellulose. • Oil Palm Empty Fruit Bunch. It is dissolved with sodium carboxymethylcellulose (NaCMC) in a sodium hydroxide/urea system to produce regenerated cellulose hydrogel.	• Stock preparation phase. • Pulping.	• Enhance efficiency in anionic pulp suspensions. • Strength, durability, and smoothness of paper. • Paper thickness, density, air permeability, and opacity.
Hemicellulose	• Pentosans. • Hexosans.	• Complex carbohydrate found in plant cell walls, alongside cellulose. • It is extracted from biomass, such as wood, straw, and agricultural residues, through different pulping processes.	• Pulping	• Enhance printability, strength, and flexibility of the paper.
Starch and its derivatives	• Starch. • Cationic starch. • Oxidized starch. • Acetylated starch. • Hydroxypropyl starch.	• Derived from agricultural sources such as corn, wheat, rice, and potatoes. • Extracted by separating it from other plant components, such as proteins and fibers, through washing and centrifugation steps.	• Wet-end phase of paper production. • coating process.	• Improve paper strength. • Enhance printability and smoothness.

Chitosan	• Cyanoethyl chitosan. • CMC • Other biopolymers.	• Derived from chitin, which is obtained from crustacean shells like crabs, shrimp, and lobsters. • Obtained in enzymatic deacetylation process.	• Wet-end phase of paper production.	• With low molecular weight-low concentration: Enhances the dry strength of paper. • In acetic acid: Enhance the antimicrobial properties of paper. • Lower the hardness and roughness. • Improve dielectric properties and thermal stabilities of the paper: Enhance strength properties.
Proteins	• Casein. • Soy protein.	• Casein is separated from milk through precipitation. • Soy protein is extracted from soybeans after removing the oil.	• Coatings. • Wet-end phase of paper production.	• Improve strength and functional properties
Gums (polysaccharides)	• Guar gum. • Gum Arabic.	• Guar gum is derived from the seeds of the guar plant. • Gum Arabic is obtained from the sap of the Acacia tree.	• Sizing stage. • Coating.	• Enhance strength, flexibility, printability, and resistance to water.
Other bio-based polymers	• Lignin. • Alginate. • Others.	• Lignin is a complex organic polymer found in woods and barks. It is a by-product of the pulping process. • Alginate is extracted from brown seaweeds.	• Coating.	• Improve paper quality and printability.

the dry and wet strength of the paper. Chitosan is derived from chitin, obtained from crustacean shells like crabs, shrimp, and lobsters. The deacetylation process involves treating chitin with an alkali, typically sodium hydroxide, which removes acetyl groups and converts them into chitosan.

Proteins such as casein from milk and soy protein from soybeans are used as additives in the paper production process to improve strength and functional properties. Casein is separated from milk through precipitation, while soy protein is extracted from soybeans after oil removal. These proteins are applied in coatings and used as wet-end additives to enhance paper quality.

Gums are additives in paper production, added in the sizing and coating stages. They improve paper quality and functionality by enhancing strength, flexibility, printability, and water resistance. Gums like guar gum and gum Arabic are natural polysaccharides extracted from plants. Guar gum is derived from the seeds of the guar plant, while gum Arabic is obtained from the sap of the Acacia tree. Before being used in paper manufacturing, these gums are processed and purified.

Other bio-based polymers used in paper production, such as lignin and alginate, are employed in different stages to improve mechanical properties, act as fillers, and enhance surface characteristics through coatings. Lignin is a complex organic polymer in plant cell walls, especially in woods and barks. It is obtained as a by-product of the pulping process. Alginate, extracted from brown seaweeds, is known for its gel-forming capabilities, which improve paper quality and printability. These bio-based polymers are sourced from renewable resources, making them environmentally friendly alternatives to synthetic chemicals.

3.4 Effluent handling challenges in the manufacturing processes of the P&P industry

This section describes the main stages of transforming woody biomass, from its handling as the main raw material of P&P mills to the final paper manufacturing step. The follow-up of the process only concerns the kraft pulping method. Emphasis is placed on which chemicals are fed to each stage, the conversions ensuing, and the pollutants derived from them. The focus is as well on how water recirculation and waste recovery are fulfilled. The survey brings about the challenges in growing the choice of feedstock type, making the key equipment of the plant efficient and the processes safe.

3.4.1 Receipt, storage, and handling of fibrous materials and chemicals

In the P&P mills, the receiving, storing, and handling of fibrous materials and chemicals involve critical steps. Firstly, the wood handling stage encompasses preparing, storing, and unloading wood raw material. Other tasks are storing roundwood, debarking, chipping, chip screening, and storing chips. Quality and consistency are priorities at this stage. Modern facilities must develop effective computer control, measurement, and monitoring systems.

After wood preparation, the logs are debarked, looking after the uniformity in size, which favors the efficiency of the pulping process. Debarking methods are chosen to prevent wood loss and pollution. Dry debarking is often preferred due to its lower environmental impact.

Storing and handling chemicals and additives is critical in P&P production. These substances must be handled safely and efficiently, so compliance with regulations is imperative. The Regulation on the REACH is the dominant law in the European Union to protect human health and the environment against harmful and hazardous chemicals. This law moreover promotes assessing and controlling chemical risks. It likewise delivers safety information on chemical substances. The chemicals used in handling fibrous materials change following the specific stage of the process.

The chemicals used in the handling and processing of fibrous materials vary depending on the specific stage of the process and need to be stocked safely. These chemicals can include (Suhr et al., 2015): In stock preparation, fillers such as calcium carbonate and kaolin, dyes, and strength additives like starch and synthetic polymers are used to improve the properties of the paper.

Cooking chemicals are used during the pulping process to separate lignin from cellulose fibers. Common chemicals used in the Kraft process include sodium hydroxide and sodium sulfide.

Bleaching chemicals are employed to increase the brightness of the pulp. Typical bleaching agents include chlorine dioxide, oxygen, ozone, and hydrogen peroxide.

Additives for paper making, such as fillers (such as calcium carbonate and clay), sizing agents (like starch and rosin), and strength agents (such as polyacrylamides [PAMs]), are introduced during the paper making process to enhance the quality of the paper.

In coating, binders like starch and synthetic latex, pigments such as calcium carbonate and kaolin, and additives are used to improve surface properties.

In water treatment, flocculants and coagulants are used for water clarification and fiber recovery.

In general, biocides are added for microbial control, defoamers are used to reduce foam, and dispersants are included to maintain pulp fluidity.

Each chemical is carefully chosen based on its ability to achieve the desired effect on the fibrous materials, while additionally taking into consideration environmental impact and efficiency. Fig. 3.6 illustrates the handling of fibrous materials stage in P&P mills.

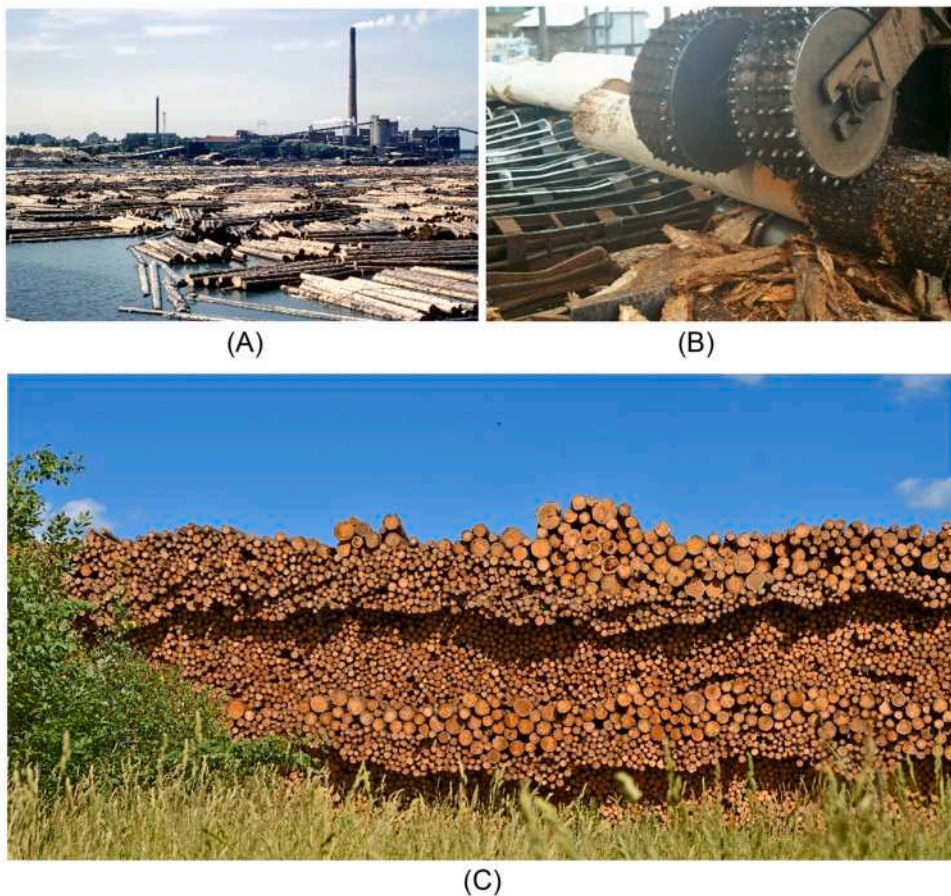


Figure 3.6 Fibrous handling stage in P&P mills. (A) Jean-Pierre Bazard, Wood processing plant Kotkamills Oy. Kotka plant. In the foreground, logs floating in the mill's basins, which will be used to produce, among other things, paper pulp. Kotkamills Oy is one of Finland's leading manufacturers of laminated products. Kotka, Kymenlaakson maakunta (region), Finland, 1984. This file is licensed under the Creative Commons Attribution - Share Alike 3.0 (non-transposed), 2.5 Generic, 2.0 Generic and 1.0 Generic licenses. (B) Author: USDA NRCS Montana, Wood debarker stripping bark off of tree at mill near Darby, September 1978. A work of the Natural Resources Conservation Service, part of the United States Department of Agriculture. The image is in the public domain in the United States. (C) Author: Ludvig14, Logs near Svetogorsk Pulp and Paper Mill, Svetogorsk, Leningrad, Russia. This file is licensed under the Creative Commons Attribution-Share Alike 4.0 International License.

3.4.1.1 A challenge in handling fibrous materials in P&P mills

A challenge in the P&P mills is processing fibrous materials from non-wood biomass. China, India, and Pakistan are the three leading countries producing non-wood pulp. According to [Abd El-Sayed et al. \(2020\)](#), non-wood plant fibers can be categorized into agricultural residues, annual plants, and non-wood crops. The first category encloses low-valued agricultural wastes, available in large quantities and medium quality. Potential biomass for P&P production includes sugarcane bagasse and rice and wheat straw in the first category, bamboo, switch grass, and reed grass in the second, and jute, ramie, and leaf fibers in the third one. For non-woody biomass, the cellulose content ranges from 30% to 59%, the hemicellulose content varies from 17.5% to 39%, and lignin is present in 12.5%–31%.

To illustrate the usage of alternative materials, advances in analyzing the potential to use fibers other than wood for paper production is revised here.

3.4.1.1.1 Fibers other than wood for paper production

A study demonstrated the potential of four non-wood plant species—kenaf (*Hibiscus cannabinus*), giant reed (*Arundo donax*), switchgrass (*Panicum virgatum*), and miscanthus (*Miscanthus × giganteus*)—for paper production ([Ververis et al., 2004](#)). The suitability of these plants for paper production was evaluated based on their fiber dimensions, lignin, and cellulose content. The findings of the study concluded as follows:

Kenaf and Giant Reed have fibers with proper dimensions and cellulose content. These features make the plants helpful in producing various paper types, including writing, printing, wrapping, and packaging papers.

Switchgrass and Miscanthus have shorter fibers, but their slenderness ratios are still satisfactory for paper production. Their attributes make them valuable for use in newsprint and writing papers.

The studied plants species can be primarily utilized in the pulping stage, where their cellulose content is sufficient to obtain paper pulp. Their lower lignin content, compared to traditional wood sources, allows for reducing energy and chemical requirements in pulp processing.

Another study demonstrated the potential of ribbon-retted jute for pulping and papermaking ([Jahan et al., 2016](#)) in the P&P production chain. This material is suitable due to its high alpha-cellulose content (41.04%) and low lignin content (12.25%), compared to traditionally retted jute sticks. High alpha-cellulose content favors paper strength and quality, while lower lignin content

simplifies the pulping process and improves the brightness and quality of the final paper product.

The ribbon retting process for jute is a method introduced by the Bangladesh Government to improve the efficiency of peeling jute fibers. The procedure removes the bark from jute plants in ribbon form. The next step is coiling these ribbons and allowing them to ret in water with or without microbial inoculum. This method requires less water, reduces environmental impact, and enhances fiber quality compared to conventional retting. The ribbon retting improves fiber quality and needs less water usage. However, a likely disadvantage is that this procedure may result in less uniform retting. The chemical properties of ribbon-retted jute sticks, and fiber are distinct, affecting their pulping process. The lignin, cellulose, and other chemical components differ from conventionally retted counterparts.

3.4.2 The kraft pulping process

Pulping technologies in the P&P industry transform woody or nonwoody feedstocks into pulp (Mboowa, 2021; Singh & Chandra, 2019; Suhr et al., 2015). The chemical Kraft process is the standard strategy, as it brings about 80% of the pulp produced in the world (Suhr et al., 2015). The chemical pulping method aims to release the cellulose fibers from the wood chips or other biomass types by dissolving the lignin into a chemical solution known as white liquor at high temperatures and pressures in a cooking digester. The hemicellulose is, in part, dissolved too. The most used chemical agents in the cooking stage are sodium hydroxide (NaOH) and sodium sulfide (Na_2S). For this alkaline pulping process, the pH lies between 13 and 14. The cooking temperature ranges from 155 to 188 C, which decreases during the cooking because the pulping reaction forms organic acids. Then, the steam pressure attains 800 kPa.

In the Kraft mills, the recycling of chemicals and energy is feasible. Detailed aspects are given by Singh and Chandra (2019), Tran and Vakkilainen (2008), but essential features are summarized here. The pulping chemicals are restocked with sodium salts before being reused in the cooking digester. First, weak black liquor is conducted to evaporation and dehydration. The product is a heavy black liquor introduced in a recovery boiler to burn it within an oxygen-poor atmosphere. A molten smelt is formed, composed of Na_2S and sodium carbonate (Na_2CO_3). It is then melted in water to compose green liquor. The green liquor is yet reduced in a causticizing chamber with NaOH and lime mud (CaCO_3) as products. The obtained white liquor is sent for reuse to the digester pulping process. The solid product, lime mud, is then burned in a

kiln and washed to obtain $\text{Ca}(\text{OH})_2$ for reuse. A black liquor with a fuel value is a Kraft pulping yield that retains lignin, hemicellulose, and extractives such as oils, resins, and terpenes. The lignin and hemicellulose contained in the black liquor is burned to co-generate electricity and steam. A boiler recovers the heat from the black liquor combustion as superheated steam. After that, the high-pressure steam moves a turbine to generate electric energy. In the end, the lowered-pressure steam from the turbine serves in different processes in the mill.

The kraft or sulfate pulping leads to higher pulp strength properties than the sulfite pulping and applies to all wood species. On the other hand, to remove foul odors from this process is a demanding task. In his concern, modern mills use gas collection systems to prevent foul odors. Moreover, chemical reactions and the pH level during cooking form compounds cause the pulp to become darker than the original biomass. The Kraft pulping yields more chromophores than sulfite pulping, which are chemical species that absorb light at a specific wavelength and then emit color. The resultant pulp has low brightness, which must be bleached to produce white paper in the papermaking stage.

Fig. 3.7 illustrates the Kraft pulping process, including representative images of the pulp refiner.

3.4.2.1 Challenges from Kraft chemical recovery process and potential solutions

Some operational problems in the chemical recovery process concern unit operations and processes working. The main drawbacks are mechanical failures and damages, chemical issues, deposit or sludge formation, unwanted deposition, or accumulation, lowering of thermal performance and process efficiency, shutdowns, process instability, poor production, and gas emissions. Table 3.5 summarizes the operational problems in different equipment used in the chemical recovery process of pulping process. These operational problems induce poor liquor and pulp quality, decrease energy consumption efficiency and production capacity in the mill. A critical issue is indeed for the mills to treat more polluted and toxic effluents and to meet the rigorous eco-friendly regulations (Tran and Vakkilainen, 2008). Depending mainly on the performance of the recovery boiler and the causticizing plant, accumulation of undesired chemical compound can be originated, such as chloride (Cl) and potassium (K).

The recovery process plays a crucial role in the pulping process. A proper recycling circuit resolves the quality of the white liquor and, in turn, enhances the pulping performance and pulp quality.

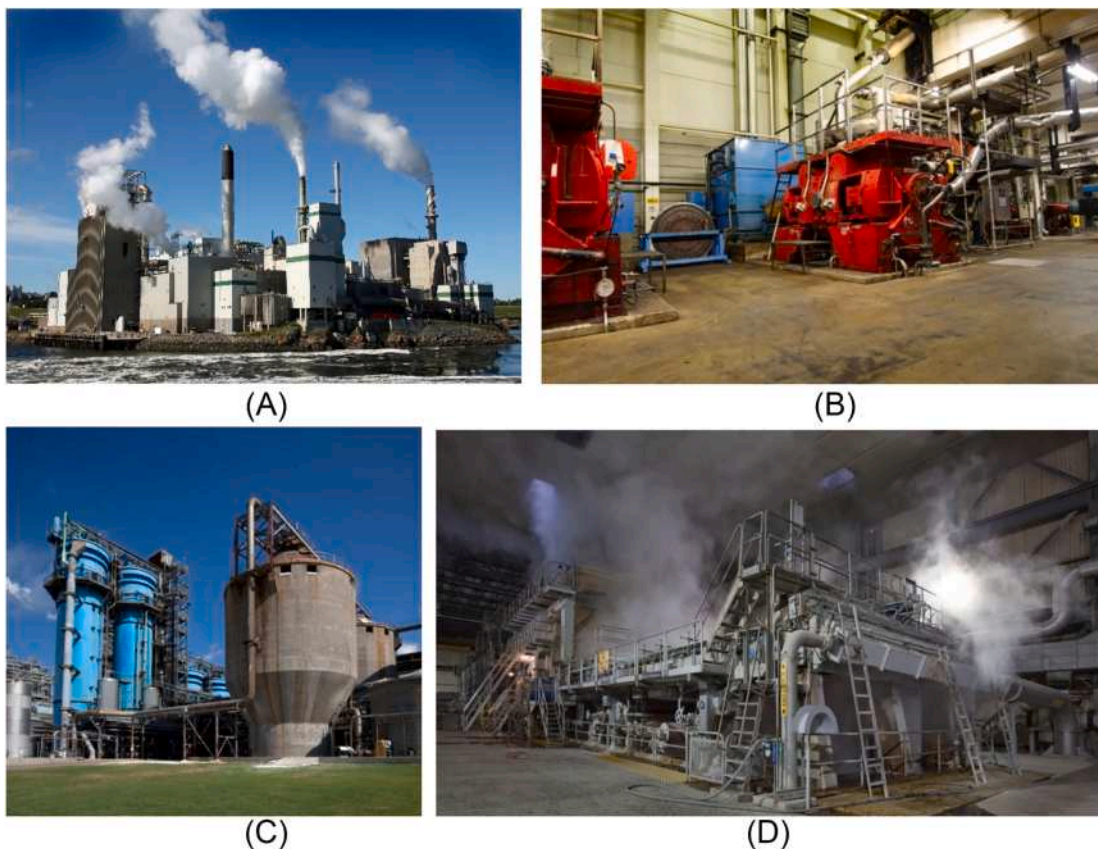


Figure 3.7 Pulping process (A) Marc-Lautenbacher. Plant of Irving Pulp & Paper Limited in Saint John, New Brunswick, Canada. Irving Pulp & Paper Limited produces softwood and hardwood grades of kraft pulp. It is with Irving Paper Limited, Irving Tissue Company Limited part of the Irving Forest Products & Services which is owned and operating by the holding company J.D. Irving, Ltd. 1 September 2019. https://commons.wikimedia.org/wiki/File:Irving_Pulp_%26_Paper_Ltd_in_Saint_John_Canada.jpg. This file is licensed under the Creative Commons Attribution-Share Alike 4.0 International license. (B) Author: Work With Sounds, This german made pulp refiner, manufactured by Andritz Sprout-Bauer, processes and refines paper pulp. At Bravikens paper mill in Norrköping, Sweden, 2014. 9 October 2014. https://commons.wikimedia.org/wiki/File:Pulp_refiner.JPG. Library of Congress's Prints and Photographs division. This file is licensed under the Creative Commons Attribution-Share Alike 4.0 International license. (C) Carol M. Highsmi, The Alabama River Pulp Company and the Claiborne Mill Complex, Claiborne, Alabama, 2010. Library of Congress's Prints and Photographs division. no known copyright restrictions. <http://hdl.loc.gov/loc.pnp/highsm.07933>. George F. Landegger Collection of Alabama Photographs. (D) Carol M. Highsmi, The Alabama River Pulp Company and the Claiborne Mill Complex, Claiborne, Alabama, 2010. Library of Congress, Prints and Photographs Division. no known copyright restrictions. <http://hdl.loc.gov/loc.pnp/highsm.07942>. The George F. Landegger Collection of Alabama Photographs.

The actions recommended in the literature to improve the recovery circuit include operating the recovery boiler to burn the black liquor at a solids content greater than 75% and at high pressure and temperature. This practice generates more steam, enhances

Table 3.5 Main operational problems in the chemical recovery process unit operations and processes of the Kraft pulping process (Tran and Vakkilainen, 2008).

Unit operations and processes	Operational problems	Process degradation issues
Multi-effect evaporators	• Fouling, • Corrosion, • Foaming.	• Boilouts, • Increase steam needs, • Lower solids in the liquid product.
Boilers	• Fouling, • Corrosion, • Plugging, • Cracking, • Explosions, • Deposits, • Issues with standard sootblowing, • Run-off / instability.	• Limit availability of the boiler. • Lower production, • Air emissions (such as CO₂). • Substantial costs.
Kilns	• Ringing, • Balling, • Dusting, • Mechanical damage.	• Low thermal efficiency, • High fuel consumption, • Poor product quality, • Air emissions.
Causticizing plant	Corrosion in storage tanks	Overliming Poor settling Poor product quality Low washing and causticizing efficiency

combustion stability, and lowers undesirable emissions. It is likewise suggested to prevent sediment accumulation. Other approaches concern reducing the liquor viscosity with heating to facilitate its processing. The energy consumption can be reduced by increasing the contact surface and using feedwater and air preheaters.

A defly is to annihilate Cl and K and to avoid noncondensable gases producing foul odors. In the causticizing plant, good practices involve:

- reducing dusting,
- Installing filtering instead of settlement for liquid-solid separation.
- Ensuring effective lime mud dewatering in the calcining.
- Implement auto causticizing.

Auto causticizing is done by adding sodium borate into the liquor system in such a way as to reach partial causticizing in a recovery boiler. Subsequently, this operation is completed in the causticizing plant with reduced lime consumption.

There is moreover an option to choose different fuels for operating the kiln based on wastes and emissions in the plant. A solid fuel can be gas produced from wood waste. Liquid fuel can be methanol, produced from noncondensable gases.

In the industrial practice, at the P&P mills, the encountered challenges and proposed solutions coupled with fouling and soot-cleaning for recovery boilers are the following ([Heat Management, 2019](#)):

- A problem is that the steam on the return stroke is sent mainly to waste, increasing costs and CO₂ emissions.
- Deposits and plugging on the boiler.
- Heavy fouling that conducts to unexpected water washes.
- Traditional soot-blowing requires opening and closing the high-pressure steam flow, which drives water hammer and, in turn, grave wear on the boiler tubes. Condensate on the soot-blower lances induces erosion.
- Precipitator clogging reduces its performance and limits boiler load while increasing fan load. Other problems include differential pressure destabilization and the need for unplanned shutdowns for manual cleaning.
- The above problems result in CO₂ emissions. Wasted steam could be used to generate energy, which would be an advantage over fossil energy.

Optimizing the recovery boiler and managing cleanliness effectively mitigate the fouling problem and the originating issues. A heat management system is required to allow the user to improve soot blowing starts without consuming more steam or significantly affecting cleanliness.

Soot blowers in recovery boilers are usually operated continuously to prevent fouling and sintering of accumulations on heat exchanger surfaces. However, this measure may need to be revised, as the regular cleaning of the equipment takes a lot of time and resources. The practical solution is to implement a local control system to operate the soot-blower's steam valves. In summary, the solution is to achieve continuous operation of the soot-blowers by means of automatic control actions ([Heat Management, 2023](#)).

3.4.3 Bleaching process evolution

The evolution of bleaching processes has shifted from chlorine-based to eco-friendly bleaching agents like ozone, peroxides, and

enzyme-based to tackle health and environmental issues ([Bajpai \(2004\)](#); [Torén and Blanc \(1997\)](#); and [Solomon \(1996\)](#)). The bleaching progress can be described in three periods as:

3.4.3.1 Prechlorine period

Include the methods employed before the widespread adoption of chlorine in industrial processes, predominantly encompassed exposure to sunlight, lye, and lactic acid from sour milk.

3.4.3.2 Chlorine period

The discovery and introduction of industrial utilization of chlorine and chlorine-based compounds for bleaching occurred in this period. The chlorine-based process markedly enhances efficiency. In turn, it pushes health concerns and environmental implications due to toxic byproducts. It may furthermore pose risks to the environment and food chain.

Certain enzymes are developed as substitutes for pulp bleaching, reducing reliance on harmful chemicals while enhancing the brightness and quality of the pulp. These enzymes achieve more ease of lignin removal without directly attacking it, thereby sweetening the penetration of bleaching chemicals. The most used enzymes in the biobleaching process include:

Xylanases: These enzymes are valued for deigning xylan, a form of hemicellulose found in plant cell walls. By breaking down xylan, xylanases enhance the penetration of bleaching agents into the fiber, thus lowering the necessity for harsh chemical treatments. Studies have demonstrated that xylanases can decrease chlorine usage by 31% and enhance pulp brightness by 2.1–4.9 points.

Laccases: These are oxidase enzymes that promote the oxidation of phenolic and non-phenolic lignin-related compounds and diverse other molecules. They serve in the P&P industry for delignification and bleaching functions. Laccases exhibit heightened effectiveness when paired with mediators such as 1-hydroxybenzotriazole and 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid). These mixtures intensify the enzyme's efficacy and the overall bleaching process.

Cellulases and other enzymes are supplementary enzymes integrated into the pulp bio-bleaching system. Some examples are cellulases, amylases, and lipases. These enzymes target specific elements of the wood fibers to boost the bleaching efficacy.

Enzymatic bleaching techniques reduce the energy required for the bleaching process and lower the expenses associated with effluent management. It is worth noting that commercial enzymes for the biobleaching process are available in the market. The

challenge is to improve biobleaching in such a way to feature various enzyme combinations suitable for diverse papermaking demands.

3.4.3.3 *Postchlorine period*

This generation underscores the innovation and integration of alternative bleaching approaches that eschew chlorine compounds, including ozone, peroxides, and enzyme-based or biobleaching processes. This transition aims to mitigate the environmental and health concerns associated with chlorine utilization.

The prevalent challenge in the bleaching stage of P&P mills is to decrease chemical usage and minimize environmental impact. The current state of bleaching practices covers both laboratory and industrial applications of enzymes. Additionally, an approach that targets significant chemical cost reductions is applying lignin-oxidizing enzymes and WRF for pulp delignification.

The challenge of the bleaching process is moving towards more sustainable and less harmful bleaching methods fueled by environmental, health, and technological advancements.

[Fig. 3.8](#) illustrates the bleaching stage and wastewater effluents in P&P mills.

3.4.4 Papermaking processes and challenges

The papermaking consists of several stages. The brief description below offers insights into the defies in effluent handling at this step ([Suhr et al., 2015](#)):

Stock preparation: This step initiates the conversion of raw stock into finished stock for paper production. This process involves blending different pulps, diluting, and adding chemicals. The goal of this step is to improve the optical and quality properties of paper by means of fillers. Some typical fillers are calcium carbonate, kaolin, and dyes. The addition of auxiliary agents aids in the retention of fillers and fines in the paper. The sought-after attributes in papers are printing and write-ability qualities, dimensional stability, and greenness.

Paper machine: This is an industrial machine where the paper is formed, and most of its properties are defined. The machine has a headbox, wire, press, and dryer sections. The tasks in these units are paper sheet making, water removal, and sheet drying. In these units, sizing agents such as starch, rosin, and synthetic polymers are dosed to increase water resistance.

Water circuits and fiber recovery: relates to water recirculation control to ensure the effective use and recovery of fibers.



Figure 3.8 Bleaching stage wastewater effluents. (A) Author: Velvet. View of the former Mahieu bleaching plant, Rue des Frères Mahieu, in Erquinghem-Lys. 26 January 2024. This file is licensed under the Creative Commons Attribution-Share Alike 4.0 International license. https://commons.wikimedia.org/wiki/File:Erquinghem_lys_usine_blanchiment_mahieu.jpg. (B) Wilson, Doug. Pumping waste water in Bellingham waterway, site of the Georgia Pacific pulp mill and other industrial plants. bleaching agent causes foam. lack of good flushing by tidal flow results in heavier buildup of pollutants here than in most other mill locations on Puget sound. May 1973. This file was provided to Wikimedia Commons by the National Archives and Records Administration as part of a cooperation project. The National Archives and Records Administration provides images depicting American and global history which are public domain or licensed under a free license.

Broke system: This step involves handling and recycling of broke, that is, the wastepaper produced during papermaking. The broke goal is to ensure uniformity and quality in the stock flowing to the paper machine.

Optional steps depend upon the type of paper and board to produce; some examples are below:

Sizing: entails application of starch or synthetic sizing agents to adjust the paper's absorption properties.

Coating: refers to dosing a mixture of pigments and additives to improve the surface quality for printing. In the end, the coating improves surface properties with binders like starch and synthetic latex, pigments such as calcium carbonate and kaolin, and additives.

Dyeing of paper: applies to adding the desired colors to the paper.

Addition of chemicals: alludes to dosing chemicals to achieve specific paper properties.

Calendering: hints at processing the paper through rollers to improve smoothness.

Reeling/cutting/dispatch: These final steps involve preparing the paper according to customer specifications.

Chemicals are dosed at different stages of the papermaking process, still for water treatment. For example, flocculants and coagulants clarify water and recover fiber. Then, biocides keep microbial control, defoamers reduce foam, and dispersants maintain pulp fluidity.

During the papermaking process, some outflows, which consist of a mixture of substances, occur. The outflows from stock preparation and paper machine stages contain fibers, fillers, chemicals, and water. They are released from operations like washing, screening, and dewatering. The waste streams from coating and sizing may include excess coating materials, sizing agents, and water. The effluents from water treatment may contain residual chemicals, biological matter, and treated solids. To handle these outflows mitigates their environmental impacts. The challenge is then to implement advanced suitable treatments to remove contaminants and recover valuable materials.

The process meets significant challenges in reducing the environmental impact of air emissions and effluent discharge. New technology can give rise to valuable solutions.

Fig. 3.9 illustrates the papermaking process, including machinery.

3.4.4.1 Challenges in papermaking processes. Papermaking sludge-based flocculant

Obtaining and using papermaking sludge-based flocculant is adequate in wastewater treatment. The performance of this type of flocculant and commercial lignin is advantageous compared to conventional flocculants. Typical flocculants are polyaluminium chloride (PAC) and PAM. Papermaking sludge-based flocculants can be incorporated in three ways in the process: as a standalone flocculant, as a supplement to PAC, and to treat the effluent from the PAC system. The treatment scheme has been reported as effective in removing color, COD, and tryptophan-like pollutants at different pH levels of wastewater. These alternative flocculants and lignin are furthermore suitable for removing reactive turquoise blue and dispersing red dyes. It seems that the combination of PAC and the sludge-based flocculant in a secondary coagulation-flocculation process allows for improved effluent quality.

The application of these alternative flocculants has been reported by Guo et al. (2021), who examined the use of sludge-based flocculants for printing and dyeing wastewater treatment. The reported findings indicate that the sludge-based flocculants surpassed PAC and PAM regarding COD removal and displayed less sensitivity to pH variations than PAC and PAM. Additionally, they exhibited remarkable proficiency in eliminating tryptophan-like pollutants.

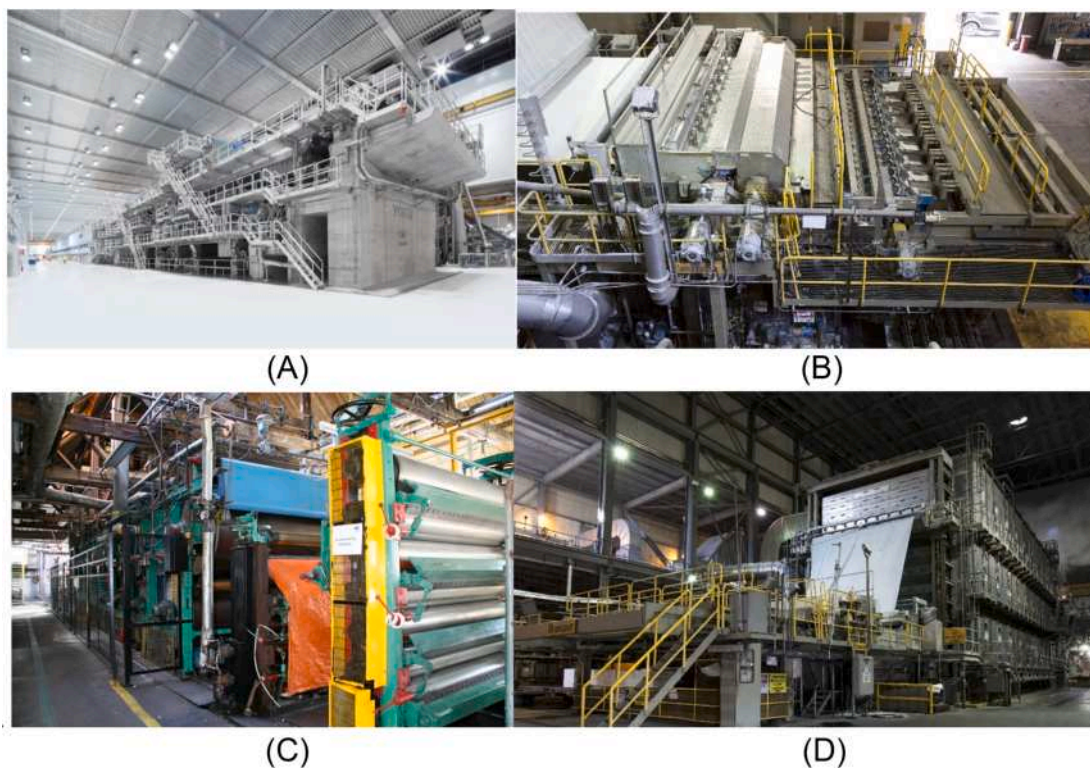


Figure 3.9 Papermaking process (A) Jan Hosan; Copyright holder Voith GmbH & Co. KGaA, Heidenheim, Germany. The most modern, most efficient and largest board machine in the world, was successfully commissioned at the BillerudKorsnäs production facility in Gruvön, Sweden. The Voith XcellLine board machine has been equipped with a pioneering technological setup that sets new performance benchmarks for production lines for four different board grades. At a design speed of 1200 m/min and web width of 8800 mm, the capacity of the BM 7 is 550,000 metric tons per year. Start-up took just seven days from stock on wire to paper on reel. 1 August 2019. https://commons.wikimedia.org/wiki/File:Gruvoen_KM7_delivered_by_Voith_in_2019.png. (B) Carol M. Highsmith. Since 1978, the Alabama River Pulp Company and the Claiborne Mill Complex have been producing southern softwood and hardwood kraft pulps for the paper producers service markets around the globe. Parsons & Whittemore manages the plant. 30 April 2010. <http://hdl.loc.gov/loc.pnp/highsm.07940>. Library of Congress-no known copyright restrictions, (C) Chris Allen. Fourdrinier paper machine, Frogmore Mills This is a very historic site and was apparently where this machine (not this particular one) was first used in the UK in 1803. This more modern machine is operated by a charitable trust and is still in use. It is of great interest as it is driven by a steam engine - one of very, very few still in commercial service in the UK. 11 March 2007. https://commons.wikimedia.org/wiki/File:Fourdrinier_paper_machine,_Frogmore_Mills_-_geograph.org.uk_-_1544694.jpg. This file is licensed for reuse under the Creative Commons Attribution-ShareAlike 2.0 license. (D) Carol M. Highsmith, The Alabama River Pulp Company and the Claiborne Mill Complex, Claiborne, Alabama, 2010. Library of Congress, Prints and Photographs Division. no known copyright restrictions. The George F. Landegger Collection of Alabama Photographs. <http://hdl.loc.gov/loc.pnp/highsm.07934>.

Source: (A) From Voith Media Database. This file is licensed under the Creative Commons Attribution-Share Alike 4.0 International license.

In a similar research, [Feng et al. \(2021\)](#) provided a comprehensive analysis of the characteristics and structures of alkaline lignin, commercial lignin, and papermaking sludge-based flocculants, highlighting their charge properties, molecular weights, zeta potentials, and functional groups. The research findings emphasize that flocculants, synthesized from papermaking sludge, exhibit similar flocculation performance to lignin, and both are superior to traditional flocculants in the removal of reactive turquoise blue and dispersing red dyes. The research concludes that flocculants derived from papermaking sludge offer an efficient solution for dye wastewater treatment with practical application potential.

3.4.4.2 Challenges in papermaking processes. Monitoring and control systems

Wastewater streams from pulping and papermaking are critical pollution sources and are challenging to treat due to their well-studied heterogeneous and complex composition. One option to face the challenge of improving wastewater treatments is the integration of advanced control strategies, which should be considered. Hybrid control systems are classified into two types. The first type lies in well-established regulatory control systems, whereas the second type matters in decision-making systems. The later systems deal with the design, modeling, and analysis at a high control level engaged in the supervision and management tasks ([Awad, 2018](#)).

Advanced monitoring schemes allow for detecting sensor faults or virtual sensor designs. The measurement of process variables collects dynamic data holding noise and other transient behaviors. Thus it is essential to combine dynamic analysis and modeling. The control supervisory system needs good capabilities to process dynamic data. Plant modeling is an essential step in the supervisory system synthesis procedure. The standard technique uses multivariate statistical process monitoring methods to estimate the model parameters. The principal component analysis and partial least squares (PLS) are essential approaches to obtain suitably fitting process models. In particular, PLS is a basis for comparing and evaluating new schemes ([Awad, 2018](#)).

Monitoring systems for the industry bear an energy-saving and cost-effective process and direct to good product quality. Driving online sensors in wastewater treatments boosts water effluent quality and guides to safe release. The supervisory approach in papermaking wastewater treatment proposed by [Yang et al. \(2022\)](#) is a reference work dealing with strategies for detecting process faults. The considered wastewater treatment includes a primary settling tank for TSS removal ahead of a chemical treatment. The assessed variables were the reagent addition time, the chemical reaction temperature, and

pH. In addition, dynamic information due to unmeasurable noise disturbances and feedback regulation mechanisms is considered for the dynamics log. The failure detection system in the cited work was called the dynamic multiblock partial least squares method for monitoring papermaking wastewater treatment processes. A model is needed to design the model-based fault detection system. The strategy involves dividing the entire process variables into several blocks. In the sequence of industrial steps, the relationships between variables are obtained. The variables from the same unit are divided into one block. Then, the model fits the dynamic characteristics of the original data by an augmented matrices technique.

The quality monitoring scheme for papermaking wastewater treatment proposed by [Zhang et al. \(2021\)](#) is another work dealing with online modeling of papermaking wastewater treatments. The model combines variable significance in projection with dynamic Bayesian networks to effectively address the dynamic nature, nonlinearity, and uncertainty of the plant. The practical application concerns soft sensor modeling for decision-making in papermaking effluent treatments. It is an approach that overcomes the limitations of existing soft sensor methods, which have a basis on modeling methods.

3.5 Wastewater treatment technologies and challenges in the P&P industry

In the P&P industry, the process units are fed with substantial volumes of water and release polluted stream loads at the end. In this scene, it seems a good option to benefit from the potential for energy and water recovery and stream recirculation. Or else, it should be enough to release sufficiently clean effluents. In all instances, wastewater treatments are critical units in P&P mills. The treatment strategies differ greatly from elementary mechanical procedures to the vast application of microbial technology and cover advanced technologies, whose main challenge is hybridization.

3.5.1 Basic treatments classification

The treatment strategy of the P&P in mills' wastewater relies on the pulp type, amount, and markers of the effluents. The standard techniques are primary and secondary treatments. Thorough advances of these techniques are given by [Jagaba et al. \(2022\)](#); [Singh and Tripathi \(2020\)](#), [Achaw and Danso-Boateng \(2021\)](#); [Thompson et al. \(2001\)](#); and [Kamali and Khodaparast \(2015\)](#) and recapped below. As another option, or to add-on, tertiary or advanced treatments help remove non-biodegradable material.

3.5.1.1 Primary treatments

Separate water in the P&P mill effluents from suspended, floating, and settled solids, particulate matter, and organic material, via mechanical methods, for example clarification by sedimentation or flotation. These units have a high performance on suspended solid removal. In spite of that, primary treatments do not comply with the legal emission standards for effluent discharged into natural waters as they produce minor removal of BOD and COD. Hence, to improve effluent handling, secondary or tertiary treatments are binding to follow these former stages. A primary treatment prevents interference with biological treatment processes and makes the overall process more efficient.

Wastewater handling in the primary treatment process is as follows: Wastewater is first passed through a screening step to remove large debris such as paper, plastics, and metals. This step prevents damage and blockages in the treatment plant equipment. In the second step, the wastewater moves to a sedimentation tank (or primary clarifier), where gravity helps settle solid particles to the bottom, forming a sludge. The sludge is regularly removed and further treated or discharged. The sludge gathered in sedimentation tanks holds significant organic material and requires further treatment. The sludge treatment can be achieved with anaerobic digestion, composting, or incineration. The choice depends on the plant's capacity and ecological regulation constraints.

The effluent from primary treatment contains fewer solids but still has a high level of dissolved and particulate organic matter. Indeed, it needs secondary treatment to reduce the organic content further.

3.5.1.2 Secondary treatments

Secondary treatments remove biodegradable matter in the P&P mill effluents via micro-organisms that speed up the inherent degradation of organic wastes. The most widely known secondary treatments are aerated stabilization and activated sludge treatment, together being aerobic. Often, the second one goes above and beyond at BOD and TSS removal, but enhanced secondary treatment plants moreover aim at lowering levels of AOX and COD (Rosa et al., 2010; Thompson et al., 2001). Sometimes secondary treatments remove nutrients such as nitrogen and phosphorus, which are not effectively removed by physical processes alone.

3.5.1.2.1 Biological treatment processes

ASP: This is one of the most common secondary treatment approaches. The process applies aeration of the wastewater to stimulate the growth of aerobic bacteria and other microorganisms

that consume organic matter in the wastewater. The wastewater and microorganisms form a mixed liquor. The mixture is later settled in a secondary clarifier to separate the treated water from the biomass.

Fixed film systems: These systems comprise trickling filters and rotating biological contactors. In them, wastewater passes over a coated medium holding bacteria and microorganisms, which consume the organic matter.

Nutrient removal: This is a process in which operations of nitrification-denitrification and phosphorus precipitation occur. The process is conceived to remove nutrients like nitrogen and phosphorus. Otherwise, a surplus of nutrients, known as eutrophication, ensues and can give rise to complex interactions between different factors.

An important problem with secondary treatments is that they cause an excess of biological sludge that needs to be treated before disposal or reuse. Operations to solve this problem are thickening, digestion, dewatering, and, in some cases, conversion to bioenergy or soil amendments.

The effluent from secondary treatment is much cleaner than that from primary treatment. It has low levels of BOD, COD, and SS. However, it may still require tertiary treatment, especially if the water is to be released into a sensitive environment or reused.

Secondary treatment is essential to comply with regulatory standards, which often specify the maximum allowable BOD, COD, and SS levels in the effluent released into water bodies.

In the P&P industry, secondary treatments are decisive for mitigating the environmental impact of effluent release. This stage is critical to guarantee that the wastewater treatment is performed to a level that protects a wide range of ecosystems and meets regulatory standards for water quality.

According to [Thompson et al. \(2001\)](#), two critical challenges of activated sludge treatment:

1. To control the concentration of the oxygen dissolved that is contained in the aeration tank.
2. To prevent a poor settling of sludge, assessed from the stirred sludge volume index (SSVI), calculated as stated in equation ([Mehmood et al., 2019](#)).

$$\text{SSVI} \left[\frac{\text{mL}}{\text{g}} \right] = \frac{V_{ss}^w \left[\frac{\text{mL}}{\text{L}} \right]}{C_{ss} \left[\frac{\text{g}}{\text{L}} \right]} \quad (3.2)$$

where V_{ss}^w is the wet settled sludge volume, C_{ss} is the SS concentration. Elevated SSVI results if the solids concentration in the process waste is in excess as the solid concentration in the final settlement tank go beyond the capacity limit.

As a case in point, advanced reactor technologies based on microbial degradation are effective strategies to treat wastewater from P&P mills. Systems developed for the industry are, for instance, MBR and MBBR. There are anaerobic and aerobic systems at play. The top goal is to bring more sustainable systems into operation. A criterion to commit to this purpose is fusing the mentioned types of reactors into refined hybrid technologies that meet strict wastewater treatment standards and prospects ([Patel et al., 2021](#)).

The MBR is a biological reactor in which a membrane unit is added to perform a solid-liquid separation. MBRs offer several advantages over traditional treatment methods, as can be the ASP. MBRs yield high-quality effluent that is fair for reuse, with less sludge production, higher separation efficiency, and down retention of LMW organic micropollutants. However, a notable drawback of MBR systems is membrane fouling, which affects their performance. To address the fouling issue, an effort should be made to integrate the MBR technology with advanced oxidation, RO, or other methods to form a hybrid system.

The MBBR is an advanced technique for treating wastewater. It involves thousands of polyethylene biofilm carriers that move around in an aerated basin. These biofilm carriers provide a surface area for the growth of both heterotrophic and autotrophic bacteria, which improves productivity. This setup enables efficient degradation of pollutants. MBBR technology is known for its simplicity and cost-effectiveness.

The treated wastewater can be recycled after filtration, disinfection, or other advanced treatments to remove the remaining pollutants. The yield of high-purity water makes it suitable for reuse in agricultural irrigation, industrial processes, groundwater replenishment, and even potable water supplies. The specific recycling process depends on the intended reuse, which dictates the level of treatment required to ensure safety and compliance with regulatory standards. This recycling invests in sustainable water management practices.

3.5.1.2.2 Membrane treatment processes

There are several methods available to treat papermaking effluent, including flocculation, alkali recovery, acidulation precipitation, concentrate treatment, biological methods, oxidation, and membrane separation.

In particular, the technique for mixture separation by membrane is performed by passing the wastewater through a synthetic membrane (see [Neves & Souza, 2017](#)). The material being eliminated is small organic and inorganic matter. The process excludes biological and chemical transformations. [Table 3.6](#) briefly describes the membrane separation technologies.

Table 3.6 Membrane separation technologies (Neves & Souza, 2017).

Membrane filtration technique	General description	Size of the membrane pores
Microfiltration	Used as prefiltration method, and for screening bacteria. Size of membrane pores: 50 nm–5 μ m.	Filtration processes based on particle size elimination.
Ultrafiltration	Have open porous. Used in pressure-driven separations to eliminate micro-organisms, bacteria, and solids from a liquid. Size of membrane pores: 5–100 nm.	
Nanofiltration	Separate fairly small organic compounds and ions from a solvent. Size of membrane pores: 1–10 nm.	
Reverse osmosis	The water is transported through membranes at high pressure, retaining most of the ions and larger solids in the liquid. This process yields high quality water.	Separation at a molecular scale by solution-diffusion mechanisms. The process driven force can be solubility gradients into the membrane, or diffusion velocity gradients through the membrane.
Pervaporation	Liquid-liquid separation. For azeotropic mixtures or blends with low difference in volatility.	
Electrodialysis	Uses bipolar membranes. It is a process that can replace electrolysis and has a wider diversity of applications.	The transport depends on the charge of the molecules. Likewise, ions can be exchanged selectively by another ion.

The cost of membrane-based treatment has become competitive compared to other established treatments. Even so, the operation should be at the lowest possible pressure for a more economical operation. Factors such as membrane fouling lower filtration effectiveness and demand more energy and cleaning, increase chemicals needs and operational costs. Optimizing the permeate flux, feed flow rate, and pressure solves the problem of fouling and allows for optimizing the operational parameters of the filtration unit.

3.5.1.2.3 Application of a composite membrane for the treatment of papermaking effluent via ultrafiltration

The membrane technique has been explored to treat paper-making effluent. In the P&P industry, UF is the most common membrane technology (Zhou et al., 2012). An issue is designing membranes with suitable properties to obtain optimal filtration.

An effective membrane should show chemical stability with heat and pressure resistance.

For the illustration of this type of treatment, reference is made to a study describing the application of a cellulose nanocrystalline (CNC) / polysulfone composite membrane as an UF membrane in the treatment of papermaking effluent. The membrane properties include the cross-sectional morphology analysis via SEM. The mechanical characterization is given by the tensile strength, measured by a tensile testing instrument. The composition characterization includes determining the lignin content, COD, and SS. An UV spectrophotometer can be used for this purpose. Membrane performance indicators are retention rate and water flux. The membrane design should always balance retention and flow rate levels suitably.

The retention rate R is defined as in (3):

$$R[\%] = \left(1 - \frac{C_{fs} \left[\frac{g}{L} \right]}{C_{is} \left[\frac{g}{L} \right]} \right) \times 100\% \quad (3.3)$$

where C_i and C are the concentrations of the initial and filtered solutions, respectively.

The pure water flux $J(\text{L}/\text{m}^2\text{h})$ can be estimated as in (4),

$$J \left[\frac{\text{L}}{\text{m}^2\text{h}} \right] = \frac{V_{fw}[\text{L}]}{A[\text{m}^2] \cdot t [\text{h}]} \quad (3.4)$$

Where V_{fw} stands for the volume of filtered water, A is the membrane surface area, and t is the processing time.

The CNC content impacts the membrane properties and the effectiveness of the composite membrane in reducing the lignin content, SS, and COD in the treated effluent.

3.5.1.3 Tertiary treatmentsg

Section 3.2.5 provides a classification of the main advanced tertiary treatments. Table 3.7 describes some research works in which advanced industrial wastewater treatment methods suitably convert non-biodegradable organic matter to harmless compounds, highlighting the application and the technology applied.

3.5.2 Effluent treatment challenges in pulp and paper mills

An effective wastewater treatment should be cost competitive, and combine a sequence of physicochemical, biological, and hybrid

Table 3.7 Description of advanced wastewater treatment methods and related research.

Advanced treatment	Objective of the treatment	Treatment description	References
Fenton oxidation process	Reduction of chemical oxygen demand (COD) and lignin concentrations in pulp and paper (P&P) effluents. The treated water can be reused due to low pH.	The Fenton reaction is a way to produce $\cdot\text{OH}$, but it has the problems of high reagent consumption and ferric sludge formation. The electro-Fenton overcome the problems by means of the controlled synthesis of H_2O_2 . It is produced by a two-electron reduction of O_2 in an electrochemical cell at an acidic medium of about pH of 3. The Fenton's reagent is continuously produced and controlled in an electrochemical reactor. (Oturán & Oturan, 2018). Optimizing operation involves suitably choose current density, electrode materials, air pressure, treatment time and the presence of NaCl. It is useful for the treatment of bleaching processes. Effectively removes total organic carbon (TOC). Coagulation-flocculation-sedimentation can precede this advanced oxidation treatment for enhanced results.	Klidi et al. (2019) Grötzner, et al. (2018) Gautham et al. (2018)
Ozone oxidation	Color removal and conversion of refractory materials into biodegradable matter. Catalysts and ultraviolet light and ultrasonic improve degradation.	Ozone (O_3) is highly reactive and has a high oxidation-reduction potential. In aqueous media it instantaneously produce more powerful oxidants, like $\cdot\text{OH}$. In wastewater treatment, O_3 can be used along with other treatments to improve biological processes (Paraskeva and Graham (2002)).	Covinich et al. (2014)
Electrocoagulation	COD, TOC, and color removal.	During this process, coagulants are generated by dissolving aluminum or mild steel used as sacrificial electrode. Under a potential is applied by an external power source, the sacrificial electrodes undergo oxidation reactions which produce iron hydroxide $\text{Fe}(\text{OH})_n$ that destabilize the pollutants by charge neutralization. Pollutants can be then separated by electro-flotation. The process can be optimized in function of current density, pH, treatment time, and inter-electrode distance.	Kumar and Sharma (2019) Shankar et al. (2014)

(Continued)

Table 3.7 (Continued)

Advanced treatment	Objective of the treatment	Treatment description	References
Electrodialysis	Separation of heavy metals, such as Nickel (Ni), copper (Cu), zinc (Zn), chromium (Cr), calcium (Ca).	It is a separation process where the action of an electric field produces selective transport of ions across ion-exchange membranes.	Gurreri et al. (2020)
Membrane bioreactors	Treatment of eucalyptus P&P wastewater.	It is a reactor in which a sedimentation tank is replaced by membrane filtration for solid-liquid separations without the use of chemicals. The membrane fouling is a persistent problem.	Poojamnong et al. (2020)
Hybrid Airlift Membrane Bioreactor	COD, ammonium, nitrite, nitrate, and total Nitrogen, organics, and nutrients removal, with diminished fouling.	It is a hybrid membrane bioreactor, which integrates oxic, anoxic and anaerobic zones. In anoxic conditions free oxygen is absent but bounded oxygen and nitrogen are present. In oxic water, the oxygen dissolved is the favored electron acceptor.	Izadi et al. (2020)
Photocatalytic treatment nanomaterials	Hazardous material, Color, aromatic compounds, COD removal. Nanomaterials degrade organic matter and reduce metals content.	Semiconductor photocatalysis is an advanced oxidation method based on reactions occurring on the surface of semiconductors. Nanomaterials are used as semiconductors that increase surface area and thus the adsorption capability.	Nogueira et al. (2018)
Ion exchange	Color and lignin residual removal.	The batch process is performed in columns filled with solids, called ion exchange resins. These resins remove organics, and mono or divalent salts. The challenge is to choose the suitable solid to achieve the salt and organic separation in the membrane filtration. The resin beds are modulars and the regeneration of the resins is done by acids and bases.	Bassandeh, et al. (2013)

processes to overcome the drawbacks of single standard methods (Singh & Tripathi, 2020).

Advanced treatment processes often consume significant amounts of energy and require costly chemicals and maintenance, resulting in high operational costs. In effect, striking a balance between treatment efficiency and operational costs presents a significant challenge. Continued research and development are necessary to identify more efficient, cost-effective, and sustainable treatment solutions.

Effluents contain a wide range of pollutants; each type needs a different treatment approach. Certain pollutants, such as dioxins, furans, and AOX, pose challenges due to their toxicity, persistence, and potential for bioaccumulation. Effectively removing these substances necessitates advanced treatment technologies such as ozone, AOPs, or activated carbon adsorption.

Treatment processes generate substantial amounts of sludge, which can be voluminous and potentially toxic depending on the contaminants removed from the wastewater. Managing, treating, reusing sludge represents a significant challenge.

The need of eco-friendly processes has conducted to stringent environmental regulations. Compliance with strict and evolving regulations needs monitoring and the upgrading of treatment systems. This includes meeting discharge quality limits for physico-chemical measurements and pollution indicators.

Implementing real-time monitoring systems and adaptable treatment processes that can accommodate changes in wastewater composition and flow rates is essential to maintaining compliance.

Achieving the necessary water quality for reuse within the mill, particularly for processes like cooling or washing, necessitates the utilization of advanced treatment technologies and stringent quality control measures.

Adopting new technologies can pose challenges due to the risks associated with scaling up novel technologies, the requirement for substantial capital investment, and the need for skilled personnel.

Other specific technological challenges are described in the next Sections.

3.5.2.1 Advanced hybrid treatments

Mitigating sludge production: The challenge of further mitigating the sludge production in P&P mills after the ASP can be faced by secondary reduction processes that integrate physical, chemical, and biological procedures. Two approaches rely on process modifications or post-treatments.

Process modifications can be achieved through operational control, which consists of plant operations that minimize the waste-

activated sludge. Another alternative is to treat the return-activated sludge. The second approach is to implement post-treatments involving oxidation operations of different natures, such as heat treatment, chemical oxidation, and sludge digestion.

Mitigating refractory material content: In general, biological treatments are the most relevant in breaking down organic matter; on the other hand, they are weak to destroy refractory compounds. Thus in P&P, refractory compounds in wastewater are not broken down by biological treatment. For this purpose, tertiary treatments are necessary. More valuable techniques to clear refractory material are the AOPs. As the central point of these methods, oxidation is the loss of electrons from an electron donor and the ensuing transfer to an electron acceptor. The losses and gains of electrons return ions or radicals, which are unstable and thus reactive species. Further reactions follow the formation of new radicals until thermodynamically stable species are obtained.

The oxidation potential measures the oxidation capacity of species. The most potent oxidants under this value are hydroxyl radicals ($\text{HO}\bullet$) and ozone. The well-known AOPs regroup treatment units that benefit from the high oxidation capacity of hydroxyl radicals. In these treatments, the energy of the oxidant radicals boosts the decay of organic species, such as resin acids, volatile organic compounds (VOC), and fatty acids. The degradation is performed in greater or lesser degrees. The primary level of degradation induces structural changes; then, middle degradation lowers toxicity, and the final degradation causes the mineralization of organic molecules. Mineralization means changing recalcitrant compounds into inorganic compounds. Strategies from this group include Fenton, photo-Fenton, and advanced ozonation processes, and photocatalysis (Covinich et al., 2014; Hermosilla et al., 2015).

Tertiary treatments often integrate physical and chemical unit operations to remove TSS, colloids, color, toxic compounds, and recalcitrant COD. Membrane-based processes includes UF, NF, and RO that are highly effective. Some issues of these technologies are their high energy demand, reduced lifespan, and maintenance problems, and the need for pretreatment. In the same line, ozonation that breaks down organic compounds and pathogens, consumes a significant amount of electricity. Adsorption through porous media is an efficient separation process, with micropollutants release capability. Its limitations include performances decay for substantial contaminants loads, and continuous adsorbent regeneration. To address the disadvantages of the practice with these advanced methods, strategies from this group include Fenton, photo-Fenton, and ozonation processes, and photocatalysis.

The challenge in selective and complex advanced schemes is to hybridize the treatment system configuration. As a reference work, the research of Mainardis et al. (2024) is recommended, where a life cycle

assessment methodology was used to assess and compare tertiary technologies for P&P wastewater treatment. The proposed scenarios to evaluate include inorganic and organic coagulation-flocculation, ozonation, ozonation combined with adsorption by activated carbon, and UF combined with RO. Regardless of the outcome of this study, the choice of the most suitable wastewater treatment scenario depends upon factors, such as effluent quality specification, environmental regulations, investment, and operating costs, among others.

Another water treatment option, UV radiation, is currently used to disinfect water, but it is not enough to treat effluents (Covinich et al., 2014). Hybridization of UV with powerful oxidants produces treatment scenarios relevant in P&P mills. PMS and hydrogen peroxide (H_2O_2) are oxidants that yield reactive oxygen species. Integrated with UV radiation, it results in UV/O₃ and UV/ H_2O_2 hybrid-derived methods. These hybrid methods and their combinations are suitable for treating the organic components of the effluents. The challenge is optimizing the strategies to make UV/AOP more effective than the non-enhanced AOPs. A published comparison of these methods has found that the UV/PMS hybridization is more performant than the UV/ H_2O_2 process, tested for different reaction conditions and pH levels (Wang et al., 2022).

3.5.2.2 Energy recovery strategies within wastewater treatment and sludge handling

A problem to consider is that intense energy consumption in wastewater treatments offsets the potential energy recovery in the sludge handling systems. One option is that the energy consumed in wastewater treatment should prioritize good effluent treatment rather than sludge reduction. This idea backs the proposal of rising secondary sludge formation as long as it is utilized for heat, biogas, or electricity production. Targeting aeration in wastewater treatment to minimize overall energy consumption is challenging but provides insights into the potential for energy recovery through different sludge handling strategies. Stoica et al. (2009) supported these tactics by analyzing process data from three Swedish mills and a mathematical model projection that assessed several sludge-handling methods.

3.6 Conclusion and future trends

In conclusion, to properly deal with the release, handling, and treatment challenges of wastewater from the P&P industry, it is meaningful to search for advances in technology and renewal of the P&P processes and wastewater treatments. The objective is to

adhere to environmental regulations and fulfill standard limits for the permissible release of effluent from the P&P mills. Sustainable practices and processes can reach these targets. In this vein, investment is demanded in resource conservation, which assumes alternative feedstock and more diversified intakes. Meanwhile, characterization tests and techniques must be improved to routinely monitor the P&P effluent properties. In parallel, good practices involve to delve into new biochemicals to be used in the processes, water and heat recirculation maximization, and waste reuse. Alike, demanding duties engage further valorization strategies. On the other hand, cutting-edge hybrid treatment systems are required in P&P effluents to break down pollutants. The general trend in the P&P industry is towards radical step-forward strategies. Thus the industry needs to move towards near-zero wastewater shots gradually. Summing up, the P&P industry is moving toward diversifying raw materials, including more green chemicals. There is, likewise, a tendency to transform waste into valued products for reuse in the P&P industry or other industries. Concerning the treatment units, the choice leans toward hybrid methods to succeed in waste biodegradability or removal. Furthermore, treatment methods are currently under development to meet avant-garde technology. In the end, for feedstock processing, the choice is to promote closed-cycle functions in the mills. All the practices and advances advanced for the P&P industry are looking to meet eco-friendly approaches.

Acronyms

AOP	advanced oxidation processes
AOX	adsorbable organic halogens
APHA	American Public Health Association
ASP	activated sludge process
BAT	best available technique
BOD	biological oxygen demand
CEDED	chlorination-alkaline extraction-chlorine dioxide-alkaline extraction-chlorine dioxide
CMC	carboxymethyl cellulose
CNC	cellulose nanocrystalline
COD	chemical oxygen demand
CPCB	Central Pollution Control Board
DMBPLS	dynamic multiblock partial least squares
EC	electrical conductivity
EF	electro-fenton
EEPA	Ethiopian Environmental Protection Authority
FAO	Food and Agriculture Organization
FID	flame ionization detectors
FTIRS	Fourier transform infrared spectroscopy
GC	gas chromatography

HMW	high-molecular-weight
ICMR	Indian Council of Medical Research
IR	infrared spectroscopy
ISI	Indian Standards Institute
LC	liquid chromatography
LPF	lignin separated by the coagulation-flocculation process
LMW	low-molecular-weight
MBR	membrane bioreactors
MBBR	moving-bed biofilm reactor
MF	microfiltration
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MSPM	multivariate statistical process monitoring
NaCMC	sodium carboxymethylcellulose
NADT	nitrogen adsorption-desorption technique
NCC	nano-crystalline cellulose
NF	nanofiltration
NFC	nano-fibrillated cellulose
NMR	nuclear magnetic resonance spectroscopy
NRCS	Natural Resources Conservation Service
PAC	polyaluminium chloride
PAH	polycyclic aromatic hydrocarbons
PAM	polyacrylamide
PCA	principal component analysis
PLS	partial least squares
PMS	peroxymonosulfate
P&P	pulp and paper
PSF	polysulfone
REACH	Registration, Evaluation, Authorization, and Restriction of Chemicals
RO	reverse osmosis
SEM	scanning electron microscope
SPM	suspended particulate matter
SS	suspended solids
SSVI	Stirred Sludge Volume Index
TA	total alkalinity
TDS	total dissolved solids
TGA	thermogravimetric analysis
TH	total hardness
TN	total nitrogen
TOC	total organic carbon
TP	total phosphorus
TS	total solids
TSS	total suspended solids
UASB	up-flow anaerobic sludge blanket
UF	ultrafiltration
UNECE	United Nations Economic Commission for Europe
USDA	United States Department of Agriculture
UV	ultraviolet
VOC	volatile organic compounds
WHO	World Health Organization
WRF	white-rot fungi
XRF	X-ray fluorescence

Symbols

A	membrane surface area (m^2)
C	concentration ($\text{g} \cdot \text{L}^{-1}$)
H^+	concentration of hydrogen ions in a solution (moles $\cdot \text{L}^{-1}$)
J	water flux ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)
pH	potential of hydrogen
R	retention rate (%)
$SSVI$	stirred sludge volume index ($\text{mL} \cdot \text{g}^{-1}$)
t	processing time (h)
V	volume (L)
V^w	wet volume ($\text{mL} \cdot \text{L}^{-1}$)

Subscript

fs	filtered solution
fw	filtered water
is	initial solution
ss	settled sludge
SS	suspended solids

Glossary

Adsorbable Organic Halogens (AOX) term commonly used in the field of wastewater treatment, particularly in industries such as paper manufacturing. It serves as a collective description for a group of organic compounds that are bound to halogens like chlorine, bromine, or iodine. AOX is utilized as an indicator to measure the presence and levels of organ-halogen compounds in wastewater. These compounds can vary from chlorinated solvents and pesticides to dioxins and furans.

Aerobic Treatment wastewater treatment process that uses oxygen and micro-organisms to downfall organic material. It is commonly implemented in the P&P industry to treat effluents retaining organic pollutants.

Anaerobic Treatment wastewater treatment that does not use oxygen. In these processes, the remedy relies on bacteria that thrive in oxygen-free environments to decompose organic matter, often producing biogas (like methane) as a byproduct. It is used for treating high-strength wastewater.

Clarifier tank used in wastewater treatment to facilitate settling solid particles or flocs. It aids in removing suspended solids in wastewater.

Delignification: process with a vital role in P&P manufacturing to extract lignin from wood or plant material. Lignin, a complex organic polymer that binds cellulose and hemicellulose fibers in plant cell walls, contributes to rigidity and resistance to degradation. Its elimination is essential to produce premium-quality pulp used in paper and other cellulose-based goods.

Significance of delignification:

- **Pulp Quality:** The removal of lignin enhances the brightness and whiteness of pulp, which are desirable characteristics for paper production and other applications.
- **Paper Strength:** Delignification improves fiber bonding, essential for mechanical properties such as strength and durability.

- **Processability:** The elimination of lignin makes cellulose fibers more suitable for subsequent processing, including bleaching and paper formation.

Delignification Methods:

- **Kraft Process:** This widely utilized technique involves cooking wood chips in a solution of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) to effectively remove lignin while preserving cellulose fiber strength, resulting in high-strength pulp suitable for various paper products.
- **Sulfite Process:** This method utilizes sulfurous acid and sulfite salts to dissolve lignin, enabling the production of pulps with varied properties, making it ideal for writing and printing papers.
- **Organosolv Process:** An environmentally friendly alternative that employs organic solvents (for example, ethanol, methanol, or acetic acid) to dissolve lignin, resulting in high-quality pulp and facilitating solvent recovery and reuse, thereby reducing environmental impact.
- **Mechanical and Chemimechanical Processes:** While these processes do not entirely eliminate lignin like chemical methods, they modify or partially degrade lignin to produce pulp. Mechanical pulping retains most lignin, yielding high volume but lower strength pulp, whereas chemimechanical processes enhance fiber separation and pulp properties using chemicals.

Effluent wastewater current with or without previous treatment, released outside a P&P mill. Its quality is regulated to prevent environmental contamination.

Fungi organisms that play various roles in the paper industry, including treating pulp and paper mill effluents and converting lignocellulosic waste into valuable products. The unique biological and enzymatic capabilities of fungi make them highly valuable in different stages of paper production and waste management.

pH measure of the acidity or alkalinity of water. In wastewater treatment, it is crucial to maintain its value at a specific level to ensure the effectiveness of processes.

Pulp fibrous material that plays a crucial role in the papermaking process. It is derived from extracting cellulose fibers from wood, non-wood plants, or recycled paper items. The quality, characteristics, and type of pulp significantly influence the texture, strength, and final properties of the paper or paper products being manufactured.

Sludge semi-solid material produced during wastewater treatment. It often contains a concentrated mix of pollutants and is treated separately.

Suspended Solids (SS) tiny particles or solids suspended in wastewater. In the P&P industry, examples include wood fibers, fillers, and other particulates.

Tertiary Treatment advanced wastewater treatment stage following primary and secondary treatment. It involves processes to eliminate nutrients such as nitrogen and phosphorus, together with additional filtration and disinfection steps.

Total Organic Carbon (TOC) measure of all the living and non-living carbon in organic compounds in water. It furthermore comprises particulate and dissolved organic carbon. TOC originates from various sources, such as wood fibers, paper additives, and chemicals used in pulping and bleaching processes. High levels of TOC in wastewater can indicate inefficient treatment.

Volatile Organic Compounds (VOCs) organic compounds having elevated vapor pressure at standard temperature. The elevated vapor pressure causes significant evaporation or sublimation of the compound to become liquid or solid. The primary sources are the coatings and solvents used in printing and packaging, the inks, and the pulping chemicals.

References

- Abd El-Sayed, E. S., El-Sakhawy, M., & El-Sakhawy, M. A.-M. (2020). Non-wood fibers as raw material for pulp and paper industry. *Nordic Pulp & Paper Research Journal*, 35, 215–230. <https://doi.org/10.1515/npjprj-2019-0064>.
- Achaw, O.-W., & Danso-Boateng, E. (2021). Pulp and paper technology. In *Chemical and process industries: With examples of industries in Ghana*. Springer International Publishing, 171–193. <https://doi.org/10.1007/978-3-030-79139-1>.
- Aprianti, T., Miskah, S., Selpiana, Komala, R., & Hatina, S. (2018). Heavy metal ions adsorption from pulp and paper industry wastewater using zeolite/activated carbon-ceramic composite adsorbent. *Presented at the proceedings of the 17th international conference on ion sources*, p. 020127. <https://doi.org/10.1063/1.5054531>
- Awad, H. (2018). Supervisory control systems: Theory and industrial applications. In R. Campos-Rodriguez, & M. Alcaraz-Mejia (Eds.). *Petri nets in science and engineering* InTech <https://doi.org/10.5772/intechopen.75166>.
- Badar, S., & Farooqi, I. H. (2012). Pulp and paper industry—Manufacturing process, wastewater generation and treatment. In A. Malik, & E. Grohmann (Eds.). *Environmental protection strategies for sustainable development* (pp. 397–436). Springer Netherlands. https://doi.org/10.1007/978-94-007-1591-2_13.
- Bajpai, P. (2004). Biological bleaching of chemical pulps. *Critical Reviews in Biotechnology*, 24, 1–58. <https://doi.org/10.1080/07388550490465817>.
- Bajpai, P. (2015). *Management of pulp and paper mill waste*. Springer International Publishing. <https://doi.org/10.1007/978-3-319-11788-1>.
- Bajpai, P., & Bajpai, P. K. (1992). Biobleaching of kraft pulp. *Process Biochemistry*, 27, 319–325. [https://doi.org/10.1016/0032-9592\(92\)87009-6](https://doi.org/10.1016/0032-9592(92)87009-6).
- Bassandeh, M., Antony, A., Le-Clech, P., Richardson, D., & Leslie, G. (2013). Evaluation of ion exchange resins for the removal of dissolved organic matter from biologically treated paper mill effluent. *Chemosphere*, 90, 1461–1469. <https://doi.org/10.1016/j.chemosphere.2012.09.007>.
- Basu, S., Malik, S., Joshi, G., Gupta, P. K., & Rana, V. (2021). Utilization of bio-polymeric additives for a sustainable production strategy in pulp and paper manufacturing: A comprehensive review. *Carbohydrate Polymer Technologies and Applications*, 2, 100050. <https://doi.org/10.1016/j.carpta.2021.100050>.
- Buyukkamaci, N., & Koken, E. (2010). Economic evaluation of alternative wastewater treatment plant options for pulp and paper industry. *Science of The Total Environment*, 408, 6070–6078. <https://doi.org/10.1016/j.scitotenv.2010.08.045>.
- Camberato, J. J., Gagnon, B., Angers, D. A., Chantigny, M. H., & Pan, W. L. (2006). Pulp and paper mill by-products as soil amendments and plant nutrient sources. *Canadian Journal of Soil Science*, 86, 641–653. <https://doi.org/10.4141/S05-120>.
- CEPI. (2021). *Key statistics 2020. European pulp & paper industry*. Confederation of European Paper Industries.
- CEPI. (2023). *Key statistics 2022. European pulp & paper industry*. Confederation of European Paper Industries.
- Covinich, L. G., Bengoechea, D. I., Fenoglio, R. J., & Area, M. C. (2014). Advanced oxidation processes for wastewater treatment in the pulp and paper industry: A review. *ajee*, 4, 56–70. <https://doi.org/10.5923/j.ajee.20140403.03>.
- Dagar, S., Singh, S. K., & Gupta, M. K. (2022). Economics of advanced technologies for wastewater treatment: Evidence from pulp and paper industry. *Frontiers in Environmental Science*, 10, 960639. <https://doi.org/10.3389/fenvs.2022.960639>.
- Ebrahimi, A., & Najafpour, G. D. (2016). Biological treatment processes: Suspended growth vs attached growth. *IJEE*, 7, 114–123. <https://doi.org/10.5829/idosi.ijee.2016.07.02.05>.

- Feng, Q., Gao, B., Yue, Q., & Guo, K. (2021). Flocculation performance of papermaking sludge-based flocculants in different dye wastewater treatment: Comparison with commercial lignin and coagulants. *Chemosphere*, 262, 128416. <https://doi.org/10.1016/j.chemosphere.2020.128416>.
- Foth, H., & Hayes, A. (2008). Concept of REACH and impact on evaluation of chemicals. *Human & Experimental Toxicology*, 27, 5–21. <https://doi.org/10.1177/0960327107087801>.
- Gautham, S. K., Dhaneesh, V. V., & Manu, B. (2018). Fenton's treatment of pulp and paper mill effluent. In V. P. Singh, S. Yadav, & R. N. Yadava (Eds.). *Water quality management, water science and technology library* (pp. 241–246). Springer Singapore. https://doi.org/10.1007/978-981-10-5795-3_20.
- Gavrilescu, D. (2008). Energy from biomass in pulp and paper mills. *Environmental Engineering and Management Journal*, 7, 537–546.
- Grötzner, M., Melchior, E., Schroeder, L. H., Dos Santos, A. R., Moscon, K. G., De Andrade, M. A., Martinelli, S. H. S., & Xavier, C. R. (2018). Pulp and paper mill effluent treated by combining coagulation-flocculation-sedimentation and Fenton processes. *Water, Air, and Soil Pollution*, 229, 364. <https://doi.org/10.1007/s11270-018-4017-5>.
- Guo, K., Gao, B., Wang, J., Pan, J., Yue, Q., & Xu, X. (2021). Flocculation behaviors of a novel papermaking sludge-based flocculant in practical printing and dyeing wastewater treatment. *Frontiers of Environmental Science & Engineering*, 15, 103. <https://doi.org/10.1007/s11783-021-1390-x>.
- Gurreri, L., Tamburini, A., Cipollina, A., & Micale, G. (2020). Electrodialysis applications in wastewater treatment for environmental protection and resources recovery: A systematic review on progress and perspectives. *Membranes*, 10, 146. <https://doi.org/10.3390/membranes10070146>.
- Hackett, G. A. R., Easton, C. A., & Duff, S. J. B. (1999). Composting of pulp and paper mill fly ash with wastewater treatment sludge. *Bioresource Technology*, 70, 217–224. [https://doi.org/10.1016/S0960-8524\(99\)00048-6](https://doi.org/10.1016/S0960-8524(99)00048-6).
- Haile, A., Gelebo, G. G., Tesfaye, T., Mengie, W., Mebrate, M. A., Abuhay, A., & Limeneh, D. Y. (2021). Pulp and paper mill wastes: Utilizations and prospects for high value-added biomaterials. *Bioresources and Bioprocessing*, 8, 35. <https://doi.org/10.1186/s40643-021-00385-3>.
- Han, N., Zhang, J., Hoang, M., Gray, S., & Xie, Z. (2021). A review of process and wastewater reuse in the recycled paper industry. *Environmental Technology & Innovation*, 24, 101860. <https://doi.org/10.1016/j.eti.2021.101860>.
- Heat Management. (2019). *Solutions for recovery boilers on pulp mills (White paper)*.
- Heat Management. (2023). *Challenges for recovery boilers (White paper)*.
- Hermosilla, D., Merayo, N., Gascó, A., & Blanco, Á. (2015). The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: A review. *Environmental Science and Pollution Research*, 22, 168–191. <https://doi.org/10.1007/s11356-014-3516-1>.
- Hubbe, M. A., Metts, J. R., Hermosilla, D., Blanco, M. A., Yerushalmi, L., Haghghat, F., Lindholm-Lehto, P., Khodaparast, Z., Kamali, M., & Elliott, A. (2016). Wastewater treatment and reclamation: A review of pulp and paper industry practices and opportunities. *BioResources*, 11, 7953–8091.
- Izadi, A., Hosseini, M., Pajoum Shariati, F., Najafpour Darzi, G., & Nabi Bidhendi, G. (2020). Treatment of real paper-recycling wastewater in a novel hybrid airlift membrane bioreactor (HAMBR) for simultaneous removal of organic matter and nutrients. *Iranian Journal of Chemistry and Chemical Engineering*, 39. <https://doi.org/10.30492/ijcce.2020.34793>.
- Jagaba, A. H., Kutty, S. R. M., Baloo, L., Birniwa, A. H., Lawal, I. M., Aliyu, M. K., Yaro, N. S. A., & Usman, A. K. (2022). Combined treatment of domestic and pulp and paper industry wastewater in a rice straw embedded activated sludge bioreactor to achieve

- sustainable development goals. *Case Studies in Chemical and Environmental Engineering*, 6, 100261. <https://doi.org/10.1016/j.cscee.2022.100261>.
- Jahan, M. S., Mostafizur Rahman, J. N. M., Islam, M., & Quaiyyum, M. A. (2016). Chemical characteristics of ribbon retted jute and its effect on pulping and papermaking properties. *Industrial Crops and Products*, 84, 116–120. <https://doi.org/10.1016/j.indcrop.2016.01.054>.
- Jebessa, Z. F., & Wondemagegnehu, E. B. (2018). Physicochemical characterization of upper awash river of ethiopia polluted by anmol product paper factory. *International Journal of Water and Wastewater Treatment*, 4. <https://doi.org/10.16966/2381-5299.154>.
- Jiang, J., Wang, X., Ren, H., Cao, G., Xie, G., Xing, D., & Liu, B. (2020). Investigation and fate of microplastics in wastewater and sludge filter cake from a wastewater treatment plant in China. *Science of The Total Environment*, 746, 141378. <https://doi.org/10.1016/j.scitotenv.2020.141378>.
- Kamali, M., & Khodaparast, Z. (2015). Review on recent developments on pulp and paper mill wastewater treatment. *Ecotoxicology and Environmental Safety*, 114, 326–342. <https://doi.org/10.1016/j.ecoenv.2014.05.005>.
- Khamdahsag, P., Jarichanon, T., Yan, D. Y. S., Grisdanurak, N., & Tanboonchuy, V. (2023). Utilization of lignin separated from pulp and paper wastewater for lead removal. *Materials Today: Proceedings*, 75, 112–118. <https://doi.org/10.1016/j.matpr.2022.11.443>.
- Klidi, N., Proietto, F., Vicari, F., Galia, A., Ammar, S., Gadri, A., & Scialdone, O. (2019). Electrochemical treatment of paper mill wastewater by electro-Fenton process. *Journal of Electroanalytical Chemistry*, 841, 166–171. <https://doi.org/10.1016/j.jelechem.2019.04.022>.
- Kumar, A., Gautam, A., & Dutt, D. (2020). Bio-pulping: An energy saving and environment-friendly approach. *Physical Sciences Reviews*, 5. <https://doi.org/10.1515/psr-2019-0043>.
- Kumar, A., Srivastava, N. K., & Gera, P. (2021). Removal of color from pulp and paper mill wastewater- methods and techniques- A review. *Journal of Environmental Management*, 298, 113527. <https://doi.org/10.1016/j.jenvman.2021.113527>.
- Kumar, D., & Sharma, C. (2019). Remediation of pulp and paper industry effluent using electrocoagulation process. *JWARP*, 11, 296–310. <https://doi.org/10.4236/jwarp.2019.113017>.
- Kumar, M., & Puri, A. (2012). A review of permissible limits of drinking water. *Indian Journal of Occupational and Environmental Medicine*, 16, 40. <https://doi.org/10.4103/0019-5278.99696>.
- Kumar, R., Maurya, A., & Raj, A. (2023). Emerging technological solutions for the management of paper mill wastewater: Treatment, nutrient recovery and fourth industrial revolution (IR 4.0). *Journal of Water Process Engineering*, 53, 103715. <https://doi.org/10.1016/j.jwpe.2023.103715>.
- Lindholm-Lehto, P. C., Knuutinen, J. S., Ahkola, H. S. J., & Herve, S. H. (2015). Refractory organic pollutants and toxicity in pulp and paper mill wastewaters. *Environmental Science and Pollution Research*, 22, 6473–6499. <https://doi.org/10.1007/s11356-015-4163-x>.
- Liu, Z., Wang, H., & Hui, L. (2018). Pulping and papermaking of non-wood fibers. In S. N. Kazi (Ed.). *Pulp and paper processing*. InTech. <https://doi.org/10.5772/intechopen.79017>.
- Mainardis, M., Ferrara, C., Cantoni, B., Di Marcantonio, C., De Feo, G., & Goi, D. (2024). How to choose the best tertiary treatment for pulp and paper wastewater? Life cycle assessment and economic analysis as guidance tools. *Science of The Total Environment*, 906, 167598. <https://doi.org/10.1016/j.scitotenv.2023.167598>.

- Mboowa, D. (2021). A review of the traditional pulping methods and the recent improvements in the pulping processes. *Biomass Conversion and Biorefinery*, 14, 1–12. <https://doi.org/10.1007/s13399-020-01243-6>.
- Mehmood, K., Rehman, S. K. U., Wang, J., Farooq, F., Mahmood, Q., Jadoon, A. M., Javed, M. F., & Ahmad, I. (2019). Treatment of pulp and paper industrial effluent using physicochemical process for recycling. *Water*, 11, 2393. <https://doi.org/10.3390/w11112393>.
- Michniewicz, M., Nalecz-Jawecki, G., Stufka-Olczyk, J., & Sawicki, J. (2000). Comparison of chemical composition and toxicity of wastewaters from pulp industry. In G. Persoone, C. Janssen, & W. De Coen (Eds.). *New microbiotests for routine toxicity screening and biomonitoring* (pp. 401–411). Springer US. https://doi.org/10.1007/978-1-4615-4289-6_45.
- Mostafa, N. A., Farag, A. A., Abo-dief, H. M., & Tayeb, A. M. (2018). Production of biodegradable plastic from agricultural wastes. *Arabian Journal of Chemistry*, 11, 546–553. <https://doi.org/10.1016/j.arabjc.2015.04.008>.
- Neves, L. C., & Souza, J. B. D. (2017). Pulp and paper mill effluent post-treatment using microfiltration and ultrafiltration membranes. *Cellulose Chemistry and Technology*, 51, 579–588.
- Nogueira, V., Lopes, I., Rocha-Santos, T. A. P., Gonçalves, F., & Pereira, R. (2018). Treatment of real industrial wastewaters through nano-TiO₂ and nano-Fe₂O₃ photocatalysis: Case study of mining and kraft pulp mill effluents. *Environmental Technology*, 39, 1586–1596. <https://doi.org/10.1080/09593330.2017.1334093>.
- Ochoa De Alda, J. A. G. (2008). Feasibility of recycling pulp and paper mill sludge in the paper and board industries. *Resources, Conservation and Recycling*, 52, 965–972. <https://doi.org/10.1016/j.resconrec.2008.02.005>.
- Oturan, N., & Oturan, M. A. (2018). Electro-Fenton process: Background, new developments, and applications. In *Electrochemical water and wastewater treatment*. Elsevier, 193–221. <https://doi.org/10.1016/B978-0-12-813160-2.00008-0>.
- Paraskeva, P., & Graham, N. J. D. (2002). Ozonation of municipal wastewater effluents. *Water Environment Research*, 74, 569–581. <https://doi.org/10.2175/106143002X140387>.
- Patel, K., Patel, N., Vaghamsi, N., Shah, K., Duggirala, S. M., & Dudhagara, P. (2021). Trends and strategies in the effluent treatment of pulp and paper industries: A review highlighting reactor options. *Current Research in Microbial Sciences*, 2, 100077. <https://doi.org/10.1016/j.crmicr.2021.100077>.
- Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater—A review. *Science of The Total Environment*, 333, 37–58. <https://doi.org/10.1016/j.scitotenv.2004.05.017>.
- Poojamnong, K., Tungsudjawong, K., Khongnakorn, W., & Jutaporn, P. (2020). Characterization of reversible and irreversible foulants in membrane bioreactor (MBR) for eucalyptus pulp and paper mill wastewater treatment using fluorescence regional integration. *Journal of Environmental Chemical Engineering*, 8, 104231. <https://doi.org/10.1016/j.jece.2020.104231>.
- Priadi, C., Wulandari, D., Rahmatika, I., & Moersidik, S. S. (2014). Biogas production in the anaerobic digestion of paper sludge. *APCBEE Procedia*, 9, 65–69. <https://doi.org/10.1016/j.apcbee.2014.01.012>.
- Ramalingam, G., Priya, A. K., Gnanasekaran, L., Rajendran, S., & Hoang, T. K. A. (2024). Biomass and waste derived silica, activated carbon and ammonia-based materials for energy-related applications – A review. *Fuel*, 355, 129490. <https://doi.org/10.1016/j.fuel.2023.129490>.
- Reid, I. (1991). Biological pulping in paper manufacture. *Trends in Biotechnology*, 9, 262–265. [https://doi.org/10.1016/0167-7799\(91\)90085-V](https://doi.org/10.1016/0167-7799(91)90085-V).

- Rosa, R., Moreira-Santos, M., Lopes, I., Silva, L., Rebola, J., Mendonça, E., Picado, A., & Ribeiro, R. (2010). Comparison of a test battery for assessing the toxicity of a bleached-kraft pulp mill effluent before and after secondary treatment implementation. *Environmental Monitoring and Assessment*, 161, 439–451. <https://doi.org/10.1007/s10661-009-0759-2>.
- Shankar, R., Singh, L., Mondal, P., & Chand, S. (2014). Removal of COD, TOC, and color from pulp and paper industry wastewater through electrocoagulation. *Desalination and Water Treatment*, 52, 7711–7722. <https://doi.org/10.1080/19443994.2013.831782>.
- Sharma, R., Chandra, S., Singh, A., & Singh, K. (2014). Degradation of pulp and paper mill effluents. *The IIOAB Journal*, 5, 6–12.
- Shokunbi, O., & Omenka, R. O. (2022). Physicochemical parameters and purification of pulp effluent (black liquor). *Journal of Tropical Pharmacy and Chemistry*, 6, 49–54. <https://doi.org/10.25026/jtpc.v6i1.394>.
- Simão, L., Hotza, D., Raupp-Pereira, F., Labrincha, J. A., & Montedo, O. R. K. (2018). Wastes from pulp and paper mills - A review of generation and recycling alternatives. *Cerâmica*, 64, 443–453. <https://doi.org/10.1590/0366-69132018643712414>.
- Singh, A. K., & Chandra, R. (2019). Pollutants released from the pulp paper industry: Aquatic toxicity and their health hazards. *Aquatic Toxicology*, 211, 202–216. <https://doi.org/10.1016/j.aquatox.2019.04.007>.
- Singh, A. K., Kumar, A., & Chandra, R. (2022). Environmental pollutants of paper industry wastewater and their toxic effects on human health and ecosystem. *Bioresource Technology Reports*, 20, 101250. <https://doi.org/10.1016/j.biteb.2022.101250>.
- Singh, U. S., & Tripathi, Y. C. (2020). Characteristics and treatment of pulp and paper mill effluents - A review. *International Journal of Engineering & Technical Research*, 10, 19–26. <https://doi.org/10.31873/IJETR.10.11.43>.
- Solomon, K. R. (1996). Chlorine in the bleaching of pulp and paper. *Pure and Applied Chemistry*, 68, 1721–1730. <https://doi.org/10.1351/pac199668091721>.
- Stoica, A., Sandberg, M., & Holby, O. (2009). Energy use and recovery strategies within wastewater treatment and sludge handling at pulp and paper mills. *Bioresource Technology*, 100, 3497–3505. <https://doi.org/10.1016/j.biortech.2009.02.041>.
- Suhr, M., Klein, G., Kourti, I., Rodrigo Gonzalo, M., Giner Santonja, G., Roudier, S., & Delgado Sancho, L. (2015). *Best available techniques (BAT) reference document for the production of pulp, paper and board* (No. JRC95678). Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). EUR 27235. Publications Office of the European Union.
- Tajik, M., Jalali Torshizi, H., Resalati, H., & Hamzeh, Y. (2021). Effects of cellulose nanofibrils and starch compared with polyacrylamide on fundamental properties of pulp and paper. *International Journal of Biological Macromolecules*, 192, 618–626. <https://doi.org/10.1016/j.ijbiomac.2021.09.199>.
- Tekere, M. (2019). Microbial bioremediation and different bioreactors designs applied. In E. Jacob -Lopes, & L. Queiroz Zepka (Eds.). *Biotechnology and bioengineering*. IntechOpen. <https://doi.org/10.5772/intechopen.83661>.
- Thompson, G., Swain, J., Kay, M., & Forster, C. F. (2001). The treatment of pulp and paper mill effluent: A review. *Bioresource Technology*, 77, 275–286. [https://doi.org/10.1016/S0960-8524\(00\)00060-2](https://doi.org/10.1016/S0960-8524(00)00060-2).
- Tofani, G., De Nys, J., Cornet, I., & Tavernier, S. (2021). Alternative filler recovery from paper waste stream. *Waste and Biomass Valorization*, 12, 503–514. <https://doi.org/10.1007/s12649-020-01011-7>.
- Torén, K., & Blanc, P. D. (1997). The history of pulp and paper bleaching: Respiratory-health effects. *The Lancet*, 349, 1316–1318. [https://doi.org/10.1016/S0140-6736\(96\)10141-0](https://doi.org/10.1016/S0140-6736(96)10141-0).

- Tran, H., & Vakkilainen, E. (2008). *The kraft chemical recovery process* [WWW Document]. Research Gate. URL https://www.researchgate.net/publication/267565045_THE_KRAFT_CHEMICAL_RECOVERY_PROCESS.
- UNECE/FAO (2023). *Forest products annual market review 2022–2023*.
- Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P., & Santas, R. (2004). Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production. *Industrial Crops and Products*, 19, 245–254. <https://doi.org/10.1016/j.indcrop.2003.10.006>.
- Wang, L., Fei, Y., Gong, C., Shan, Y., Zhang, Z., Zhang, F., & Cheng, H. (2022). Comparative study of UV/H₂O₂ and UV/PMS processes for treating pulp and paper wastewater. *Water Science and Technology*, 86, 2032–2044. <https://doi.org/10.2166/wst.2022.326>.
- Wang, L. K., Hung, Y.-T., Lo, H. H., & Yapijakis, C. (2004). *Handbook of industrial and hazardous wastes treatment*. CRC Press.
- Xia, G., Wan, J., Zhang, J., Zhang, X., Xu, L., Wu, J., He, J., & Zhang, J. (2016). Cellulose-based films prepared directly from waste newspapers via an ionic liquid. *Carbohydrate Polymers*, 151, 223–229. <https://doi.org/10.1016/j.carbpol.2016.05.080>.
- Yang, J., Zhang, Y., Zhou, L., Zhang, F., Jing, Y., Huang, M., & Liu, H. (2022). Quality-related monitoring of papermaking wastewater treatment processes using dynamic multiblock partial least squares. *Journal of Bioresources and Bioproducts*, 7, 73–82. <https://doi.org/10.1016/j.jobab.2021.04.003>.
- Zhang, H., Yang, C., Shi, X., & Liu, H. (2021). Effluent quality prediction in papermaking wastewater treatment processes using dynamic Bayesian networks. *Journal of Cleaner Production*, 282, 125396. <https://doi.org/10.1016/j.jclepro.2020.125396>.
- Zhou, Y., Zhao, H., Bai, H., Zhang, L., & Tang, H. (2012). Papermaking effluent treatment: A new cellulose nanocrystalline/polysulfone composite membrane. *Procedia Environmental Sciences*, 16, 145–151. <https://doi.org/10.1016/j.proenv.2012.10.020>.

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Methods of pulp and paper wastewater treatment and their challenges

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Overview and comparison of various pulp and paper wastewater treatment techniques

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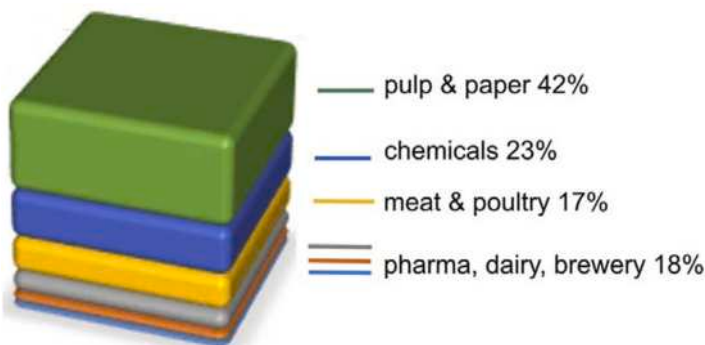
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4.1 Introduction

Global industrial development has accelerated significantly over the past few decades. The environment has changed since the start of the industrial revolution (Belousov, Parkhacheva, Suleimanov, Shafiq, 2023; Janicke & Jacob, 2013; Shafiq, Shafique, Akhter, Yang, et al., 2022). The pulp and paper (P&P) industry is well-established and regarded as one of the most significant industries worldwide (Hubbe et al., 2016). One of the biggest issues with this freshwater-using industry is environmental contamination. Water was usually used extensively in the P&P industry for various phases of the process, including washing, pulping, bleaching, and paper-making (Kamali & Khodaparast, 2015). Based on current data, the production of one ton of paper in the P&P industry requires 250–300 m³ of water (Chandra et al., 2011). Thus a large amount of hazardous chemical-filled liquid waste is released into the environment from the P&P industry, as shown in Fig. 4.1.

Research revealed that over 250 chemical compounds are produced at various phases involved in producing paper (Kumar et al., 2018). Lignin and other naturally occurring polymers are used to create xenobiotic compounds such as chlorinated phenol, chlorinated lignin, dioxins, chlorinated resin acid, phenols, chlorophenols, halogens, metal ions, adsorbable organic halogens, extractable organic acids, etc. (Chaudhry & Paliwal, 2018). The improper or nonexistent wastewater treatment system used by the industry causes the release of these compounds into water bodies. These substances have mutagenic, carcinogenic, and clastogenic

Figure 4.1 Worldwide production of commercial wastewater.
 Source: Reproduced with permission from ref Toczyłowska-Mamińska, R. (2017). *Limits and perspectives of pulp and paper industry wastewater treatment – A review*. Renewable Sustainable Energy Reviews, 78, 764–772. <https://doi.org/10.1016/j.rser.2017.05.021>. Copyright 2017 Elsevier.



effects, as well as producing slime and scum and causing thermal, esthetic, and other problems. The typical properties of wastewater generated from the paper industry are presented in Table 4.1.

Because of this, the wastewater has unusually high biological oxygen demand (BOD) and chemical oxygen demand (COD) contents owing to the existence of lignin and hazardous compounds. The dark brown effluent depletes dissolved oxygen, alters the potential of hydrogen (pH) of the water, and inhibits photosynthesis, all of which are detrimental to aquatic life (Haq & Raj, 2020). However, developed nations in North America and Europe have long-standing wastewater treatment plants (WWTPs), and their environmental regulatory bodies impose stringent limitations on the release of chlorinated compounds (Cabrera, 2017). Consequently, to reduce environmental harm, wastewater treatment is required. Therefore removal is imperative; failure to do so could pose a serious risk to the environment, including the loss of natural beauty, harm to aquatic life, and an increase in soil salinity due to nutrient imbalance, all of which could have an impact on a nation's economic prosperity (Mahesh et al., 2016). Environmental researchers are always developing new methods to treat P&P wastewater to address these worries. In this regard, a huge amount of work has been dedicated to this topic, as shown in Fig. 4.2.

The Scopus statistics from 1990 to 2023 show that 14,298 documents have been published to cater to this ongoing issue. Water consumption and P&P wastewater generation have decreased as a result of numerous experimental and analytical studies. Strategies for accomplishing contaminant-reduction objectives in P&P processes have also been provided by sources such as the

Table 4.1 Typical properties of wastewater from paper industries.

Studies	Color (co-pt)	pH	Chemical oxygen demand (mg L ⁻¹)	Biological oxygen demand (mg L ⁻¹)	Sulfate (mg L ⁻¹)	Phenol (mg L ⁻¹)	Lignin (mg L ⁻¹)	Total solids (mg L ⁻¹)
Study 1	1065 ± 89.3	8.1 ± 1.0	774 ± 43.7	426 ± 30.6	866 ± 47.0	39.3 ± 12.0	529 ± 20.10	859 ± 45.3
Study 2	8942 ± 15.0	7 ± 0.20	22,189 ± 39	8296 ± 45	1089 ± 19.67	364 ± 20.13	1124 ± 12.09	1799 ± 17.61
Study 3	660–1230	6.4–7.3	1170–1510	142–221	—	—	133–265	354–563
Study 4	2242 ± 56	8.2 ± 1.0	792 ± 70	385 ± 12	993 ± 6	42 ± 2.5	436 ± 18	850 ± 30
Study 5	1761 ± 2.3	7.4 ± 0.1	2420 ± 17	185 ± 2.9	—	—	—	2359 ± 14.2
Study 6	7253 ± 64.2	9.8 ± 1.3	6735 ± 45.3	2934 ± 38.3	852.4 ± 34.1	—	1863 ± 52.6	1753 ± 34.2
Study 7	2538 ± 53.3	8.5 ± 1.0	16,550 ± 507.2	7250 ± 123.0	1003 ± 5.3	—	800 ± 18.4	977 ± 7.2
Study 8	1202 ± 6.53	7.7 ± 0.02	584 ± 3.62	180.54 ± 4.70	—	—	—	1686 ± 10.58

Source: Reproduced with permission from Patel, N., Vaghamshi, N., Shah, K., Duggirala, S. M., & Dudhagara, P. (2021). Trends and strategies in the effluent treatment of pulp and paper industries: A review highlighting reactor options. *Current Research in Microbial Sciences*, 2, 100077. Copyright 2021 Elsevier.

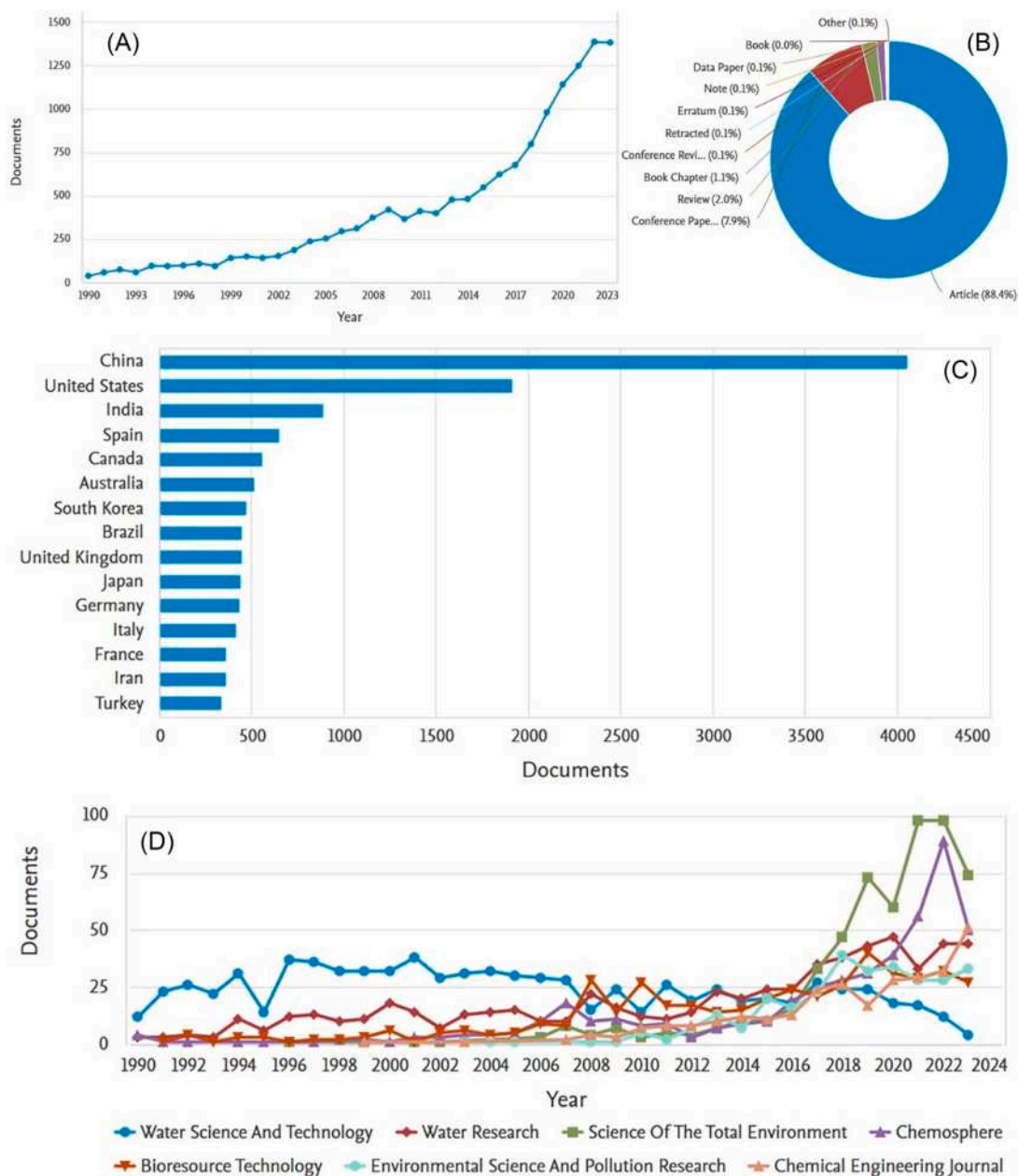


Figure 4.2 Scopus statistic with keywords “P&P wastewater treatment” (A) Publications by year, (B) Publications by type, (C) Publications by country, and (D) Publications by source (Updated on December 10, 2023).

European Commission. In addition, rising environmental consciousness and new, stringent environmental laws from national, provincial, and federal agencies have compelled the commercial sector to treat effluent before releasing it into water bodies (Dilpazeer et al., 2023; Rashid et al., 2021). Therefore it appears that the primary, secondary, and tertiary treatment processes are still the best options for safely releasing wastewater into the receiving environment. Conversely, large molecule degradation by physical and chemical treatment methods is associated with high energy requirements, high costs, incomplete mineralization, and increased effluent toxicity. These days, research and proposals have been made on hybrid treatment approaches to address these issues (Shabir et al., 2022).

Even though P&P wastewater treatment has been the subject of numerous studies over the years, the results have been inconsistent. For example, although various works have demonstrated the complete treatment of P&P wastewater through the use of a combination of treatment techniques, other studies have demonstrated subpar outcomes through the application of the same methodology. The developments in wastewater treatment within the P&P industry have been examined in several studies to date. While some have concentrated primarily on biological approaches, others have prioritized approaches. In addition, review papers have examined various reactor types, operating factors, laboratory, pilot, and full-scale studies in the literature (Hubbe et al., 2016). This chapter aims to provide insight into the role operating parameters play in wastewater treatment, highlight the significance of researching hybrid treatment technologies, and guide future P&P wastewater treatment research so that the outcomes are more comparable. It focuses on recent advancements in P&P wastewater treatment over the past decade. By conducting thorough analysis and comparison, our goal is to provide researchers, industry experts, and environmentalists with the knowledge necessary to make wise decisions when searching for environmentally friendly and sustainable wastewater treatment options. Wastewater treatment methods must adapt to the changing P&P production industry. We will set out on this insightful journey together, hoping to bring about a cleaner, greener, and more optimistic future for the industry.

4.2 Physical methods

The P&P sector has a complex difficulty in managing effluent, which calls for a variety of treatment strategies. Physical procedures are

among the most effective means of eliminating pollutants and toxins. This chapter highlights the distinct qualities, uses, and efficacy of the many physical wastewater treatment methods that are employed in the industry by providing an overview and comparison of them. Physical material treatment methods include several techniques that are elaborated below.

4.2.1 Coagulation–flocculation

Coagulation–flocculation is the process of small particle agglomeration and the subsequent production of large-sized flocs aimed for the settlement and subsequent removal as sludge, hence minimizing organic pollutants such as color, adsorbable organic halides (AOX), COD, and lignin. The P&P business has strongly commended this approach. It can also remove color entirely, as opposed to just a little bit (Kumar & Srivastava, & Gera, 2021). Furthermore, because the wastewater contains lignin colloids, which have a size of around 500 nm, this procedure is effective for removing lignin (Zahrim et al., 2015).

Selecting the appropriate coagulation agent for the breakdown of certain pollutants is essential since their characteristics have a direct impact on how effectively a treatment performs. For instance, the surface of lignin particles in water has a negative charge. Thus adding cationic polymer coagulants can eradicate lignin from P&P effluent (Zahrim et al., 2015). Adjusting pH levels is another important consideration when making changes to the process. One of the common coagulants, alum ($\text{Al}_2(\text{SO}_4)_3$), offers complete recovery in the pH range of 2–7 because of the hydrolysis product and the opposing charges of lignin (Nawaz et al., 2014). Coagulants are often used for lignin-containing P&P wastewater treatment because coagulants can effectively remove phenolic derivatives. Coagulants are substances like iron and aluminum (Irfan et al., 2017). Metal hydroxide polymers, concerning color pollution, possess an amorphous assembly and a substantial surface area, contributing to the improvement of color removal (Irfan et al., 2017).

Alum, ferric chloride (FeCl_3), and polyaluminum chloride (PAC) fall into the categories of inorganic iron and organic coagulants. These substances are frequently employed for P&P wastewater treatment as metal-based coagulants. Because PAC is less expensive, performs better in coagulation, and works better across larger pH options than traditional coagulants (such as alum or FeCl_3), it has been used to treat paper effluent (Chaudhry & Paliwal, 2018). Three polymeric coagulants were tested in research for their ability to reduce COD from black liquor (BL): polyethyleneoxide, polymeric

ammonium chloride, and polydimethyldiallyl ammonium chloride. The results showed that at acidic pH, the coagulants could remove 50%–70% of the COD. Since most of the BL's original COD was soluble, this probably contributed to the poorer removal effectiveness when compared to paper mill effluent (Domínguez-Robles et al., 2020).

Because the coagulation-flocculation technique has been thoroughly studied for removing total suspended solids (TSS), it was proposed that it be combined with various physicochemical treatment techniques to gain an improved knowledge of its potential for removing lignin, color, and AOX. The combination of sedimentation along with the coagulation-flocculation, coupled with the acidic pH-based Fenton procedure using highly concentrated hydrogen peroxide (H_2O_2), provided 76% lignin removal from P&P wastewater (Grötzner et al., 2018). In a different case, the integration of the settling with the coagulation procedure was examined for generating water used for the P&P manufacturing process's criteria. Subsequently, following a primary settling duration of 4 hours and the introduction of 3400 mg/L of MgSO_4 as a coagulant, a substantial decrease in COD by 84% and color by 89% was accomplished (Mehmood et al., 2019).

A major concern associated with the coagulation-flocculation procedure is the potential noxiousness and health-related issues associated with the coagulants. This employs the use of the natural coagulants—like chitosan, oleifera seed powder, both shelled and unshelled, *Cecropia obsifolia* seed gum, and *Ocimum basicum* mucilage—a preferable substitute for potentially destructive inorganic polymeric coagulants for P&P wastewater treatment. Besides mitigating noxiousness, the Oleifera-seed ash effectively removed more than 90% of the total organic matter from the paper mill effluent, which initially had a neutral pH at a concentration of 10,752 mg/L. Because of this, the powder was a preferable choice to alum coagulant, which was more toxic but had the same COD elimination efficacy (Boulaadjoul et al., 2018). In general, the coagulation-flocculation technique does not have sufficient tendency to be considered as the key approach for treating P&P effluents, given the uncertainty surrounding its capacity to break down lignin and AOX.

4.2.2 Membrane technologies

Research conducted over the last 20 years has shown that membranes are an excellent way to cleanse wastewater produced during the paper-making process. The size of a membrane's pores, which controls the degree to which particular pollutants, such as

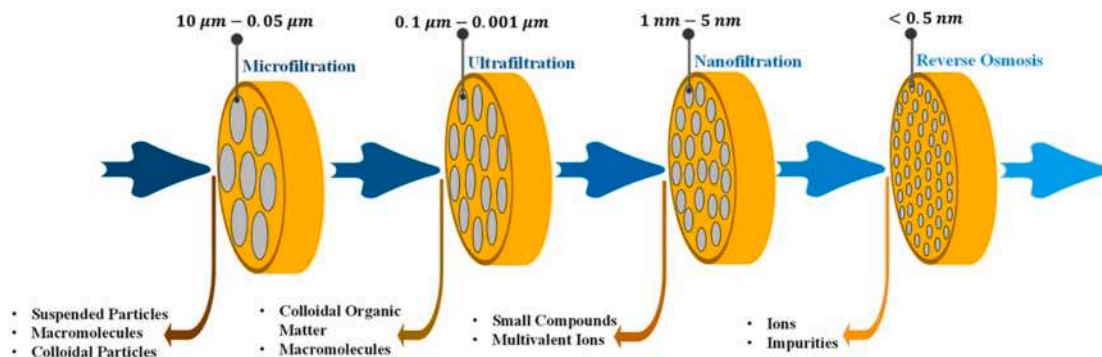


Figure 4.3 Characteristics of different membrane-based separation technologies.

Source: Reproduced with permission from Esmaeeli, A., Sarrafzadeh, M.-H., Zeighami, S., Kalantar, M., Bariki, S.G., Fallahi, A., Asgharnejad, H., & Ghaffari, S.-B. (2023). A comprehensive review on pulp and paper industries wastewater treatment advances. *Industrial & Engineering Chemistry Research*, 62(21), 8119–8145. <https://doi.org/10.1021/acs.iecr.2c04393>. Copyright 2023 American Chemical Society.

ions, lignin, organic detritus, and AOX, may be filtered out, is commonly used to categorize membranes, as shown in Fig. 4.3 (Courbalay et al., 2021; Polizzi et al., 2020).

The two primary types of membranes are polymeric and ceramic, and each has its own pros and cons. If fouling or scaling occurs, ceramic membranes, as opposed to polymeric membranes, may be cleaned using a range of strong cleaning solutions. However, because ceramic membranes are more expensive initially and have lower packing densities than polymeric membranes, many industrial P&P businesses confront formidable obstacles (Hong et al., 2007; Moslehi, 2018; Sousa et al., 2018; Subramonian et al., 2017).

Lignin, polysaccharides, and their destructive byproducts are prevalent foulants encountered during filtration in P&P wastewater, alongside wood extractives such as fatty acids, resin acids, steroids, and phenolic extracts. P&P effluents can therefore have a variety of properties, and membrane filtering is likely to produce both organic and inorganic foulants (Gönder et al., 2011). Nonetheless, a few setups, such as pH adjustment, polymeric adsorbents, and enzyme pretreatment, can greatly enhance the efficiency of membrane filtering (Bokhary et al., 2018).

Since P&P mill effluents often have harsh properties (high pH and temperature) and high organic strength, it is important to carefully consider membrane/module features and operating conditions while designing a process. If not, a lot of cleaning work will need to be done (Weis et al., 2005).

4.2.3 Adsorption

Previous research has demonstrated that coal ash, activated carbon, fuller's earth, silica, and other adsorbents may successfully decolorize and remove obstinate pollutants from P&P effluent (Samsami et al., 2020). However, it was revealed that the adsorption procedures of ion exchange resin and granular activated carbon only operate with high molecular weight and hydrophobic fractions (Barhoumi et al., 2019). According to their research, the means of granular activated carbon and ion exchange resin reduced the amount of dissolved organic carbon by 72% and 76%, respectively (Ribeiro et al., 2023).

Xilei et al. used inexpensive bentonite as the adsorbent and poly-aluminum silicate chloride as the coagulant in a tertiary treatment that included adsorption and coagulation. Under ideal circumstances, they eliminated 60.87% and 41.38% of COD and color, respectively, at coagulant and adsorbent doses of 400 and 450 mg/L (Duan et al., 2010).

4.3 Chemical methods (advanced oxidation processes)

In the P&P industry, advanced oxidation processes (AOPs) are gaining traction. AOPs are thought to be an effective technique for treating water. AOPs may result in mineralization, the organic matter conversion to inorganic matter, or the production of biodegradable materials (Covinich et al., 2014). AOPs, which contain nonbiodegradable components like lignin, are a necessary step before traditional biological treatment (Lal & Garg, 2017). AOPs proceed through the production of a hydroxyl-free radical ($\text{OH}^\bullet$), a potent oxidant that efficiently cleans discharges. Radicals employ their extreme energy to damage organic materials. One benefit of this approach is thought to be the short half-life of OH radicals, which exhibit selectivity for contaminants (Al Mayyahi & Al-Asadi, 2018; Can-Güven et al., 2021; Khare et al., 2021).

Even though many AOPs, such as the Fenton processes, can only function at acidic or neutral pH levels, there are surprisingly few effective AOPs for commercial discharges. While P&P discharges are produced at basic pH levels, choosing the right AOP for the treatment of P&P wastewater is crucial (Boczka & Fernandes, 2017).

It should be mentioned that the treatment plans for AOPs would not work if any of the transitional products utilized in the procedure were prone to dimerization and cross-reactions. It has been demonstrated that reactive nitrogen species (RNs) play a crucial

part in the conversion of organic pollutants during wastewater treatment, leading to the production of additional harmful byproducts. $\text{NO}_3^\bullet$, $\text{NO}_2^\bullet$, and $\text{NO}^\bullet$ can recombine as nitrating and nitrosating agents with P&P pollutants that include functional groups that donate electrons, including derivatives of phenol. It has been demonstrated that RNs reacting with the lignin and chlorinated chemicals present in P&P effluent formed the corresponding nitro-products. However, the low nitrogen level of P&P effluent suggests that nitrated byproduct formation is improbable (Rayaroth et al., 2022).

Among the suggested process methods are ozonation, hydrodynamic cavitation, photocatalysis, Fenton oxidation, and persulfate oxidation. These techniques can be combined or applied alone to create hybrid systems (Portela et al., 2016).

4.3.1 Fenton-based processes

Fenton and photo-Fenton procedures are the two types of Fenton-based processes. The Fenton procedure is among the AOPs that employs a combination of soluble Fe^{2+} and H_2O_2 (Fenton's reagents) to carry out coagulation and oxidation tasks in order to eliminate COD, lignin, and color from paper mill effluent (Brink et al., 2017; Samsami et al., 2020). However, because of photo-Fenton's high rates of organic elimination and Fenton's powers owing to ultraviolet (UV) absorption, it is preferred over the traditional Fenton procedure (Boczkaj & Fernandes, 2017; Fernandes et al., 2014; Ribeiro et al., 2023). More metal catalyst recovery, reduced sludge production, and smaller reaction periods are thought to be the key advantages of photo-Fenton technology over the traditional Fenton procedure. The most important variables for the Fenton-based processes were found to be the temperature, pH, oxidant concentrations, and treatment duration. For example, larger amounts of Fe^{2+} or Fe^{3+} enhanced the Fenton reaction by producing more $\text{OH}^\bullet$ radicals. Furthermore, it was shown that a pH range of 2.5–3.0 was ideal for raising COD and color removal (Şefika & Yeliz, 2019). Because of lignin's high oxidation capacity, pH independence at room temperature, and propensity for structural degradation by the $\text{OH}^\bullet$ radical, fert-based methods are appropriate for removing lignin from P&P streams (Muryanto et al., 2017). The most difficult obstacle to Fenton-based methods would be modest lignin solubilization because iron hydroxides precipitate in acidic settings (Mendes et al., 2021). This suggests that when lignin is the target pollutant, Fenton-based methods are ineffective for treating the acidic effluent from P&P bleaching units.

4.3.2 Ozonation

Ozone gas (O_3) is one of the strongest oxidants since it is made up of three oxygen atoms. The ozone injection into the water is the foundation of this water treatment process. Ozone has a brief half-life; hence, ozone generation for ozonation therapy needs to be ongoing. Ozonation alters the molecular weights (MW), transitioning to a lower MW, and improves the P&P wastewater effluents' biodegradability (Hermosilla et al., 2015). Oxygen-rich compounds with two carbon-carbon double bonds are first oxidized by ozone, then those with just one. Ozonation is therefore a simple method for handling AOX and lignin-enriched effluents (Hermosilla et al., 2015; Mainardis et al., 2020). This method works in the P&P business because of the comparatively high solubility and selectivity of organic molecules. Ozonation effectiveness is dependent on the type of target organic molecules, concentration, pH, ozone dose, and competition between the target chemical and biodegradable byproducts. The maximum COD reductions were attained early in the process, and the procedure proceeded without incident regardless of an increase in ozone dose, demonstrating the effectiveness of oxidation-affinity product breakdown at the commencement of ozonation treatment (Hermosilla et al., 2015). Furthermore, ozonation in the presence of H_2O_2 improves color removal but has a detrimental effect on COD elimination (Ko & Fan, 2010).

While pH=4.5–11 does not affect the removal of COD, pH levels greater than 9 encourage the oxidation of lignin products. The research indicated that a basic environment generates additional $OH^\bullet$ radicals compared to the acidic one. When the level of pH rises, the therapy becomes more effective because O_3 is broken down into $OH^\bullet$ by the OH^- anions and O_2 and H_2O by the H^+ protons. On the other hand, H_2O_2 processes are inefficient at basic pH, with very few exceptions. The reason the efficacy of the therapy increases when H_2O_2 moves toward neutral or acidic pH values is that it reduces H_2O_2 oxidative potential at alkaline pH levels. Overall, because ozonation may produce strong oxidants that can break down complex organic molecules, it may be utilized to remove lignin and AOX from P&P streams.

4.3.3 Photocatalytic treatment

“Photocatalysis” represents the employment of light in conjunction with certain semiconductors to accelerate photochemical processes (Belousov & Shafiq, 2023; Belousov, Parkhacheva, Suleimanov, Shafiq, 2023; Chen et al., 2024; Zhu et al., 2023). Because hydroxyl radicals are produced during the excitation of electrons from valence to conduction band, resulting in separation of charges to produce a pair of electron and hole (Belousov & Shafiq, 2022; Belousov & Shafiq, 2023; Belousov,

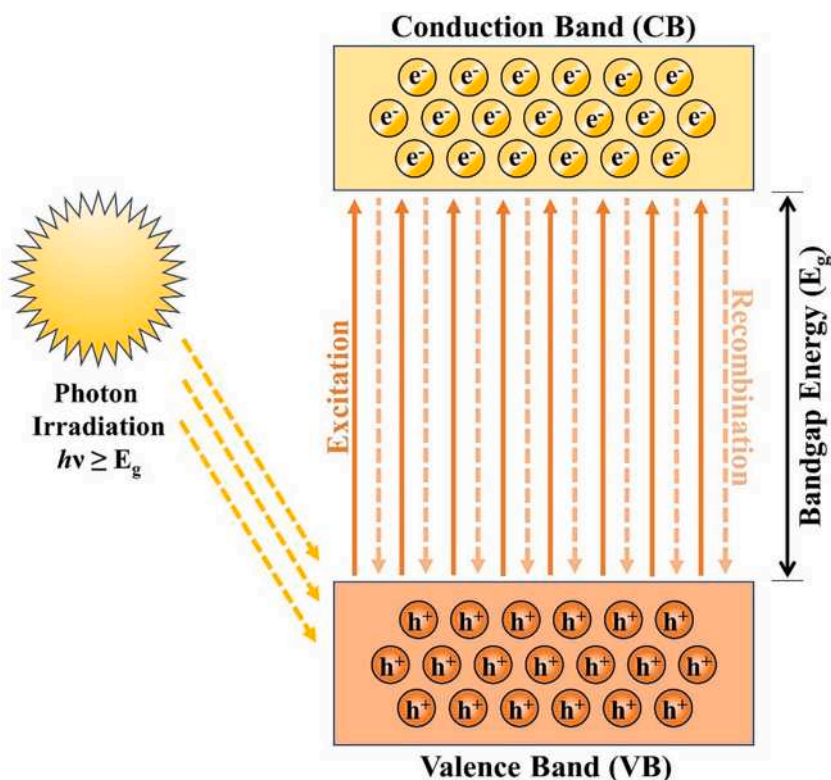


Figure 4.4 Electron-hole pair generation mechanism in photocatalysis.

Source: Reproduced with permission from Shafiq, I., Shafique, S., P. Akhter, P., G. Abbas, G., Qurashi, A., M.J.C.R. Hussain, M. J. C. R. (2022). Efficient catalyst development for deep aerobic photocatalytic oxidative desulfurization: Recent advances, confines, and outlooks, 64(4) (2022) (pp. 789–834). Copyright 2022 Taylor & Francis Group – Informa UK Limited.

Parkhacheva, Suleimanov, Shafiq, 2023; Belousov, Parkhacheva, Suleimanov, Fukina, et al., 2023; Mahboob et al., 2023; Shafiq, Hussain, Shafique, Akhter, et al., 2021; Shafiq, Hussain, Shafique, Rashid, et al., 2021), as shown in Fig. 4.4 (Shafiq, Shafique, Akhter, Abbas, Qurashi, et al., 2022).

The highest amounts of COD in closed circuits yielded the greatest outcomes from photocatalytic (PC) methods, perhaps because photocatalysis breaks down phenolic contaminants more efficiently. Contamination clearance is influenced by a variety of semiconductor surface properties, such as particle size, excited state lifetime, surface area, and charge migration and recombination parameters. Titanium dioxide (TiO_2) particles have been the subject of several investigations because of their good chemical stability, high removal efficiency, and great availability within the spectrum of semiconductor oxides (Rashid et al., 2021, 2023; Shafiq, Hussain,

Rashid, et al., 2021). By boosting the generation of OH radicals, the air flow rate, and the semiconductor dose (TiO_2) have a direct influence on the elimination of lignin and COD. The pH of the solution affects how quickly semiconductors break down complicated structures (Uğurlu et al., 2008).

Both the point of zero charge (PZC) of the catalyst and acid dissociation constant (pKa) of the compounds influence the success of the PC process. TiO_2 , with a PZC of 6.25, exhibits a negative charge above and a positive charge below this value. If both the substance and the catalyst surface share the same charge, whether negative or positive, it discourages adsorption. Consequently, with increasing pH, the catalyst acquires a negative charge. This negatively charged state hampers the effectiveness of the PC process for organic contaminants in P&P effluent, particularly compounds like chlorophenols that bear negative surface charges (Boczka & Fernandes, 2017). For example, in an acidic environment, the surface of the Fe_2O_3 – TiO_2 catalyst had a net positive charge, whereas the organic contaminants carried a negative charge, increasing the photodegradation efficiency (Subramonian et al., 2017).

According to some research, solar photocatalysis is a more effective means of reducing energy use than UV radiation (Hermosilla et al., 2015). Furthermore, it has been demonstrated that using solar photocatalysis to oxidize paper mill effluent enhances the biodegradability of the wastewater, suggesting that this method might be used to improve biological P&P wastewater post-treatment (Devi et al., 2013; Ghaly et al., 2011). Notwithstanding, TiO_2 /UV PC devices for P&P wastewater treatment, eliminating organic pollutants, have been extensively studied. Just 4%–6% of the solar spectrum is made up of UV light, and because TiO_2 exclusively reacts to UV light, its usage in wastewater treatment is limited because of its high bandgap value. To tackle this issue, a visible-light-based TiO_2 doped with Eosin-Y was created utilizing the dye sensitization approach (Khan et al., 2020). Furthermore, the solar-sulfite-Eosin- TiO_2 is a viable alternative to environmentally friendly since it generates a sizable amount of hydrogen (H_2) in an atmosphere with visible light (Khan et al., 2020).

When exposed to light, doping of metal-oxide changes the textural characteristics of a catalyst, causing a shift in the band gap energy and an increase in activity (Yeber et al., 2007). AgO-doped ZnO, for instance, demonstrated the highest COD reduction activity, measuring 66%. Conversely, ZnO lowered the color by 60% (Marques et al., 2017). In recent research, the discharge from kraft pulp mills and mining activities were the two true hazardous wastewaters that were photocatalyzed to be treated using TiO_2 and Fe_2O_3 (Nogueira et al., 2018). Research using the organic effluent revealed that the

color, lignin, and COD levels were reduced by over 80% in an acidic atmosphere. In a separate study, electro-synthesized zirconia nanoparticles (EGZrO_2) achieved complete degradation of a phenol solution at pH nine within an hour. It was observed that the biodegradability of treated wastewater mostly stays similar, while the operating costs of the $\text{O}_3/\text{H}_2\text{O}_2$ and O_3 technologies reduce with the inclusion of TiO_2 . With COD declines of 38% and 19%, respectively, $\text{TiO}_2/\text{UV}/\text{O}_3/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{UV}$ treatments were shown to be the most effective in reaching the goals of sulfide ions degradation and COD reduction. It was also demonstrated that the $\text{UV}/\text{O}_3/\text{H}_2\text{O}_2$ technique could remove 46% of COD and 92% of volatile organic compounds of wastewater; however, TiO_2 significantly abridged the number of chemicals required and the time required for the degradation process, resulting in a low cost (Fernandes et al., 2019).

4.3.4 Persulfate application

P&P wastewater was processed with ferric chloride, electrocoagulation (EC), permanganate, and electro-Fenton (EF) in the literature before sulfate radical-advanced oxidation processes (SR-AOPs) were further treated to assess the combined procedure for color and COD reduction (Kumar & Verma, 2023; Kumar & Srivastava, & Gera, 2021). The findings demonstrated that the BOD/COD ratios of EC-PMS/UV and EC-PDS/UV (PMS is peroxymonosulfate and PDS is peroxydisulfate) could be increased to more than 0.4, suggesting that they are appropriate for biodegradation. Additionally, electro-activated PMS fared better in COD and color reduction than EF. Furthermore, it was demonstrated that smaller PMS doses could be more effective than H_2O_2 at breaking down larger organic materials (Jaafarzadeh et al., 2016). In addition, the pH of the solution decreased sharply from 6.15 to 3.8, and it was demonstrated that 99% of the COD could be removed using PDS, Fe^{2+} , and heat (Gholami et al., 2017). An additional post-treatment technique for P&P wastewater treatment is the use of SR-AOPs. The P&P industry's major worries concerning the usage of SR-AOPs are still the rise of total dissolved solids and a noticeable change in pH. Moreover, when using SR-AOPs as a pretreatment for biological processes, large quantities of sulfate ions may prevent microorganisms from functioning (Fernandes et al., 2021). Researchers are fascinated by this method's potential for treating P&P wastewater and its efficacy in eliminating aromatic chemicals, lignin, and AOX.

4.3.5 Electrochemical methods

There are generally two types of electrochemical methods for treating P&P wastewater, that is, electro-coagulation and EF. EC

works in a small space at room temperature and pressure using basic equipment. Additionally, it reduces the amount of sludge that is enriched with minerals, shortens retention periods, and improves the capacity to absorb both organic and mineral contaminants (Chaturvedi, 2013). By increasing conductivity, NaCl can reduce the amount of energy required for EC (because there are no chemical additives required), saving energy. Selectivity and automation flexibility are two further benefits of EC. First-order rate kinetics is the most likely reason for the COD decline in EC. EC may be used to quantify the color loss caused by the oxidative coupling unit of lignin and other organic and inorganic compounds vanishing. The evolution of lignin's chemical and physical characteristics, which in turn affect how efficiently it absorbs metal ions, depends on the presence of hydroxyl groups. Thus lignin and ion metals are removed at the same time. For AOX, EC is a reliable therapy. However, at first, EC is extra reliant on the mass load of AOX compared to that of concentration. The elimination of pollutants in electrochemical cells is affected by several important variables, including pH, treatment duration, applied current density and potential, and others (Nasrullah et al., 2019; Öztürk & Özcan, 2021).

On the other hand, by controlled H_2O_2 production and electrochemical regeneration of Fe^{2+} to initiate the Fenton reaction, EF seeks to overcome the limitations of the Fenton process. Several anodes ($\text{Ti}/\text{IrO}_2\text{--Ta}_2\text{O}_5$ and boron-doped diamond) and cathodes (carbon felt, modified carbon felt, and gas diffusion electrode [GDE]) have been investigated in EF. All things considered, EF is less expensive and more environmentally friendly than Fenton as it uses safer chemicals (iron catalysts and H_2O_2). Some advantages of EF over Fenton include cathodic regeneration of Fe^{2+} , continuous electro-generation of H_2O_2 , improved process control, and the absence of secondary pollutants, particularly for lignin removal, that do not result in reddish-brown precipitates. However, because of oxygen's poor solubility, the sluggish bulk transit of oxygen to the cathode typically limits EF's efficiency. More energy is often needed to remove more lignin and COD when the current density is increased. H_2O_2 concentration also affects EF efficiency. However, an overdose of H_2O_2 in EF can reduce efficiency because the unreacted H_2O_2 scavenges the hydroxyl radical. Moreover, pH has a significant impact on the production of hydrogen peroxide and its oxidative strength. Lastly, it has been proposed that EF be used in conjunction with either anodic oxidation or GDE to improve EF performance.

The performances for various P&P processes are tabulated in Table 4.2.

Table 4.2 chemical oxygen demand (COD) removal performances of various pulp and paper wastewater treatment physicochemical technologies.

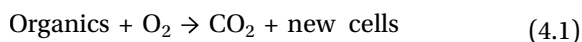
Process parameters	COD (mg/L)	Removal (%)	References
Electrocoagulation (Al)	426	75	Uğurlu et al. (2008)
Electrocoagulation (Al)	2500	95	Shankar et al. (2015)
Flocculation (Polyaluminium chloride)	500–1800	40–45	Renault et al. (2009)
Flocculation (Chitosan)	500–1800	80	Renault et al. (2009)
Flocculation (Polydiallyldimethylammonium)	2900	90	Razali et al. (2011)
Electrocoagulation (EC/Fe ⁰) + flotation + solar photocatalytic degradation (UV/TiO ₂ /H ₂ O ₂)	1310	88	Boroski et al. (2008)
Precipitation (CaO)	1510	90	Eskelinen et al. (2010)
Laccase-polymerized membrane filtration	785	60	Ko and Fan (2010)
Ozonation	1315	20	Mänttari et al. (2008)
Ozonation + electrolysis	1382	50	Kishimoto et al. (2010)
Solar photocatalytic degradation (nTiO ₂ /UV)	2075	75	Ghaly et al. (2011)
Solar photo-Fenton (Fe ²⁺ /H ₂ O ₂ /UV)	899	90	Lucas et al. (2012)
Fungi + solar photo-Fenton (cryptococcus + Fe ²⁺ /H ₂ O ₂)	1802	90	Fernandes et al. (2014)

4.4 Biological treatment

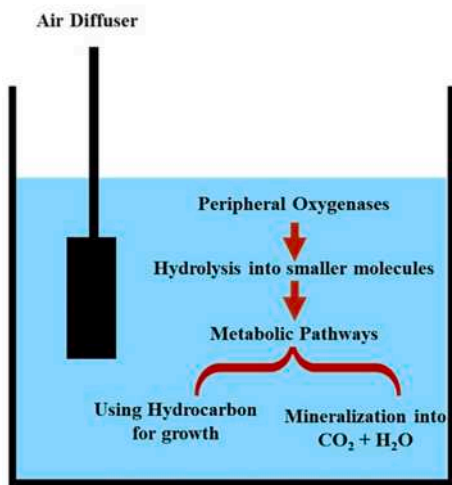
Biological processes are characterized by high efficiency in treating newly created P&P manufacturing effluents but are less effective for removing refractory paper manufacturing effluents (Jagaba et al., 2023; Mustafa et al., 2020). It is well known that P&P mill effluent contains persistent organic contaminants that are usually not biodegradable due to their BOD/COD ratios of 0.02–0.07. Normally, complete biodegradation requires an index of 0.40 (Birjandi et al., 2016).

The main advantages of biological-based treatment are low cost, eco-friendliness, and effectiveness in reducing organic debris. However, the biological processes are considered a secondary treatment due to pretreatment is required to remove persistent elements that may be hazardous to microorganisms (Garg et al., 2010). Biological treatment processes can be categorized into two categories (Fig. 4.5) (Esmaeeli et al., 2023):

1. Aerobic systems



(A) Aerobic



(B) Anaerobic

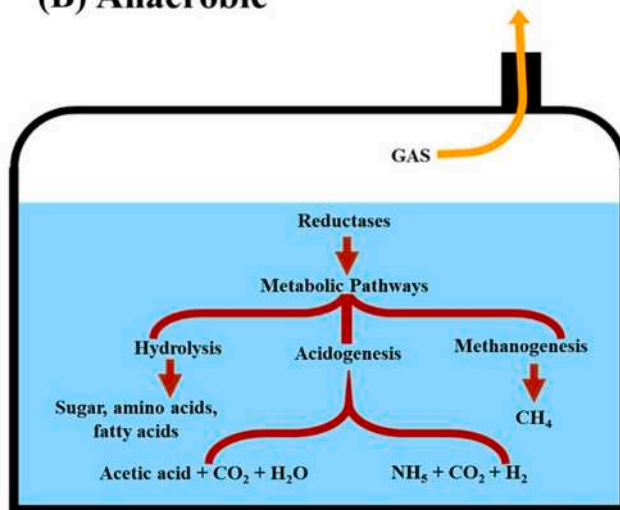
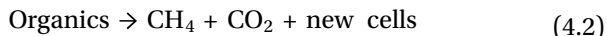


Figure 4.5 Comparison of (A) aerobic treatment and (B) anaerobic treatment.

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2. Anaerobic systems



Aerobic methods are preferred due to their simplicity and low capital and operational costs. Activated sludge (AS) (Jagaba, Kutty, Baloo, et al., 2022), long-time aerated sludge (Jagaba, Kutty, Noor, et al., 2022), sequential batch reactor (Singh et al., 2022), aerated lagoon (Peitz & Xavier, 2019), aerated stabilization basins (Lewis et al., 2018), aerated/stabilization ponds and moving-bed bioreactors (Liu et al., 2022) are the most widely used aerobic methods in the wastewater treatment. AS technique has been the main treatment process for P&P effluents (Buyukkamaci & Koken, 2010). Aerated lagoons processes are effective for BOD removal (more than 95%), but have reasonable competence toward COD (40%–60%) (Pokhrel & Viraraghavan, 2004). Also, aerobic processes produce carbon dioxide and a large amount of sludge through the removal of organic contaminants. It was shown that 330 g CO₂/kg BOD is released by the AS process and 190 g sludge/kg BOD is produced (Ashrafi et al., 2013). Another disadvantage of aerobic methods is the high oxygen consumption, which determines the main energy consumption. Ashrafi et al. (2013) demonstrated that 452 g O₂/kg BOD and 227 kWh/day electricity are needed, respectively, for the biological treatment.

Anaerobic processes are promising techniques for P&P mill wastewater treatment because, compared to aerobic methods, they are characterized by lesser chemical depletion, lesser sludge creation, design simplicity, lesser terrestrial necessities, and energy generation in the form of biogas (methane and CO₂) (Esmaeeli et al., 2023). The anaerobic treatment includes anaerobic lagoon (Owusu-Twum & Sharara, 2020), sludge contact process (Bokhary et al., 2022), up-flow anaerobic sludge blanket (UASB) reactor (Ravichandran & Balaji, 2020), internal circulation reactor (Irizar et al., 2018), packed-bed reactor (Namdarimonfared et al., 2023), up-flow anaerobic filter (Deshmukh et al., 2009), expanded granular sludge bed (Rodrigues et al., 2023), and fluidized-bed reactor (Dornelles et al., 2023).

During the anaerobic processes, a large amount of CH₄ can be formed. It is well-known that methane is a greenhouse gas (GHG) with a global warming potential of 34 times higher than CO₂ and may be used as an energy source (Ashrafi et al., 2015). The use of anaerobic processes can be more promising and cost-effective compared to aerobic methods if the generated methane is recovered and used to satisfy the energy requirements of the WWTPs. It was reported that 235 g CO₂/kg BOD, 124 g CH₄/kg BOD, and 25 g sludge/kg BOD were produced through the anaerobic process (Ashrafi et al., 2015), which is significantly lower than for the aerobic

method. On the other hand, anaerobic processes require the supply of alkalinity that increases energy consumption and GHG generation. The average alkalinity requirement is commonly 2000–4000 mg CaCO_3/L to control and maintain the pH value.

In general, anaerobic systems are employed for highly polluted wastewater treatment, whereas aerobic methods are appropriate for treating lower to moderately polluted waters. Aerobic processes typically provide superior waste management in comparison with anaerobic techniques.

As can be seen from Table 4.3, biological treatment includes the application of bacteria (Abhishek et al., 2015; Chandra et al., 2011; Haq et al., 2017; Hooda et al., 2018; Jiang et al., 2019; Kumar & Chandra, 2021; Majumdar et al., 2019; Rasool et al., 2023; Sonkar et al., 2019; Verma et al., 2020), fungi (Costa et al., 2017; Freitas et al., 2009; Heinz et al., 2019; Liu et al., 2011; Rajwar et al., 2017; Singhal & Thakur, 2009a; 2009b), and algae (Tao et al., 2017; Tarlan et al., 2002; Usha et al., 2016) with the various conventional (aerobic, anaerobic, and combination treatments) processes for the removal of organic contaminants (Patel et al., 2021; Pokhrel & Viraraghavan, 2004).

4.4.1 Bacteria-based process

For industrial wastewater treatment, bacteria have been the most commonly used microorganisms due to their abundance in sewage water and diverse enzymatic activity (Aditya et al., 2022; Dhanker et al., 2023; Li et al., 2022). In P&P wastewater treatment, aerated lagoons (Fan et al., 2023; Oliveiraesquerre et al., 2004; Oliveira-Esquerre et al., 2004) and AS (Clauss et al., 1999; Dalentoft & Thulin, 1997), which can accelerate the breakdown of organic substances into CO_2 and H_2O , have generally been used. Aerobic biodegradation of organics is an autocatalytic reaction, and aerobic bacteria are characterized by a much faster metabolic rate compared to anaerobic ones. On the other hand, the realization of the aerobic process may lead to the generation of a large amount of biomass (Esmaeeli et al., 2023). As a result, severe ecological concerns, for example, GHG releases (Pan et al., 2023; Yang et al., 2023), could arise due to this huge amount of sludge. One of the major applications of sewage sludge is as a fertilizer in agriculture, but the existence of heavy metals along with added hazardous chemicals in sludge requires the treatment of sludge prior to the ultimate discarding on land (Dede et al., 2023; D'Imporzano & Adani, 2023; Nyashanu et al., 2023; Zhang et al., 2022).

Tiku et al. (2010) demonstrated that a consortium of three bacteria, namely *Pseudomonas aeruginosa* (DSMZ 03504), *P. aeruginosa* (DSMZ 03505), and *Bacillus megaterium* (MTCC 6544),

Table 4.3 Efficiency of different microbial species in the treatment of pulp and paper mill wastewater.

Microbial species	Removal efficiency	References
Bacteria		
<i>Serratiamarcescens</i> , <i>Citrobacter</i> sp., and <i>Klebsiella Pneumonia</i>	COD (83%), BOD (74%), color (85%)	Chandra et al. (2011)
<i>Planococcus</i> sp. TRC1	COD (85%), phenol (96%), lignin (74%), color (81%)	Majumdar et al. (2019)
<i>Typha latifolia</i>	COD (80%), BOD (81%), lignin (83%)	Rasool et al. (2023)
<i>Bacillus cereus</i> AKRC03	Total organic carbon (TOC) (80%)	Kumar and Chandra (2021)
<i>Brevibacillus parabrevis</i> MTCC 12,105	COD (60%), lignin (43%), color (52%)	Hooda et al. (2018)
<i>Citrobacter freundii</i> and <i>Serratia marcescens</i>	COD (80%), color (87%)	Abhishek et al. (2015)
<i>C. freundii</i>	COD (45%), color (65%)	Abhishek et al. (2015)
<i>S. marcescens</i>	COD (33%), color (60%)	Abhishek et al. (2015)
<i>Bacillus velezensis</i>	Lignin (43%), color (56%)	Verma et al. (2020)
<i>Arthrobacter</i> sp. C2	Lignin (40%)	Jiang et al. (2019)
<i>Serratia liquefaciens</i>	COD (84%), lignin (61%), color (72%)	Haq et al. (2017)
<i>Bacillus</i> sp. IITRDVM-5	COD (90%), lignin (64%), color (73%), AOX (75%)	Sonkar et al. (2019)
Fungi		
<i>Cryptococcus</i> sp.	Lignin (50%), color (40%)	Singhal and Thakur (2009a)
<i>Bjerkandera adusta</i> and <i>Phanerochaete chrysosporium</i>	Lignin (74%–97%) TOC (35%)	Costa et al. (2017)
<i>Pleurotus ostreatus</i> EB 016	COD (99%), phenol (92%)	Heinz et al. (2019)
<i>Nigrospora</i> sp. LDF00204 and <i>Curvularia lunata</i> LDF21	COD (80%), lignin (76%), color (82%)	Rajwar et al. (2017)
<i>Emericella nidulans</i> var. <i>nidulans</i>	Lignin (37%), color (67%)	Singhal and Thakur (2009b)
<i>Aspergillus niger</i>	Color (43%)	Liu et al. (2011)
<i>Pleurotus sajor caju</i> , <i>Trametes versicolor</i> , <i>P. chrysosporium</i> and <i>Rhizopus oryzae</i>	COD (80%)	Freitas et al. (2009)
Algae		
<i>Scenedesmus</i> sp.	COD (75%), BOD (82%)	Usha et al. (2016)
<i>Scenedesmus acuminatus</i>	COD (29%–39%), color (74%–80%)	Tao et al. (2017)
<i>Chlorella</i>	COD (58%), color (79%)	Tarlan et al. (2002)

successfully decreased the COD content by about 76% within 10 hours with higher efficiency compared to single cell cultures. Similar results were obtained by Chandra et al. (2011) who developed a bacterial consortium comprising *Serratia marcescens*, *Citrobacter* sp., and *Klebsiella pneumoniae* for the decolorization of BL from rayon grade pulp plant having 18,700 mg/L COD. Nevertheless, comparatively great sedimentation happened throughout the AS procedures owing to the extreme growth of bacteria having filaments in sludge suspension, which offered a serious issue in downstream P&P effluent treatment (Esmaeeli et al., 2023; Kamali & Khodaparast, 2015).

Recently, Majumdar et al. (2019) presented a “waste-treats-waste” strategy for the bioremediation of paper mill effluent in FBR using another waste of the same industry, *that is*, paper mill sludge (PMSD) as an immobilizing matrix for *Planococcus* sp. TRC1. It was found that the PMSD immobilized bacteria are capable of removing phenol, lignin, color, and COD from the effluent by 96%, 74%, 81% and 85%, respectively after 60 hours of treatment. Application of the “waste-treats-waste” technology may be an attractive way from an economic and ecological point of view (Bai et al., 2023; Lu et al., 2023; Luo et al., 2023). It was also demonstrated that *Bacillus velezensis* is an efficient and economical process capable of removing a high percentage of color (56%) from P&P wastewater using response surface methodology to optimize the nutritional and physical factors (Verma et al., 2020).

It should be noted that in recent years the combination of anaerobic and aerobic processes has been actively developing to get the most out of the treatment benefits and final process effects (Guo et al., 2023; Yan et al., 2023). However, some studies (Table 4.3) reveal that anaerobic and aerobic methods are non-competent in degrading large and complex compounds, for instance, lignin (Balcioglu et al., 2007; Zhao et al., 2022). It is stated, for instance, that the conversion rate of lignin into value-added chemicals by bacteria is very less compared to fungi (Ahmad et al., 2010; Beckham et al., 2016).

4.4.2 Fungi-based process

The main advantage of fungi is associated with their survivability at a complex waste loading in comparison with that of bacteria (Chu et al., 2021; Singhal & Thakur, 2009b). White rot and wood-decay fungi, which belong to *Basidiomycotina* and *Ascomycotina*, are widely used for the degradation of lignin (Haq et al., 2016). Lignin represents a complex polyphenolic macromolecule, and its degradation pertains to the oxidation procedure ascribed to a restricted admittance to sulfur, nitrogen, and carbon (Wan et al., 2023; Wu et al., 2005).

Interestingly, recent studies have shown that wastewater treatment by fungi may be combined with fatty acid methyl esters or biodiesel production (Sundaramahalingam & Sivashanmugam, 2023; Vasiliadou et al., 2016).

Singhal and Thakur (2009b) investigated the effectiveness of a biological process to decolorize and detoxify P&P effluents using *Emericella nidulans* var. *nidulans* (anamorph: *Aspergillus nidulans*) based on rDNA ITS1 and rDNA ITS2 region sequences. They showed that decolorization of wastewater was improved by 31%, decreasing 67% pigment and 37% of lignin when treated by *E. nidulans* var. *nidulans*. It was also demonstrated that temperature rise has no influence on this method, while pH series between 5 and 6 offers the utmost influence on dye removal, which was attributed to adsorption and precipitation. Costa et al. (2017) compared the lignin-degrading ability of white rot fungi, such as *Bjerkandera adusta* and *Phanerochaete cryosporium*, grown in different media. Both fungal strains were able to accomplish 100% delignification in 8–10 days with a significant reduction of total organic carbon (TOC).

Unfortunately, the main limitation of fungi for practical P&P effluent treatment is their sensitivity to severe ecological situations, for instance, higher pH value. Other disadvantages are associated with the high glucose requirement and the necessity of a longer detention time due to the slow metabolism of microorganisms (Esmaeeli et al., 2023). As a result, scientists are aiming to test other microorganisms, such as algae.

4.4.3 Algae-based process

Micro-algae have fascinated noteworthy consideration since they are skilled for proficiently fixing CO₂ and concurrent production of biomass (Li et al., 2023; Xu et al., 2023). Nowadays, anthropogenic CO₂ emission is considered among the major reasons for global warming, and the development of new strategies for CO₂ application is the most important task of modern chemical science (Belousov & Suleimanov, 2021; Belousov et al., 2021). Nevertheless, the use of microalgae for wastewater treatment is also of interest and has great practical significance due to low cost, less energy intensive, useful biomass production, reduced sludge production, and heavy metals removal (Chen, Li, et al., 2023; Hasan et al., 2023; Najjar-Almanzor et al., 2023).

Usha et al. (2016) reported a mixed culture of microalgae, containing two *Scenedesmus* species, is capable of removing 82% and 75% of BOD and COD, respectively. Also, NO₃-N and PO₄-P removal of up to 65% and 71%, respectively, was detected after 28 days. It was observed that palmitic acid, oleic acid, linoleic acid, and α -linolenic acid are major fatty acids in the composition of mixed

microalgal culture cultivated with effluent. The cultivation of *Scenedesmus acuminatus* led to partial removal of color (74%–80%) and soluble COD (29%–39%) (Tao et al., 2017). Green algae (*Chlorella*) can remove 58%, 79% and 80% of COD, color, and AOX, respectively, from P&P effluent (Tarlan et al., 2002).

However, in the P&P wastewater, there is a great carbon content, whereas phosphorus and nitrogen are comparatively low. As a result, it may inhibit the microalgae cells' growth (Bhatti et al., 2021). Other algae cell growth inhibitory substances are resins, sterols, tannins, peroxides, alcohols, fatty acids, furfurals, and phenols (Scragg, 2006; Toczyłowska-Mamińska, 2017).

4.5 Hybrid technologies

The application of hybrid systems (Fig. 4.6), also known as integrated systems, has gained much attention in order to improve the efficiency of P&P wastewater treatment. These systems may be a combination of single-stage treatment techniques, such as chemical treatment, physical treatment, and biological treatment. The use of integrated systems may solve the main limitations inherent in single-stage methods. Some examples of the use of hybrid systems to treat P&P effluent are tabulated in Table 4.4.

Buzzini et al. (2006) investigated electrochemical oxidation (EO) with a UASB reactor for the treatment of bleached pulp mill

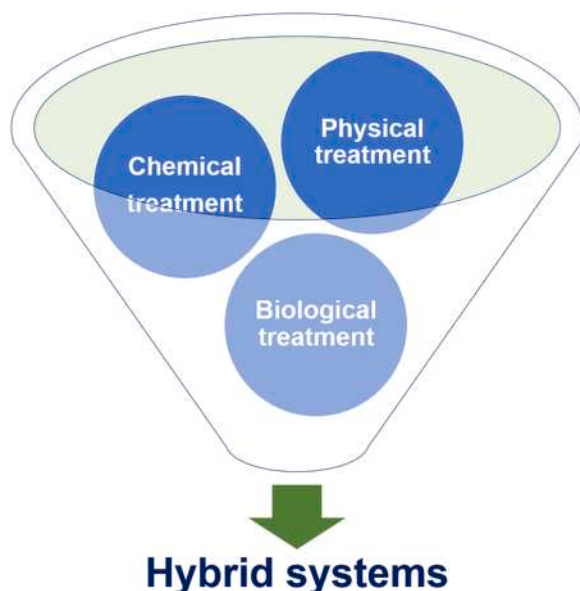


Figure 4.6 Hybrid systems construction.

Table 4.4 Efficiency of integrated systems in the treatment of pulp and paper mill wastewater.

Hybrid technology	Reactor	Removal efficiency	References
Anaerobic + membrane	Submerged anaerobic membrane bioreactor	COD (93%–99%)	Xie et al. (2010)
Aerobic MBR + electrochemical oxidation (Ti/SnO ₂ –Sb ₂ O ₅ –IrO ₂)	TSAMBR	COD (97%), color (100%)	Qu et al. (2012)
Electrochemical + membrane	Batch membrane reactor	COD (97%), color (98%)	Chanworrawoot and Hunsom (2012)
Anaerobic + slow sand filter	Upflow fixed-bed anaerobic bioreactor	COD (87%)	Mishra et al. (2015)
Enzymatic + membrane	–	Initial lignin content of 1,300 ppm	Krawczyk et al. (2013)
Fungal + photo-Fenton	Air-lift bioreactor + photoreactor	COD (99%), total phenols (92%)	Heinz et al. (2019)
Flotation + anaerobic treatment + AS + nanofiltration	UASB	COD (99%), color (100%)	Diniz Caldeira et al. (2021)
Ozone oxidation + photocatalysis + AS	–	COD (81%), BOD (92%), TOC (85%)	Jiang et al. (2023)

wastewater and compared the efficiency with that obtained from single-stage processes. The authors used Ti/Ru_{0.3}Ti_{0.7}O₂ as an anode and stainless steel as a cathode. The results indicated the technical feasibility and prospects of the electrochemical treatment as post-treatment for UASB since the hybrid system can remove about 93% and 96% of COD and color, respectively. On the other hand, the high operating costs of the electrochemical process may be a limiting factor for industrial applications and should be taken into account before modeling. Other examples of the electrochemical methods application in hybrid systems for water treatment include studies made by [Qu et al. \(2012\)](#) and [Chanworrawoot and Hunsom \(2012\)](#). The use of an integrated thermophilic submerged aerobic membrane bioreactor (TSAMBR) and EO allowed the removal of 98% COD with complete decolorization ([Qu et al., 2012](#)). The EO of the TSAMBR permeate was performed using a Ti/SnO₂–Sb₂O₅–IrO₂ electrode.

A further improvement of the integrated methods based on EO can be achieved by the realization of photoelectrocatalyst treatment, a combination of PC and electrocatalytic (EC) reactions. It is believed that the coupling of PC and EC for wastewater treatment is beneficial for restricting the charge carriers recombination and catalyst extraction from the mixture (Liu et al., 2020; Zhang et al., 2023; Zhou et al., 2023). It is also possible to combine electrochemical methods with ozonation, leading to oxidative reaction and a synergic regime for efficient removal of dye (Behin et al., 2015; Mehralian et al., 2021). Ozone represents a class of powerful oxidants (2.07 V vs SHE in an acidic solution), but the direct oxidation by ozone involves a slow degradation rate and poor mineralization of ozone-resistant compounds (Bavasso et al., 2022; Chen, Ma, et al., 2023; Issaka et al., 2022; Rekhate & Srivastava, 2020).

Recently, Jiang et al. (2023) evaluated the efficiency of innovative coupling of ozone oxidation and photocatalysis–biological treatment (ICOPB) for chemical–mechanical pulp (CMP) wastewater remediation (Fig. 4.7). The ICOPB strategy showed excellent mineralization efficiency because the removal rate of COD, BOD, and TOC were 81%, 92% and 85%, respectively. It was also demonstrated that *Proteobacteria* were actively involved in the subsequent biodegradation of CMP wastewater treated by the ICOPB system. Overall, the use of photocatalysis could be a promising approach to treating P&P

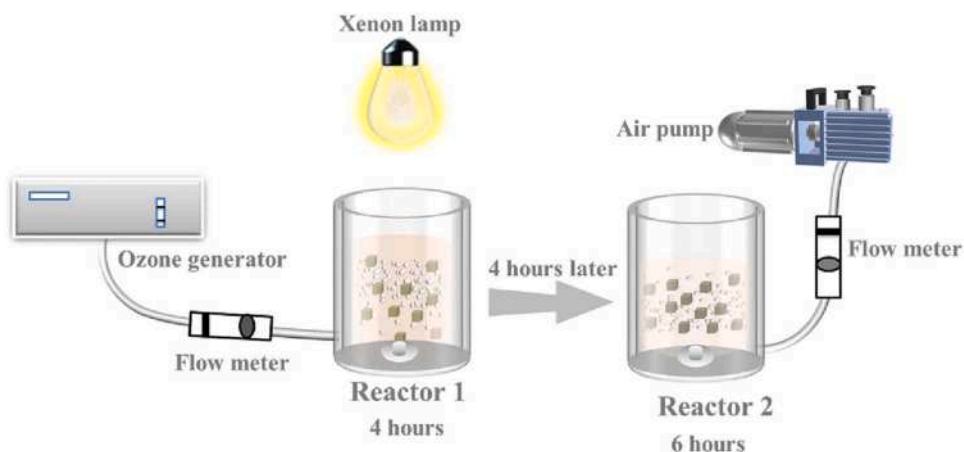


Figure 4.7 Schematic representation of the ICOPB reactor.

Source: Reproduced with permission from Jiang, Z., Abdoulaye, M.G., Wei, T., Xiao, X., Liang, Y., Xiong, J., Chen, G., & Chen, Y. (2023). Treatment of Eucalyptus chemical-mechanical pulp wastewater by coupling system of advanced catalytic oxidation and biodegradation: synergistic effect of ozonation photocatalytic-microbial. *Journal of Water Process Engineering*, 55, 104071. <https://doi.org/10.1016/j.jwpe.2023.104071>. Copyright 2023 Elsevier.

Table 4.5 Comparison of various pulp and paper wastewater technologies.

Treatment method	Pros	Cons
Physical treatment	• Efficient removal of solids and suspended matter. • Simple and cost-effective. • Reduced chemical consumption.	• Limited effectiveness for organic contaminant removal. • Ineffective against persistent organic compounds.
Chemical treatment	• Effective for color removal. • Suitable for complex effluents. • Reduction of toxic substances.	• High chemical costs. • May generate sludge requiring additional treatment.
Physico-chemical treatment	• Combines advantages of both physical and chemical. • Effective in removing diverse contaminants. • Can handle variable effluent characteristics.	• High operational and maintenance costs. • May require skilled personnel for operation.
Biological treatment	• Low-cost and eco-friendly. • High efficiency in reducing organic debris. • Anaerobic processes produce biogas for energy.	• Requires pre-treatment for persistent elements. • Aerobic processes result in CO₂ and sludge generation. • – High oxygen consumption in aerobic processes.
Bacteria-based process	• Abundant microorganisms for industrial wastewater. • Consortium of bacteria can efficiently decrease COD. • The “Waste-treats-waste” strategy can be cost-effective.	• Generation of clarification sludge in aerobic processes. • Filamentous bacteria may cause sedimentation issues.
Fungi-based process	• Efficient degradation of lignin by white-rot fungi. • Some fungi can produce biodiesel during treatment. • Decolorization and detoxification capabilities.	• Sensitivity to extreme environmental conditions. • High glucose requirement and slow metabolism.
Algae-based process	• Microalgae fix CO₂ efficiently. • Low energy requirement and heavy metal removal.	• Inhibition of microalgae growth due to high carbon content. • Sensitivity to inhibitory substances in wastewater.
Hybrid technologies	• Improved efficiency through integrated systems. • Addresses limitations of single-stage treatments. • Versatility in combining different treatment steps.	• High operating costs for some electrochemical methods. • Potential limitations in practical application.

wastewater using solar light. Other advantages of photocatalysis are environmental friendliness, economy (expensive equipment is not required), and ambient reaction conditions (Belousov & Shafiq, 2023; Belousov, Parkhacheva, Suleimanov, Shafiq, 2023).

The chapter concludes by following the pros and cons of various P&P wastewater treatment technologies, as shown in Table 4.5.

4.6 Conclusion and future trends

In conclusion, the comprehensive analysis of wastewater treatment methods for the paper and pulp industry reveals a diverse range of approaches, each with its unique advantages and challenges. The four major treatment categories explored in this chapter (physical, chemical, biological, and hybrid technologies) provide a holistic overview of the options available for mitigating the environmental impact of paper and pulp mill effluents.

Physical treatment methods, such as screening, sedimentation, and flotation, offer effective initial steps in the removal of solid contaminants and large particulate matter. These processes significantly reduce the overall pollutant load, facilitating subsequent treatments. However, their limited efficiency in handling dissolved and refractory pollutants necessitates a combination with other advanced treatments for comprehensive efficacy. Similarly, chemical treatments, particularly coagulation and flocculation, play a crucial role in the removal of colloidal and dissolved contaminants. Precipitation of undesirable compounds through the addition of chemical agents enhances the efficiency of subsequent processes. Nevertheless, the generation of chemical sludge and the need for proper disposal pose environmental challenges, emphasizing the importance of responsible chemical management.

On the other hand, biological processes emerge as environmentally friendly and cost-effective solutions for the degradation of organic pollutants in paper and pulp mill effluents.

Aerobic and anaerobic systems, each with distinct advantages, harness the metabolic activities of microorganisms to break down complex organic compounds. Bacteria, fungi, and algae exhibit varying degrees of efficiency in removing pollutants, providing a spectrum of options for tailored treatment strategies. Despite their high energy demand, aerobic methods like AS have been widely employed, showcasing proficiency in organic debris reduction. The challenge lies in the substantial carbon footprint associated with aerobic processes, emphasizing the need for energy-efficient alternatives. Anaerobic processes present promising alternatives, marked by lower chemical consumption, reduced sludge production, and potential energy recovery through biogas generation. The use of

anaerobic treatments becomes particularly attractive when coupled with the capture and utilization of methane as an energy source, demonstrating a more sustainable approach. The efficiency of various microbial species, including bacteria, fungi, and algae, highlights the potential for tailored biological treatments. The selection of specific microorganisms can be optimized for targeted pollutant removal, showcasing the adaptability and versatility of biological approaches.

The integration of multiple treatment techniques in hybrid systems represents a frontier in enhancing overall efficiency. By combining chemical, physical, and biological processes, hybrid technologies address the limitations inherent in single-stage methods. Notable examples include anaerobic-membrane hybrid systems, EO coupled with membrane bioreactors, and the innovative ICOPB reactor, showcasing the potential for advanced treatment strategies. The application of electrochemical methods, despite high operational costs, proves effective in removing COD and color, highlighting the technical feasibility of these advanced technologies. The integration of ozone oxidation, photocatalysis, and biological treatment in the ICOPB system demonstrates promising results in the remediation of CMP wastewater. This approach not only enhances the removal of COD, BOD, and TOC but also actively involves specific microbial communities, further contributing to the overall efficiency of the treatment.

The disadvantages, which are characteristic of treatment techniques, may be eliminated by fine-tuning treatment unit's parameters and integrating different approaches. The hybrid techniques have resulted in higher removal rates compared to other proposed techniques. Thus further investigations should be directed to the synergic effects when different treatment techniques are combined.

In summary, addressing the environmental challenges posed by paper and pulp mill effluents requires a synergistic approach that leverages the strengths of physical, chemical, and biological treatments. The continual exploration and development of hybrid technologies showcase a commitment to advancing sustainable practices in wastewater treatment. The selection of appropriate treatment strategies should consider the specific characteristics of effluents and aim to strike a balance between efficiency, cost-effectiveness, and environmental impact. As industries navigate increasingly stringent environmental regulations, the findings presented in this chapter offer valuable insights into evolving wastewater treatment methodologies for the paper and pulp sectors.

Acknowledgment

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List of acronyms

AOPs	advanced oxidation processes
AOX	adsorbable organic halides
AS	activated sludge
ASB	aerated stabilization basins
BL	black liquor
BOD	biological oxygen demand
CB	conduction band
CMP	chemical-mechanical pulp
COD	chemical oxygen demand
EC	electrocoagulation
EF	electro-Fenton
EGSB	expanded granular sludge bed
ELC	electrocatalytic
EO	electrochemical oxidation
FAMEs	fatty acid methyl esters
FBR	fluidized-bed reactor
GDE	gas diffusion electrode
GHG	greenhouse gas
IC	internal circulation reactor
ICOPB	innovative coupling of ozone oxidation and photocatalysis-biological treatment
LAS	long-time aerated sludge
MBBR	moving-bed bioreactors
MCF	modified carbon felt
MW	molecular weight
PAC	polyaluminum chloride
PBR	packed-bed reactor
PC	photocatalytic
PDS	peroxydisulfate
PEC	photoelectrocatalytic
PMS	peroxymonosulfate
PMSD	paper mill sludge
P&P	pulp and paper
PPME	pulp and paper mill effluent
PZC	point of zero charge
RNs	reactive nitrogen species
SBR	sequential batch reactor
SR	sulfate radical
TDS	total dissolved solids
TOC	total organic carbon
TSAMBR	thermophilic submerged aerobic membrane bioreactor
TSS	total suspended solids
UAF	up-flow anaerobic filter
UASB	up-flow anaerobic sludge blanket
UV	ultraviolet
VB	valence band
WWTPs	wastewater treatment plants

List of symbols

E_g	band gap energy

<i>h</i>	Planck's constant
<i>v</i>	frequency
pH	potential of hydrogen
pKa	acid dissociation constant

References

- Abhishek, A., Dwivedi, A., Tandan, N., & Kumar, U. (2015). Comparative bacterial degradation and detoxification of model and kraft lignin from pulp paper wastewater and its metabolites. *Applied Water Science*, 7(2), 757–767. <https://doi.org/10.1007/s13201-015-0288-9>.
- Aditya, L., Mahlia, T. M. I., Nguyen, L. N., Vu, H. P., & Nghiem, L. D. (2022). Microalgae-bacteria consortium for wastewater treatment and biomass production. *The Science of the Total Environment*, 838, 155871. <https://doi.org/10.1016/j.scitotenv.2022.155871>.
- Ahmad, M., Taylor, C. R., Pink, D., Burton, K., Eastwood, D., Bending, G. D., & Bugg, T. D. H. (2010). Development of novel assays for lignin degradation: Comparative analysis of bacterial and fungal lignin degraders. *Molecular Biosystems*, 6(5), 815–821. <https://doi.org/10.1039/b908966g>.
- Al Mayyahi, A., & Al-Asadi, H. A. A. (2018). Advanced oxidation processes (AOPs) for wastewater treatment and reuse: A brief review. *Asian Journal of Applied Science and Technology*, 2, 18–30.
- Ashrafi, O., Yerushalmi, L., & Haghighat, F. (2013). Greenhouse gas emission by wastewater treatment plants of the pulp and paper industry – Modeling and simulation. *International Journal of Greenhouse Gas Control*, 17, 462–472. <https://doi.org/10.1016/j.ijggc.2013.06.006>.
- Ashrafi, O., Yerushalmi, L., & Haghighat, F. (2015). Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management*, 158, 146–157. <https://doi.org/10.1016/j.jenvman.2015.05.010>.
- Bai, H., He, P., Hao, L., Fan, Z., Niu, R., Tang, T., & Gong, J. (2023). Waste-treating-waste: upcycling discarded polyester into metal-organic framework nanorod for synergistic interfacial solar evaporation and sulfate-based advanced oxidation process. *Chemical Engineering Journal*, 456, 140994. <https://doi.org/10.1016/j.cej.2022.140994>.
- Balcioğlu, I. A., Tarlan, E., Kivılcımdan, C., & Türker Saçan, M. (2007). Merits of ozonation and catalytic ozonation pre-treatment in the algal treatment of pulp and paper mill effluents. *Journal of Environmental Management*, 85(4), 918–926. <https://doi.org/10.1016/j.jenvman.2006.10.020>.
- Barhoumi, A., Ncib, S., Chibani, A., Brahmi, K., Bouguerra, W., & Elaloui, E. (2019). High-rate humic acid removal from cellulose and paper industry wastewater by combining electrocoagulation process with adsorption onto granular activated carbon. *Industrial Crops and Products*, 140, 111715.
- Bavasso, I., Montanaro, D., & Petrucci, E. (2022). Ozone-based electrochemical advanced oxidation processes. *Current Opinion in Electrochemistry*, 34, 101017. <https://doi.org/10.1016/j.coelec.2022.101017>.
- Beckham, G. T., Johnson, C. W., Karp, E. M., Salvachúa, D., & Vardon, D. R. (2016). Opportunities and challenges in biological lignin valorization. *Current Opinion in Biotechnology*, 42, 40–53. <https://doi.org/10.1016/j.copbio.2016.02.030>.
- Behin, J., Farhadian, N., Ahmadi, M., & Parvizi, M. (2015). Ozone assisted electrocoagulation in a rectangular internal-loop airlift reactor: Application to

- decolorization of acid dye. *Journal of Water Process Engineering*, 8, 171–178. <https://doi.org/10.1016/j.jwpe.2015.10.003>.
- Belousov, A. S., Esipovich, A. L., Kanakov, E. A., & Otopkova, K. V. (2021). Recent advances in sustainable production and catalytic transformations of fatty acid methyl esters. *Sustainable Energy Fuels*, 5(18), 4512–4545. <https://doi.org/10.1039/d1se00830g>.
- Belousov, A. S., Parkhacheva, A. A., Suleimanov, E. V., Fukina, D. G., Koryagin, A. V., Shafiq, I., Krashenninnikova, O. V., & Kuzmichev, V. V. (2023). Doping vs. heterojunction: A comparative study of the approaches for improving the photocatalytic activity of flower-like Bi₂WO₆ for water treatment with domestic LED light. *Catalysis Communications*, 106705.
- Belousov, A. S., Parkhacheva, A. A., Suleimanov, E. V., & Shafiq, I. (2023). Potential of Bi₂WO₆-based heterojunction photocatalysts for environmental remediation. *Materials Today Chemistry*, 32, 101633. <https://doi.org/10.1016/j.mtchem.2023.101633>.
- Belousov, A. S., & Shafiq, I. J. C. (2022). Towards the sustainable production of ultra-low-sulfur fuels through photocatalytic oxidation. *Catalysts*, 12(9), 1036.
- Belousov, A. S., & Shafiq, I. (2023). Heterogeneous photocatalysis for C–H bond activation. *Journal of Environmental Chemical Engineering*, 11(5), 110970. <https://doi.org/10.1016/j.jece.2023.110970>.
- Belousov, A. S., & Suleimanov, E. V. (2021). Application of metal–organic frameworks as an alternative to metal oxide-based photocatalysts for the production of industrially important organic chemicals. *Green Chemistry: an International Journal and Green Chemistry Resource: GC*, 23(17), 6172–6204. <https://doi.org/10.1039/d1gc01690c>.
- Bhatti, S., Richards, R., & McGinn, P. (2021). Screening of two freshwater green microalgae in pulp and paper mill wastewater effluents in Nova Scotia, Canada. *Water Science and Technology: a Journal of the International Association on Water Pollution Research*, 83(6), 1483–1498. <https://doi.org/10.2166/wst.2021.001>.
- Birjandi, N., Younesi, H., & Bahramifar, N. (2016). Treatment of wastewater effluents from paper-recycling plants by coagulation process and optimization of treatment conditions with response surface methodology. *Applied Water Science*, 6(4), 339–348. <https://doi.org/10.1007/s13201-014-0231-5>.
- Boczka, G., & Fernandes, A. (2017). Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. *Chemical Engineering Journal*, 320, 608–633.
- Bokhary, A., Leitch, M., & Liao, B. Q. (2022). Effect of organic loading rates on the membrane performance of a thermophilic submerged anaerobic membrane bioreactor for primary sludge treatment from a pulp and paper mill. *Journal of Environmental Chemical Engineering*, 10(3), 107523. <https://doi.org/10.1016/j.jece.2022.107523>.
- Bokhary, A., Tikka, A., Leitch, M., & Liao, B. (2018). Membrane fouling prevention and control strategies in pulp and paper industry applications: A review. *Journal of Membrane Science and Research*, 4(4), 181–197.
- Boroski, M., Rodrigues, A. C., Garcia, J. C., Gerola, A. P., Nozaki, J., & Hioka, N. (2008). The effect of operational parameters on electrocoagulation–flotation process followed by photocatalysis applied to the decontamination of water effluents from cellulose and paper factories. *Journal of Hazardous Materials*, 160(1), 135–141.
- Boulaadjou, S., Zemmouri, H., Bendjama, Z., & Drouiche, N. (2018). A novel use of *Moringa oleifera* seed powder in enhancing the primary treatment of paper mill effluent. *Chemosphere*, 206, 142–149.

- Brink, A., Sheridan, C., & Harding, K. (2017). The Fenton oxidation of biologically treated paper and pulp mill effluents: A performance and kinetic study. *Process Safety and Environmental Protection*, 107, 206–215.
- Buyukkamaci, N., & Koken, E. (2010). Economic evaluation of alternative wastewater treatment plant options for pulp and paper industry. *The Science of the Total Environment*, 408(24), 6070–6078. <https://doi.org/10.1016/j.scitotenv.2010.08.045>.
- Buzzini, A. P., Miwa, D. W., Motheo, A. J., & Pires, E. C. (2006). Use of electrochemical oxidation process as post-treatment for the effluents of a UASB reactor treating cellulose pulp mill wastewater. *Water Science and Technology: a Journal of the International Association on Water Pollution Research*, 54(2), 207–213. <https://doi.org/10.2166/wst.2006.507>.
- Cabrera, M. N. (2017). Pulp mill wastewater: Characteristics and treatment. *Biological Wastewater Treatment and Resource Recovery*, 2, 119–139.
- Can-Güven, E., Guvenc, S. Y., Kavan, N., & Varank, G. (2021). Paper mill wastewater treatment by Fe²⁺ and heat-activated persulfate oxidation: Process modeling and optimization. *Environmental Progress & Sustainable Energy*, 40(2), e13508.
- Chandra, R., Abhishek, A., & Sankhwar, M. (2011). Bacterial decolorization and detoxification of black liquor from rayon grade pulp manufacturing paper industry and detection of their metabolic products. *Bioresource Technology*, 102(11), 6429–6436.
- Chanworrawoot, K., & Hunsom, M. (2012). Treatment of wastewater from pulp and paper mill industry by electrochemical methods in membrane reactor. *Journal of Environmental Management*, 113, 399–406. <https://doi.org/10.1016/j.jenvman.2012.09.021>.
- Chaturvedi, S. I. (2013). Electrocoagulation: A novel waste water treatment method. *International Journal of Modern Engineering Research*, 3(1), 93–100.
- Chaudhry, S., & Paliwal, R. (2018). Techniques for remediation of paper and pulp mill effluents: Processes and constraints. *Handbook of Environmental Materials Management*, 12.
- Chen, S., Li, X., Ma, X., Qing, R., Chen, Y., Zhou, H., Yu, Y., Li, J., & Tan, Z. (2023). Lighting the way to sustainable development: Physiological response and light control strategy in microalgae-based wastewater treatment under illumination. *The Science of the Total Environment*, 903, 166298. <https://doi.org/10.1016/j.scitotenv.2023.166298>.
- Chen, X., Ma, J., Chen, J., & Wang, Z. (2023). Ceramic membrane filtration coupled with ozonation for water purification: Principles, applications and perspectives. *Journal of Water Process Engineering*, 55, 104127. <https://doi.org/10.1016/j.jwpe.2023.104127>.
- Chen, Z., Xiong, J., & Cheng, G. (2024). Recent advances in brookite phase TiO₂-based photocatalysts toward CO₂ reduction. *Fuel*, 357, 129806. <https://doi.org/10.1016/j.fuel.2023.129806>.
- Chu, R., Li, S., Zhu, L., Yin, Z., Hu, D., Liu, C., & Mo, F. (2021). A review on co-cultivation of microalgae with filamentous fungi: Efficient harvesting, wastewater treatment and biofuel production. *Renewable Sustainable Energy Rev*, 139, 110689. <https://doi.org/10.1016/j.rser.2020.110689>.
- Clauss, F., Balavoine, C., Hélaine, D., & Martin, G. (1999). Controlling the settling of activated sludge in pulp and paper wastewater treatment plants. *Water Science and Technology: a Journal of the International Association on Water Pollution Research*, 40(11–12), 223–229. [https://doi.org/10.1016/s0273-1223\(99\)00722-2](https://doi.org/10.1016/s0273-1223(99)00722-2).
- Costa, S., Dedola, D., Pellizzari, S., Blo, R., Rugiero, I., Pedrini, P., & Tamburini, E. (2017). Lignin biodegradation in pulp-and-paper mill wastewater by selected white rot fungi. *Water*, 9(12), 935. <https://doi.org/10.3390/w9120935>.

- Courbalay, M., Villain-Gambier, M., Klem, A., Ziegler-Devin, I., Dumarcay, S., & Trebouet, D. (2021). Influence of pH and fouling characterization during membrane process for lignin recovery from the process water of thermomechanical pulping. *Separation and Purification Technology*, 275, 119162.
- Covinich, L. G., Bengoechea, D. I., Fenoglio, R. J., Area, M. C. (2014). Advanced oxidation processes for wastewater treatment in the pulp and paper industry: A review.
- D'Imporzano, G., & Adani, F. (2023). Measuring the environmental impacts of sewage sludge use in agriculture in comparison with the incineration alternative. *The Science of the Total Environment*, 905, 167025. <https://doi.org/10.1016/j.scitotenv.2023.167025>.
- Dalentoft, E., & Thulin, P. (1997). The use of aerobic selectors in activated sludge systems for treatment of wastewater from the pulp and paper industry. *Water Science and Technology: a Journal of the International Association on Water Pollution Research*, 35(2-3), 181-188. [https://doi.org/10.1016/s0273-1223\(96\)00930-4](https://doi.org/10.1016/s0273-1223(96)00930-4).
- Dede, G., Banu Sasmaz, Z., Ozdemir, S., Caner, C., & Dede, C. (2023). Investigation of heavy metal and micro-macro element speciation in biomass ash enriched sewage sludge compost. *Journal of Environmental Management*, 344, 118330. <https://doi.org/10.1016/j.jenvman.2023.118330>.
- Deshmukh, N. S., Lapsiya, K. L., Savant, D. V., Chiplonkar, S. A., Yeole, T. Y., Dhakephalkar, P. K., & Ranade, D. R. (2009). Upflow anaerobic filter for the degradation of adsorbable organic halides (AOX) from bleach composite wastewater of pulp and paper industry. *Chemosphere*, 75(9), 1179-1185. <https://doi.org/10.1016/j.chemosphere.2009.02.042>.
- Devi, A., Singhal, A., & Gupta, R. J. I. J. O. E. S. (2013). *A Review on Spent Pickling Liquor*, 4(3), 284-295.
- Dhanker, R., Khatana, K., Verma, K., Singh, A., Heena, Kumar, R., & Mohamed, H. I. (2023). An integrated approach of algae-bacteria mediated treatment of industries generated wastewater: Optimal recycling of water and safe way of resource recovery. *Biocatalysis and Agricultural Biotechnology*, 54, 102936. <https://doi.org/10.1016/j.bcab.2023.102936>.
- Dilpazeer, F., Munir, M., Baloch, M. Y. J., Shafiq, I., Iqbal, J., Saeed, M., Abbas, M. M., Shafique, S., Aziz, K. H. H., & Mustafa, A. (2023). A comprehensive review of the latest advancements in controlling arsenic contaminants in groundwater. *Water*, 15(3), 478.
- Diniz Caldeira, D. C., Mudadu Silva, C., Colodette, J. L., de Ávila Rodrigues, F., Da Mata, R. A., da Silva Menezes, K., Vieira, J. C., & Vinha Zanuncio, A. J. (2021). A case study on the treatment and recycling of the effluent generated from a thermo-mechanical pulp mill in Brazil after the installation of a new bleaching process. *The Science of the Total Environment*, 763, 142996. <https://doi.org/10.1016/j.scitotenv.2020.142996>.
- Domínguez-Robles, J., Palenzuela, M. D. V., Sánchez, R., Loaiza, J. M., Espinosa, E., Rosal, A., & Rodríguez, A. (2020). Coagulation-flocculation as an alternative way to reduce the toxicity of the black liquor from the paper industry: Thermal valorization of the solid biomass recovered. *Waste and Biomass Valorization*, 11, 4731-4742.
- Dornelles, H. D. S., Camargo, F. P., Silva, E. L., & Varesche, M. B. A. (2023). Microbial community stratification in scale-up anaerobic fluidized bed reactor applied for 4-nonylphenol degradation. *Bioresource Technology Reports*, 21, 101359. <https://doi.org/10.1016/j.biteb.2023.101359>.
- Duan, X., Liu, T., Duan, W., & Hu, H. (2010). Adsorption and coagulation tertiary treatment of pulp & paper mills wastewater. In *2010 4th international conference on bioinformatics and biomedical engineering* (pp. 1-4). IEEE.

- Eskelinen, K., Särkkä, H., Kurniawan, T. A., & Sillanpää, M. E. (2010). Removal of recalcitrant contaminants from bleaching effluents in pulp and paper mills using ultrasonic irradiation and Fenton-like oxidation, electrochemical treatment, and/or chemical precipitation: A comparative study. *Desalination*, 255(1-3), 179–187.
- Esmaeeli, A., Sarrafzadeh, M.-H., Zeighami, S., Kalantar, M., Bariki, S. G., Fallahi, A., Asgharnejad, H., & Ghaffari, S.-B. (2023). A comprehensive review on pulp and paper industries wastewater treatment advances. *Industrial & Engineering Chemistry Research*, 62(21), 8119–8145. <https://doi.org/10.1021/acs.iecr.2c04393>.
- Fan, L., Mohseni, A., Schmidt, J., Evans, B., Murdoch, B., & Gao, L. (2023). Efficiency of lagoon-based municipal wastewater treatment in removing microplastics. *The Science of the Total Environment*, 876, 162714. <https://doi.org/10.1016/j.scitotenv.2023.162714>.
- Fernandes, A., Gagol, M., Makoś, P., Khan, J. A., & Boczkaj, G. (2019). Integrated photocatalytic advanced oxidation system (TiO₂/UV/O₃/H₂O₂) for degradation of volatile organic compounds. *Separation and Purification Technology*, 224, 1–14.
- Fernandes, A., Nunes, M. J., Rodrigues, A. S., Pacheco, M. J., Ciriaco, L., & Lopes, A. (2021). Electro-persulfate processes for the treatment of complex wastewater matrices: Present and future. *Molecules (Basel, Switzerland)*, 26(16), 4821.
- Fernandes, L., Lucas, M. S., Maldonado, M. I., Oller, I., & Sampaio, A. (2014). Treatment of pulp mill wastewater by *Cryptococcus podzolicus* and solar photo-Fenton: A case study. *Chemical Engineering Journal*, 245, 158–165.
- Freitas, A. C., Ferreira, F., Costa, A. M., Pereira, R., Antunes, S. C., Gonçalves, F., Rocha-Santos, T. A. P., Diniz, M. S., Castro, L., Peres, I., & Duarte, A. C. (2009). Biological treatment of the effluent from a bleached kraft pulp mill using basidiomycete and zygomycete fungi. *The Science of the Total Environment*, 407(10), 3282–3289. <https://doi.org/10.1016/j.scitotenv.2009.01.054>.
- Garg, A., Mishra, I. M., & Chand, S. (2010). Effectiveness of coagulation and acid precipitation processes for the pre-treatment of diluted black liquor. *Journal of Hazardous Materials*, 180(1-3), 158–164. <https://doi.org/10.1016/j.jhazmat.2010.04.008>.
- Ghaly, M. Y., Jamil, T. S., El-Seesy, I. E., Souaya, E. R., & Nasr, R. A. (2011). Treatment of highly polluted paper mill wastewater by solar photocatalytic oxidation with synthesized nano TiO₂. *Chemical Engineering Journal*, 168(1), 446–454.
- Gholami, M., Abbasi Souraki, B., Pendashteh, A., & Bagherian Marzouni, M. (2017). Efficiency evaluation of the membrane/AOPs for paper mill wastewater treatment. *Environmental Technology*, 38(9), 1127–1138.
- Grötzner, M., Melchior, E., Schroeder, L. H., dos Santos, A. R., Moscon, K. G., de Andrade, M. A., Martinelli, S. H. S., & Xavier, C. R. (2018). Pulp and paper mill effluent treated by combining coagulation-flocculation-sedimentation and Fenton processes. *Water, Air, & Soil Pollution*, 229, 1–7.
- Guo, D., Wang, M., Zhang, J., Su, J., Shao, Y., Zhang, B., Yang, L., Ma, Y., & Ren, Y. (2023). Simultaneous removal of macromolecular microbial metabolites and nitrogen in a receiving river of wastewater treatment plants lacking ecological base flow via the combination of anaerobic and aerobic biofilters. *Journal of Cleaner Production*, 427, 139242. <https://doi.org/10.1016/j.jclepro.2023.139242>.
- Gönder, Z. B., Arayici, S., & Barlas, H. (2011). Advanced treatment of pulp and paper mill wastewater by nanofiltration process: Effects of operating conditions on membrane fouling. *Separation and Purification Technology*, 76(3), 292–302.
- Haq, I., Kumar, S., Kumari, V., Singh, S. K., & Raj, A. (2016). Evaluation of bioremediation potentiality of ligninolytic *Serratia liquefaciens* for detoxification of pulp and paper mill effluent. *Journal of Hazardous Materials*, 305, 190–199. <https://doi.org/10.1016/j.jhazmat.2015.11.046>.

- Haq, I., Kumar, S., Raj, A., Lohani, M., & Satyanarayana, G. N. V. (2017). Genotoxicity assessment of pulp and paper mill effluent before and after bacterial degradation using *Allium cepa* test. *Chemosphere*, 169, 642–650. <https://doi.org/10.1016/j.chemosphere.2016.11.101>.
- Haq, I., & Raj, A. (2020). Pulp and paper mill wastewater: Ecotoxicological effects and bioremediation approaches for environmental safety. In *Bioremediation of Industrial Waste for Environmental Safety: Volume II: Biological Agents and Methods for Industrial Waste Management* (pp. 333–356).
- Hasan, H. A., Muhamad, M. H., Ji, B., Nazairi, N. A., Jiat, K. W., Sim, S. I. S. W. A., & Poh, A. F. M. S. (2023). Revolutionizing wastewater treatment with microalgae: Unveiling resource recovery, mechanisms, challenges, and future possibilities. *Ecological Engineering*, 197, 107117. <https://doi.org/10.1016/j.ecoleng.2023.107117>.
- Heinz, O. L., Cunha, M. A. A., Amorim, J. S., Barbosa-Dekker, A. M., Dekker, R. F. H., & Barreto-Rodrigues, M. (2019). Combined fungal and photo-oxidative Fenton processes for the treatment of wood-laminate industrial waste effluent. *Journal of Hazardous Materials*, 379, 120790. <https://doi.org/10.1016/j.jhazmat.2019.120790>.
- Hermosilla, D., Merayo, N., Gascó, A., & Blanco, Á. (2015). The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: A review. *Environmental Science and Pollution Research*, 22, 168–191.
- Hong, Y.-S., Zhou, H., & Zytner, R. (2007). Combining ultrafiltration process with coagulation pretreatment for pulp mill wastewater treatment. *Environmental Technology*, 28(9), 995–1006.
- Hooda, R., Bhardwaj, N. K., & Singh, P. (2018). *Brevibacillus parabrevis* MTCC 12105: A potential bacterium for pulp and paper effluent degradation. *World Journal of Microbiology and Biotechnology*, 34(2), 31. <https://doi.org/10.1007/s11274-018-2414-y>.
- Hubbe, M. A., Metts, J. R., Hermosilla, D., Blanco, M. A., Yerushalmi, L., Haghighat, F., Lindholm-Lehto, P., Khodaparast, Z., Kamali, M., & Elliott, A. (2016). Wastewater treatment and reclamation: A review of pulp and paper industry practices and opportunities. *BioResources*, 11(3), 7953–8091.
- Irfan, M., Butt, T., Imtiaz, N., Abbas, N., Khan, R. A., & Shafique, A. (2017). The removal of COD, TSS and colour of black liquor by coagulation-flocculation process at optimized pH, settling and dosing rate. *Arabian Journal of Chemistry*, 10, S2307–S2318.
- Irizar, I., Roche, E., Beltrán, S., Aymerich, E., & Esteban-Gutiérrez, M. (2018). Model-based design of a software sensor for real-time diagnosis of the stability conditions in high-rate anaerobic reactors – Full-scale application to internal circulation technology. *Water Research*, 143, 479–491. <https://doi.org/10.1016/j.watres.2018.06.055>.
- Issaka, E., Amu-Darko, J. N.-O., Yakubu, S., Fapohunda, F. O., Ali, N., & Bilal, M. (2022). Advanced catalytic ozonation for degradation of pharmaceutical pollutants – A review. *Chemosphere*, 289, 133208. <https://doi.org/10.1016/j.chemosphere.2021.133208>.
- Jaafarzadeh, N., Omidinasab, M., & Ghanbari, F. (2016). Combined electrocoagulation and UV-based sulfate radical oxidation processes for treatment of pulp and paper wastewater. *Process Safety and Environmental Protection*, 102, 462–472.
- Jagaba, A. H., Birniwa, A. H., Usman, A. K., Mu'azu, N. D., Yaro, N. S. A., Soja, U. B., Abioye, K. J., Almahbashi, N. M. Y., Al-dhawi, B. N. S., Noor, A., & Lawal, I. M. (2023). Trend and current practices of coagulation-based hybrid systems for pulp and paper mill effluent treatment: Mechanisms, optimization techniques and performance evaluation. *Journal of Cleaner Production*, 139543. <https://doi.org/10.1016/j.jclepro.2023.139543>.

- Jagaba, A. H., Kutty, S. R. M., Baloo, L., Birniwa, A. H., Lawal, I. M., Aliyu, M. K., Yaro, N. S. A., & Usman, A. K. (2022). Combined treatment of domestic and pulp and paper industry wastewater in a rice straw embedded activated sludge bioreactor to achieve sustainable development goals. *Case Studies in Chemical and Environmental Engineering*, 6, 100261. <https://doi.org/10.1016/j.cscee.2022.100261>.
- Jagaba, A. H., Kutty, S. R. M., Noor, A., Isah, A. S., Lawal, I. M., Birniwa, A. H., Usman, A. K., & Abubakar, S. (2022). Kinetics of pulp and paper wastewater treatment by high sludge retention time activated sludge process. *Journal of Hunan University Natural Sciences*, 49(2), 242–251. <https://doi.org/10.55463/issn.1674-2974.49.2.24>.
- Janicke, M., & Jacob, K. (2013). A third industrial revolution, Long-term governance for social-ecological change (pp. 47–71).
- Jiang, C., Cheng, Y., Zang, H., Chen, X., Wang, Y., Zhang, Y., Wang, J., Shen, X., & Li, C. (2019). Biodegradation of lignin and the associated degradation pathway by psychrotrophic *Arthrobacter* sp. C2 from the cold region of China. *Cellulose*, 27(3), 1423–1440. <https://doi.org/10.1007/s10570-019-02858-3>.
- Jiang, Z., Abdoulaye, M. G., Wei, T., Xiao, X., Liang, Y., Xiong, J., Chen, G., & Chen, Y. (2023). Treatment of Eucalyptus chemical-mechanical pulp wastewater by coupling system of advanced catalytic oxidation and biodegradation: synergistic effect of ozonation photocatalytic-microbial. *Journal of Water Process Engineering*, 55, 104071. <https://doi.org/10.1016/j.jwpe.2023.104071>.
- Kamali, M., & Khodaparast, Z. (2015). Review on recent developments on pulp and paper mill wastewater treatment. *Ecotoxicology and Environmental Safety*, 114, 326–342. <https://doi.org/10.1016/j.ecoenv.2014.05.005>.
- Khan, J. A., Sayed, M., Shah, N. S., Khan, S., Zhang, Y., Boczkaj, G., Khan, H. M., & Dionysiou, D. D. (2020). Synthesis of eosin modified TiO₂ film with co-exposed {001} and {101} facets for photocatalytic degradation of para-aminobenzoic acid and solar H₂ production. *Applied Catalysis B: Environmental*, 265, 118557.
- Khare, P., Patel, R. K., Sharan, S., & Shankar, R. (2021). Recent trends in advanced oxidation process for treatment of recalcitrant industrial effluents. In *Advanced oxidation processes for effluent treatment plants*. Elsevier, 137–160.
- Kishimoto, N., Nakagawa, T., Okada, H., & Mizutani, H. (2010). Treatment of paper and pulp mill wastewater by ozonation combined with electrolysis. *Journal of Water and Environment Technology*, 8(2), 99–109.
- Ko, C.-H., & Fan, C. (2010). Enhanced chemical oxygen demand removal and flux reduction in pulp and paper wastewater treatment using laccase-polymerized membrane filtration. *Journal of Hazardous Materials*, 181(1-3), 763–770.
- Krawczyk, H., Oinonen, P., & Jönsson, A. S. (2013). Combined membrane filtration and enzymatic treatment for recovery of high molecular mass hemicelluloses from chemithermomechanical pulp process water. *Chemical Engineering Journal*, 225, 292–299. <https://doi.org/10.1016/j.cej.2013.03.089>.
- Kumar, A., & Chandra, R. (2021). Biodegradation and toxicity reduction of pulp paper mill wastewater by isolated laccase producing *Bacillus cereus* AKRC03. *Cleaner Engineering and Technology*, 4, 100193. <https://doi.org/10.1016/j.clet.2021.100193>.
- Kumar, A., Srivastava, N. K., & Gera, P. (2021). Removal of color from pulp and paper mill wastewater - methods and techniques - A review. *Journal of Environmental Management*, 298, 113527. <https://doi.org/10.1016/j.jenvman.2021.113527>.
- Kumar, D., Gaurav, V. K., & Sharma, C. (2018). Ecofriendly remediation of pulp and paper industry wastewater by electrocoagulation and its application in agriculture. *American Journal of Plant Sciences*, 9(12), 2462.
- Kumar, V., & Verma, P. (2023). A critical review on environmental risk and toxic hazards of refractory pollutants discharged in chlorolignin waste of pulp and

- paper mills and their remediation approaches for environmental safety. *Environmental Research*, 236, 116728. <https://doi.org/10.1016/j.envres.2023.116728>.
- Lal, K., & Garg, A. (2017). Utilization of dissolved iron as catalyst during Fenton-like oxidation of pretreated pulping effluent. *Process Safety and Environmental Protection*, 111, 766–774.
- Lewis, R., Cohen, J., Awad, J., Burger, H., Marzouk, J., Burch, G., Lewis, D. M., & van Leeuwen, J. A. (2018). Study of the impacts of process changes of a pulp and paper mill on aerated stabilization basin (ASB) performance. *Chemosphere*, 211, 767–774. <https://doi.org/10.1016/j.chemosphere.2018.07.178>.
- Li, S., Chang, H., Zhang, S., & Ho, S.-H. (2023). Production of sustainable biofuels from microalgae with CO₂ bio-sequestration and life cycle assessment. *Environmental Research*, 227, 115730. <https://doi.org/10.1016/j.envres.2023.115730>.
- Li, S., Ondon, B. S., Ho, S.-H., Jiang, J., & Li, F. (2022). Antibiotic resistant bacteria and genes in wastewater treatment plants: From occurrence to treatment strategies. *The Science of the Total Environment*, 838, 156544. <https://doi.org/10.1016/j.scitotenv.2022.156544>.
- Liu, T., Hu, H., He, Z., & Ni, Y. (2011). Treatment of poplar alkaline peroxide mechanical pulping (APMP) effluent with *Aspergillus niger*. *Bioresource Technology*, 102(15), 7361–7365. <https://doi.org/10.1016/j.biortech.2011.04.043>.
- Liu, X., Tang, P., Liu, Y., Xie, W., Chen, C., Li, T., He, Q., Bao, J., Tiraferri, A., & Liu, B. (2022). Efficient removal of organic compounds from shale gas wastewater by coupled ozonation and moving-bed-biofilm submerged membrane bioreactor. *Bioresource Technology*, 344, 126191. <https://doi.org/10.1016/j.biortech.2021.126191>.
- Liu, X., Zhou, H., Pei, S., Xie, S., & You, S. (2020). Oxygen-deficient WO_{3-x} nanoplate array film photoanode for efficient photoelectrocatalytic water decontamination. *Chemical Engineering Journal*, 381, 122740. <https://doi.org/10.1016/j.cej.2019.122740>.
- Lu, M., Wang, Y., Yu, J., Li, D., Zhao, Q., & Chi, R. (2023). Treating waste with waste: adsorption of anionic dyes in wastewater with surfactant-modified phosphogypsum. *Environmental Research*, 237, 116963. <https://doi.org/10.1016/j.envres.2023.116963>.
- Lucas, M. S., Peres, J. A., Amor, C., Prieto-Rodríguez, L., Maldonado, M. I., & Malato, S. (2012). Tertiary treatment of pulp mill wastewater by solar photo-Fenton. *Journal of Hazardous Materials* 225, 173–181.
- Luo, S., Zhu, X., Gong, M., Mo, R., & Yang, S. (2023). Coupling the recovery of spent lithium-ion batteries and the treatment of phenol wastewater: A “treating waste with waste” strategy. *Chemosphere*, 341, 140018. <https://doi.org/10.1016/j.chemosphere.2023.140018>.
- Mahboob, I., Shafique, S., Shafiq, I., Akhter, P., Belousov, A. S., Show, P.-L., Park, Y.-K., & Hussain, M. J. E. R. (2023). Mesoporous LaVO₄/MCM-48 nanocomposite with visible-light-driven photocatalytic degradation of phenol in wastewater, 218, 114983.
- Mahesh, S., Garg, K. K., Srivastava, V. C., Mishra, I. M., Prasad, B., & Mall, I. D. (2016). Continuous electrocoagulation treatment of pulp and paper mill wastewater: Operating cost and sludge study. *RSC Advances*, 6(20), 16223–16233.
- Mainardis, M., Buttazzoni, M., Bortoli, N. D., Mion, M., & Goi, D. (2020). Evaluation of ozonation applicability to pulp and paper streams for a sustainable wastewater treatment. *Journal of Cleaner Production*, 258, 120781.
- Majumdar, S., Priyadarshinee, R., Kumar, A., Mandal, T., & Dasgupta Mandal, D. (2019). Exploring *Planococcus* sp. TRC1, a bacterial isolate, for carotenoid

- pigment production and detoxification of paper mill effluent in immobilized fluidized bed reactor. *Journal of Cleaner Production*, 211, 1389–1402. <https://doi.org/10.1016/j.jclepro.2018.11.157>.
- Marques, R., Ferrari-Lima, A., Slusarski-Santana, V., & Fernandes-Machado, N. (2017). Ag₂O and Fe₂O₃ modified oxides on the photocatalytic treatment of pulp and paper wastewater. *Journal of Environmental Management*, 195, 242–248.
- Mehmood, K., Rehman, S. K. U., Wang, J., Farooq, F., Mahmood, Q., Jadoon, A. M., Javed, M. F., & Ahmad, I. (2019). Treatment of pulp and paper industrial effluent using physicochemical process for recycling. *Water*, 11(11), 2393.
- Mehralian, M., Khashij, M., & Dalvand, A. (2021). Treatment of cardboard factory wastewater using ozone-assisted electrocoagulation process: Optimization through response surface methodology. *Environmental Science and Pollution Research*, 28(33), 45041–45049. <https://doi.org/10.1007/s11356-021-13921-7>.
- Mendes, S. F., Rodrigues, J. S., de Lima, V. H., Botaro, V. R., Cardoso, V. L., & Reis, M. H. (2021). Forward black liquor acid precipitation: lignin fractionation by ultrafiltration. *Applied Biochemistry and Biotechnology*, 193(10), 3079–3097.
- Mishra, T., Ramola, S., Shankhwar, A. K., Rabha, A. K., & Srivastava, R. K. (2015). Pulp and paper mill effluent treatment by hybrid anaerobic upflow fixed-bed bioreactor combined with slow sand filter. *Desalination and Water Treatment*, 57(23), 10528–10536. <https://doi.org/10.1080/19443994.2015.1039596>.
- Moslehi, E. (2018). Integrating membrane filtration for water reuse in tissue mill.
- Muryanto, M., Hanifah, U., Amriani, F., Ibadurrahman, A. F., & Sari, A. A. (2017). Fenton process combined with coagulation for the treatment of black liquor from bioethanol wastewater. In *AIP conference proceedings*. AIP Publishing.
- Mustafa, H. M., Hayder, G., & Jagaba, A. H. (2020). Microalgae: A renewable source for wastewater treatment and feedstock supply for biofuel generation. *Biointerface Research in Applied Chemistry*, 11(1), 7431–7444. <https://doi.org/10.33263/briac111.74317444>.
- Mänttari, M., Kuosa, M., Kallas, J., & Nyström, M. (2008). Membrane filtration and ozone treatment of biologically treated effluents from the pulp and paper industry. *Journal of Membrane Science*, 309(1–2), 112–119.
- Najar-Almanzor, C. E., Velasco-Iglesias, K. D., Nunez-Ramos, R., Uribe-Velázquez, T., Solis-Bañuelos, M., Fuentes-Carrasco, O. J., Chairez, I., García-Cayuela, T., & Carrillo-Nieves, D. (2023). Microalgae-assisted green bioremediation of food-processing wastewater: A sustainable approach toward a circular economy concept. *Journal of Environmental Management*, 345, 118774. <https://doi.org/10.1016/j.jenvman.2023.118774>.
- Namdarimonfared, M., Zilouei, H., & Tondro, H. (2023). Biological hydrogen production from paper mill effluent via dark fermentation in a packed bed biofilm reactor. *Fuel*, 338, 127231. <https://doi.org/10.1016/j.fuel.2022.127231>.
- Nasrullah, M., Zularisam, A., Krishnan, S., Sakinah, M., Singh, L., & Fen, Y. W. (2019). High performance electrocoagulation process in treating palm oil mill effluent using high current intensity application. *Chinese Journal of Chemical Engineering*, 27(1), 208–217.
- Nawaz, A., Ahmed, Z., Shahbaz, A., Khan, Z., & Javed, M. (2014). Coagulation-flocculation for lignin removal from wastewater—A review. *Water Science and Technology*, 69(8), 1589–1597.
- Nogueira, V., Lopes, I., Rocha-Santos, T., Gonçalves, F., & Pereira, R. (2018). Treatment of real industrial wastewaters through nano-TiO₂ and nano-Fe₂O₃ photocatalysis: Case study of mining and kraft pulp mill effluents. *Environmental Technology*, 39(12), 1586–1596.
- Nyashanu, P. N., Shafodino, F. S., & Mwapagha, L. M. (2023). Determining the potential human health risks posed by heavy metals present in municipal sewage

- sludge from a wastewater treatment plant. *Scientific African*, 20, e01735. <https://doi.org/10.1016/j.sciaf.2023.e01735>.
- Oliveiraesquerre, K., Seborg, D., Mori, M., & Bruns, R. (2004). Application of steady-state and dynamic modeling for the prediction of the BOD of an aerated lagoon at a pulp and paper mill: Part II. Nonlinear approaches. *Chemical Engineering Journal*, 105(1-2), 61-69. <https://doi.org/10.1016/j.cej.2004.06.012>.
- Oliveira-Esquerre, K. P., Seborg, D. E., Bruns, R. E., & Mori, M. (2004). Application of steady-state and dynamic modeling for the prediction of the BOD of an aerated lagoon at a pulp and paper mill: Part I. Linear approaches. *Chemical Engineering Journal*, 104(1-3), 73-81. <https://doi.org/10.1016/j.cej.2004.05.011>.
- Owusu-Twum, M. Y., & Sharara, M. A. (2020). Sludge management in anaerobic swine lagoons: A review. *Journal of Environmental Management*, 271, 110949. <https://doi.org/10.1016/j.jenvman.2020.110949>.
- Öztürk, T., & Özcan, Ö. F. (2021). Effectiveness of electrocoagulation and chemical coagulation methods on paper industry wastewaters and optimum operating parameters. *Separation Science and Technology*, 56(12), 2074-2086.
- Pan, Y., Li, P., Song, K., Liu, G., Li, L., Zhang, P., Gong, J., & Huang, Q. (2023). New model for evaluating greenhouse gas emissions from sludge treatment based on fossil and biogenic carbon migration. *Journal of Cleaner Production*, 425, 138845. <https://doi.org/10.1016/j.jclepro.2023.138845>.
- Patel, K., Patel, N., Vaghamshi, N., Shah, K., Duggirala, S. M., & Dudhagara, P. (2021). Trends and strategies in the effluent treatment of pulp and paper industries: A review highlighting reactor options. *Current Research in Microbial Sciences*, 2, 100077.
- Peitz, C., & Xavier, C. R. (2019). Evaluation of aerated lagoon modified with spongy support medium treating Kraft pulp mill effluent. *Revista Facultad de Ingeniería Universidad de Antioquia*, (92), 60-69. <https://doi.org/10.17533/udea.redin.20190725>.
- Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater - A review. *The Science of the Total Environment*, 333(1-3), 37-58. <https://doi.org/10.1016/j.scitotenv.2004.05.017>.
- Polizzi, V., Servaes, K., Vandezande, P., Kouris, P. D., Panaite, A. M., Jacobs, G., Hensen, E. J., Boot, M. D., & Vanbroekhoven, K. (2020). Molecular weight-based fractionation of lignin oils by membrane separation technology. *Holzforschung*, 74(2), 166-174.
- Portela, N. A., Oliveira, E. C., Neto, A. C., Rodrigues, R. R., Silva, S. R., Castro, E. V., & Filgueiras, P. R. (2016). Quantification of biodiesel in petroleum diesel by ¹H NMR: Evaluation of univariate and multivariate approaches. *Fuel*, 166, 12-18.
- Qu, X., Gao, W. J., Han, M. N., Chen, A., & Liao, B. Q. (2012). Integrated thermophilic submerged aerobic membrane bioreactor and electrochemical oxidation for pulp and paper effluent treatment - Towards system closure. *Bioresource Technology*, 116, 1-8. <https://doi.org/10.1016/j.biortech.2012.04.045>.
- Rajwar, D., Paliwal, R., & Rai, J. P. N. (2017). Biodegradation of pulp and paper mill effluent by co-culturing ascomycetous fungi in repeated batch process. *Environmental Monitoring and Assessment*, 189(9), 482. <https://doi.org/10.1007/s10661-017-6198-6>.
- Rashid, R., Shafiq, I., Akhter, P., Iqbal, M. J., & Hussain, M. (2021). A state-of-the-art review on wastewater treatment techniques: The effectiveness of adsorption method. *Environmental Science and Pollution Research*, 28, 9050-9066.
- Rashid, R., Shafiq, I., Gilani, M. R. H. S., Maaz, M., Akhter, P., Hussain, M., Jeong, K.-E., Kwon, E. E., Bae, S., & Park, Y.-K. (2023). Advancements in TiO₂-based photocatalysis for environmental remediation: Strategies for enhancing visible-light-driven activity. *Chemosphere*, 140703.

- Rashid, R., Shafiq, I., Iqbal, M. J., Shabir, M., Akhter, P., Hamayun, M. H., Ahmed, A., & Hussain, M. (2021). Synergistic effect of NS co-doped TiO₂ adsorbent for removal of cationic dyes. *Journal of Environmental Chemical Engineering*, 9(4), 105480.
- Rasool, T., Ishtiaq Ali, M., Jamal, A., Huang, Z., & Urynowicz, M. (2023). Performance evaluation and microbial profiling of integrated vertical flow constructed wetland (IVFCW) for simultaneous treatment of domestic and pulp and paper industry wastewater. *Saudi Journal of Biological Sciences*, 103850. <https://doi.org/10.1016/j.sjbs.2023.103850>.
- Ravichandran, P., & Balaji, K. (2020). Effect of HRT on performance of hybrid upflow anaerobic sludge blanket (HUASB) reactor using bio balls in treatment of pulp and paper mill bagasse wash water. *Materials Today: Proceedings*, 22, 627–632. <https://doi.org/10.1016/j.matpr.2019.09.011>.
- Rayaroth, M. P., Aravindakumar, C. T., Shah, N. S., & Boczkaj, G. (2022). Advanced oxidation processes (AOPs) based wastewater treatment-unexpected nitration side reactions-a serious environmental issue: A review. *Chemical Engineering Journal*, 430, 133002.
- Razali, M., Ahmad, Z., Ahmad, M., & Ariffin, A. (2011). Treatment of pulp and paper mill wastewater with various molecular weight of polyDADMAC induced flocculation. *Chemical Engineering Journal*, 166(2), 529–535.
- Rekhate, C. V., & Srivastava, J. K. (2020). Recent advances in ozone-based advanced oxidation processes for treatment of wastewater – A review. *Chemical Engineering Journal Advances*, 3, 100031. <https://doi.org/10.1016/j.cej.2020.100031>.
- Renault, F., Sancey, B., Charles, J., Morin-Crini, N., Badot, P.-M., Winterton, P., & Crini, G. (2009). Chitosan flocculation of cardboard-mill secondary biological wastewater. *Chemical Engineering Journal*, 155(3), 775–783.
- Ribeiro, J. P., Cruz, N. C., Neves, M. C., Rodrigues, S. M., Tarelho, L. A., & Nunes, M. I. (2023). Granulated biomass fly ash coupled with fenton process for pulp and paper wastewater treatment. *Environmental Pollution*, 317, 120777.
- Rodrigues, C. V., Camargo, F. P., Lourenço, V. A., Sakamoto, I. K., Maintinguer, S. I., Silva, E. L., & Varesche, M. B. A. (2023). Optimized conditions for methane production and energy valorization through co-digestion of solid and liquid wastes from coffee and beer industries using granular sludge and cattle manure. *Journal of Environmental Chemical Engineering*, 11(6), 111250. <https://doi.org/10.1016/j.jece.2023.111250>.
- Samsami, S., Mohamadizani, M., Sarrafzadeh, M.-H., Rene, E. R., & Firoozbahr, M. (2020). Recent advances in the treatment of dye-containing wastewater from textile industries: Overview and perspectives. *Process Safety and Environmental Protection*, 143, 138–163.
- Scragg, A. H. (2006). The effect of phenol on the growth of *Chlorella vulgaris* and *Chlorella* VT-1. *Enzyme and Microbial Technology*, 39(4), 796–799. <https://doi.org/10.1016/j.enzmictec.2005.12.018>.
- Şefika, K., & Yeliz, A. (2019). Evaluation of color and COD removal by Fenton and photo-Fenton processes from industrial paper wastewater. *Journal of the Institute of Science and Technology*, 9(3), 1539–1550.
- Shabir, M., Yasin, M., Hussain, M., Shafiq, I., Akhter, P., Nizami, A.-S., Jeon, B.-H., & Park, Y.-K. (2022). A review on recent advances in the treatment of dye-polluted wastewater. *Journal of Industrial and Engineering Chemistry*, 112, 1–19.
- Shafiq, I., Hussain, M., Rashid, R., Shafique, S., Akhter, P., Yang, W., Ahmed, A., Nawaz, Z., & Park, Y.-K. (2021). Development of hierarchically porous LaVO₄ for efficient visible-light-driven photocatalytic desulfurization of diesel. *Chemical Engineering Journal*, 420, 130529.
- Shafiq, I., Hussain, M., Shafique, S., Akhter, P., Ahmed, A., Ashraf, R. S., Ali Khan, M., Jeon, B.-H., & Park, Y.-K. (2021). Systematic assessment of visible-light-driven

- microspherical V2O5 photocatalyst for the removal of hazardous organosulfur compounds from diesel. *Nanomaterials*, 11(11), 2908.
- Shafiq, I., Hussain, M., Shafique, S., Rashid, R., Akhter, P., Ahmed, A., Jeon, J.-K., & Park, Y.-K. (2021). Oxidative desulfurization of refinery diesel pool fractions using LaVO4 photocatalyst. *Journal of Industrial and Engineering Chemistry*, 98, 283–288. <https://doi.org/10.1016/j.jiec.2021.03.040>.
- Shafiq, I., Shafique, S., Akhter, P., Abbas, G., Qurashi, A., Hussain, M. J. C. R. (2022). Efficient catalyst development for deep aerobic photocatalytic oxidative desulfurization: Recent advances, confines, and outlooks, 64(4) (pp. 789–834).
- Shafiq, I., Shafique, S., Akhter, P., Yang, W., & Hussain, M. J. C. R. (2022). Recent developments in alumina supported hydrodesulfurization catalysts for the production of sulfur-free refinery products. *A Technical Review*, 64(1), 1–86.
- Shankar, R., Singh, L., Mondal, P., & Chand, S. (2015). Removal of lignin from wastewater through electro-coagulation. *Ecological Technologies for Industrial Wastewater Management: Petrochemicals, Metals, Semi-Conductors, and Paper Industries*, 1, 217.
- Singh, A., Srivastava, A., Saidulu, D., & Gupta, A. K. (2022). Advancements of sequencing batch reactor for industrial wastewater treatment: Major focus on modifications, critical operational parameters, and future perspectives. *Journal of Environmental Management*, 317, 115305. <https://doi.org/10.1016/j.jenvman.2022.115305>.
- Singhal, A., & Thakur, I. S. (2009a). Decolourization and detoxification of pulp and paper mill effluent by *Cryptococcus* sp. *Biochemical Engineering Journal*, 46(1), 21–27. <https://doi.org/10.1016/j.bej.2009.04.007>.
- Singhal, A., & Thakur, I. S. (2009b). Decolourization and detoxification of pulp and paper mill effluent by *Emericella nidulans* var. *nidulans*. *Journal of Hazardous Materials*, 171(1–3), 619–625. <https://doi.org/10.1016/j.jhazmat.2009.06.041>.
- Sonkar, M., Kumar, M., Dutt, D., & Kumar, V. (2019). Treatment of pulp and paper mill effluent by a novel bacterium *Bacillus* sp. IITRDVM-5 through a sequential batch process. *Biocatalysis and Agricultural Biotechnology*, 20, 101232. <https://doi.org/10.1016/j.bcab.2019.101232>.
- Sousa, M. R. S., Lora-García, J., & López-Pérez, M.-F. (2018). Modelling approach to an ultrafiltration process for the removal of dissolved and colloidal substances from treated wastewater for reuse in recycled paper manufacturing. *Journal of Water Process Engineering*, 21, 96–106.
- Subramonian, W., Wu, T. Y., & Chai, S.-P. (2017). Photocatalytic degradation of industrial pulp and paper mill effluent using synthesized magnetic Fe2O3-TiO2: Treatment efficiency and characterizations of reused photocatalyst. *Journal of Environmental Management*, 187, 298–310.
- Sundaramahalingam, M. A., & Sivashanmugam, P. (2023). Concomitant strategy of wastewater treatment and biodiesel production using innate yeast cell (*Rhodotorula mucilaginosa*) from food industry sewerage and its energy system analysis. *Renewable Energy*, 208, 52–62. <https://doi.org/10.1016/j.renene.2023.03.070>.
- Tao, R., Lakaniemi, A.-M., & Rintala, J. A. (2017). Cultivation of *Scenedesmus acuminatus* in different liquid digestates from anaerobic digestion of pulp and paper industry biosludge. *Bioresource Technology*, 245, 706–713. <https://doi.org/10.1016/j.biortech.2017.08.218>.
- Tarlan, E., Dilek, F. B., & Yetis, U. (2002). Effectiveness of algae in the treatment of a wood-based pulp and paper industry wastewater. *Bioresource Technology*, 84(1), 1–5. [https://doi.org/10.1016/s0960-8524\(02\)00029-9](https://doi.org/10.1016/s0960-8524(02)00029-9).
- Tiku, D. K., Kumar, A., Chaturvedi, R., Makhijani, S. D., Manoharan, A., & Kumar, R. (2010). Holistic bioremediation of pulp mill effluents using autochthonous

- bacteria. *International Biodeterioration and Biodegradation*, 64(3), 173–183. <https://doi.org/10.1016/j.ibiod.2010.01.001>.
- Toczyłowska-Mamińska, R. (2017). Limits and perspectives of pulp and paper industry wastewater treatment – A review. *Renewable Sustainable Energy Reviews*, 78, 764–772. <https://doi.org/10.1016/j.rser.2017.05.021>.
- Usha, M. T., Sarat Chandra, T., Sarada, R., & Chauhan, V. S. (2016). Removal of nutrients and organic pollution load from pulp and paper mill effluent by microalgae in outdoor open pond. *Bioresource Technology*, 214, 856–860. <https://doi.org/10.1016/j.biortech.2016.04.060>.
- Uğurlu, M., Gürses, A., Doğar, Ç., & Yalçın, M. (2008). The removal of lignin and phenol from paper mill effluents by electrocoagulation. *Journal of Environmental Management*, 87(3), 420–428.
- Vasiliadou, I. A., Sánchez-Vázquez, R., Molina, R., Martínez, F., Melero, J. A., Bautista, L. F., Iglesias, J., & Morales, G. (2016). Biological removal of pharmaceutical compounds using white-rot fungi with concomitant FAME production of the residual biomass. *Journal of Environmental Management*, 180, 228–237. <https://doi.org/10.1016/j.jenvman.2016.05.035>.
- Verma, M., Ekka, A., Mohapatra, T., & Ghosh, P. (2020). Optimization of kraft lignin decolorization and degradation by bacterial strain *Bacillus velezensis* using response surface methodology. *Journal of Environmental Chemical Engineering*, 8(5), 104270. <https://doi.org/10.1016/j.jece.2020.104270>.
- Wan, Y., Liu, J., Deng, F., Xie, Z., Chen, Y., Li, J., & Li, D. (2023). Screening of lignin-degrading fungi and bioaugmentation on the directional humification of garden waste composting. *Industrial Crops and Products*, 203, 117208. <https://doi.org/10.1016/j.indcrop.2023.117208>.
- Weis, A., Bird, M. R., Nyström, M., & Wright, C. (2005). The influence of morphology, hydrophobicity and charge upon the long-term performance of ultrafiltration membranes fouled with spent sulphite liquor. *Desalination*, 175(1), 73–85.
- Wu, J., Xiao, Y., & Yu, H. (2005). Degradation of lignin in pulp mill wastewaters by white-rot fungi on biofilm. *Bioresource Technology*, 96(12), 1357–1363. <https://doi.org/10.1016/j.biortech.2004.11.019>.
- Xie, K., Lin, H. J., Mahendran, B., Bagley, D. M., Leung, K. T., Liss, S. N., & Liao, B. Q. (2010). Performance and fouling characteristics of a submerged anaerobic membrane bioreactor for kraft evaporator condensate treatment. *Environmental Technology*, 31(5), 511–521. <https://doi.org/10.1080/09593330903527898>.
- Xu, P., Li, J., Qian, J., Wang, B., Liu, J., Xu, R., Chen, P., & Zhou, W. (2023). Recent advances in CO₂ fixation by microalgae and its potential contribution to carbon neutrality. *Chemosphere*, 319, 137987. <https://doi.org/10.1016/j.chemosphere.2023.137987>.
- Yan, Y., Gu, R., Zhu, M., Tang, M., He, Q., Tang, Y., & Liu, L. (2023). Environmental impacts and optimization simulation of aerobic anaerobic combination treatment technology for food waste with life cycle assessment. *Waste Management (New York, N.Y.)*, 164, 228–237. <https://doi.org/10.1016/j.wasman.2023.03.036>.
- Yang, H., Guo, Y., Fang, N., & Dong, B. (2023). Life cycle assessment of sludge anaerobic digestion combined with land application treatment route: Greenhouse gas emission and reduction potential. *Journal of Environmental Chemical Engineering*, 11(6), 111255. <https://doi.org/10.1016/j.jece.2023.111255>.
- Yeber, M. C., Oñate, K. P., & Vidal, G. (2007). Decolorization of kraft bleaching effluent by advanced oxidation processes using copper (II) as electron acceptor. *Environmental Science & Technology*, 41(7), 2510–2514.
- Zahrim, A., Nasimah, A., & Hilal, N. (2015). Coagulation/flocculation of lignin aqueous solution in single stage mixing tank system: Modeling and optimization

- by response surface methodology. *Journal of Environmental Chemical Engineering*, 3(3), 2145–2154.
- Zhang, H., Qi, H.-Y., Zhang, Y.-L., Ran, D.-D., Wu, L.-Q., Wang, H.-F., & Zeng, R. J. (2022). Effects of sewage sludge pretreatment methods on its use in agricultural applications. *Journal of Hazardous Materials*, 428, 128213. <https://doi.org/10.1016/j.jhazmat.2022.128213>.
- Zhang, X., Yu, W., Guo, Y., Li, S., Chen, Y., Wang, H., & Bian, Z. (2023). Recent advances in photoelectrocatalytic advanced oxidation processes: from mechanism understanding to catalyst design and actual applications. *Chemical Engineering Journal*, 455, 140801. <https://doi.org/10.1016/j.cej.2022.140801>.
- Zhao, L., Zhang, J., Zhao, D., Jia, L., Qin, B., Cao, X., Zang, L., Lu, F., & Liu, F. (2022). Biological degradation of lignin: A critical review on progress and perspectives. *Industrial Crops and Products*, 188, 115715. <https://doi.org/10.1016/j.indcrop.2022.115715>.
- Zhou, Y., Chai, Y., Sun, H., Li, X., Liu, X., Liang, Y., Gong, X., Wu, Z., Liu, C., & Qin, P. (2023). Design strategies and mechanisms of g-C₃N₄-based photoanodes for photoelectrocatalytic degradation of organic pollutants in water. *Journal of Environmental Management*, 344, 118545. <https://doi.org/10.1016/j.jenvman.2023.118545>.
- Zhu, W., Yue, Y., Wang, H., Zhang, B., Hou, R., Xiao, J., Huang, X., Ishag, A., & Sun, Y. (2023). Recent advances on energy and environmental application of graphitic carbon nitride (g-C₃N₄)-based photocatalysts: A review. *Journal of Environmental Chemical Engineering*, 11(3), 110164. <https://doi.org/10.1016/j.jece.2023.110164>.

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Overview of membrane-based reclamation of pulp and paper industry effluent and the need for recovery and reuse of process water

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5.1 Introduction

The evolution within the paper and pulp industry has reformed their perception, turning them into significant players in the large-scale industry. This industry sector exclusively utilizes plant-derived wood materials for manufacturing paper, pulp, cellulose-based materials, and other products. Water plays a crucial role in almost every stage of the paper and pulp manufacturing process. Significant amounts of water are required to process wood into paper pulp and, subsequently, into paper products. The paper and pulp industry is among the top four industries discharging large quantities of wastewater. The wastewater stream absorbs harmful pollutants and other unwanted substances at different phases of the paper-making process. Thus discharge of this wastewater can lead to environmental concerns, such as wastewater pollution and the depletion of freshwater resources (Nataraj et al., 2007; Zheng et al., 2015).

The factors that influence water demand and the characteristics of wastewater in pulp and paper industries are the raw material selected, the processes used, the size of the mill, and the grade and kind of the final output. The three different categories of raw materials used are wood and bamboo, agro-residue, and recycled fiber. Lignin from plant-based raw materials causes by-products, like chlorinated dibenzo-p-dioxin and chlorinated phenols, to impart color and high chemical oxygen demand (COD) ranging between

3380 and 4930 mg/L. Additionally, nanoadditives have been employed to enhance the opacity of paper, improve gas and water absorption barrier properties, serve as a bleaching agent, and act as an antimicrobial agent. The small particle size of these additives poses challenges in wastewater treatment. The mutagenic organohalogen (AOX) are reported to be transported through trophic levels and affect the ecosystem (Abdel-Fatah, 2018; Oliveira et al., 2007).

In the realm of pulp and paper manufacturing, for treating pulp and paper industry effluent containing elevated pollutant loads, conventional treatments like flotation, evaporation, and others alone are insufficient. The primary function is the retention and fractionation of the utilized process liquid, aiming to decolorize and treat effluent. Membrane-based procedures are remarkable for their minimal energy usage and significant purifying efficacy when compared to other advanced treatment options (Nataraj et al., 2007).

A membrane acts as a barrier that selectively permits the passage of certain moieties, which is termed as permselectivity or semipermeability. The separation is driven by applied pressure, and the selectivity of the membrane depends on the membrane structure and subsequent characteristics. Membrane structure is crucial for the separation process because it influences the process parameters and the filtration performance (Barjoveanu & Teodosiu, 2006).

A large spectrum of pollutants of organic and inorganic origin, bacteria, and viruses are being removed by synthetic membranes without biological and chemical transformation during the filtration. The commonly used separation strategies are electrodialysis, reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). The distinctions among these methods reside in their removal capacities, the mode of pollutant separation, and the nature and strength of the driving force applied to facilitate the separation (Neves et al., 2017). MF and UF are categorized to be low-pressure processes, and RO and NF are considered high-pressure processes (Bray et al., 2021). Fig. 5.1 gives the specifications of membrane techniques applied in industries.

According to Zheng et al. (2015) the membrane technology is advantageous in pulp and paper industries at a minimum capacity of 5000 m³ (Zheng et al., 2015). Most importantly, the economic efficiency of membrane systems hinges on the ability to operate the permeate at the lowest feasible pressure over extended periods without compromising effectiveness. Fouling of the membrane is an undesirable event that reduces the efficiency of operation and results in the reversible or irreversible deposition of particles on the membrane surface. Fouling may increase the system's demand for energy, frequent cleaning, requirement of high quantity of

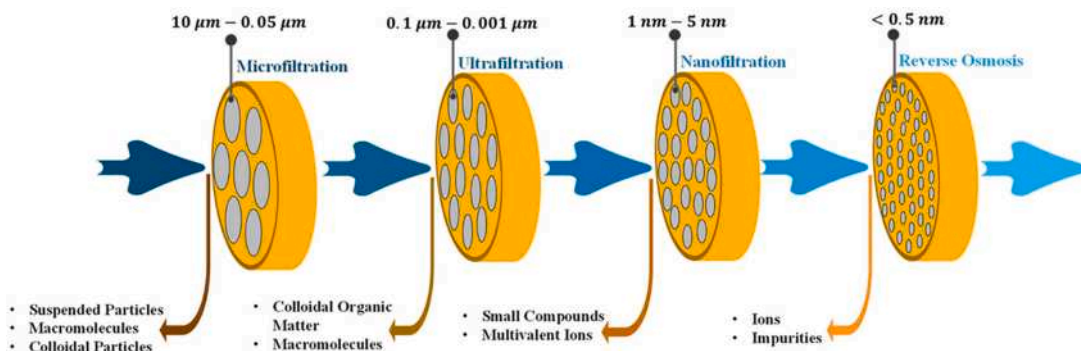


Figure 5.1 Membrane specifications for microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

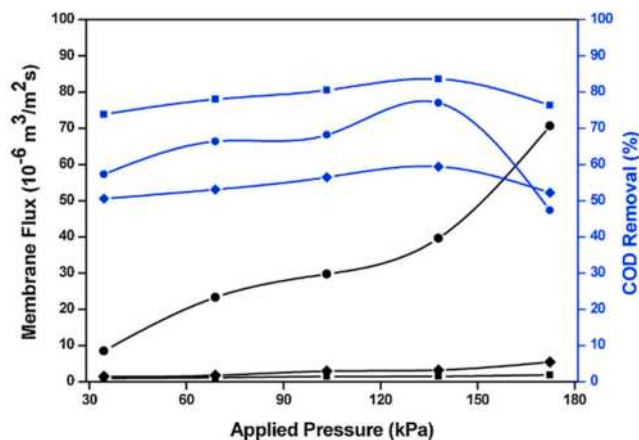
Reprinted with permission from Esmaeeli, A., Sarrafzadeh, M. H., Zeighami, S., Kalantar, M., Bariki, S.G., Fallahi, A., Asgharnejad, H., & Ghaffari, S. B. (2022). A comprehensive review on pulp and paper industries wastewater treatment advances. *Industrial & Engineering Chemistry Research*, 62, 8119–8145. <https://doi.org/10.1021/acs.iecr.2c04393>. Copyright © 2023 American Chemical Society.

chemicals, and increased costs and ultimately reduce permeate flux. Factors beyond membrane fouling, such as those associated with the feed system, filtration module, membrane porosity, and operational conditions like pressure and flow rate, can influence the overall permeate flux throughout the entire operational period (Neves et al., 2017).

5.2 Microfiltration

MF could effectively remove suspended particles by placing them as a preliminary filtration before the primary filtration in pulp and paper industries. The size of particles ranges from 0.1 to 10 μm . Prefiltration with MF has been found to enhance the permeate flux and mitigate fouling in the subsequent high-shear filtration to fractionate lignocellulosic material in the effluent. In a two-stage filtration system, lignin concentration from effluent water was improved, concurrently alleviating the load on the treatment plant. The residual lignin post-MF treatment could be further eliminated through a subsequent UF step (Esmaeeli et al., 2022). Another tubular ceramic MF membrane designed for lignin rejection was reinforced with a carboxymethyl cellulose binder, enhancing its porosity to 36% (Singh et al., 2020). Managing pore blocking due to removed solids is a consideration in MF. Consequently, MF serves as a prefiltration step, either removing colloidal particles or stabilizing so that coagulation of such particles is avoided in the subsequent processes (Nataraj et al., 2007). High chemical stability was also observed with a maximum rejection of 82.5% at 32 kPa. However, the

Figure 5.2 Effect of external pressure on membrane performance. COD reduction from dairy (■), biomass gasification (●), and paper and pulp (◆) industry wastewaters (Goswami et al., 2019).



cost-effectiveness of MF, despite its efficiency in clarifying process water and removing suspended matter, requires thorough evaluation (Esmaeeli et al., 2022).

In a study, MF was applied as a posttreatment process using a clay-born economic ceramic membrane with 1.01 μm of pore size and 44% porosity after biodegradation. Within an applied pressure range of 34–172 kPa the COD removal from pulp and paper industry process water was enhanced from 46.1% to 87.6%, respectively, using the MF system (Goswami et al., 2019). In another work an MF system treating pulp and paper wastewater, using a polypropylene hollow-fiber membrane module with 0.1 μm pore size, assumed that dissolved forms of organic or inorganic compounds are not effectively removed by MF (Mänttari et al., 2008).

The correlation of VCR with flux is given in a study using a ceramic MF module of 0.14 μm pore size operated with recycling to give an elevated (215 $\text{L}/\text{m}^2\text{h}$) and steady flux but diminished with an increase in VCR (12). In the same study a polymeric membrane was also studied with a stable flux output of 47 $\text{L}/\text{m}^2\text{h}$ when the VCR was 7.5 in a recycling mode (Pizzichini et al., 2005).

Fig. 5.2 shows the correlation between TMP (Eq. 5.3) and permeate flux during the MF process. The COD reduction from different wastewaters, including pulp and paper industry wastewater, is also shown.

5.3 Ultrafiltration

UF is a wastewater separation process employing ultrafine filtration membranes with a selective permeation function. UF assists as an internal method for recycling process water and for external effluent

treatment in the pulp and paper and allied industries. It is utilized for the reclamation of effluent water to reduce mainly organic pollutant load within wastewater treatment plants. UF stands out as an appealing process for treating pulp and paper industry wastewater, particularly due to the prevalence of HMW compounds in the pollutants, which are effectively retained by UF membranes (Siagian *et al.*, 2021; Sousa *et al.*, 2018).

The retention limit of a UF membrane is defined using MWCO, defined as a nominal rating for the size or molecular weight of a certain HMW molecule above which a certain fraction of the particles in the inlet will be retained by the membrane under controlled conditions (Al Aani *et al.*, 2020). MWCO for UF membranes ranges from 1 to 500 kDa. Filtration can be operated in two ways, dead-end filtration and cross-flow filtration, as depicted in Fig. 5.3. In the former the inlet flows perpendicular to the membrane, with only permeate flow. Here, the permeate flux reduces rapidly due to the cake formation occurring at the same operational pressure. In this aspect, cross-flow filtration is advantageous since the feed flow is tangential with the transverse flow of permeate and the flux is maintained at high values for a longer duration. Cross-filtration is adopted in most UF units (Barjoveanu & Teodosiu, 2006). Additionally, by facilitating turbulence, the movement of hollow fibers can be promoted in the membranes, which favors the filtration process (Neves *et al.*, 2017). Concentration polarization appears to be a threat in membrane systems, which can be alleviated by providing proper ventilation and improving turbulence (Oliveira *et al.*, 2007).

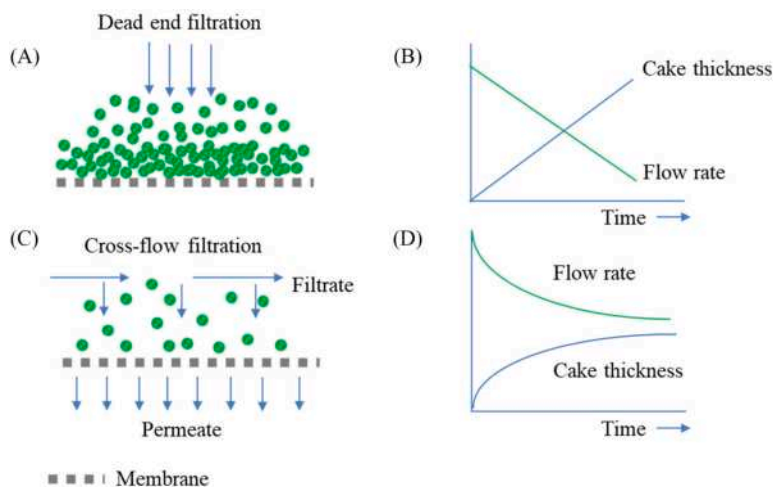


Figure 5.3 Flow configurations (A and C) and corresponding comparisons of cake layer formation and permeate flux variation (B and D) in dead-end filtration and cross-flow filtration (Abdel-Fatah, 2018).

UF helped to remove 30% of the organic load; the permeate can be utilized in paper machine shower systems, replacing mechanically treated water. Remarkably, research has shown effective treatment of kraft bleaching effluents through UF, attaining excellent efficiency of more than 85% COD. UF is commonly considered a sieve separation process, usually carried out with tangential flow (Gönder et al., 2012). In a separate evaluation, UF demonstrated efficacy in purging pollutants from a prefiltered secondary clarifier effluent generated in a paper mill handling agricultural residue. The combined filtration system showed 20%, 89%, and 74% removal of COD, lignin, and color, respectively, at optimum operational conditions (Dagar et al., 2023).

In a UF pilot plant study, whitewater was treated employing a submerged UF membrane module with hollow-fiber incorporation at a TMP of -33.8 kPa, and calcium and magnesium precipitates were removed, showing good performance. The total area of polymeric hydrophilic membrane used in this study was 1 m^2 , and the transmembrane driving force was induced by an external pump. Purification through UF is a viable method to produce bleaching water as good as fresh water in the functioning (Oliveira et al., 2007). Fig. 5.4 gives a glimpse of a pilot-scale UF system.

As mentioned before, fouling reduces the system's performance by declining flux. In a study a UF system with commercial

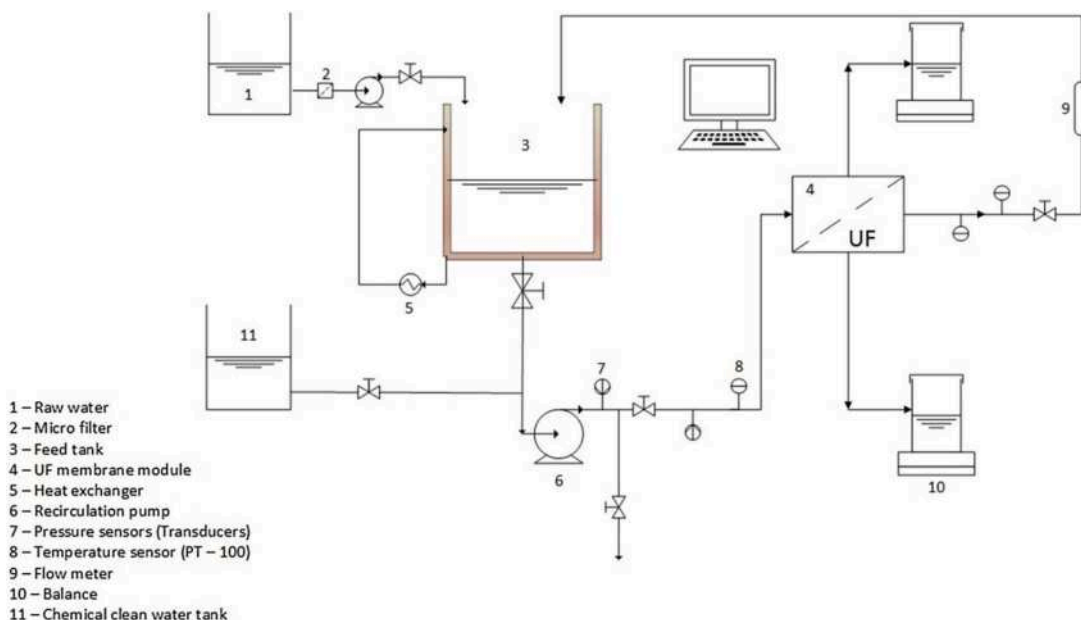


Figure 5.4 Ultrafiltration membrane system treating paper industry effluent (Sousa et al., 2018).

membranes (UH050 and UPO20) observed deposition of iron and sulfate; hence, the flux is reduced to a lower value (Dogan et al., 2023). The presence of iron and other derivatives is also reported to cause fouling of the membrane surface (Tang et al., 2021).

Membrane selection is crucial for UF applications to ensure a technological balance between maximizing the membrane productivity and minimizing the plant's dimensions and energy consumption. Inherent fouling and troubleshooting can be minimized with suitable membrane material selection. This may help to maintain sufficient permeate flux values and minimize the water demand for the cleaning of the membrane (Barjoveanu & Teodosiu, 2006).

5.4 Nanofiltration

In recent years, nanomembrane-based technology has emerged as an assuring and sustainable solution for industrial effluents and drinking water reclamation. These membranes act as physical barriers for contaminant removal, with NF being a notable technique. It operates through a pressure-driven process, separating ions, molecules, and particles in the range of 0.5–0.1 nm, combining characteristics of UF and RO. Size exclusion, Donnan exclusion, and dielectric exclusion are major mechanisms for ion rejection, as illustrated in Fig. 5.5 (Agboola et al., 2014; Madhubala et al., 2022). NF has gained attention for its catalytic property, low costs of maintenance, good permeation, disinfectant properties, minimal space requirement, less fouling, simplicity of design and handling, and lower operating and energy costs (Han et al., 2021; Kolya & Kang, 2023).

The main objective of NF is to eliminate ions and organic materials. It has demonstrated favorable outcomes while treating pulp and paper mill effluent by effectively segregating particles of varying sizes. As observed in UF, nanomembranes also exhibit size exclusion properties based on MWCO, removing compounds above the cutoff (Ruiz-Gutierrez et al., 2024). Additionally, electrostatic interactions contribute to pollutant removal, with nanomembranes being negatively charged, enhancing the removal of negatively charged components (Hu et al., 2016). The temperature adjustments while using freshwater to meet mill processing criteria might be unnecessary because of the reuse of NF permeate (Mänttari et al., 2006).

Functionalization of membranes is a way of enhancing the filtration performance. Composite NF membranes, incorporating mixed matrix and surface-functionalized membranes, are innovative and reliable. These composites enhance hydrophilic and mechanical properties, leading to improved pollutant removal. Incorporating carbon nanofibers and beta cyclodextrins improved selective

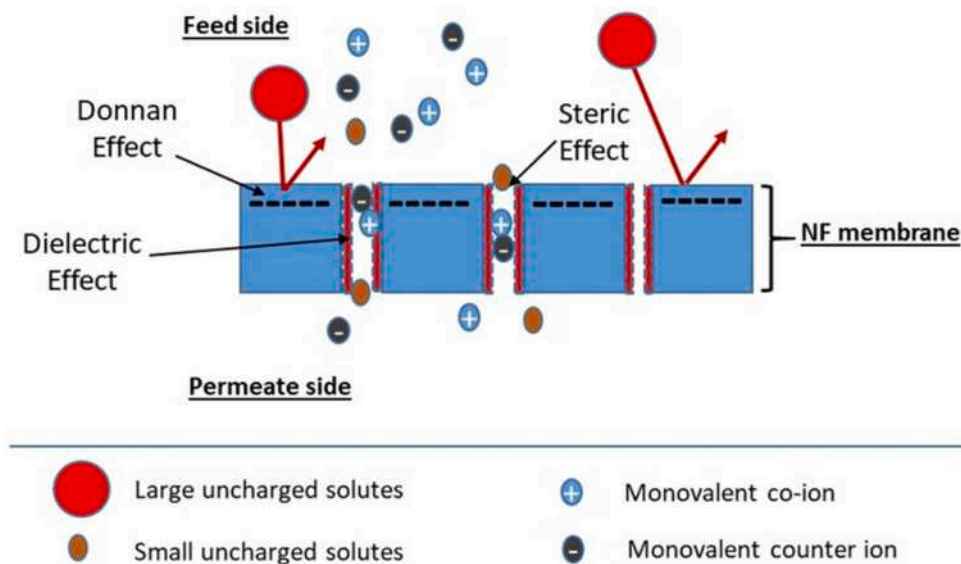


Figure 5.5 Mechanism of filtration in nanofiltration systems (Ahmad et al., 2022).

filtration and removal efficiency. Carbon nanotubes contribute to antimicrobial properties and minimize membrane fouling (Hu et al., 2016). Silver nanoparticles further inhibit bacteria adherence and mitigate biofouling when infused into polymeric membranes along with added tensile strength (Mbakop et al., 2021).

Nanocomposites, often involving carbon-based materials in polymeric matrices, exhibit thermal stability, biodegradability, solvent resistance, and effective barriers to contaminants. Incorporating metal oxide nanoparticles enhances permeability, antifouling properties, and hydrophilicity. Nanofillers with large specific surface areas, particularly those incorporating metal oxide nanoparticles, improve the mechanical and thermal stability of membranes, increasing permeate flux. NF is effective in reducing heavy metals, total dissolved solids, volatile organic compounds, nitrates, sulfates, tannins, color, and turbidity (Kolya & Kang, 2023). NF has been crucial for treating effluents, reducing wastewater from the paper and pulp industry, enabling treated water reuse, and removing hazardous components from bleaching effluents (Mänttari et al., 2021).

Studies highlight NF's economic and sustainable use in the paper and pulp industry, achieving high lignin recovery without chemical usage. Membrane-based technologies, especially NF, contribute to mitigating environmental pollution by addressing harmful organic compounds in wastewater effluents. Additionally, NF is considered to be a superior

choice for small-scale treatment trains compared to any other available process water reclamation strategies. The diverse applications and successes of nanomembrane technology underscore its potential as a transformative solution in effluent reclamation (Mänttäre et al., 2021).

NF is a process that fractionates a waste effluent stream passing through a semipermeable membrane. Postfractionation, the input stream is separated into permeate, the purified segment, and retentate or concentrate, representing the unfiltered portion. NF has demonstrated effective removal of organic material. However, it is crucial to note that chlorine disinfection plays a vital role in eliminating microbial growth, a concern reported in NF distribution systems (Park et al., 2012). To mitigate microbial growth, NF membranes with specific characteristics are employed. These membranes are designed with low detention of inorganic materials and high removal of organic substances. This tailored design aims to produce water of optimal quality by efficiently addressing both organic and microbial contaminants (Abdel-Fatah, 2018). NF can serve as a substitute for traditional treatment methods in the preparation of raw water, ensuring the production of high-quality water devoid of bacteria, metal ions like iron and manganese, and colloids irrespective of variations in the feed (Mänttäre et al., 2021). There are reports of a few challenging compounds, such as chloride ions, that may accumulate in the permeate stream (Mänttäre et al., 2021).

The performance of NF membranes can be improved with pretreatments. Chemical precipitation and settling at many stages, use of a sand filter, a backwashable screen filter, and a 5 μm bag filter are used (Mänttäre et al., 2006). Hardness, which gauges divalent cations, is effectively concentrated in NF. However, the retention of dissolved solutes is below 40%, mainly due to the undesired chloride retention, as per the Donnan phenomenon. The NF membrane demonstrates an electrostatic separation effect due to surface charge, particularly multivalent ionic species. Despite NF exhibiting good permeate flux and being less susceptible to fouling than RO, monovalent ions can permeate the filter in the presence of elevated sulfate concentrations in the water. For instance, nitrate ions pass through NF membranes even with relatively low sulfate concentrations. Consequently, in such scenarios, RO is advisable for high-end treatment, resulting in a good-quality product stream (Mänttäre et al., 2006).

5.4.1 Cost of nanofiltration

NF faces limited commercial adoption in water treatment primarily due to its elevated operational expenses. The cost sensitivity to flux and the diminishing economies of scale at larger plants contribute to this constraint. Notably, membrane-related investment

costs form a substantial proportion of the expenses, escalating with plant size. Operating and maintenance costs include various elements such as labor, routine maintenance, replacement expenditures, chemicals, and energy consumption. Achieving higher operation rates is critical for cost reduction in NF processes, emphasizing the need for efficiency improvements to enhance its economic viability in water treatment applications (Mänttari et al., 2021).

5.5 Reverse osmosis

RO systems appear to be highly effective in eliminating all inorganic pollutants present in pulp and paper mill wastewater. The contaminants, dissolved nonions, salt ions, and color up to a particle size of 0.0001 μm are removed. It is commonly used for removing hardness from water streams (Trishitman et al., 2020). Operating at elevated pressures, RO stands out as the most stringent membrane available, with a substantial permeate flux with a permeate of moderate quality. Application of RO in the pulp and paper industry enables the reuse of over 60% of wastewater after filtration, exhibiting a conductivity below 200 mS/cm and less than 15 mg/L of COD value. In a separate evaluation, RO was introduced after UF treatment to achieve complete degradation of lignin, COD, and color at an optimum pH value of 5.74 (Esmaeeli et al., 2022). Polysulphone and polyamide membranes were incorporated in research, and the membrane system outperformed in color removal compared to COD reduction when bleaching effluent of acidic and alkaline nature was fed to the RO feed side. With a 50 Da polyamide membrane system, retentate is obtained with 100% TDS removal. However, such an RO system is characterized by a high fouling index (Shukla et al., 2010).

Despite not necessitating chemicals or a heat supply and being applicable for tertiary treatment, intensely polluted effluents are not advisable to pass through the RO membrane directly. High COD and lignin concentrations may negatively impact the permeate purity and cause fouling in such instances (Esmaeeli et al., 2022). In research, RO gave good output flux of 20–25 L/m²h values when the silt density index is lower than two at operating conditions of 20 bar and a VCR of nine. For the smooth operation of RO, it is suggested to remove the soluble salts by some pretreatment methods such as chemical precipitation (Pizzichini et al., 2005). The usage of composite flocculants and combining with electrochemical systems can be used for better RO performance. Though high pathogen removal is exhibited, economic feasibility is questionable, since the disposal of retentate is required (Kamali & Khodaparast, 2015).

The pros and cons of NF and RO systems are as given in Table 5.1.

Table 5.1 Advantages and disadvantages of nanofiltration and reverse osmosis (Trishitman et al., 2020).

Advantages	Disadvantages
Nanofiltration	
NF efficiently removes calcium and magnesium ions, reducing hardness without introducing sodium ions, as seen in ion-exchange units. No additional chemical treatment for water softening, and it avoids any need for sodium resin. Unlike processes like distillation, NF does not necessitate heating or cooling of the feed, reducing separation costs. NF operates without mechanical stirring, ensuring gentle molecular separation during the filtration process. NF can handle a substantial volume of feed continuously, maintaining a stable flow rate of permeate.	NF has restricted applications due to the membrane's limited pore size, making RO and UF preferable for broader applications. NF may need high initial, operating, and maintenance costs compared to RO and UF. NF membranes have shorter lifespan and are replaced more frequently than the actual filter lifetime, increasing operational costs. The use of NF systems has led to a 60%–150% increase in energy requirements for water treatment. Although green energy might reduce consumption, its higher cost poses a challenge. Various fouling phenomena like colloidal, microbiological, and chemical fouling contribute to membrane fouling. Pretreatment is crucial for reducing fouling, involving monitoring parameters, awareness of trace contaminants, and control of pH, flow rates, and temperature. Cleaning is necessary when permeate flux falls, salinity in permeate increases, or when normalized pressure drop rises.
Reverse osmosis	
Achieving separation without a phase change leads to low-energy requirements. RO systems are characterized by their compact design, requiring less space and offering ease of operation, easy scale-up, and maintenance. Labor training is easier due to the consistent design and standardization of the RO systems.	The process requires high pressure, surpassing the osmotic pressure of the inlet to achieve permeate flow. RO membranes are prone to concentration polarization and fouling, necessitating mandatory pretreatment. Regression cleaning procedures are necessary. Time-consuming and high initial investment. Membranes lack mechanical robustness and are easily damaged by operational malfunctions.

RO, Reverse osmosis; *UF*, ultrafiltration.

5.6 Electrodialysis

Membrane separation of charged pollutants under an electric field is another method proposed for pulp and paper mill wastewater treatment. ED reportedly can be associated with a zero liquid discharge strategy in a pulp and paper mill by reducing the brine volume. Configurations such as alternate cationic and anionic membranes parted by spacers in a study have been proven effective. The ionic membranes were prepared of HDX200 and HDX100 with a polypropylene spacer (Molledo et al., 2022). Functionalization is a strategy to improve performance. A zero-discharge proposal for an agro-based paper mill to concentrate NaOH from green liquor solution used sulfonated graphene oxide. The membrane showed good stability after 50 cycles and suitability for long-term operations (Goel et al., 2021). Bipolar membrane made of inert reinforcing fibers and ion-exchange resins arranged in five compartments was used multipurposefully for the concentration of alkali and the removal of H₂S. Here, a high concentration of bathing solution declines the permselectivity and current efficiency. Similarly, the lower concentration may indirectly cause water dissociation and a lowering of current efficiency. Such troubles with concentration polarization are avoided with spacers. Elemental sulfur formation is common in sulfonated membranes (Kuldeep et al., 2023).

Pulsed ED is another strategy adopted to reduce operational cost and fouling. The high-frequency process with heterogeneous membranes claimed the removal of chloride, sodium, and sulfate by 59%, 21%, and 20%. During the ED process the monovalent cation exchange membranes to remove sodium and retain useful multivalent ions in the discharge stream might be a promising method (Gonzalez-Vogel et al., 2021).

The demineralization rate during the ED process usually depends on the ratio of the electrical conductivity of the diluted solution and the feed. Energy consumption of the ED process can be determined by Eq. (5.1).

$$\text{Energy consumption} = \frac{EIt}{v} \quad (5.1)$$

where E is the potential (V), I is the electric current (A), t is the time of operation (h), and v is volume treated (L) (Molledo et al., 2022).

5.7 Hybrid methods

Hybrid methods facilitate the benefits of two individual processes in terms of efficiency. In a study a pilot scale was set up for eliminating the color and other pollutants from a paper mill effluent combined

MF and ED system, for a recovery and reuse rate exceeding 90% of the feed effluent stream. An MF module, consisting of a stainless-steel casing and a ceramic membrane arranged in a hollow tubular configuration under constant pressure, served as the pretreatment for bulk water at both 60°C and ambient temperature. The system tolerated peak temperatures in the process effluent stream and produced a filtered portion devoid of suspended or colloidal particles. The MF-ED hybrid filtration, operated at an applied voltage of 50 V, demonstrated a high rate of removal of total dissolved solids, and COD was reduced to less than 20 mg/L. Nevertheless, the pilot plant module, constructed locally, successfully lowered the concentrations of contaminated ions in water from the paper industry to meet the standards set by the World Health Organization (Nataraj et al., 2007).

In a study a polyetherimide MF membrane and polyethersulfone UF membrane were produced by simple extrusion to treat pulp and paper industry effluent. The permeate flux values for the MF membrane exceeded by a considerable margin compared to the UF, due to the larger average pore diameter of the MF membranes. This hybrid system was able to operate under consistent transmembrane pressures (TMPs) with stable flux. Fouling caused by clogged pores and cake formation could be eliminated by simple backwash and the tangential flux. This system resulted in high removal of turbidity, lignin, and COD (Neves et al., 2017).

Another hybrid micro-ultrafiltration system operated with a cross-flow single ceramic MF membrane at the optimum temperature of 80°C, flow velocity of 3 m/s, and 0.6 bar TMP at volume reductions (VR) of 50% and 80% using an RC10PE membrane. The corresponding hemicellulose concentration values are shown. While evaluating the economics the recovery of hemicellulose by this strategy is about €1160/t_{hemi}. Also, the specific energy demand concerning the pollutant load was calculated as 674 kWh/t COD. The proposed strategy in a pulp and paper plant for hemicellulose retention may aid in energy conservation at a rate of 210 kW when the wastewater flux is 180 m³/h (Thuvander et al., 2019).

In a different study a series of different membrane systems, micro, ultra, and NF, was incorporated with a ceramic tubular membrane to treat the effluent from sulfite pulp production. The proposal as a substitute for traditional methods for effluent remediation could effectively alleviate the COD and residual lignin at a TMP of 1–5 bar and 60°C temperature. The reductions of COD and residual lignin concentrations reached over 35% and 70%, respectively. When evaluating ceramic membranes for fractionation and performance, the two-stage process configuration involving MF followed by UF emerged as a fitting choice for the effective

decontamination of alkaline bleaching effluent (Ebrahimi et al., 2016). Although MF and UF systems play the role of pretreatment, a study showed that such pretreatment caused no significant changes in the permeate flux while high-shear NF. The permeate flux rate seemed to be better with UF compared to MF. However, with the negligible effect of UF, such prefiltration does not improve the performance of high-shear systems. This is strongly supported by fouling values being 5%, 2%, and 3% calculated from pure water fluxes when microfiltered, ultrafiltered, and nanofiltered original discharge, respectively (Mänttäre et al., 2008).

Nonetheless, these hybridized and systematically integrated solutions require additional research, especially concerning various industrial wastewaters, with a focus on eco-sustainability, circular economy principles, and achieving minimum to nil liquid discharges. Comprehensive investigations into their viability on both lab-scale and industrial cases are essential, including in-depth analyses of potential for integration, energy efficiency, cost-effectiveness, and ecological impact assessment. This is crucial for facilitating green industrial transitions (Dogan et al., 2023). Table 5.2 gives different hybrid membrane systems and the process details.

5.8 Membrane fouling and its prevention

Membrane fouling is a phenomenon that occurs as a result of the adsorption of particles like lignin, organic solutes, and membrane surface polarization, leading to high hindrance for the flow of liquid fraction through the membrane pores (Goswami et al., 2019). It is expected that a continuously operated plant is prone to more fouling when compared with a small-scale batch process (Izadi et al., 2018).

Fouling layers necessitate proper cleaning procedures. HCl solution at pH 2 could be used to address CaCO_3 . This procedure converts CO_3^{2-} to CO_2 and eliminates other metal precipitates and scales formed by mineral deposition. Organics and silt removal are effective by cleaning with a 1% aqueous solution of tetrasodium EDTA. Biological fouling can be alleviated by thorough washing with deionized water followed by storage in sodium bisulfate (0.5% NaHSO_3) solution at the final stage of filtration. Water flux is significantly improved by removing dirt, oils, colloidal material, metal hydroxides, and adsorbed organics using caustic detergent, acids, and oxidizing agents, respectively (Nataraj et al., 2007).

Pore characteristics are significant factors influencing the incidence and the degree of fouling. Membranes with packed pore structures fouled to a lesser degree than did membranes with loosely packed pore structures. Fouling in smaller pore sizes occurs due to

Table 5.2 Operational details of hybrid membrane filtration systems.

Method	Membrane specification	Operational conditions	Dimension and MWCO	Cleaning	Average flux rate (L/m ² h)	Efficiency	References
MF and ED	Stainless-steel housing of hollow tubular α -alumina made ceramic membrane	4–12 bar, 25°C, Re~4000, fluid velocity 1.0 m/s	ID 32 mm, length 1000 mm, 20 kDa, 1.5 μ m pore size	HCl (pH 2) and 1% tetrasodium EDTA	113	80% wastewater recovery	Nataraj et al. (2007)
MF and UF	Polyetherimide (MF) and polyethersulphone (UF)	Tangential inflow rate of 3.9 m/s, feed flow rate 6.6 L/min, 30°C	0.4 μ m pore size, 50 kDa, filtering area 0.090 m ²	NaOCl	MF: 52.2 UF: 41.2	Lignin removal of 82.5% (UF) and 76.5% (MF)	Neves et al. (2017)
MF and UF	Regenerated cellulose on a polyester support, spiral-wound element	MF: cross-flow velocity=3 m/s, 74°C–77°C, 0.6 bar	ID (MF) 3 mm, UF, 10 kDa, area 15.75 m ²	H ₂ O ₂ or NaOCl, under alkaline conditions	MF:112 UF: 132	Hemicellulose concentrated from 2.3 to 47 g/L	Thuvander et al. (2019)
MF, UF and NF	Al ₂ O ₃ /TiO ₂ ceramic membrane	1–5 bar 60°C, 4 m/s	0.05–0.2 μ m pores, 1–20 kDa,	1% NaOH at 60°C and distilled water	MF: 186 UF: 140	Residual lignin reduction of 70%	Ebrahimi et al. (2016)
MF, UF, and NF	Semiaromatic piperazine-based polyamide-polysulphone with polyester	6.5 bar, 9 m/s (NF), 30°C	Cutoff (NF) 200–300 g/mol	Low fouling rate	60–70	30% COD (UF), inorganic carbon retention 60%– 70%	Mänttari et al. (2008)

COD, Chemical oxygen demand; *ED*, electrodialysis; *MF*, microfiltration; *MWCO*, molecular weight cutoff; *NF*, nanofiltration; *UF*, ultrafiltration.

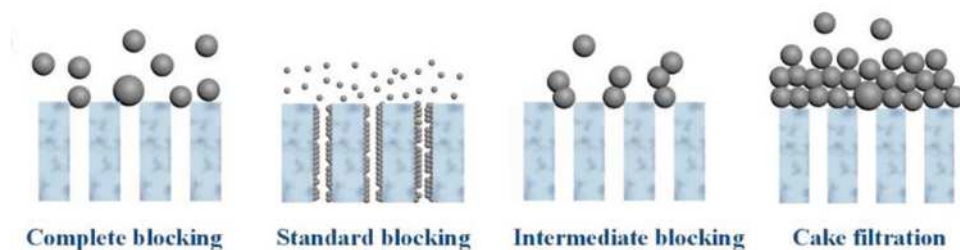


Figure 5.6 Representation of porous membrane fouling (Wang et al., 2020).

adsorption; however, pore plugging dominates fouling with increased membrane cutoff. Fouling is caused due to pore blocking in MF and absorptive fouling in the cases of UF and NF. Fig. 5.6 represents different mechanisms of fouling. Hydrophilic membranes are favorable in membrane filtration since hydrophobic membranes such as polysulphone, polyamide-imide, and polyether-imide are susceptible to frequent fouling. Similarly, membranes with higher contact angles tend to have higher fouling rates compared to those with smaller contact angles (Neves et al., 2017).

5.9 Parameters affecting membrane fouling

Membrane fouling is an intricate process guided by the interplay of various factors. It is contingent on filtration conditions and effluent properties, encompassing pH, temperature, TMP, volume reduction factor, hydrodynamics, hydrophilicity, molecular shape, concentration, and membrane characteristics. Given its direct correlation with solute properties, membrane features, and operational parameters, careful consideration must be given to the selection of membrane material, effluent strength, and process design. When fouling occurs, a range of approaches is employed, including chemical methods such as coagulation, chemical cleansing, and modification of membrane surface; hydrodynamic methods like vibrating membrane, high shear, and rotating disk; and physical techniques such as ultrasound and physical cleaning. To prevent scaling on membrane surfaces, an antiscalant such as sodium-hexametaphosphate is employed. The selection of method owes to the diversity of chemical compositions of membranes and the hydrodynamic conditions applied (Bokhary et al., 2018). Optimizing operational conditions like permeate flux, feed flow rate near the membrane surface, operating pressure, and backwash or chemical cleaning fouling could be avoided in membrane filtration (Neves et al., 2017).

5.9.1 Mathematical aspects of membrane processes

Focus on the design parameters and mathematical aspects of membrane processes is essential because of their influence on process efficiency, cost, scalability, quality control, regulatory compliance, and so on (Hosseini et al., 2023). Knowledge of these parameters helps in optimizing various aspects of the membrane filtration process, such as flow rates, pressures, and membrane surface area. This optimization leads to higher efficiency, better separation performance, and lower operational costs (Ravichandran et al., 2022).

Permeate flux is a direct indicator of the performance of the membrane system. High permeate flux typically signifies efficient filtration and good membrane condition, while a decline in flux can indicate fouling, scaling, or membrane degradation. The performance of the membrane system is predicted by determining permeate flux (J) and membrane rejection (R). Darcy's law states that the permeate flux is directly proportional to the external applied force, as shown Eq. (5.2) (Dogan et al., 2023).

$$J = \frac{1}{A_m} \frac{dV_p}{dt} \quad (5.2)$$

where J is the permeate flux (L/m^2h), A_m is the membrane filtration area (m^2), V_p is the total permeate volume (L), and t is the time of filtration (h).

Membrane separations are driven by TMP, and it is defined as the difference in the stream pressures of retentate and permeate, as given in Eq. (5.3):

$$TMP = \frac{[P_1 + P_2]}{2} - P_3 \quad (5.3)$$

where TMP is the total TMP, P_1 , P_2 , and P_3 are the pressures of the inlet stream, retentate stream, and the negative permeate pressure, respectively. A digital flowmeter can be employed to determine the permeate flow rate (Ebrahimi et al., 2016).

Another critical parameter in membrane filtration processes is the VCR, and it represents the extent to which solutes in the feed solution are concentrated (Eq. 5.4). VCR influences solute concentration, membrane fouling, process efficiency, design considerations, product quality, energy consumption, recovery rates, and operational stability. Monitoring and optimizing VCR are essential for achieving desired outcomes in various industrial and environmental applications involving membrane filtration (Nataraj et al., 2007).

$$VCR = \frac{\text{Volume of initial feed}}{\text{volume of retentate}} \quad (5.4)$$

The poor hydraulics in the reactor system, such as slow cross-flow and small Reynolds number, may cause diminished performance of certain membrane systems (Pizzichini et al., 2005). Reynolds number, Re , is calculated as

$$Re = \frac{\rho v d}{\mu} \quad (5.5)$$

where ρ is the fluid density (kg/m^3), v is the fluid velocity (m/s), d is the hydraulic diameter (m), and μ is its fluid viscosity (kg/ms).

Fouling in membrane filtration processes leading to a decline in permeate flux is a significant factor because it directly impacts the efficiency and effectiveness of the filtration process. The membrane fouling can be determined by Eq. (5.6). Here, the pure water permeability ($\text{L}/(\text{m}^2\text{h bar})$) before (PWP_b) and after (PWP_a) membrane filtration is compared (Mänttärä et al., 2008).

$$Fouling = \left(1 - \left(\frac{PWP_a}{PWP_b} \right) \right) \times 100 \quad (5.6)$$

The flux declines in the membrane process can be determined by measuring the fluxes as follows: initially, get the flux while running with pure water and the flux at steady state (J_0). Next measure the final flux (J_s) by replacing pure water with wastewater. Later determine the permeate flux of pure water with the fouled membrane (J_f) to get a stable value (Gönder et al., 2012). The flux declines can be calculated according to the following formula.

$$\text{Total flux decline} = \frac{J_0 - J_s}{J_0} \quad (5.7)$$

Reduction of flux due to concentration

$$\text{polarization} = \frac{J_f - J_s}{J_0} \quad (5.8)$$

$$\text{Reduction of flux due to fouling} = \frac{J_0 - J_f}{J_0} \quad (5.9)$$

Percent rejection (%R) gives the separation efficiency of the membrane, calculated from concentration of solute in the feed (C_f) and permeate (C_p) as,

$$\%R = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (5.10)$$

The VR is calculated according to Eq. (5.10).

$$VR = \frac{Q_p}{Q_f} = \frac{1}{1 + \frac{Q_r}{Q_p}} \quad (5.11)$$

where Q_p , Q_f , and Q_r are flow rates of permeate, feed, and retentate (L/h), respectively.

5.10 Membrane materials

The selection of membrane material is important since it influences the permeate flux rate, fouling, cost of investment, type of maintenance and cake removal, and overall performance of the system. Extensive studies have been conducted to improve the properties of materials considering energy, flux gain, hydrodynamics, and ease of membrane cleaning. A membrane material with good thermochemical stability, mechanical strength, and optimum cost is preferred. Polymers of natural as well as synthetic origin are widely employed in membrane preparation for the pulp and paper industry; regenerated cellulose, cellulose acetate, polyolefin, polysulfone, sulfonated polyethersulfone, polyethersulfone, polypiperazine amide, and polyvinylidenedifluoride were found in studies (Neves et al., 2017). Polysulphones are widely used and have good tolerance for varying pH and temperature. However, polysulfones cannot intake high-fat and polar substrates. Certain polymer membranes have also shown tolerance toward oxidizing environments, which is favorable in integrated systems. Other nonconventional materials such as polyamide, polyacrylonitrile, polyetherimide, polytetrafluoroethylene, and polycarbonates are excellent candidates with selective permeability. Polymer membranes are characterized by their lightweight, low cost, good mechanical strength, and low fouling indices, making them suitable for microporous membranes (Barjoveanu & Teodosiu, 2006; Ebrahimi et al., 2016). Organic polymer membranes are prone to microbial degradation and intolerant toward varying pH and heat. Ceramic membranes are incorporated often when polymeric membranes are not suitable to be employed. Solvent resistance and thermal stability are crucial factors for UF and MF. Membranes of ceramic origin are suitable in this aspect to be incorporated in MF and UF (Barjoveanu & Teodosiu, 2006). Additionally, ceramic materials are durable, and hydrophilic and can be used under abrasive filtering conditions to get good permeate flux (Ebrahimi et al., 2016). Hence, the material is selected according to the criteria of filtration.

Hydrophilicity is a desirable property to avoid fouling due to the repulsion of negatively charged aggregates by the membrane surface (Barjoveanu & Teodosiu, 2006). In a study a ceramic membrane for pulp industry wastewater gained stable productivity when compared to the spiral-wound polymeric system. Later one is not recommended for pulp and paper industry effluents since they are prone to fouling (Pizzichini et al., 2005).

Membranes are prepared from raw materials by several methods. Phase inversion is popular, and it can be explained as the transformation of a polymer from a liquid phase to a solid phase under a controlled environment. Four fundamental techniques are employed in the creation of phase inversion membranes. They are (1) precipitation from the vapor phase, (2) precipitation by controlled evaporation, (3) thermally induced phase separation, and (4) immersion precipitation. Among these, immersion precipitation stands out as the most commonly utilized technique for the preparation of polymeric membranes (Membranes 101, n.d.).

5.11 Physicochemical methods for pulp and paper industry wastewater

The utilization of diverse physicochemical treatment approaches, including sedimentation and flotation, coagulation and precipitation, filtration, adsorption, wet oxidation, ozonation, and other advanced oxidation processes for treating pulp and paper effluents, has been reported. These methods are recognized for their effectiveness in eliminating a range of suspended and floating materials, along with toxic compounds, from the generated wastewater (Mehmood et al., 2019).

The efficiencies of sedimentation and flotation for the reclamation of wastewater depend on the industrial processes involved as well as the secondary treatment techniques adopted. In addition, metal salts promote flocculation, and subsequent settling reduces the lignin load and turbidity in the wastewater. High molecular weight flocculants, including natural polymers (chitosan), polydiallyldimethylammonium chloride, polyaluminium chloride, and CaO, are used for pulp and paper industry wastewater. The usage of adsorbents such as activated carbon, silica, fuller's earth, and coal ash is also used for the removal of pollutants (Kamali & Khodaparast, 2015).

Hybrid methods where the combination of Fenton assisted by ultrasonic irradiation-like process, photo-Fenton degradation, and electro-oxidation are reported. Similarly, ozonation and electrolysis also were combined in a study to remove COD and color (Kishimoto et al., 2010). Although electrochemical methods are high-performing treatment options, their application in large-scale industries should

be explored further. Energy conversion from cellulose-laden waste using biological processes is an option for waste management. An anaerobic biofilm digester treating pulp and paper industry wastewater produced a high volume of biogas with a rich methane content of up to 71% and caused >70% pollutant reduction (Bakraoui et al., 2019). Depending on the properties of wastewater generated, suitable treatment strategies may be adopted.

5.12 Conclusions and future trends

Membrane filtration is an effective wastewater treatment method in the pulp and paper industry using a selectivity mechanism. Membrane processes remove lignin and other particulate matter by passing wastewater through a porous medium with an external TMP. According to the degree of purity required and the nature of contaminants, there are MF, UF, NF, RO, and ED. Among the filtration systems, RO removes the minute particles, including microorganisms, and MF is effective for particles ranging from 0.1 to 10 μm . A series of different types of membrane systems to form a hybrid treatment module is more effective than placing a single type of filter. The application of membrane filtration includes water softening, disinfection, and removal of lignin and other solids in the pulp and paper industry. Low requirements of chemical additives and a small footprint facilitate the effluent treatment more cost-effective and ecofriendly. The operation and maintenance of the membrane filtration system are simple, and in contrast with biological-based technologies, changes in environmental parameters such as feed composition and oxygen level do not affect this type of filtration process. Overall, the pulp and paper industry can operate with a zero-discharge strategy by adopting membrane technology.

However, dissolved ions are not completely removed through membrane filtration alone. Furthermore, fouling is a major concern in membrane processes, reducing membrane flux, membrane lifespan, and consequently membrane performance. Pretreatment of inlet feed before filtration helps to reduce fouling to an extent. Fouling can be removed by chemical, physical, and hydrodynamic treatments. Novel proposals for cost-effective methods to reduce the load on the membranes would be welcome in this field. Fouling can also be avoided by optimizing filtration conditions and by using antiscaling agents. Researchers shall work on cost-effective membrane materials and configurations to improve overall performance by reducing fouling for recycle and reuse of pulp and paper industry wastewater. Furthermore, membrane process combined with advanced oxidation process has enormous scope, and it shall be explored in detail for operational improvement.

List of acronyms

AOX	Mutagenic organo-halogens
ED	Electrodialysis
EDTA	Ethylenediaminetetraacetic acid
HMW	High molecular weight compounds
ID	Inner diameter
MF	Microfiltration
MWCO	Molecular weight cutoff
NF	Nanofiltration
PT100	Platinum-based temperature detector
TDS	Total dissolved solids
UF	Ultrafiltration
VCR	Volume concentration ratio
VR	Volume reductions

List of symbols

Symbol	Abbreviation	Unit
A_m	Membrane filtration area	m^2
C_f	Feed solute concentration	ppm
COD	Chemical oxygen demand	ppm
C_p	Permeate solute concentration	ppm
d	Hydraulic diameter	m
E	Potential	V
I	Electric current	A
J	Permeate flux	L/m^2h
J_0	Pure water flux at steady state	L/m^2h
J_f	Pure water flux with the fouled membrane	L/m^2h
J_s	Wastewater final flux	L/m^2h
P_1	Inlet stream pressure	bar
P_2	Retentate stream pressure	bar
P_3	Negative permeate pressure	bar
pH	Potential hydrogen	–
PWP_a	Pure water permeability and after membrane filtration	$L/(m^2h\ bar)$
PWP_b	Pure water permeability before membrane filtration	$L/(m^2h\ bar)$
Q_f	Feed flow rate	L/h
Q_p	Permeate flow rate	L/h
Q_r	Retentate flow rate	L/h
t	Time of operation/filtration	h
TMP	Transmembrane pressure	bar
V	Volume treated	L
v	Fluid velocity	m/s
V_p	Total permeate volume	L
μ	Fluid viscosity	kg/ms
ρ	Fluid density	kg/m^3

References

- Abdel-Fatah, M. A. (2018). Nanofiltration systems and applications in wastewater treatment: Review article. *Ain Shams Engineering Journal*, 9, 3077–3092. <https://doi.org/10.1016/j.asej.2018.08.001>.
- Agboola, O., Maree, J., & Mbaya, R. (2014). Characterization and performance of nanofiltration membranes. *Environmental Chemistry Letters*, 12, 241–255. <https://doi.org/10.1007/s10311-014-0457-3>.
- Ahmad, N. N. R., Ang, W. L., Teow, Y. H., Mohammad, A. W., & Hilal, N. (2022). Nanofiltration membrane processes for water recycling, reuse and product recovery within various industries: A review. *Journal of Water Process Engineering*, 45, 102478. <https://doi.org/10.1016/j.jwpe.2021.102478>.
- Al Aani, S., Mustafa, T. N., & Hilal, N. (2020). Ultrafiltration membranes for wastewater and water process engineering: A comprehensive statistical review over the past decade. *Journal of Water Process Engineering*, 35, 101241. <https://doi.org/10.1016/j.jwpe.2020.101241>.
- Bakraoui, M., Hazzi, M., Karouach, F., Ouhammou, B., & El Bari, H. (2019). Experimental biogas production from recycled pulp and paper wastewater by biofilm technology. *Biotechnology Letters*, 41, 1299–1307. <https://doi.org/10.1007/s10529-019-02735-w>.
- Barjoveanu, G., & Teodosiu, C. (2006). Advanced treatment for pulp and paper wastewater recycling by membrane processes. *Environmental Engineering and Management Journal*, 5, 145–167. <https://doi.org/10.30638/eemj.2006.012>.
- Bokhary, A., Tikka, A., Leitch, M., & Liao, B. (2018). Membrane fouling prevention and control strategies in pulp and paper industry applications: A review. *Journal of Membrane Science and Research*, 4, 181–197. <https://doi.org/10.22079/JMSR.2018.83337.1185>.
- Bray, R. T., Jankowska, K., Kulbat, E., Łuczkiwicz, A., & Sokołowska, A. (2021). Ultrafiltration process in disinfection and advanced treatment of tertiary treated wastewater. *Membranes (Basel)*, 11. <https://doi.org/10.3390/membranes11030221>.
- Dagar, S., Singh, S. K., & Gupta, M. K. (2023). Integration of Pre-treatment with UF/RO membrane process for waste water recovery and reuse in agro-based pulp and paper industry. *Membranes (Basel)*, 13. <https://doi.org/10.3390/membranes13020199>.
- Dogan, E. C., Pişkin, E. D., Narcı, A. O., Mert, B. K., Yakin, S. T., Demirözlü, T. N., Atasoy, M. S., & Aydinler, C. (2023). Eco-sustainable paper wastewater management by water-resource recovery and concentrate minimization using a membrane oxidation reactor and membrane distillation system. *Environmental Science: Water Research & Technology*, 9, 3398–3416. <https://doi.org/10.1039/d3ew00520h>.
- Ebrahimi, M., Busse, N., Kerker, S., Schmitz, O., Hilpert, M., & Czermak, P. (2016). Treatment of the bleaching effluent from sulfite pulp production by ceramic membrane filtration. *Membrane*, 6, 7. <https://doi.org/10.3390/MEMBRANES6010007>.
- Esmaeeli, A., Sarrafzadeh, M. H., Zeighami, S., Kalantar, M., Bariki, S. G., Fallahi, A., Asgharnejad, H., & Ghaffari, S. B. (2022). A comprehensive review on pulp and paper industries wastewater treatment advances. *Industrial & Engineering Chemistry Research*, 62, 8119–8145. <https://doi.org/10.1021/acs.iecr.2c04393>.
- Goel, P., Mandal, P., Bhuvanesh, E., Shahi, V. K., & Chattopadhyay, S. (2021). Sulfonated poly (ether ether ketone) composite cation exchange membrane for NaOH production by electro-electrodialysis using agro-based paper mill green liquor. *Journal of Environmental Chemical Engineering*, 9, 106409. <https://doi.org/10.1016/j.JECE.2021.106409>.
- Gonzalez-Vogel, A., Moltedo, J. J., Reyes, R. Q., Schwarz, A., & Rojas, O. J. (2021). High frequency pulsed electrodialysis of acidic filtrate in kraft pulping. *Journal of*

- Environmental Management*, 282, 111891. <https://doi.org/10.1016/J.JENVMAN.2020.111891>.
- Goswami, L., Kumar, R. V., Pakshirajan, K., & Pugazhenth, G. (2019). A novel integrated biodegradation—Microfiltration system for sustainable wastewater treatment and energy recovery. *Journal of Hazardous Materials*, 365, 707–715. <https://doi.org/10.1016/j.jhazmat.2018.11.029>.
- Gönder, Z. B., Arayici, S., & Barlas, H. (2012). Treatment of pulp and paper mill wastewater using ultrafiltration process: Optimization of the fouling and rejections. *Industrial & Engineering Chemistry Research*, 51, 6184–6195. <https://doi.org/10.1021/ie2024504>.
- Han, R., Zhang, S., & Sui, Y. (2021). Chapter 4 – Nanofiltration membranes for challenging environment. In *Handbook of nanotechnology applications: Environment, energy, agriculture and medicine*. Elsevier, 99–123. <https://doi.org/10.1016/B978-0-12-821506-7.00004-1>.
- Hu, J., Lv, Z., Xu, Y., Zhang, X., & Wang, L. (2016). Fabrication of a high-flux sulfonated polyamide nanofiltration membrane: Experimental and dissipative particle dynamics studies. *Journal of Membrane Science*, 505, 119–129. <https://doi.org/10.1016/j.memsci.2016.01.034>.
- Hosseini, M. K., Liu, L., Hosseini, P. K., Lee, K., & Miao, J. (2023). Performance evaluation of a pilot-scale membrane filtration system for oily wastewater treatment: CFD modeling and scale-up design. *Journal of Water Process Engineering*, 52, 103570. <https://doi.org/10.1016/j.jwpe.2023.103570>.
- Izadi, A., Hosseini, M., Darzi, G. N., Bidhendi, G. N., Shariati, F. P., & Mosaddeghi, M. R. (2018). Perspectives on membrane bioreactor potential for treatment of pulp and paper industry wastewater: A critical review. *Journal of Applied Biotechnology Reports*, 5, 139–150. <https://doi.org/10.29252/JABR.05.04.02>.
- Kamali, M., & Khodaparast, Z. (2015). Review on recent developments on pulp and paper mill wastewater treatment. *Ecotoxicology and Environmental Safety*, 114, 326–342. <https://doi.org/10.1016/j.ecoenv.2014.05.005>.
- Kishimoto, N., Nakagawa, T., Okada, H., & Mizutani, H. (2010). Treatment of paper and pulp mill wastewater by ozonation combined with electrolysis. *Journal of Water and Environment Technology*, 8, 99–109. <https://doi.org/10.2965/jwet.2010.99>.
- Kolya, H., & Kang, C.-W. (2023). Next-generation water treatment: Exploring the potential of biopolymer-based nanocomposites in adsorption and membrane filtration. *Polymers (Basel)*, 15, 3421. <https://doi.org/10.3390/polym15163421>.
- Kuldeep, T., Ahonen, M. K., Rosenthal, L., & Murtomäki (2023). Bipolar membrane electrodialysis of Na₂CO₃ and industrial green liquor for producing NaOH: A sustainable solution for pulp and paper industries. *Chemical Engineering Journal Advances*, 14, 100450. <https://doi.org/10.1016/J.CEJA.2023.100450>.
- Madhubala, G., Abiramasundari, S., Rumjit, N. P., Padmanabhan, V. C., & Lai, C. W. (2022). Nano-driven processes toward the treatment of paper and pulp industrial effluent: From the view of resource recovery and circular economy. In *Nanotechnology in paper and wood engineering*. Elsevier, 471–492.
- Mänttari, M., Viitikko, K., & Nyström, M. (2006). Nanofiltration of biologically treated effluents from the pulp and paper industry. *Journal of Membrane Science*, 272, 152–160. <https://doi.org/10.1016/j.memsci.2005.07.031>.
- Mänttari, M., Kuosa, M., Kallas, J., & Nyström, M. (2008). Membrane filtration and ozone treatment of biologically treated effluents from the pulp and paper industry. *Journal of Membrane Science*, 309, 112–119. <https://doi.org/10.1016/j.memsci.2007.10.019>.
- Mänttari, M., Nyström, M., Nuortila-Jokinen, J., & Kallioinen, M. (2021). Nanofiltration in the pulp and paper industry. *Nanofiltration: Principles and Applications with New Materials*, 1 2(1–2), 599–620. <https://doi.org/10.1002/9783527824984.ch13>.

- Mbakop, S., Nthunya, L. N., & Onyango, M. S. (2021). Recent advances in the synthesis of nanocellulose functionalized-hybrid membranes and application in water quality improvement. *Processes*, 9. <https://doi.org/10.3390/pr9040611>.
- Mehmood, K., Rehman, S. K., Wang, J., Farooq, F., Mahmood, Q., Jadoon, A. M., Javed, M. F., & Ahmad, I. (2019). Treatment of pulp and paper industrial effluent using physicochemical process for recycling. *Water*, 11. <https://doi.org/10.3390/w1112393>.
- Molledo, J. J., Schwarz, A., & Gonzalez-Vogel, A. (2022). Evaluation of percrystallization coupled with electrodialysis for zero liquid discharge in the pulping industry. *Journal of Environmental Management*, 303, 114104. <https://doi.org/10.1016/J.JENVMAN.2021.114104>.
- Nataraj, S. K., Sridhar, S., Shaikha, I. N., Reddy, D. S., & Aminabhavi, T. M. (2007). Membrane-based microfiltration/electrodialysis hybrid process for the treatment of paper industry wastewater. *Separation and Purification Technology*, 57, 185–192. <https://doi.org/10.1016/J.SEP PUR.2007.03.014>.
- Neves, L. C., De Souza, J. B., De Sousa, C. M., Vidal, K. G. M., & Manago, B. L. (2017). Pulp and paper mill effluent post-treatment using microfiltration and ultrafiltration membranes. *Cellulose Chemistry and Technology*, 51, 579–588. <https://doi.org/10.2175/106143017x15023776270494>.
- Oliveira, C. R., Silva, C. M., & Milanez, A. F. (2007). Application of ultrafiltration in the pulp and paper industry: Metals removal and whitewater reuse. *Water Science and Technology*, 55, 117–123. <https://doi.org/10.2166/wst.2007.219>.
- Park, S.-K., Choi, J.-H., & Hu, J. Y. (2012). Assessing bacterial growth potential in a model distribution system receiving nanofiltration membrane treated water. *Desalination*, 296, 7–15. <https://doi.org/10.1016/j.desal.2012.03.022>.
- Pizzichini, M., Russo, C., & Meo, C. D. D. (2005). Purification of pulp and paper wastewater, with membrane technology, for water reuse in a closed loop. *Desalination*, 178, 351–359. <https://doi.org/10.1016/j.desal.2004.11.045>.
- Ravichandran, S. R., Venkatachalam, C. D., Sengottian, M., Sekar, S., Ramasamy, B. S. S., Narayanan, M., Gopalakrishnan, A. V., Kandasamy, S., & Raja, R. (2022). A review on fabrication, characterization of membrane and the influence of various parameters on contaminant separation process. *Chemosphere*, 306, 135629. <https://doi.org/10.1016/j.chemosphere.2022.135629>.
- Ruiz-Gutierrez, A., Lasobras, J., Coronas, J., Menéndez, M., & Luque-Alled, J. M. (2024). Lindane removal by membrane nanofiltration. *Journal of Water Process Engineering*, 57. <https://doi.org/10.1016/j.jwpe.2023.104649>.
- Shukla, S. K., Kumar, V., & Bansal, M. C. (2010). Treatment of combined bleaching effluent by membrane filtration technology for system closure in paper industry. *Desalination and Water Treatment*, 13, 464–470. <https://doi.org/10.5004/dwt.2010.1034>.
- Siagian, U. W. R., Khoiruddin, K., Wardani, A. K., Aryanti, P. T. P., Widiasta, I. N., Qiu, G., Ting, Y. P., & Wenten, I. G. (2021). High-performance ultrafiltration membrane: Recent progress and its application for wastewater treatment. *Current Pollution Reports*, 7, 448–462. <https://doi.org/10.1007/s40726-021-00204-5>.
- Singh, P., Manikandan, N. A., Purnima, M., Pakshirajan, K., & Pugazhenth, G. (2020). Recovery of lignin from water and methanol using low-cost kaolin based tubular ceramic membrane. *Journal of Water Process Engineering*, 38, 101615. <https://doi.org/10.1016/j.jwpe.2020.101615>.
- Sousa, M. R. S., Lora-Garcia, J., & López-Pérez, M. F. (2018). Modelling approach to an ultrafiltration process for the removal of dissolved and colloidal substances from treated wastewater for reuse in recycled paper manufacturing. *Journal of Water Process Engineering*, 21, 96–106. <https://doi.org/10.1016/j.jwpe.2017.11.017>.
- Tang, X., Wang, J., Zhang, H., Yu, M., Guo, Y., Li, G., & Liang, H. (2021). Respective role of iron and manganese in direct ultrafiltration: From membrane fouling to

- flux improvements. *Separation and Purification Technology*, 259, 118174. <https://doi.org/10.1016/j.seppur.2020.118174>.
- Thuvander, J., Lipnizki, F., & Jönsson, A. S. (2019). On-site recovery of hemicelluloses from thermomechanical pulp mill process water by microfiltration and ultrafiltration. *Journal of Wood Chemistry and Technology*, 39, 214–223. <https://doi.org/10.1080/02773813.2019.1565865>.
- Membranes 101, (n.d.). Synder Filtration. <https://synderfiltration.com/learning-center/artic>.
- Trishitman, D., Cassano, A., Basile, A., & Rastogi, N. K. (2020). Reverse osmosis for industrial wastewater treatment. In *Current trends and future developments on (Bio-) membranes: Reverse and forward osmosis: Principles, applications, advances*. Elsevier, 207–228. <https://doi.org/10.1016/B978-0-12-816777-9.00009-5>.
- Wang, J., Cahyadi, A., Wu, B., Pee, W., Fane, A. G., & Chew, J. W. (2020). The roles of particles in enhancing membrane filtration: A review. *Journal of Membrane Science*, 595, 117570. <https://doi.org/10.1016/j.memsci.2019.117570>.
- Zheng, X., Zhang, Z., Yu, D., Chen, X., Cheng, R., Min, S., Wang, J., Xiao, Q., & Wang, J. (2015). Overview of membrane technology applications for industrial wastewater treatment in China to increase water supply. *Resources, Conservation and Recycling*, 105, 1–10. <https://doi.org/10.1016/j.resconrec.2015.09.012>.

Physiochemical methods for pulp and paper wastewater treatment

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6.1 Introduction

The pulp and paper industry is one of the largest industrial water users, generating significant volumes of wastewater during various stages of production. This wastewater is characterized by its high load of organic and inorganic pollutants, including lignin, cellulose fibers, chlorinated compounds, and heavy metals. The complex composition of pulp and paper mill effluents poses considerable challenges for effective treatment and disposal.

During the pulping process, wood is broken down into fibers, releasing organic substances such as lignin and hemicellulose. Subsequent bleaching stages, especially those involving chlorine-based chemicals, contribute to the formation of chlorinated organic compounds, which are toxic and recalcitrant. The wastewater also contains suspended solids, color, chemical oxygen demand (COD), and biological oxygen demand (BOD), making it a significant environmental concern.

Managing this wastewater is crucial not only for regulatory compliance but also for minimizing the environmental footprint of the industry. Various treatment methods, including physicochemical and biological processes, are employed to remove contaminants and reduce the impact on receiving water bodies (Kumar et al., 2020; Toczyłowska-Mamińska, 2017). The selection of appropriate treatment technologies depends on the specific characteristics of the wastewater and the desired quality of the treated effluent.

The complexity and variability of pulp and paper wastewater necessitate a comprehensive and integrated approach to treatment,

incorporating multiple stages and technologies to achieve optimal results. Advances in treatment methods continue to evolve, aiming to enhance efficiency, reduce costs, and improve the sustainability of wastewater management in the pulp and paper industry.

Wastewater treatment is vital for environmental protection, public health, and sustainable industrial operations. In industries such as pulp and paper, where large volumes of water are used and substantial amounts of pollutants are generated, effective wastewater treatment is crucial. Untreated wastewater can contain organic and inorganic pollutants, toxic substances, and high levels of BOD and COD, posing severe risks to aquatic ecosystems and human health.

Effective wastewater treatment reduces the pollutant load, ensuring that the effluent released into the environment meets regulatory standards. This protects water bodies from contamination, preserving aquatic life and maintaining the ecological balance. Additionally, it prevents the accumulation of harmful substances in the food chain, safeguarding public health. For the pulp and paper industry, wastewater treatment is not only a regulatory requirement but also a component of corporate social responsibility and sustainability initiatives. By implementing efficient treatment processes, companies can reduce their environmental footprint, conserve water resources, and enhance their reputation among consumers and stakeholders (Wang et al., 2016).

Moreover, advanced wastewater treatment technologies can enable water reuse and recycling within industrial processes, reducing the overall demand for fresh water and lowering operational costs. This is particularly important in regions facing water scarcity. In summary, wastewater treatment is essential for environmental sustainability, regulatory compliance, public health protection, and resource conservation, making it a critical aspect of industrial operations and environmental management.

Treating pulp and paper wastewater presents a range of complex challenges due to the diverse and variable nature of the effluent generated during the manufacturing process. One of the primary challenges is the high organic load, particularly lignin and cellulose fibers, which contribute to elevated levels of COD and BOD. These organic compounds are resistant to biodegradation, making it difficult to achieve effective removal using conventional biological treatment methods.

The presence of toxic and recalcitrant substances, such as chlorinated organic compounds formed during the bleaching process, poses another significant challenge. These compounds are not only harmful to aquatic life but also persist in the environment, requiring advanced treatment technologies for effective removal. Additionally, the wastewater often contains suspended solids, color, and heavy metals, each demanding specific treatment approaches.

Another challenge is the high variability in wastewater composition and flow rates, influenced by the different stages of the pulping and papermaking processes. This variability complicates the design and operation of treatment systems, necessitating flexible and adaptive solutions. Furthermore, the industry's large water consumption generates substantial volumes of wastewater, creating a need for efficient and scalable treatment systems.

Economic factors also play a critical role, as the cost of implementing and operating advanced treatment technologies can be significant. Balancing cost-effectiveness with regulatory compliance and environmental sustainability is a constant challenge for pulp and paper mills.

Overall, the multifaceted nature of pulp and paper wastewater requires a comprehensive and integrated treatment approach, combining multiple technologies to address the diverse contaminants and meet stringent environmental standards.

6.2 Characteristics and composition of pulp and paper wastewater

Since the optimization and efficiency of wastewater treatments strongly depend on its composition, the next paragraph will provide a short overview of physical, chemical, and biological parameters to be taken into account for selecting and optimizing the treatment technology. For instance, high-suspended solids may necessitate pretreatment steps like sedimentation or filtration, while temperature control may be required to optimize biological treatment efficiency. As another example the presence of chlorinated compounds may necessitate advanced oxidation processes (AOPs) or adsorption techniques to achieve effective removal and compliance with environmental regulations ([Cabrera, 2017](#)).

6.2.1 Physical characteristics

The physical characteristics of pulp and paper wastewater are crucial in determining the appropriate treatment methods. This wastewater typically contains high levels of suspended solids, primarily composed of cellulose fibers, wood particles, and bark residues. These suspended solids contribute to the turbidity and color of the wastewater, making it visually unappealing and potentially harmful to aquatic life due to reduced light penetration and oxygen transfer.

Temperature is another important physical parameter, as the pulping process often generates heat, resulting in elevated temperatures of the effluent. High temperatures can affect the solubility of gases

and the activity of microorganisms in biological treatment processes. Additionally, the temperature of the wastewater can vary significantly depending on the specific manufacturing processes and the season.

Other physical characteristics include the pH and conductivity of the wastewater. The pH can fluctuate widely, influenced by the use of chemicals in various stages of production, such as bleaching agents and caustic solutions. Conductivity is an indicator of the total dissolved solids present in the wastewater, which includes inorganic salts and other dissolved substances.

6.2.2 Chemical composition

The chemical composition of pulp and paper wastewater is complex and varies depending on the raw materials, production processes, and chemicals used. One of the primary chemical constituents is lignin, a natural polymer released during the pulping process. Lignin and its derivatives contribute significantly to the COD and color of the wastewater.

Additionally, the effluent contains various organic compounds, such as carbohydrates, fatty acids, and resin acids, which result from the breakdown of wood fibers. These organic compounds can be challenging to treat due to their recalcitrant nature and potential toxicity ([Kesalkar et al., 2012](#)).

Chlorinated organic compounds are of particular concern in wastewater from bleaching operations. These include chlorophenols, chloroform, and other chlorinated by-products formed when chlorine or chlorine-based chemicals react with organic matter. These compounds are highly toxic and persistent in the environment, requiring advanced treatment technologies for effective removal.

The chemical composition also includes inorganic substances, such as sulfates, chlorides, and various metal ions. Heavy metals like mercury, cadmium, and lead can be present, albeit in smaller concentrations, depending on the raw materials and production processes ([Sharma et al., 2022](#)).

6.2.3 Biological constituents

Biological constituents in pulp and paper wastewater primarily consist of microorganisms, including bacteria, fungi, and protozoa, which originate from the raw materials and production processes. These microorganisms play a significant role in the biodegradation of organic matter present in the wastewater. However, their presence also poses challenges for treatment and environmental management.

The BOD of the wastewater is a critical parameter that indicates the amount of biodegradable organic matter. High BOD levels suggest a high concentration of readily biodegradable substances,

which can be effectively treated using biological processes such as activated sludge or anaerobic digestion. However, the presence of recalcitrant organic compounds, such as lignin and chlorinated substances, can inhibit microbial activity and reduce the efficiency of biological treatment.

Pathogenic microorganisms may also be present in the wastewater, posing health risks to workers and downstream ecosystems. Effective disinfection methods, such as chlorination or UV treatment, are essential to mitigate these risks and ensure the safety of the treated effluent. Furthermore, the microbial community structure in the wastewater can vary significantly, influenced by factors such as the type of raw materials, production processes, and environmental conditions (Meyer & Edwards, 2014; Meyer et al., 2024).

6.2.4 Seasonal and process variability

The composition and characteristics of pulp and paper wastewater can exhibit significant seasonal and process variability, impacting the performance and efficiency of treatment systems. Seasonal variations are primarily driven by changes in raw material availability, production schedules, and environmental conditions.

For instance, during certain seasons, mills may switch to different types of wood or nonwood fibers, resulting in variations in the organic and inorganic constituents of the wastewater. These changes can affect the efficiency of treatment processes, necessitating adjustments in operational parameters and treatment strategies.

Process variability is another critical factor, as different stages of the pulping and papermaking processes generate wastewater with distinct characteristics. For example, the kraft pulping process produces highly alkaline wastewater with high lignin content, while mechanical pulping generates effluent with high concentrations of suspended solids and fibers. The use of different bleaching agents, such as chlorine, chlorine dioxide, or hydrogen peroxide, can also lead to variations in the chemical composition of the wastewater.

6.3 Physicochemical treatment methods

This section will provide an overview of physicochemical treatment methods, which will be described in full detail in the next sections. This introductory overview is aimed at describing the advantages and drawbacks of specific physicochemical technologies and at providing a comparison with the biological treatments.

6.3.1 Overview of physicochemical techniques

Physicochemical treatment methods encompass a spectrum of processes designed to remove contaminants from paper and pulp wastewater. These techniques leverage principles such as coagulation, flocculation, sedimentation, filtration, adsorption, and chemical precipitation. Coagulation involves destabilizing colloidal particles through the addition of coagulants, while flocculation promotes the agglomeration of destabilized particles into larger flocs. Sedimentation then facilitates the separation of these flocs from the water phase, with filtration providing additional polishing. Adsorption processes, utilizing activated carbon or other adsorbents, target dissolved organic compounds and colorants, whereas chemical precipitation precipitates dissolved ions. These methods can be tailored to efficiently address the complex composition of paper and pulp wastewater, offering robust treatment solutions.

[Table 6.1](#) below contains a simplified overview of the main physicochemical treatment methods for paper wastewater management, which will be described in full detail in the next paragraphs.

6.3.2 Comparison with biological treatment methods

In contrast to biological treatment methods, which rely on microbial activity to degrade organic matter, physicochemical methods excel in handling high-strength and variable wastewater streams typical of the paper and pulp industries. Physicochemical treatments are particularly effective in removing nonbiodegradable pollutants such as lignin derivatives and dyes, which are challenging for biological systems. While biological processes require longer retention times and are sensitive to fluctuations in pH and temperature, physicochemical methods offer rapid treatment and are less affected by variations in wastewater characteristics. Moreover, physicochemical treatments often produce sludge that is easier to dewater and manage compared to the biomass generated in biological systems. However, the energy-intensive nature and the requirement for chemical inputs in physicochemical treatments necessitate careful consideration of operational costs and environmental impacts. Selecting between physicochemical and biological methods depends on specific wastewater characteristics, regulatory requirements, and sustainability goals, highlighting the importance of integrated approaches in wastewater management for the paper and pulp industry. It is also worth mentioning that physicochemical and biological methods can be integrated together in hybrid systems, as described in [Section 6.11](#).

Table 6.1 Overview of paper and pulp wastewater physicochemical treatment methods.

Technique	Description	Advantages	Drawbacks
Coagulation	Addition of coagulants (e.g., aluminum sulfate and ferric chloride) to destabilize colloidal particles and promote aggregation.	– Effective in removing colloidal particles and some dissolved organics. – Can improve subsequent filtration processes. – Generally, fast process. – Compatible with other treatment methods.	– Requires careful dosing to avoid overdosing. – Generates sludge that requires disposal. – Chemical cost and handling considerations.
Flocculation	Gentle mixing to promote the formation of larger, settleable flocs from destabilized particles through the addition of flocculants (e.g., polymers).	– Enhances settleability of particles, improving sedimentation efficiency. – Reduces suspended solids and turbidity. – Can be tailored to specific wastewater characteristics.	– Requires energy for mixing. – Polymer selection is critical for effectiveness. – Sludge production and disposal are required.
Sedimentation	Gravity-driven separation of flocs and solids from water by allowing them to settle in a clarifier or sedimentation tank.	– Removes settleable solids effectively. – Simple operation and maintenance. – Can handle high hydraulic loads.	– Large footprint required. – Efficiency is affected by hydraulic variations. – Sludge management and disposal are needed.
Filtration	Passage of water through media (e.g., sand and activated carbon) to remove residual suspended solids and impurities after sedimentation.	– High removal efficiency for particulate matter. – Polishing step improves water quality. – Can be automated for continuous operation.	– Requires frequent backwashing and media replacement. – Energy-intensive for pumping. – Initial setup and maintenance costs.

(Continued)

Table 6.1 (Continued)

Technique	Description	Advantages	Drawbacks
Adsorption	Use of adsorbents (e.g., activated carbon and zeolites) to capture dissolved organic compounds, colorants, and other contaminants from wastewater.	– Highly effective in removing specific organic pollutants. – Versatile for treating various contaminants. – Regeneration potential for some adsorbents.	– Adsorbent cost and disposal of spent adsorbent. – Limited capacity for high-volume wastewater streams. – Adsorbent regeneration can be complex.
Chemical precipitation	Addition of chemicals (e.g., lime and alum) to precipitate dissolved ions (e.g., phosphates and heavy metals) as insoluble solids for subsequent removal by sedimentation.	– Effective in removing dissolved metals and phosphates. – Can improve effluent quality significantly. – Often used for targeted pollutant removal.	– Chemical handling and storage requirements. – pH adjustment needed. – Sludge disposal and management challenges. – Potential for residual chemical presence.

6.4 Coagulation and flocculation

This section will describe the application of coagulation and flocculation technologies to pulp and paper wastewater treatment. After a general description of principles and mechanisms, a focus will be provided on the most common additives and on the optimization.

6.4.1 Principles and mechanisms

Coagulation and flocculation are fundamental processes in the physicochemical treatment of paper and pulp wastewater, crucial for the removal of suspended solids, organic matter, and colorants.

These processes involve the addition of chemicals to destabilize and aggregate particles, facilitating their separation from the wastewater matrix.

Coagulation initiates the treatment process by neutralizing the electrostatic charges of suspended colloidal particles. Common coagulants such as aluminum sulfate (alum) and ferric chloride are added to the wastewater. These coagulants dissociate in water to form positively charged metal ions (e.g., Al^{3+} and Fe^{3+}), which neutralize the negatively charged surfaces of colloids. This neutralization reduces the repulsive forces between particles, causing them to coalesce and form larger aggregates known as microflocs.

Flocculation follows coagulation and involves gentle mixing to enhance the formation of larger, macroscopic flocs from the destabilized microflocs. Flocculants, typically high-molecular-weight polymers like polyacrylamide (PAM) or polyaluminum chloride (PAC), are added to aid particle aggregation. These polymers adsorb onto the surfaces of the microflocs, bridging them together to form larger, settleable flocs (Gholami et al., 2022). The process of flocculation requires controlled mixing to ensure effective collision and attachment of particles, promoting the growth of flocs of sufficient size and density for subsequent separation.

6.4.2 Common coagulants and flocculants

The most common flocculation agents are listed in Table 6.2, with a short description of their effects and a simplified overview of their advantages and disadvantages.

6.4.3 Process parameters and optimization

Optimizing coagulation and flocculation processes is crucial for achieving effective treatment of paper and pulp wastewater, ensuring high removal efficiencies of suspended solids, organic compounds, and colorants. Several key parameters and factors influence the performance and efficiency of these physicochemical processes. Continuous monitoring of these parameters, coupled with proactive adjustments based on real-time data and laboratory analysis, allows operators to optimize coagulation and flocculation processes effectively, reduce operational costs, minimize chemical usage, and ensure compliance with regulatory standards for discharged effluent (Birjandi et al., 2016).

pH: It plays a critical role in coagulation and flocculation processes, as it affects the speciation and charge of both the contaminants and the coagulant/flocculant chemicals. For instance, aluminum-based coagulants like alum typically work optimally in the pH range from 5.5 to 8.5, where they form

Table 6.2 Common coagulants and flocculants for paper and pulp wastewater treatment.

Agent	Effect	Advantages	Drawbacks
Aluminum sulfate	Destabilizes colloids, aids in coagulation	– Effective for wide pH range. – Reduces turbidity and color. – Cost-effective.	– pH adjustment may be necessary. – Generates significant sludge. – Potential for residual aluminum.
Ferric chloride	Rapid coagulation and phosphorus removal	– Effective at low doses. – Suitable for phosphorus removal. – Less impact on pH compared to alum.	– Higher chemical cost. – Handling and storage challenges. – May increase chloride levels in effluent.
Polymers (e.g., PAC)	Enhances flocculation	– Improves settleability of flocs. – Effective in low turbidity waters. – Reduces sludge volume.	– Polymer selection is critical. – Can be expensive. – Potential for residual monomers in effluent.
Polyacrylamide (PAM)	Improves floc formation and settling	– Enhances particle removal efficiency. – Reduces sludge production. – Works well in diverse wastewater.	– Requires precise dosing. – Long-term environmental impacts. – High initial cost.

hydrolyzed species that neutralize the negative charges on colloidal particles. Ferric salts, another common coagulant, are effective at a lower pH range but can raise the chloride concentration in the effluent, necessitating careful pH control.

Coagulant/flocculant dosage: The amount of coagulant and flocculant added is critical for achieving efficient particle destabilization and floc formation. Overdosing can lead to increased chemical costs, residual chemical presence in the effluent, and the generation of excess sludge. Underdosing, on the contrary, can result in incomplete particle removal and compromised water quality. Dosage requirements vary depending on the type and concentration of contaminants present in the wastewater, necessitating frequent monitoring and adjustment.

Mixing intensity and duration: Proper mixing during flocculation is essential to promote the collision and attachment of destabilized particles, facilitating the formation of larger flocs. Gentle mixing ensures uniform distribution of the coagulant and flocculant throughout the wastewater, while excessive mixing can lead to floc breakage or poor settling. Optimizing mixing intensity and duration helps achieve the desired floc size and density for effective sedimentation or filtration.

Temperature: It influences the reaction kinetics of coagulation and flocculation processes. Warmer temperatures generally accelerate chemical reactions and enhance mixing efficiency but can also affect the viscosity and solubility of chemicals and the stability of formed flocs. Temperature control is crucial to maintaining process stability and consistency in treatment performance, especially in seasonal climates where water temperature variations are significant.

Wastewater characteristics: Understanding the specific composition and characteristics of paper and pulp wastewater is essential for optimizing coagulation and flocculation processes. Factors such as the concentration of suspended solids, organic content, colorants, and variability in wastewater flow rates dictate the selection of appropriate chemicals and the adjustment of process parameters to ensure consistent and effective treatment.

6.5 Sedimentation and clarification

This section is focused on sedimentation and clarification, describing the underlying principles and mechanisms, with a special focus on equipment and design and on efficiency factors.

6.5.1 Basic principles

Sedimentation and clarification are common processes in the treatment of paper and pulp wastewater, very useful and efficient for the removal of suspended solids and particulate matter following coagulation and flocculation. Sedimentation involves the gravity-driven settling of solid particles from the wastewater, allowing for their separation and removal. This process is predicated on the principle that particles with a higher density than the surrounding water will settle to the bottom of a sedimentation basin or clarifier over time. The efficiency of sedimentation is influenced by particle size, shape, and density, as well as the viscosity and flow characteristics of the wastewater. Larger and denser particles settle more rapidly compared to smaller and lighter ones. To enhance sedimentation, prior treatment steps such as coagulation and

flocculation are employed to form larger, denser flocs from smaller colloidal particles, thereby improving their settleability. Clarification is the process of separating the settled solids (sludge) from the clarified water. In a clarifier the settled sludge is collected at the bottom and removed periodically, while the clarified effluent overflows from the top or is drawn from a specific zone designed to minimize disturbance and ensure the highest quality effluent.

6.5.2 Equipment and design considerations

Sedimentation and clarification technologies are particularly useful in scenarios where the wastewater contains significant amounts of suspended solids, colloidal particles, and flocculated material. These processes are highly effective in removing particulate matter that has been aggregated through prior coagulation and flocculation steps, making them ideal for industries like paper and pulp, where such contaminants are prevalent. They are also advantageous in situations requiring robust, high-throughput treatment systems, as they can handle large volumes of wastewater with relatively low operational costs and energy requirements. Furthermore, sedimentation and clarification provide a straightforward, gravity-driven approach that can be integrated into various treatment schemes, enhancing overall process flexibility. However, these technologies are less favored in situations where the wastewater contains high concentrations of dissolved organic compounds, oils, greases, or very fine colloidal particles that do not readily settle. In such cases, additional treatments like AOPs, dissolved air flotation, or membrane filtration may be required to achieve the desired effluent quality. Sedimentation and clarification can also be less effective in cold climates, where lower temperatures increase water viscosity and reduce settling efficiency. Additionally, the generation and management of sludge, which requires further treatment and disposal, can be a significant drawback. Therefore, while sedimentation and clarification are invaluable in many contexts, their application must be carefully evaluated against specific wastewater characteristics and treatment goals to determine their suitability and effectiveness within a comprehensive treatment strategy.

The design and selection of sedimentation and clarification equipment are critical for achieving efficient solid–liquid separation in the treatment of paper and pulp wastewater (Han et al., 2021). Common equipment includes rectangular and circular sedimentation tanks, clarifiers, and lamella separators.

- **Rectangular sedimentation tanks:** These tanks are characterized by their long, narrow shape, which allows wastewater to flow

horizontally. They are equipped with baffles to distribute the flow evenly and reduce turbulence. Sludge is collected at the bottom and removed via mechanical scrapers.

- **Circular clarifiers:** They have a central feed well that distributes the wastewater radially, promoting uniform flow and reducing short-circuiting. The settled sludge is scraped toward a central hopper for removal. These clarifiers are often preferred for their efficient hydraulic performance and ease of sludge removal.
- **Lamella separators:** These, or inclined plate settlers, use a series of inclined plates to increase the effective settling area. Wastewater flows upward between the plates, allowing solids to settle onto the plates and slide down to a collection area. This design is compact and offers high settling efficiency in a smaller footprint.

When designing sedimentation and clarification systems, several factors must be considered, as described in [Table 6.3](#). Recommended ranges are based on [Vieira et al. \(2022\)](#) and [Riffat and Husnain \(2022\)](#).

6.5.3 Efficiency factors

Several factors influence the efficiency of sedimentation and clarification processes in treating paper and pulp wastewater ([Zhou et al., 2020](#)):

- **Particle characteristics:** The size, shape, and density of particles influence their settling velocity. Flocculated particles, being larger and denser, settle more rapidly compared to smaller colloidal particles.

Table 6.3 Operating parameters for paper and pulp wastewater sedimentation and clarification.

Parameter	Effect	Typically recommended range
Surface loading rate	Influences the size and efficiency of the clarifier. Lower rates result in better settling performance.	1–3 m ³ /m ² /h
Detention time	Affects the extent of particle settling. Longer times allow more particles to settle but require larger tanks.	2–4 h
Sludge removal mechanism	Prevents accumulation of sludge, which can reduce tank volume and degrade performance.	Continuous or periodic removal using mechanical scrapers or suction devices
Flow distribution	Ensures uniform flow to avoid dead zones and short-circuiting, enhancing settling efficiency.	Achieved through the use of baffles and other flow control structures

- **Wastewater flow rate:** High flow rates can lead to turbulence and reduced settling efficiency. Controlling the flow rate to maintain optimal hydraulic conditions is essential for effective sedimentation.
- **Temperature:** It affects the viscosity of water and the settling velocity of particles. Higher temperatures reduce water viscosity, enhancing particle settling, whereas lower temperatures increase viscosity, hindering settling.
- **Chemical conditioning:** The use of coagulants and flocculants improves particle agglomeration, forming larger flocs that settle more efficiently. The type and dosage of chemicals must be optimized based on wastewater characteristics.
- **Tank geometry:** The shape and size of sedimentation tanks or clarifiers impact flow patterns and settling efficiency. Rectangular tanks promote horizontal flow, while circular clarifiers facilitate radial flow, each with its own advantages.

Finally, it is also worth mentioning the importance of sludge management. Regular and efficient removal of settled sludge is crucial to maintain the effective volume of the sedimentation tank or clarifier. Accumulated sludge can lead to resuspension of settled particles, reducing overall efficiency.

6.6 Filtration techniques

This section will describe the treatment of pulp and paper wastewater by means of filtration technologies, including the different forms of filtration mechanisms. Sand, multimedia, and membrane filtration are compared, with an analysis of different polymers. Finally, operational parameters are discussed.

6.6.1 Mechanisms of filtration

Filtration is highly useful in the treatment of paper and pulp wastewater, particularly when a high degree of clarity and removal of fine particulates, colloidal substances, and residual flocs is required. It serves as an effective polishing step following primary treatment processes like coagulation, flocculation, and sedimentation. Filtration is beneficial in achieving low turbidity levels and removing fine suspended solids that other treatment methods may leave behind. This makes it essential for processes where high-quality effluent is necessary for reuse or discharge into sensitive environments. However, filtration can be less favored in certain conditions. High operational and maintenance costs, especially for advanced filtration systems like membranes, can be a drawback. Filtration systems can

also be sensitive to influent quality; high concentrations of suspended solids or organic matter can lead to rapid fouling and reduced efficiency, necessitating frequent cleaning or replacement of filter media. Additionally, for very large volumes of wastewater, filtration may not be cost-effective as a primary treatment method due to the significant infrastructure and operational requirements. In such cases, it is typically employed as a secondary or tertiary treatment step following more cost-effective bulk solid removal processes. Filtration mechanisms vary depending on the type of filtration technology used (Haq et al., 2020; Hube et al., 2020; Jiang et al., 2020) but generally involve several common processes:

- **Mechanical straining:** This is the primary mechanism in granular media filtration, where particles larger than the pore spaces of the filter media are physically trapped and removed from the water. Sand and multimedia filters primarily rely on this mechanism.
- **Adsorption:** In granular media filters, fine particles and dissolved substances can adhere to the surface of the filter media through physical and chemical interactions. This process enhances the removal of smaller particles and some dissolved contaminants. Next paragraph 7 will describe this process in more detail.
- **Cake filtration:** As particles accumulate on the surface of the filter media, they form a layer or “cake” that acts as an additional filter, trapping more particles. This mechanism is common in membrane filtration and enhances the removal efficiency over time.
- **Diffusion and interception:** Fine particles in the water can be removed as they diffuse and are intercepted by the filter media or the cake layer. This mechanism is particularly important in membrane filtration, where smaller pores are involved.
- **Electrostatic attraction:** Some filters, particularly those with charged media or membranes, can remove particles and dissolved substances through electrostatic attraction. This mechanism is effective for removing colloidal particles and dissolved ions.
- **Sieving:** Membrane filters primarily use sieving, where particles larger than the pore size of the membrane are physically blocked and removed from the water. This mechanism provides high removal efficiency for fine particles and microorganisms.

6.6.2 Types of filtration

Table 6.4 summarizes the most common filtration technologies.

As for the membrane filtration, in the treatment of paper and pulp wastewater, polyethersulfone (PES) membranes are among the most commonly used, despite membrane technology is undergoing rapid innovation (Bera et al., 2022; Hube et al., 2020; Xiang et al., 2022). This preference is due to several key factors, including high mechanical

Table 6.4 Overview of paper and pulp wastewater filtration types.

Filtration type	Technology description	Advantages	Drawbacks
Sand filtration	Utilizes a bed of sand to trap particles as water flows through it.	Simple, cost-effective, and suitable for removing suspended solids and turbidity.	Requires regular backwashing; less effective for very fine particles or dissolved contaminants.
Multimedia filtration	Employs multiple layers of granular materials (sand, anthracite, and gravel) with varying densities and sizes.	Provides higher flow rates and longer filter runs; effective for removing a range of particle sizes.	Requires periodic backwashing; less effective with high organic content.
Membrane filtration	Uses semipermeable membranes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) to separate contaminants.	Highly effective for removing fine particulates, bacteria, viruses, and dissolved substances; produces high-quality effluent.	More complex and expensive to install and operate; sensitive to fouling, requiring regular maintenance.

strength, chemical and thermal resistance, and optimal hydrophobicity. Indeed, PES membranes can withstand the rigorous conditions often present in paper and pulp wastewater treatment, including high solids content and abrasive particles, and are resistant to a wide range of chemicals, which is important in the paper industry, where various chemical additives and residuals might be present in the wastewater. Hydrophilicity makes PES membranes less prone to fouling, a significant advantage in dealing with the complex mixtures of organic and inorganic substances found in paper and pulp wastewater. Potential alternatives to PES are as follows:

- Polyvinylidene Fluoride (PVDF): These membranes are highly resistant to chemicals, thermal degradation, and oxidation. They have excellent mechanical properties and are widely used in applications requiring durability and resistance to harsh conditions.
- Polysulfone (PSF): These membranes are known for their toughness, high-temperature resistance, and chemical stability. They are hydrophobic, which can lead to fouling issues, but they provide good filtration performance for a range of applications.
- Polyamide (PA): These membranes, often used in reverse osmosis, are valued for their excellent salt rejection and high-flux rates.

They have good mechanical strength and resistance to a variety of chemicals, although they can be sensitive to chlorine.

- **Cellulose Acetate (CA):** These membranes are hydrophilic and provide good resistance to fouling. They are less chemically resistant than synthetic polymers and are susceptible to hydrolysis at extreme pH levels, but they offer good filtration properties for specific applications like water treatment.

6.6.3 Operational parameters

Due to the specific features of paper and pulp wastewater composition described in [Section 6.2](#), effective filtration in the treatment of paper and pulp wastewater requires careful consideration of several key operational parameters.

Flow rate: The flow rate of wastewater through the filter determines the contact time between the water and the filter media. In paper and pulp wastewater treatment the flow rate must be optimized to balance filtration efficiency and operational capacity. Higher flow rates can reduce the effectiveness of contaminant removal, leading to lower effluent quality. Conversely, lower flow rates increase contact time, enhancing filtration performance but potentially reducing the overall throughput. Typically, flow rates for sand and multimedia filters range from 5 to 15 m³/m²/h, while membrane filtration systems operate at lower rates to ensure effective separation.

Backwashing frequency: It directly affects the performance of granular media filters, since paper and pulp wastewater can contain high levels of suspended solids and organic matter, leading to rapid clogging of the filter media. Regular backwashing removes accumulated particles and prevents filter bed compaction. The frequency of backwashing depends on the influent quality and the filter media type. For instance, sand and multimedia filters may require backwashing every 24–72 hours, depending on the solids load.

Filter media characteristics: Finer media provide better removal of small particles and colloidal substances but may require more frequent backwashing. Coarser media allow higher flow rates and longer filter runs but might be less effective for fine particle removal. Common filter media include silica sand, anthracite, and garnet in multimedia filters, each selected based on specific wastewater characteristics.

Pressure drop: Monitoring the pressure drop across the filter allows both detecting clogging and scheduling maintenance. A higher pressure drop indicates that the filter media is becoming clogged with particles, necessitating backwashing or media replacement. In paper and pulp wastewater treatment, maintaining an optimal pressure drop is crucial to prevent excessive energy consumption and ensure consistent filter performance. Typically, a pressure drop of 0.5 to

2.0 bar is maintained across membrane filtration systems, while granular media filters operate within a lower range of 0.1 to 0.5 bar.

Together with process monitoring, feedstock monitoring is also particularly important in filtration technology. The characteristics of the influent water, including turbidity, suspended solids concentration, and organic content, significantly impact the filtration process. Paper and pulp wastewater often contains high levels of organic matter, fibers, and chemical additives. Pretreatment processes like coagulation and flocculation can improve the influent quality by aggregating fine particles and reducing the load on the filtration system. Effective pretreatment enhances filtration efficiency and extends the filter media's lifespan.

6.7 Adsorption methods

In this section an overview of adsorption methods is provided.

Adsorption is a valuable method in wastewater treatment, particularly in the paper and pulp industry, where it is effective in removing specific contaminants that are challenging to treat by conventional methods (Rathi & Kumar, 2021). Adsorption isotherms describe the equilibrium relationship between the concentration of a solute in the liquid phase and its concentration on the surface of a solid adsorbent at a constant temperature. The two most commonly used adsorption isotherms are the Langmuir and the Freundlich isotherms.

- **Langmuir isotherm:** It assumes a monolayer adsorption on a homogeneous surface with a finite number of identical sites. It is expressed as $q/C = 1/b + q_{\max}/B$, where q is the amount of solute adsorbed per unit weight of adsorbent, C is the equilibrium concentration of the solute in the liquid phase, $q_{\max}$ is the maximum adsorption capacity, and b is the Langmuir constant related to the energy of adsorption.
- **Freundlich isotherm:** It describes multilayer adsorption on a heterogeneous surface with sites of varying energies. It is represented as $q/C = K_F \cdot C^{1/n}$, where K_F and $1/n$ are Freundlich constants related to adsorption capacity and intensity, respectively.

Adsorption is highly effective when dealing with wastewater containing low to moderate concentrations of organic compounds, heavy metals, and dyes. It can achieve high removal efficiencies for these pollutants, producing treated effluent that meets stringent discharge regulations or can be safely reused within the production process. Adsorption is particularly advantageous for targeting specific contaminants due to the selective affinity of adsorbents like activated carbon, zeolites, and char toward certain molecules.

In industries such as paper and pulp, where wastewater composition can vary widely depending on the production processes and raw materials used, adsorption offers versatility. It can be applied as a standalone treatment or as part of a polishing step following primary treatment processes like sedimentation or biological treatment. Moreover, adsorption processes are typically robust and can operate effectively over a wide range of pH and temperature conditions, making them adaptable to diverse wastewater characteristics.

Adsorption may be less favored in scenarios where the wastewater contains high concentrations of contaminants or where the pollutants are not effectively adsorbed by available adsorbents. For instance, adsorption can be less efficient for treating wastewater with highly soluble organic compounds or dissolved ions that do not readily bind to adsorbent surfaces. In such cases, other treatment methods like AOPs or membrane filtration may be more suitable for achieving the required effluent quality. Additionally, adsorption processes can be cost-intensive, particularly when high-capacity adsorbents like activated carbon are used, and when frequent regeneration or replacement of the adsorbent is necessary. The operational costs associated with adsorption, including energy consumption for regeneration and disposal of spent adsorbents, can make it less economically viable compared to alternative treatment technologies in certain industrial applications.

Therefore, while adsorption remains a valuable tool for wastewater treatment in the paper and pulp industry, its application should be carefully evaluated based on the specific characteristics of the wastewater and the treatment goals to ensure optimal efficiency and cost-effectiveness.

Zeolites and char are the most commonly used adsorbents.

- **Zeolites** are crystalline aluminosilicates with a porous structure and high surface area, making them effective adsorbents for various contaminants in paper and pulp wastewater. Their ion exchange capacity and selective adsorption properties make them suitable for removing heavy metals, organic compounds, and colorants from effluents. In the paper and pulp industry, zeolites can be used in fixed-bed columns or batch reactors to treat wastewater before discharge or reuse. Their stability and recyclability make them economically viable for continuous treatment processes (Magalhães et al., 2022; Rad & Anbia, 2021).
- **Char** (activated carbon derived from charred biomass or coal) is widely used in the paper and pulp industry for adsorbing organic contaminants, colorants, and odorous compounds from wastewater. Char adsorption is effective due to its high surface area and microporous structure, which provide numerous adsorption sites. It is applied in both powdered and granular forms, often in filtration

beds or as part of a multistage treatment process. However, its effectiveness can be influenced by the presence of inorganic compounds and its susceptibility to fouling, requiring periodic regeneration or replacement (Lewoyehu, 2021; Wang et al., 2021).

In addition to zeolites and activated carbon, other adsorbents such as clay minerals, biosorbents (e.g., agricultural wastes and algae), and polymeric resins are used in the paper and pulp industry for specific applications (Chai et al., 2021). Clay minerals like bentonite and kaolinite are valued for their ion exchange capacity and cost-effectiveness. Biosorbents offer environmentally friendly alternatives and can be tailored for the selective removal of specific contaminants. Polymeric resins provide high selectivity and are used in specialized processes where precise control over adsorption and desorption is required. These diverse adsorbents contribute to sustainable wastewater treatment practices in the paper and pulp industry, addressing varying contaminant profiles and regulatory requirements efficiently.

6.8 Advanced oxidation processes

This section will describe the application of oxidation processes to pulp and paper wastewater treatment. AOPs involve the generation of highly reactive hydroxyl radicals ($\bullet\text{OH}$) through chemical or photochemical reactions. These radicals are capable of oxidizing and decomposing organic pollutants into harmless products like water and carbon dioxide. AOPs are characterized by their ability to mineralize organic compounds rather than merely transferring them to a different phase.

AOPs are highly effective for treating recalcitrant organic pollutants in wastewater, including those found in the paper and pulp industry. They are particularly useful when dealing with complex wastewater streams containing persistent organic compounds, colorants, and toxic substances. AOPs can achieve significant removal efficiencies by generating highly reactive hydroxyl radicals ($\bullet\text{OH}$) or other oxidizing species capable of breaking down these contaminants into simpler, less harmful by-products. This makes AOPs suitable for achieving stringent effluent quality standards and for treating wastewater for reuse purposes.

However, AOPs may not be efficient in treating large volumes of wastewater or in scenarios where the contaminants are present at very low concentrations. The high energy requirements and operational costs associated with AOPs, such as the use of ozone or UV radiation, can make them economically impractical for continuous large-scale treatment. Additionally, the effectiveness of AOPs can be influenced by water quality parameters, such as pH, temperature, and the presence of organic and inorganic constituents, which may require careful optimization and monitoring.

6.8.1 Types of advanced oxidation processes

Table 6.5 summarizes the different types of AOPs, based on the chemical intermediate used to generate the hydroxy radical.

Table 6.5 Overview of advanced oxidation processes for paper and pulp wastewater treatment.

Name	Description	Advantages	Drawbacks	Recommended operational conditions
Ozone	Ozone (O_3) is a strong oxidant generated on-site and injected into wastewater to oxidize organic contaminants.	Effective against a wide range of organic pollutants; no residual chemicals in treated water.	High operational costs; requires careful handling due to toxicity; limited solubility in water.	pH: 6–8; temperature: 15°C–25°C; contact time: 10–30 min.
UV radiation	UV light (254 nm) produces hydroxyl radicals ($\bullet OH$) in water, which oxidize organic pollutants.	Rapid treatment; no chemical addition; effective for micropollutants.	Limited penetration depth; potential need for pretreatment to reduce turbidity.	Low turbidity; direct sunlight exposure; short contact time.
Fenton's reaction	Involves the catalytic decomposition of hydrogen peroxide (H_2O_2) with ferrous ions (Fe^{2+}) to produce hydroxyl radicals.	Effective for treating refractory organic pollutants; operates under ambient conditions.	High chemical consumption; generates sludge requiring disposal.	pH: 3–5; Fe^{2+} concentration: 1–10 mM; H_2O_2 concentration: 10–100 mM.
Photocatalysis	Uses semiconductors (e.g., TiO_2) activated by UV light to generate electron-hole pairs, producing $\bullet OH$ radicals.	Degrades a wide range of pollutants; operates under ambient conditions.	Limited by catalyst availability and efficiency; potential catalyst deactivation.	Near-neutral pH; UV or visible light irradiation; catalyst loading: 0.1–1 g/L.

Table 6.6 Operational parameters for advanced oxidation of paper and pulp wastewater.

Parameter	Effect	Recommended range
pH	Influences the generation and stability of hydroxyl radicals ($\bullet\text{OH}$) and the efficiency of oxidation reactions.	2–9 (depending on the AOP type)
Temperature	Affects reaction kinetics and the stability of oxidizing species.	Ambient to moderate (15°C – 35°C)
Hydrogen peroxide (H_2O_2)	Concentration of H_2O_2 influences the rate of hydroxyl radical generation in Fenton's reaction.	10–100 mM (for Fenton's reaction)
Contact time	Duration of exposure between contaminants and oxidizing species affects treatment efficiency.	Varies (typically minutes to hours)
UV intensity	Directly impacts the generation of hydroxyl radicals in UV-based AOPs.	High intensity (254 nm for UV AOPs)

Notes: AOP, Advanced oxidation process.

6.8.2 Operational parameters and efficiency

Table 6.6 outlines key operational parameters critical for optimizing AOPs in treating paper and pulp wastewater.

6.9 Chemical precipitation

This section aims to describe the application of chemical precipitation to pulp and paper wastewater management. The section provides a description of the chemical principles and main chemical reactions and includes a focus on process design and parameter optimization.

6.9.1 Mechanisms and chemistry

Chemical precipitation is a widely used method for removing dissolved metals and other contaminants from wastewater in various industries, including pulp and paper production. It involves adding chemicals that react with dissolved ions to form insoluble precipitates, which can then be separated from the water (Mainardis et al., 2020; Ribeiro et al., 2020). Involved mechanisms are summarized as follows:

- **Complexation and hydrolysis:** Many metal ions in wastewater exist in soluble forms due to complexation with ligands or as hydrolyzed species. By adjusting the pH and adding suitable chemicals, such as hydroxides or sulfides, these complexed ions can be destabilized. This leads to the formation of insoluble hydroxides [e.g., $\text{Fe}(\text{OH})_3$] or sulfides (e.g., PbS), which precipitate out of solution.

- Redox reactions: Some metal ions undergo oxidation-reduction (redox) reactions during chemical precipitation. For instance, in Fenton's reaction, ferrous ions (Fe^{2+}) react with hydrogen peroxide (H_2O_2) to form hydroxyl radicals ($\bullet\text{OH}$) and ferric ions (Fe^{3+}). The hydroxyl radicals then oxidize organic contaminants while simultaneously promoting the precipitation of metals like chromium and arsenic as their hydroxides.
- Formation of metal hydroxides: The addition of hydroxide ions (OH^-) or alkalis like lime ($\text{Ca}(\text{OH})_2$) raises the pH of wastewater. This causes metal ions such as aluminum, iron, and manganese to precipitate as their respective hydroxides.
- Formation of metal sulfides: Sodium sulfide (Na_2S) or hydrogen sulfide gas (H_2S) can be used to precipitate metals like lead, cadmium, and zinc as insoluble sulfides.

Common precipitating agents are listed below in [Table 6.7](#), together with an overview of their effects, advantages, and drawbacks.

6.9.2 Design and operational considerations

Chemical precipitation is effective in treating wastewater streams with high concentrations of metals, such as copper, zinc, and lead, which can form stable precipitates with suitable chemical agents. It is particularly useful in industries like paper and pulp, where effluents often contain elevated levels of these metals due to additives and

Table 6.7 Precipitating agents for paper and pulp wastewater.

Name/ Formula	Effect	Advantages	Drawbacks
Lime ($\text{Ca}(\text{OH})_2$)	Precipitates metals as hydroxides [e.g., $\text{Fe}(\text{OH})_3$]	Cost-effective; raises pH for subsequent treatment	High pH requirements; sludge disposal
Sodium hydroxide (NaOH)	Raises pH and precipitates metals as hydroxides	Effective for large-scale operations	High chemical cost; pH adjustment needed
Sodium sulfide (Na_2S)	Precipitates metals as sulfides (e.g., PbS)	Low cost; effective for sulfide-forming metals	Toxicity concerns; odor issues
Sodium carbonate (Na_2CO_3)	Precipitates metals as carbonates (e.g., CaCO_3)	Raises pH; effective for calcium and magnesium removal	Limited effectiveness for other metals; pH control

processing chemicals. Precipitation can significantly reduce metal concentrations to meet discharge limits and facilitate further treatment processes. Chemical precipitation may be less efficient for treating wastewater with low metal concentrations or where metals are present in complex forms that are not easily precipitated. In such cases, additional treatment methods like adsorption or membrane filtration may be required for effective removal. Moreover, the effectiveness of chemical precipitation can be influenced by factors such as pH, temperature, and the presence of interfering substances, which may require careful optimization and monitoring to achieve desired results cost-effectively (Ribeiro et al., 2020; Wu, 2022). The following factors should be considered:

- **pH control:** Maintaining precise pH conditions is critical for optimizing the precipitation of metals as hydroxides, sulfides, or carbonates. In pulp and paper wastewater, which can vary in pH due to different stages of production and chemical additives, controlling pH within the optimal range (typically pH 6.5–9.0) ensures efficient removal of contaminants without causing excessive chemical usage or compromising treatment performance.
- **Chemical selection and dosage:** Choosing the appropriate precipitating agent depends on the specific contaminants present in the wastewater. Commonly used chemicals such as lime ($\text{Ca}(\text{OH})_2$), sodium hydroxide (NaOH), sodium sulfide (Na_2S), and sodium carbonate (Na_2CO_3) each have distinct advantages and recommended concentrations based on the target metals and wastewater characteristics. For example, lime is effective for precipitating metals like iron and aluminum, while sodium sulfide is suitable for sulfide-forming metals such as lead and cadmium.
- **Mixing and reaction time:** Adequate mixing ensures uniform distribution of chemicals and enhances contact between contaminants and precipitating agents. Efficient mixing is crucial in pulp and paper wastewater treatment to achieve rapid and thorough reaction kinetics, minimizing chemical usage and optimizing the formation of insoluble precipitates. Additionally, sufficient reaction time allows for complete precipitation of metals and facilitates the settling of precipitates, which is essential for subsequent separation processes like sedimentation or filtration.

6.10 Electrochemical treatment methods

This section reports the principles and applications of electrochemical treatment methods: in particular, electrocoagulation and electrooxidation are described, including their equipment, operational parameters, and advantages.

6.10.1 Electrocoagulation

Electrocoagulation (EC) is an electrochemical process used extensively for the treatment of industrial wastewater, including that from the pulp and paper industry. It involves the generation of coagulant species directly in the wastewater through the application of an electric current across metal electrodes, typically made of aluminum or iron (Das et al., 2022; Tahreen et al., 2020). The mechanism involves the following steps:

- 1. Electrolysis of water:** When an electric current is applied to the electrodes submerged in water, water molecules undergo electrolysis, producing hydrogen gas (H_2) at the cathode and hydroxyl ions (OH^-), which increase the pH locally. At the anode, metal cations (such as Fe^{2+} or Al^{3+}) are released into the solution through oxidation reactions.
- 2. Formation of hydroxide flocs:** The metal cations generated at the anode hydrolyze in the alkaline environment created by the cathode's hydrogen evolution. For instance: $Fe^{2+} + 2 OH^- \rightarrow Fe(OH)_2$. These metal hydroxides further react to form larger and more oxidized flocs: $Fe(OH)_2 + Fe^{2+} + 2OH^- \rightarrow Fe(OH)_3$.
- 3. Floc formation and contaminant removal:** The metal hydroxide flocs formed are highly effective in destabilizing colloidal particles, emulsified oils, and organic matter, leading to their aggregation and subsequent sedimentation or filtration. This process also aids in the removal of heavy metals and other contaminants through adsorption onto the flocs.

EC is relatively simple to implement and can be highly effective at lower chemical dosages compared to traditional coagulation. It is effective across a wide range of pH levels and can treat various contaminants, including heavy metals, dyes, and organic compounds. The on-site generation of coagulants reduces the need for external chemicals, decreasing costs and minimizing chemical sludge production. Overall, electrocoagulation provides a powerful and flexible solution for the treatment of complex wastewater streams, making it particularly suited for the diverse and challenging wastewater characteristics of the pulp and paper industry.

6.10.2 Electrooxidation

Electrooxidation (EO) is an advanced electrochemical process used for the treatment of industrial wastewater, including applications in the pulp and paper industry. Unlike electrocoagulation, which focuses on coagulation and precipitation, electrooxidation employs direct oxidation reactions to degrade organic pollutants and oxidize inorganic contaminants present in wastewater. In

electrooxidation an electric current is applied to electrodes immersed in wastewater. Typically, the anode is made from materials like platinum, titanium, or graphite, which can withstand the harsh oxidative conditions. As the current passes through the wastewater, oxidation reactions occur at the anode surface, generating powerful oxidizing agents such as hydroxyl radicals ($\bullet\text{OH}$), ozone (O_3), and hydrogen peroxide (H_2O_2) (Divyapriya et al., 2021; Magnisali et al., 2022). The process involves the following steps:

1. **Hydroxyl radical formation:** The primary mechanism involves the generation of hydroxyl radicals ($\bullet\text{OH}$) through the electrolysis of water at the anode: $\text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{H}^+ + \text{e}^-$.
2. **Oxidation of contaminants:** Hydroxyl radicals are highly reactive species that rapidly oxidize organic pollutants, breaking down complex molecules into simpler, less harmful compounds.
3. **Generation of ozone and hydrogen peroxide:** Depending on the electrolysis conditions, ozone and hydrogen peroxide may also be produced, contributing further to the oxidation capacity of the process.

EO efficiently degrades a wide range of organic pollutants, including persistent compounds resistant to biological treatments. It operates without the need for additional chemicals, reducing operational costs and chemical handling risks, and can operate under various pH conditions, and is effective in treating complex wastewater compositions. In the pulp and paper industry, EO can effectively treat effluents containing lignin, dyes, and other organic contaminants. It complements traditional treatment methods by targeting difficult-to-treat pollutants, improving overall wastewater quality and compliance with environmental regulations. However, the process can be energy-intensive and requires careful monitoring of operational parameters to optimize treatment efficiency and minimize operational costs.

6.10.3 Equipment and operational parameters

Electrochemical treatment systems used in the pulp and paper industry typically consist of specialized equipment designed to facilitate electrocoagulation and electrooxidation processes. These systems include an electrolytic cell containing electrodes—usually made of materials like iron, aluminum, or graphite—that serve as both anodes and cathodes depending on the process requirements (Divyapriya et al., 2021; Mousset & Hatton, 2022). Optimization of operational parameters should include the following considerations:

- **Current density:** Adjusting the current density influences the rate of electrochemical reactions. Higher current densities increase the

production of coagulants (in electrocoagulation) or reactive oxygen species (in electrooxidation), enhancing treatment efficiency but also affecting energy consumption and electrode wear.

- **Electrode material:** The choice of electrode material affects the type and effectiveness of reactions occurring in the cell. For example, iron electrodes are effective in generating iron hydroxide coagulants in electrocoagulation, while graphite electrodes are commonly used for their stability and resistance to corrosion in electrooxidation processes.
- **Electrolyte concentration:** The concentration of electrolytes (e.g., sodium chloride or sulfuric acid) influences the conductivity of the electrolyte solution, which in turn affects the efficiency of electrochemical reactions and the conductivity of the wastewater.
- **Reaction time:** The duration of treatment (reaction time) allows sufficient contact between contaminants and the generated reactive species. This parameter is critical for achieving desired treatment outcomes, such as high removal efficiencies of pollutants.

6.10.4 Advantages and limitations

Electrochemical methods are highly versatile, capable of effectively treating a wide range of contaminants such as heavy metals, organic compounds, and colorants. They exhibit rapid treatment kinetics and high removal efficiencies, reducing overall treatment time and space requirements. Electrochemical processes also provide precise control over operational parameters, allowing for tailored treatment solutions that meet specific discharge standards. Importantly, they typically involve minimal chemical usage and produce fewer harmful by-products compared to conventional chemical treatment methods.

Despite their effectiveness, electrochemical methods have notable drawbacks. They tend to be energy-intensive, especially in electrooxidation processes, where significant electrical energy is required to generate reactive species like hydroxyl radicals or ozone. This high energy demand can lead to increased operational costs, which may be prohibitive for some facilities. Electrochemical systems also require careful maintenance and operational expertise to manage electrode fouling, scaling, and corrosion, which can impact treatment efficiency and longevity. Additionally, the initial capital investment for establishing electrochemical treatment facilities can be substantial, and scaling up from laboratory-scale to industrial applications may pose challenges due to variations in wastewater composition and flow rates.

While electrochemical treatment methods offer promising benefits for treating pulp and paper wastewater, including efficient

contaminant removal and environmental compatibility, their adoption should consider the specific operational and economic considerations to ensure sustainable and cost-effective wastewater treatment solutions.

6.11 Hybrid treatment systems

This section is a short overview of hybrid technologies and systems, integrating physicochemical and biological methods.

Hybrid treatment systems represent a synergistic approach to wastewater treatment by combining the strengths of physicochemical and biological methods. These integrated systems are increasingly recognized for their ability to achieve enhanced treatment efficiencies, robustness, and flexibility in managing complex wastewater streams, including those from the pulp and paper industry (Dhangar & Kumar, 2020; Jagaba et al., 2023; Khader et al., 2023).

By integrating physicochemical processes like coagulation, flocculation, and oxidation with biological processes such as activated sludge, membrane bioreactors, or constructed wetlands, hybrid systems can effectively target a broad spectrum of contaminants. Physicochemical methods excel at rapid and targeted removal of pollutants like heavy metals, colorants, and refractory organics, while biological processes excel at biodegradation and nutrient removal. Hybrid systems offer redundancy and resilience against fluctuations in wastewater characteristics and flow rates. Physicochemical processes can handle shock loads and sudden changes in influent composition, while biological processes provide stability and long-term treatment efficiency by adapting to gradual changes over time. Integrating physicochemical and biological treatments often results in superior effluent quality compared to standalone methods. This is crucial for meeting stringent discharge limits and environmental regulations, particularly in industries like pulp and paper, where effluents may contain complex and persistent contaminants.

Designing a successful hybrid treatment system involves careful consideration of several factors, including selecting physicochemical and biological processes that complement each other and operate synergistically; ensuring efficient integration of unit operations to maximize treatment efficiency and minimize operational costs; implementing robust monitoring and control strategies to optimize performance and ensure compliance with regulatory standards; and balancing the space requirements and capital costs associated with different treatment technologies to achieve cost-effective solutions.

6.12 Conclusions and future trends

The effective treatment of wastewater from the pulp and paper industry remains a pivotal challenge in environmental management and regulatory compliance. This chapter has provided a comprehensive exploration of various physicochemical treatment techniques essential for managing the complex characteristics of pulp and paper wastewater. Each method—coagulation and flocculation, sedimentation, clarification, filtration, adsorption, AOPs, chemical precipitation, and electrochemical methods—offers unique advantages in addressing specific contaminants and achieving desired effluent quality standards.

Physicochemical methods such as coagulation and flocculation excel in the rapid removal of suspended solids, colorants, and certain dissolved contaminants like heavy metals. These processes are crucial initial steps in wastewater treatment, preparing effluents for further biological degradation or advanced treatment methods. Sedimentation and clarification processes further refine effluents by separating settled solids from clarified water, essential for reducing turbidity and improving clarity before discharge.

Filtration techniques, including sand, multimedia, and membrane filtration, provide efficient means to remove fine particles and colloidal matter from wastewater, enhancing overall water quality. Adsorption methods utilizing materials like activated carbon, zeolites, and char are effective in capturing organic compounds, dyes, and other pollutants, contributing significantly to wastewater remediation efforts.

AOPs, such as ozone, UV radiation, Fenton's reaction, and photocatalysis, offer powerful oxidation capabilities for degrading recalcitrant organic pollutants and chemical contaminants. These processes are increasingly integrated into treatment schemes to achieve stringent effluent standards and address emerging contaminants in wastewater streams.

Chemical precipitation and electrochemical methods provide additional tools for treating wastewater, targeting specific ions and contaminants through controlled chemical reactions and electrooxidation processes. These methods are instrumental in removing heavy metals, phosphates, and other inorganic pollutants, complementing biological treatment strategies.

Hybrid treatment systems represent a promising approach by combining the strengths of physicochemical and biological methods, offering enhanced treatment efficiencies, resilience to fluctuating wastewater characteristics, and superior effluent quality. These integrated systems optimize contaminant removal while minimizing environmental impact and operational costs, making them increasingly favored in sustainable wastewater management practices.

Moving forward, continuous research and innovation in treatment technologies, process optimization, and operational strategies will be essential to meet evolving environmental regulations and sustainability goals. The pulp and paper industry must continue to prioritize investments in advanced treatment technologies, interdisciplinary collaborations, and regulatory compliance to mitigate its environmental footprint effectively. In conclusion, while challenges persist in managing pulp and paper wastewater, the integration of diverse physicochemical treatment methods, coupled with innovative hybrid approaches, provides a pathway toward sustainable water management practices. By advancing technological solutions and embracing environmental stewardship, the industry can achieve significant strides in environmental protection and resource conservation for future generations.

List of acronyms

AOPs	Advanced oxidation processes
BOD	Biological oxygen demand
COD	Chemical oxygen demand
EC	Electrocoagulation
EO	Electrooxidation
PAC	Polyaluminum chloride
PAM	Polyacrylamide
TDS	Total dissolved solids
UV	Ultraviolet

References

- Bera, S. P., Godhaniya, M., & Kothari, C. (2022). Emerging and advanced membrane technology for wastewater treatment: A review. *Journal of Basic Microbiology*, 62(3-4), 245-259. <https://doi.org/10.1002/jobm.202100259>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1521-4028](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1521-4028).
- Birjandi, N., Younesi, H., & Bahramifar, N. (2016). Treatment of wastewater effluents from paper-recycling plants by coagulation process and optimization of treatment conditions with response surface methodology. *Applied Water Science*, 6, 339-348.
- Cabrera, M. N. (2017). Pulp mill wastewater: Characteristics and treatment. *Biological Wastewater Treatment and Resource Recovery*, 2, 119-139.
- Chai, W. S., Cheun, J. Y., Kumar, P. S., Mubashir, M., Majeed, Z., Banat, F., Ho, S. H., & Show, P. L. (2021). A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application. *Journal of Cleaner Production*, 296, 126589. <https://doi.org/10.1016/j.jclepro.2021.126589>.
- Das, P. P., Sharma, M., & Purkait, M. K. (2022). Recent progress on electrocoagulation process for wastewater treatment: A review. *Separation and Purification Technology*, 292. <https://doi.org/10.1016/j.seppur.2022.121058>, <http://www.journals.elsevier.com/separation-and-purification-technology/>.

- Dhangar, K., & Kumar, M. (2020). Tricks and tracks in removal of emerging contaminants from the wastewater through hybrid treatment systems: A review. *Science of the Total Environment*, 738, 140320. <https://doi.org/10.1016/j.scitotenv.2020.140320>.
- Divyapriya, G., Scaria, J., Singh, T. A., Nidheesh, P. V., Babu, D. S., & Kumar, M. S. (2021). Advanced treatment of real wastewater effluents by an electrochemical approach. *Water Pollution and Remediation: Heavy Metals*, 85–122.
- Gholami, M., Ghaneian, M. T., Fatemi, S. S., Talebi, P., & Dalvand, A. (2022). Investigating the efficiency of coagulation and flocculation process in wastewater treatment of paper and cardboard recycling industry. *International Journal of Environmental Analytical Chemistry*, 102(17), 5860–5872. <https://doi.org/10.1080/03067319.2020.1804891>, <http://www.tandf.co.uk/journals/titles/03067319.asp>.
- Han, N., Zhang, J., Hoang, M., Gray, S., & Xie, Z. (2021). A review of process and wastewater reuse in the recycled paper industry. *Environmental Technology & Innovation*, 24, 101860. <https://doi.org/10.1016/j.eti.2021.101860>.
- Haq, I., Mazumder, P., & Kalamdhad, A. S. (2020). Recent advances in removal of lignin from paper industry wastewater and its industrial applications – A review. *Bioresource Technology*, 312, 123636. <https://doi.org/10.1016/j.biortech.2020.123636>.
- Hube, S., Eskafi, M., Hrafnkelsdóttir, K. F., Bjarnadóttir, B., Bjarnadóttir, M. Á., Axelsdóttir, S., & Wu, B. (2020). Direct membrane filtration for wastewater treatment and resource recovery: A review. *Science of the Total Environment*, 710. <https://doi.org/10.1016/j.scitotenv.2019.136375>, <http://www.elsevier.com/locate/scitotenv>.
- Jagaba, A. H., Birniwa, A. H., Usman, A. K., Mu'azu, N. D., Yaro, N. S. A., Soja, U. B., Abioye, K. J., Almahbashi, N. M. Y., Al-dhawi, B. N. S., Noor, A., & Lawal, I. M. (2023). Trend and current practices of coagulation-based hybrid systems for pulp and paper mill effluent treatment: Mechanisms, optimization techniques and performance evaluation. *Journal of Cleaner Production*, 429. <https://doi.org/10.1016/j.jclepro.2023.139543>, <https://www.journals.elsevier.com/journal-of-cleaner-production>.
- Jiang, J., Wang, X., Ren, H., Cao, G., Xie, G., Xing, D., & Liu, B. (2020). Investigation and fate of microplastics in wastewater and sludge filter cake from a wastewater treatment plant in China. *Science of The Total Environment*, 746, 141378. <https://doi.org/10.1016/j.scitotenv.2020.141378>.
- Kesalkar, V. P., Khedikar, I. P., & Sudame, A. M. (2012). Physico-chemical characteristics of wastewater from paper industry. *International Journal of Engineering Research and Applications*, 2(4), 137–143.
- Khader, E. H., Mohammed, T. J., Albayati, T. M., Harharah, H. N., Amari, A., Saady, N. M. C., & Zendejboudi, S. (2023). Current trends for wastewater treatment technologies with typical configurations of photocatalytic membrane reactor hybrid systems: A review. *Chemical Engineering and Processing-Process Intensification*, 109503.
- Kumar, V., Thakur, I. S., & Shah, M. P. (2020). Bioremediation approaches for treatment of pulp and paper industry wastewater: Recent advances and challenges. In *Microbial Bioremediation & Biodegradation*. India: Springer Singapore, 1–48. <http://doi.org/10.1007/978-981-15-1812-6>, https://doi.org/10.1007/978-981-15-1812-6_1.
- Lewoyehu, M. (2021). Comprehensive review on synthesis and application of activated carbon from agricultural residues for the remediation of venomous pollutants in wastewater. *Journal of Analytical and Applied Pyrolysis*, 159, 105279.
- Magalhães, Silva, & Peres, A. E. C. (2022). *Zeolite application in wastewater treatment*. Adsorption Science & Technology.

- Magnisali, E., Yan, Q., & Vayenas, D. V. (2022). Electrocoagulation as a revived wastewater treatment method-practical approaches: A review. *Journal of Chemical Technology & Biotechnology*, 97(1), 9–25.
- Mainardis, M., Buttazzoni, M., De Bortoli, N., Mion, M., & Goi, D. (2020). Evaluation of ozonation applicability to pulp and paper streams for a sustainable wastewater treatment. *Journal of Cleaner Production*, 258, 120781. <https://doi.org/10.1016/j.jclepro.2020.120781>.
- Meyer, T., & Edwards, E. A. (2014). Anaerobic digestion of pulp and paper mill wastewater and sludge. *Water Research*, 65, 321–349.
- Meyer, T., Yang, M. L., Nesbø, C. L., Master, E. R., & Edwards, E. A. (2024). Microbial community organization during anaerobic pulp and paper mill wastewater treatment. *ACS ES&T Engineering*, 4(6), 1286–1301. <https://pubs.acs.org/page/aecco/about.html>, <https://doi.org/10.1021/acsestengg.3c00554>, <https://pubs.acs.org/page/aecco/about.html>.
- Mousset, E., & Hatton, T. A. (2022). Advanced hybrid electro-separation/electro-conversion systems for wastewater treatment, reuse and recovery: Compromise between symmetric and asymmetric constraints. *Current Opinion in Electrochemistry*, 35, 101105. <https://doi.org/10.1016/j.coelec.2022.101105>.
- Rad, L. R., & Anbia, M. (2021). Zeolite-based composites for the adsorption of toxic matters from water: A review. *Journal of Environmental Chemical Engineering*, 9(5), 106088.
- Rathi, B. S., & Kumar, P. S. (2021). Application of adsorption process for effective removal of emerging contaminants from water and wastewater. *Environmental Pollution*, 280. <https://doi.org/10.1016/j.envpol.2021.116995>, <https://www.journals.elsevier.com/environmental-pollution>.
- Ribeiro, J. P., Marques, C. C., Portugal, I., & Nunes, M. I. (2020). AOX removal from pulp and paper wastewater by Fenton and photo-Fenton processes: A real case-study. *Energy Reports*, 6, 770–775. <https://doi.org/10.1016/j.egy.2019.09.068>.
- Riffat, R., & Husnain, T. (2022). *Fundamentals of Wastewater Treatment and Engineering*. CRC Press. <https://doi.org/10.1201/9781003134374>.
- Sharma, P., Iqbal, H. M. N., & Chandra, R. (2022). Evaluation of pollution parameters and toxic elements in wastewater of pulp and paper industries in India: A case study. *Case Studies in Chemical and Environmental Engineering*, 5, 100163. <https://doi.org/10.1016/j.cscee.2021.100163>.
- Tahreem, A., Jami, M. S., & Ali, F. (2020). Role of electrocoagulation in wastewater treatment: A developmental review. *Journal of Water Process Engineering*, 37. <https://doi.org/10.1016/j.jwpe.2020.101440>, <http://www.journals.elsevier.com/journal-of-water-process-engineering/>.
- Toczyłowska-Mamińska, R. (2017). Limits and perspectives of pulp and paper industry wastewater treatment – A review. *Renewable and Sustainable Energy Reviews*, 78, 764–772. <https://doi.org/10.1016/j.rser.2017.05.021>.
- Vieira, P. R., Tonon e Rocha, N. L., Matheus, M. C., & Bassin, J. P. (2022). Processes and technologies for water reuse in the industry. In *Environmental sustainability and industries: Technologies for solid waste, wastewater, and air treatment*. Brazil: Elsevier, 3–54. <https://www.sciencedirect.com/book/9780323900348>, <https://doi.org/10.1016/B978-0-323-90034-8.00021-X>.
- Wang, H., Xu, J., Liu, X., & Sheng, L. (2021). Preparation of straw activated carbon and its application in wastewater treatment: A review. *Journal of Cleaner Production*, 283, 124671.
- Wang, Y., Yang, X., Sun, M., Ma, L., Li, X., & Shi, L. (2016). Estimating carbon emissions from the pulp and paper industry: A case study. *Applied Energy*, 184, 779–789.

- Wu, Q. (2022). Wastewater treatment by enhanced H_2O_2 - Based advanced oxidation process (AOP) methods: A review. *Journal of Physics: Conference Series*, 2152(1), 012011. <https://doi.org/10.1088/1742-6596/2152/1/012011>.
- Xiang, H., Min, X., Tang, C.-J., Sillanpää, M., & Zhao, F. (2022). Recent advances in membrane filtration for heavy metal removal from wastewater: A mini review. *Journal of Water Process Engineering*, 49, 103023. <https://doi.org/10.1016/j.jwpe.2022.103023>.
- Zhou, G. J., Lin, L., Li, X. Y., & Leung, K. M. Y. (2020). Removal of emerging contaminants from wastewater during chemically enhanced primary sedimentation and acidogenic sludge fermentation. *Water Research*, 175, 115646.

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Application of membrane technology in pulp and paper industry

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7.1 Introduction

Pulping and paper production demand significant amounts of freshwater, ranging from 10 to 40 m³/ton of paper, depending on the kind of product and the age of the facility (Nuortila-Jokinen et al., 2003). This value has reduced from approximately 300 m³/ton in the 20th century (Judd & Jefferson, 2003). Water, while making up less than 10% of the final product, serves as a carrier throughout the manufacturing process. It is used throughout many stages of the process, ranging from debarking to papermaking, with a consumption rate of 1 to 16 m³/ton depending on the specific stage. Besides water, chemicals, fillers, and sizing agents are often used; therefore wastewater generated during related processes is an important source of environmental pollution.

The paper and pulp business has long been considered one of the most polluting sectors due to the substantial quantity of effluent or wastewater it produces, ranging from 6 to 200 ML/ton. Pulp and paper mill effluents include significant levels of biological oxygen demand (BOD) and chemical oxygen demand (COD), color, suspended particles, and other additives (including acids, fillers, starch, and bases) that may cause environmental contamination if released untreated (Biermann, 1996) and potentially induce aquatic toxicity, especially at the reproductive level (Pokhrel & Viraraghavan, 2004).

Typical processes of the pulp and paper processing industry and polluting substances contained in related wastewaters are summarized in Table 7.1.

The pulp and paper sector is seeking better ways to cleanse its incoming water and effluents in response to stricter environmental restrictions and the rising expense of fresh water, particularly in

Table 7.1 Typical steps of pulp and paper processing industry and pollutants in related wastewaters.

Process	Description	Typical pollutants of produced wastewater
Wood preparation	Removal of soil, dirt, and bark from the wood and chips. Water is used to clean the wood.	Suspended solids, BOD, dirt, grit, fibers, etc.
Chemical pulping	The wood chips are cooked with appropriate chemicals in an aqueous solution at elevated temperature and pressure to break chips into a fibrous mass. Chemical pulping can be carried out in an alkaline media (<i>Kraft process</i> , by using NaOH and Na ₂ S) or acidic media (<i>Sulfite process</i> , by using a combination of H ₂ SO ₃ and HSO ₃ ⁻ ions).	Resins, fatty acids, color, BOD, COD, AOX, and VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, etc.).
Pulp washing	Cleaning and screening processes to remove impurities and improve the quality of the pulp.	Suspended solids, BOD, COD, and color.
Pulp bleaching	Bleaching removes residual lignin and other impurities from the fibers, which can cause the paper to turn yellow over time. It can be performed by using different chemical agents such as chlorine gas, chlorine dioxide gas, oxygen gas, H ₂ O ₂ , and ozone gas.	Dissolved lignin, carbohydrate, color, COD, AOX, inorganic chlorine compounds, organo chlorine compounds (dioxins, furans, chlorophenols), and VOCs (acetone, methylene chloride, carbon disulfide, chloroform, etc.).
Paper making	The pulp is treated up to the required degree of fitness; then the treated pulp is passed through continuous molds/wires to form sheets.	Particulate waste, inorganic dyes, COD, acetone, etc.

AOX, Adsorbable organic halides; BOD, biochemical oxygen demand; COD, chemical oxygen demand; VOC, volatile organic compound.

Modified from Pokhrel, D., Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater—A review. *Science of The Total Environment*, 333(1–3), 37–58. <https://doi.org/10.1016/j.scitotenv.2004.05.017>.

industrialized nations. Nowadays, different physicochemical (sedimentation, coagulation, precipitation, adsorption, membrane filtration, ozonation, and advanced oxidation processes) and biological (fungal treatment and aerobic and anaerobic digestion) methodologies are available to recycle process water of pulp and paper industry as well to reduce the polluting load of the produced wastewater to satisfy stringent environmental guidelines (Kamali & Khodaparast, 2015). Among them, membrane separation processes offer a great technological and economical potential for the treatment of internal circulation water, partial flows containing coating colors, and biologically treated effluents (Han et al., 2021; Simstich & Oeller, 2010).

These processes are not only cost-effective if compared with conventional methodologies but also offer simple operation conditions, high-output production with lower energy consumption and chemicals (Shamsuddin et al., 2015). In particular, pressure-driven membrane operations such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), as well as membrane bioreactors (MBRs), represent today well-established technologies in pulp and paper industry. They find applications for a wide variety of operations, including the recovery of waste material, impurities and by-products from process effluents, the fractionation, concentration and purification of valuable compounds (i.e., the fractionation and purification of lignosulfonate from spent sulfite liquor and the fractionation and purification of lignin from kraft black liquor), and the removal of BOD and COD from pulp and paper mill effluents (Adnan et al., 2009; Olsen, 1980). Innovative membrane processes, such as electrodialysis (ED) and membrane distillation (MD), offer new opportunities in the treatment of pulp industry raw wastewater. Finally, the implementation of hybrid systems in which membrane operations are combined with other unit processes (i.e., coagulation, ion exchange, adsorption, and advanced oxidation processes) has been proven to be an efficient tool for a sustainable growth of the pulp and paper industry in agreement with the principles of zero liquid discharge and circular economy.

An overview of typical membrane applications in the pulp and paper industry is depicted in Fig. 7.1.

7.2 Pressure-driven membrane operations

Pressure-driven membrane processes are based on the use of permselective barriers through which solvent fluids with permeable solutes are selectively transported under a hydrostatic pressure applied on the feed side. As a result the feed solution is divided into a permeate fraction containing all components which have

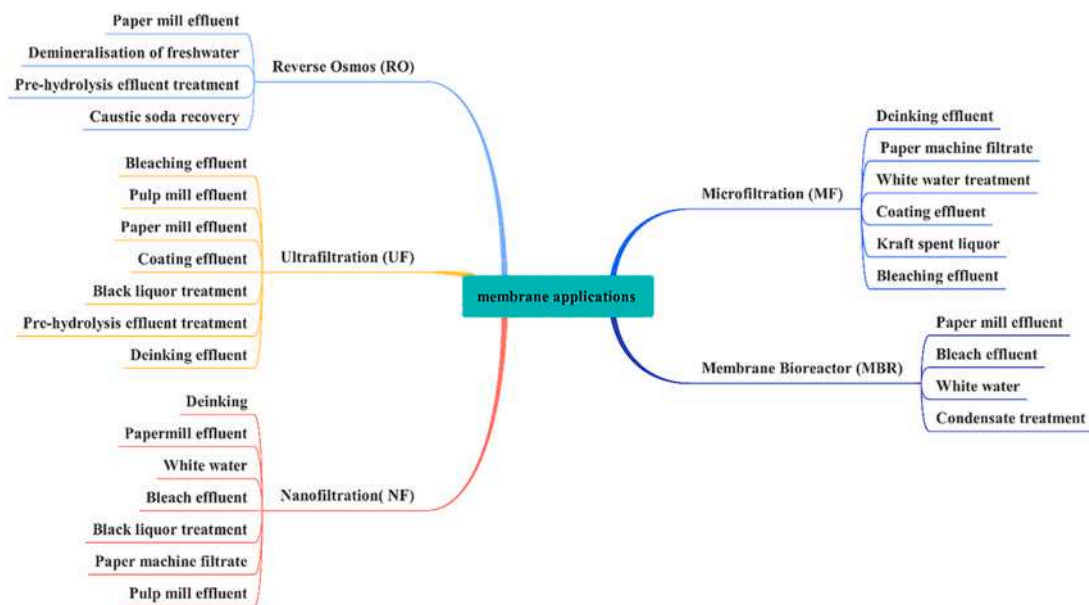


Figure 7.1 Overview of typical membrane uses in the pulp and paper sector.

permeated the membrane and a retentate fraction containing all rejected compounds, within some of the solvent. These processes are classified into four categories, which include MF, UF, NF, and RO, according to the membrane pore size, the required transmembrane pressure (TMP), and the separation mechanism.

7.2.1 Microfiltration

Particles ranging from 0.1 to 10 μm (10^{-7} to 10^{-5} m) are often separated using the MF process, which can eliminate impurities from both gases and liquids (Scott, 1995). Some of the most common uses for MF are in microelectronics, medicines, sewage treatment, chemical processing, food manufacturing, and bacterial control of drinking water. The pulp and paper industry did not begin using MF until the 1990s, when a pilot study was carried out on evaporator condensate from a kraft pulp manufacturing process to remove terpene oils, and obtained 90% removal (Minami et al., 1991). The technology was first developed in Germany in the 1930s. To avoid membrane deterioration caused by terpene oils, this research employed a Teflon membrane instead of a polysulphone (PS) one. This was a precursor to the difficulties of using membrane separation in a pulp and paper mill, which is known for its hostile environment. Later on, ceramic membranes with great chemical resistance and

thermal stability were developed, allowing membrane separation technology to be used in almost every sector. The strong mechanical robustness of ceramic membranes allows for the use of back flushing, which in turn reduces the need for chemical foulant elimination.

The pulp and paper sector has many applications for MF, including treating white water, deinking effluent, filtrate from paper machines, wasted liquor from paper mills, coating effluent, and bleaching effluent (Liu et al., 2004; Mänttari et al., 2008; Nataraj et al., 2007; Richardson et al., 2008; Silva et al., 1999; Widsten et al., 2004). Silva et al. (1999) reported on four MF uses in the pulp and paper sector. Bleached-Chemi-Thermo-Mechanical Pulping (BCTMP) effluent concentrations rose sevenfold, whereas deinking, coating, and paper-recycling mill effluents had suspended particles removed at a rate of 99% to 100%. The same research found that deinking, coating, and recycling effluents may remove COD by 85%–99%. The high organic content of the BCTMP effluent meant that the MF treatment had no discernible impact on COD, in contrast to the other three applications, which resulted in substantial fouling of the polymer hydrophilic membrane.

In research, MF was used at operating temperatures of 91°C in conjunction with back flushing to remove pitch or colloidal suspended materials from black liquors. A week of operation yielded fluxes exceeding 200 L/m²h in the testing, which did not need chemical cleaning (Cortiñas et al., 2002). The alumina ceramic membranes used in this research were sourced from United States Filter (USF) Shumacher and are capable of withstanding temperatures as high as 120°C. Due to the reduced viscosity and reduced chance of organic material precipitation within the pores, which leads to fouling, high-temperature filtration is very advantageous when dealing with black liquors. With fluxes above 200 L/m²h a comparable application on straw kraft spent liquor demonstrated lignin retention of up to 80% after 42 days of operation (Liu et al., 2004). In addition, inorganic MF membranes were able to remove an average of 80% of silica in this research, which is encouraging news in the quest to find a remedy for the silica buildup issue in nonwood pulping processes that have impeded commercialization efforts thus far.

To reduce concentrations of COD and total organic carbon (TOC) and to remove suspended particles, MF may be used by paper mills that treat recycled papers, whether or not a deinking process is performed (Pizzichini et al., 2005; Park et al., 2007). To make pulp and paper mill effluents less visible and less cloudy, MF might be used (Nataraj et al., 2007; Park et al., 2007). Suspended solids, bleaching effluents, inks, and coating materials with colloidal particles are the culprits responsible for the color and cloudiness of pulp and paper mill wastewater. MF has the potential to successfully remove these particles.

7.2.2 Ultrafiltration

The UF method operates within a membrane pore radius range of 0.005 to 0.1 μm (5×10^{-9} to 10^{-7} m) (Richardson et al., 2002) and is capable of purifying, separating, and concentrating macromolecules (Fig. 7.2A). UF can separate particle sizes with molecular weight cut-off (MWCO) ranging from 10 to 1000 kDa. The operational pressure varies from 0.5 to 1 MPa. Commercially, phase inversion is often used to produce porous and asymmetric polymeric UF membranes. UF may be used independently or as a preliminary step of other membrane processes such as NF and RO. It is susceptible to fouling over time because of concentration polarization that occurs at the membrane surface.

The pulp and paper sector in Japan was the first to use UF in the early 1980s, primarily for the treatment of bleach plant effluents (Scott, 1995). White water treatment, coating effluent, deinking effluent, and pulping liquor chemical recovery are among other typical uses.

Research on treating bleaching effluents has shown that UF may effectively separate and concentrate lignin components (Oliveira et al., 2007), carbohydrates (Chabot et al., 1999), extractives, and multivalent inorganic ions (Upton et al., 1999). UF has been shown to decrease COD levels in bleaching effluents by separating high

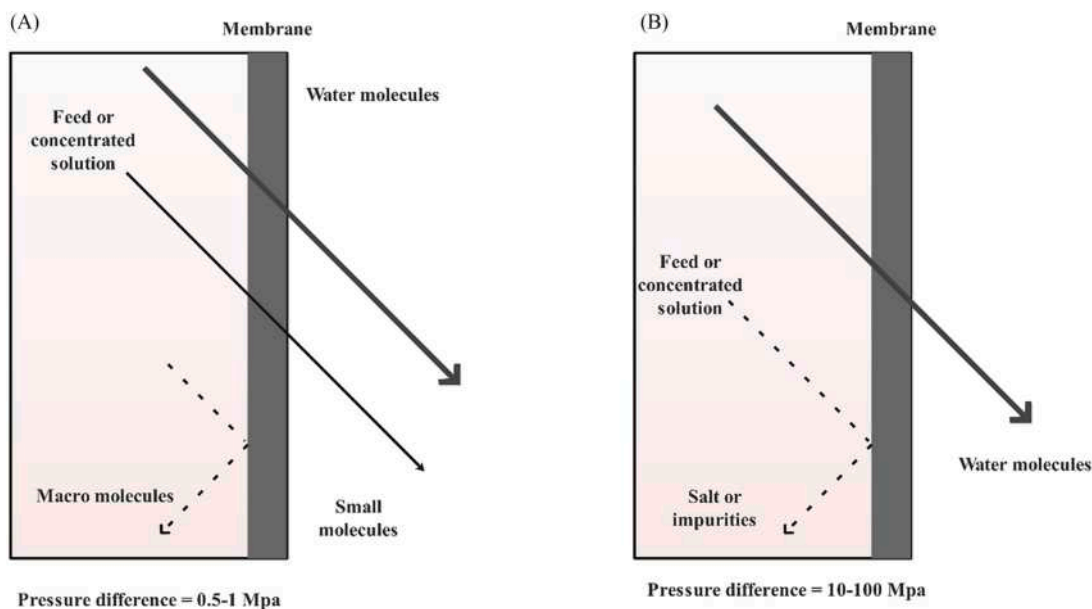


Figure 7.2 Principles of (A) ultrafiltration and (B) reverse osmosis.

molecular weight and nonbiodegradable organic substances efficiently (Klepaczka, 2004; Tizon et al., 2005). Zaidi et al. (1992) evaluated the performance of different UF membranes in the treatment of kraft bleaching effluents and achieved a COD removal in the range of 85%–90%. UF also eliminates some of the fibrous debris found in the bleaching effluents.

Pretreatment technologies are able to improve the performance of UF membranes, reducing membrane fouling and extending membrane lifetime. Xu et al. (2019) evaluated the effect of coagulation and Fenton as pretreatment of secondary effluent from recycled paper mill on the performance of a flat-sheet PS membrane with a MWCO of 5 kDa. The combination of Fenton and UF produced the best results in terms of reduction of organic compounds and fouling mitigation. In particular, the Fenton pretreatment degraded macromolecules into smaller organic compounds, prolonged the transition from pore blocking to cake filtration, thereby reducing fouling.

The coagulation pretreatment with both alum and ferric chloride greatly reduced the permeate flux decline rates of UF membranes when used in the treatment of kraft pulp mill wastewater (Hong et al., 2009). The coagulant dose was identified as the most important factor affecting the permeate flux.

Polyethersulphone (PES) UF membranes characterized by a 5-kDa MWCO were able to remove 97% of sulfate and 89% of COD from pulp and paper mill wastewater under optimized conditions of pH (10), temperature (25°C), TMP (6 bar), and volume concentration ratio (VCR) (3). The flux decline caused by fouling in these conditions was estimated to be 35% (Gönder et al., 2012). UF membranes can also be a useful approach to eliminate suspended particulates and calcium carbonate crystals from the whitewater coming from the wet end of the paper machines (Oliveira et al., 2007). The treated whitewater is suitable for its reuse in some processes in the paper machine, but not in the bleaching plant due to the high content of the soluble calcium. The combination of precipitation and UF was proposed as a proper methodology for reusing the ultrafiltered whitewater in the bleach plant. Kallioinen et al. (2010) compared the performance of different MF and UF membranes with different material and pore dimension in the treatment of acidic clear filtrate. Among the investigated membranes, a regenerated cellulose (RC) membrane with MWCO of 30 kDa exhibited the best filtration capacity and the lower fouling tendency. A similar trend was also observed by Puro et al. (2010), which compared the performance of RC and PES membranes of 30 kDa in the treatment of chemithermomechanical pulp mill process water. The 30 kDa RC membrane also exhibited higher permeation fluxes and lower propensity to fouling phenomena in the treatment of spent sulfite liquor when compared with PS and PES

membranes of the same MWCO (Weis et al., 2005). This behavior was attributed to the hydrophilic character of the RC membranes. For PS and PES membranes, having a similar hydrophobicity, flux decline was found more significant for the PS membrane, which displayed a higher roughness value (Weis et al., 2005).

According to Su et al. (2016) the addition of metal ions in the filtration of filtering whitewater with a PES membrane of 10 kDa resulted in an increase of the specific resistance of the cake layer and, consequently, in a greater membrane fouling due to their chelation with dissolved organics.

Cake layer formation was identified as the main responsible of fouling when treating the water samples at high concentration of metal ions; on the contrary, intermediate blocking was found to be the dominant fouling mechanism when treating the solution without metal ions.

In the deinking step of a paper mill that relies on recycling, UF has the ability to eliminate fine flexographic pigments derived from old newspapers (Chabot et al., 1999; Upton et al., 1999). Coating effluent (Klepaczka, 2004; Tizon et al., 2005) and black liquor treatments are two further applications of UF membranes in this field (Holmqvist et al., 2005; Liu et al., 2004; Wallberg et al., 2003).

MF and UF membranes also represent an efficient alternative for posttreatment of pulp and paper mill wastewater aimed at removing color, COD, turbidity, lignin/tannin, and total solids (Neves et al., 2017).

Recently, Burts et al. (2022) evaluated the performance of PS UF membranes prepared through the addition of polyacrylic acid to the coagulation bath in the treatment of thermomechanical pulp mill process water. The prepared membranes showed better antifouling stability in the treatment of process water, exhibiting higher flux, fouling recovery ratio, and hemicellulose rejection in comparison with unmodified membranes. Rudolph et al. (2018) developed a two-step cleaning process of UF membranes fouled by thermomechanical pulping process water based on the use of an enzyme cocktail containing a mixture of enzymes that degrade wood-derived compounds, followed by a cleaning step with an alkaline detergent. This approach allowed to restore the initial water permeability of the membranes. Fourier-transform infrared spectroscopy revealed the adsorption of both polysaccharides and extractives onto the membrane surface of fouled membranes.

7.2.3 Nanofiltration

NF is one of the membrane technologies that have been applied for water recycling and reuse within various industries, thanks to its unique features such as higher selectivity toward divalent/polyvalent ions while allowing permeation for monovalent ions and small

molecules of less than 100 Da (Ahmad et al., 2022). Demineralizing groundwater, removing organic waste, and polyvalent cations are all possible applications. Pore sizes for NF may vary from 0.001 to 0.01 μm (10^{-9} to 10^{-8} m) (Scott, 1995).

The NF process can be useful to remove color and organic compounds from discharge water coming from an activated sludge process in the pulp and paper industry, with the production of a purified effluent containing low amounts of monovalent ions (Mänttari et al., 2006). Semiaromatic piperazine-based polyamide NF membranes with MWCO of 200–300 Da showed a very high retention for organic compounds and initial permeate flux of 110 L/m²h at a TMP of 6.5 bar. A further decrease in color, UV-absorbing materials (lignin), and turbidity can be achieved by treating the NF concentrate by ozonation (Mänttari et al., 2008).

Integrating the NF process in the treatment of alkaline bleach plant effluent from a softwood pulp mill has been shown to enhance the elimination of small organic molecules and biodegradable chemicals before ozonation and biological treatment (Bijan & Mohseni, 2008). Different research conducted on the same effluent with ceramic NF membranes, operating at 10 bar pressure and 4 m/s velocity, achieved very high fluxes exceeding 265 L/m²h (Tomani & Seisto, 1999). These membranes can eliminate both organic molecules and metal complexes like iron and manganese that are produced due to the inclusion of chelating agents in the completely chlorine-free bleaching process. Keyoumu et al. (2004) investigated the use of UF and NF ceramic membranes coated with ZrO₂ (with MWCO of 1000, 5000, and 15,000 Da) to remediate kraft black liquors made from either hardwoods or softwoods. According to their findings, NF may remove organic pollutants, especially lignins, from black liquors, relieving pressure on the recovery boiler. An alternative to the recovery boiler is to burn the separated lignin in the lime kiln. Important by-products, such as phenols and adhesives, may be made from the removed lignins (Jönsson & Wallberg, 2009). The amount of energy that may be recovered or utilized as fuel can be as high as 4.88×10^4 MJ if a mill produces 50 tons of unbleached pulp daily and 2 tons of lignin, which has a heating value of around 24.4 MJ/kg (Francey et al., 2009; Ghatak, 2009). (Kaya et al., 2010) proposed a combination of loose and tight NF membranes (PES membranes with a MWCO of 1000 and 400 Da, respectively) for the treatment of paper machine circulation wastewater (whitewater). This combination achieved reduction of both COD and total hardness greater than 90% suggesting the reuse of whitewater as shower water of paper machine.

UF membranes allow to separate high MW lignin from kraft black liquors, allowing permeation of low MW lignin. Vives et al. (2022)

evaluated the performance of different NF membranes (with MWCO ranging from 100 to 2000 Da) in the concentration of low MW lignin from UF permeates.

Among the investigated membranes the best performances were provided by two flat-sheet membranes with MWCO of 350 and 1000 Da. These membranes provided lignin retention of 90% and 84%, respectively, and permeate fluxes of 37 and 72 L/m²h in selected conditions of TMP (35 bar), temperature (50°C), and cross-flow velocity (0.5 m/s).

Ceramic hollow-fiber membranes with pore size of 3, 8, and 20 nm were tested by [Humpert et al. \(2019\)](#) for the recovery of lignin from spent sulfate liquors. It was observed that lignosulfonate retention increased with TMP and volume concentration factor (VCF), while decreased with MWCO. The 3 nm ceramic hollow-fiber membrane achieved the highest retention (up to 69%), and at a VCF 8, the flux loss was lower than that of the 8 nm ceramic hollow-fiber membrane.

Graphene oxide (GO) NF membranes supported on porous PES supports can be effective for concentration of kraft black liquors. These membranes were also scaled up to ~660 cm² sheets and exhibited excellent characteristics over more than 1500 hours onstream in real black liquor at 70°C for separation of lignin, organics, and salts ([Wang et al., 2019](#)).

[Mänttari et al. \(2000\)](#) did extensive study on how different membrane materials, operating conditions, and fouling affect nanofiltration's performance in the treatment of pulp and paper effluents. For many commercial membranes, such as the NTR-7450 (from Nitto Denko) and the Desal-5 (from Osmonics) membranes, their optimal operating parameters were elucidated. Based on laboratory- and pilot-scale experiments the NF270 membrane (from Filmtec-Dow) exhibited a very interesting performance for the treatment of paper mill wastewater due to its hydrophilicity, high retention, and high permeability ([Mänttari & Nyström, 2004](#); [Mänttari et al., 2004](#)). Effluents with total dissolved carbon retention rates between 64% and 95% were successfully processed by the membrane. The membrane's narrow working temperature range below 45°C severely limits its application.

New logic international's commercial vibratory shear enhanced processing is one solution to membrane fouling problems; it works with RO, UF, MC, and polymer NF membranes. Using vibration, this technique reduces concentration polarization on membrane surfaces, which in turn reduces fouling. Whitewater treatment, black liquor concentration, paper mill effluent, paper coating effluent, and paperboard mill effluent are just a few of the applications for which

this approach has been studied in the paper and pulp industry (Dexter, 1996; Farlow, 1996).

7.2.4 Reverse osmosis

Most municipal drinking water and ultrapure industrial water are produced using the RO or hyperfiltration process, which typically operates at pressures ranging from 10 to 100 bar (Nunes & Peinemann, 2001). MWCO particles range from 0.05 to 10 kDa, or less than 0.001 micron (10^{-9} m) in size, which RO membranes are able to separate (Scott, 1995). RO has many potential uses, including those in desalination, the processing of food and drink, cleaning up polluted freshwater, organic and aqueous wastewater, leachates, and more. Research into RO membrane materials has yielded many promising candidates, the most significant of which being cellulose acetate, polyamide (PA), and aryl-alkyl polyether urea. Chemical and microbiological resistance, the required separation qualities, and mechanical and structural durability over extended periods are ideal attributes of RO membranes.

Fig. 7.2B illustrates the main concept of RO. The solvent, often water, will migrate over a semipermeable membrane from a solution with a lower concentration to one with a higher concentration, and so on, until the two solutions reach a concentration equilibrium. Solvent transfer cannot be avoided without first overcoming the osmotic pressure differential, which grows in direct proportion to the temperature and concentration gradients between the solutions. Water molecules are compelled to cross the membrane and enter a solution with a lower concentration when the osmotic pressure difference between two solutions is large enough. On the high-pressure side, concentrated pollutants or salts are filtered out, while on the low-pressure side, just water is filtered out. To get the necessary quality in the permeate, one may use a variety of design combinations or phases (Adnan et al., 2009).

In 1976, RO was first used to concentrate sulfite pulping liquors in the pulp and paper sector (Scott, 1995). Before the liquids go through further evaporation and eventual disposal, this concentration procedure helps to remove even more water from them. Kraft liquors, bleaching effluents, and paper machine effluents were concentrated using RO from the 1970s until the 1990s. Using a mix of RO and freeze concentration approach, the effluents from three mills' bleach plants were successfully concentrated from 5 g/L to 200 g/L solids (Wiley et al., 1978). Using a RO membrane at a high pressure of 41 bar (Slater et al., 1983), field research was conducted that successfully reduced color and COD by 95% for pulp and paper wastewater.

A very clean permeate can be produced by RO-activated sludge discharge fluids from pulp and paper industry due to the high retention of RO membranes toward organic molecules (Slater et al., 1983). This trend is positive since the organic components in these effluents lead to elevated levels of COD and BOD, which are crucial factors in determining the efficiency of wastewater treatments.

A preliminary investigation found that RO may recover caustic soda for pulp and paper industry uses by concentrating diluted NaOH solution (Slater et al., 1983). RO is also used in the dissolving pulp business to treat the prehydrolyzed liquor produced during rayon manufacturing. The alcohol undergoes fermentation to turn carbohydrates into yeast, and then it is ultrafiltered to eliminate the yeasts. The permeate is further filtered by RO, leading to the near-total elimination of the residual low molecular weight carbohydrates (Bhattacharya et al., 2005; Rath et al., 2005). Saif et al. (2013) formulated a mathematical programming model to determine the optimal RO network configuration in the treatment of wastewater streams within the kraft pulp and paper process. The model also allowed to identify optimal operating conditions to reduce the salt concentration to predetermined acceptable levels required by the pulp and paper processes. Preliminary cost estimates indicated that the RO is an effective technology for wastewater management in the pulp and paper process.

7.3 Membrane bioreactors

MBRs integrate membrane technologies like MF and UF with biological approaches. Microorganisms, in an aerobic or anaerobic procedure, are introduced to the feed as part of the biological method to break down the organic contents (Minami et al., 1991; Stahl et al., 2004).

The two basic MBR configurations are the side stream or external cross-flow MBR (Fig. 7.3A) and the submerged or internal MBR (Fig. 7.3B). The former is a combination of the traditional bioreactor with a membrane filtration device into a single unit process. High molecular weight substances are rejected by the membrane and can be further decomposed. The biomass concentration in the system can reach values 10 times higher than those obtained in conventional plants. In the submerged configuration the membrane is placed inside the bioreactor and operates under subatmospheric pressure instead of hydraulic pressure. It is more commonly used due to less energy-intensive and lower fouling potential.

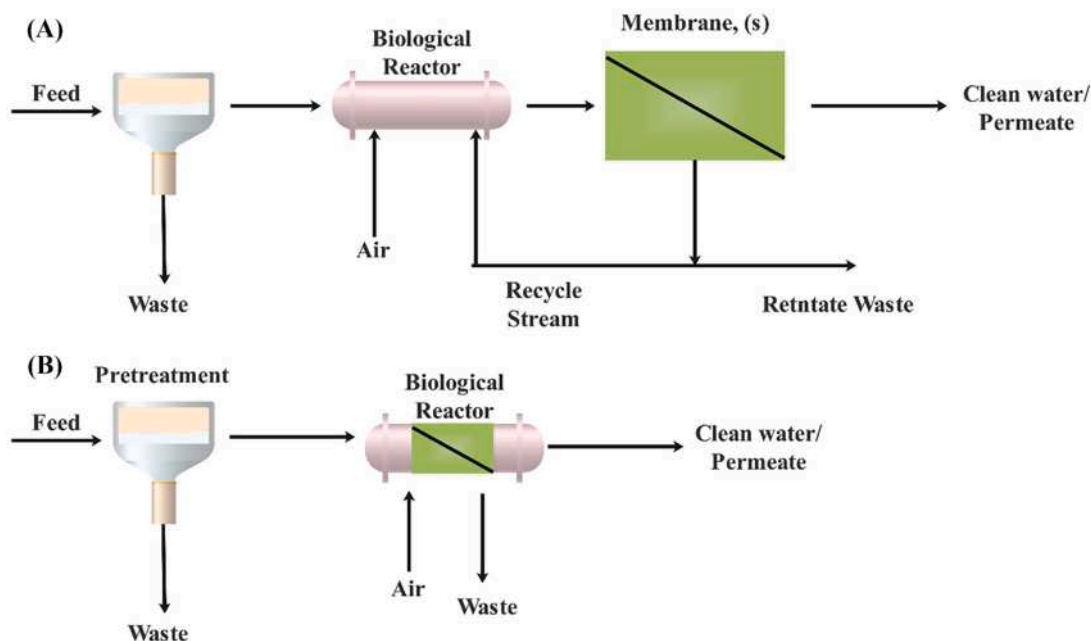


Figure 7.3 Two different types of membrane bioreactor (A) internal and (B) external.

The pulp and paper industry has discovered that the MBR is more effective than the traditional activated sludge process (ASP) in decreasing levels of BOD and COD (Dufresne et al., 1998; Lerner et al., 2007). By adding an ozonation step the COD level may be further lowered (Gommers et al., 2007). Also, when comparing suspended solids, MBR is much better than ASP (Stahl et al., 2004). There have been reports of more than 90% efficiency when using MBR to extract methanol from evaporator condensate (Bérubé & Hall, 2001). According to Bérubé and Hall (2001) the total cost of removing methanol with MBR is 40% less than the steam stripper procedure. Anaerobic MBRs were more effective than anaerobic conventional bioreactors in eliminating organic materials and suspended particles from white fluids produced during papermaking using bleached kraft pulps (Adnan et al., 2009; Tenno & Paulapuro, 1999). Erkan and Engin (2017) obtained removal efficiencies for COD, ammoniacal nitrogen ($\text{NH}_3\text{-N}$), and total phosphorous (TP) of 98%, 95.99%, and 96.36%, respectively, in the treatment of paper mill industry wastewater though a submerged MBR operated at 35 hours of hydraulic retention time (HRT) and 40 days of sludge retention time. Accordingly, the process was considered a suitable approach for the removal of organic matter and nutrients from

the treated wastewater, except for the problem of calcium accumulation.

In the work of [Bokhary et al. \(2021\)](#) the anaerobic digestion of primary sludge of a thermomechanical pulp mill was carried out by using a thermophilic anaerobic MBR. Best results were achieved under conditions of lower organic loading rate (OLR) and higher HRT, respectively of 2.5 kg COD/m³ and 192 hours. The biogas production resulted in the range of 0.059–0.334 L biogas per g of mixed liquor suspended solids (MLSS) removed. Biogas production and sludge biomass degradation decreased in conditions of increased OLR and decreased HRT.

Carbon nanotube/PS nanocomposite membranes prepared through the phase inversion method were coupled by [Mulopo \(2017\)](#) to an anaerobic MBR to assess their performance in the removal of COD from a bleach effluent. The system was operated at an HRT of 12 hours and temperature of 25°C. The COD removal under these conditions was of about 92%. The addition of carbon nanotubes to the PS membrane enhanced the membrane performance by improving the permeate flux, which resulted higher than 6 L/m²h. This phenomenon was attributed to the presence of the O-H bonds that alters the contact angles and the roughness of the membrane.

Recently, [Kalshan et al. \(2024\)](#) evaluated the performance of an advanced MBR equipped with a polyvinylidene difluoride flat-sheet membrane in the treatment of pulp and paper industry wastewater. The best pollution removal of about 97.5% was achieved operating at 12 hours of HRT. It was found that the dynamic link between MLSS and HRT is a key parameter for optimizing the biological treatment procedure, and that 25°C was the ideal temperature for the MBR operation.

7.4 Electrodialysis

ED is a membrane-based process promoting the migration of ions from one solution to another through a semipermeable membrane under an electric field. In a typical ED cell feed and the permeate streams are separated by cationic membranes (i.e., poly[vinyl benzyl trimethyl ammonium hydroxide]) or anionic membranes (i.e., poly[styrene sulfonic acid] or Nafion®). Cation- and anion-exchange membranes are arranged alternately to form thin compartments called stacks. The ED process offers several advantages over many other desalting processes especially when the concentration of salt ions in the feed stream is low and the ions are highly mobile ([Chua et al., 2020](#)). In addition, this process is characterized by high water recovery and does not require the use of chemicals or high pressures

for performing desalination. This makes ED a very ecofriendly and sustainable technology for the treatment of industrial wastewater, including those produced in paper and pulp industry.

ED with monovalent selective anion and cation-exchange membranes showed very good selectivity for chloride over sulfate when used in the treatment of feed streams with very high ionic strength, including model solutions and pulp mill wastewater (Pfromm, 2006). Particulate pollutants, noncharged molecules with a larger molecular weight, and weakly ionized molecules like silica are not removed by ED procedures.

7.5 Membrane distillation

MD is a method of separation that makes use of a vapor pressure gradient, which is generated by the temperature differential between two membrane surfaces. To keep the hot feed solution from mixing with the cold receiving stream, a microporous hydrophobic membrane is used. Only vapor forms of the feed's volatile components may permeate past the hydrophobic barrier. Vapor condenses as soon as it contacts the chilly surface across the barrier. Depending on the arrangement the receiving end of the membrane might be in the vapor or liquid phase, with four distinct MD configurations. The solutions to be separated dictate the choice of MD configuration; the most frequent and preferable arrangement for obtaining clean water is direct contact MD (Curcio & Drioli, 2005).

Although most research on MD focuses on desalination and fruit juice concentration, it may also be used for water purification, wastewater treatment, concentrating biological fluids, and in bio-refineries. Experiments separating volatile liquids, including methanol, ethanol, and isopropanol, using MD shown a flow of up to 12.5 kg/m²h may be achieved (García-Payo et al., 2000). This suggests the potential use of MD to eliminate the volatile elements from unpleasant pulping condensates. MD may be powered by low-grade energy sources or waste heat, both of which are plentiful in the pulp and paper sector.

7.6 Hybrid membrane systems

The combination of one or more membrane techniques with other unit processes like coagulation, ion exchange, adsorption, or other membrane processes offers interesting opportunities in the treatment of pulp and paper wastewater providing a better performance than either of the technologies as a standalone process, enhanced quality of the water produced, energy savings, environmental

friendliness, and reductions in the capital and operating costs of the plants (Ang et al., 2015). Shukla et al. (2015) evaluated the combination of the ASP with different pressure-driven membrane processes (including MF, UF, NF, and RO) as an alternative methodology to recycle water from the already established paper mill wastewater treatments. Experimental results clearly indicated that a treatment scheme based on the sequential design ASP - MF - UF - NF - RO was the best option, allowing to remove 100% of total dissolved solids (TDS), total suspended solids and color, 94.2% of COD, and 86% of adsorbable organic halides.

An integrated membrane process for the purification of pulp and paper wastewater based on the combination of MF and RO membranes was proposed by Pizzichini et al. (2005). In the proposed process (Fig. 7.4) a VCR lower than eight was proposed for the MF process performed with a ceramic membrane with a pore size of 0.14 μm to minimize fouling phenomena. A similar VCR in the RO step, performed with a spiral-wound polymeric membrane, allowed to produce a purified water as RO permeate with a conductivity of about 70 $\mu\text{S}/\text{cm}$, COD lower than 25 ppm of O_2 , and TOC of about 1 mg/L. The volume of the produced permeate was about 80% of the total wastewater volume.

An integrated membrane system based on a prefiltration step followed by UF and RO processes was also investigated by Dagar et al. (2023) to assess the water reuse of an effluent coming from the

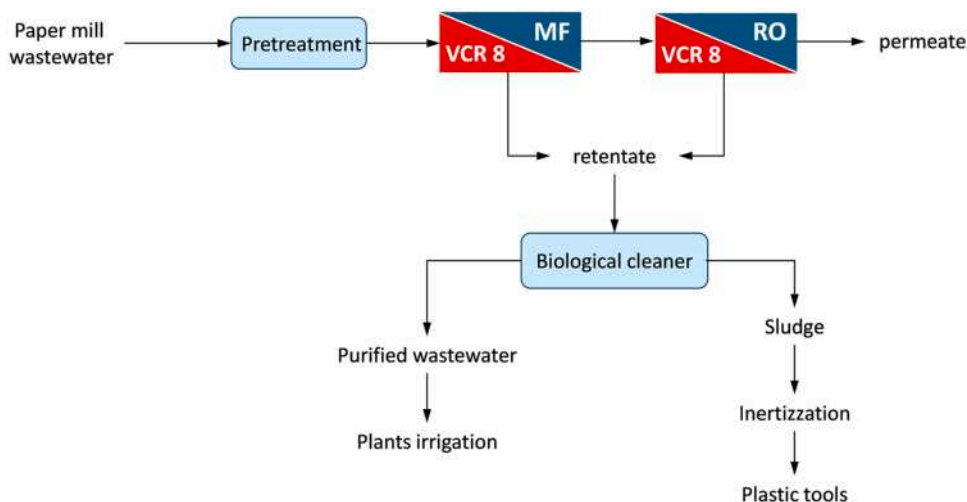


Figure 7.4 Membrane process scheme for the treatment of paper mill wastewater. Modified from Pizzichini, M., Russo, C. & Meo, C. Di. (2005). Purification of pulp and paper wastewater, with membrane technology, for water reuse in a closed loop. *Desalination*, 178(1–3), 351–359. <https://doi.org/10.1016/j.desal.2004.11.045>.

secondary clarifier of the conventional treatment of pulp and paper wastewater. More than 88% of the contaminants of the effluent were reduced with the use of RO. The quality of the RO permeate adequately complied with the quality standard required for its reuse in the making of all grades of paper.

A membrane-based process for the efficient treatment of the alkaline bleaching effluent based on the use of MF, UF, and NF ceramic membranes was proposed by Ebrahimi et al. (2016). This effluent is highly polluted due to the presence of high levels of lignin and their partially aromatic degradation products, as well as polymeric materials that resist biological degradation. Membrane filtration of the effluent was achieved using two stirred batch-reactor systems with the membrane modules arranged in parallel according to the setup illustrated in Fig. 7.5 Among the investigated configurations the two-step MF/UF provided the best results with reduction of COD and lignin of more than 35% and 70%, respectively.

In the process proposed by Valderrama et al. (2021) the combination of UF and NF membranes in a sequential design was suggested for the recovery of valuable organic and inorganic compounds from black liquors. In this approach the UF process is employed as pretreatment step for the recovery of inorganic compounds (most of the hemicellulose is retained by UF membranes); the UF permeate, containing NaOH, water, low MW lignin, and low molecular mass sugar, is then concentrated by NF (Fig. 7.6).

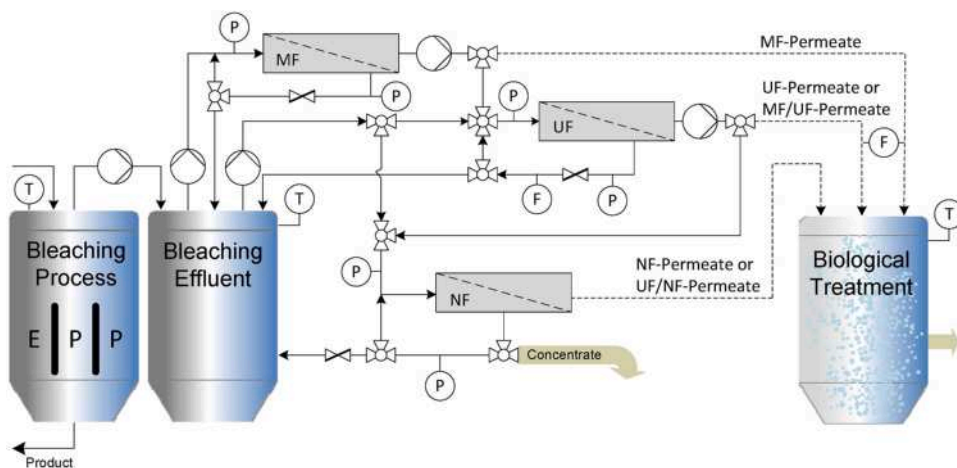


Figure 7.5 Multistage cross-flow filtration system for the treatment of the bleaching effluent from sulfite pulp production (Ebrahimi et al., 2016).

From Ebrahimi, M., Busse, N., Kerker, S., Schmitz, O., Hilpert, M., & Czermak, P. (2016). Treatment of the bleaching effluent from sulfite pulp production by ceramic membrane filtration. *Membranes*, 6(1). <https://doi.org/10.3390/membranes6010007>.

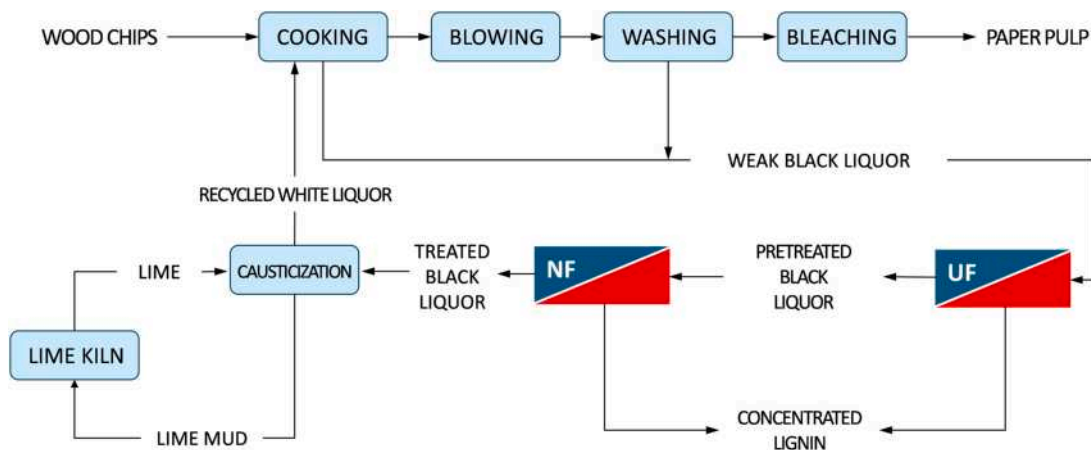


Figure 7.6 Treatment of black liquor by integrated ultrafiltration/nanofiltration process.

Modified from Valderrama, O.J., Zedda, K.L., & Velizarov, S. (2021). Membrane filtration opportunities for the treatment of black liquor in the paper and pulp industry. *Water*, 13(16). <https://doi.org/10.3390/w13162270>.

Specifically, authors evaluated the filtration performance of self-made NF membranes in the filtration of a simulated black liquor. One of the prepared membranes showed the best performance for this application, exhibiting permeate fluxes of about 24 L/m²h at TMP of 21.5 bar, high rejection of organic components (i.e., 92.5% for TOC) and salts (i.e., 84.10% for CO₃²⁻, 88.7% for sulfates, and 99.9% for Mg²⁺), as well as negative rejection to OH⁻ ions (-317.9% in average) and, consequently, high OH⁻ concentration in the permeate side. Johakimu et al. (2016) proposed a conceptual process for recovering water and caustic soda from effluents produced in the alkaline extraction stage, where caustic soda, oxygen, and peroxide are applied as pulp bleaching chemicals. The effluent is previously submitted to a clarifier unit where most of suspended solids are removed. The clarified effluent is then ultrafiltered to remove colloidal particles and some dissolved solids. Typically, the UF permeate is submitted to the RO unit while the retentate is forwarded to the caustic soda recovery tank. The RO membranes separate inorganic dissolved solids (such as the sodium salts) from water producing a purified water fraction (RO permeate) and a concentrated fraction rich in caustic soda (Fig. 7.7).

The economic viability of the integrated process is strictly dependent on the effluent flow rates and the amount of water recovered. Optimal effluent flow rates and water recovery rates were estimated to be 480 m³/d and higher than 70%, respectively. In these conditions the process cost is estimated to be R 19/m³ (calculations based on eThekweni municipality water tariffs: 1 kl=R 16.47). The

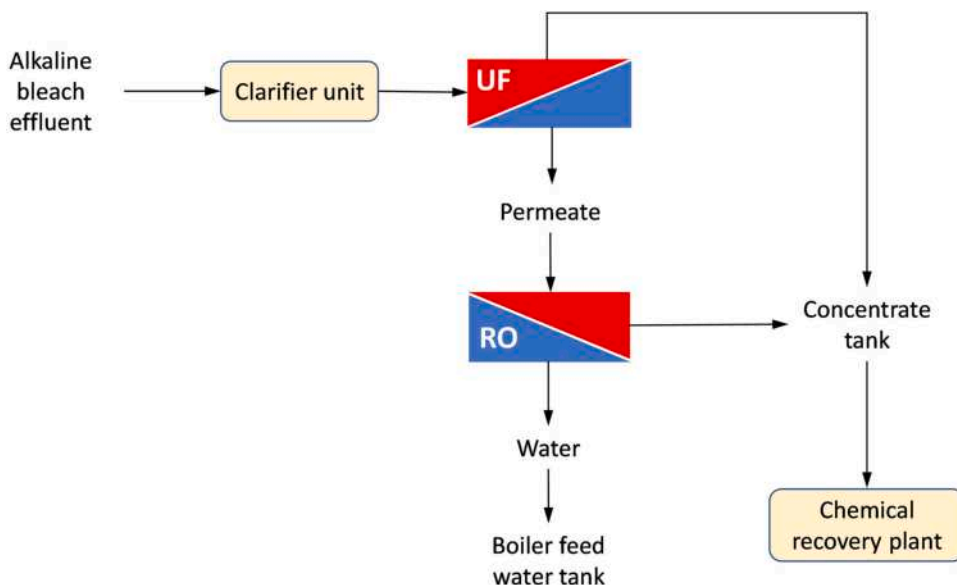


Figure 7.7 Conceptual process design for the recovery of water and caustic soda from alkaline bleach effluents. Modified from Johakimu, J.K., Andrew, J., Sithole, B.B., & Syphus, E. (2016). Preliminary techno-economic assessment of recovering water and caustic soda from alkaline bleach plant effluent. *Journal of Cleaner Production*, 139, 914–921. <https://doi.org/10.1016/j.jclepro.2016.08.088>.

investment cost and the payback time were estimated in the range of R 5–25 million and 3–4 years, respectively.

The combination of membrane filtration systems with advanced oxidation processes (AOPs) offers interesting opportunities to reduce the pollution load of pulp and paper mill wastewater. Hermosilla et al. (2012) investigated the combination of different AOPs (conventional Fenton, photo-Fenton, and photo-catalysis) for the removal of COD in the RO retentate from a paper mill. Among the investigated processes the photo-Fenton process was the most effective, achieving the total reduction of COD and TOC.

A hybrid approach based on the combination of UF and AOPs for the treatment of pulp and paper mill wastewater was investigated at a bench scale by Gholami et al. (2017). The UF process was performed by using a flat-sheet membrane vertically fixed inside the feed tank. The separation of the pollutants was achieved by suction applied by a vacuum pump. The UF permeate was then forwarded to the AOPs reactor, where oxidants, such as persulfate ($\text{S}_2\text{O}_8^{2-}$) and H_2O_2 , activated by $\text{Fe}(\text{II})$, were added. In the optimized conditions of temperature, pH, and dosage of oxidant the removal efficiency of COD, UV_{254} , and UV_{280} with the filtration/persulfate/ $\text{Fe}(\text{II})$ combined system reached 94.96%, 92.04%, and 90.16%,

respectively. [Geraldes and de Pinho \(1995\)](#) proposed a hybrid process based on the use of NF and ED for the recovery of water from alkaline pulp bleaching effluents. The NF process was performed by using a thin film composite membrane module in spiral-wound configuration. It allowed to remove organo- and organo-chlorinated compounds of low molecular weight, providing also a partial demineralization of the treated effluent. The NF permeate was then treated with an ED pilot plant equipped with 33 ion exchange membrane pairs with an effective area of 206 cm²/cell. This process allowed to reduce the NaCl content of the NF permeate within 350 ppm so meeting the quality requirements of washing water for pulp bleaching. The proposed process block diagram ([Fig. 7.8](#)) involved different levels of NF (from 1 to 4) depending on the water recovery factor to be achieved.

An integrated process based on the use of MF and ED was investigated by [Nataraj et al. \(2007\)](#) for the treatment of effluent wastewater collected from a paper mill in India. Effluents were pretreated with tubular ceramic MF membranes and then submitted to ED by using a pilot unit equipped with 11 cation-exchange and 10 anion-exchange membrane pairs. The hybrid MF/ED process allowed to recover and reuse more than 90% of original wastewater. The produced permeate showed a low content of TDS (about 546 mg/L), a conductivity of 0.61 mS/cm, and a COD of less than 20 mg/L.

The combination of MBR with other technologies such as AOPs, RO, granulation technology, and moving bed biofilm reactor is an efficient approach to overcome fouling problems, which negatively

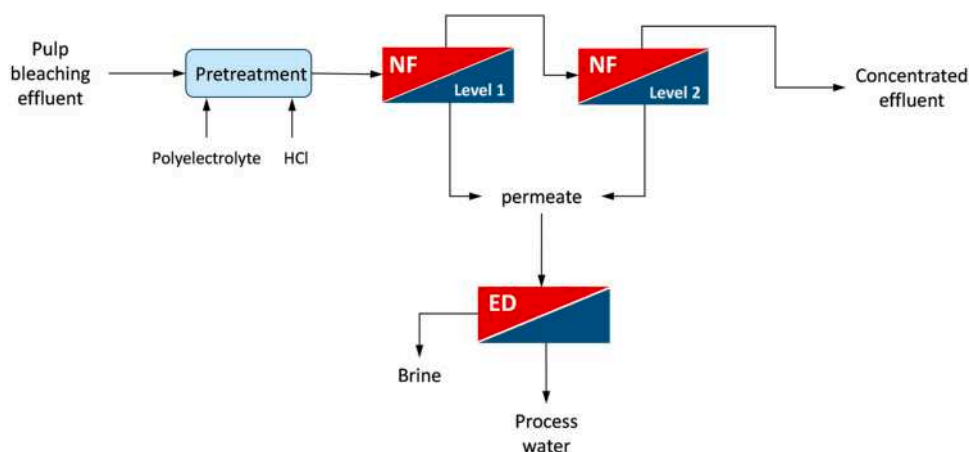


Figure 7.8 Hybrid NF/ED process for the recovery of process water from pulp bleaching effluents.

Modified from [Geraldes, V., & de Pinho, M.N. \(1995\). Process water recovery from pulp bleaching effluents by an NF/ED hybrid process. Journal of Membrane Science, 102\(C\), 209–221. \[https://doi.org/10.1016/0376-7388\\(94\\)00325-S\]\(https://doi.org/10.1016/0376-7388\(94\)00325-S\).](#)

impact the MBR performance (Patel et al., 2021). Qu et al. (2012) developed an integrated process for the treatment of thermomechanical pulping pressate based on a combination of a thermophilic submerged aerobic MBR and electrochemical oxidation. The MBR treatment was performed by using a flat-sheet MF membrane made of PVDF with a pore size of $0.3 \mu\text{m}$. It was able to remove up to 92% of COD under the OLR of $3.98 \text{ kg COD/m}^3\text{d}$; an optimal HRT of $1.1 \pm 0.1 \text{ d}$ was identified for COD removal. The electrochemical oxidation of the permeate stream by using a $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5\text{-IrO}_2$ electrode produced a total decolorization of the effluent and a further removal of the COD up to 96%. COD and BOD_5 elimination rates of 83% and 99%, respectively, were also observed by Simstich et al. (2012) in the treatment of circuit wastewater from the paper industry through a submerged flat-sheet MBR under thermophilic conditions at 50°C . Merayo et al. (2013) evaluated the performance of different combinations of AOPs and MBR in the treatment of effluents of both recycled paper mill and kraft pulp mill. Among the investigated processes the ozone treatment achieved the highest efficiency, providing a 60% COD reduction in the treatment of the effluent from the kraft pulp mill and a 35% COD removal for the effluent of the recycled paper mill. Izadi et al. (2020) obtained high removal efficiencies of COD (up to 99% through an HRT of 36 hours) in the treatment of a real paper-recycling wastewater through a novel integrated hybrid airlift membrane bioreactor (HAMBR) composed of oxic, anoxic, and anaerobic zones. The evaluation of membrane fouling through the monitoring of TMP revealed a good resistance of the membrane against fouling phenomena.

Recently, Dogan et al. (2023) implemented an innovative process for the treatment of paper industry raw wastewater, which provides comprehensive liquid discharge minimization and resource recovery. It was based on the combination of Fenton reaction with both submerged UF process, to meet current discharge standards, and MD to provide water recovery. The combination of the Fenton/UF process provided COD removal higher than 87% while the MD wastewater was recovered at a rate of 50%–60% for reuse as process water with a permeate flux of about $14 \text{ L/m}^2\text{h}$.

A major hurdle to using membrane technology in the pulp and paper industry is the associated costs. When it comes to pulp and paper, there are not many articles that provide price data for membrane technology applications. Energy, chemicals, personnel, and equipment maintenance are part of the operating costs, whereas design, equipment, materials, and construction are all part of the capital expenditures included in the membrane cost analysis (Bérubé & Hall, 2001; Madwar & Tarazi, 2003).

Whereas the volumes of clean water or permeate produced are used to calculate the costs for RO, NF, and UF applications in wastewater and circulation water treatment, the amounts of pulp produced per metric tonne are used to calculate the costs for MF and MBR applications in foul pulping condensates and kraft black liquor treatment.

7.7 Development, research, and application trends on a global scale

In 2004, membrane technology in the pulp and paper sector accounted for around 5.3% of the worldwide membrane market, which was projected to decrease to less than 5% by 2009 (Sutherland, 2004). The majority of published research in the pulp and paper industry concentrated on the use of UF at 37% and MBR at 16% (Fig. 7.9). R&D trends show a preference for enhancing traditional membrane technologies like UF and hybrid membrane systems rather than exploring whole new research fields, perhaps because of their better success rates and lower risks. Between 1999 and 2008, less than 160 papers on

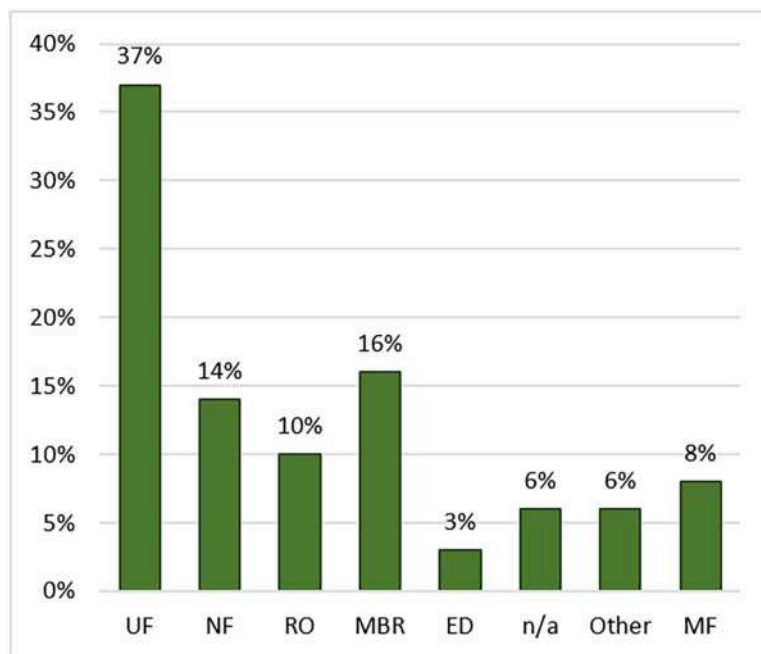


Figure 7.9 Analysis of 159 papers showing the distribution of research and development expenditures in the pulp and paper sector from 1999 to 2008 by membrane type.

the use of membrane technology in the pulp and paper sector were published. Local environmental laws, water shortages, and the yearly rate of 4% to 15% increase in the cost of clean water (in Melbourne) (Adnan et al., 2009) are among the reasons that will likely lead this amount to climb consistently in the next years. The pulp and paper industry is expected to be significantly impacted by membrane technology going forward.

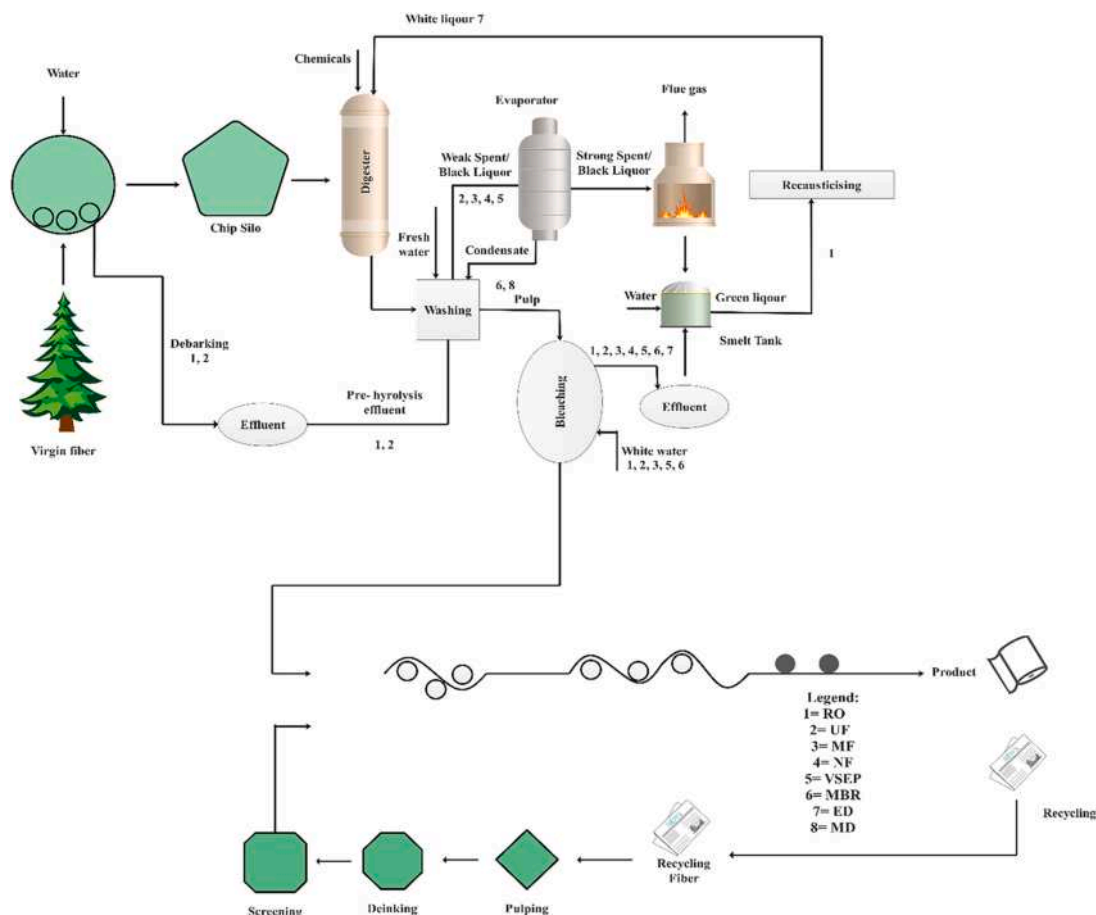


Figure 7.10 Exploring the present and future possibilities of using membrane technology in the pulp and paper industries.

Modified from Adnan, S., Hoang, M., & Wang, H. (2009). *Research, development and application of membrane technology in the pulp and paper industry*. In Appita Annual Conference (pp. 241–246).

7.8 Other membrane advances

The pulp and paper industry is now the focus of research into the potential applications of new membrane technologies such as electrodialysis, hybrid membranes, and MD (Adnan et al., 2009; Liu et al., 2004; Singh, 2006). To ensure these technologies are technically and economically viable for use in the pulp and paper industry, more work is needed. Present and prospective applications of membrane processes in the pulp and paper sector are depicted in Fig. 7.10.

7.9 Challenges for membrane operations implementation for industrial scale-up

The primary obstacles to implementing membrane processes at an industrial level are membrane fouling, selectivity, and the need to maintain competitive prices to ensure the economic viability of compound recovery for large-scale operations.

7.9.1 Fouling

Choosing the right membrane material reduces adsorptive fouling, whereas pore blockage may be managed by selecting a membrane with an adequate MWCO (Tolbert et al., 2014). Polyacrylonitrile, PS, PES, polyamide-imide, and polyether-imide membranes saw a significant reduction in pure water permeability, ranging from 60% to 80%, due to adsorptive fouling from presses originating from the semichemical mechanical pulp mill. Hydrophilic membranes (Arkell, 2015) and RC and thin film composite membranes (Tolbert et al., 2014) have a reduced tendency to accumulate fouling compared to other types of membranes. Various techniques investigated for reducing or avoiding fouling in membranes include using flotation as a preliminary treatment, optimizing operating temperature and cross-flow velocity, and modifying membranes with substances like Praestol 859 or Pluronic F108 to enhance fouling resistance. Membrane cleaning using nonionic detergents has also been suggested (Maitz et al., 2023).

7.9.2 Selectivity

The coexistence of chemicals with similar particle sizes, such as lignosulfonates and hemicelluloses, in pulp and paper industrial process streams poses a challenge for their separation due to fouling (Aro & Fatehi, 2017). Therefore membrane selectivity is crucial for effectively separating pulp components. The process of choosing and getting membranes ready for certain uses has been extensively

studied and is well recorded. Studies by [Al-Rudainy et al. \(2019\)](#) have shown that hydrophilic membranes exhibit less retention of lignin due to their lower affinity, resulting in decreased fouling. Inorganic membranes have superior mechanical, chemical, and thermal stability, prolonged durability, reduced membrane resistance, and excellent filtering capabilities compared to organic membranes. In particular, ceramic membranes have greater hydrophilicity than other inorganic membranes and offer lesser lignin retention and greater capital expenditures to polymeric membranes ([Arkell et al., 2014](#); [Ebrahimi et al., 2021](#); [Li et al., 2021](#); [Liao et al., 2017](#)).

Air sparging is useful in reducing energy consumption and boosting hemicellulose retention from wheat bran in UF membranes. There is a possibility of transferring this process to streams from the pulp and paper industry, although it has not been documented yet ([Thuvander et al., 2018](#)). Other potential methods for scaling up membrane technology include assisted liquid membrane extraction and permeation. Liquid membrane permeation using supported membranes has shown promise as a future separation solution for treating process streams from the PPI ([Kienberger et al., 2020](#)).

7.10 Conclusions and future trends

The pulp and paper industry has been using membrane technology for commercial purposes since the 1970s. A literature assessment of over 150 papers from 1998 to 2008 shows that UF and MBR are preferred for research and development as well as in industrial use in the pulp and paper sector.

A significant portion of the research and development has focused on traditional membrane technologies such as MF, NF, RO, UF, and MBR. Advanced membrane technologies like ED have been evaluated and shown promising outcomes. Other promising technologies, including MD, have not been fully investigated. Advancements in these sophisticated technologies have been hindered by the challenge of addressing fouling issues and lowering the substantial capital and operational expenses. Creativity in research, such as integrating several membrane separation techniques or using various mechanical and chemical approaches to address challenges, is essential. The main obstacles which limit the use of membrane processes at industrial level are fouling, selectivity, and prices. However, several sectors have successfully addressed these issues by integrating other separation technologies, showing significant promise for expanding membrane systems to industrial use with economic viability.

In the future, membrane technology is expected to become a more cost-effective, technically viable, and environmentally benign solution for the pulp and paper sector as research focuses on investigating different membrane technologies and optimizing processes.

List of acronyms

AOPs	advanced oxidation processes
AOX	adsorbable organic halides
ASP	activated sludge process
BCTMP	bleached-chemi-thermo-mechanical pulping
BOD	biochemical oxygen demand
COD	chemical oxygen demand
ED	electrodialysis
GO	graphene oxide
HAMBR	hybrid airlift membrane bioreactor
HRT	hydraulic retention time
MD	membrane distillation
MBR	membrane bioreactor
MF	microfiltration
MLSS	mixed liquor suspended solids
MWCO	molecular weight cut-off
NF	nanofiltration
OLR	organic loading rate
PA	polyamide
PAI	polyamide-imide
PAN	polyacrylonitrile
PEI	polyether-imide
PES	polyethersulphone
PS	polysulphone
PVDF	polyvinylidene fluoride
RC	regenerated cellulose
RO	reverse osmosis
SRT	sludge retention time
TMP	transmembrane pressure
TN	total nitrogen
TP	total phosphorus
TDC	total dissolved carbon
TDS	total dissolved solids
TSS	total suspended solids
UF	ultrafiltration
VCR	volume concentration ratio
VOC	volatile organic compound
VSEP	vibratory shear enhanced processing

References

- Adnan, S., Hoang, M., & Wang, H. (2009). Research, development and application of membrane technology in the pulp and paper industry. In Appita annual conference (pp. 241–246). Australia.

- Ahmad, N. N. R., Ang, W. L., Teow, Y. H., Mohammad, A. W., & Hilal, N. (2022). Nanofiltration membrane processes for water recycling, reuse and product recovery within various industries: A review. *Journal of Water Process Engineering*, 45. <https://doi.org/10.1016/j.jwpe.2021.102478>, <https://www.sciencedirect.com/science/journal/22147144>.
- Al-Rudainy, B., Galbe, M., Lipnizki, F., & Wallberg, O. (2019). Galactoglucomannan recovery with hydrophilic and hydrophobic membranes: Process performance and cost estimations. *Membranes*, 9(8), 99. <https://doi.org/10.3390/membranes9080099>.
- Ang, W. L., Mohammad, A. W., Hilal, N., & Leo, C. P. (2015). A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants. *Desalination*, 363, 2–18. <https://doi.org/10.1016/j.desal.2014.03.008>, <https://www.journals.elsevier.com/desalination>.
- Arkell, A. (2015). *Membrane filtration for fractionation of biomass compounds-process design for the separation of hemicelluloses and lignin from alkaline solutions*.
- Arkell, A., Olsson, J., & Wallberg, O. (2014). Process performance in lignin separation from softwood black liquor by membrane filtration. *Chemical Engineering Research and Design*, 92(9), 1792–1800. <https://doi.org/10.1016/j.cherd.2013.12.018>.
- Aro, T., & Fatehi, P. (2017). Production and application of lignosulfonates and sulfonated lignin. *ChemSusChem*, 10(9), 1861–1877. <https://doi.org/10.1002/cssc.201700082>.
- Bhattacharya, P. K., Jayan, R., & Bhattacharjee, C. (2005). A combined biological and membrane-based treatment of prehydrolysis liquor from pulp mill. *Separation and Purification Technology*, 45(2), 119–130. <https://doi.org/10.1016/j.seppur.2005.03.003>.
- Biermann, C. J. (1996). *Handbook of pulping and papermaking*. Academic Press.
- Bijan, L., & Mohseni, M. (2008). Novel membrane pretreatment to increase the efficiency of ozonation-biooxidation. *Environmental Engineering Science*, 25(2), 229–238. <https://doi.org/10.1089/ees.2006.0264>.
- Bokhary, A., Leitch, M., & Liao, B. Q. (2021). Effect of organic loading rate on the biological performance of the thermophilic anaerobic membrane bioreactor treating pulp and paper primary sludge. *Clean Technologies and Environmental Policy*, 23(9), 2669–2681. <https://doi.org/10.1007/s10098-021-02186-w>.
- Burts, K. S., Plisko, T. V., Bilyukevich, A. V., Rodrigues, G., Sjölin, M., Lipnizki, F., & Ulbricht, M. (2022). Development of polysulfone ultrafiltration membranes with enhanced antifouling performance for the valorisation of side streams in the pulp and paper industry. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 632, 127742. <https://doi.org/10.1016/j.colsurfa.2021.127742>.
- Bérubé, P. R., & Hall, E. R. (2001). Cost comparison between a high-temperature membrane bioreactor and a steam stripper for the treatment of foul evaporator condensate for reuse. *Tappi Journal*, 84(6), 62.
- Chabot, B., Krishnagopalan, G. A., & Abubakr, S. (1999). Flexographic newspaper deinking: Treatment of wash filtrate effluent by membrane technology. *Journal of Pulp and Paper Science*, 25(10), 337–343.
- Chua, S.-C., Isa, M. H., & Ho, Y.-C. (2020). Electrodialysis (ED): A review on the fundamental concept, advantages, limitations and future trend. *Platform: A Journal of Science and Technology*, 3(2), 14. <https://doi.org/10.61762/pjstvol3iss2art6146>.
- Cortiñas, S., Luque, S., Álvarez, J. R., Canaval, J., & Romero, J. (2002). Microfiltration of kraft black liquors for the removal of colloidal suspended matter (pitch). *Desalination*, 147(1-3), 49–54. [https://doi.org/10.1016/s0011-9164\(02\)00575-1](https://doi.org/10.1016/s0011-9164(02)00575-1).
- Curcio, E., & Drioli, E. (2005). Membrane distillation and related operations—A review. *Separation & Purification Reviews*, 34(1), 35–86. <https://doi.org/10.1081/spm-200054951>.

- Dagar, S., Singh, S. K., & Gupta, M. K. (2023). Integration of pre-treatment with UF/RO membrane process for waste water recovery and reuse in agro-based pulp and paper industry. *Membranes*, 13, 199. <https://doi.org/10.3390/membranes13020199>.
- Dexter, R. J. (1996). Industry's efforts at effluent closure must focus on competitive innovation. *Pulp and Paper*, 70(2), 55–59.
- Dogan, E. C., Pişkin, E. D., Narcı, A. O., Mert, B. K., Yakın, S. T., Demirözlü, T. N., Atasoy, M. S., & Aydinler, C. (2023). Eco-sustainable paper wastewater management by water-resource recovery and concentrate minimization using a membrane oxidation reactor and membrane distillation system. *Environmental Science: Water Research and Technology*, 9(12), 3398–3416. <https://doi.org/10.1039/d3ew00520h>, <http://pubs.rsc.org/en/journals/journal/ew>.
- Dufresne, R., Lavallee, H. C., Lebrun, R. E., & Lo, S. N. (1998). Comparison of performance between membrane bioreactor and activated sludge system for the treatment of pulping process wastewaters. *Technical Association of the Pulp and Paper Industry Journal*, 81(4), 131–135.
- Ebrahimi, M., Busse, N., Kerker, S., Schmitz, O., Hilpert, M., & Czermak, P. (2016). Treatment of the bleaching effluent from sulfite pulp production by ceramic membrane filtration. *Membranes*, 6, 7. <https://doi.org/10.3390/membranes6010007>.
- Ebrahimi, M., Humpert, D., Schönherr, S., & Czermak, P. (2021). Ceramic membrane technology for the availability of biogenic material streams. *Chemie-Ingenieur-Technik*, 93(1-2), 154–167. <https://doi.org/10.1002/cite.202000160>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1522-2640](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1522-2640).
- Erkan, H. S., & Engin, G. O. (2017). The investigation of paper mill industry wastewater treatment and activated sludge properties in a submerged membrane bioreactor. *Water Science and Technology*, 76(7), 1715–1725. <https://doi.org/10.2166/wst.2017.351>, <http://wst.iwaponline.com/content/76/7/1715.full.pdf>.
- Farlow, M. (1996). Water management critical for mills making effort at whitewater closure. *Pulp and Paper*, 70(5), 6.
- Francey, S., Tran, H., & Jones, A. (2009). Current status of alternative fuel use in lime kilns. *Technical Association of the Pulp and Paper Industry Journal*, 8(10), 33–39. <https://doi.org/10.32964/tj8.10.33>.
- García -Payo, M., Izquierdo-Gil, M. A., & Fernández-Pineda, C. (2000). Air gap membrane distillation of aqueous alcohol solutions. *Journal of Membrane Science*, 169, 61–80. [https://doi.org/10.1016/S0376-7388\(99\)00326-9](https://doi.org/10.1016/S0376-7388(99)00326-9).
- Geraldes, V., & de Pinho, M. N. (1995). Process water recovery from pulp bleaching effluents by an NF/ED hybrid process. *Journal of Membrane Science*, 102(C), 209–221. [https://doi.org/10.1016/0376-7388\(94\)00325-S](https://doi.org/10.1016/0376-7388(94)00325-S).
- Ghatak, H. R. (2009). Reduction of organic pollutants with recovery of value-added products from soda black liquor of agricultural residues by electrolysis. *Technical Association of the Pulp and Paper Industry Journal*, 8(7), 4–10.
- Gholami, M., Souraki, B. A., Pendashteh, A., & Marzouni, M. B. (2017). Efficiency evaluation of the membrane/AOPs for paper mill wastewater treatment. *Environmental Technology*, 38, 1127–1138. <https://doi.org/10.1080/09593330.2016.1218553>.
- Gommers, K., De Wever, H., Brauns, E., & Peys, K. (2007). Recalcitrant COD degradation by an integrated system of ozonation and membrane bioreactor. *Water Science and Technology*, 55(12), 245–251. <https://doi.org/10.2166/wst.2007.410>.
- Gönder, Z. B., Arayici, S., & Barlas, H. (2012). Treatment of pulp and paper mill wastewater using ultrafiltration process: Optimization of the fouling and rejections. *Industrial and Engineering Chemistry Research*, 51(17), 6184–6195. <https://doi.org/10.1021/ie2024504>.

- Han, N., Zhang, J., Hoang, M., Gray, S., & Xie, Z. (2021). A review of process and wastewater reuse in the recycled paper industry. *Environmental Technology and Innovation*, 24. <https://doi.org/10.1016/j.eti.2021.101860>, <http://www.journals.elsevier.com/environmental-technology-and-innovation/>.
- Hermosilla, D., Merayo, N., Ordóñez, R., & Blanco, Á. (2012). Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill. *Waste Management*, 32(6), 1236–1243. <https://doi.org/10.1016/j.wasman.2011.12.011>.
- Holmqvist, A., Wallberg, O., & Jönsson, A.-S. (2005). Ultrafiltration of kraft black liquor from two Swedish pulp mills. *Chemical Engineering Research and Design*, 83(8), 994–999. <https://doi.org/10.1205/cherd.04204>.
- Hong, Y.S., Zhou, H., & Zytner, R.G. Combining ultrafiltration process with coagulation pretreatment for pulp mill wastewater treatment. *Environmental Technology*, 28 995–1006. <https://doi.org/10.1080/09593332808618860>.
- Humpert, D., Ebrahimi, M., Stroh, A., & Czermak, P. (2019). Recovery of liginosulfonates from spent sulfite liquor using ceramic hollow-fiber membranes. *Membranes*, 9(4), 45. <https://doi.org/10.3390/membranes9040045>.
- Izadi, A., Hosseini, M., Shariati, F. P., Darzi, G. N., & Bidhendi, G. N. (2020). Treatment of real paper-recycling wastewater in a novel hybrid airlift membrane bioreactor (Hambr) for simultaneous removal of organic matter and nutrients. *Iranian Journal of Chemistry and Chemical Engineering*, 39(3), 203–211. http://www.ijcce.ac.ir/article_34793_340da50fd2e58180fa7f235496b076c5.pdf.
- Johakimu, J. K., Andrew, J., Sithole, B. B., & Syphus, E. (2016). Preliminary techno-economic assessment of recovering water and caustic soda from alkaline bleach plant effluent. *Journal of Cleaner Production*, 139, 914–921. <https://doi.org/10.1016/j.jclepro.2016.08.088>.
- Judd, S., & Jefferson, B. (2003). *Membranes for industrial wastewater recovery and reuse*. United Kingdom: Elsevier Inc, 1–291. <https://doi.org/10.1016/B978-1-85617-389-6.X5000-0>, <http://www.sciencedirect.com/science/book/9781856173896>.
- Jönsson, A. S., & Wallberg, O. (2009). Cost estimates of kraft lignin recovery by ultrafiltration. *Desalination*, 237(1–3), 254–267. <https://doi.org/10.1016/j.desal.2007.11.061>.
- Kallioinen, M., Mänttari, M., Nyström, M., Nuortila-Jokinen, J., Nurminen, P., & Sutela, T. (2010). Membrane evaluation for the treatment of acidic clear filtrate. *Desalination*, 250(3), 1002–1004. <https://doi.org/10.1016/j.desal.2009.09.090>.
- Kalshan, S., Dhankhar, R., Narwal, S., Chhillar, A., Yadav, P., & Yadav, S. (2024). Achieving high removal efficiency and membrane sustainability in pulp and paper industry MBR system. *Oriental Journal Of Chemistry*, 40(1), 209–219. <https://doi.org/10.13005/ojc/400126>.
- Kamali, M., & Khodaparast, Z. (2015). Review on recent developments on pulp and paper mill wastewater treatment. *Ecotoxicology and Environmental Safety*, 114, 326–342. <https://doi.org/10.1016/j.ecoenv.2014.05.005>.
- Kaya, Y., Gönder, Z. B., Vergili, I., & Barlas, H. (2010). The effect of transmembrane pressure and pH on treatment of paper machine process waters by using a two-step nanofiltration process: Flux decline analysis. *Desalination*, 250(1), 150–157. <https://doi.org/10.1016/j.desal.2009.06.034>.
- Keyoumu, A., Sjödhall, R., Henriksson, G., Ek, M., Gellerstedt, G., & Lindström, M. E. (2004). Continuous nano- and ultra-filtration of kraft pulping black liquor with ceramic filters: A method for lowering the load on the recovery boiler while generating valuable side-products. *Industrial Crops and Products*, 20(2), 143–150. <https://doi.org/10.1016/j.indcrop.2004.04.017>.
- Kienberger, M., Demmelmayer, P., Weiß, M., Zankl, A., & Spirk, S. (2020). Biobased support layers for the fractionation and selective extraction of liginosulfonates.

- Solvent Extraction and Ion Exchange*, 38(1), 132–141. <https://doi.org/10.1080/07366299.2019.1691764>, <http://www.tandf.co.uk/journals/titles/07366299.asp>.
- Klepaczka, A. (2004). Ultrafiltracja w oczyszczaniu wod obiegowych. *Przegląd Papierniczy*, 60(11), 606–608.
- Lerner, M., Stahl, N., & Galil, N. I. (2007). Comparative study of MBR and activated sludge in the treatment of paper mill wastewater. *Water Science and Technology*, 55(6), 23–29. <https://doi.org/10.2166/wst.2007.208>.
- Liao, B., Bohkary, A., Cui, L., & Li, H. (2017). A review of membrane technology for integrated forest biorefinery. *Journal of Membrane Science and Research*, 3, 120–141. <https://doi.org/10.22079/JMSR.2016.22839>.
- Liu, G., Liu, Y., Ni, J., Shi, H., & Qian, Y. (2004). Treatability of kraft spent liquor by microfiltration and ultrafiltration. *Desalination*, 160(2), 131–141. [https://doi.org/10.1016/S0011-9164\(04\)90003-3](https://doi.org/10.1016/S0011-9164(04)90003-3), <https://www.sciencedirect.com/science/journal/00119164>.
- Li, K., Kollberg, L., Almqvist, H., Xu, B., & Hulteberg, C. (2021). Maximizing yield of liquid-lignin from membrane filtration retentate of kraft black liquor. *Industrial Crops and Products*, 169, 113657. <https://doi.org/10.1016/j.indcrop.2021.113657>.
- Madwar, K., & Tarazi, H. (2003). Desalination techniques for industrial wastewater reuse. *Desalination*, 152(1–3), 325–332. [https://doi.org/10.1016/S0011-9164\(02\)01080-9](https://doi.org/10.1016/S0011-9164(02)01080-9).
- Maitz, S., Wernsperger, L., & Kienberger, M. (2023). Isolation of carboxylic acids and NaOH from kraft black liquor with a membrane-based process sequence. *Membranes*, 13(1), 92. <https://doi.org/10.3390/membranes13010092>.
- Merayo, N., Hermosilla, D., Blanco, L., Cortijo, L., & Blanco, Á. (2013). Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry. *Journal of Hazardous Materials*, 262, 420–427. <https://doi.org/10.1016/j.jhazmat.2013.09.005>.
- Minami, K., Okamura, K., Ogawa, S., & Naritomi, T. (1991). Continuous anaerobic treatment of wastewater from a kraft pulp mill. *Journal of Fermentation and Bioengineering*, 71(4), 270–274. [https://doi.org/10.1016/0922-338x\(91\)90280-t](https://doi.org/10.1016/0922-338x(91)90280-t).
- Mulopo, J. (2017). Bleach plant effluent treatment in anaerobic membrane bioreactor (AMBR) using carbon nanotube/polysulfone nanocomposite membranes. *Journal of Environmental Chemical Engineering*, 5(5), 4381–4387. <https://doi.org/10.1016/j.jece.2017.08.027>.
- Mänttari, M., Kuosa, M., Kallas, J., & Nyström, M. (2008). Membrane filtration and ozone treatment of biologically treated effluents from the pulp and paper industry. *Journal of Membrane Science*, 309, 112–119. <https://doi.org/10.1016/j.memsci.2007.10.019>.
- Mänttari, M., & Nyström, M. (2004). Ultrafiltration and nanofiltration in the pulp and paper industry using cross-rotational (CR) filters. *Water Science and Technology*, 50(3), 229–238. <https://doi.org/10.2166/wst.2004.0200>.
- Mänttari, M., Pekuri, T., & Nyström, M. (2004). NF270, a new membrane having promising characteristics and being suitable for treatment of dilute effluents from the paper industry. *Journal of Membrane Science*, 242, 107–116. <https://doi.org/10.1016/j.memsci.2003.08.032>.
- Mänttari, M., Puro, L., Nuortila-Jokinen, J., & Nyström, M. (2000). Fouling effects of polysaccharides and humic acid in nanofiltration. *Journal of Membrane Science*, 165, 1–17. [https://doi.org/10.1016/S0376-7388\(99\)00215-X](https://doi.org/10.1016/S0376-7388(99)00215-X).
- Mänttari, M., Viitikko, K., & Nyström, M. (2006). Nanofiltration of biologically treated effluents from the pulp and paper industry. *Journal of Membrane Science*, 272, 152–160. <https://doi.org/10.1016/j.memsci.2005.07.031>.
- Nataraj, S. K., Sridhar, S., Shaikha, I. N., Reddy, D. S., & Aminabhavi, T. M. (2007). Membrane-based microfiltration/electrodialysis hybrid process for the treatment

- of paper industry wastewater. *Separation and Purification Technology*, 57(1), 185–192. <https://doi.org/10.1016/j.seppur.2007.03.014>.
- Neves, L. C., De Souza, J. B., Vidal, C. M. D., Martins, K. G., & Managó, B. L. (2017). Pulp and paper mill effluent post-treatment using microfiltration and ultrafiltration membranes. *Cellulose Chemistry and Technology*, 51(5-6), 579–588. [http://www.cellulosechemtechnol.ro/pdf/CCT5-6\(2017\)/p.579-588.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT5-6(2017)/p.579-588.pdf).
- Nunes, S. P., & Peinemann, K.-V. (2001). Membrane technology in the chemical industry: Future directions. In *Membrane technology: In the chemical industry*. Wiley, 268–295. <https://doi.org/10.1002/3527600388.ch13>.
- Nuortila-Jokinen, J., Huuhilo, T., & Nyström, M. (2003). Closing pulp and paper mill water circuits with membrane filtration. *Annals of the New York Academy of Sciences*, 984, 39–52. <https://doi.org/10.1111/j.1749-6632.2003.tb05991.x>, <http://www.blackwellpublishing.com/0077-8923>.
- Oliveira, C. R., Silva, C. M., & Milanez, A. F. (2007). Application of ultrafiltration in the pulp and paper industry: Metals removal and whitewater reuse. *Water Science and Technology*, 55(6), 117–123. <https://doi.org/10.2166/wst.2007.219>.
- Olsen, O. (1980). Membrane technology in the pulp and paper industry. *Desalination*, 35, 291–302. [https://doi.org/10.1016/s0011-9164\(00\)88617-8](https://doi.org/10.1016/s0011-9164(00)88617-8).
- Park, J. Y., Choi, S. J., & Park, B. R. (2007). Effect of N₂-back-flushing in multichannels ceramic microfiltration system for paper wastewater treatment. *Desalination*, 202, 207–214. <https://doi.org/10.1016/j.desal.2005.12.056>.
- Patel, K., Patel, N., Vaghamsi, N., Shah, K., Duggirala, S. M., & Dudhagara, P. (2021). Trends and strategies in the effluent treatment of pulp and paper industries: A review highlighting reactor options. *Current Research in Microbial Sciences*, 2, 100077. <https://doi.org/10.1016/j.crmicr.2021.100077>.
- Pfromm, P. H. (2006). Low effluent processing in the pulp and paper industry: Electrodialysis for continuous selective chloride removal. *Separation Science and Technology*, 32, 2913–2926. <https://doi.org/10.1080/01496399708000787>.
- Pizzichini, M., Russo, C., & Di Meo, C. (2005). Purification of pulp and paper wastewater, with membrane technology, for water reuse in a closed loop. *Desalination*, 178(1-3), 351–359. <https://doi.org/10.1016/j.desal.2004.11.045>.
- Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater—A review. *Science of the Total Environment*, 333(1-3), 37–58. <https://doi.org/10.1016/j.scitotenv.2004.05.017>.
- Puro, L., Kallioinen, M., Mänttari, M., Natarajan, G., Cameron, D. C., & Nyström, M. (2010). Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters. *Desalination*, 264(3), 249–255. <https://doi.org/10.1016/j.desal.2010.06.034>.
- Qu, X., Gao, W. J., Han, M. N., Chen, A., & Liao, B. Q. (2012). Integrated thermophilic submerged aerobic membrane bioreactor and electrochemical oxidation for pulp and paper effluent treatment – Towards system closure. *Bioresource Technology*, 116, 1–8. <https://doi.org/10.1016/j.biortech.2012.04.045>.
- Rath, R. L., Bhattacharjee, C., Jain, S., & Bhattacharya, P. K. (2005). Treatment of prehydrolysis liquor from pulp mill using a biological route followed by reverse osmosis. *Chemical Engineering & Technology*, 28(10), 1201–1211. <https://doi.org/10.1002/ceat.200500249>.
- Richardson, D., Blom, L., & Reeves, E. (2008). Pilot plant investigations into the feasibility of membrane treatment of paper machine and deinking plant filtrates. In *Appita annual conference* 383–387.
- Richardson, J. F., Harker, J. H., Backhurst, J. R., & Coulson, J. M. (2002). *Coulson and Richardson's chemical engineering*. Butterworth-Heinemann, 2.
- Rudolph, G., Schagerlöf, H., Krogh, K. B. M., Jönsson, A. S., & Lipnizki, F. (2018). Investigations of alkaline and enzymatic membrane cleaning of ultrafiltration

- membranes fouled by thermomechanical pulping process water. *Membranes*, 8(4). <https://doi.org/10.3390/membranes8040091>, <https://www.mdpi.com/2077-0375/8/4/91/pdf>.
- Saif, Y., Almansoori, A., & Elkamel, A. (2013). Wastewater minimization in pulp and paper industries through energy-efficient reverse-osmosis membrane processes. *Chemical Engineering & Technology*, 36(3), 419–425. <https://doi.org/10.1002/ceat.201200445>.
- Scott, K. (1995). *Handbook of industrial membranes*.
- Shamsuddin, N., Das, D. B., & Starov, V. M. (2015). Filtration of natural organic matter using ultrafiltration membranes for drinking water purposes: Circular cross-flow compared with stirred dead end flow. *Chemical Engineering Journal*, 276, 331–339. <https://doi.org/10.1016/j.cej.2015.04.075>, www.elsevier.com/inca/publications/store/6/0/1/2/7/3/index.htm.
- Shukla, S. K., Kumar, V., Van Doan, T., Yoo, K., Kim, Y., & Park, J. (2015). Combining activated sludge process with membrane separation to obtain recyclable quality water from paper mill effluent. *Clean Technologies and Environmental Policy*, 17(3), 781–788. <https://doi.org/10.1007/s10098-014-0836-2>, <https://link.springer.com/journal/10098>.
- Silva, C. M., Reeve, D. W., Woodhouse, K. A., Husain, H., & Behmann, H. (1999). Water reuse in the pulp and paper industry: Evaluation of four microfiltration applications. *Pulp and Paper Canada*, 100(5), 38–43.
- Simstich, B., Beimfohr, C., & Horn, H. (2012). Lab scale experiments using a submerged MBR under thermophilic aerobic conditions for the treatment of paper mill deinking wastewater. *Bioresource Technology*, 122, 11–16. <https://doi.org/10.1016/j.biortech.2012.04.029>.
- Simstich, B., & Oeller, H.-J. (2010). Membrane technology for the future treatment of paper mill effluents: Chances and challenges of further system closure. *Water Science and Technology*, 62(9), 2190–2197. <https://doi.org/10.2166/wst.2010.947>.
- Singh, R. (2006). *Hybrid membrane systems for water purification: technology, systems design and operations hybrid membrane systems for water purification: Technology, systems design and operations*. United States: Elsevier, 1–291. <https://doi.org/10.1016/B978-1-85617-442-8.X5000-3>, <https://www.elsevier.com/books/hybrid-membrane-systems-for-water-purification/singh/978-1-85617-442-8>.
- Slater, C. S., Ahlert, R. C., & Uchirin, C. G. (1983). Applications of reverse osmosis to complex industrial wastewater treatment. *Desalination*, 48(2), 171–187. [https://doi.org/10.1016/0011-9164\(83\)80015-0](https://doi.org/10.1016/0011-9164(83)80015-0).
- Stahl, N., Tenenbaum, A., & Galil, N. I. (2004). Advanced treatment by anaerobic process followed by aerobic membrane bioreactor for effluent reuse in paper mill industry. *Water Science and Technology*, 50(3), 245–252. <https://doi.org/10.2166/wst.2004.0202>.
- Sutherland, K. S. (2004). *Profile of the international filtration and separation industry: Market prospects to 2009*. Oxford, UK: Elsevier Science.
- Su, W., Chen, C., Xu, H., Yang, W., & Dai, H. (2016). Filtering whitewater with an ultrafiltration membrane: Effects of the interaction between dissolved organics and metal ions on membrane fouling. *North Carolina State University, China BioResources*, 11(1), 1108–1124. [10.15376/biores.11.1.1108-1124](https://doi.org/10.15376/biores.11.1.1108-1124), https://www.ncsu.edu/bioresources/BioRes_11/BioRes_11_1_1108_Su_CXYD_Filtering_Whitewater_Effects_Interac_Dissol_Organics_Metal_Ions_8216.pdf.
- Tenno, R., & Paulapuro, H. (1999). Removal of dissolved organic compounds from paper machine whitewater by membrane bioreactors: A comparative analysis. *Control Engineering Practice*, 7(9), 1085–1099. [https://doi.org/10.1016/S0967-0661\(99\)00079-9](https://doi.org/10.1016/S0967-0661(99)00079-9).
- Thuvander, J., Arkell, A., & Jönsson, A. S. (2018). Reduction of energy demand by use of air sparging during ultrafiltration of alkali-extracted wheat bran hemicelluloses. *Chemical Engineering Research and Design*, 138, 43–50.

- <https://doi.org/10.1016/j.cherd.2018.08.001>, http://www.elsevier.com/wps/find/journaldescription.cws_home/713871/description#description.
- Tizon, B., Boivin, P., Bayle, S., Pradelle, H., & Bloch, J. H. (2005/12). France ultrafiltration treatment of coating effluents from paper machine. In *Annual meeting of the Pulp and Paper Technical Association of Canada (PAPTAC)* 14947722115–119.
- Tolbert, A., Akinosho, H., Khunsupat, R., Naskar, A. K., & Ragauskas, A. J. (2014). Characterization and analysis of the molecular weight of lignin for biorefining studies. *Biofuels, Bioproducts and Biorefining*, 8(6), 836–856. <https://doi.org/10.1002/bbb.1500>, <http://www3.interscience.wiley.com>.
- Tomani, P., & Seisto, A. (1999). Separation methods for closed-loop manufacture of bleached kraft pulp—Overview of an EU project. *Desalination*, 124(1–3), 217–223. [https://doi.org/10.1016/s0011-9164\(99\)00106-x](https://doi.org/10.1016/s0011-9164(99)00106-x).
- Upton, B. H., Krishnagopalan, G. A., & Abubakr, S. (1999). Ultrafiltrative deinking of flexographic ONP: The role of surfactants. *Technical Association of the Pulp and Paper Industry Journal*, 82(11), 104–114.
- Valderrama, O. J., Zedda, K. L., & Velizarov, S. (2021). Membrane filtration opportunities for the treatment of black liquor in the paper and pulp industry. *Water*, 13(16), 2270. <https://doi.org/10.3390/w13162270>.
- Vives, M. B., Thuvander, J., Arkell, A., & Lipnizki, F. (2022). Low-molecular-weight lignin recovery with nanofiltration in the kraft pulping process. *Membranes*, 12(3). <https://doi.org/10.3390/membranes12030310>, <https://www.mdpi.com/2077-0375/12/3/310/pdf>.
- Wallberg, O., Jönsson, A. S., & Wimmerstedt, R. (2003). Fractionation and concentration of kraft black liquor lignin with ultrafiltration. *Desalination*, 154(2), 187–199. [https://doi.org/10.1016/S0011-9164\(03\)80019-X](https://doi.org/10.1016/S0011-9164(03)80019-X), <https://www.sciencedirect.com/science/journal/00119164>.
- Wang, Z., Ma, C., Sinquefield, S. A., Shofner, M. L., & Nair, S. (2019). High-performance graphene oxide nanofiltration membranes for black liquor concentration. *ACS Sustainable Chemistry and Engineering*, 7(17), 14915–14923. <https://doi.org/10.1021/acssuschemeng.9b03113>, <http://pubs.acs.org/journal/ascecg>.
- Weis, A., Bird, M. R., Nyström, M., & Wright, C. (2005). The influence of morphology, hydrophobicity and charge upon the long-term performance of ultrafiltration membranes fouled with spent sulphite liquor. *Desalination*, 175(1), 73–85. <https://doi.org/10.1016/j.desal.2004.09.024>.
- Widsten, P., Nguyen, T., Laine, J. E., Malmqvist, Å., & Welander, T. (2004). In-mill removal of TMP whitewater contaminants by biological treatment in an aerobic biokidney used in conjunction with microfiltration and laccase treatment. *Nordic Pulp & Paper Research Journal*, 19(3), 379–383. <https://doi.org/10.3183/npprj-2004-19-03-p379-383>.
- Wiley, A. J., Dambruch, L. E., Parker, P. E., & Dugal, H. S. (1978). Treatment of bleach plant effluents. A combined reverse osmosis/freeze concentration process. *Technical Association of the Pulp and Paper Industry Journal*, 61(12), 77–80.
- Xu, Y., Li, Y., & Hou, Y. (2019). Reducing ultrafiltration membrane fouling during recycled paper mill wastewater treatment using pretreatment technologies: A comparison between coagulation and Fenton. *Journal of Chemical Technology and Biotechnology*, 94(3), 804–811. <https://doi.org/10.1002/jctb.5826>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1097-4660](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1097-4660).
- Zaidi, A., Buisson, H., Sourirajan, S., & Wood, H. (1992). Ultra- and nano-filtration in advanced effluent treatment schemes for pollution control in the pulp and paper industry. *Water Science and Technology*, 25(10), 263–276. <https://doi.org/10.2166/wst.1992.0254>.

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Biological methods for pulp and paper wastewater treatment

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8.1 Introduction

From the beginning of the paper-manufacturing process, pulp and paper (P&P) global industries have been reported to consume vast amounts of water, which consequently leads to notable highly contaminated wastewater bulk generation. Papermaking and the first traces of the P&P industries were introduced during the Han dynasty by Ts'ai Lun at 105 AD, whereas the invention of the papyrus is located in ancient Egypt around 2400 BC (Mleziva & Wang, 2012). However, the Chinese version of the paper, which is considered to be the precursor of contemporary used paper, is mainly formed by a wood pulp mixture, specifically cellulose fibers. Lun may have been the inventor of modern paper, yet more civilizations around the globe grew an interest in papermaking, such as the Central American Mayans around 100 AD, who created a thin sheet of paper mat called “amatl,” the Koreans and Japanese later on (Mleziva & Wang, 2012).

Europe was introduced to the papermaking technique by the Arabs around 1150 AD, while in 1453, Gutenberg innovatively increased the demand for paper by inventing the printing press. Hence, among others, Gutenberg triggered the universal industrialization of papermaking that bloomed during the 19th century and resulted in the mass production of newspapers, magazines, and the physical form of currency (Aytac & Korkmaz, 2022; Del Rio et al., 2022).

Wastewater treatment has been a research trend, as industries and governments all over the globe are recruiting groups of scientists to do

research and propose possible depollution ways. Dating back to the origins of humankind, humans developed the first wastewater constructs like dams, aqueducts, wells, and drainage systems, yet hygiene was ignored for the most part, a situation that caused dysentery and other infectious diseases to spread within the populations. The past main engineering goal was to build systems able to tackle any property destruction caused by natural phenomena while essentially providing people with fresh water (De Feo et al., 2011). Hippocrates emphasized the quality of drinkable water affecting human health and later on introduced a conical water treatment filter (De Namor, 2007). Between 500 BC and 1000 AD, methods like distillation and boiling under direct exposure to sunlight were developed. Furthermore, some civilizations actively used natural materials like sand, herbs, seeds, rhizomes of algae, roots of Kanal, rocks, and iron to filtrate water (De Namor, 2007). From the Mesopotamian Empire to the Indus, Egyptian, Greek, and Roman civilizations, no serious wastewater treatment was started during the Middle Ages. Moreover, an immense historical regression was reported by Sorcinelli (Lofrano & Brown, 2010) in Italy because of the nonexistent sewer system. It was not until the 19th century that the global industries noticed that the water used for manufacturing purposes was polluted both biologically and chemically, and the need for cleansing techniques and methods started to arise (Lofrano & Brown, 2010).

The 20th century marks the beginning of thorough scientific research. Most importantly the eighth report in 1912 was introduced by the Royal Commission on Sewage Disposal, and the term biochemical oxygen demand (BOD) was proposed (Sun et al., 2022). Two different research groups in 1925 and 1932, respectively, designed aeration and deaeration models for BOD levels on surface water prediction. This was the moment when governmental interest was drawn to serious waste treatment methods research. Unfortunately, World War I's outbreak initially intercepted the function of the already constructed wastewater treatment facilities in European. Moreover, many of those facilities were severely damaged and abandoned due to the fact that not all political parties were supportive of the given methods by the time World War II commenced; thus water pollution drastically increased. The end of the war impelled the United Kingdom and the United States to reinstate the operation of wastewater treatment plants. In the following years, water pollution debates inspired the formation of waste management policies, while gas chromatography and atomic absorption spectrophotometry, introduced around 1970, empowered scientists to classify toxic compounds present in wastewater (Faisal et al., 2023; Sun et al., 2022).

The first semimodern treatment plant was constructed in Prague during 1900–06. Subsequently, this resulted in 1926 in the construction of the first biological wastewater treatment plant, called the

“Jones Island Sewage Treatment Plant,” in the United States. Using this treatment method, biosolids were collected, and the produced sludge was converted into fertilizer with the brand name “Milorganite,” which is a predecessor to the inorganic urea fertilizer that entered the market by the end of World War II (Faisal et al., 2023). China is currently producing the most treatment patents in the last five decades, whereas the United States has been exporting its technological advances internationally (Angelakis et al., 2023).

Nowadays, modern aquatic sewage treatment focuses on combining chemical, biological, and physical methods so as to increase its effectiveness in purifying the wastes while simultaneously decreasing the energy and equipment costs (Angelakis et al., 2023; Sun et al., 2022). The P&P industry has been claimed to belong among the top 10 environmental polluting industries worldwide, a position attributed to the generation of wastewater that contains harmful pollutants, such as phenols, lignin, absorbable organo-halogens (AOX), and chlorinated organic substances (Sharma et al., 2022), and is characterized by increased BOD and chemical oxygen demand (COD). Hence, the demand for biodegradation techniques has increased drastically, since the legal pressure for more environmentally friendly options has proportionally increased by environmental nongovernmental organizations (ENGOS) as well as world governments (Roy et al., 2021). Circumstances have brought forth the need for hybrid process exploration instead of employing traditional methods, with an aim to reduce humankind’s wastewater pollution footprint on the planet. Gray et al. (2014) have claimed that the Environmental Protection Agency introduced to all P&P factories a combination of air and water regulations so as to diminish their natural negative impact. Therefore worldwide corporations ardently aim to develop the most beneficial means for wastewater control in the dawn of environmental crisis (Gray et al., 2014).

In this chapter the matter of biologically treating wastewater is further analyzed on its major parameters of techniques, energy, and infrastructure expenses, considering the P&P industry. These analyzed processes are then compared to propose the most economical yet effective alternatives to conventional methods.

8.2 Pulp and paper wastewater: characteristics and challenges

The P&P manufacturing process can be generally divided into three steps: pulp-making, pulp-processing, and papermaking, summarized in Fig. 8.1. P&P Industries convert raw materials (virgin or recycled fibers) into value-added matter through the aforementioned steps.

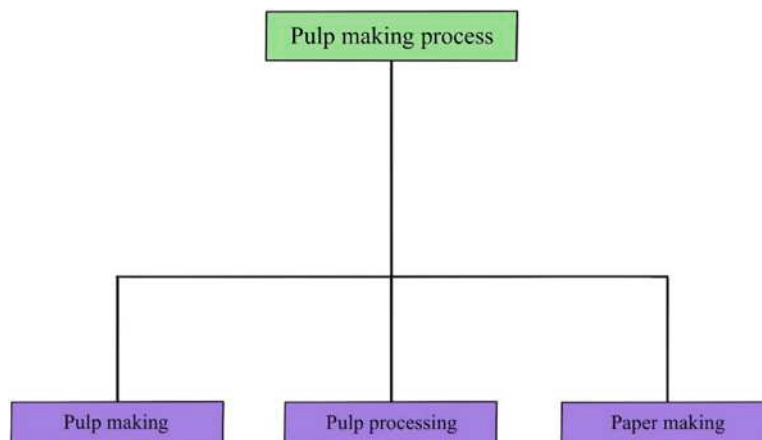


Figure 8.1 The pulp-making process (Ashrafi et al., 2015; Sharma et al., 2022).

Firstly, the raw materials are cut into small pieces after necessary preparation and debarking. Afterwards, they are cooked under high temperatures and pressure, using different pulp cooking methods (for instance, mechanical, chemical, or thermomechanical). Thirdly, during the bleaching step, the quality and brightness of the brown pulp are improved by various bleaching agents, including oxygen and chlorine. The following step is the washing of the produced pulp and the removal of all bleaching agents and other hardly biodegradable compounds. Then, the pulp is specifically treated to achieve a proper degree of fitness by combining it with materials such as dyes and resins. Finally, the treated pulp is dewatered, and the resulting sheets are dried using air or heat (Esmaeeli et al., 2023; Sharma et al., 2022).

Pulp wastewater refers to the liquid waste generated during the production of pulp, which is primarily used for papermaking. Pulp is produced by mechanically or chemically breaking down wood fibers to extract cellulose, which is the main component of paper. In fact, in the P&P industry, the majority of wastewater production originates from wood preparation, paper-making processes, pulp bleaching, and pulp washing. From the process of P&P-manufacturing explained above, it is evident that the generated wastewater is comprised mainly of various organic and inorganic substances, including lignin, color, organochlorides, chlorinated phenols, and AOX (Ashrafi et al., 2015; Hämäläinen et al., 2022; Sharma et al., 2022).

8.2.1 Key pollutant indicators of pulp and paper wastewater

COD could be characterized as the most general indicator of organic pollutants being released at each stage of the P&P

production process. It is known that the biodegradability of P&P wastewater is relatively low, with a minimum BOD to COD ratio of 0.095 at the bleaching state, and a maximum of 0.574 at the paper machine (Esmaeeli et al., 2023).

Moving on to lignin, it is a polyaromatic compound made by cross-linking phenolic precursors. Lignin is characterized by its stability, slight biodegradability, complexity, and hydrophobic behavior. In fact, kraft lignin is the most dominant and common type of lignin in the P&P industry (Esmaeeli et al., 2023).

Another key pollutant indicator of P&P wastewater is color. Colored wastewater occurs by specific materials, such as $-\text{CH}=\text{CH}-$ groups conjugated with aromatic rings, free radicals, and metal-organic complexes. It is common for P&P wastewater to contain high amounts of color, since its content of lignin and dissolved organic matter is high. Color compounds are a type of refractory organic material in P&P wastewater, which can either be converted into smaller substances rather than minerals or even utilized by microorganisms in conventional biobased treatment systems as energy and carbon sources. Furthermore, it is important to note that, in the P&P industry, the major sources of color are pulping, bleaching, and chemical recovery sections (Esmaeeli et al., 2023).

Finally, AOX is extremely harmful to the ecosystem and is responsible for the prevention of microorganism activity, ranging from mutagenic all the way to carcinogenic. Owing to this exact toxic effect of AOX, several European countries were led to set restricted regulations for wastewater disposal from P&P wastewater industries (Muhamad et al., 2013). Moreover, in the bleaching of pulp with the use of chlorine-based agents, about 8% of the chlorine will be converted into AOX. Since AOX can be absorbed into activated carbon, they are defined as “adsorbable organic halides” (Esmaeeli et al., 2023).

8.2.2 Pulp and paper wastewater challenges

While wastewater consists primarily of liquid waste, it is important to clarify that it additionally contains high concentrations of suspended solids (SS) and floating matter. The P&P processes are bound to produce wastewater, and the generated volume in each of these processes is closely related to the quantity of produced pulp. Pulp wastewater is typically characterized by its high BOD, COD, SS, and color. It can be highly polluting if not properly treated before being discharged into the environment. Effective treatment methods are employed to remove or reduce the pollutants present in pulp wastewater, ensuring compliance with environmental regulations and minimizing the impact on water bodies and ecosystems (Ashrafi et al., 2015; Jagaba et al., 2022; Sharma et al., 2022).

8.2.3 Water bodies and ecosystems pollution

The recycling and reuse of the generated wastewater are suggested to minimize the impact on water bodies and ecosystems. This process is of high importance to the P&P industry, since it helps reduce freshwater consumption while simultaneously minimizing the external discharges to the environment. To reuse the generated wastewater, the contaminants must be removed. That can be done by a series of biological, physicochemical, and integrated treatment processes. It is important to highlight the fact that during those processes, energy consumption is inevitable. As a result an emission of greenhouse gases (GHGs) takes place ([Jagaba et al., 2022](#)).

8.2.4 Air pollution

GHGs are gaseous constituents of the atmosphere that absorb and emit radiation in the thermal infrared range. Traces of GHG, both natural and anthropogenic, are present in the troposphere. The most abundant GHGs are water vapor, carbon dioxide (CO₂), methane (CH₄), nitrogen oxides (NO_x), and ozone (O₃). It is worth noting that GHG percentages vary daily, seasonally, and annually ([Cassia et al., 2018](#)), and the magnitude of the GHG emissions from P&P industries' wastewater treatment processes depends on the concentration of nutrients present in said wastewater, operating reactors' temperature, treatment process type, and the efficiency of the contaminant's removal ([Esmaeeli et al., 2023](#)).

During the pulping process, when wood waste and sludges are burned, the production of ashes does not cease to occur. Heavy metals are mostly found in black liquor in the pulp (by-product from the kraft process) and paper industries. In the paper-making process, black liquor is a liquid containing about 70% solids and is added to the digester. P&P aquatic waste contains a lot of organic compounds, like chlorinated phenols and lignin. Hence, when wastewater containing all these dangerous contaminants is discharged into rivers and lakes, it contributes to the overall toxicity of the aquatic environment. Some of the heavy metals that are harmful to the environment ([Muhamad et al., 2013](#)) are lead (Pb), mercury (Hg), barium (Ba), cadmium (Cd), arsenic (As), and chromium (Cr). By these heavy metals' discharge to the environment, they are in turn infiltrating the food chain and can easily wind up in the human body, in high concentrations as well.

However, the protection of the environment, and by extension, human itself, from all these harmful pollutants was not always a priority. For centuries, wastewater management was not given much, if any, consideration, to say the least. Wastewater was being disposed of near residential areas, with this impacting not only public health but nature as well. It was not until the 19th century

and the evident numerous epidemics that occurred throughout Europe that forced wastewater management to change. Since then, P&P wastewater management has been introduced to many different biological methods that can be utilized for its remediation and, consequently, contribute to severely less environmental pollution (Lofrano & Brown, 2010).

8.3 Biological methods concerning pulp and paper wastewater treatment

As mentioned, wastewater in general is the waterborne waste material known to contain several toxic chemicals, residues, substances, and even contaminants and their derivatives emanating from human domestic, urban, industrial, or commercial activity (Wastewater Treatment Water Use | U.S. Geological Survey; What Is the Definition of Wastewater? Pumps and Systems Magazine, 2021). Among the assorted industrial applications the quantity of water consumed in the P&P industry is considered to be the greatest worldwide, since water is utilized at almost every manufacturing stage (Jagaba et al., 2022). Thus significant wastewater volume is generated, emerging in various compositions and colors, and with comparatively higher BOD, COD, SS, and AOX concentrations than any other related industrial process (Hämäläinen et al., 2022).

For the sake of human health and environmental wellness, it is essential that this vast amount of P&P wastewater is properly treated in the most beneficial way possible (Hämäläinen et al., 2022; Jagaba et al., 2022). Considering the paper-manufacturing procedure, wastewater may be produced both in creating pulp from wood processes, while mostly compressing, digesting, washing, bleaching, or removing ink and fiber, and from the creating paper from this pulp, during the usage of washers, screens, beaters, mixing tanks, and other paper-making machines (Ahn & Lim, 2009). Therefore all global paper mill industries should lean toward seeking eco-friendly, economically viable, and technologically advanced treatment methods for the purpose of reusing the treated water and reducing overall water consumption (Ahn & Lim, 2009; Netnapid et al., 2004).

Many physical and chemical processes have been employed throughout the years, including the most commonly used coagulation-flocculation method, as well as physicochemical adsorption, membrane filtration, advanced chemical oxidation, and other methods (Bajpai, 2018; Esmaeeli et al., 2023; Gandhi, 2010; Ghosh & Thakur, 2017; Haq et al., 2016; Mir-Tutusa et al., 2018; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019; Yeber & Silva,

2022). All the above technologies focus especially on the deduction of SS, floating and colloidal particles, besides wastewater decolorization and detoxification (Ghosh & Thakur, 2017; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes). Nonetheless, the expensive application and disposal followed by sludge burning, air, water, and soil pollution, in addition to massive sludge generation affiliated with traditional physico-chemical methods, set an urgent global demand for greener effluent treatment (Archibald et al., 1997; Kumar, Thakur, et al., 2020; Lee et al., 1978; Meena et al., 2022; Patel et al., 2017; Pellinen et al., 1989; Sátiro et al., 2022; Selvam et al., 2002; Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002).

In contrast to the existing physicochemical processes, cost-effective, eco-friendly biological methods are considered the ideal pathway at P&P industrial scale (Ahn & Lim, 2009; Patel et al., 2021). The cornerstone of every biomethod is the connection formed between generated wastewater and bacteria, which feed upon the organic materials and consequently lower pollutants' concentration (Ahn & Lim, 2009; Bajpai, 2018). Biological treatment includes mostly technologies that utilize microbial groups, such as fungi, algae, bacteria, and their enzymes, due to their distinctive ability to biotransform and biodegrade profitably by converting waste sewage into energy and primal raw matter (Esmaeeli et al., 2023; Mir-Tutusaus et al., 2018; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes). This treatment is applied either as a single or joined with multiple standard processes, including aerobic, anaerobic, or even integrated methods (Esmaeeli et al., 2023; Lee et al., 1978; Mir-Tutusaus et al., 2018; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).

The selection of the particular microbes or microbial consortia highly depends on the specific wastewater composition and the coveted treatment goals. By adjusting and optimizing all system conditions, such as pH, temperature, and oxygen availability, the crucial support of the growth and activity of those microbes is secured (Esmaeeli et al., 2023). Since desired conditions are ensured, microbes isolated from industrial paper mill residues, sewage, and distillery sludges are able to secrete enzymes and organic acids, committed to providing the biodegradation and total decontamination (Esmaeeli et al., 2023; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sátiro et al., 2022). Some of the existing biological techniques utilized in P&P industries are further analyzed in the following sections. Fig. 8.2 involves, in a summary, the biological,

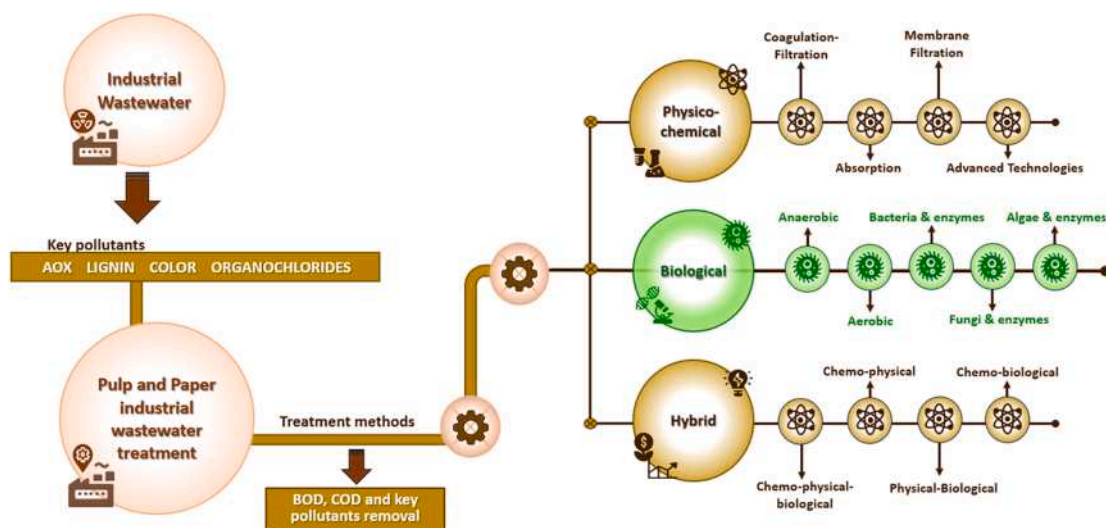


Figure 8.2 Treatment methods in the pulp and paper industry (Esmaeeli et al., 2023; Vidal et al., 2021; What is Industrial Effluent - Etch2o, 2023).

physicochemical, and hybrid treatment methods that are also applied in such industries.

8.3.1 Standard biological treatment technologies

In an attempt to limit and possibly eliminate contaminants in the wastewater and for the treated water to be suitable for future reuse, many standard biological treatment technologies have been practiced. Considered nowadays standard, aerobic and anaerobic biological processes have been put to use and evaluated in the past so as to determine the most efficient method among them (Ahn & Lim, 2009; Esmaeeli et al., 2023; Meena et al., 2022; Patel et al., 2021; Selvam et al., 2002).

Depending on oxygens' presence or absence, aerobic and anaerobic methods, respectively, have been considered ideal for the removal of unsanitary pollutants from P&P effluents. Aerobic biological treatment involves activated sludge (AS) processes, aerated lagoons, and proper biological reactors; while anaerobic treatment methods enclose filters, up-flow sludge blanket processes, fluidized-bed methods, deaerated lagoons, and anaerobic biological contact reactors (Ghosh & Thakur, 2017). However, efficiency lies upon the merger of aerobic and anaerobic methods with micro-organisms (Ghosh & Thakur, 2017; Patel et al., 2021).

Currently, the biological treatment of paper mill waste effluent using different types of bioreactors is considered the best approach from all accessible methods (Meena et al., 2022; Patel et al., 2021). A range of widely utilized bioreactors, like the membrane bioreactor (MBR), sequencing batch reactor (SBR), up-flow anaerobic sludge blanket reactor (UASBR), and the fluidized-bed reactor (FBR), are excessively exploited for the effective treatment of different polluted wastewater containments (Esmaeeli et al., 2023; Meena et al., 2022). Bioreactors' operation, either independently or merged with other methods, holds enormous potential in successfully handling numerous naturally occurring issues (Esmaeeli et al., 2023; Meena et al., 2022; Patel et al., 2021; *Pulp and paper industry wastewater treatment: Use of microbes and their enzymes*; Yel, Dilek, et al., 2002).

The AS technique is the most commonly used aerobic biological method (over 95% BOD, yet only 40%–60% COD reduction) (Esmaeeli et al., 2023). Conversely, anaerobic treatment processes are an optimizing solution, counting many advantages, such as minimized chemical ingestion, less sludge generation, and small land occupation, due to only a few needed reactors and high biogas production. However, deaerated bacterial systems exhibit sensitivity to highly toxic lignocellulose chemical substances, a situation that causes lower COD decline (Esmaeeli et al., 2023; Meena et al., 2022; Patel et al., 2021; *Pulp and paper industry wastewater treatment: Use of microbes and their enzymes*).

Aerobic and anaerobic processes are functional toward all different P&P waste compositions; their systems are suitable for high-strength effluent and low- to moderate-strength wastewaters, respectively. Moreover, by selecting an aerobic method, better-quality and highly decontaminated treated water is sealed in comparison to anaerobic methods. However, hybrid processes, which combine mainly biological with physical or chemical methods, have been reported to contribute to high-quality and cost-effective treated wastewater rather than any single process (Esmaeeli et al., 2023).

8.3.1.1 Aerobic biological treatment

Aerobic treatment is based upon the biological oxidation of wastewater pollutants when air or oxygen proximity is secured. Given that excessive BOD and organochlorides removal, as well as inexpensive and profitable application, is achieved, P&P mills all over the globe have invested in aerobic treatments (Swamy et al., 2011). Commonly employed and commercially scaled aerobic biological methods are aerated lagoons, AS processes, aerobic bioreactor enrollment (Ahn & Lim, 2009; Patel et al., 2021; Selvam et al., 2002; Swamy et al., 2011), and many more. AS process is an indicative

aerobic treatment method widely utilized in several P&P mills since high BOD reduction is recorded (Esmaeeli et al., 2023).

The AS process is hinged on aerobe activity forming a flocculent mass with organic substances. AS is performed using two basins that are functioning simultaneously (Ahn & Lim, 2009). The first basin allows air bubbles that provide oxygen to accelerate inside wastewater and create turbulent circumstances, while the second basin—settling tank—provides low water flow for faster gravitational settling and removal. BOD and COD decrease, and efficiency in AS methods increases drastically by applying floating biological beds, whereas significant color, AOX, SS, phenolics, sulfides, and chlorides reduction is noted (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Swamy et al., 2011; Virkutyte, 2017). Modified AS processes, claimed to affect toxicity removal, are step and tapered aeration plus oxidation ditch methods (Ahn & Lim, 2009).

Aerated lagoons, otherwise known as stabilization basins (ASBs), are regularly utilized for wastewater biotreatment. This method's success depends upon two different tasks: the total conversion of BOD to CO₂ or CH₄ and the reduction of accumulated solids by AS and Benthic stabilization (Mahmood & Paice, 2011). ASBs are less expensive compared to AS, although operative difficulties exist due to high SS and nutrient discharge (Mahmood & Paice, 2011; Savant et al., 2006). COD and color reduction were strengthened with Fenton's oxidation posttreatment, while nitrogen affluent conditions enhanced the overall removal of pollutants (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Virkutyte, 2017).

A modified process with an aim to lower sludge production (LSP) has been introduced in wastewater treatment. LSP systems produced strikingly less sludge while assisting in the decrease of significant BOD, COD, and AOX percentages deriving from bleach kraft effluents and increasing dewatering properties. However, LSP processes demand 25% extra aeration than AS or ASB systems, thus higher energy appeal (Kumar, Thakur, et al., 2020; Virkutyte, 2017).

High removals of kraft mill wastewater contaminants are attributed to biological reactors (Ahn & Lim, 2009; Patel et al., 2021; Savant et al., 2006; Sharma et al., 2019; Swamy et al., 2011). Sequencing batch reactors (SBR) consisted of a reactor that performs as an aeration and a secondary settling tank that carries out both nitrification and denitrification in the reaction cycle (Ahn & Lim, 2009; Sharma et al., 2019; Swamy et al., 2011). Removal efficiencies of 100% methanol, 95% nitrogen, and 90% COD decrease, as well as other pollutant degradation, have been reported (Ghodeif, 2013; Meena et al., 2022; Sharma et al., 2019; Swamy et al., 2011). SBR

treatment drawbacks like expensive maintenance systems that are in constant need of energy, as well as the unsafety due to the high flammability of biogas supplies, must be assessed (Ghodeif, 2013; Meena et al., 2022; Sharma et al., 2019). In general, rotating biological contactor (RBC), moving-bed biofilm reactors (MBBR), MBR, trickling filter process (TFP), and many other types of bioreactors have been demonstrated to be efficient representatives of moderate to high total removal (Ahn & Lim, 2009; Swamy et al., 2011). Some reported advantages and disadvantages of the main aerobic processes are further introduced in Table 8.1.

8.3.1.2 Anaerobic biological treatment

In general, in anaerobic treatment processes, all anaerobes exploit the bounded oxygen within ions like CO_3^{2-} , SO_4^{2-} , NO_3^- , and PO_4^{3-} (not the atmospheric oxygen). Cell synthesis and metabolic functions of anaerobes are enhanced by the obtained energy from depolymerization and conversion of organic matter into CH_4 , CO_2 , and other products such as H_2S , H_2 , and N_2 (Ahn & Lim, 2009). Several deaerated methods like anaerobic digestion (AD), anaerobic filters (AFs), and UASBR-FBR processes have been outlined as fertile mostly for COD, BOD, AOX, and SS decontamination (Ahn & Lim, 2009; Bajpai, 2018; Mir-Tutusa et al., 2018; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Swamy et al., 2011).

Anaerobes catalyze the displacement of chloride ions by protons in chlorinated molecules, an act that enhances reactivity, thereby the decrease of P&P waste pollution and increasing generated energy (Kumar, Thakur, et al., 2020). Anaerobic treatment methods are uncomplicated, relatively economical, and low-sludge-generating technologies that demand less space. High toxicity levels, though, may be inhibitory (Savant et al., 2006; Swamy et al., 2011; Yel, Dilek, et al., 2002). All anaerobes withstand being denourished for a long period without any serious activity collapse, which implies their viability for high-strength effluents (Savant et al., 2006). Reviews have highlighted evident soluble and biodegradable compound removal by combining aerobic and anaerobic processes (Swamy et al., 2011). Frequently used anaerobic treatment methods are AD, deaerated lagoons, AF processes, fluidized-bed reactors FBR, UASB, and anaerobic contact reactor (ACR) technologies (Ahn & Lim, 2009; Patel et al., 2021; Savant et al., 2006; Swamy et al., 2011).

AD processes employ microbes to perform oxygen-deprived biodegradation of organic material to methane and biogas in the form of CO_2 via hydrolysis, acetogenesis, acidogenesis, and methanogenesis (Ahn & Lim, 2009; Meyer & Edwards, 2014). Benefits of AD methods, such as inexpensiveness, biogas production, COD,

Table 8.1 Comparison of the main aerobic biological treatment processes.

Aerobic processes	Advantages	Disadvantages
Activated sludge (AS) (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Swamy et al., 2011)	Wide application, high effluent' removal, simple upgrade and modification, reduction of odorous gases	Instability, mass sludge generation, difficult sludge-wastewater separation, constant oxygen and energy needs, expensive operation
Aerated lagoons (stabilization basins -ASBs) (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020; Mahmood & Paice, 2011; Patel et al., 2021; Savant et al., 2006; Swamy et al., 2011)	High effluent removal, cost-effective methods, effective dechlorination, COD/BOD efficient decrease	Instability, mass sludge generation, and solids/nutrients accumulation, difficult sludge-wastewater separation, constant oxygen and energy needs, expensive function
Low-sludge production systems (LSP) (Kumar, Thakur, et al., 2020)	Less sludge generation, increased de-watering properties, and COD/BOD/AOX efficient drop	Higher aeration demand, constant energy and power supply, and expensive operation systems
Sequencing batch reactor (SBR) (Ahn & Lim, 2009; Ghodeif, 2013; Meena et al., 2022; Sharma et al., 2019; Swamy et al., 2011)	COD decline, N ₂ and CH ₃ OH almost total removal, BOD drop, TOC, AOX, and lignin efficient removal, high flexibility, potential for electricity production from biogas	Low pathogen riddance, constant energy and power supply, expensive operation and maintenance systems, low automation properties, and the explosiveness of hazardous biogas

Notes: AOX, Absorbable organo-halogens; BOD, biochemical oxygen demand; COD, chemical oxygen demand.

dewatering properties, and nutrient recovery, are followed by many safety issues and microbial and biomass-inhibited growth due to toxicity and maintenance problems that must be resolved directly (Ahn & Lim, 2009; Esmaeeli et al., 2023; Meyer & Edwards, 2014).

The UASB is widely utilized since this type of reactor functions even when dealing with high organic loads (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Morya, et al., 2020). Wastewater enters the bottom of the reactor as the generated sludge slowly accumulates in the remaining space, and agitation starts due to biogas formation. Biogas rises upward and is slowly collected and stored at the appropriate tank so as to be converted later into manageable energy, whereas the treated wastewater flows upward and is withdrawn by an

opening at the top of the UASB reactor for further posttreatment ([Ahn & Lim, 2009](#); [Kumar, Morya, et al., 2020](#); [Meena et al., 2022](#)). Moderate to high pollutant removal and BOD/COD indicator values decrease, reportedly achieved (80%–93% COD, 50% BOD, and 71%–99% chlorinated residues recorded riddance) ([Kumar, Morya, et al., 2020](#); [Kumar, Thakur, et al., 2020](#); [Patel et al., 2021](#); [Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Swamy et al., 2011](#)). Despite all the economic, nature-friendly, and productive advantages of UASB systems, some marked drawbacks like the lack of gas-solid total division, wastewater diffusion, and stability must be confronted for the utmost UASB future development ([Esmaeeli et al., 2023](#); [Kumar, Morya, et al., 2020](#); [Meena et al., 2022](#)).

Fluidized-bed bioreactors (FBR) are an alternative established method that includes a two-phase fluid-solid mixture, where the solid biomass carrier particles are fluidized by liquid/gas flow streams ([Fluidized bed bioreactor for multiple environmental engineering solutions. ScienceDirect](#)). By the addition of ligninolytic fungi in FBR systems for P&P wastewater remedial, studies reported COD decline and decolorization improvement, while the utilization of an up-flow anaerobic filter (UAF) is believed to remove 50% of COD, 70% of BOD, and 50% of AOX in total. Less capital cost, short hydraulic and long biomass retention time, close-packed reactor size, high conversion and biomass transfer rates without flow channeling, and flow recycling benefits battle against size limitations, continuous energy supplement demand, and slow biofilm creation ([Fluidized bed bioreactor for multiple environmental engineering solutions. ScienceDirect](#); [Meena et al., 2022](#); [Patel et al., 2021](#)). Scientists, by merging UASBR-FBR processes, have confirmed almost double the overall pollutant reduction in P&P effluents ([Fluidized bed bioreactor for multiple environmental engineering solutions. ScienceDirect](#); [Kumar, Thakur, et al., 2020](#); [Meena et al., 2022](#)).

Finally, the AF process is characterized as a promising secondary waste treatment method. Many filtration chambers are perpetually connected with supporting media and enhance bacterial growth and exopolysaccharide production ([Ahn & Lim, 2009](#); [Kumar, Morya, et al., 2020](#)). Depending on flow direction, filters are divided into up-flow and down-flow types ([Kumar, Morya, et al., 2020](#)). Many advantages, including low and high pollutant concentrations, equal treatment, low-temperature conditions (20°C), simple structure, and less generated sludge, are not enough for industries to neglect drawbacks like long start-up time, expensive filling media, low treated wastewater quality in case of high SS presence, and easily clogged filters possibility ([Ahn & Lim, 2009](#); [Esmaeeli et al., 2023](#); [Kumar, Morya, et al., 2020](#); [Stanbury et al., 2017](#)). The advantages and disadvantages of the main anaerobic methods are represented in [Table 8.2](#).

8.3.2 Biological treatment technologies utilizing microorganisms—bioaugmentation/biostimulation processes

Against the lack of sustainability of physicochemical methods, microbiological treatment of P&P industrial waste has become a requisite solution universally due to increased treated water quality and future reuse insurance (Patel et al., 2021). Lately, industries have reached sufficient removal of effluents' toxicity by following many "bioremediation pathways." Fungi, bacteria, algae, and enzymes, individually, combined, or affiliated with further standard treatment technologies, successfully catalyze P&P sewages' degradation and biotransformation of complex chemical compounds to plain matter (Pulp and paper industry wastewater treatment: Use of microbes and their enzymes). This alternative solution has been reported to offer evident color removal, COD and BOD decline, low-molecular-weighted and chlorinated lignin degradation (Ghosh & Thakur, 2017). Detoxification, organic load reduction, and significant conversion of harmful complex residues to simple matter and energy rightfully dignify microbial-based biological methods as the best solution to P&P industries' wastewater management issues (Ghosh & Thakur, 2017; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).

8.3.2.1 Biological treatment using bacteria—bacterial bioaugmentation

Their remarkable environmental adaptability and vast versatility place bacteria among the top biological treatment approaches for P&P wastewater. Due to the presence of many heavy phenolic compounds such as lignin, large quantities of highly colored, P&P industrial effluent are discharged, which is confirmed to be extremely harmful to nature's aquatic and soil flora and fauna (Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Yeber & Silva, 2022). Bacterial populations' responsibility lies upon the decolorization and detoxification of polluted wastewater generated by paper mills' manufacture (Haq et al., 2016; Yeber & Silva, 2022). In general, bacteria catalyze organic matter's decay by transforming it into CO₂, H₂O, and energy (Esmaeeli et al., 2023). Bacterial strains of bacterial genera, such as *Bacillus*, *Pseudomonas*, *Micrococcus*, *Paenibacillus*, and many more, are capable of lignin degradation, color and total phenol removal, and COD and BOD decline from the P&P industries' wastewater (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).

Low-molecular-weight lignin components are easily demeaned by bacteria. However, single bacterial strains lack all the necessary

Table 8.2 Comparison of the main anaerobic biological treatment processes.

Anaerobic processes	Advantages	Disadvantages
Anaerobic digestion (AD) (Ahn & Lim, 2009; Esmaeeli et al., 2023; Meyer & Edwards, 2014; Swamy et al., 2011)	Biogas may be converted to electricity, cost-effective COD anaerobic decrease, low waste sludge generation when AD precedes aerobic AS method, high dewaterability, nutrient restoration, and less required land	Slow microbial substrate riddance and biomass growth rates, biogas explosivity, wastewater toxicity inhibits microbial growth, long-term sludge residence, and high-maintenance reactors
Anaerobic filter process (AF) (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Morya, et al., 2020)	Suitable for both low and high effluents, contain removal, cost-effective method, low temperatures functioning, simple structure, easily handled, unnecessary less generated sludge, potential for sludge recycling, COD/BOD efficient decrease	Expensive function and filling media, long start-up time, low treated wastewater quality in case of high suspended solids presence, possibility of easily clogged filters
Anaerobic fluidized-bed reactors (FBR) (Ahn & Lim, 2009; Kumar, Thakur, et al., 2020; Meena et al., 2022; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	Low organic wastewater concentration treatment, compact FBR reactor size, little capital cost, short hydraulic and long biomass retention time, high conversion and biomass transfer rates, no flow channeling, flow recycle, efficient pollutants removal	Constant energy and power supply for flow recycling, expensive and high-maintenance operation systems, reactor vertical size limitations, long-period biofilm formation, expensive pumping, difficult control of the generated biomass amounts
Up-flow anaerobic sludge blanket reactor (UASB) (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Morya, et al., 2020; Meena et al., 2022; Meyer & Edwards, 2014; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Swamy et al., 2011)	COD and organochlorides high total removal, electricity generation from biogas, lower energy and space demand, lower sludge production, adjustable microbial retention time, unnecessary effluent recirculation, and no mechanical support requirement	Lower pathogen riddance, system lacks of effective gas-solid division, wastewater diffusion at the bottom tank, and stable operational mechanism, explosivity of biogas

Notes: AS, Activated sludge; BOD, biochemical oxygen demand; COD, chemical oxygen demand.

lignin-degrading enzymes and are unable to perform this degradation. Therefore applications of two or more mutually synergistic bacterial strains along with fungi enable efficient lignin removal from P&P wastewater (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes). Even though fungi have been widely reported to successfully biodegrade lignin, they unfortunately exhibit instability under extreme natural conditions like high pH or oxygen-deprived environments. Unlike fungi, bacteria species manage to grow at neutral to alkaline pH conditions (7–9), showing extensive tolerance to lower oxygen and higher pH or temperature existing limitations (Gandhi, 2010).

It has been identified that both aerobic and anaerobic biodegradation bacteria are able to efficiently treat wastewater. Aerobic bacteria act as biocatalysts inside oxygen-rich enzymatic systems, while anaerobic bacteria conduct organic pollutant disintegration inside oxygen-deprived enzymatic systems by pumping energy from nitrates and sulfates. Although rapid metabolic rate is achieved by aerobic bacteria in opposition to anaerobic ones, the mass-produced biomass-clarification sludge still remains a disadvantage (Esmaeeli et al., 2023; Patel et al., 2021). Recently, scientists have prioritized combining aerobic and anaerobic bacterial treatment for maximum decontamination efficiency (Sonkar et al., 2019).

Comparative studies have been conducted for decades over several single or mutually synergistic bacterial strains and appropriate conditions under which efficient biological effluent treatment is reached (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).

These studies have confirmed that biological P&P wastewater treatment using two or more cooperating bacterial strains displays greater results than single bacterial strains (Esmaeeli et al., 2023). Concurrently, as seen in Table 8.3, the bacterial group of *Bacillus subtilis* and *Micrococcus luteus* is adequately prone to COD-BOD reduction, lignin's degradation, and almost total decolorization and detoxification of P&P mill's effluent (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019). *Pseudochrobactrum glaciale*, *Providencia rettgeri*, and *Pantoea* sp. consortium offered almost perfect color, BOD, and COD decrease, not notably affecting lignin and other phenolic groups' reduction (Esmaeeli et al., 2023; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019). *Bacillus subtilis* as a single strain affected moderately to well all aforementioned key pollutants (Gandhi, 2010; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019).

Table 8.3 Bacterial biological treatment of pulp and paper wastewaters.

Bacteria	Pollution parameters reduction (%)					Ability
	Color	Lignin	BOD	COD	Phenol	
<i>Pseudomonas fluorescens</i> (Patel et al., 2021)	75.0	45.0	–	79.0	66.0	Color, lignin, total phenol, and COD reduction
<i>Serratia liquefaciens</i> (Esmaeeli et al., 2023; Sonkar et al., 2019)	72.0	58.0–61.0	–	84.0–85.0	–	Color, lignin, and COD reduction
<i>Bacillus subtilis</i> and <i>Klesbiella pneumonia</i> (Sonkar et al., 2019)	80.0	–	62.0	73.0	–	Color, BOD, and COD reduction
<i>Brevibacillus parabrevis</i> (Sonkar et al., 2019)	59.0	53.8	–	62.0	–	Color, lignin, and COD reduction
<i>Brevibacillus agri</i> (Esmaeeli et al., 2023; Sonkar et al., 2019)	47.0	37.0	–	69.0	–	Color, lignin, and COD reduction
<i>Aeromonas formicans</i> (Esmaeeli et al., 2023; Patel et al., 2021)	86.0	78.0	–	71.0	–	Color, lignin, and COD reduction
<i>Paenibacillus</i> sp. (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	68.0	28.0–54.0	83.0	52.0–78.0	–	Color, lignin, BOD, and COD reduction
<i>Aneurinibacillus aneurinilyticus</i> and <i>Bacillus</i> sp. (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	39.0–61.0	–	65.0–82.0	–	64.0–77.0	Decolorization, total phenol, and BOD reduction
<i>Pseudochrobactrum glaciale</i> , <i>Providencia rettgeri</i> , and <i>Pantoea</i> sp. (Esmaeeli et al., 2023; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019)	96.02	–	92.59	91.0	–	Color, BOD, and COD reduction

<i>Bacillus subtilis</i> (Gandhi, 2010; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019)	61.0–65.2	53–64.8	64.1–82	75.6–78	60.9	BOD, COD, total phenol, and color reduction – lignin's degradation
<i>Bacillus subtilis</i> and <i>Micrococcus luteus</i> (Patel et al., 2021)	> 90.0	97.0	87.2	94.7	–	Significant color, lignin, BOD, and COD reduction of P&P wastewater
<i>Bacillus megaterium</i> , <i>Pseudomonas aeruginosa</i> (DSMZ 03504), and <i>P. aeruginosa</i> (Esmaeeli et al., 2023; Sonkar et al., 2019)	76.0	–	76.0	70.0–76.0	–	Color, BOD, and COD reduction
<i>Bacillus subtilis</i> bacterium (Patel et al., 2021)	61.3	59.6	–	64.1	–	Color, lignin, and COD reduction
<i>Serratia marcescens</i> , <i>Citrobacter</i> sp., and <i>Klebsiella</i> sp. (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	85.0	–	74.0	83.0	–	Reduction of the chemical and biochemical O ₂ demand in a sequential batch reactor—Color, BOD, and COD reduction
<i>Klebsiella</i> sp., <i>Alcaligenes</i> sp., and <i>Cronobacter</i> sp. (Ghosh & Thakur, 2017; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019)	55.0	–	91.1	72.3	–	Color, BOD, and COD reduction
<i>Pseudomonas</i> , <i>Bacillus</i> , <i>Pannonibacter</i> , and <i>Ochrobacterum</i> (Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	–	–	–	66.0–86.0	–	COD reduction in affluent in nitrogen and sulfate systems

(Continued)

Table 8.3 (Continued)

Bacteria	Pollution parameters reduction (%)					Ability
	Color	Lignin	BOD	COD	Phenol	
<i>Bacillus cereus</i> and <i>Serratia marcescens</i> (Ghosh & Thakur, 2017; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Sonkar et al., 2019)	62.0	54.0	70.0	90.0	—	Color, lignin, BOD, and COD reduction
<i>Comamonas</i> sp. (Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	—	—	—	32.0	—	Treatment of kraft lignin into low-molecular-weight compounds

Notes: BOD, Biochemical oxygen demand; COD, chemical oxygen demand; P&P, pulp and paper.

8.3.2.2 Biological treatment using fungi—fungi bioremediation

Fungi are eucaryotic microorganisms present in P&P aquatic waste that perform as biological degrading agents against lignin and other compound's depolymerization. Their distinctive enzyme-tank system and well-built extracellular structure made by an extrapoly-saccharide matrix are responsible for fungi's survival rate, adaptation, and resistance toward inhibitory molecules, in comparison to bacteria (Esmaeeli et al., 2023; Ghosh & Thakur, 2017; Patel et al., 2017, 2021; Pellinen et al., 1989). Fungi have been reported to break down intricate organochlorine molecules and absorb heavy metals from P&P industries' aquatic waste (Patel et al., 2021). Moreover, specific fungi species have been claimed to perform lipid synthesis by utilizing light lignin monomers stemming from delignification (Esmaeeli et al., 2023; Mir-Tutusaus et al., 2018; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Yel, Yetis, et al., 2002).

White-rot fungi, otherwise known as wood-decay fungi, belong mostly to Basidiomycotina and only a few to Ascomycotina fungi kingdom divisions. White-rot fungi (WRF) are threadlike, grown via mycelia microorganisms, and are responsible for fast delignification. Delignification is an oxidative activity linked either to restricted accessibility to carbon, nitrogen, or sulfur or to secondary organic metabolites' presence (Esmaeeli et al., 2023; Gandhi, 2010; Ghosh & Thakur, 2017; Pellinen et al., 1989). WRF activity rests upon their ability to demean many toxic organic compounds such as chlorogenic, synthetic, and aromatic residues, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and a wide range of other similar substances (Ghosh & Thakur, 2017; Pellinen et al., 1989). The fungus most relevantly degrades lignin so as to secure carbohydrate accessibility, due to lignin's high molecular weight and unobtainability as an energy source (Pellinen et al., 1989; Selvam et al., 2002).

When functioning in proper environments, WRFs secrete lignin-modifying enzymes (LMEs), including laccase or lignin, manganese, and versatile peroxidases, among other degradative compounds. Laccases, in contrast to peroxidases, exploit atmospheric oxygen instead of hydrogen peroxide (Esmaeeli et al., 2023; Mir-Tutusaus et al., 2018). Furthermore, the production of oxidation-reduction mediators assists in electron transference and substrate scope expansion of lignin-degrading enzymes (Ghosh & Thakur, 2017; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).

Multiple species of the fungi family assist in lignin/phenol depolymerization. Nonetheless, the most active species participating in P&P wastewater treatment that perform contaminants' degradation are *Phanerochaete chrysosporium*, *Fomes lividus*, and *Trametes versicolor*, working in cooperation with many assistant ligninolytic

and accessory enzymes, organic acids, and mediators (Esmaeeli et al., 2023; Ghosh & Thakur, 2017; Mir-Tutusaous et al., 2018; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Selvam et al., 2002). It is vital to note the importance of mill and reactors' type, treatment method, time estimation as well as conditions careful regulation, which may affect maximum pollutant removal (%), considering fungal utilization (Esmaeeli et al., 2023; Ghosh & Thakur, 2017; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).

Table 8.4 highlights that fungal biological methods induce bioremediation, focusing chiefly on decolorizing waste and later on delignifying effluents (Esmaeeli et al., 2023; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes). Moreover, fungi in consortia with other fungi, bacteria, or algae, when used in the P&P wastewater treatment, highly influence pollutant removal, with the *Merulius aureus* and *Fusarium sambucinum* fungal groups standing out (Patel et al., 2021; Pellinen et al., 1989; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Selvam et al., 2002).

Results suggested *P. chrysosporium* and *T. versicolor* relation to delignification and chlorinated phenols total removal, besides color, COD, and even BOD—by *T. versicolor*—reduction (Archibald et al., 1997; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).

WRF's family member known as *Trametes* (*Coriolus*) *versicolor* has the best decolorization potential upon effluents originating from kraft mills by sulfate pulping (Archibald et al., 1997; Selvam et al., 2002). This fungus's huge attribution in laboratory and pilot scale contaminants removal should not be negligible. In addition, *P. chrysosporium* fungal species have resulted in efficient decolorization and great COD, lignin, and chloro-phenol removal when working under optimized conditions (RF mill, batch flask for 9 days) (Archibald et al., 1997; Ghosh & Thakur, 2017; Pellinen et al., 1989; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Selvam et al., 2002). Ultimately, *F. lividus* seems to be an inexpensive candidate in favor of wastewater dechlorination, when used in laboratory and pilot scales for 4- and 6-day incubation, respectively (Selvam et al., 2002).

Fungal treatment of effluents containing organic pollutants is a feasible alternative (Mir-Tutusaous et al., 2018). Regardless of the numerous advantages linked to fungal-based biological treatment, paramount environmental conditions like high pH and oxygen depletion in conjunction with slow metabolism features and great glucose demand are defined as some serious drawbacks. Such disadvantages slowly led to a wide global requirement for higher

Table 8.4 Fungal biological treatment of pulp and paper wastewaters.

Fungi	Pollution parameters reduction (%)					Ability
	Color	Lignin	BOD	COD	Phenol	
<i>Trametes versicolor</i> (Archibald et al., 1997; Esmaeeli et al., 2023; Ghosh & Thakur, 2017; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Selvam et al., 2002)	63.9–93.8	> 80	69.0	57.0–82.0	> 90.0	Color, lignin, total phenol, and COD reduction in the laboratory and pilot scale
<i>Phanerochaete chrysosporium</i> (Archibald et al., 1997; Esmaeeli et al., 2023; Ghosh & Thakur, 2017; Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes; Selvam et al., 2002)	78.6–86.4	71.0–99.1	–	79.4–98.5	91.0	Color, lignin, COD, and chloro-phenol reduction (Optimized conditions: RF mill, batch flask, 9 days)
<i>Fomes lividus</i> (Selvam et al., 2002)	66.7 72.8	–	–	59.32 59.30	227 57.7	Color, COD, and chloro-phenol removal in the laboratory and pilot scale (4- and 6-day incubation), respectively
<i>Phanerochaete chrysosporium</i> and <i>Trametes versicolor</i> (Selvam et al., 2002)	40.0–80.0	–	–	32.0–70.0	-	Color and COD reduction
<i>Merulius aureus</i> and <i>Fusarium sambucinum</i> (Patel et al., 2021)	78.6	79.0	–	85.0	81.0	Color, BOD, and COD reduction
<i>Cryptococcus</i> sp. (Esmaeeli et al., 2023; Patel et al., 2021).	27.0–53.0	24.0–40.0	–	–	–	Color reduction - lignin's degradation (optimized conditions: shaking flask 24 h)

(Continued)

Table 8.4 (Continued)

Fungi	Pollution parameters reduction (%)					Ability
	Color	Lignin	BOD	COD	Phenol	
<i>Emericella nidulans</i> var. <i>nidulans</i> (optimized pH: batch culture, 5.0–6.0 and T: 30°C–35°C) (Esmaeeli et al., 2023; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	66.66–71.0	37.0	–	–	–	Decolorization and delignification
<i>Aspergillus flavus</i> Strain F10 (Esmaeeli et al., 2023; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	33.7–66.3	39.0–61.0	–	–	–	Color, lignin, and COD reduction after 10 days of incubation
<i>Aspergillus flavus</i> (Esmaeeli et al., 2023; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	31.0–84.0	94.0	–	45.0	–	Color, lignin, and COD reduction, mainly delignification
<i>Pleurotus sajor caju</i> , <i>Trametes versicolor</i> , <i>Phanerochaete chrysosporium</i> , and <i>Rhizopus oryzae</i> (Esmaeeli et al., 2023; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	72.0–74.0	25.0–46.0	–	74.0–81.0	–	Mainly treatment of kraft lignin of P&P waste and COD reduction, as well as mild decolorization
<i>Phellinus</i> sp. (Pulp and paper industry wastewater treatment: Use of microbes and their enzymes).	62.2	–	–	42.1	–	Color and COD reduction in the laboratory scale

<i>Schizophyllum commune</i> (Ghosh & Thakur, 2017; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	90.0	—	70.0	72.0	—	Color, BOD, and COD reduction
<i>Pleurotus streatus</i> (Pulp and paper industry wastewater treatment: Use of microbes and their enzymes)	80.0	77.0	76.8	60.0	—	Color, lignin, BOD, and COD reduction
<i>Phanerochaete</i> sp. (Fungus) and <i>Pseudomonas</i> sp. (Bacteria) (Ghosh & Thakur, 2017)	45.4	—	—	76.9	—	Color and COD reduction
<i>Trametes versicolor</i> and <i>Flavodon flavus</i> (Ghosh & Thakur, 2017)	60.0–78.0	—	52.0–69.0	52.0–69.0	—	Immobilization on PUF cubes: Color, BOD, and COD reduction

Notes: BOD, Biochemical oxygen demand; COD, chemical oxygen demand; P&P, pulp and paper.

resistance solutions in order for mass production of the needed extracellular ligninolytic enzymes (Esmaeeli et al., 2023; Ghosh & Thakur, 2017). To a large extent, bacteria and algae have been tested as suitable for fungi replacement under existing jangling circumstances (Ghosh & Thakur, 2017; Patel et al., 2017; Pellinen et al., 1989).

8.3.2.3 *Biological treatment using algae (phyco-remediation)*

The microalgal phyco-remediation approach has attracted attention lately for P&P industrial contaminated aquatic waste treatment (Esmaeeli et al., 2023; *Pulp and paper industry wastewater treatment: Use of microbes and their enzymes*). The expansive metabolic action of algae holds their ability to decolorize, discard, and degrade chromophore lignin compounds by lignin fragmentation to simple colorless matter (Lee et al., 1978; Patel et al., 2021; Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002). Studies have already reported the metabolic transformation of colored and chlorinated molecules to noncolored and nonchlorinated molecules. Specifically, wastewater chlorinated and nonchlorinated compound content was primarily dechlorinated and then discharged from all colored pollutants (Esmaeeli et al., 2023; Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002). Therefore it was concluded that the main removal mechanism was metabolic wastes' degradation rather than simple adsorption (Sátiro et al., 2022; Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002).

Microalgal species minimize CO₂ emissions while engaging in photosynthesis and clear away nutrients from paper mill wastewater by utilizing their ample nutrient uptake capacity (Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020; Sátiro et al., 2022; Yel, Dilek, et al., 2002). Profitability, small energy demand, increased biomass, and reduced sludge generation, as well as heavy metals (for instance, chromium) mass riddance, are indisputable algal benefits (Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020; Sátiro et al., 2022). However, color content and P&P wastes' high carbon and low nitrogen/phosphorus containment may inhibit microalgal action and growth (Esmaeeli et al., 2023; Lee et al., 1978). An encouraging algal bioremediation solution is the dilution and mix of highly nutritional civic or dairy farm wastewater with P&P aquatic waste, a situation that may sadly lead to toxic chemicals like tannins, sterols, or sodium peroxide increase, which may hinder algal growth irreversibly (Esmaeeli et al., 2023; Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002).

P&P wastewater in many studies was examined in batch reactors under several conditions for the assessment of color and other pollutants' algal removal efficiency. Mixed algal strains exhibit faster degradation than single species (Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020; Yel, Dilek, et al., 2002). For this purpose an algal mixture

called “inoculum” was microscopically inspected for composition characterization, and results showed that this culture was composed mainly of green algal substances (*Chlorella*, *Chlamydomonas*, *Chlorococcum*, *Pandorina*, and *Eudorina*), some microscopic diatoms like *Nitzschia* and *Cyclotella*, flagellates such as *Euglena*, and blue-green colored algae like *Microcystis* and *Anabaena* (Sátiro et al., 2022; Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002).

Furthermore, systems that exploit microalgae and bacterial bioflocculation, enhance resource recovery potential and circular economy (CE), as wastewater treatment plants (WWTP) that utilize this synergistic consortium are well known for biomass growth and significant removal of pharmaceutical pollutants (Sátiro et al., 2022).

Sequencing Batch Reactors (SBR) are widely utilized in microalgal biological treatment methods, as flexible reactors are able to deal even with highly contaminated wastewater and are easily affected by the filling period (Yel, Yetis, et al., 2002). During an SBR analysis, algal cells were able to grow desirably in both mixotrophic and heterotrophic growth modes, favoring mixotrophic conditions (Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002). COD and color reduction were not strongly affected by brightness and wastewater strength alteration; however, AOX removals were notably reduced. COD and color high content, moreover, led to slower chlorine riddance. In carbons' presence, mainly green algae, diatoms, and flagellates of the P&P effluents survived, as high COD initial quantities accelerated diatoms' growth while light intensity pleased more green algae's existence (Yel, Dilek, et al., 2002; Yel, Yetis, et al., 2002).

The potential of microalgal treatment is unquestionable, yet many comparative studies must be conducted for maximum accuracy insurance. Even though, microalgal biological treatment aids future work, evaluations from different studies claim that the microalgae-bacterial consortium is able to lead, under the proper conditions, to efficient biological treatment (Sátiro et al., 2022).

Once more a synergy between two or more algae and diatoms is confirmed to be more fruitful than single algae methods (Esmaeeli et al., 2023; Patel et al., 2021). By evaluating and comparing different single or combined algal mixed cultures in Table 8.5, the above assumptions are certified. The mixed culture of algal *Chlorella*, *Chlorococcum*, *Chlamydomonas*, *Pandorina*, *Eudorina*, *Nitzschia*, *Cyclotella*, *Microcystis*, and *Anabaena* determined high overall color, COD, and AOX reduction in a laboratory scale (Patel et al., 2021; Pulp and paper industry wastewater treatment: Use of microbes and their enzymes). Simultaneously, *Scenedesmus* sp. as a single strain enhanced to a significant level of BOD and COD reduction, while two *Scenedesmus* sp. combined removed greater amounts of COD

Table 8.5 Algal biological treatment of pulp and paper wastewaters.

Algae and Diatoms	Pollution parameters reduction (%)					Ability
	Color	Lignin	BOD	COD	AOX	
<i>Chlorella</i> , <i>Chlorococcum</i> , <i>Chlamydomonas</i> , <i>Pandorina</i> , <i>Eudorina</i> , <i>Nitzschia</i> , <i>Cyclotella</i> , <i>Microcystis</i> , and <i>Anabaena</i> (Patel et al., 2021)	75.0	–	–	85.0	93.0	Color, COD, and AOX reduction in laboratory scale
<i>Chlorella</i> , <i>Chlorococcum</i> , <i>Chlamydomonas</i> , <i>Pandorina</i> , and <i>Eudorina</i> (Patel et al., 2021)	84.0	–	–	75.0	80.0	Color, COD, and AOX reduction in laboratory scale
<i>Chlorella</i> , <i>Chlorococcum</i> , <i>Chlamydomonas</i> , <i>Microcystis</i> , <i>Anabaena</i> , <i>Euglena</i> , <i>Phacus</i> , <i>Nitzschia</i> , <i>Cyclotella</i> , <i>Pandorina</i> , <i>Eudorina</i> , <i>Gonium</i> , and <i>Prymnesium</i> (Esmaeeli et al., 2023)	80.0	–	–	–	70.0	Color and AOX reduction in laboratory scale
<i>Scenedesmus</i> sp. (Patel et al., 2021)	–	–	82.0	75.0	–	Maximum COD and BOD reduction
Mixed culture of two <i>Scenedesmus</i> sp. (Esmaeeli et al., 2023)	–	–	–	89.0	–	Better COD removal than that of a single diatom
<i>Planktochlorella nurekis</i> and <i>Chlamydomonas reinhardtii</i> (Patel et al., 2021)	–	–	–	–	–	COD, nitrate, phosphate, and many heavy metals removal
Green algae <i>Chlorella</i> (Patel et al., 2021)	84.0	–	–	68.0	80.0	Color, COD, and AOX reduction in laboratory scale
<i>Scenedesmus acuminatus</i> (Esmaeeli et al., 2023)	74.0–80.0	–	–	29.0–39.0	–	Color and COD reduction
Green algae <i>Chlorella</i> and diatom species (Esmaeeli et al., 2023)	79.0	–	–	58.0	50.0	Color, COD, and AOX reduction in laboratory scale

Notes: AOX, Absorbable organo-halogens; BOD, biochemical oxygen demand; COD, chemical oxygen demand.

(Esmaeeli et al., 2023; Patel et al., 2021). Furthermore, green algae *Chlorella* was effective toward color and AOX reduction, but less helpful in COD decrease (Patel et al., 2021).

8.3.2.4 Role of enzymes in the biological treatment

Enzymatic catalysis is broadly applied in many biological treatment methods as enzymes expertise in providing in less time the desirable results. P&P industrial effluent remedy over the years has employed numerous microbial enzymes, including laccases, peroxidases, cellulases, xylanases, catalases, proteases, and many more, that are in charge of controlling P&P industrial organic effluent (Patel et al., 2021). Nonetheless, high temperatures, pH levels, and enzymatic inhibitory factors must be properly regulated to achieve enzymatic efficiency (Kumar, Thakur, et al., 2020; Patel et al., 2021; *Pulp and paper industry wastewater treatment: Use of microbes and their enzymes*).

Microbial ligninolytic enzymes implicated in lignin's oxidization (ligninases) are classified into two primal categories: the LMEs and lignin-degrading auxiliary (LDAs) enzymes. Microbial LMEs are categorized into heme-containing peroxidases such as lignin (LiP), manganese (MnP), versatile (VP), and dye-decolorizing (DyP) peroxidase, and phenol oxidase that includes laccase (Lac). LDAs, on the contrary, are oxidative enzymes unable to facilitate lignin's degradation without LME presence, numbering glyoxal and aryl alcohol oxidase and glucose and cellobiose dehydrogenase, often traced in WRF residues (Kumar, Thakur, et al., 2020).

Laccase and some WRF peroxidases degrade organic pollutants. Especially, laccase has been reported to control almost the entire oxidization of phenolic substances like monophenols, diphenols, and polyphenols, as well as aromatic amines and nonphenolic compounds, wastes' decolorization, and BOD and COD quantities present in the P&P wastewater riddance (Patel et al., 2021). Peroxidases, on the contrary, are the main candidates in the removal of color and organic load effluent (*Pulp and paper industry wastewater treatment: Use of microbes and their enzymes*).

Biodegradation of lignin represents one of the most challenging problems in biological treatment methods since degradation is demanding, and the presence of lignin is negative against cellulose utility in the P&P industry. Microorganisms like fungi and bacteria degrade lignin efficiently in cooperation with secreted extracellular ligninolytic and accessory enzymes (Kumar, Thakur, et al., 2020). WRF mass production of extracellular ligninolytic enzymes and bacterial remediation in enzymatic systems, which were previously assessed, imply the need for enzymes in most biological method applications (Patel et al., 2021; *Pulp and paper industry wastewater*

treatment: Use of microbes and their enzymes). However, further investigation is required until maximum enzymatic yield is globally achieved (Kumar, Thakur, et al., 2020).

8.3.3 Advanced combined biological technologies— hybrid/integrated treatment

Currently, hybrid advanced technologies regarding wastewater treatment have been imported into many P&P industries for achieving more effective results and for overcoming existing obstacles (Ahn & Lim, 2009; Kumar, Thakur, et al., 2020). Hybridization of biological, physical, and chemical processes (Fig. 8.3) and modification of already established methods requires extra investigation for these processes' compatibility against effluents' composition variation, with a focus on addressing the immediate need for technologically, environmentally, and economically viable treatment solutions (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020; Mishra et al., 2015). Numerous methods have been conducted in the hope of discovering the best P&P industrial technique that combines efficiency, safety, greener perspective, and economic viability.

A promising integrated biological treatment is that of membrane filtration and low-pressure reverse osmosis (GWF). An anaerobic microbial alternative method is used for wastewater pretreatment, without air and electricity demand, and followed by high biogas production (Ahn & Lim, 2009; Kumar, Thakur, et al., 2020).

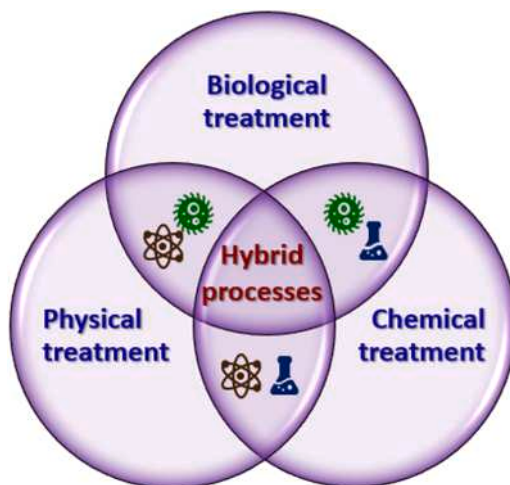


Figure 8.3 Hybrid treatment depiction (Esmaeeli et al., 2023).

Membrane filtration is then performed on the biologically treated water, where vertically arranged membranes filters draw wastewater to separate it from sludge. For recycling purposes, the filtered water progresses to a reverse osmosis process, which is recorded to remove 90% of salt's containments using a porous semipermeable membrane (Ahn & Lim, 2009).

The utilization of membrane techniques in cooperation with biological effluent treatment has been launched in many P&P industries globally. A hybrid unit connecting an up-flow fixed-bed anaerobic bioreactor (UFBAB) with a slow sand filter (SSF) has exhibited high depollution. Later on, UFBAB and SSF, when combined to a sMBR otherwise submerged membrane bioreactor, are able to eliminate possible dissolved substances in paper mill effluents except for calcium residues (98% COD, 92.99% ammonia-nitrogen consortium, and 96.36% phosphorus removal efficiencies) (Kumar, Thakur, et al., 2020; Mishra et al., 2015). High decontamination records have placed the UFBAB-SSF-sMBR method among the most auspicious future hybrid treatment options (Kumar, Thakur, et al., 2020; Mishra et al., 2015).

Hybrid biological coagulation-filtration (CF) has been implemented as a highly effective technique concerning treating P&P contaminated wastewater. Inside a fed-batch reactor, high-strength polluted wastewater is slowly added into an aeration tank that discharges effluent only when it is full. Fed-batch reactor's process followed by coagulation and sand filtration (SF) led to 93% COD and 96.5% BOD decrease (Ahn & Lim, 2009). Coagulation coupled with biological processes is broadly preferred, especially when this method is integrated first with anaerobic up-flow fixed bacterial film bioreactors and then with aerobic techniques using *Pseudomonas aeruginosa*. Aromatic amine degradation, 94% of COD, and 85%–89% of color removal reports make this technology more profitable than single approaches (Ahn & Lim, 2009; Kumar, Thakur, et al., 2020). Hybridization of sequencing CF unit, UASB, AS, and nanofiltration membrane (NF) enhances color, COD decrease, and lignin removal (Ahn & Lim, 2009; Esmaeeli et al., 2023).

Various alternative ways of wastewater treatment have been introduced, such as MBBR combination with chemical precipitation, aerobic AS merged with thermo-alkaline processes or chemical surfactants, ultrafiltration followed by anaerobic and aerobic treatment (80% COD and AOX reduction), preozonation and postozonation either on algal or on fungal biological treatment, and physical-bioabsorption of microbes, mainly bacteria such as *Shewanella putrefaciens* bacterial cells on granular activated carbon (GAC). All prementioned methods are considered adequate in regard to decontamination efficiency. However, supplementary studies must

be conducted for humanity to reach full hybrid methods potential (Ahn & Lim, 2009; Esmaeeli et al., 2023; Kumar, Thakur, et al., 2020). Wastewater treatment success seems to rely upon the expansion of hybrid processes, which are reportedly appropriate options for P&P effluents depollution and satisfactory greener candidates for low overall GHG emissions future potential (Kumar, Thakur, et al., 2020; Mishra et al., 2015).

8.4 Discussion and evaluation of biological treatment methods

In the previous section, several biological methods have been scrutinized and examined so as to effectively clarify their significant role in the P&P mills. A plethora of treatment methods, including those utilizing bacteria, fungi, algae, and enzymes, as well as the revolutionary hybrid processes, which combine the advantages of both biological and physicochemical techniques, have been extensively analyzed.

As a consequence, it is now of great importance to summarize all existing advantages and disadvantages while stating possible challenges deriving from the utilization of the prementioned biological treatment methods. Hence, a comparative analysis of traditional and innovative biological treatment systems is provided. Furthermore, all global industries, including the P&P ones, rely heavily on the current global markets' economic profile. Thus some recent statistics and reviews concerning the energy consumption fingerprint and the potential for resource recovery of P&P industries are further evaluated in the following subsections along with a commentary upon the economic viability and CE sustainable benefits.

8.4.1 Advantages, disadvantages, and challenges of biological treatment methods

Taking into account the above-mentioned, the P&P industry withholds many advantages while dealing with generated wastewater during the paper-making process. Bioremediation methods have been gaining considerable interest recently, since biological treatments offer greener options from the perspective of commonly past used traditional physicochemical methods. These methods employ microbes like bacteria, fungi, algae, and their enzymes power to break down environmental pollutants present in wastewater and eventually convert them into convenient products. Biotechnological treatment systems are capable of decreasing COD

by exploiting natural microbial functions (Ghangrekar & Behera, 2014; Skouteris et al., 2020; Uçkun Kiran et al., 2016).

Aerobic biological processes play a key role in managing highly polluted waste. AS, aerated lagoons, and sequencing batch reactor aerobic methods are frequently merged with aerobic bacteria that flourish in the presence of oxygen and actively biodegrade complex organic residues (Skouteris et al., 2020). On the contrary, anaerobic treatment processes like digestion, filter processes, fluidized-bed and up-flow sludge blanket bioreactors, when bound to microbial activity, are able to biodegrade organic matter, reduce BOD, COD, and many key pollutants, while emitting renewable biogas in the form of methane able for electricity production (Skouteris et al., 2020). Aerobic and anaerobic technologies in cooperation with specificity and adaptability characterizing microorganisms simply offer attractive solutions in eco-friendly wastewater management due to notably reducing the environmental impact of effluents (Ghangrekar & Behera, 2014).

An innovative hybridization of biotechnological methods with other biological or physicochemical processes has been proven to have enormous cost-effective and natural potential for optimizing future wastewater treatment. For instance the most common hybrid method, combining sequencing coagulation-flotation units with an UASB, AS method, and nanofiltration membrane technologies, is a widely preferred solution that enables more sustainable and efficient resource utility and recovery within the P&P industries (Ghangrekar & Behera, 2014; Skouteris et al., 2020; Uçkun Kiran et al., 2016).

Compared with physicochemical processes, in all aforementioned technologies, microorganisms' activity usually does not require excessive energy input and land occupation; thus operating costs and negative environmental impact are reduced without affecting pollutant removal efficiency (Ghangrekar & Behera, 2014; Skouteris et al., 2020). However, certain limitations and difficulties bound to biodegradation methods still exist despite recent developments. Generally, such treatment methods are often time-consuming and may require prolonged retention times in case of engaging with complicated polluted effluents. Moreover, aerobic treatment may be effective, but the constant oxygen supply demand results in higher energy consumption and expensive aeration systems, since large biomass amounts are created and are in need of immediate handling (Ranade & Bhandari, 2014). Anaerobic treatment, on the other hand, which is intended to produce biogas, is not suitable for the complete elimination of a few pathogens, and this method is relatively expensive and risky due to biogas's high flammability (Parr).

Small paper and pulp producers with limited resources may be challenged by applying novel hybrid treatment methods that could entail increased capital expenditure and complex operating requirements. Another serious challenge lies in maintaining and adjusting the optimal environment suitable for microbial growth, because microbial ecosystems are prone to disruption by extreme environmental conditions and inhibition due to toxicity (Parr; Ranade & Bhandari, 2014). Furthermore, difficulties like the complexity and diverse nature of effluents, considering developing bioreactors that fit all biological treatment styles, still afflict global P&P industries (Alisawi, 2020; Parr).

P&P industries are facing the constant challenge of balancing the need for effective treatment with the necessity of reduced operating costs. Stability and performance issues of biological treatment systems are under strain on account of seasonal changes, extreme weather conditions, or other environmental factors (Alisawi, 2020). For worldwide corporations to ensure sustainable and environmentally friendly practices, these challenges must be addressed promptly by continuous research, technological improvements, and tailored solutions (Alisawi, 2020; Parr).

8.4.2 Concise comparative analysis of traditional and innovative biological treatment systems in the pulp and paper industry

Paper-manufacturing mills all over the globe have depended on conventional aerobic/anaerobic biological treatment for long periods of time, with the purpose of dealing with high wastewater-generated volumes (Mazhar et al., 2019). Despite the fact that traditional methods are essential in organic substances' deconstruction, they are followed by a lot of restrictions impacting their final profitability and yield (Alisawi, 2020; Mazhar et al., 2019). Considerable toxicity sensitivity, large land occupation, huge processing basins, and lack of consistent compliance in removing specific pollutants are only a few of the existing drawbacks that cause infrastructure costs in paper production (Mazhar et al., 2019).

Under those circumstances, P&P industries searched for novel options so as to provide factories with sustainable solutions against the shortcomings of existing treatments (Toczyłowska-Mamińska, 2017). Bioreactors like sequencing batch and membrane reactors combined with microbial utility and physicochemical methods employment are reportedly innovative techniques that offer almost flawless contaminants removal, highly cleansed water, and vast biogas production, hence, cost-effectiveness, electricity generation,

nature-friendly operation, and renewable-economical manufacturing (Al-Asheh et al., 2021; Toczyłowska-Mamińska, 2017). In addition, these hybrid/integrated technologies apply to both large- and small-scale pulp, paper WWTPs, and factories, with equally ensured efficiencies (sbr_new.pdf).

The selection of the appropriate integrated process is dependent on factors such as sewage composition, required efficiency, land availability, and budgetary constraints. Innovative bioremediation systems may be providing significant benefits to P&P plants and industries. However, wastewater stream complexity evaluation and overall cost analysis of the industry's life cycle expenditure, including initial investments, operating and maintenance expenses, as well as energy consumption and possible revenue from biogas production, must be carefully assessed before deciding on traditional or hybrid bioremediation systems selection in a P&P corporation (sbr_new.pdf).

8.4.3 Energy consumption and potential for resource recovery

P&P industries are known to be the 4th most energy-consuming factories worldwide (Furszyfer Del Rio et al., 2022; Lin et al., 2014). For instance, it has been reported that the Taiwanese paper industry energy prerequisites dramatically increased in 2011, a situation that evoked Taiwanese authorities to propose new policies concerning carbon footprint minimization. The implemented policy suggested technological improvements on the given pulp systems and high-concentration pulpers so as to conserve energy up to 30%–40% and reduce 80% of total energy costs from the pulpers (Lin et al., 2014).

Processes like chemical pulping, paper drying, and black liquor evaporation require both electricity and heat generation by fossil factories, which mitigate the greenhouse effect by increasing GHG emissions by 1.3% (van Ewijk et al., 2021). Nevertheless, it must be noted that during paper production, wastes like biogenic feedstock are used as biomass for energy generation that covers half of P&P industries' energy needs. Thus most energy requirements are covered by renewable sources like biomass (Furszyfer Del Rio et al., 2022).

The AS disposal withholds up to 60% of total treatment expenses (Silva & Rosa, 2022; Stoica et al., 2009), while in Europe and North America, the cost escalated due to natural variations, hence higher treatment standards (Kaur et al., 2020). Furthermore, Stoica et al. (2009) mentioned that the aeration of the biological wastewater treatment units holds out more than 50% of the electricity energy costs of the total expenses of WWTP; hence, an alternative treatment plan would be to exclude oxygen and employ anaerobic processes. This approach could lead to almost 10 times less sludge production than during aerobic

processes. In addition, in AS systems, the energy expenses are not equally dispersed in each unit. For example, recirculation systems require excessive energy amounts similar to aeration systems to pump the given sludge and circulate nutrients inside the unit, with the purpose to ensure phosphorus and nitrogen even delivery in all reactors. It has been found that among WWTP aeration methods that utilize mechanical aerators, they are the most energy-consuming processes in contrast to air diffuser utilization, which are superior alternatives providing energy cost efficiency (Silva & Rosa, 2022).

The potential for resource recovery is considerably high for P&P industries, as wastes are collected and treated with various physico-chemical and biological processes (Gopal et al., 2019; Kaur et al., 2020; Kumar et al., 2011). Typically, AD of waste-activated sludge has been proven to be a more adaptable technique, where AS is treated with a variety of microorganisms, a process that leads to mass biogas formation, which is used as an electricity source (Kamali et al., 2016). Additionally, biodiesel production as a result of toxicity extraction from the industry's effluents may be achieved by some fungus equal to the yeast strain of *Rhodospiridium kratochvilovae*, an action that allows all produced biodiesel to be a great transportation fuel. In addition, methane discharge as biogas during secondary sludge treatment of AD was observed to cover experimentally 88% of the net energy reserves (Resource recovery assessment at a pulp mill wastewater treatment plant in Uruguay - ScienceDirect).

Although phosphorus plays a serious role in bacterial development, the external feed of these nutrients should be limited for resource reservation and discharged biomass decrease (Slade et al., 2004). Nonetheless, Daneshgar et al. (2019) claimed that phosphorus can be recovered through precipitation of the solid phosphorus minerals drawn from the generated sludge and in the form of struvite, a magnesium ammonium phosphate crystal (MAP) (Daneshgar et al., 2019; Resource recovery assessment at a pulp mill wastewater treatment plant in Uruguay - ScienceDirect). Struvite is formed when magnesium salts precipitate phosphorus during the phosphorus recovery phase in aquatic waste treatment and is considered to be a high-quality fertilizer (Karunanithi et al., 2016; Rahman et al., 2014; Shih & Yan, 2016). Moreover, studies suggest lignocellulosic fiber recovery and their utility as biofuels for numerous organic compounds like PAHs, pesticides, dioxins, furans, and heavy metal contaminants, such as arsenic, lead, and mercury absorption (Kumar et al., 2011; Mandeep et al., 2020).

8.4.4 Economic viability and circular economy

The findings of a survey conducted on P&P industrial expenditures in 1978 projected a total of \$363 million in capital expenses regarding

air-water quality assurance and solid waste management, whereas less than 26% was spent on costs toward environmental protection ([Pulp and paper industry wastewater management on JSTOR](#)).

Sustainable economic benefits have been claimed to derive from the promotion of a CE. Contaminated aquatic waste from paper mills raises safety concerns about agricultural, environmental, and human consumption uses of recycled wastewater, which refer to studies claiming that significant organic residue volume remained in wastewater, even after controlled recycling remediation ([Pulp and paper industry wastewater management on JSTOR](#); [Shogren et al., 2019](#)). The CE pattern correlates to a closed net-zero waste cycle that results in multiple benefits, counting less required primal matter and boosting renewable resource use, and waste-biomass management ([Amândio et al., 2022](#); [Leppänen et al., 2020](#); [Li & Ma, 2015](#)). CE resembles nature, given that just like our environment, no generated waste is useless to some organisms is not merely useful to other living beings ([Amândio et al., 2022](#); [Leppänen et al., 2020](#)). Thus industrial symbiosis is a collective approach that empowers industries' separation and mass exchange of resources, energy, water, and by-products, according to geographic proximity ([Leppänen et al., 2020](#)).

China's papermaking eco-industries pay much attention to source conservation and are constantly seeking greener alternative methods practically based on CE ([Li & Ma, 2015](#)). High energy, resources, and fuel wasting, and thus excessive air, water, and soil pollutant emissions, set an urgent need for the Chinese government to develop harmonious CE solutions ([Li & Ma, 2015](#); [Shogren et al., 2019](#)). One decade has passed since Chinese P&P industries introduced the establishment of eco-industrial CE parks that formed energy and matter bonds among the existing factories inside them. Regional and industrial characteristics were thoroughly assessed before eco-park construction. Eco-parks plan hinged on CE principles and involved centralized heat, power, and cold supplies appropriate for all seasons, in addition to CE chains of energy, water, and solid matters' utility ([Li & Ma, 2015](#)). Such innovative, eco-viable methods, placed Chinese industries among the most rapidly evolving and ecological paper-manufacturing enterprises on the globe ([Li & Ma, 2015](#); [Pulp and paper industry wastewater management on JSTOR](#)).

Eleven million tons of waste are generated annually by European P&P factories. In 2004, in an attempt to jump into greener papermaking industries transition, the European Union prioritized landfills abolishment. On the contrary, commonly used waste cremation in an attempt to achieve energy recovery is harmful due to mass air pollutant emissions and wastes' unlikely revalorization ([Amândio et al., 2022](#); [Leppänen et al., 2020](#)).

Except for eco-park establishment, developed CE processes, which utilize bioethanol, polyhydroxy-alkanoates, and biogas, are fully capable of converting P&P wastes into high-value bioproducts. The feasibility of these methods relies on factors like feedstocks' availability, technological receptivity, operation expenses, and total revenues (Amândio et al., 2022; Leppänen et al., 2020). Hence, it is indisputably acknowledged that the CE planning concept is in the right direction for relieving our planet from resource exhaustion and ongoing pollution (Amândio et al., 2022; Leppänen et al., 2020; Li & Ma, 2015).

8.5 Conclusions and future trends

The P&P industry's biological wastewater treatment is about to embark on a revolutionary journey characterized by cutting-edge methods, eco-friendly energy practices, and reduced infrastructure costs. These developments promise to meet regulatory requirements and drive economic viability through resource efficiency and innovation, while the industry works toward greater environmental responsibility. Paper-manufacturing processes inside P&P industries generate vast wastewater's amounts, considered to be contaminated by high BOD and COD pollutants. The recognition of wastewater impact on the environment urged global P&P corporations to seek eco-friendly, viable, and sustainable treatment alternatives. Single physicochemical and standard aerobic/anaerobic conventionally applied remediation processes are followed by several economic, manufacturing, and environmental limitations. Comparatively, integrated processes combining microbial assistance and other bioremediation or physicochemical methods are confirmed to be remarkably efficient decontamination approaches. Hybrid technologies are excessively prone to participating in resource recovery and CE patterns inside the global market. However, further studies must be conducted for industries to profitably tackle any existing drawbacks and obstacles, as well as to completely develop active bioremediation and hybrid techniques.

Nomenclature

ACR	Anaerobic Contact Reactor
AD	Anaerobic Digestion
AF	Anaerobic Filter process
AOX	Absorbable Organo-Halogens
AS	Activated Sludge process
ASBs	Aerated Lagoons (Aerated stabilization basins)
BC	Before Christ
BOD	Biological Oxygen Demand
CE	Circular Economy
CF	Coagulation-Filtration

COD	Chemical Oxygen Demand
DOM	Dissolved Organic Matter
DyP	Dye-decolorizing Peroxidase
ENGO	Environmental Non-Governmental Organizations
EPA	Environmental Protection Agency
FBR	Fluidized-Bed Reactor
GAC	Granular Activated Carbon
GHG	Green-House Gas emissions
GWF	Membrane Filtration and Low-Pressure Reverse Osmosis
Lac	Laccase
LDAs	Lignin-Degrading Auxiliary enzymes
LiP	Lignin Peroxidase
LMEs	Lignin-Modifying Enzymes
LSP	Low-Sludge Production systems
MAP	Magnesium-Ammonium-Phosphate crystal
MBR	Membrane BioReactor
MBBR	Moving-Bed Biofilm Reactors
MnP	Manganese Peroxidase
NF	NanoFiltration membrane
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	PolyChlorinated Biphenyls
P&P	Pulp and Paper industry
RBC	Rotating Biological Contactor
RF	Re-Finer (mill type)
SBR	Sequencing Batch Reactor
SF	Sand Filter
sMBR	Submerged Membrane Bio-Reactor
SS	Suspended Solids
SF	Sand Filter
SSF	Slow Sand Filter
TFP	Trickling Filter Process
UAF	Up-Flow Anaerobic Filter
UASBR-FBR	Up Flow - Anaerobic Sludge Blanket - Fluidized-Bed Reactor
UASBR	Up Flow - Anaerobic Sludge Blanket Reactor
UFBAB	Up-flow Fixed-Bed Anaerobic Bioreactor
VP	Versatile Peroxidase
WRF	White-Rot Fungi
WWTP	Waste-Water Treatment Plants

References

- Ahn, J.-W., & Lim, M. (2009). Characteristics of wastewater from the pulp. Paper Industry and its biological treatment technologies. *Journal of the Korean Institute of Resources Recycling*, 18.
- Al-Asheh, S., Bagheri, M., & Aidan, A. (2021). Membrane bioreactor for wastewater treatment: A review. *Case Studies in Chemical and Environmental Engineering*, 4, 100109.
- Alisawi, H. A. O. (2020). Performance of wastewater treatment during variable temperature. *Applied Water Science*, 10, 89.

- Amândio, M. S. T., Pereira, J. M., Rocha, J. M. S., Serafim, L. S., & Xavier, A. M. R. B. (2022). Getting value from pulp and paper industry wastes: On the way to sustainability and circular economy. *Energies*, 15, 4105.
- Angelakis, A. N., Capodaglio, A. G., & Dialynas, E. G. (2023). Wastewater management: From ancient Greece to modern times and future. *Water*, 15, 43.
- Archibald, F. S., Bourbonnais, R., Jurasek, L., Paice, M. G., & Reid, I. D. (1997). Kraft pulp bleaching and delignification by *Trametes versicolor*. *Journal of Biotechnology*, 53, 215–236.
- Ashrafi, O., Yerushalmi, L., & Haghighat, F. (2015). Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management*, 158, 146–157.
- Aytac, A., & Korkmaz, M. (2022). An analysis of the world paper industry with a focus on Europe and trade perspective. *Studia Universitatis "Vasile Goldis" Arad - Economics Series*, 32, 24–40.
- Bajpai, P. (2018). Biological treatment of pulp and paper mill effluents. In P. Bajpai (Ed.). *Biotechnology for pulp and paper processing* (pp. 313–369). Singapore: Springer.
- Cassia, R., Nocioni, M., Correa-Aragunde, N., & Lamattina, L. (2018). Climate change and the impact of greenhouse gasses: CO₂ and NO, friends and foes of plant oxidative stress. *Frontiers in Plant Science*, 9, 273.
- Daneshgar, S., Buttafava, A., Callegari, A., & Capodaglio, A. G. (2019). Economic and energetic assessment of different phosphorus recovery options from aerobic sludge. *Journal of Cleaner Production*, 223, 729–738.
- De Feo, G., Mays, L. W., & Angelakis, A. N. (2011). 4.01 – Water and wastewater management technologies in the Ancient Greek and Roman Civilizations. In P. Wilderer (Ed.). *Treatise on Water Science* (pp. 3–22). Oxford: Elsevier.
- De Namor, A. D. (2007). Water purification: From ancient civilization to the XXI Century. *Water Science & Technology: Water Supply*, 7. <https://doi.org/10.2166/ws.2007.004>.
- Del Rio, D. D. F., Sovacool, B. K., Griffiths, S., Bazilian, M., Kim, J., Foley, A. M., et al. (2022). Decarbonizing the pulp and paper industry: A critical and systematic review of sociotechnical developments and policy options. *Renewable and Sustainable Energy Reviews*, 167, 112706.
- Esmaeeli, A., Sarrafzadeh, M.-H., Zeighami, S., Kalantar, M., Bariki, S. G., Fallahi, A., et al. (2023). A comprehensive review on pulp and paper industries wastewater treatment advances. *Industrial & Engineering Chemistry Research*. <https://doi.org/10.1021/acs.iecr.2c04393>.
- Faisal, M., Muttaqi, K. M., Sutanto, D., Al-Shetwi, A. Q., Ker, P. J., & Hannan, M. A. (2023). Control technologies of wastewater treatment plants: The state-of-the-art, current challenges, and future directions. *Renewable and Sustainable Energy Reviews*, 181, 113324.
- Fluidized bed bioreactor for multiple environmental engineering solutions. ScienceDirect. <https://www.sciencedirect.com/science/article/pii/S0043135418309904>. Accessed 27 July, 2023.
- Gandhi, M. S. (2010). Biological treatment of pulp and paper mill effluent using immobilized bacillus subtilis. *International Journal of Biological Sciences*, 1, 131–140.
- Ghangrekar, M. M., & Behera, M. (2014). 3.5 – Suspended growth treatment processes. In S. Ahuja (Ed.). *Comprehensive water quality and purification* (pp. 74–89). Waltham: Elsevier.
- Ghodeif, K. (2013). *Baseline assessment study for wastewater treatment plant for Al Gozayyera village, West Kantara City, Ismailia Governorate, Egypt* <https://doi.org/10.13140/RG.2.2.34897.63844>.
- Ghosh, P., & Thakur, I. S. (2017). Treatment of landfill leachate using fungi: An efficient and cost-effective strategy. In T. Satyanarayana, S. K. Deshmukh, & B. N.

- Johri (Eds.). *Developments in fungal biology and applied mycology* (pp. 341–357). Singapore: Springer.
- Gopal, P. M., Sivaram, N. M., & Barik, D. (2019). Chapter 7 – Paper industry wastes and energy generation from wastes. In D. Barik (Ed.). *Energy from toxic organic waste for heat and power generation* (pp. 83–97). Woodhead Publishing.
- Gray, W. B., Shadbegian, R. J., Wang, C., & Meral, M. (2014). Do EPA regulations affect labor demand? Evidence from the pulp and paper industry. *Journal of Environmental Economics and Management*, 68, 188–202.
- Hämäläinen, A., Kokko, M., Kinnunen, V., Hilli, T., & Rintala, J. (2022). Hydrothermal carbonization of pulp and paper industry wastewater treatment sludges – Characterization and potential use of hydrochars and filtrates. *Bioresource Technology*, 355, 127258.
- Haq, I., Kumar, S., Kumari, V., Singh, S. K., & Raj, A. (2016). Evaluation of bioremediation potentiality of ligninolytic *Serratia liquefaciens* for detoxification of pulp and paper mill effluent. *Journal of Hazardous Materials*, 305, 190–199.
- Jagaba, A. H., Kutty, S. R. M., Baloo, L., Birniwa, A. H., Lawal, I. M., Aliyu, M. K., et al. (2022). Combined treatment of domestic and pulp and paper industry wastewater in a rice straw embedded activated sludge bioreactor to achieve sustainable development goals. *Case Studies in Chemical and Environmental Engineering*, 6, 100261.
- Kamali, M., Gameiro, T., Costa, M. E. V., & Capela, I. (2016). Anaerobic digestion of pulp and paper mill wastes – An overview of the developments and improvement opportunities. *Chemical Engineering Journal*, 298, 162–182.
- Karunanithi, R., Szogi, A., Bolan, N. S., Naidu, R., Ok, Y. S., Krishnamurthy, S., et al. (2016). Chapter 27 – Phosphorus recovery from wastes. In M. N. V. Prasad, & K. Shih (Eds.). *Environmental materials and waste* (pp. 687–705). Academic Press.
- Kaur, R., Tyagi, R. D., & Zhang, X. (2020). Review on pulp and paper activated sludge pretreatment, inhibitory effects and detoxification strategies for biovalorization. *Environmental Research*, 182, 109094.
- Kiran, E. K., Stamatelatos, K., Antonopoulou, G., & Lyberatos, G. (2016). 10 – Production of biogas via anaerobic digestion. In R. Luque, C. S. K. Lin, K. Wilson, & J. Clark (Eds.). *Handbook of biofuels production* (pp. 259–301). Woodhead Publishing 2nd ed.
- Kumar, M., Morya, R., Gupta, A., & Thakur, I. S. (2020). Chapter 3 – Anaerobic biovalorization of pulp and paper mill waste. In N. K. Rathinam, & R. K. Sani (Eds.). *Biovalorisation of wastes to renewable chemicals and biofuels* (pp. 41–61). Elsevier.
- Kumar, S., Loganathan, V. A., Gupta, R. B., & Barnett, M. O. (2011). An assessment of U(VI) removal from groundwater using biochar produced from hydrothermal carbonization. *Journal of Environmental Management*, 92, 2504–2512.
- Kumar, V., Thakur, I. S., & Shah, M. P. (2020). Bioremediation approaches for treatment of pulp and paper industry wastewater: Recent advances and challenges. *Microbial Bioremediation & Biodegradation*, 1–48.
- Lee, E. G.-H., Mueller, J. C., & Walden, C. C. (1978). Decolorization of bleached kraft mill effluents by algae. *TAPPI*, 61, 59–62.
- Leppänen, T., Mustonen, E., Saarela, H., Kuokkanen, M., & Tervonen, P. (2020). Productization of industrial side streams into by-products—Case: Fiber sludge from pulp and paper industry. *Journal of Open Innovation: Technology, Market, and Complexity*, 6, 185.
- Li, Y., & Ma, C. (2015). Circular economy of a papermaking park in China: A case study. *Journal of Cleaner Production*, 92, 65–74.
- Lin, H.-C., Chan, D. Y.-L., Lin, W.-C., Hsu, C.-H., & Hong, G.-B. (2014). Status of energy conservation in Taiwan's pulp and paper industry. *Energy*, 73, 680–685.

- Lofrano, G., & Brown, J. (2010). Wastewater management through the ages: A history of mankind. *Science of the Total Environment*, 408, 5254–5264.
- Mahmood, T., & Paice, M. (2011). Aerated stabilization basin design and operating practices in the canadian pulp and paper industry. *Journal of Environmental Engineering and Science*, 5, 383–395.
- Mandeep, Gupta, G. K., & Shukla, P. (2020). Insights into the resources generation from pulp and paper industry wastes: Challenges, perspectives and innovations. *Bioresource Technology*, 297, 122496.
- Mazhar, S., Ditta, A., Bulgariu, L., Ahmad, I., Ahmed, M., & Nadiri, A. A. (2019). Sequential treatment of paper and pulp industrial wastewater: Prediction of water quality parameters by Mamdani Fuzzy Logic model and phytotoxicity assessment. *Chemosphere*, 227, 256–268.
- Meena, M., Yadav, G., Sonigra, P., & Shah, M. P. (2022). A comprehensive review on application of bioreactor for industrial wastewater treatment. *Letters in Applied Microbiology*, 74, 131–158.
- Meyer, T., & Edwards, E. A. (2014). Anaerobic digestion of pulp and paper mill wastewater and sludge. *Water Research*, 65, 321–349.
- Mir-Tutusaus, J. A., Baccar, R., Caminal, G., & Sarrà, M. (2018). Can white-rot fungi be a real wastewater treatment alternative for organic micropollutants removal? A review. *Water Research*, 138, 137–151.
- Mishra, T., Ramola, S., Shankhwar, A. K., Rabha, A., & Srivastava, D. R. (2015). Pulp and paper mill effluent treatment by hybrid anaerobic upflow fixed-bed bioreactor combined with slow sand filter. *Desalination and water treatment*, 57. <https://doi.org/10.1080/19443994.2015.1039596>.
- Mleziva, M. M., & Wang, J. H. (2012). 10.23 – Paper. In K. Matyjaszewski, & M. Möller (Eds.). *Polymer science: A comprehensive reference* (pp. 397–410). Amsterdam: Elsevier.
- Muhamad, M. H., Abdullah, S. R. S., Mohamad, A. B., Abdul Rahman, R., & Kadhum, A. A. H. (2013). Application of response surface methodology (RSM) for optimisation of COD, NH₃-N and 2,4-DCP removal from recycled paper wastewater in a pilot-scale granular activated carbon sequencing batch biofilm reactor (GAC-SBBR). *Journal of Environmental Management*, 121, 179–190.
- Netnapid, T., Wirojanagud, W., & Santi, S. (2004). Removal of color, COD and lignin of pulp and paper wastewater using wood ash. *Songklanakarin Journal of Science and Technology*, 26.
- Parr J. Anaerobic treatment of municipal wastewater: How appropriate is it for low-income countries?.
- Patel, A., Arora, N., Pruthi, V., & Pruthi, P. A. (2017). Biological treatment of pulp and paper industry effluent by oleaginous yeast integrated with production of biodiesel as sustainable transportation fuel. *Journal of Cleaner Production*, 142, 2858–2864.
- Patel, K., Patel, N., Vaghamshi, N., Shah, K., Duggirala, S. M., & Dudhagara, P. (2021). Trends and strategies in the effluent treatment of pulp and paper industries: A review highlighting reactor options. *Current Research in Microbial Sciences*, 2, 100077.
- Pellinen, J., Abuhasan, J., Joyce, T. W., & Chang, H.-M. (1989). Biological delignification of pulp by *Phanerochaete chrysosporium*. *Journal of Biotechnology*, 10, 161–170.
- Pulp and paper industry wastewater management on JSTOR. https://www.jstor.org/stable/40586464?saml_data=eyJzYW1sVG9rZW4iOiI1YjRkYzU1OS05NzRmLTQwZTMtYTQ2OC00ZGI5OWEwM2ZlZjgiLCJlbWFPbC16Im1haW50emVAaWh1LmdyIiwiaW5zdGl0dXRpb25JZHMlOlsiZDYxMjEwNDYtMTdmYy00YTl0LTg1NDItY2JiMDgyZGQyNWYlIl19 (Accessed 27 July 2023).

Pulp and paper industry wastewater treatment: Use of microbes and their enzymes.

<https://www.degruyter.com/document/doi/10.1515/psr-2019-0050/html>

(Accessed 27 July 2023).

Rahman, M. M., Salleh, M. A. M., Rashid, U., Ahsan, A., Hossain, M. M., & Ra, C. S. (2014). Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review. *Arabian Journal of Chemistry*, 7, 139–155.

Ranade, V. V., & Bhandari, V. M. (2014). Chapter 1 - Industrial wastewater treatment, recycling, and reuse: An overview. In V. V. Ranade, & V. M. Bhandari (Eds.).

Industrial wastewater treatment, recycling and reuse (pp. 1–80). Oxford: Butterworth-Heinemann.

Resource recovery assessment at a pulp mill wastewater treatment plant in Uruguay -

ScienceDirect. <https://www.sciencedirect.com/science/article/pii/S0301479719314367>

(Accessed 27 July 2023).

Roy, P., Ashton, L., Wang, T., Corradini, M. G., Fraser, E. D. G., Thimmanagari, M., et al. (2021). Evolution of drinking straws and their environmental, economic and societal implications. *Journal of Cleaner Production*, 316, 128234.

Sátiro, J., Cunha, A., Gomes, A. P., Simões, R., & Albuquerque, A. (2022). Optimization of microalgae–bacteria consortium in the treatment of paper pulp wastewater.

Applied Sciences, 12, 5799.

Savant, D. V., Abdul-Rahman, R., & Ranade, D. R. (2006). Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater.

Bioresource Technology, 97, 1092–1104.

sbr_new.pdf. https://www3.epa.gov/npdes/pubs/sbr_new.pdf (Accessed 27 July 2023).

Selvam, K., Swaminathan, K., Hoon Song, M., & Chae, K.-S. (2002). Biological treatment of a pulp and paper industry effluent by *Fomes lividus* and *Trametes versicolor*. *World Journal of Microbiology and Biotechnology*, 18, 523–526.

Sharma, P., Iqbal, H. M. N., & Chandra, R. (2022). Evaluation of pollution parameters and toxic elements in wastewater of pulp and paper industries in India: A case study. *Case Studies in Chemical and Environmental Engineering*, 5, 100163.

Sharma, S., Sarma, S. J., & Tay, J.-H. (2019). Chapter 4 - Aerobic granulation in wastewater treatment: A general overview. In M. P. Shah, & S. Rodriguez-Couto (Eds.). *Microbial Wastewater Treatment* (pp. 57–81). Elsevier.

Shih, K., & Yan, H. (2016). Chapter 26 - The crystallization of struvite and its analog (K-Struvite) from waste streams for nutrient recycling. In M. N. V. Prasad, & K. Shih (Eds.). *Environmental Materials and Waste* (pp. 665–686). Academic Press.

Shogren, R., Wood, D., Orts, W., & Glenn, G. (2019). Plant-based materials and transitioning to a circular economy. *Sustainable Production and Consumption*, 19, 194–215.

Silva, C., & Rosa, M. J. (2022). A comprehensive derivation and application of reference values for benchmarking the energy performance of activated sludge wastewater treatment. *Water*, 14, 1620.

Skouteris, G., Rodriguez-Garcia, G., Reinecke, S. F., & Hampel, U. (2020). The use of pure oxygen for aeration in aerobic wastewater treatment: A review of its potential and limitations. *Bioresource Technology*, 312, 123595.

Slade, A., Ellis, R., van den Heuvel, M., & Stuthridge, T. R. (2004). Nutrient minimisation in the pulp and paper industry: An overview. *Water Science & Technology*, 50, 111–122.

Sonkar, M., Kumar, M., Dutt, D., & Kumar, V. (2019). Treatment of pulp and paper mill effluent by a novel bacterium *Bacillus* sp. IITRDVM-5 through a sequential batch process. *Biocatalysis and Agricultural Biotechnology*, 20, 101232.

- Stanbury, P. F., Whitaker, A., & Hall, S. J. (2017). Chapter 11 – Effluent treatment. In P. F. Stanbury, A. Whitaker, & S. J. Hall (Eds.). *Principles of fermentation technology* (pp. 687–723). Oxford: Butterworth-Heinemann 3rd ed.
- Stoica, A., Sandberg, M., & Holby, O. (2009). Energy use and recovery strategies within wastewater treatment and sludge handling at pulp and paper mills. *Bioresource Technology*, 100, 3497–3505.
- Sun, X., Jin, L., Zhou, F., Jin, K., Wang, L., Zhang, X., et al. (2022). Patent analysis of chemical treatment technology for wastewater: Status and future trends. *Chemosphere*, 307, 135802.
- Swamy, N. K., Singh, P., & Sarethy, I. P. (2011). Aerobic and anaerobic treatment of paper industry wastewater. *Research in Environment Life and Science*, 4(4), 141–148.
- Toczyłowska-Mamińska, R. (2017). Limits and perspectives of pulp and paper industry wastewater treatment – A review. *Renewable and Sustainable Energy Reviews*, 78, 764–772.
- van Ewijk, S., Stegemann, J. A., & Ekins, P. (2021). Limited climate benefits of global recycling of pulp and paper. *Nature Sustainability*, 4, 180–187.
- Vidal, G., González, Y., Piña, B., Jarpa, M., & Gómez, G. (2021). Minimization of environmental impact of kraft pulp mill effluents: Current practices and future perspectives towards sustainability. *Sustainability*, 13, 9288.
- Virkutyte, J. (2017). *Aerobic treatment of effluents from pulp and paper industries* 103–130.
- Wastewater Treatment Water Use | U.S. Geological Survey. <https://www.usgs.gov/special-topics/water-science-school/science/wastewater-treatment-water-use> (Accessed 27 July 2023).
- What is Industrial Effluent - Etch2o. 2023. <https://www.etch2o.com/what-is-industrial-effluent/> (Accessed 21 January 2024).
- What is the definition of wastewater? Pumps and systems magazine. 2021. <https://www.pumpsandsystems.com/what-definition-wastewater> (Accessed 27 July 2023).
- Yeber, M. C., & Silva, T. (2022). The ability of a bacterial strain to remove a phenolic structure as an approach to pulp and paper mill wastewater treatment: Optimization by experimental design. *Water*, 14, 3296.
- Yel, E., Dilek, F., & Yetis, U. (2002). Effectiveness of algae in treatment of a wood-based pulp and paper industry wastewater. *Bioresource Technology*, 84, 1–5.
- Yel, E., Yetis, U., & Dilek, F. (2002). Algal treatment of pulp and paper industry wastewaters in SBR systems. *Water Science and Technology*, 45, 151–158.

Photocatalysis methods for pulp and paper wastewater treatment

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9.1 Introduction

The water deficiency and its pollution are the major challenges of the 21st century (Das et al., 2023). This is caused by a variety of circumstances, such as industrialization, population growth, climate change, contaminating water sources, and wasting or using excessive amounts of pure water (Moravvej et al., 2020). An estimated 2000 million people throughout the world do not have free admittance to safe drinking water, and 7.8 million people die each year as a result of poor sanitation and water hygiene. Furthermore, the annual cost of the crisis resulted in more than USD 5 billion in economic losses for about 55 million people. Since 1980, annual water demand has improved by 1%, and this inclination is predicted to proceed up to 2050 (Das et al., 2023). The three sectors that utilize the most water globally are domestic use (11%), industrial use (19%), and agricultural activities (70%). The annual population growth rate crosses over 80 million people. So, the increase in water consumption is unavoidable for future generations (Moravvej et al., 2020). Despite this, there is a sharp increase in the volume of wastewater entering the environment, which leads to water pollution and causes detrimental effects on the environment (Kumar & Verma, 2023). According to the United Nations World Water Development Report, more than 80% of the wastewater in the world is dumped into the environment without treatment (Asfaha et al., 2021).

The rapidly expanding paper and pulp industry emits around 170 million tonnes of hazardous pollutants annually. These pollutants are the sixth-leading cause of freshwater body pollution globally (Kumar & Verma, 2023; Madhubala et al., 2022). The untreated pulp and paper mill wastewater (PPMW) with high BOD, COD, lignin, resin acids, fatty acids, tannins, blackish hue, suspended particles, and sulfur

compounds affects the receiving water channels severely (Panizza, 2018). These pollutants impact aquatic life, causing metabolic issues, endocrine disruptions, physiological dysfunctions, accumulation in body tissues, and an imbalance of microflora. They also prevent sunlight from penetrating water, obstruct photosynthetic activity, and create low-oxygen environments in aquatic ecosystems. The translocation technique used by root plants to transport pollutants through the food chain poses a serious health risk (Kumar & Verma, 2023). Therefore, before being discharged into the environment, these effluents must be thoroughly treated. Conventional wastewater treatment consists of three major steps: primary, secondary, and tertiary. Primary treatment includes a bar screen and sedimentation basin to remove suspended particles, whereas secondary treatment involves biological processes, such as the biological filter process and the activated sludge process, to convert complex organic molecules into harmless chemicals (Das et al., 2023). Tertiary treatments employ advanced oxidation techniques like ozonation, peroxidation, photocatalysis, membrane processes (ultrafiltration, nanofiltration, and reverse osmosis), adsorption, or coagulation (Panizza, 2018).

Photocatalysis is a widely used process for treating PPMW because it is based on photon absorption rather than thermal activation. The term photocatalysis comes from the words photo (light) and catalysis (the catalyst-assisted reaction of a reactant that affects the rate of a chemical reaction). Therefore photocatalysis uses light to activate that substance, which assists in enhancing the rate of a chemical reaction without contributing to the reaction. Photocatalysis is done directly or indirectly by irradiating a catalyst, which drops the activation energy required for the primary process. In the presence of irradiation semiconductors, photocatalysis initiates redox processes. Natural photocatalysis occurs when chlorophyll absorbs light and changes carbon dioxide and water into oxygen and glucose. Artificial photocatalysis, on the contrary, uses photocatalysts to produce strong oxidizing agents and electronic holes that dissociate organic matter into CO_2 and H_2O . Over the past 40 years, photocatalysis has found several uses in energy and environment (Mandade, 2021). Photocatalytic treatment has been found to effectively remove TOC and toxicity from PPMW compared to UV, UV/ H_2O_2 , and UV/ $\text{H}_2\text{O}_2/\text{TiO}_2$ (Levchuk et al., 2015). Due to its rapid degradation rate, reasonable mineralization efficiency, low toxicity, and optimal progress of CO_2 and H_2O as end products, photocatalytic degradation is extremely promising (Bibi et al., 2023). Photocatalysis for PPMW treatment has been extensively investigated and developed. However, further research and studies are needed for photocatalysis to continue its practical uses. This chapter provides an overview of photocatalytic techniques and their effects on PPMW treatment.

9.2 Overview of pulp and paper making and wastewater generation

Woods, straws, grasses, bamboo, canes, and reeds are the most common sources of pulp fibers (Pokhrel & Viraraghavan, 2004). There are three types of paper mills: (1) wood/forest-based mills, (2) agro-based residue mills, and (3) wastepaper mills. The main processes in the paper and pulp industries include raw material preparation, pulping, washing, bleaching, and paper manufacturing. Mechanical or hydraulic methods are used to convert plant fiber into chips, while mechanical, semichemical, and chemical (kraft, sulfite) pulping processes are used in pulping (Madhubala et al., 2022). Mechanical and chemical pulping account for approximately 60% of total pulp production (Virkutyte, 2017). Among different chemical pulping, kraft pulping accounts for 90% of worldwide paper production (Ribeiro et al., 2020). The pulp and paper industry typically has three to five washing steps. Among these, multistage countercurrent washing is the most effective (Madhubala et al., 2022). Bleaching is performed after cooking to eliminate residual lignin in the pulp, and chlorine-based chemical agents (chlorine, chlorine dioxide, and hypochlorite) are usually utilized as bleaching agents (Sadhasivam et al., 2010). Chlorine dioxide is widely used as a bleaching agent because it creates less hazardous ECF, COD, BOD, and AOX than other bleaching agents (Liang et al., 2022). Because of consumer reluctance and environmental regulations, pulp manufacturers are switching to O_2 , O_3 , and peroxide bleaching even though it is more costly and less successful than chlorine-based chemical agents (Sadhasivam et al., 2010). The process of making paper requires a variety of raw materials and a lot of water (Haq et al., 2020). The pulp and paper industry consumes 5–20 m³ of water per ton of product, and up to 1000 m³ in some cases (Levchuk & Sillanpaa, 2020). The paper industry globally utilizes around 905.8 million m³ of water per year (Haq et al., 2020). The water consumption varies depending on the process (Virkutyte, 2017). In chemical pulping, more amount of wastewater is found in the pulping stage of the papermaking process (Sadhasivam et al., 2010). The bleaching plant is one of the heaviest consumers of water (Balcioglu & Cecen, 1999). The industry, like pulp and paper, textile, food processing, leather, pharmaceutical, and explosive manufacturing, produces enormous amounts of wastewater (Bhanot et al., 2020). The paper industry generates around 695.7 million m³ of effluent globally (Haq et al., 2020). The numerous components found in wood (lignin, carbohydrates, and extractives) are difficult to biodegrade and are washed away from the fibers during the washing, dewatering, and screening processes (Pokhrel & Viraraghavan, 2004). Based on the assumption that each ton of pulp and paper generates

200 m³ of effluent, pulp and paper mills emit approximately 40,000 million m³ of wastewater per year (Virkutyte, 2017). Globally, the pulp and paper sector produces 42% of wastewater, making it the third largest generator (Kumar et al., 2021). The following processes are the principal sources of pollution in the various stages of production: wood preparation, pulping, washing, bleaching, screening, paper machine, and coating operations (Pokhrel & Viraraghavan, 2004). The pulping and bleaching operations, which are the two main steps in the production of paper, create a substantial amount of wastewater (Madhubala et al., 2022). Pulping and bleaching processes can produce 225 m³ of effluent per ton of product (Parilti & Akten, 2011). The bleaching process contributes around 85% of the overall effluent of the industry (Madhubala et al., 2022). The washing and bleaching section in pulp and paper mills frequently contributes the most toxicity among all the other sections (Virkutyte, 2017). Different pulp and paper industry processes produce wastewater with variable characteristics depending on the sort of process, kind of wood used, methods employed, management strategies, internal recirculation of the effluent for recovery, and amount of water required in the particular process (Pokhrel & Viraraghavan, 2004). The elimination of structurally integrated lignin is a critical problem in the pulp and paper industry for producing high-quality paper (Sadhasivam et al., 2010). Every year the pulp and paper industry produces 50–70 million tons of lignin worldwide, of which about one million tons are traded for use in industry. The lignin output increases by 225 million tons annually by 2030 (Haq et al., 2020). Lignin and chlorolignin are mainly responsible for the color of wastewater (Parilti & Akten, 2011). For each ton of paper produced the effluents from bleach production plants comprise 100 kg of chemicals that impart color and 2–4 kg of organochlorines (Kansal et al., 2008). A complex mixture of cellulose, hemicellulose, dyes, inks, and lignin and its derivatives makes up CPBL. The CPBL concentrated almost 90% of the pollutants in the pulping process and had a strong odor, rich color, high COD, and strong alkalinity (Sun et al., 2022). Table 9.1 lists the many contaminants that reside at each stage of the pulping and papermaking process.

9.3 Impact of pulp and paper mill wastewater

The waste generated by the pulp and paper industry contains hazardous compounds that are by-products of the manufacturing process and have varied degrees of environmental toxicity. The summary of the detrimental impacts of PPMW on three components of the environment is summarized in Table 9.2.

Table 9.1 Lists of pollutants in the different stages of the pulping and papermaking process (Pokhrel & Viraraghavan, 2004).

Serial no.	Stage	Pollutant
1	Wood preparation	Suspended solids, dirt, grit, bark, and fibers
2	Digester house	Resins, fatty acids, AOX, and VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform)
3	Pulp washing	Suspended solids
4	Pulp bleaching	AOX, dissolved lignin, carbohydrate, inorganic chlorine compounds (chlorate ion), organic chlorine compounds (dioxins, furans, chlorophenols), and VOCs (acetone, methylene chloride, carbon disulfide, chloroform, chloromethane, and trichloroethane)
5	Papermaking	Waste particulates, organic compounds, inorganic dyes, and acetone

AOX, Absorbable organic halogen; VOC, volatile organic compound.

Table 9.2 Summary of the detrimental impact of PPMW on several environmental components (Kumar & Verma, 2023).

Components of environment	Impact
Aquatic organism	The heavy metals, like zinc, nickel, copper, lead, chromium, and cadmium, present in PPMW alter the physicochemical properties of received water bodies. The PPMW causes endocrine and reproductive abnormalities, mutations in tested organisms, carcinogenic and clastogenic diseases, respiratory stress, liver damage, genotoxicity, and discoloration and disintegration of the body.
Terrestrial flora and fauna	It slows plant growth and development, leads to metallic element bioaccumulation in plants, inhibits seed germination, reduces alpha-amylase activity, and causes phytotoxicity and genotoxicity.
Human health hazards	It causes lung cancer, respiratory disease, chronic problems, skin irritation, genetic and reproductive problems, and failure of the kidney and liver.

PPMW, Pulp and paper mill wastewater.

9.4 Methods for pulp and paper wastewater treatment

There have been many attempts to minimize the amounts of toxicity, organic charge, color, and AOX in PPMW. The treatment strategies

for PPMW are illustrated in Fig. 9.1 and encompass various approaches. These approaches can be categorized into physical methods, such as membrane filtration and adsorption; chemical methods, including coagulation-flocculation, electrochemical methods, electrochemical advanced oxidation processes, and advanced oxidation processes; biological methods, such as bacterial assisted treatment, algal assisted treatment, and fungal assisted treatment; and emerging methods, which comprise phytoremediation, constructed wetland plant treatment, microbial fuel cell technology, photoreforming, nanoremediation, biofilm-mediated remediation, and integrated treatment approaches.

9.4.1 Physical method

The removal of Cr^{6+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} , and Cd^{2+} ions from PPMW involves the use of activated neem bark, an adsorbent-like material. Under the best possible circumstances the color and lignin in PPMW are reduced using activated carbon formed from the pyrolysis of plastic mix waste. The implementation of membrane filtration techniques allows the PPMW plant to effectively decrease its chemical burden while simultaneously achieving efficient impurity removal with little energy consumption. The effectiveness of PPMW decontamination has been demonstrated due to the ability of

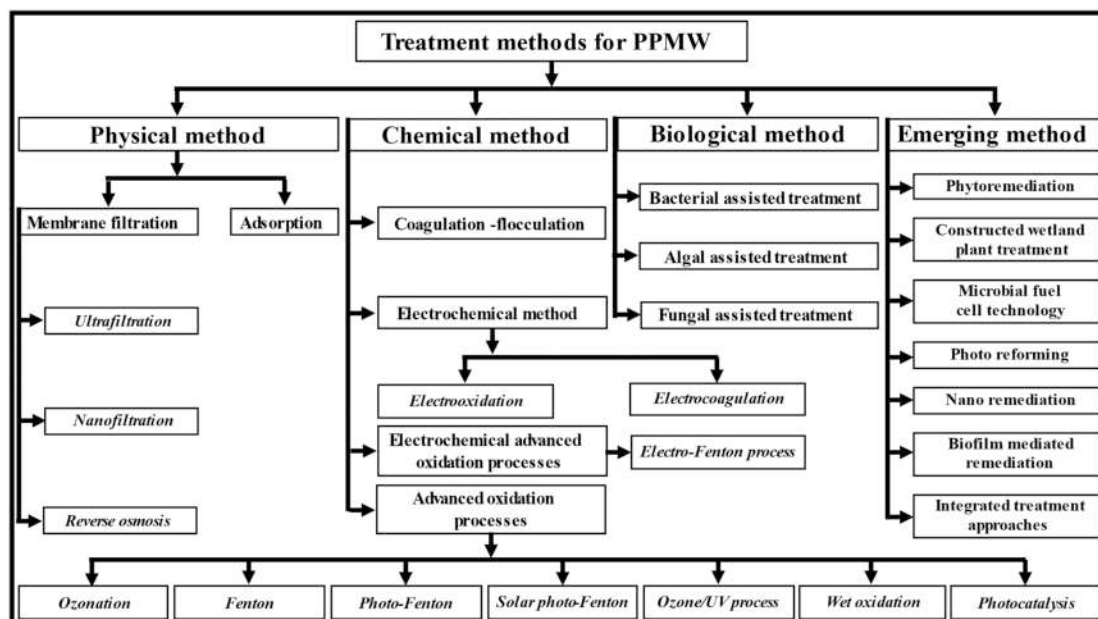


Figure 9.1 Different methods for pulp and paper mill wastewater treatment.

ultrafiltration to eliminate chemicals with high molecular weight. The ultrafiltration process can remove around 30% of the organic load, resulting in the production of permeate that can serve as a substitute for mechanically treated water. The two-step nanofiltration technology is an additional membrane filtering method employed to purify biotreated PPMW for reutilization. To reduce salt concentrations in parts per million by weight for recycling, reverse osmosis is used as an intercepting separation process.

9.4.2 Chemical methods

Coagulation-flocculation is a common process for eliminating large quantities of organics, metals, and color from PPMW. It requires the addition of inorganic coagulants (aluminum, synthetic organic polymers, and/or iron-based salts). Electrochemical degradation techniques are used for removing resistant contaminants from a range of PPMW before disposal since it is not harmful to the environment. With the use of heterogeneous and homogeneous catalysts and the electrocoagulation and electrooxidation mechanisms, electrochemical methods such as electro-Fenton are used to remove pollutants. A more practical and effective method for breaking down PPMW with a variety of resistant pollutants is electrocoagulation. The pollutants are destabilized during this procedure by the coagulants dissolved in the anodes. The combinations of iron and aluminum electrodes enable the effective treatment of PPMW by the electrocoagulation method. With graphite plates serving as electrodes and kaolin modified with transition metals (cobalt and copper) acting as catalysts, an electrochemical oxidation process incorporating catalyst adsorption and synergetic oxidation mechanisms is used to reduce the COD of PPMW. The galvanostatic electrolyzer is used in the electro-Fenton method to achieve electrochemical-enhanced oxidation of organic pollutants in PPMW (Kumar & Verma, 2023).

The advanced oxidation processes (ozonation, Fenton, photo-Fenton, solar photo-Fenton, ozone/UV process, wet oxidation, and photocatalysis) are used for the disintegration of persistent substances in PPMW. The strong oxidizing agent (hydroxyl radicals) produced by these processes oxidizes organic compounds in wastewater. Ozonation is used in the industry to remove color from PPMW. The Fenton method is based on the equilibrium concentration of hydroxyl radicals and catalytic formation. With minimal sludge production the photo-Fenton method performed traditional Fenton in the removal of AOX from PPMW. Under optimum conditions the photo-Fenton method can remove 90% AOX and 80% color reduction and improve the degradability of PPMW. The

solar photo-Fenton process is a viable alternative to traditional advanced oxidation processes for the decontamination of PPMW because of its faster rate of deterioration. Under ideal conditions the ozonation/UV process is a feasible wastewater treatment method to remove color and COD from black liquor discharged by pulp and paper mills. Wet oxidation, which employs air or O₂ as an oxidant, is a potential hydrothermal method for incompletely or totally breaking down resistant chemical contaminants present in effluents at high temperatures (125°C–320°C) and pressures (0.5–20 MPa) (Kumar & Verma, 2023). Photocatalysis is a prominent technology that completely degrades organic pollutants into harmless inorganic compounds under mild conditions without generating substantial secondary pollution (Chen et al., 2003).

9.4.3 Biological method

In comparison with more expensive methods, biological technology offers an environmentally sustainable alternative for treating PPMW, using fungus, bacteria, and actinomycetes to remove and detoxify hazardous chemicals. Bacteria are being used as bioaugmentation for treating PPMW due to their adaptability, metabolic diversity, and ease of use. They can also serve as bioindicators for environmental pollution levels and facilitate the degradation of harmful organic compounds, reducing toxicity associated with PPMW. Various bacterial strains, including *Rhodococcus* sp. NCIM 2891, *Achromobacter xylosoxidans* 15DKVB, *Serratia liquefaciens* LD-5, *Brevibacillus agri* strain RJH-1, *Rhodococcus pyridinivorans* PDB9TN-1, *Brevibacillus parabrevis* MTCC 12105, and *Bacillus* sp., have been evaluated for their ability to remove PPMW color and reduce its toxicity (Kumar & Verma, 2023).

The use of PPMW for algae cultivation is an exciting method because it reduces freshwater and nutrient necessities. The use of microalgae in PPMW is quickly changing to combine bioremediation with the production of useful products. However, low nutrient concentrations, high color, turbidity, and possible toxicity issues prevent microalgae from growing in wastewater. For the PPMW treatment the algae-like *Scenedesmus*, *Selenastrum minutum*, *Scenedesmus dimorphus*, and *S. minutum* are employed (Kumar & Verma, 2023).

The biodegradation of organochlorine compounds in municipal wastewater can be facilitated by fungal strains due to their observed higher resistance to inhibitory substances and adaptation to difficult conditions. They have also been used in traditional tertiary biotreatment procedures for color removal and detoxification of biorefractory contaminants. Fungal strains are used to biodegrade organochlorine compounds in municipal wastewater, as well as to remove color and detoxify biorefractory contaminants in conventional tertiary

biotreatment methods. Fungal species like *Pleurotus ostreatus*, *Aspergillus nidulans*, *Phanerochaete chrysosporium*, *Lentinus edodes*, *Trametes versicolor* F200, *T. versicolor*, *Cryptococcus* sp., *Aspergillus flavus* strain F10, *T. versicolor* U80, *Phanerochaete sordida*, *Pycnoporus sanguineus*, *Trametes elegans*, *Pleurotus ostreatus*, *T. versicolor* INACC F200, and *Rhizopus oryzae* are used in biostimulation and bioaugmentation strategies for remediating persistent petroleum-contaminated groundwater (Kumar & Verma, 2023).

9.4.4 Emerging methods

The emerging advanced methods include phytoremediation, constructed wetland plant treatment, microbial fuel cell technology, photoreforming, nanoremediation, biofilm-mediated remediation, and integrated treatment approaches used to attain the maximum decomposition, decolorization, and detoxification of PPMW.

Phytoremediation is a viable, low-cost, and environmentally benign method for removing harmful and emerging chemical pollutants from polluted environments. To expedite the disintegration or removal of pollutants within the plant and in the surrounding environment, this sustainable method involves growing plants in polluted surface water, groundwater, sediment, and soil (Kumar & Verma, 2023).

Constructed wetland plant treatment is an intricate, low-cost artificially integrated system in which water, plants, microorganisms, and substrate interact to reduce harmful substances and pathogens from wastewater. They are already widely employed to decompose and detoxify wastewater from a variety of industries, acid mine drainage, stormwater runoff, and landfill leachates. The pollutant remediation efficiency of man-made wetlands is primarily governed by interactions in the rhizosphere involving microorganisms, plant roots, soil, and pollutants (Kumar & Verma, 2023).

PPMW is treated using bioelectrochemical systems, which combine electrochemistry and biological methods within the circumstances of a redox reaction. Bioelectrochemical systems, such as microbial fuel cells, are used to treat PPMW while also generating power from the chemical energy trapped in organic materials. Microorganisms act as biocatalysts in these biocatalyzed electrochemical cells, propelling the process. The cationic-specific membrane in microbial fuel cells is used to divide the anode and cathode. At the anode the oxidation of organic molecules in the wastewater takes place by microorganisms to produce protons and electrons. The protons flow across the membrane to the cathode, and electrons move from the anode to an external circuit that generates current (Kumar & Verma, 2023).

The photoreformation of organic molecules has the potential to produce hydrogen gas more quickly than water splitting and to help mineralize organic pollutants in wastewater or water. By serving as hole scavengers and oxidizing more quickly than H_2O , organic contaminants aid in the process of photocatalytic water splitting (Kumar & Verma, 2023).

In the nanoremediation process, nanomaterials are used as a catalyst for pollutant degradation processes such as oxidation, adsorption, and degradation. The removal of heavy metals, anions, color, and COD from PPMW is accomplished by using composite materials (polyaniline/sawdust and polymer polypyrrole/sawdust), which remove anions, metals, and color more effectively than COD (Kumar & Verma, 2023).

Complex organic substrates found in PPMW, particularly lignin derivatives, are broken down by biofilm-mediated remediation because it reduces the amount of sludge produced, accepts erratic environmental stresses, gets rid of clogging issues, and makes the process overall more economical and environmentally benign (Kumar & Verma, 2023).

In contrast to other methods the integrational treatment approach removed the most amounts of turbidity, TSS, BOD, COD, and TDS. For PPMW, combining physical-chemical and biological methods is preferable to utilizing separate treatments (Kumar & Verma, 2023). Because of the existence of resistant contaminants, conventional wastewater treatment technologies are sometimes not enough to meet regulations for PPMW disposal. Even after additional treatment the PPMW effluent contains a high amount of hazardous substances (color component, organic, and chlorinated compounds) (Kumar & Verma, 2023). It is therefore more practical to use hybrid, two-stage sequential/phase separation, or sequential procedures for PPMW treatment to achieve better degradability than single treatments.

9.5 Photocatalysis

In this process the photocatalyst is subjected to ultraviolet (UV) or solar light within the wavelength range of less than 390 nm. After the catalyst is exposed to this radiation, electron-hole pairs start to form on its surface, resulting in the production of radical-reduced oxygen species. The produced radicals have high reactivity and are not very selective oxidizing agents (Yeber et al., 1999). Through the use of light for activating a substance, photocatalysis accelerates chemical reactions without the material being involved (Mandade, 2021). The effectiveness of photocatalysis is contingent upon the mechanism by

which the electron is extracted from the surface of the semiconductor and the subsequent recombination of the electron and vacancy, resulting in the liberation of thermal energy (Barreto-Rodrigues et al., 2009). Photocatalysis has been established as an extremely efficient approach for removing nonbiodegradable contaminants from PPMW. The efficacy of the solar photocatalytic treatment utilizing synthesized TiO_2 has been demonstrated in the degradation of nonbiodegradable compounds inside heavily contaminated PPMW (Kumar & Verma, 2023). Visible light irradiation is regarded as the most efficient form of light exposure, as UV light comprises just 5% of sunlight and is not suitable for industrial-scale use (Kumar et al., 2021). Tropical regions get a consistent and abundant supply of bright sunshine throughout the year. The cost-effectiveness of solar photocatalytic degradation of pollutants in parts per million by weight is higher. Nevertheless, the process of UV-photocatalytic degradation is both perilous and costly due to the substantial amount of electrical power required to produce UV irradiation. The solar photocatalytic degradation process does not result in any material damage. Hence, to implement a cost-effective heterogeneous photocatalytic process on an industrial level, researchers have also investigated the potential of solar photocatalytic water detoxification (Kansal et al., 2008). Photocatalysis can be performed in two ways: directly or through a catalyst. The photocatalysis through a catalyst effectively reduces the activation energy required (Mandade, 2021). The presence of three critical components is required for the photocatalytic reaction to effectively degrade environmental contaminants such as organic pollutants, microorganisms, and inorganic pollutants: (1) a photocatalyst like TiO_2 , ZnO , or Ag_2WO_4 ; (2) an energy-rich light source (solar, visible, or UV light); and/or (3) an oxidizing agent (air or O_2 or H_2O_2 , or O_3) (Jabbar & Ebrahim, 2022). During photocatalysis the five following processes are identified and are depicted in Fig. 9.1: (1) transfer of pollutants to the photocatalyst surface, (2) adsorption of pollutants on the surface of catalyst, (3) activation and degradation of adsorbed molecules by photons, (4) product desorption, and (5) elimination of products from the photocatalyst surface (Rueda-Marquez et al., 2020) (Fig. 9.2).

9.5.1 Photocatalyst

A substance known as a photocatalyst absorbs UV light to increase energy intensity and triggers the formation of electron-hole pairs through chemical processes (Khan & Mondal, 2021). The photocatalyst remains chemically unchanged throughout the reaction and subsequent processes. The measurement of the rate at

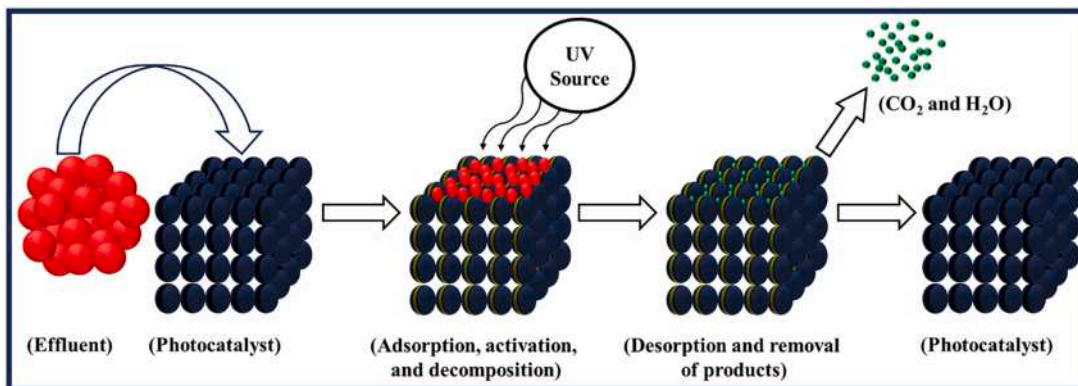


Figure 9.2 Systematic steps for photocatalytic treatment of pulp and paper mill wastewater.

which a photocatalytic process occurs is known as photocatalytic activity (Rueda-Marquez et al., 2020). The electrical structure, light absorption capacities, charge transport qualities, and excited-state lifetimes of semiconductors all have an impact on photocatalytic activity (Mandade, 2021). The substance utilized as a catalyst needs to possess the qualities of being nontoxic, cost-effective, and capable of being reused (Shalini & Setty, 2022). Various photocatalysts are utilized in wastewater treatment across different industries to effectively eliminate contaminants. These catalysts include ZnS-CuS-CdS, ZnS-WS₂-CdS, C₃N₄-CdS, carbon spheres/CdS, Pd-Cr₂O₃-CdS (Mandade, 2021), ZnO, BaTiO₃, Ag-ZnO, KNbO₃, SrBi₄, Ti₄O₁₅ (Shalini & Setty, 2022), WO₃ (Moravvej et al., 2020), TiO₂ (Degussa P25), CuO, CeO₂, Fe₂O₃, Bi₂O₃, CdS, CuS, ZnS, Ge₃N₄, SbSI (Kusworo et al., 2022), ZnAl₂O₄/BiPO₄ composites, BiPO₄, ZnO/ZnAl₂O₄ (Tian et al., 2020), Nb₂O₅, Ag₂O/ZnO (Marques et al., 2017), LaFeO₃, BiVO₄ (Lin et al., 2021), and ZrO₂ (Motamedi et al., 2022).

For the photodegradation process, titanium oxide is the most extensively utilized photocatalyst material because of several advantages, including its high catalysis efficiency, energy savings, low cost, and absence of pollution (Shavisi et al., 2014), noncorrosive, nontoxic, photochemically stable to strong acids and bases, and commercially available in different crystalline forms (Mandade, 2021), chemical inertness, and having oxidation capacity (Zulkiflee, Khan, & Harunsani, 2023), safety for both human and animal (Sampaio et al., 2013). However, the TiO₂ photocatalyst has various limitations. They are as follows: (1) the low quantum efficiency results in a high recombination rate for photo-induced electron-hole pairs, decreasing photocatalyst efficiency, (2) titanium dioxide is only active in the UV part of the solar spectrum, which accounts for only 4% of the total solar spectrum, due to its high

bandgap, (3) a strong proclivity for agglomeration during the synthesis process, (4) a propensity to create a colloidal suspension, making recovery difficult (Khasawneh & Palaniandy, 2021), (5) photocatalytic activity of TiO_2 nanoparticles is reduced under increased scattering conditions, (6) poor affinity for organic pollutants, (7) limited adsorption of organic contaminants on the TiO_2 surface causes delayed photocatalytic disintegrate rates, (8) provide a specific affinity for the target pollutants, (9) aggregation reduces the photocatalytic activity of titanium oxide by blocking light from reaching the active centers, (10) recovery of nanoscale TiO_2 particles from treated water efficiently and securely, (11) the original TiO_2 photocatalyst has a high band energy, making it challenging to drive by sunlight (Chen et al., 2020), (12) problem in maintaining continual stirring for full disintegration and separation of catalyst for reuse (Shalini & Setty, 2022), and (13) UV light scattering disrupts light availability (Haghighi et al., 2019). As a result, TiO_2 is modified through doping with various elements (platinum or palladium) or semiconductors (nickel oxide, tungsten oxide, strontium titanate, ruthenium (IV) oxide, or cadmium sulfide) (Mandade, 2021), morphological change, oxygen vacancies formation, and surface modification (Zulkiflee, Khan, & Harunsani, 2023). The photocatalytic process by TiO_2 photocatalyst is affected by factors like the kind of TiO_2 used, the number of layers of TiO_2 , and the durability of the catalyst films which affect how efficient the degrading process is in terms of photoactivity (Sampaio et al., 2013).

In contrast to TiO_2 powder, TiO_2 colloids have excellent dispersibility, a significant specific surface area, convenient recovery, and cost-effectiveness. So, the use of TiO_2 colloids in the field of wastewater treatment is an exceptional choice (Lin et al., 2021). When employing TiO_2 photocatalyst in a powdered state, the particles scatter within the wastewater, resulting in an elevation of turbidity, and the level of light penetration into the wastewater is reduced. The light, on the contrary, is directly exposed to the wastewater in the case of the TiO_2 /LECA photocatalyst. Because of its high porosity and low density, LECA granules provide enough support in photocatalytic reactions (Shavisi et al., 2014).

Illuminating all catalyst particles in slurry systems is difficult due to the shading effect generated by particles adjacent to the light source, which prevents radiation from reaching particles farther away. To bypass such constraints the catalyst particles are immobilized by coatings or films applied to various surfaces such as polypropylene fabrics, stainless steel, beads, glass slides, and Raschig rings (Sampaio et al., 2013). The immobilized photocatalysts also help to accelerate the separation process and maximize the usefulness of the photocatalytic process (Rueda-Marquez et al., 2020).

Because of the increased concentration of catalyst per unit volume, TiO_2 suspensions degrade aqueous effluents faster than films. However, as the catalyst dose is raised, the powdered catalyst is difficult to remove from the slurry and causes particle aggregation. Furthermore, the utilization of TiO_2 particles in continuous processes is technologically impractical (Sampaio et al., 2013). The nanomaterial has significant advantageous physicochemical characteristics, including extensive surface areas, varied morphologies, and crystalline structures, which are very conducive to the process of photocatalysis for wastewater treatment (Mandade, 2021). Nano- TiO_2 is considered to be a viable photocatalyst for the treatment of PPMW. Catalytic effectiveness is decreased by the increased recombination ratio of hole–electron pairs produced by light. Nano- TiO_2 has undergone many alterations to improve its catalytic performance and study new photocatalytic functionalities (Chen et al., 2003). There are two demerits of nanophotocatalysis, including the issue of increased energy consumption and the constraints imposed by mass transfer. The issue of electron–hole recombination has been effectively addressed through the utilization of nanocomposites and the implementation of new nanophotocatalytic reactor designs (Madhubala et al., 2022).

Zinc oxide is used as a highly efficient photocatalyst in wastewater treatment. This is due to its notable photocatalytic activity, straightforward production method, cost-effectiveness, environmentally friendly nature (Rueda-Marquez et al., 2020), substantial binding energy for free excitons, high oxidation capacity, and a huge band gap in the near-UV spectral area (Lee et al., 2016). However, it amplifies the toxicity of wastewater (Rueda-Marquez et al., 2020). The use of a composite material consisting of ZnO and carbon materials enhances the rate of electron transfer in photo-generated systems, while simultaneously inhibiting the recombination of electron–hole pairs (Wang et al., 2017). Whether it is immobilized on glass or not, TiO_2 is more efficient than ZnO at alkaline pH conditions (Marques et al., 2017) for degrading various organic pollutants and colors (Madhubala et al., 2022).

Due to its high sensitivity, ease of production, and low cost, cerium dioxide is used as a photocatalyst to break the organic contaminants in wastewater treatment and as an agent to prevent the adhesion of biological substances (Yin et al., 2023). Due to cost-effectiveness, widespread availability, magnetic characteristics, straightforward synthesis methods, enhanced photocatalytic performance, lower toxicity, and eco-friendly nature, Iron oxides are also used as a photocatalyst. Iron oxides ($\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4) and other magnetic materials can be used to recover the TiO_2 photocatalyst (Khasawneh & Palaniandy, 2021). Under UV light the rate of

degradation of methylene blue over BiPO_4 is twice that of P25 (Degussa). However, the photocatalytic use of BiPO_4 is hindered by its inadequate adsorptive performance, substantial bulk, and considerable band gap energy. Therefore the performance of this kind of catalyst is enhanced by the use of secondary semiconductor heterostructures, such as Ag/BiPO_4 , $\text{SrTiO}_3/\text{BiPO}_4$, $\text{C}_3\text{N}_4/\text{BiPO}_4$, $\text{Bi}_2\text{SiO}_5/\text{BiPO}_4$, BiOI/BiPO_4 , and $\text{Ag}_3\text{PO}_4/\text{BiPO}_4$ composites (Tian et al., 2020).

Repetitive usage of a photocatalyst reduces its efficiency. There are two methods for deactivating a photocatalyst: reversible and irreversible. The two processes by which photocatalysts deactivate are as follows: (1) the production of photocatalytic by-products on their surface and (2) the emergence of surface species that have a higher adsorption capacity than the reactants (Rueda-Marquez et al., 2020).

9.5.2 Photocatalytic reactor

The photocatalytic reactor, also known as a photochemical reactor, is a device used for carrying out photocatalytic reactions. Unlike conventional reactors, which depend upon thermal or thermal-catalytic principles, photocatalytic reactors have unique properties. The presence of a radiation field, which enhances catalyst activation, is a unique characteristic of photocatalytic reactors. Titanium dioxide, the catalyst that is frequently used in the photocatalytic reactor, can absorb radiation in the nonvisible range, at least near-UV, of the light spectrum. Artificial lights or solar radiation can produce the required radiation field (Alfano et al., 2000). However, the use of artificial lights has some inherent physical harm and specific problems. For instance the use of high-pressure mercury lamps is reduced due to inherent problems such as physical harm and the risk of mercury leakage. In their place, UV-LED photoreactors are used due to advantages like reduction of power consumption, prolonged operational lifespan, and the absence of disposal concerns (Haghighi et al., 2019). The photocatalytic reactor must be designed depending upon the optimization of the light-activated phase and the choice of suitable catalyst in both artificial light or solar radiation. The design of a photocatalytic reactor has three major challenges: (1) selecting a suitable catalyst, as well as an exhaustive examination of the reaction, which includes paths, processes, products, and efficiencies. (2) reaction kinetics studies and the development of reactor design methods for various reactor geometries, and (3) ensuring adequate irradiation throughout the entire volume of the reactor (Alfano et al., 2000). Various types of photoreactors are employed in the process of

photocatalysis of PPMW. For the photocatalytic treatment of PPMW, continuous-flow reactors are more significant than batch and fluidized bed reactors. When catalyst material becomes blocked on the surface of the reactor, the batch reactors experience loss of the catalyst, and hence the efficiency of the reactor is lowered (Binjhade et al., 2022). Supported catalyst fluidized bed reactors offer an effective remedy for mass transfer limitations (Kabir et al., 2006). The photocatalysis carried out in a continuous photocatalytic reactor by using nano-TiO₂ colloid for PPMW treatment is controlled using an industry personal computer that has six main functions: (1) adjusting the concentration in the regulating pool, (2) changing the pH by pumping alkali and acid solutions into the regulating pool, (3) adjusting the titanium oxide dosage by magnetically swirling the nano-TiO₂ colloid into the regulating pool, (4) degradation of PPMW utilizing UV light in a horizontal plug flow photocatalytic reactor, (5) supplying dissolved oxygen to PPMW by external circulation aeration, and (6) utilizing a human-machine interface, the TiO₂ dosage, pH, level, and photocatalytic time are displayed (Lin et al., 2021).

9.5.3 Type of photocatalytic reactions

There are two types of photocatalytic reactions: (1) homogeneous photocatalytic reaction and (2) heterogeneous photocatalytic reaction.

9.5.3.1 Homogeneous photocatalytic reaction

The catalyst and the reaction system are in the same phase during homogeneous photocatalysis (Ramalingam et al., 2022). It is used for water self-purification by the utilization of the UV component of solar light (Saravanathamizhan & Perarasu, 2021). It involves the use of photo-Fenton systems (Fe⁺ and Fe⁺/H₂O₂), ozone, and transition metal oxide (Mandade, 2021). It mostly occurs on hydro complexes of transition metals such as iron, copper, chromium, and others, which exist in higher oxidation states. Therefore the hydroxyl radicals produced in this process undergo a reaction with the substrate, which is employed to degrade the effluent (Saravanathamizhan & Perarasu, 2021). In this reaction the charge carrier recombination occurs with a high degree of ease. However, it is challenging to generate holes and charges using materials with a wide bandgap. It is dependent on the pH level, light intensity, and hydrogen peroxide concentration in the Fenton system (Ramalingam et al., 2022). The demerits of homogeneous catalytic reaction are as follows: (1) generates significant amounts of waste, (2) offers significant difficulty in separating the catalyst from the reaction mixture, (3) raises issues with environmental and ecological stability, and (4) accumulation of

homogeneous catalysts on the inner walls of the reactor which lead to corrosion of different types of industrial materials (Mandade, 2021), and photocatalysts have a relatively poor photosynthetic capacity (Ramalingam et al., 2022).

9.5.3.2 *Heterogeneous photocatalytic reaction*

It uses a catalyst and a reaction mechanism that undergoes several phases (Ramalingam et al., 2022). It is more efficient than flocculation and coagulation-based wastewater treatment technologies. The organic pollutants in the PPMW are separated into carbon dioxide and water during this process. This reaction requires oxygen and ultra-band gap energy, both of which can be obtained from natural sources such as air and sunlight (Shalini & Setty, 2022). The heterogeneous photocatalysts are TiO_2 , ZnO , MgO , WO_3 , FeO , CdS , ZnS (Rodrigues et al., 2008), and CeO (Katal & Pahlavanzadeh, 2011). The heterogeneous photocatalyst has the potential to be immobilized on various inert matrices, such as polymers, glasses, and graphene oxides (Shalini & Setty, 2022). Two types of reactors, namely suspension and fixed film systems, are primarily used for the PPMW treatment in this reaction (Rodrigues et al., 2008). Heterogeneous semiconductor photocatalysis is an efficient technique owing to its cost-effectiveness, environmentally friendly nature, rapid degradation rate, little toxicity, and capacity to fully convert organic pollutants into comparatively benign by-products, such as water and carbon dioxide (Jabbar & Ebrahim, 2022). However, it is unsuitable for large-scale implementation because of (1) difficult separation of the colloidal catalyst from the water suspension after treatment, and (2) difficulties with immobilized catalysts in mass transfer (Moravvej et al., 2020).

Three different types of heterogeneous photocatalysis exist: (1) type I, (2) type II, and (3) Z-scheme photocatalyst. There are two semiconductors with distinct energy band gaps involved in the type I photocatalytic process. As compared to semiconductor II, semiconductor I has a higher energy band gap. The excitement of photons in semiconductor I leads to the transfer of charge carriers from semiconductor I to semiconductor II. The holes move from the valence band of semiconductor I to the valence band of semiconductor II, whereas the electrons pass from the conduction band of semiconductor I to the conduction band of semiconductor II. The redox process has been found to occur at the surface of semiconductor II. Furthermore, the redox potential of the photocatalytic process of type I is significantly smaller.

Electrons migrate from the conduction band of semiconductor I to the conduction band of semiconductor II, which has a moderately negative potential, in the type II heterojunction photocatalyst.

Similarly, the application of a moderate positive potential promotes the transfer of holes from the valence band of semiconductor II to the valence band of semiconductor I. The presence of electrostatic repulsion between identical charge carriers (either holes or electrons) hinders the formation of meaningful interactions in this phenomenon.

Z-scheme heterojunction photocatalysts and type II heterogeneous photocatalysts with two different semiconductors are very similar. Excited electrons are transported from the conduction band of semiconductor I to the valence band of semiconductor II in this condition. Furthermore, photon excitations cause holes in the valence band of semiconductor II to transfer into the conduction band of semiconductor I. When there are significant obstacles to charge carrier combination, substantial oxidation and reduction processes are found in the valence and conduction bands, respectively (Ramalingam et al., 2022).

Based on the fundamental concepts and applications, photocatalysis can be divided into three types: photovoltaic cells, photoelectrolyzing cells, and photocatalytic cells (Ahmad et al., 2020).

9.5.4 Basic principle of photocatalysis

According to the principle of photocatalysis, electron-hole pairs are produced when a photocatalytic material is exposed to light with energy equal to or greater than the band gap of the photocatalyst. The produced electron-hole pairs disintegrate, separating electrons in the conduction band and holes in the valence band. The transport of electrons and holes causes the reduction and oxidation of molecules adsorbed on the surface of a photocatalytic material. However, on the surface of the photocatalytic material, electron-hole recombination occurs, preventing the progression of oxidation and reduction reactions. An increase or decrease in reaction rate corresponds to an increase or decrease in electron-hole recombination, respectively (Rueda-Marquez et al., 2020).

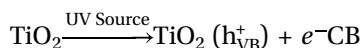
9.5.5 Mechanism of photocatalysis of pulp and paper mill wastewater

The process of absorbing sunlight in natural photocatalysis is accomplished through chlorophyll, whereas photocatalysts are used in artificial photocatalysis. Photocatalysis initiates redox processes in the presence of semiconductors under irradiation. When titanium dioxide is exposed to UV radiation from sunlight or other sources, the electron in the VB of the material becomes energetically excited. The excess energy that the electron possesses enables it to move into

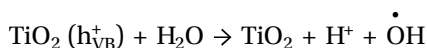
the titanium dioxide CB, where it produces a positively charged hole (h^+) and a negatively charged electron (e^-). The band gap is the difference in energy levels between the valence bands and conduction bands, and the current phase of the semiconductor is known as the photoexcitation stage (Mandade, 2021).

In the presence of light the holes and electrons on the surface of the semiconductor undergo the following reactions.

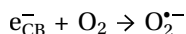
1. The hole created in the VB oxidizes the water in the medium, forming the $\cdot OH$ radical (García et al., 2020).



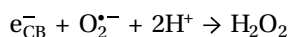
2. The oxygen is reduced by the CB electron to form superoxide radicals which are further reduced to form H_2O_2 . The superoxide radicals can also react with H_2O_2 to produce the $\cdot OH$ radical (Cho et al., 2004).



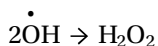
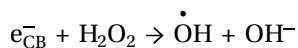
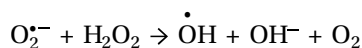
3. H_2O_2 is reduced by CB electron to produce the $\cdot OH$ radical which can undergo recombination with other $\cdot OH$ radicals to produce H_2O_2 (Cho et al., 2004).



4. The VB hole reacts with OH^- to form the $\cdot OH$ radical (Cho et al., 2004).



The great oxidizing power of generated hydroxyl radicals is responsible for the breakdown of contaminants into CO_2 and H_2O (Cho et al., 2004).



However, the presence of an excessive amount of hydrogen peroxide can hinder the process of photocatalysis due to two main reasons. Firstly, there is a competition for light absorption between hydrogen peroxide and titanium dioxide, which reduces the photo-excitation of the catalyst. Secondly, the excess hydrogen peroxide leads to the conversion of a portion of the hydroxyl radical into the hydroperoxyl radical, resulting in the suppression of other hydroxyl radicals that produce water and oxygen (Borowski et al., 2008). Fig. 9.3 represents the reaction mechanism of the photocatalytic reaction of PPMW.

9.5.6 Factor affecting photocatalysis

The photocatalyst dosage, pH of the solution, the beginning concentration of the contaminant, intensity of the light, and presence of dissolved oxygen are all parameters that influence photocatalysis.

1. A higher photocatalyst loading rate produces a higher number of active sites. However, the excessive photocatalyst loading rate

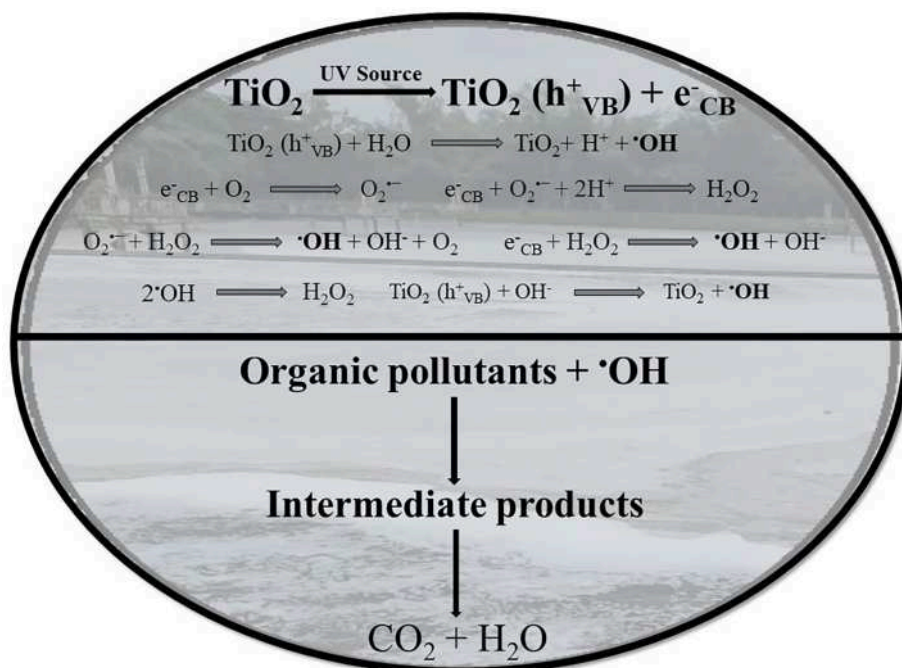


Figure 9.3 Reaction mechanism of photocatalytic reaction of PPMW.

- increases the solution opacity and particle aggregation which causes a decrease in photocatalytic activity.
2. As pollutant concentrations rise, more pollutants adsorb on the photocatalyst surface, resulting in a reduction in the number of photons reaching the photocatalyst surface. As a result, increasing the initial concentration of contaminants reduces photocatalytic activity.
 3. The pH solution influences various properties, including surface charge (adsorption process), surface of the photocatalyst, degree of ionization, and band edge position (Mandade, 2021). At pH 11 the photocatalytic reaction performs better (Marques et al., 2017).
 4. In the photocatalytic process, two sorts of light sources have been used: visible light sources and UV light sources. The wavelengths of the visible light sources range from 420–680 nm, while the wavelengths of the UV light sources range from 400–300 nm (Saravanathamizhan & Perarasu, 2021). The photocatalyst absorbs more photons as the light intensity (UV or visible light) rises, resulting in a large number of electron/hole pairs on the photocatalyst surface and improving photocatalytic removal efficiency.
 5. Dissolved oxygen boosts or degrades photocatalytic degradation depending on the pathway and mechanism of the photocatalytic process. It also improves the generated reactive species by improving photogenerated electron/hole pair separation.
 6. H_2O_2 acts as a catalyst in the formation of hydroxyl radicals. As a result, increasing the concentration of H_2O_2 leads to increased concentration of hydroxyl radicals and enhanced photocatalytic activity.
 7. The photocatalytic degradation efficiency of organic molecules decreases as the reaction temperature rises (Mandade, 2021).
 8. The photocatalyst has a bandgap energy range from 3.09 to 4.13 eV for the UV source region and a bandgap energy range from 2.95 to 1.82 eV for the visible light source region (Saravanathamizhan & Perarasu, 2021).

9.5.7 Advantages and disadvantages of photocatalytic technology for pulp and paper mill wastewater

Photocatalysis technology for PPMW has various advantages, but it also has a few drawbacks. The merits and demerits of photocatalytic technology for PPMW are summarized in Table 9.3.

Table 9.3 Summary of the merits and demerits of photocatalytic technology for PPMW.

Advantages	Disadvantages
(i) It is a low-cost process (Jabbar & Ebrahim, 2022), requires low energy to operate (Bibi et al., 2023), and uses renewable and pollution-free solar energy. (ii) It produces harmless compounds with minimal secondary waste, requires mild reaction conditions, and the reaction time is modest with lesser chemical input (Mandade, 2021). (iii) It uses cheap, nontoxic, and noncorrosive catalysts. Since it is a recyclable process, the catalyst can be recovered and reused (Bibi et al., 2023). (iv) It can break the very stable chemicals that are difficult to decompose using other methods, and it causes the mineralization of organic pollutants to CO₂ and H₂O (Jabbar & Ebrahim, 2022). (v) Photocatalysis provides a solution to problems associated with a faulty understanding of daylight, which is seen as a limitless and enormously strong energy source capable of managing the activities of Earth (Mandade, 2021).	(i) It causes the generation of sludge (Madhubala et al., 2022) along with a greater quantity of hazardous by-products (Yeber et al., 1999). (ii) Most of the semiconductors used in photocatalysis exhibit limited reactivity toward visible light and necessitate a large band gap energy (Bibi et al., 2023). (iii) The photocatalysts only operate inside the UV or near-UV region of the electromagnetic spectrum. (iv) The photocatalytic efficacy is determined by the chemical composition of the surface and the degree of contact. So, the optimization of overall efficiency in photocatalysis is a crucial concern (Mandade, 2021). (v) The agglomeration of the nanomaterial employed in photocatalysis occurs. So, the catalyst separation and reusability from the aqueous solution is difficult (Bibi et al., 2023).

PPMW, Pulp and paper mill wastewater.

9.6 Conclusions and future trends

The amount of wastewater produced by the pulp and paper industry increases with its growth. There exist multiple types of incurable diseases linked to the PPMW. Hence, it is imperative to grow sustainable and eco-friendly techniques for pulp and paper production, as well as explore novel approaches for economic benefit treatment. The water use of the pulp and paper industry in 1974 is recorded as 600 m³/ton. As a result of the implementation of contemporary paper mills, the water consumption per tonne of paper has been diminished to a range of 4–100 m³/ton. In addition, wastewater production has decreased significantly from 46 m³/ton of paper in 1974 to about 15 m³/ton currently. However, rules and regulations must be drafted and implemented to reduce PPMW. For instance the effluent discharge regulations for modern paper mills are becoming more and more strict. The effluent generated during

paper manufacture must be treated before it can be discharged into natural bodies of water or reused in the papermaking process. To decrease the use of freshwater resources the modern pulp and paper industries are progressively employing zero-liquid effluent solutions, such as the development of closed-water circuits. The global implementation of management rules has led to a significant reduction in water usage within the paper sector. It is imperative to foster public knowledge regarding the negative impacts of pulp and paper effluent on both the environment and human health. Necessary steps must be taken for water conservation in the pulp and paper industries. The cost-effectiveness, technological difficulties, and possible health and environmental hazards provide serious impediments to the development and commercialization of photocatalysis. Therefore there is a need for modification and development of PPMW technology for water treatment. There are many future aspects regarding about the modification and development of photocatalytic process for PPMW treatment: (1) innovation of cost-efficiency, sustainability, robustness, optimal effectiveness, reliability, and easily applicable photocatalytic processes, (2) production of a photocatalyst that is ecologically sustainable and can be used to degrade persistent organic contaminants in wastewater, (3) integration of photocatalytic technology with conventional technology and other advanced oxidation processes, (4) prioritization of using by-products resulting from the photocatalytic treatment of PPMW, (5) use of photocatalytic techniques for the treatment of persistent organic pollutants in wastewater at a continuous operation and on a big scale, (6) development of stable, efficient, and low-cost novel nanomaterials photocatalyst for photocatalysis, (7) development of photocatalysts and photocatalytic reactors which are more reliable and able to be activated by UV/visible radiation from sunshine or visible light; these developments are especially significant because of their potential application in a wide range of geographical conditions, including tropical places, (8) use of immobilized photocatalytic materials exhibiting exceptional rates of organic contaminant adsorption and desorption, (9) prevention of degradation of photocatalysts in aquatic environments due to the presence of suspended particles, ions, and variations in pH, (10) design of photoreactor for effective adsorption of low concentrations of reactants, (11) contaminants have dispersed within the water and have subsequently adhered to the surface of the photocatalyst, (12) optimization of photocatalyst immobilization processes to provide the maximum feasible surface area with limiting agglomeration and catalyst recovery problems, and (13) preventing long-term nanomaterial accumulation and environmental discharge during photocatalytic pyrolysis.

List of abbreviations

AOX	absorbable organic halogen
BOD	biochemical oxygen demand
CB	conduction band
COD	chemical oxygen demand
CPBL	cotton pulp black liquor
ECF	elemental chlorine-free
LECA	light-expanded clay aggregate
LEDs	light emitting diodes
PPMW	pulp and paper mill wastewater
TDS	total dissolved solids
TOC	total organic carbon
TSS	total suspended solids
USD	United States dollar
UV	ultraviolet
VB	valance band
VOCs	volatile organic compounds

References

- Ahmad, K., Ghatak, H. R., & Ahuja, S. M. (2020). *Photocatalytic technology: A review of environmental protection and renewable energy application for sustainable development*. Environmental Technology.
- Alfano, O. M., Bahnemann, D., Cassano, A. E., Dillert, R., & Goslich, R. (2000). Photocatalysis in water environments using artificial and solar light. *Catalysis Today*, 58(2-3), 199–230. [https://doi.org/10.1016/S0920-5861\(00\)00252-2](https://doi.org/10.1016/S0920-5861(00)00252-2).
- Asfaha, Y. G., Tekile, A. K., & Zewge, F. (2021). Hybrid process of electrocoagulation and electrooxidation system for wastewater treatment: A review. *Cleaner Engineering and Technology*, 4. <https://doi.org/10.1016/j.clet.2021.100261>, <https://www.journals.elsevier.com/cleaner-engineering-and-technology>.
- Balcioğlu, I. A., & Cecen, F. (1999). Treatability of kraft pulp bleaching wastewater by biochemical and photocatalytic oxidation. *Water Science and Technology*, 40(1), 281–288.
- Barreto-Rodrigues, M., Souza, J. V. B., Silva, E. S., Silva, F. T., & Paiva, T. C. B. (2009). Combined photocatalytic and fungal processes for the treatment of nitrocellulose industry wastewater. *Journal of Hazardous Materials*, 161(2-3), 1569–1573. <https://doi.org/10.1016/j.jhazmat.2008.05.012>.
- Bhanot, P., Celin, S. M., Sreekrishnan, T. R., Kalsi, A., Sahai, S. K., & Sharma, P. (2020). Application of integrated treatment strategies for explosive industry wastewater—A critical review. *Journal of Water Process Engineering*, 35, 101232. <https://doi.org/10.1016/j.jwpe.2020.101232>.
- Bibi, A., Bibi, S., Abu-Dieyeh, M., & Al-Ghouti, M. A. (2023). Towards sustainable physiochemical and biological techniques for the remediation of phenol from wastewater: A review on current applications and removal mechanisms. *Journal of Cleaner Production*, 417, 137810. <https://doi.org/10.1016/j.jclepro.2023.137810>.
- Binjhade, R., Mondal, R., & Mondal, S. (2022). Continuous photocatalytic reactor: Critical review on the design and performance. *Journal of Environmental Chemical Engineering*, 10(3), 107746. <https://doi.org/10.1016/j.jece.2022.107746>.
- Boroski, M., Rodrigues, A. C., Garcia, J. C., Gerola, A. P., Nozaki, J., & Hioka, N. (2008). The effect of operational parameters on electrocoagulation-flotation process followed by photocatalysis applied to the decontamination of water effluents

- from cellulose and paper factories. *Journal of Hazardous Materials*, 160(1), 135–141. <https://doi.org/10.1016/j.jhazmat.2008.02.094>.
- Chen, D., Cheng, Y., Zhou, N., Chen, P., Wang, Y., Li, K., Huo, S., Cheng, P., Peng, P., Zhang, R., Wang, L., Liu, H., Liu, Y., & Ruan, R. (2020). Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review. *Journal of Cleaner Production*, 268. <https://doi.org/10.1016/j.jclepro.2020.121725>, <https://www.journals.elsevier.com/journal-of-cleaner-production>.
- Chen, J., Liu, M., Zhang, L., Zhang, J., & Jin, L. (2003). Application of nano TiO₂ towards polluted water treatment combined with electro-photochemical method. *Water Research*, 37, 3815–3820.
- Cho, M., Chung, H., Choi, W., & Yoon, J. (2004). Linear correlation between inactivation of *E. coli* and OH radical concentration in TiO₂ photocatalytic disinfection. *Water Research*, 38(4), 1069–1077. <https://doi.org/10.1016/j.watres.2003.10.029>.
- Das, P. P., Sontakke, A. D., & Purkait, M. K. (2023). Electrocoagulation process for wastewater treatment: Applications, challenges, and prospects. In *Development in wastewater treatment research and processes: Advances in industrial wastewater treatment technologies: Removal of contaminants and recovery of resources*. India: Elsevier, 23–48. <https://www.sciencedirect.com/book/9780323956840>.
- Garcia, B. B., Lourinho, G., Romano, P., & Brito, P. S. D. (2020). Photocatalytic degradation of swine wastewater on aqueous TiO₂ suspensions: Optimization and modeling via Box-Behnken design. *Heliyon*, 6(1), e03293. <https://doi.org/10.1016/j.heliyon.2020.e03293>.
- Haghighi, M., Rahmani, F., Kariminejad, F., & Sene, R. A. (2019). Photodegradation of lignin from pulp and paper mill effluent using TiO₂/PS composite under UV-LED radiation: Optimization, toxicity assessment and reusability study. *Institution of Chemical Engineers, Iran Process Safety and Environmental Protection*, 122, 48–57. <https://doi.org/10.1016/j.psep.2018.11.020>, http://www.elsevier.com/wps/find/journaldescription.cws_home/713889/description#description.
- Haq, I., Mazumder, P., & Kalamdhad, A. S. (2020). Recent advances in removal of lignin from paper industry wastewater and its industrial applications – A review. *Bioresource Technology*, 312, 123636. <https://doi.org/10.1016/j.biortech.2020.123636>.
- Jabbar, Z. H., & Ebrahim, S. E. (2022). Recent advances in nano-semiconductors photocatalysis for degrading organic contaminants and microbial disinfection in wastewater: A comprehensive review. *Environmental Nanotechnology. Monitoring & Management*, 17, 100666.
- Kabir, M. F., Vaisman, E., Langford, C. H., & Kantzas, A. (2006). Effects of hydrogen peroxide in a fluidized bed photocatalytic reactor for wastewater purification. *Chemical Engineering Journal*, 118(3), 207–212. <https://doi.org/10.1016/j.cej.2006.02.003>.
- Kansal, S. K., Singh, M., & Sud, D. (2008). Effluent quality at kraft/soda agro-based paper mills and its treatment using a heterogeneous photocatalytic system. *Desalination*, 228(1–3), 183–190. <https://doi.org/10.1016/j.desal.2007.10.007>.
- Katal, R., & Pahlavanzadeh, H. (2011). Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: Application to the treatment of paper mill wastewater. *Desalination*, 265(1–3), 199–205. <https://doi.org/10.1016/j.desal.2010.07.052>.
- Khan, A. A., & Mondal, M. (2021). Effective materials in the photocatalytic treatment of dyestuffs and stained wastewater. In *Photocatalytic degradation of dyes: Current trends and future perspectives*. India: Elsevier, 91–111. <https://www.sciencedirect.com/book/9780128238769>.

- Khasawneh, O. F. S., & Palaniandy, P. (2021). Removal of organic pollutants from water by $\text{Fe}_2\text{O}_3/\text{TiO}_2$ based photocatalytic degradation: A review. *Environmental Technology & Innovation*, 21, 101230.
- Kumar, A., Srivastava, N. K., & Gera, P. (2021). Removal of color from pulp and paper mill wastewater- methods and techniques- A review. *Journal of Environmental Management*, 298, 113527.
- Kumar, V., & Verma, P. (2023). A critical review on environmental risk and toxic hazards of refractory pollutants discharged in chlorolignin waste of pulp and paper mills and their remediation approaches for environmental safety. *Environmental Research*, 236, 116728.
- Kusworo, T. D., Budiyono, Kumoro, A. C., & Utomo, D. P. (2022). Photocatalytic nanohybrid membranes for highly efficient wastewater treatment: A comprehensive review. *Journal of Environmental Management*, 317. <https://doi.org/10.1016/j.jenvman.2022.115357>, <https://www.sciencedirect.com/journal/journal-of-environmental-management>.
- Lee, K. M., Lai, C. W., Ngai, K. S., & Juan, J. C. (2016). Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Research*, 88, 428–448. <https://doi.org/10.1016/j.watres.2015.09.045>, www.elsevier.com/locate/watres.
- Levchuk, I., & Sillanpää, M. (2020). Titanium dioxide-based nanomaterials for photocatalytic water treatment. *Advanced Water Treatment*, 1–56.
- Levchuk, I., Rueda-Márquez, J. J., Suihkonen, S., Manzano, M. A., & Sillanpää, M. (2015). Application of UVA-LED based photocatalysis for plywood mill wastewater treatment. *Separation and Purification Technology*, 143, 1–5. <https://doi.org/10.1016/j.seppur.2015.01.007>.
- Liang, Y., Feng, Q., Zhang, J., Jiao, C., Xiong, J., Wang, S., & Yang, Q. (2022). Coupling of photocatalysis and biological treatment for elemental chlorine free bleaching wastewater: Application of factorial design methodology. *Journal of Environmental Management*, 302, 114111. <https://doi.org/10.1016/j.jenvman.2021.114111>.
- Lin, Z., Li, J., Shen, W., Corriou, J.-P., Chen, X., & Xi, H. (2021). Different photocatalytic levels of organics in papermaking wastewater by flocculation-photocatalysis and SBR-photocatalysis: Degradation and GC-MS experiments, adsorption and photocatalysis simulations. *Chemical Engineering Journal*, 412, 128715. <https://doi.org/10.1016/j.cej.2021.128715>.
- Madhubala, G., Abiramasundari, S., Rumjit, N. P., Padmanaban, V. C., & Lai, C. W. (2022). Nano-driven processes toward the treatment of paper and pulp industrial effluent: From the view of resource recovery and circular economy. In *Nanotechnology in paper and wood engineering: Fundamentals, challenges and applications*. India: Elsevier, 471–492. <https://www.sciencedirect.com/book/9780323858359>.
- Mandade, P. (2021). *Introduction, basic principles, mechanism, and challenges of photocatalysis*. Elsevier BV, 137–154.
- Marques, R. G., Ferrari-Lima, A. M., Slusarski-Santana, V., & Fernandes-Machado, N. R. C. (2017). Ag_2O and Fe_2O_3 modified oxides on the photocatalytic treatment of pulp and paper wastewater. *Journal of Environmental Management*, 195, 242–248. <https://doi.org/10.1016/j.jenvman.2016.08.034>.
- Moravvej, Z., Soroush, E., & Rahimpour, M. R. (2020). Achievements in hybrid processes for wastewater and water treatment. In *Current trends and future developments on (bio-) membranes: Recent achievements in wastewater and water treatments*. Iran: Elsevier, 239–262. <https://www.elsevier.com/books/current-trends-and-future-developments-on-bio-membranes/basile/978-0-12-817378-7>.

- Motamedi, M., Yerushalmi, L., Haghighat, F., & Chen, Z. (2022). Recent developments in photocatalysis of industrial effluents: A review and example of phenolic compounds degradation. *Chemosphere*, 296, 133688. <https://doi.org/10.1016/j.chemosphere.2022.133688>.
- Panizza, M. (2018). Fine chemical industry, pulp and paper industry, petrochemical industry and pharmaceutical industry. In *Electrochemical water and wastewater treatment*. Italy: Elsevier, 335–364. <http://www.sciencedirect.com/science/book/9780128131602>.
- Parilti, N. B., & Akten, D. (2011). Optimization of TiO₂/Fe(III)/solar UV conditions for the removal of organic contaminants in pulp mill effluents. *Desalination*, 265, 37–42.
- Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater—A review. *Science of The Total Environment*, 333(1-3), 37–58. <https://doi.org/10.1016/j.scitotenv.2004.05.017>.
- Ramalingam, G., Pachaiappan, R., Kumar, P. S., Dharani, S., Rajendran, S., Vo, D. V. N., & Hoang, T. K. A. (2022). Hybrid metal-organic frameworks as an Exotic material for the photocatalytic degradation of pollutants present in wastewater: A review. *Chemosphere*, 288.
- Ribeiro, J. P., Marques, C. C., Portugal, I., & Nunes, M. I. (2020). Fenton processes for AOX removal from a kraft pulp bleaching industrial wastewater: Optimisation of operating conditions and cost assessment. *Journal of Environmental Chemical Engineering*, 8.
- Rodrigues, A. C., Boroski, M., Shimada, N. S., Garcia, J. C., Nozaki, J., & Hioka, N. (2008). Treatment of paper pulp and paper mill wastewater by coagulation-flocculation followed by heterogeneous photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry*, 194(1), 1–10. <https://doi.org/10.1016/j.jphotochem.2007.07.007>.
- Rueda-Marquez, J. J., Levchuk, I., Fernández Ibañez, P., & Sillanpää, M. (2020). A critical review on application of photocatalysis for toxicity reduction of real wastewaters. *Journal of Cleaner Production*, 258. <https://doi.org/10.1016/j.jclepro.2020.120694>, <https://www.journals.elsevier.com/journal-of-cleaner-production>.
- Shalini, & Setty, Y. P. (2022). Fenton/Photo-Fenton processes for wastewater treatment and disinfection. *Novel Approaches Towards Wastewater Treatment and Resource Recovery Technologies*, 241–252.
- Sadhasivam, S., Savitha, S., & Swaminathan, K. (2010). Deployment of *Trichoderma harzianum* WL1 laccase in pulp bleaching and paper industry effluent treatment. *Journal of Cleaner Production*, 18(8), 799–806. <https://doi.org/10.1016/j.jclepro.2009.11.014>.
- Sampaio, M. J., Silva, C. G., Silva, A. M. T., Vilar, V. J. P., Boaventura, R. A. R., & Faria, J. L. (2013). Photocatalytic activity of TiO₂-coated glass raschig rings on the degradation of phenolic derivatives under simulated solar light irradiation. *Chemical Engineering Journal*, 224(1), 32–38. <https://doi.org/10.1016/j.cej.2012.11.027>, www.elsevier.com/inca/publications/store/6/0/1/2/7/3/index.htm.
- Saravanathamizhan, R., & Perarasu, V. T. (2021). *Improvement of biodegradability index of industrial wastewater using different pretreatment techniques*. Elsevier BV, 103–136.
- Shavisi, Y., Sharifnia, S., Zendehebzan, M., Mirghavami, M. L., & Kakehazar, S. (2014). Application of solar light for degradation of ammonia in petrochemical wastewater by a floating TiO₂/LECA photocatalyst. *Journal of Industrial and Engineering Chemistry*, 20(5), 2806–2813. <https://doi.org/10.1016/j.jiec.2013.11.011>.
- Sun, J., Maimaiti, H., Xu, B., Feng, L., Bao, J., & Zhao, X. (2022). Photo electrocatalytic degradation of wastewater and simultaneous hydrogen production on copper nanorod-supported coal-based N-carbon dot composite nanocatalysts. *Applied Surface Science*, 585.

- Tian, Q., Ran, M., Fang, G., Ding, L., Pan, A., Shen, K., & Deng, Y. (2020). ZnAl₂O₄/BiPO₄ composites as a heterogeneous catalyst for photo-Fenton treatment of textile and pulping wastewater. *Separation and Purification Technology*, 239, 116574. <https://doi.org/10.1016/j.seppur.2020.116574>.
- Virkutyte, J. (2017). *Aerobic treatment of effluents from pulp and paper industries*. Elsevier BV, 103–130. <http://doi.org/10.1016/b978-0-444-63665-2.00004-7>.
- Wang, H., Qiu, X., Zhong, R., Fu, F., Qian, Y., & Yang, D. (2017). One-pot in-situ preparation of a lignin-based carbon/ZnO nanocomposite with excellent photocatalytic performance. *Materials Chemistry and Physics*, 199, 193–202. <https://doi.org/10.1016/j.matchemphys.2017.07.009>.
- Yeber, M. C., Rodríguez, J., Baeza, J., Freer, J., Zaror, C., Durán, N., & Mansilla, H. D. (1999). Chile toxicity abatement and biodegradability enhancement of pulp mill bleaching effluent by advanced chemical oxidation. *Water Science and Technology*, 40(11-12), 337–342. [https://doi.org/10.1016/S0273-1223\(99\)00736-2](https://doi.org/10.1016/S0273-1223(99)00736-2).
- Yin, Z., Li, Z., Deng, Y., Xue, M., Chen, Y., Ou, J., Xie, Y., Luo, Y., Xie, C., & Hong, Z. (2023). Multifunctional CeO₂-coated pulp/cellulose nanofibers (CNFs) membrane for wastewater treatment: Effective oil/water separation, organic contaminants photodegradation, and anti-bioadhesion activity. *Industrial Crops and Products*, 197, 116672. <https://doi.org/10.1016/j.indcrop.2023.116672>.
- Zulkiflee, A., Khan, M. M., & Harunsani, M. H. (2023). Bismuth oxyhalides: Recent progress and its applications in photocatalysis, hydrogen production, antibacterial studies, and sensors. *Darussalam Materials Science in Semiconductor Processing*, 163. <https://doi.org/10.1016/j.mssp.2023.107547>, <https://www.journals.elsevier.com/materials-science-in-semiconductor-processing>.

Ozonation method for pulp and paper wastewater treatment

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10.1 Introduction

This chapter aims to shed light on the most innovative approaches of ozonation, which hold substantial promise for addressing the unique wastewater challenges faced by the pulp and paper industry. Proper wastewater management in the pulp and paper industry is undeniably vital for safeguarding the environment and the health of ecosystems and human communities. This sector's significance stems from its substantial water consumption and the complex nature of the effluents it generates, necessitating specialized treatment methods. This chapter sets out to elucidate one such innovative approach, ozonation, and its potential to revolutionize how the pulp and paper industry tackles its wastewater-related concerns.

Ozonation, explored in depth in this chapter, stands as a powerful and versatile treatment method. Its exceptional oxidizing properties make it adapt to remove various contaminants present in pulp and paper effluents. By understanding the intricacies of ozonation, its mechanisms, and the key operational parameters, readers will gain valuable insights into how it can effectively address the industry's wastewater challenges. Furthermore, this work emphasizes the method's inherent advantages and limitations, providing a holistic overview of its applications and impact. In essence, this chapter will hopefully serve as a crucial stepping stone toward comprehending how ozonation could be the solution the pulp and paper industry seeks to

balance sustainable production with environmental responsibility. To achieve this goal, the chapter was structured into four sections.

[Section 10.2](#) delves into the fundamental principles of ozonation, a process that utilizes ozone's powerful oxidation capabilities to remove contaminants from wastewater. It covers the chemical reactions involved, the ozone generation methods, and the key operational parameters. Additionally, it presents the advantages and limitations of ozonation for drinking water and wastewater treatment.

[Section 10.3](#) reviews the existing scientific literature on ozonation application in pulp and paper wastewater treatment. It offers insights from case studies, research findings, and practical experiences, including pollutant removal efficiency and comparative analyses with alternative treatment methods. Both ozonation alone and ozone combined with other processes are discussed, giving useful insight to the reader about the most recent literature advances.

[Section 10.4](#) examines the environmental and economic aspects of ozonation. It discusses the formation of byproducts and energy consumption, along with capital and operating cost considerations, offering a balanced perspective on the method's sustainability and affordability, especially in comparison with other alternatives for tertiary pulp and paper wastewater treatment.

Finally, [Section 10.5](#) synthesizes the key take-home messages and outlines the full-scale potential of ozonation for pulp and paper wastewater treatment. It also highlights future research directions, emphasizing the need for further innovation and sustainability.

10.2 Ozonation: characteristics, production, and applications

[Section 10.2.1](#) reports the general ozone characteristics, while [Section 10.2.2](#) focuses on the oxidation potential of ozone, compared to other common oxidants. [Section 10.2.3](#) describes ozone solubility and stability, and is followed by the applicable measurement methods ([Section 10.2.4](#)). Ozone production and formation in nature and at the industrial level are successively outlined in [Sections 10.2.5](#) and [10.2.6](#), respectively. Finally, [Section 10.2.7](#) focuses on ozone applications for wastewater treatment.

10.2.1 Definition and general characteristics

The ozone molecule (O_3) is a colorless, unstable, and highly reactive gas, composed of three oxygen atoms. Ozone chemistry in water has been intensively studied in the past decades and

is now well-established (von Sonntag & Gunten, 2012). The main physicochemical properties of ozone are reported in Table 10.1 (Epelle et al., 2023).

Despite being about 13 times more soluble in water than oxygen, ozone can only partially dissolve at atmospheric pressure; a higher dissolution capacity is observed in organic solvents (Biř, 2006). The presence of a peak in the 580–590 nm range (up to 5.12 l/M cm at 588 nm) indicates that ozone in aqueous solutions tends to have an eye-detectable blue color (Gorshelev et al., 2014; Hart et al., 1983). Another absorption band is present in the ultraviolet (UV) region, where the 260 nm peak possesses a molar absorption coefficient of 3300 l/M cm (Hart et al., 1983; Oh et al., 2016). However, recent research reported a more conservative molar absorption coefficient of 3150 l/M cm (Hoigné, 1998). It can be perceived as a clear blue color exclusively at high concentrations; the strong ozone odor, instead, is evident even at low concentrations.

Ozone is recognized as one of the strongest oxidants for heavily polluted wastewater treatment (Rekhate & Srivastava, 2020). The early trials of ozone applications in the wastewater sector occurred

Table 10.1 Main physicochemical ozone properties.

Property	Value
Chemical Abstracts Service (CAS) number	10028-15-6
Absorbance peak (ultraviolet region)	260 nm
Absorbance peak (visible region)	588 nm
Odor	Strong and pungent (perception threshold 0.02 ppm)
Molecular weight	49.997 g/mol
Boiling point (at 1 atm)	−111.9°C
Melting point (at 1 atm)	−192.7°C
Critical temperature	−12.1°C
Critical pressure	54.62 atm
Density (at 0°C and 1 atm)	2.144 g/L
Bond length	1.28 Å
Bond angle	116 degrees
Solubility at 10°C (1 atm)	0.39 m ³ O ₃ /m ³ H ₂ O
Half-life time in air	12 h
Half-life time in water (pH=7)	20 min
Oxidation potential	2.07 V

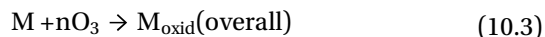
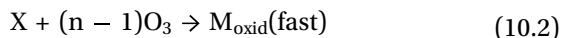
Source: Modified from Epelle E.I., Macfarlane A., Cusack M., Burns A., Okolie J.A., Mackay W., Rateb M., Yaseen M. (2023). Ozone application in different industries: A review of recent developments. *Chemical Engineering Journal*. 454. <https://doi.org/10.1016/j.cej.2022.140188>, <https://www.elsevier.com/inca/publications/store/6/0/1/2/7/3/index.htm>.

in the early 1970s (Xu et al., 2002). Besides wastewater treatment, drinking water can also be disinfected with ozone, reducing the required dosages of conventional chlorine disinfectants (Loeb et al., 2012). However, the instability of this gas in aqueous solutions and the high operational costs still hinder its widespread usage for water and wastewater treatment (Chavoshani et al., 2020).

10.2.2 Oxidation potential

Ozone is one of the strongest oxidants for organic compound removal, having an oxidant potential much higher than oxygen (2.07 V against 1.23 V). To give a thorough overview to the reader, the most common and powerful oxidant agents are reported in Table 10.2, including their oxidation potential.

Ozone removal of organic compounds shows an average reaction constant k_D from 10^{-1} to 10^6 1/M s (Bromberg, 2016; Hoigné & Bader, 1983). The following simplified reactions explain the ozone effect on organic pollutants in aqueous solutions:



The initial pollutant (M) concentration is reduced by ozone and transformed into the final product (M_{oxid}) through the formation of a primary intermediate X; a relatively stable final product (M_{oxid}) is obtained when no more ozone is consumed by the reaction (Hoigné & Bader, 1983). The stoichiometric factor n represents the number of ozone molecules consumed per molecule M transformed to M_{oxid} , and is typically between 1 and 5.

Hydroxyl ($OH^\bullet$) and superoxide ($O_2^{\bullet-}$) radicals originate from ozone decomposition and are characterized by a stronger oxidative capacity than ozone (Table 10.2) (Guo et al., 2023); thus, ozone oxidation is performed both directly by the ozone molecule and indirectly by the produced radicals.

Radicals' marked instability forces an immediate reaction with other molecules to get their missing electrons (Wang & Xu, 2012). The reaction constant k_D of hydroxyl radicals is several orders of magnitude higher than that of ozone alone, up to 10^8 – 10^{10} 1/M s (Hoigné & Bader, 1983). Radical chain reactions are more complex than common first-order oxidation and are reported in-depth in the literature. A comprehensive explanation can be found in Gottschalk et al. (2009).

It is possible to conclude that direct and indirect ozone reactions in aqueous solutions are second only to fluorine, considering the oxidation potential. Ozone's first-order reaction with organic

Table 10.2 Most powerful oxidant agents and their related oxidation potential.

Oxidant agent (formula)	Oxidation potential (V)
Fluorine (F ₂)	3.06
Hydroxyl radical (OH [•])	2.80
Superoxide radical (O ₂ ^{•-})	2.40
Ozone (O ₃)	2.07
Hydrogen peroxide (H ₂ O ₂)	1.80
Oxygen gas (O ₂)	1.23

Source: Modified from Epelle E.I., Macfarlane A., Cusack M., Burns A., Okolie J.A., Mackay W., Rateb M., Yaseen M. (2023). Ozone application in different industries: A review of recent developments. *Chemical Engineering Journal*. 454. <https://doi.org/10.1016/j.cej.2022.140188>, <https://www.elsevier.com/inca/publications/store/6/0/1/2/7/3/index.htm>.

compounds is selective and slower than the nonselective and fast radical chain mechanisms. The joint action of ozone and radicals launched the widely applied ozone-based advanced oxidation processes (AOPs). In fact, from the 1980s, the discovery of ozone's indirect strong oxidative capacities led to widened ozone applications (Staelin & Hoigne, 1985).

10.2.3 Solubility and stability

The mean ozone solubility ratio (R_t) in aqueous solutions at 20°C, which represents the ratio between the concentration in water and the concentration in the gas phase (both expressed as mg/L), obtained from Henry's law, can be estimated as 0.3 in neutral or weakly acidic environments (Egorova et al., 2015). However, significant interferences are linked to solvent properties and initial conditions, including (1) temperature; (2) initial ozone content (% by weight); (3) pH; (4) pressure; and (5) electric conductivity (Table 10.3).

The solubility ratio is halved from 0°C to 15°C and is reduced to one-sixth at 40°C. Furthermore, the dissolved ozone concentration in water changes based on the initial percentage by weight (% w/w) of ozone. A linear dependence exists between ozone's initial concentration and its solubility in water; as a reference, 1% by weight corresponds to 14.3 g O₃/m³ O₂. pH may also affect ozone solubility: a higher pH reduces ozone dissolution (Andoyo et al., 2018). The R_t of ozone in water is stable around 0.3 ± 0.1 for a pH of 2–6 (Egorova et al., 2015); solutions with pH lower than two or higher than seven present a reduced R_t value (0.16–0.24).

Table 10.3 Effect of temperature, pressure, and concentration of ozone in water.

Tested condition			Ozone solubility in water (mg/L)
Ozone concentration	Temperature	Pressure	
3% w/w O ₃	5°C	1 atm	21.450
9% w/w O ₃			64.350
15% w/w O ₃			107.25
6% w/w O ₃	0°C	1 atm	52.91
	10°C		33.46
	20°C		20.59
	30°C		12.87
	40°C		8.580
6% w/w O ₃	15°C	1 atm	26.598
		2 atm	53.196
		3 atm	79.794

Source: Modified from Epelle E.I., Macfarlane A., Cusack M., Burns A., Okolie J.A., Mackay W., Rateb M., Yaseen M. (2023). Ozone application in different industries: A review of recent developments. *Chemical Engineering Journal*. 454. <https://doi.org/10.1016/j.cej.2022.140188>, <https://www.elsevier.com/inca/publications/store/6/0/1/2/7/3/index.htm>.

As well as the initial concentration, ozone solubility shows a linear dependence on pressure increase. So, pressure is a useful control variable for improved ozone dissolution in water.

The presence of salt ions may reduce ozone solubility. However, limited literature data is available due to difficulties in measuring the residual ozone concentration in water at high salinity levels, due to salt ion interferences (Egorova et al., 2015).

Dissolved ozone stability in aqueous solutions is limited, especially in alkaline environments. Hydroxyl radical (OH[•]) formation is promoted by the OH⁻ anion, which is part of the total alkalinity, and the subsequent reaction of OH[•] with ozone enhances O₃ instability (von Gunten, 2007). Despite reacting more slowly than at higher pH, neutral pH environments present a similar decomposition behavior. Acidic pH, instead, may lengthen ozone retention, reducing its decomposition rate (Briñ, 2004).

In general, the half-life is the time needed to reduce by half the initial ozone concentration in water (Hallare & Gerriets, 2023). Ozone in gaseous form presents a longer half-life compared to its dissolution in liquids (McClurkin et al., 2013). Once again, temperature and pH play a key role in the ozone decay mechanism (Harding et al., 2013).

The ozone half-life in aqueous solutions is inversely proportional to temperature. Lower internal kinetic energy, resulting in slower

movement of the gas particles, produces less frequent collisions that keep ozone for longer intervals inside the solution. Vice versa, higher temperatures stimulate faster ozone decomposition due to the continuous contact between particles (Harding et al., 2013).

The same behavior appears while modifying the pH: several literature studies confirmed that working at a higher pH shows a faster ozone decay compared to acidic environments. Ozone half-life based on pH (at a fixed temperature) is longer in strongly acidic solutions; vice versa, its half-life in alkaline media approaches zero (Gardoni et al., 2012).

10.2.4 Measurement methods

The extensive development of ozone applications within the wastewater sector calls for proper analytical methodologies to assess the dissolved ozone concentrations in water (Harding et al., 2013). Interferences from several compounds in real wastewater streams may misrepresent the real ozone concentration, so standardized approaches must be used. The Standard Methods for the Examination of Water and Wastewater are the commonly adopted guidelines for all experimental tests, interference avoidance, and analytical calculations in the water and wastewater sector (Standard Methods for the Examination of Water and Wastewater, 2022).

Schönbein, the father of ozone discovery, developed a quantification method called Indigo, which is still one of the most widely adopted laboratory tests to trace the residual ozone concentration in aqueous solutions (Bader & Hoigné, 1981). This procedure measures the ozone concentration through the decolorization of the Indigo trisulfonate solution after entering in contact with an ozonated sample. The difference in absorbance at a fixed wavelength (600 ± 5 nm) between a reference sample and the processed sample can be directly related to the ozone concentration. However, interferences may occur when chlorine and manganese are present: in these situations, corrections with the addition of malonic acid and glycine, respectively, are required (Bader & Hoigne, 1982).

Gilbert and Hoigné proposed N,N-diethyl-p-phenylenediamine (DPD) as an agent for dissolved ozone estimation (Buchan et al., 2005). However, similarly to the Indigo method, the presence of manganese and bromine in the aqueous solutions alters the measured ozone concentration due to the unavoidable reactions between DPD and these compounds during ozonation (von Sonntag & Gunten, 2012).

Additional approaches proposed in the literature are iodometric titration (KI solution reaction with ozone followed by starch titration to an endpoint) (Rakness et al., 1996), UV absorption at 254 nm,

amperometric membranes, stripping, and gas phase detection (Lozina et al., 2021; Majewski, 2012). Online sensors are also more and more adopted for ozone measurement in aqueous solutions (Korotcenkov et al., 2018).

10.2.5 Ozone production: natural formation

Ozone is naturally produced in the ozono layer, almost coincident with the stratosphere (the part of the atmosphere at a distance between 10 and 50 km from the Earth's surface), through the interaction of the UV spectrum of sunlight (mainly wavelength < 200 nm) (Vázquez et al., 2010) with oxygen molecules (O_2). When the solar ultraviolet radiation breaks the O_2 molecules, the produced oxygen atoms react with oxygen molecules (O_2) and recombine, producing ozone (O_3) molecules (Fig. 10.1).

The stratospheric ozone, or the so-called “ozone layer,” beneficially impacts human health and all biological activities by absorbing intense solar radiation (Rowland, 2006).

On the contrary, ozone natural production in the troposphere, the part of the atmosphere up to 18 km from the Earth's surface, is driven by photochemical reactions from solar radiation and chemical precursors, or by lightning and thunderstorm-induced corona effect.

In the first case, the interaction between UV sunlight and some classes of precursor compounds, including volatile organic compounds (VOC), nitrogen oxides (NO_x), carbon monoxide (CO), and methane (CH_4), breaks the O_2 chemical bonds, and the generated

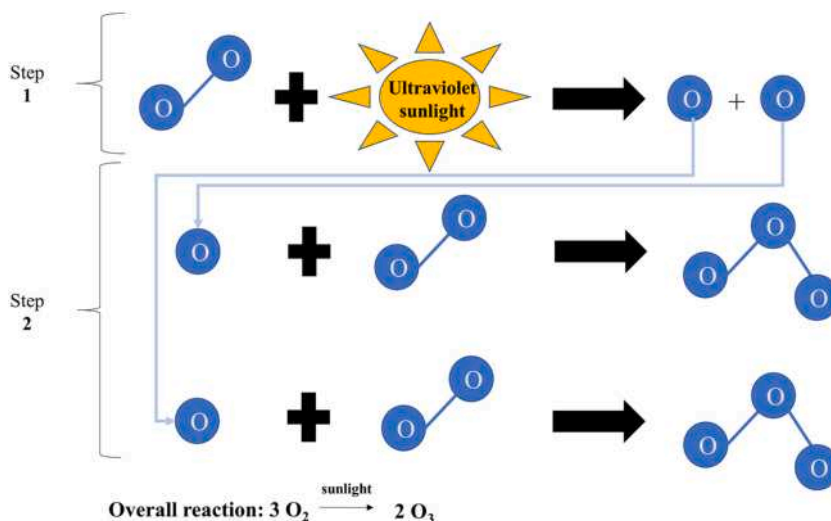


Figure 10.1 Simplified scheme of natural ozone formation in the stratosphere.

oxygen atoms (O) recombine with atmospheric oxygen molecules, producing ozone (Singh et al., 2021).

In the second case, the thunderstorm-induced corona effect and the UV radiation from lightning break the oxygen molecule bonds, creating oxygen atoms (O) that again recombine with oxygen molecules (O_2) to produce ozone molecules (O_3) (Shlanta & Moore, 1972).

Contrary to the stratospheric ozone formation, tropospheric ozone (or “ground level” ozone) is considered a priority pollutant since it is a green house gas (GHG) and can have significant negative effects on human health, causing mild to severe respiratory problems (Ground-level Ozone Pollution, 2023).

10.2.6 Industrial ozone production

Industrial ozone generation processes mimic those found in nature. It is possible to generate ozone industrially using UV radiation, by mimicking the stratospheric ozone production processes, or through the use of electrical discharges (electric arc in nonthermal ionized plasma or an electrolytic cell), as happens in the tropospheric natural ozone production. As previously mentioned, given its highly reactive nature, ozone cannot be stored but must be produced on-site and immediately used.

The most commonly used industrial technique to produce ozone in high amounts is nonthermal ionized plasma generated by electrical discharges (Pekárek, 2003).

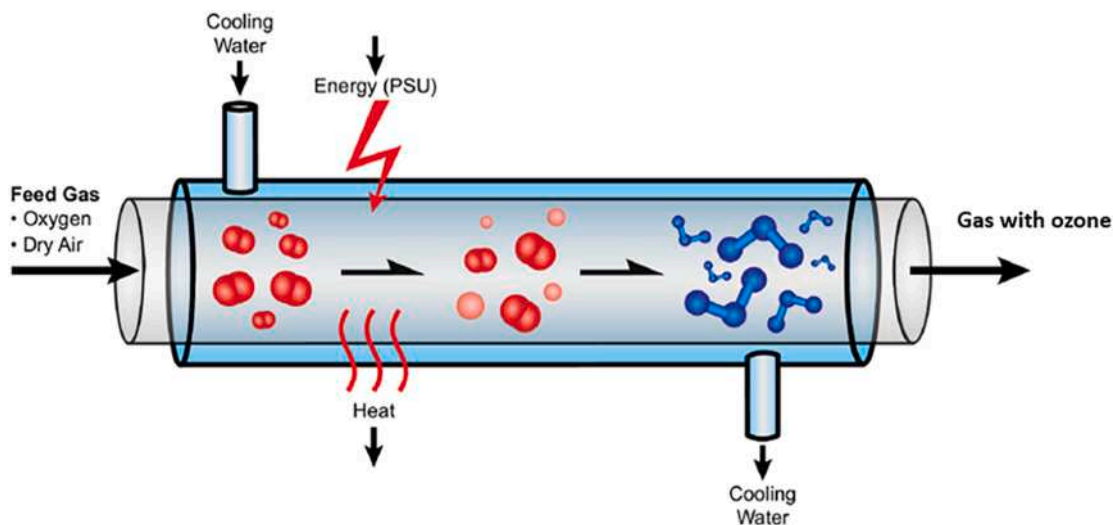


Figure 10.2 Conceptual scheme of an ozone generator (Courtesy of De Nora Water Technologies Italy S.r.l.) (De Nora Water Technologies, 2023).

Inside the ozone generator, whose process scheme is reported in Fig. 10.2, a high-voltage alternating current is applied through a dielectric discharge gap where the feed gas flows, breaking the oxygen molecules' chemical bonds. The feed gas can be either pure oxygen or dry air. Obviously, with the same generator, the amount of ozone produced (g/h) is higher when pure oxygen is supplied as the feed gas source. A cooling system is required to maintain the optimum temperature to get the highest ozone production efficiency; in general, in fact, the cooler the temperature, the higher the efficiency during the reaction process (De Nora Water Technologies, 2023).

Ozone can be used in combination with other oxidizing agents, such as UV and H_2O_2 (hydrogen peroxide), to form extremely reactive radicals and enable AOPs. AOPs are used for quaternary processes in municipal and industrial wastewater treatment plants (WWTPs) and are widely employed for the oxidation of micropollutants, Contaminants of Emerging Concern (CECs), industrial and pharmaceutical residues, and metabolites from drugs.

The gas flow rich in ozone must then be dissolved in water and react with the wastewater requiring treatment in a dedicated contact tank. To be efficiently exploited in wastewater treatment, gaseous ozone must be dissolved in water as much as possible using systems

How it works

Inside the generator, ozone is produced when oxygen molecules are separated by an energy source into oxygen atoms, which collide with an oxygen molecule to form ozone. A high voltage alternating current is applied across a dielectric discharge gap that contains an oxygen-bearing feed gas. When ozone is dissolved in water, the free radicals that are formed have excellent oxidizing capacity on pollutants and molecules.

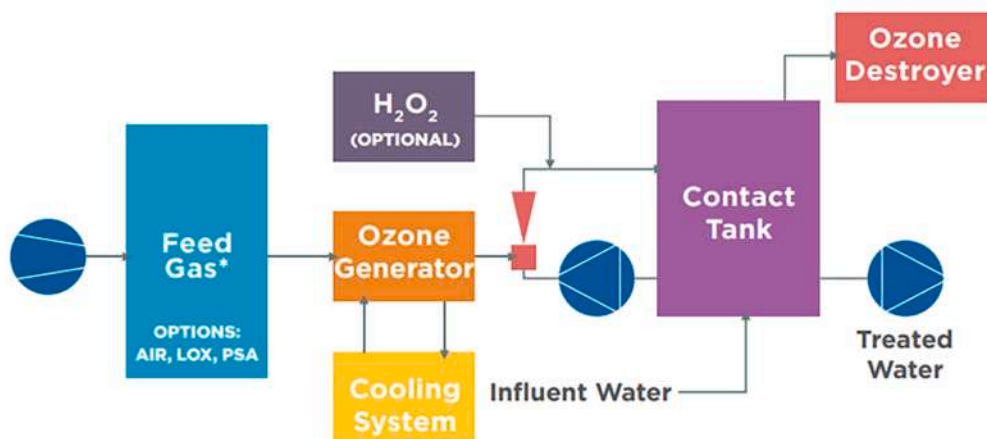


Figure 10.3 Process scheme of an ozonation reactor at industrial scale (Courtesy of De Nora Water Technologies Italy S.r.l.) (De Nora Water Technologies, 2023).

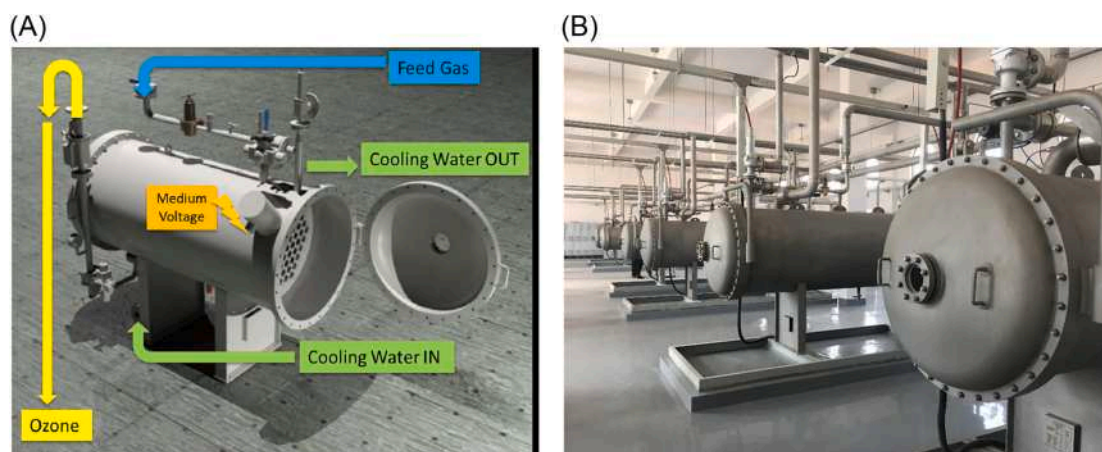


Figure 10.4 De Nora ozone generator in vessels.

such as pump ejectors (Venturi), disk diffusers with a diffusion water column, static mixing, and rotating systems. Since, as already mentioned, ozone is harmful to human health if inhaled, and is a GHG, ozone sensors are always installed in the equipment room, and the unreacted ozone must be destroyed by an ozone catalytic destructor, which converts it back to oxygen.

The scheme described above is resumed in [Fig. 10.3](#).

Industrial ozone generators from nonthermal ionized plasma may have different configurations; in [Fig. 10.4](#) an example of ozone generators in vessels is reported ([De Nora Water Technologies, 2023](#)).

10.2.7 Applications in wastewater treatment

As previously introduced, ozone is a widely adopted disinfectant and oxidant agent, first introduced in the drinking water sector and later applied in wastewater treatment ([Ikehata & Li, 2018](#); [Lim et al., 2022](#)). In the beginning, ozone was mostly employed for odor control and color removal and then for organic and inorganic substances oxidation, especially micropollutants removal ([von Gunten, 2003](#)). Later, literature studies aimed to enhance the ozone's oxidative capacities, for example, by combining ozone with metal catalysts, ultrasounds, UV radiation, and hydrogen peroxide ([Rekhate & Srivastava, 2020](#)). These ozone-based processes are known as AOPs. More recently, ozone has also been investigated as a pretreatment before the anaerobic digestion of sewage sludge, with the aim of enhancing sludge solubility and subsequently the methane yields that can be obtained ([Catenacci et al., 2022](#)).

Table 10.4 Ozonation advantages and downsides in wastewater treatment.

Advantages	Drawbacks
High pollutant removal efficiency	Expensive generation process
Hybrid processes can be performed (AOPs)	Difficult to exactly describe the chemical reactions happening during the AOPs
Adaptable to several process stages, limited to negligible disinfection byproducts, suitable for wastewater reuse	In situ production is required (almost impossible to store)
Applicable to quaternary treatments (micropollutant removal)	Unstable in aqueous solutions
Odor and color removal	No residual action
Removal of antibiotic-resistant genes (ARGs) and antibiotic-resistant bacteria (ARBs)	Toxic in air at high concentrations (leakages)

AOPs, Advanced oxidation processes.

The main advantages and drawbacks of ozone-based wastewater treatment are summarized in [Table 10.4](#).

Despite requiring an expensive generation process and in situ production, due to the impossibility of being stored, the high efficiency on a wide range of pollutants suggests ozonation application for refractory (i.e., poorly biodegradable) wastewater streams, as conventional biological processes show a limited efficiency on recalcitrant organic matter ([Mainardis et al., 2020](#)). Moreover, recent findings suggest that ozonation is applicable to limit the diffusion of antibiotic-resistant genes and antibiotic-resistant bacteria in the environment ([Czekalski et al., 2016](#); [Iakovides et al., 2019](#)).

As previously mentioned the revision of the 91/271/EEC Directive concerning Urban Wastewater Treatment (UWWTD) ([Council Directive of 21 May 1991 concerning Urban Waste Water Treatment, 1991](#)), approved in 2024 (Directive 2024/3019) introduces the requirement of a quaternary treatment for the removal of persistent compounds (micropollutants), such as pharmaceuticals and CECs ([Proposal for a Directive of the European Parliament and the Council concerning Urban Waste Water Treatment, 2022](#)). In this framework, ozone will probably be one of the most useful technologies to attain this purpose ([Maniakova et al., 2023](#)), eventually in combination with other technologies, such as granular activated carbon filtration.

The most recent ozone applications for pulp and paper wastewater treatment, according to the scientific literature, are specifically detailed in [Section 10.3](#). Ozonation byproducts, instead, are

discussed in Section 10.4 together with the most relevant economic aspects.

10.3 Ozonation application to pulp and paper wastewater

A significant interest has been dedicated in the last years to ozone application to pulp and paper (P&P) wastewater (WW) treatment, due to the general refractoriness of this stream to conventional biological processes. This feature often asks for a dedicated tertiary treatment to reach the desired high-quality standards for effluent discharge or reuse (Table 10.5). Different water quality classes are defined in P&P mills for effluent reuse, according to the specific usage of the treated effluents; overall, organic matter (COD) appears as a key parameter to define the specific quality class of the effluents. Water of lower quality can be exclusively used for cleaning purposes, while high-quality water can be employed in different process operations.

In the P&P sector, ozone has been investigated in the latest year as a potential alternative solution to conventional physicochemical coagulation–flocculation (which is still the prevalent method for tertiary P&P WW treatment at a full-scale level), improving effluent quality for reuse and limiting, at the same time, the negative environmental impacts connected to chemicals' usage and chemical sludge generation.

Table 10.5 Water quality criteria for effluent reuse in pulp and paper mills.

Parameter	Unity of measure	High quality	Medium quality	Low quality
Conductivity	μS/cm	< 500	< 500	< 500
Chlorides	mg/L	< 200	< 200	< 300
Calcium	mg/L	< 60	< 60	< 200
Color	–	None	Not specified	Not specified
Solids	mg/L	10	10–15 (< 5 μm)	Coarse filtration
COD	mg/L	< 50	< 200	Not specified
BOD	mg/L	< 3	Low	Reduced

BOD, Biochemical oxygen demand; *COD*, chemical oxygen demand.

Source: Modified from Mainardis M., Buttazzoni M., De Bortoli N., Mion M., Goi D. (2020). Evaluation of ozonation applicability to pulp and paper streams for a sustainable wastewater treatment. *Journal of Cleaner Production*. 258, 120781. <https://doi.org/10.1016/j.jclepro.2020.120781>.

Table 10.6 Recent literature studies related to ozone application to P&P WW treatment.

Treated stream	Aim of the work	Main results	References
High-strength pulp and paper (P&P) wastewater (WW)	Study the performances of combined acid precipitation and ozonation	25 min ozonation increased effluent biodegradability (BOD ₅ / COD ratio up to 0.29); final ozonation products from lignin degradation included fumaric, maleic, malonic, and formic acid	De los Santos Ramos et al. (2009)
Low-strength P&P WW	Compare ozonation with other AOPs, including ultraviolet (UV) irradiation and hydrogen peroxide (H ₂ O ₂)	Ozonation leads to improved effluent biodegradability, together with 30%–40% COD removal and excellent color removal at a dosage of 0.8 g O ₃ /g COD	Bierbaum et al. (2012)
Black liquor from P&P industry	Assess lignin removal by ozone and determine the required ozone dosage	Lignin degradation ranged from 40% to 96.6% for applied ozone dosages of 0.1–3.6 mg O ₃ /mg COD, while COD removal was 8.8%–69.6%. Color removal was observed as well	Michniewicz et al. (2012)
Kraft pulp mill and recycled paper mill WW	Assess ozonation and photocatalysis performances on different P&P WW streams	Higher ozonation efficiency than photocatalysis; O ₃ is more suitable for kraft pulp mill WW (60% COD removal vs 35% for recycled paper mill WW), enhancing effluent biodegradability. A combination of membrane bioreactor and postozonation achieved 90% COD and 95% color removal	Merayo et al. (2013)
Secondary P&P WW effluent	Assess the performances of Fe supported on activated carbon (AC) for catalytic ozonation	After 60 min of ozonation, COD removal reached 35% by ozone alone, 56% in the presence of Fe/ AC, and 43% using AC as a catalyst. Ozone alone reached satisfactory color removal	He et al. (2016)
Secondary P&P WW effluent	Develop a new Cu-Ce catalyst supported on Al ₂ O ₃ for catalytic ozonation	Total organic carbon (TOC) removal increased by 6.5%, 9.5%, 24.5%, and 35.5% compared to Ce/Al ₂ O ₃ /O ₃ , Cu/Al ₂ O ₃ /O ₃ , Al ₂ O ₃ /O ₃ , and O ₃ alone, respectively, due to enhanced •OH radical formation	He et al. (2018)

Secondary P&P effluent	Assess the performances of waste rice straw-derived activated carbon-supported manganese oxides for catalytic ozonation	A significant increase in effluent biodegradability was observed after catalytic ozonation (from 0.16 to 0.46). The effluent met all discharge standards, showing 59% color and 78% COD removal. The acute toxicity decreased by 59.1%	Zhuang, Guo and Hong (2018)
Black liquor from P&P industry	Compare ozonation alone and ozone+UV irradiation for COD and color removal	The combined process was more effective than O_3 alone, with maximum efficiencies (56% of COD and 71% of color removal) at pH 9.8 and O_3 dose of 0.2 mg/mL in the O_3 /UV process	Munir et al. (2019)
P&P WW before and after biological treatment	Assess the techno-economic feasibility of ozonation as an alternative to coagulation–flocculation for tertiary treatment	Ozone was more effective on secondary effluents than raw influent streams (from 46% to 81% COD removal). At a dosage of 100 mg/L, comparable COD removal to coagulation–flocculation (50%) was obtained	Mainardis et al. (2020)
Black liquor from P&P industry	Compare Fe-zeolite with raw zeolite catalyst for P&P WW ozonation and optimize process parameters	The maximum COD (71%) and color (88%) removals were obtained at natural pH (6.8). Fe-zeolite catalyst led to a 23%–29% increase in efficiency when compared to ozonation alone and 17%–19% when compared to raw zeolite ozonation. The catalyst remained stable after five cycles	Munir et al. (2022)
Anaerobically treated P&P stream	Investigate the performances of catalytic ozonation, the catalyst being a polyurethane sponge loaded with titanium dioxide	A COD reduction of 52% was obtained under optimal process conditions (pH=9, ozone concentration=16 mg/L, treatment time=8 min, catalyst filling ratio=7.5%), with an increase in BOD_5 /COD ratio from 0.26 to 0.37	Zhou et al. (2023)

BOD_5 , 5-day biochemical oxygen demand; COD , chemical oxygen demand.

The most recent literature studies related to ozone application to P&P WW treatment are summarized in [Table 10.6](#) to give an updated overview to the reader.

Most of the studies were conducted on biologically treated (i.e., secondary) effluents, in most cases through conventional activated sludge, even if, interestingly, some studies were focused on the treatment of raw (or anaerobically treated) P&P effluents. Obviously, treating high-loaded streams through ozonation leads to a remarkable increase in overall energy consumption, as both biodegradable and nonbiodegradable organic matter are nonspecifically targeted by ozone, and the required ozone dosages are thus higher. On the contrary, ozone application as a tertiary treatment is generally preferable to enhance the process performances and improve its techno-economic sustainability, as the biodegradable COD fraction has already been assimilated by the biomass in the biological treatment. This can markedly reduce operating costs, as the ozone dosage required to reach the desired process efficiency is significantly lower.

From the results reported in [Table 10.6](#), it is generally accepted that ozonation leads to an improvement in effluent biodegradability, which is typically assessed through the BOD₅/COD ratio: this can be beneficial not only for a downstream biological treatment but also to decrease effluent toxicity, limiting the negative effects on the receiving water bodies. A combination of different advanced treatment technologies, as previously mentioned, can be proficient in reaching the high-quality standards required for internal reuse in the P&P factory ([Table 10.5](#)). As an example, biofiltration positioned downstream of the ozonation reactor can be a useful solution, as more than 80% COD removal can be obtained, reducing at the same time the required ozone dosage, and consequently the energy request of the process ([Möbius & Helble, 2004](#)). Multiple ozonation-biofiltration steps can be even performed to further enhance the pollutant removal capability, optimizing ozone dosages; however, this leads to a complication in system operations and a requirement for additional reactors, so a compromise between efficiency and simplicity must be reached.

Ozone can be particularly useful for removing adsorbable organic halogens (AOX) and lignin derivatives, due to its capacity to oxidize electron-rich molecules with carbon-carbon double bonds ([Esmaeeli et al., 2023](#)). More specifically, the oxidation of phenols, chlorophenol, and trichlorophenol takes place in a single stage thanks to aromatic ring opening reactions, while other pollutants (e.g., catechol, vanillin, guaiacol, and syringaldehyde) are oxidized in two stages, as they generate intermediates that are more resistant to ozone attack ([Hermosilla et al., 2015](#)). The carboxylic acids

formed by the opening of the aromatic rings, instead, are very resistant to ozone oxidation, and are responsible for the limitation in the overall total organic carbon (TOC) and COD removal. However, they are highly biodegradable; thus, the negative environmental effects are narrowed compared to their precursors.

In general, the performances of ozonation treatment are widely affected by pH, temperature, ozone dosage, and type and concentration of target substances, but also by the competition of the target pollutants with the biodegradable compounds still present in the effluents. The oxidation of lignin derivatives is normally improved at alkali pH (> 9), due to a more effective generation of hydroxyl radicals, while COD removal is not strongly affected in a wide range of pH (4.5–11.0) (Esmaeeli et al., 2023). No remarkable differences have been observed in process performances by varying the environmental temperature from 20°C to 60°C, despite ozone solubilization being obviously higher at lower temperatures. The ozone consumption rate decreases during the ozonation process due to the ongoing reactions with the organic matter; the rate of this decrease depends on the specific nature of the treated stream, being proportional to the amount of easily oxidizable compounds present in the effluents (Hermosilla et al., 2015).

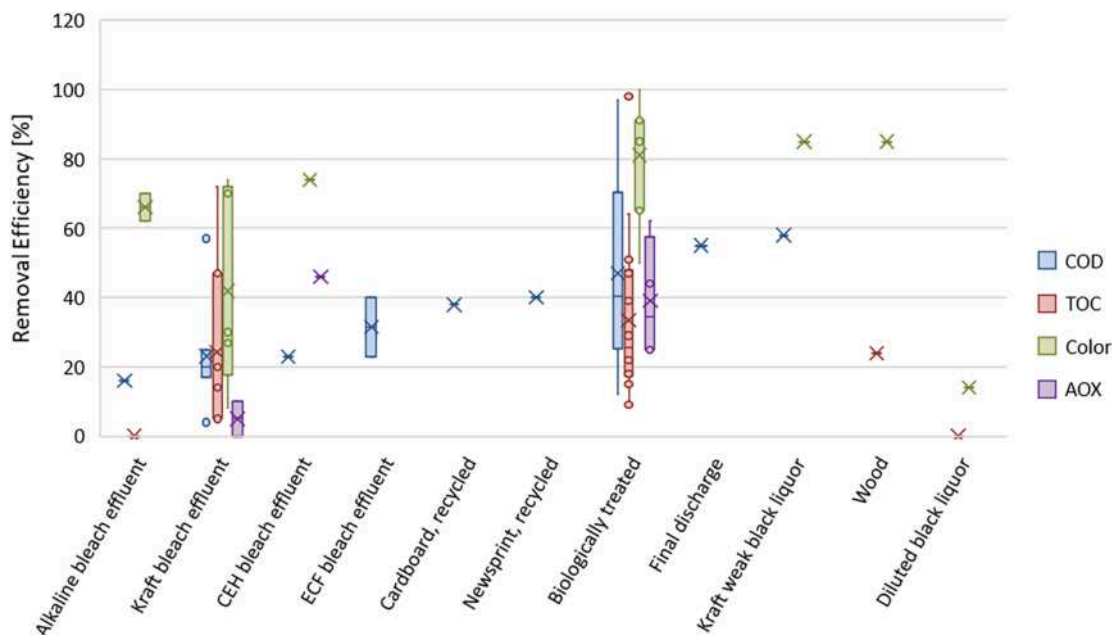


Figure 10.5 Literature results on COD, TOC, color, and AOX removal obtained through ozone treatment of different pulp and paper streams. AOX, adsorbable organic halogens; COD, chemical oxygen demand; TOC, total organic carbon.

The significant variability of ozone effectiveness reported in the scientific literature (Table 10.6) depends on the extreme diversity in P&P WW characteristics, which in turn rely on the specific process conditions in the upstream factories. This variability is further underlined in Fig. 10.5, where the removal efficiency of COD, TOC, color, and AOX obtained in different literature studies forecasting P&P effluent ozonation is summarized.

Besides ozonation alone, another innovative solution mentioned in the scientific literature is nanofiltration followed by ozonation: the high-molecular-weight fraction can be separated as concentrate through the membranes and is successively ozonated, while the low-molecular-weight fraction, which is more biodegradable, can be treated by conventional biological processes (Hermosilla et al., 2015). Generally, the coupling of two (or more) technical solutions (e.g., O_3 +UV irradiation and O_3 + granular activated carbon-GAC filtration) leads to an improvement both in effluent quality and energy/economic burdens, leading to higher applicability and profitability when compared to stand-alone solutions. More specifically, the combination of O_3 and other oxidizing agents (such as UV radiation) can lead to superior performances, addressing the well-known disadvantages of O_3 (i.e., significant electricity consumption and possible generation of unwanted byproducts).

Catalytic ozonation has been recently investigated as a further amelioration of O_3 alone. Several catalysts have been studied in the literature (Fe-zeolite, Fe-activated carbon, and Cu-Ce/ Al_2O_3), typically highlighting superior performances to ozonation alone (Table 10.6). In this case, ozone can react both through direct reactions of O_3 molecules and catalyzed processes. Even complete pollutant mineralization can be reached in some cases with catalytic processes, with lower ozone dosages (Hermosilla et al., 2015).

Interestingly, effluents including relatively high amounts of biodegradable organic matter, such as those generated from recycled P&P mills, highlighted lower removal efficiencies than virgin fiber effluents in catalytic ozonation. It was proved that O_3 alone is, in most cases, sufficient to reach a satisfactory color removal, thanks to the easiness in lignin double and triple bond oxidation by ozone (Hermosilla et al., 2015), but the abatement of recalcitrant COD requires higher dosages, especially if high efficiencies must be reached (Mainardis et al., 2020). However, no indication of the scale-up feasibility of catalytic ozonation was found in the scientific literature, as up to now most of the studies have been conducted at the laboratory level. Further investigations are thus needed at pilot-scale conditions to better ascertain

the sustainability of applying catalytic ozonation at full-scale (industrial) conditions.

Ozone and hydrogen peroxide combination (the so-called peroxone process) has been studied as well in the literature, as H_2O_2 stimulates a faster ozone degradation, rapidly producing hydroxyl radicals. However, differently to what was obtained on other effluents, the results related to P&P WW treatment were discordant and even negative in some cases: thus, ozonation alone is generally preferable to $\text{O}_3+\text{H}_2\text{O}_2$ in the remediation of these effluents

Table 10.7 Advantages and downsides of ozonation alone and ozonation combined with other advanced treatment processes for pulp and paper wastewater treatment.

Process	Advantages	Downsides	References
Ozonation alone	Efficient color removal; effluent biodegradability increase; partially effective on nonbiodegradable organics	High electric energy consumption; impossibility of reaching complete COD removal; competition with the residual BOD	Hermosilla et al. (2015) ; Mainardis et al. (2020)
Ozone+UV	Improvement in decolorization and dechlorination	Effluent turbidity limits the UV effect; higher ozone consumption, which increases operating costs	Hermosilla et al. (2015)
Ozone+ H_2O_2 (peroxone)	Faster ozone degradation	Conflicting literature results on COD and color removal; higher operating costs	Hermosilla et al. (2015)
Ozone +biofilter	Simultaneous removal of AOX, color, COD; possibility of effluent reuse by applying two-stage ozonation; process ready for industrial scale	Limited industrial experience	Möbius and Helble (2004)
Ozone +granular activated carbon (GAC) filtration	Supplementary hydroxyl radicals' generation; improvement of COD, AOX, and color removal; reduced effluent toxicity; reduction of ozone dosages	Limited industrial experience	Balçioğlu and Moral (2008)
Catalytic ozonation	Higher organic matter removal at lower ozone dosages; catalyst stability and reusability; effluent biodegradability increase	Lower efficiency on more biodegradable effluents (e.g., recycled paper mills); uncertain full-scale applicability; mostly lab-scale studies	Munir et al. (2022) ; Zhou et al. (2023)

AOX, Adsorbable organic halogens; BOD, biochemical oxygen demand; COD, chemical oxygen demand.

(Hermosilla et al., 2015), also due to the higher operational expenses required for the peroxone process.

In a combined O_3 +UV process, instead, the short-wave UV energy (< 310 nm) interacts with ozone, stimulating fast hydroxyl radicals' generation; however, despite O_3 +UV has shown synergistic effects in the treatment of starch degradation products, in the specific case of P&P WW nonsignificant differences from ozonation alone were claimed, due to its high turbidity, which hinders UV light penetration (Hermosilla et al., 2015). Also, a higher ozone consumption is normally observed in combined O_3 +UV processes, due to the synergistic interaction of UV light with ozone.

The advantages and downsides of ozonation alone and ozone combined with other processes are summarized in Table 10.7. It is generally demonstrated that the combination of ozone with other AOPs allows for the reduction of the required ozone dosages, lowering the energy requirements, and subsequently the operating costs. However, some advanced processes (e.g., ozone + UV and the peroxone process), which have demonstrated their effectiveness on different WW streams, were shown not to be as efficient in the treatment of P&P WW. Other combined treatments (e.g., ozone + biofiltration and ozone + GAC filtration), on the contrary, appear more promising, even if limited literature studies are available.

The applied processes and the type of generated products at the P&P factory level, including the utilization of virgin or recycled fibers, determine the peculiar wastewater features and its biodegradability, which make every WWTP substantially unique. Thus, it is highly recommended in all cases to conduct specific pilot studies at the WWTP level to select the most appropriate point where positioning ozonation (e.g., before or after the biological treatment), assess the specific ozone dosage required to achieve the desired pollutant removal, and finally ascertain the techno-economic sustainability of the upgraded treatment chain. The combination of ozone with other processes (especially GAC filtration and catalytic processes) appears particularly promising to reach wider industrial applications in the near future; however, more scientific studies are required, addressing not only the technical performances of the upgraded treatment chain but also the environmental burdens and the economic convenience compared to conventional treatment solutions. A compromise must be reached between excellent pollutant removal and the increased complexity of the WW treatment train. Finally, treated effluent reuse, both at the factory level and for other industrial uses, can be a forcing agent to boost the application of advanced treatment technologies, such as ozonation.

10.4 Environmental and economic aspects

This section discusses the environmental and economic aspects of ozone application to P&P WW treatment. First, the economic aspects are addressed, followed by considerations on the environmental aspects related to ozone application.

10.4.1 Economic aspects

The economic burdens of ozone application to P&P WW treatment are mostly linked to the capital costs (i.e., installation of the ozonation reactor) and the energy requirements in electricity form to run the ozone production unit. Further elements to be considered in an economic assessment are the ozone transfer system and the contact reactor, as well as the application of either ozone alone or ozone in a train of different operational units (Section 10.3). The potential revenues from ozone application are linked to the reduced amounts of waste to manage (especially sludge), and the improved possibility of effluent reuse thanks to its higher quality when compared to conventional solutions for tertiary WW treatment, such as physico-chemical coagulation-flocculation. These aspects, and others, are addressed in the following paragraphs, first discussing the capital and operating costs, and then considering the possible revenues.

10.4.1.1 Capital costs

The main capital cost for ozone application is linked to the installation of the ozone production system. The capital costs, also called investment costs, required by O_3 production systems for P&P WW treatment are in the order of magnitude of 1.5–2 M€ for a plant capacity of 1200 m³/h and an ozone dosage of 84 kg O_3 /h, as reported by Mainardis et al. (2020), while evaluating the full-scale applicability of ozonation as a tertiary WW treatment in a P&P mill in Northern Italy. The order of magnitude of the investment cost for the ozone production system was later confirmed by Peyrelasse et al. (2022), who reported a cost of approximately 2.5 M\$ for an ozone generator of 46 kg O_3 /h.

The oxygen needed for ozone production can be alternatively supplied through liquid oxygen (LOX) cylinders (O_2 purity 99.99%), through an oxygen-rich stream produced on-site by pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA) (O_2 purity 92%–95%), or using ambient dry air as gas feed (O_2 content around 21%).

The use of ambient dry air to produce the same quantity of ozone is slightly cheaper in terms of operating expenses (OPEX) since no LOX supply is needed, as well as in terms of Capital Expenditure (CAPEX), since the building of a PSA/VPSA system is not required;

on the contrary, the concentration of ozone produced is lower compared to O_3 produced from LOX, PSA, or VPSA.

Among the gas feed streams that provide pure (PSA or VPSA) or ultrapure (LOX) oxygen, LOX systems show higher OPEX but lower CAPEX. Generally speaking, considering a constant amount of ozone produced (g/h), the ozone concentration in the gas is higher when the equipment is fed with pure or ultrapure oxygen. Such solutions are preferred when a high concentration of ozone is required against (micro)pollutants in WWTPs, and especially when the ozone is also dosed in the upstream P&P industrial process as a bleaching agent. [Mainardis et al. \(2024\)](#) reported a current cost of liquid oxygen of 120 €/ton in Italy. Therefore, the choice of oxygen production or on-site storage, as well as the choice of the specific ozone production system, depends on the amount of oxygen required to obtain the desired ozone concentration in WW treatment and the eventual additional use of ozone in the P&P production line. The oxygen stream needed for ozone production is often produced on-site when ozone is also needed in the production line ([Xylem, 2012](#)).

Regarding the ozone transfer system, the investment cost of fine bubble diffusers is higher than that of the Venturi system, due to the need for a dedicated basin for the ozone transfer. The Venturi system, instead, shows higher operational costs; however, it is the most commonly applied solution at an industrial level, due to its higher transfer efficiency compared to fine bubble reactors, easier maintenance, and the lower space requirements ([Rakness et al., 2018](#)).

Regarding ozone contact reactors, the investment cost depends on the wastewater volume to be treated and the type of contact reactors. Pressurized ozone tank reactors are well-suited to work with Venturi systems, as they guarantee a high transfer efficiency and allow for easy off-gas control ([Hostachy et al., 2014](#)). Moreover, if a biological unit follows the ozone reactor, following the indications of the best available technologies (BAT) of the European Joint Research Center (JRC) ([Roudier et al., 2015](#)), the stream reaching such biological treatment is oxygen-rich, increasing the overall process efficiency and reducing the costs for basin aeration ([Hostachy et al., 2014](#)). Indeed, as indicated by the BAT, ozone should be ideally implemented in a unit train composed of the ozone unit and a successive biological filter ([Roudier et al., 2015](#)). This combination helps reduce the overall ozone amount required to obtain the desired COD removal, therefore reducing the operational costs. In any case, both the investment costs related to the ozone contact reactor and those of the subsequent biological unit are much lower than the investment cost for the ozone production unit, which is always the preponderant term.

10.4.1.2 Operational costs

The most relevant term of operational costs for ozone WW treatment is related to the electric energy requirements of the ozone production system. The energy ratio for ozone production is in the order of magnitude of 10 kWh/kg O₃, which includes the need for a cooling water supply to avoid an excessive temperature increase (Xylem, 2012). The energy requirement for on-site O₂ production is about an order of magnitude lower than that required for ozone production (Bisio et al., 2002; “OSI 125/250/500/1000 Oxygen Concentrator,” 2019). However, the ozone production efficiency from pure oxygen streams is about 10% in weight; therefore, the operational costs of on-site oxygen production should be carefully evaluated considering the system efficiency, the required amount of oxygen, the maintenance of the oxygen production plant or, in alternative, the purchase and transportation costs of liquid oxygen in cylinders.

The energy requirements of ozone transfer depend on the specific system used, its peculiar design, and the applied operational parameters. Venturi (or side-stream injection units) require a flux of pressurized water and, therefore, are more energy-intensive than bubble diffusers, although more efficient in gas transfer. Regarding the downstream ozone destruction unit, which is needed to avoid the harmful release of unreacted ozone into the atmosphere, the development of catalytic ozone destructors has helped significantly reduce the energy requirements of this unit, which previously exploited thermal processes.

As previously mentioned, at full-scale conditions, the ozonation unit in P&P WW treatment is often followed by a biofilter. The energy requirements of the biofilter are significantly lower than the ozone production unit. To quantitatively evaluate the operating costs, considering the ozone requirements previously mentioned, the electricity cost for nonhousehold units in the EU can be considered, which rose from 0.15 €/kWh in the first semester of 2019 to 0.25 €/kWh in the first semester of 2023, according to Eurostat data (Eurostat, 2023). The overall estimate of the annual operating costs of ozone application to P&P WW as a tertiary treatment can be found by Mainardis et al. (2024), where an annual expense of about 2 M€/yr was reported for the sole O₃ unit. Such expenses can be almost halved if ozone is used in a train with another treatment unit (specifically, GAC filtration), thanks to the significant reduction in the required ozone dosages (Mainardis et al., 2024).

10.4.1.3 Revenues

The possible revenues obtainable by ozone application to P&P WW treatment are linked to the enhanced feasibility of effluent reuse

within the upstream factory (Table 10.5) and the consistent reduction in sludge production. These aspects are particularly important when comparing alternative solutions for advanced P&P WW treatment, providing useful insight to decision-makers regarding the pros and cons of each technology. The reduction in sludge production, which is due to partial organic matter mineralization, is very appealing when considering that the most frequently exploited solution for full-scale tertiary P&P WW, i.e., coagulation–flocculation, generates significant sludge amounts that must be properly managed and disposed of. Regarding water reuse within the P&P plant, the revenues calculated by Mainardis et al. (2024) can be more than half of the yearly operational costs of the ozone unit, depending on the local freshwater tariff and the availability of alternative freshwater sources, which will probably be scarcer in the future due to accelerating climate change.

10.4.2 Environmental aspects

The most important environmental aspects related to ozone application are linked to the quality of the treated effluent and the possible generation of unwanted byproducts.

10.4.2.1 *Quality of the final effluent*

One of the most notable positive features of employing ozonation for treating real wastewater from P&P mills, regardless of whether the WW has undergone prior biological treatment or not, lies in its well-demonstrated ability to facilitate the effective degradation of toxic lignin byproducts and complex chlorophenol compounds, as well as to achieve a substantial reduction in color (Hermosilla et al., 2015). As previously described, ozonation has been effectively harnessed for the oxidation of various chemical constituents in P&P mill effluents, encompassing compounds such as eugenol, catechol, vanillin, guaiacol, syringaldehyde, phenol, chlorinated phenols, and cinnamic acid derivatives (Hubbe et al., 2016). In addition to its improvement in COD removal, the impact of ozonation on the treated effluent varies depending on the specific WW characteristics, the eventual pretreatment (e.g., upstream biological reactor), and the applied ozone dosage. Ozone can also yield meaningful reductions in effluent color, AOX, poorly biodegradable chelating agents such as diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA) (Mainardis et al., 2024), and effluent toxicity (Mainardis et al., 2020). As previously mentioned, ozonation is a viable and widely applied method for the final disinfection of treated wastewater effluents. The combined influence of these factors contributes to the improvement of final effluent quality, thereby widening its applicability for reuse within the same industrial facility or for other industrial applications.

As previously underlined, ozone treatment is seldom employed as a stand-alone solution in the treatment of P&P WW. More frequently, it is employed in conjunction with other treatment processes, such as biological treatment, coagulation, and filtration, to enhance the overall efficacy and cost-effectiveness. Furthermore, the design and operations of an ozone treatment system necessitate meticulous optimization to attain the desired outcomes and must take into account critical factors such as ozone dosage, contact time, and the complete removal of ozone residues before effluent discharge or reuse.

Ozonation combined with biofiltration was defined as a BAT for P&P WW treatment (Roudier et al., 2015) and has the inherent merit of a limited production of excess biological sludge from the biofilters, where the polluting substances are not merely separated but effectively removed. Consequently, this treatment protocol avoids the generation of a concentrated stream necessitating a subsequent dedicated treatment, which is often the case when membranes or evaporation processes are employed. In instances where the removal of organic compounds remains insufficient following conventional biological treatment, the implementation of ozonation in conjunction with subsequent biofiltration can be an efficient and affordable option. Advanced effluent treatment is typically required for P&P mills located near ecologically sensitive or relatively small receiving water bodies, but it will be more and more required in the future due to stricter discharge standards. Tertiary treatment solutions are also adopted by mills undergoing substantial capacity expansion and that do not possess the permits to increase the pollutant loads discharged into the environment accordingly (Kamali & Khodaparast, 2015). These treatments can also be necessary when the produced paper has a high brightness grade, which results in higher organic loads in the produced wastewater, requiring additional treatment steps.

10.4.2.2 *Byproducts/transformation products*

Regarding the byproducts and transformation products generated by ozone, it is important to keep in mind that ozonation, when employed as a tertiary WW treatment, can potentially give rise to the generation of several harmful substances, which can be toxic at very low concentrations. The specific byproducts generated in each condition depend on various factors, including the initial wastewater composition, the employed ozone concentration, and the prevailing reaction conditions. Among the compounds that may result from the oxidation (or partial oxidation) of the organic substances present in the P&P effluents, aldehydes, ketones, carboxylic acids, and simple organic acids (such as formic acid and acetic acid) are particularly relevant (Kienle et al., 2022). However, it is worth mentioning that widely

recognized ozonation byproducts, such as bromate, have not been observed in ozonated effluents from P&P processes: a remarkable study by [De los Santos Ramos et al. \(2009\)](#) identified fumaric, maleic, malonic, and formic acids as the ultimate ozonation products. This mixture of acids is known to be biodegradable and nontoxic, showing limited environmental burdens. Additionally, a recent investigation demonstrated that the *Daphnia Magna* toxicity in ozonated streams is comparable to that of secondary effluents ([Mainardis et al., 2020](#)).

10.5 Conclusions and future trends

Nowadays, ozone is a widely applied technology in both the drinking water and wastewater sectors, to remove pathogens and oxidize refractory organic compounds, including emerging pollutants. Ozone is an excellent oxidant agent, and the oxidation reactions are performed both by the ozone molecule and the hydroxyl radicals produced during its decomposition. Ozone can be even exploited to improve sludge biodegradability for anaerobic digestion processes. However, ozone cost-effectiveness is often hindered by its limited solubility in water and the necessity to produce it on-site, requiring significant electric energy inputs and pure oxygen in cylinders (or, alternatively, on-site pure oxygen production). A wider application of ozone in full-scale wastewater treatment plants can be easily forecast in the near future, also due to the more stringent requirements for effluent discharge or reuse (e.g., UWWTD revision).

P&P WW, in particular, is generally characterized by a significant fraction of poorly biodegradable organic matter that cannot be removed by conventional biological processes, requiring tertiary treatment, which is often a physicochemical treatment of coagulation-flocculation at the industrial scale, to reach high-quality standards for discharge or reuse.

Ozone application to P&P effluents is still limited at full-scale conditions, but good efficiency in removing the recalcitrant COD fractions has been demonstrated in the scientific literature. The literature studies on ozonation performance in P&P WW treatment, despite being quantitatively limited, present a compelling narrative of the method's potential and efficacy in addressing the complex challenges of treating this specific industrial effluent. These findings collectively underline the potential of ozonation as a formidable solution for tertiary P&P WW treatment; on the contrary, given the specificity of each P&P factory, which in turn shapes the characteristics of the generated effluents, it is not always possible to draw general conclusions about the best position to install ozone and the required ozone dosages to get the desired pollutant removal efficiency. Thus,

specific investigations must be accomplished case by case at the WWTP level to get representative data before moving to full-scale applications.

The literature studies consistently demonstrate that ozonation is highly effective in removing various pollutants commonly found in P&P WW, such as lignin, color compounds, and organic matter (COD and TOC), even if in most cases it is not possible to obtain complete organic pollutant mineralization. The removal efficiency is not only substantial but also often superior to conventional treatment methods such as physicochemical coagulation–flocculation, showcasing its ability to tackle the specific contaminants present in these effluents. The coupling of ozonation with other processes, such as GAC filtration or catalysts, often leads to a further improvement in its effectiveness, reducing at the same time the related energy burdens, which are the main drawbacks still hindering a fast increase of full-scale ozone applications.

The comparative analyses with alternative treatment technologies reveal that ozonation often holds a competitive edge in terms of performance, making it a valuable choice for improved treatment outcomes. The economic burdens are mostly linked to the capital costs for ozone reactor installation, on the one hand, and the operating costs related to electricity consumption for ozone generation, on the other hand. The combination of ozone with other processes may allow for the reduction of the required ozone dosages, improving the economic balance. Possible revenues from effluent reuse, either as additional income due to industrial effluent selling or as savings in freshwater purchase for the upstream P&P mill, may be obtained when considering the higher effluent quality than that obtained with conventional technologies. As concerns the environmental aspects, the generation of harmful byproducts is limited in the specific case of P&P effluents, and the toxicity of the treated streams is typically comparable to that obtained after conventional biological processes. Furthermore, a remarkable reduction in sludge generation is observed in comparison to traditional physicochemical methods (e.g., coagulation–flocculation), with evident benefits on the treatment and disposal costs.

In summary, the available literature studies highlight the robust and reliable performance of ozonation in treating P&P WW, especially when coupled with other advanced processes such as biofiltration and GAC filtration. The conducted research provides a strong foundation for considering ozonation as a sustainable and efficient solution in this industrial context. However, additional studies are required to better prove the upscale feasibility of ozonation alone and combined processes (such as catalytic ozonation), as up to now most of the scientific studies have been conducted at a laboratory scale. A wider application of life cycle assessment methods can allow to compare in a standardized way alternative advanced treatment solutions for P&P effluents.

List of acronyms

AC	Activated carbon
AOP	Advanced oxidation process
ARB	Antibiotic-resistant bacteria
ARG	Antibiotic-resistant genes
BAT	Best available technologies
CAPEX	Capital expenditure
CAS	Chemical Abstracts Service
CEC	Contaminant of emerging concern
DPD	N,N-diethyl-p-phenylenediamine
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EEC	European Economic Community
EU	European Union
GAC	Granular activated carbon
GHG	Green-house gas
JRC	Joint Research Center
LOX	Liquid oxygen
M	Initial pollutant to be ozonized
M_{oxid}	Final product of the ozonation process
OPEX	Operating expenses
P&P	Pulp and paper
PSA	Pressure swing adsorption
UV	Ultraviolet
UWWTD	Urban wastewater treatment Directive
VPsA	Vacuum pressure swing adsorption
WW	Waste-water
WWTP	Waste-water treatment plant
X	Ozonation reaction intermediate

List of symbols

AOX	Adsorbable organic halogens
BOD₅	5-day biochemical oxygen demand
COD	Chemical oxygen demand
k_p	Reaction constant for pollutant removal
n	Stoichiometric factor
pH	Potential of hydrogen
R_t	Ozone solubility ratio
TOC	Total organic carbon
VOC	Volatile organic compounds

References

- Andoyo, R., Prawitasari, I. A. P., Mardawati, E., Cahyana, Y., Sukarminah, E., Rialita, T., Djali, M., Zaida, I. H., & Setiasih, I. S. (2018). Retention time of ozone at various water condition. *Journal of Physics: Conference Series*, 1080(1), 012033. <https://doi.org/10.1088/1742-6596/1080/1/012033>.

- Bader, H., & Hoigne, J. (1982). Determination of ozone in water by the indigo method; A submitted standard method. *Ozone: Science & Engineering*, 4(4), 169–176. <https://doi.org/10.1080/01919518208550955>.
- Bader, H., & Hoigné, J. (1981). Determination of ozone in water by the indigo method. *Water Research*, 15(4), 449–456. [https://doi.org/10.1016/0043-1354\(81\)90054-3](https://doi.org/10.1016/0043-1354(81)90054-3).
- Balcioğlu, I. A., & Moral, Ç. K. (2008). Homogeneous and heterogeneous catalytic ozonation of pulp bleaching effluent. *Journal of Advanced Oxidation Technologies*, 11(3). <https://doi.org/10.1515/jaots-2008-0314>.
- Bierbaum, S., Escabasse, J. Y., Well, B., Kompare, D., & Drev, A. (2012). Klemencic, reducing fresh water consumption in paper industry by recycling AOP-treated effluents. *Fresenius Environmental Bulletin*, 21.
- Bisio, G., Bosio, A., & Rubatto, G. (2002). Thermodynamics applied to oxygen enrichment of combustion air. *Energy Conversion and Management*, 43(18), 2589–2600. [https://doi.org/10.1016/s0196-8904\(01\)00194-7](https://doi.org/10.1016/s0196-8904(01)00194-7).
- Biń, A. (2006). Ozone solubility in liquids. *Ozone: Science and Engineering*, 28(2), 67–75. <https://doi.org/10.1080/01919510600558635>.
- Biń, A. K. (2004). Ozone dissolution in aqueous systems treatment of the experimental data. *Experimental Thermal and Fluid Science*, 28(5), 395–405. <https://doi.org/10.1016/j.expthermflusci.2003.03.001>.
- Bromberg, P. A. (2016). Mechanisms of the acute effects of inhaled ozone in humans. *Biochimica et Biophysica Acta - General Subjects*, 1860(12), 2771–2781. <https://doi.org/10.1016/j.bbagen.2016.07.015>, www.elsevier.com/locate/bbagen.
- Buchan, K. A. H., Martin-Robichaud, D. J., & Benfey, T. J. (2005). Measurement of dissolved ozone in sea water: A comparison of methods. *Aquacultural Engineering*, 33(3), 225–231. <https://doi.org/10.1016/j.aquaeng.2005.02.002>.
- Catenacci, A., Peroni, M., Gievers, F., Mainardis, M., Pasinetti, E., & Malpei, F. (2022). Integration of sludge ozonation with anaerobic digestion: From batch testing to scenario analysis with energy, economic and environmental assessment. *Resources, Conservation and Recycling*, 186, 106539. <https://doi.org/10.1016/j.resconrec.2022.106539>.
- Chavoshani, A., Hashemi, M., Amin, M. M., & Ameta, S. C. (2020). Pharmaceuticals as emerging micropollutants in aquatic environments. In *Micropollutants and challenges: Emerging in the aquatic environments and treatment processes*. Iran: Elsevier, 35–90. [10.1016/B978-0-12-818612-1.00002-7](https://doi.org/10.1016/B978-0-12-818612-1.00002-7), <https://www.elsevier.com/books/micropollutants-and-challenges/chavoshani/978-0-12-818612-1>.
- Council Directive of 21 May 1991 concerning Urban Waste Water Treatment. (1991). European Commission.
- Czekalski, N., Imminger, S., Salhi, E., Veljkovic, M., Kleffel, K., Drissner, D., Hammes, F., Bürgmann, H., & von Gunten, U. (2016). Inactivation of antibiotic resistant bacteria and resistance genes by ozone: From laboratory experiments to full-scale wastewater treatment. *Environmental Science & Technology*, 50(21), 11862–11871. <https://doi.org/10.1021/acs.est.6b02640>.
- De los Santos Ramos, W., Poznyak, T., Chairez, I., & Córdova, I. (2009). R., Remediation of lignin and its derivatives from pulp and paper industry wastewater by the combination of chemical precipitation and ozonation. *Journal of Hazardous Materials*, 169(1–3), 428–434. <https://doi.org/10.1016/j.jhazmat.2009.03.152>.
- Egorova, G. V., Voblikova, V. A., Sabitova, L. V., Tkachenko, I. S., Tkachenko, S. N., & Lunin, V. V. (2015). Ozone solubility in water. *Moscow University Chemistry Bulletin*, 70(5), 207–210. <https://doi.org/10.3103/s0027131415050053>.
- De Nora Water Technologies Italy S.r. (2023).
- Epelle, E. I., Macfarlane, A., Cusack, M., Burns, A., Okolie, J. A., Mackay, W., Rateb, M., & Yaseen, M. (2023). Ozone application in different industries: A review of recent

- Hermosilla, D., Merayo, N., Gascó, A., & Blanco, Á. (2015). The application of advanced oxidation technologies to the treatment of effluents from the pulp and

- paper industry: A review. *Environmental Science and Pollution Research*, 22(1), 168–191. <https://doi.org/10.1007/s11356-014-3516-1>.
- Hoigné, J., & Bader, H. (1983). Rate constants of reactions of ozone with organic and inorganic compounds in water—I: Non-dissociating organic compounds. *Water Research*, 17(2), 173–183. [https://doi.org/10.1016/0043-1354\(83\)90098-2](https://doi.org/10.1016/0043-1354(83)90098-2).
- Hoigné, J. (1998). *Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation processes*. Springer Science and Business Media LLC, 83–141. https://doi.org/10.1007/978-3-540-68089-5_5.
- Hostachy, J. C., Van Wyk, B., & Metcís, A. (2014). The use of ozone in the pulp and paper industry. *Paper Asia*, 30(2), 22–28.
- Hubbe, M. A., Metts, J. R., Hermosilla, D., Blanco, M. A., Yerushalmi, L., Haghghat, F., Lindholm-Lehto, P., Khodaparast, Z., Kamali, M., & Elliott, A. (2016). Wastewater treatment and reclamation: A review of pulp and paper industry practices and opportunities. *BioResources*, 11(3), 7953–8091. <https://doi.org/10.15376/biores.11.3.hubbe>.
- Iakovides, I. C., Michael-Kordatou, I., Moreira, N. F. F., Ribeiro, A. R., Fernandes, T., Pereira, M. F. R., Nunes, O. C., Manaia, C. M., Silva, A. M. T., & Fatta-Kassinos, D. (2019). Continuous ozonation of urban wastewater: Removal of antibiotics, antibiotic-resistant *Escherichia coli* and antibiotic resistance genes and phytotoxicity. *Water Research*, 159, 333–347. <https://doi.org/10.1016/j.watres.2019.05.025>.
- Ikehata, K., & Li, Y. (2018). Ozone-based processes. In *Advanced oxidation processes for wastewater treatment: Emerging green chemical technology*. United States: Elsevier Inc, 115–134. <http://www.sciencedirect.com/science/book/9780128104996>, <https://doi.org/10.1016/B978-0-12-810499-6.00005-X>.
- Kamali, M., & Khodaparast, Z. (2015). Review on recent developments on pulp and paper mill wastewater treatment. *Ecotoxicology and Environmental Safety*, 114, 326–342. <https://doi.org/10.1016/j.ecoenv.2014.05.005>.
- Kienle, C., Werner, I., Fischer, S., Lüthi, C., Schifferli, A., Besselink, H., Langer, M., McArdell, C. S., & Vermeirssen, E. L. M. (2022). Evaluation of a full-scale wastewater treatment plant with ozonation and different post-treatments using a broad range of in vitro and in vivo bioassays. *Water Research*, 212. <https://doi.org/10.1016/j.watres.2022.118084>, <http://www.elsevier.com/locate/watres>.
- Korotcenkov, G., Brinzari, V., & Cho, B. K. (2018). In2O3- and SnO2-based ozone sensors: Design and characterization. *Critical Reviews in Solid State and Materials Sciences*, 43(2), 83–132. <https://doi.org/10.1080/10408436.2017.1287661>, <http://www.tandf.co.uk/journals/titles/10408436.asp>.
- Lim, S., Shi, J. L., von Gunten, U., & McCurry, D. L. (2022). Ozonation of organic compounds in water and wastewater: A critical review. *Water Research*, 213. <https://doi.org/10.1016/j.watres.2022.118053>, www.elsevier.com/locate/watres.
- Loeb, B. L., Thompson, C. M., Drago, J., Takahara, H., & Baig, S. (2012). Worldwide ozone capacity for treatment of drinking water and wastewater: A review. *Ozone: Science and Engineering*, 34(1), 64–77. <https://doi.org/10.1080/01919512.2012.640251>, <http://www.tandf.co.uk/journals/titles/01919512.asp>.
- Lozina, A., Garkusha, I., Taran, A., Nezoviba'ko, Y., & Chechel'nitskyi, O. (2021). Development of ozone monitoring system in ozone-treated water. *Review of Scientific Instruments*, 92(12). <https://doi.org/10.1063/5.0073328>.
- Mainardis, M., Buttazzoni, M., De Bortoli, N., Mion, M., & Goi, D. (2020). Evaluation of ozonation applicability to pulp and paper streams for a sustainable wastewater treatment. *Journal of Cleaner Production*, 258, 120781. <https://doi.org/10.1016/j.jclepro.2020.120781>.
- Mainardis, M., Ferrara, C., Cantoni, B., Di Marcantonio, C., De Feo, G., & Goi, D. (2024). How to choose the best tertiary treatment for pulp and paper wastewater?

- Life cycle assessment and economic analysis as guidance tools. *Science of The Total Environment*, 906, 167598. <https://doi.org/10.1016/j.scitotenv.2023.167598>.
- Majewski, J. (2012). Methods for measuring ozone concentration in ozone-treated water. Wydawnictwo SIGMA - N O T Sp. z o.o. *Poland Przegląd Elektrotechniczny*, 88(9 B), 253–255. <http://www.pe.org.pl/archive.php?lang=1>.
- Maniakova, G., López, M. I. P., Oller, I., Malato, S., & Rizzo, L. (2023). Ozonation vs sequential solar driven processes as simultaneous tertiary and quaternary treatments of urban wastewater: A life cycle assessment comparison. *Journal of Cleaner Production*, 413, 137507. <https://doi.org/10.1016/j.jclepro.2023.137507>.
- McClurkin, J. D., Maier, D. E., & Ileleji, K. E. (2013). Half-life time of ozone as a function of air movement and conditions in a sealed container. *Journal of Stored Products Research*, 55, 41–47. <https://doi.org/10.1016/j.jspr.2013.07.006>.
- Merayo, N., Hermosilla, D., Blanco, L., Cortijo, L., & Blanco, Á. (2013). Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry. *Journal of Hazardous Materials*, 262, 420–427. <https://doi.org/10.1016/j.jhazmat.2013.09.005>.
- Michniewicz, M., Stufka-Olczyk, J., & Milczarek, A. (2012). Ozone degradation of lignin; Its impact upon the subsequent biodegradation. *Fibres and Textiles in Eastern Europe*, 96(6 B), 191–196. [http://www.fibtex.lodz.pl/file-Fibtex_\(ksq678azqqzbs3ap\).pdf-FTEE_96_191.pdf](http://www.fibtex.lodz.pl/file-Fibtex_(ksq678azqqzbs3ap).pdf-FTEE_96_191.pdf).
- Munir, H. M. S., Feroze, N., Ikhlaiq, A., Kazmi, M., Javed, F., & Mukhtar, H. (2019). Removal of colour and COD from paper and pulp industry wastewater by ozone and combined ozone/UV process. *Desalination and Water Treatment*, 137, 154–161. <https://doi.org/10.5004/dwt.2019.23186>, <http://www.deswater.com/readfulltextopenaccess.php?id=RFdUX2FydGJlbGVzL3ZvbF8xMzdfcGFwZXJzLzEzN18yMDE5XzE1NC5wZGY=>.
- Munir, H. M. S., Feroze, N., Ramzan, N., Sagir, M., Babar, M., Tahir, M. S., Shamshad, J., Mubashir, M., & Khoo, K. S. (2022). Fe-zeolite catalyst for ozonation of pulp and paper wastewater for sustainable water resources. *Chemosphere*, 297. <https://doi.org/10.1016/j.chemosphere.2022.134031>, <http://www.elsevier.com/locate/chemosphere>.
- Möbius, C. H., & Helble, A. (2004). Combined ozonation and biofilm treatment for reuse of papermill wastewaters. *Water Science and Technology*, 49(4), 319–323. <https://doi.org/10.2166/wst.2004.0294>.
- Oh, J. S., Yajima, H., Hashida, K., Ono, T., Ishijima, T., Serizawa, I., Furuta, H., & Hatta, A. (2016). In-situ UV absorption spectroscopy for observing dissolved ozone in water. *Journal of Photopolymer Science and Technology*, 29(3), 427–432. <https://doi.org/10.2494/photopolymer.29.427>, https://www.jstage.jst.go.jp/article/photopolymer/29/3/29_427/_pdf.
- OSI 125/250/500/1000 Oxygen Concentrator. Oxygen Solutions. (2019).
- Pekárek, S. (2003). Non-thermal plasma ozone generation. *Acta Polytechnica*, 43(6). <https://doi.org/10.14311/498>.
- Peyrelasse, C., Jacob, M., & Lallement, A. (2022). Multicriteria comparison of ozonation, membrane filtration, and activated carbon for the treatment of recalcitrant organics in industrial effluent: A conceptual Study. *Environmental Processes*, 9(1). <https://doi.org/10.1007/s40710-022-00563-1>.
- Proposal for a Directive of the European Parliament and the Council concerning Urban Waste Water Treatment (recast. European Commission. (2022).
- Rakness, K., Gordon, G., Langlais, B., Masschelein, W., Matsumoto, N., Richard, Y., Robson, C. M., & Somiya, I. (1996). Guideline for measurement of ozone concentration in the process gas from an ozone generator. *Ozone: Science and Engineering*, 18(3), 209–229. <https://doi.org/10.1080/01919519608547327>, <http://www.tandf.co.uk/journals/titles/01919512.asp>.

- Rakness, K. L., Hunter, G., Lew, J., Mundy, B., & Wert, E. C. (2018). Design considerations for cost-effective ozone mass transfer in sidestream systems. *Ozone: Science and Engineering*, 40(3), 159–172. <https://doi.org/10.1080/01919512.2018.1424532>, <http://www.tandf.co.uk/journals/titles/01919512.asp>.
- Rekhate, C. V., & Srivastava, J. K. (2020). Recent advances in ozone-based advanced oxidation processes for treatment of wastewater- A review. *Chemical Engineering Journal Advances*, 3, 100031. <https://doi.org/10.1016/j.cej.2020.100031>.
- Roudier, S., Kourti, I., Sancho, G.M. Suhr, S.G.K. (2015). *Best available techniques (BAT) reference document for the production of pulp, paper and board*. Publications Office of the European Union. <https://doi.org/10.2791/370629>.
- Rowland, F. S. (2006). Stratospheric ozone depletion. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 361(1469), 769–790. <https://doi.org/10.1098/rstb.2005.1783>, <http://rstb.royalsocietypublishing.org/>.
- Shlanta, A., & Moore, C. B. (1972). Ozone and point discharge measurements under thunderclouds. *Journal of Geophysical Research*, 77(24), 4500–4510. <https://doi.org/10.1029/jc077i024p04500>.
- Singh, P., Yadav, D., & Pandian, E. S. (2021). Link between air pollution and global climate change. In *Global Climate Change*. India: Elsevier, 79–108. <https://doi.org/10.1016/B978-0-12-822928-6.00009-5>, <https://www.sciencedirect.com/book/9780128229286>.
- von Sonntag, & Gunten (2012). *Chemistry of ozone in water and wastewater treatment: From basic principles to applications*. IWA Publishing. <https://doi.org/10.2166/9781780400839>.
- Staehelin, J., & Hoigne, J. (1985). Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environmental Science & Technology*, 19(12), 1206–1213. <https://doi.org/10.1021/es00142a012>.
- Standard Methods for the Examination of Water and Wastewater. (2022).
- Vázquez, M., Pallé, E., & Rodríguez, P. M. (2010). The earth in time. In M. Vázquez, E. Pallé, & P. M. Rodríguez (Eds.). *The earth as a distant planet: A Rosetta stone for the search of earth-like worlds* (pp. 35–105). Springer. https://doi.org/10.1007/978-1-4419-1684-6_2.
- Wang, J. L., & Xu, L. J. (2012). Advanced oxidation processes for wastewater treatment: Formation of hydroxyl radical and application. *Critical Reviews in Environmental Science and Technology*, 42(3), 251–325. <https://doi.org/10.1080/10643389.2010.507698>, <http://www.tandf.co.uk/journals/titles/10643389.asp>.
- Xu, P., Janex, M. L., Savoye, P., Cockx, A., & Lazarova, V. (2002). Wastewater disinfection by ozone: Main parameters for process design. *Water Research*, 36(4), 1043–1055. [https://doi.org/10.1016/S0043-1354\(01\)00298-6](https://doi.org/10.1016/S0043-1354(01)00298-6), <http://www.elsevier.com/locate/watres>.
- Xylem, Ozone in the Pulp & Paper Industry. (2012).
- Zhou, C., Zhang, J., Cai, Y., & Xiong, J. (2023). Catalytic ozonation for pulp and paper mill wastewater treatment: COD reduction and organic matter degradation mechanism. *Separations*, 10(3), 148. <https://doi.org/10.3390/separations10030148>.
- Zhuang, H., Guo, J., & Hong, X. (2018). Advanced treatment of paper-making wastewater using catalytic ozonation with waste rice straw-derived activated carbon-supported manganese oxides as a novel and efficient catalyst. *Polish Journal of Environmental Studies*, 27(1), 451–457. <https://doi.org/10.15244/pjoes/74483>.

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Advanced oxidation processes for pulp and paper wastewater treatment

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11.1 Introduction

The pulp and paper industry (PP) plays a crucial role in global economic development, supplying essential products for sectors such as packaging, printing, hygiene, footwear, and furniture. However, the industry generates approximately 700 million m³ of wastewater per year (Kumar & Verma, 2023). The composition of PP wastewater is influenced by raw materials and production processes, often resulting in complex mixtures of organic and inorganic pollutants (Shafeeyan, 2024).

The major organic constituents in PP wastewater include lignin, cellulose, hemicellulose, extractives, and additives, leading to high chemical oxygen demand (COD > 1 g·L⁻¹) and biochemical oxygen demand (BOD). Additionally, these wastewaters contain recalcitrant organic compounds such as terpenes, volatile organic compounds, sterols, tannins, chlorinated organics, furan, dioxins, and adsorbable organic halides (AOX). Inorganic contaminants in PP wastewater include brine salts, sulfites, sulfides, and heavy metals such as arsenic, chromium, iron, lead, nickel, and zinc (Kumar & Verma, 2023; Shafeeyan, 2024). Some of these pollutants pose significant environmental and health hazards due to their potential to cause cytotoxicity, mutagenicity, genotoxicity, hormonal interference, and endocrine disruption (Lindholm-Lehto et al., 2015; Ribeiro & Nunes, 2021; Sharma et al., 2022).

Treating PP wastewater is challenging due to its complex composition and recalcitrant nature. Conventional treatment methods, such as biological and physical-chemical processes, often have limited efficacy, especially under conditions of fluctuating wastewater quality and stringent regulatory standards (Ochando-Pulido et al., 2017; Trapido et al., 2017). Advanced oxidation processes (AOPs) are frequently explored as solutions to these challenges, aiming to break down and completely mineralize organic pollutants (Lindholm-Lehto et al., 2015). AOPs can be implemented independently or in conjunction with other technologies, enhancing the overall wastewater treatment efficiency. Furthermore, AOPs can be easily tailored to specific wastewater characteristics and operating conditions, making them versatile and adaptable to different industrial settings.

This chapter reviews the fundamentals of AOPs and their application in the treatment of PP wastewater. It discusses the principles, mechanisms, and factors influencing the efficiency of AOPs, and reviews successful case studies from the past decade. Finally, it outlines future challenges and research directions. By exploring the potential of AOPs as sustainable solutions for PP wastewater treatment, this chapter aims to contribute to the environmental sustainability of this key manufacturing sector, particularly regarding wastewater pollution control.

11.2 Fundamentals of advanced oxidation processes

Over the past decades, significant progress has been made in the research of AOPs, particularly in applications such as groundwater purification, soil remediation, volatile organic compound treatment, odor control, and, most extensively, water and wastewater treatment (Umair et al., 2023). This section provides a comprehensive understanding of the fundamental principles underlying the main AOPs applied in PP wastewater treatment.

11.2.1 Basic principles of advanced oxidation processes

AOPs are based on the supply or *in situ* generation of reactive oxygen species (ROS) with high oxidation capacities, which can degrade a wide range of organic and some inorganic pollutants. These ROS include non-radical oxidants such as hydrogen peroxide (H_2O_2 , redox potential (E) ranging between +0.77 and +1.77 V), peroxymonosulphate (PMS, $E=+1.75$ V), peroxydisulphate (PDS,

$E=+1.96$ V), or ozone (O_3 , $E=+2.07$ V), and free radicals including hydroxyl radical ($\cdot OH$, $E=+2.80$ V), sulfate radical ($SO_4^{\cdot -}$, $E=+2.40$ – 3.10 V), carbonate radical ($CO_3^{\cdot -}$, $E=+1.81$ V), hydroperoxyl radical ($\cdot O_2H$, $E=+1.48$ V), or superoxide radical ($\cdot O_2^-$, $E=+0.59$ V) (Guerra-Rodríguez et al., 2018; Phaniendra et al., 2015; Qiu et al., 2020; Roslan et al., 2024).

The detailed fragmentation pathways of many recalcitrant compounds during advanced oxidation remain a research challenge (Roslan et al., 2024). For a wide range of organic compounds, oxidation involves several pathways, including hydrogen addition, abstraction, and electron transfer (Lee et al., 2020). Regarding selectivity, different ROS exhibit varying levels of selectivity. For instance, PMS and PDS can directly oxidize alcohols, ketones, phenols, amines, and sulfides (Roslan et al., 2024). Ozone, another highly selective oxidant, preferentially reacts with compounds containing double bonds, aromatic moieties, and certain sulfur-containing compounds (Razumovskii & Zaikov, 1980). In contrast, hydroxyl radicals are highly reactive and non-selective, reacting with pollutants primarily through addition to double bonds, hydrogen abstraction, and electron transfer mechanisms (Ribeiro & Nunes, 2021). They have a very short half-time of approximately 20 ns and react with organic molecules at rates ranging between 10^8 – $10^{10} M^{-1} \cdot s^{-1}$ (Bokare & Choi, 2014; Feijoo et al., 2023). Conversely, sulfate radicals are slightly more selective than hydroxyl radicals, have a longer half-time (30–40 μs), and react more efficiently with compounds containing electron-rich functional groups such as amines and phenols (Lee et al., 2020; Li et al., 2019). Sulfate radicals mainly react through electron transfer processes but can also engage in hydrogen abstraction and addition reactions under certain conditions (Luo et al., 2017). The selectivity of these ROS can be exploited to target specific pollutants.

AOPs can also be categorised based on the route of ROS generation, distinguishing between chemical-based and energy-based AOPs, as shown in Fig. 11.1. Chemical-based AOPs rely on the addition of chemical oxidizing agents (e.g., H_2O_2 , O_3) to wastewater to generate radicals through chemical reactions. Examples of these processes include Fenton, ozonation, and sulfate radical-based processes. Energy-based AOPs comprise electrochemical, ultrasonic, and photochemical processes, which use radiation to increase ROS generation and enhance pollutant abatement. In most AOPs, catalysts play a crucial role in improving process efficiency by enhancing radical generation and even contributing to the regeneration of some ROS (Hassan et al., 2022; Jiang et al., 2023; Kumar & Verma, 2023; Roslan et al., 2024). Detailed

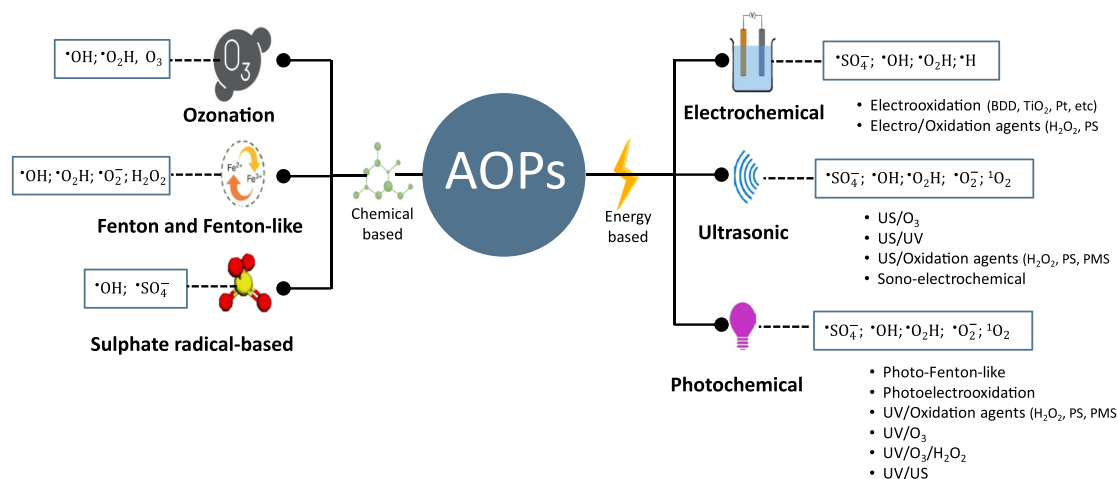


Figure 11.1 Advanced oxidation processes applied to pulp and paper industry wastewater treatment, and their main oxidant species.

discussion of the principles and mechanisms of the different AOPs is presented in [Section 11.3](#).

11.2.2 Factors influencing AOPs efficiency

The efficiency of AOPs is affected by several interrelated factors. Effective pollutant destruction depends not only on the availability of the oxidizing agents but also on factors such as hydrodynamics and the mass transfer of radicals within the system ([Umair et al., 2023](#)). Therefore understanding factors like wastewater composition, operating conditions, and reactor design and configuration, as well as their interactions ([Fig. 11.2](#)), is critical to optimizing the removal of contaminants from wastewater through AOPs.

11.2.2.1 Wastewater matrix

The efficiency of AOPs in treating wastewater is influenced by the concentration and nature of organic pollutants. Wastewater with high organic content often demands higher doses of chemicals, increased energy inputs, and longer reaction times to achieve the desired removal levels. Additionally, the presence of inorganic ions, suspended solids, and other matrix components can compete with target pollutants for ROS, thereby reducing their availability for degrading pollutants and decreasing AOPs efficiency.

Certain components in the wastewater matrix can influence the reaction kinetics of AOPs, as some may promote or inhibit the

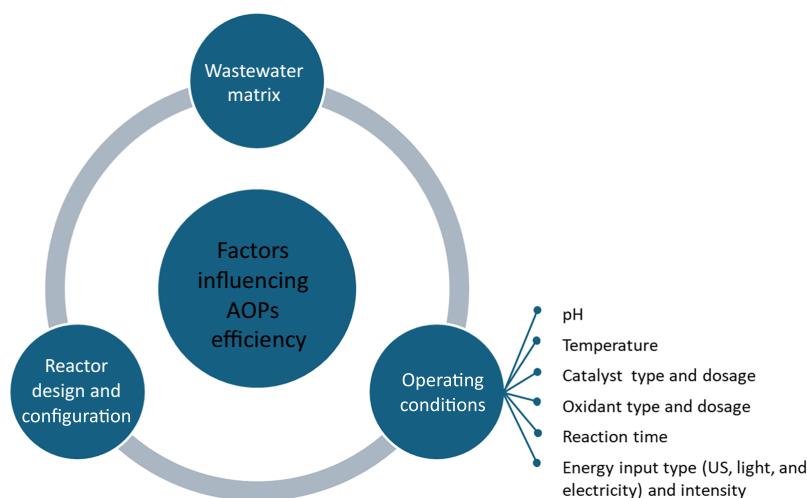


Figure 11.2 The main factors affecting the advanced oxidation processes efficiency.

formation of oxidizing radicals or even destroy them. For example, the presence of iron salts ($\text{Fe}^{2+}/\text{Fe}^{3+}$) in the wastewater can boost the formation of hydroxyl radicals in the Fenton process. Similarly, chloride ions (Cl^-) in electrooxidation processes favor the formation of chlorine-based oxidizing radicals. Conversely, Cl^- can act as radical scavenger in hydroxyl radical-based (HR-AOPs) and sulfate radical-based (SR-AOPs) processes, leading to decreased process efficiency (Lee et al., 2020). Other scavengers, such as carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-) ions, can react with $\cdot\text{OH}$ to form less reactive carbonate radicals, thereby reducing treatment performance. Moreover, different ROS may be affected by different scavenging species, each with distinct impacts on the degradation process. Treatment efficiency may also decrease due to the consumption of ROS by background organic matter (Lee et al., 2020). To address this issue, it may be advisable to implement a hybrid treatment approach, where background organic matter is first removed by a biological process before applying the AOP.

11.2.2.2 Operating conditions

Effective control of operating parameters is needed for maximizing AOP efficiency and ensuring stable treatment performance. Key operating conditions that influence AOP performance include:

- **pH:** each AOP has its optimum pH value. For instance, in HR-AOPs, hydroxyl radicals are typically formed in higher amounts

under acidic conditions, usually between 2.5 and 4.2 (Brink et al., 2018; Guo et al., 2018; Hermosilla et al., 2015). In SR-AOPs, pH affects the dissociation of the oxidant agents (PMS and PDS), and these processes operate efficiently over a wider pH range ($2 < \text{pH} < 8$) (Guerra-Rodríguez et al., 2018). Direct ozonation prevails at acidic pH, as ozone is less stable in alkaline conditions, while radical-driven ozonation prevails under alkaline conditions (Boczka & Fernandes, 2017; Mainardis et al., 2020). pH affects the speciation of pollutants, influencing their activity with oxidizing radicals, and can also impact the occurrence of side reactions, leading to the formation of undesired (potentially toxic) by-products.

- **Temperature:** higher temperatures usually promote faster reaction kinetics and radical production. However, excessively high temperatures can result in the thermal decomposition of reactants, decreased solubility of oxidant gases like O_3 , and reduced overall process efficiency.
- **Oxidant type and dosage:** different oxidants generate different oxidizing radicals with varying reactivity and selectivity. An adequate dosage of the oxidant ensures sufficient generation of oxidizing radicals for pollutant abatement. Insufficient dosage can lead to incomplete treatment and lower efficiency. However, there is an optimal concentration for each oxidant beyond which no significant increase in degradation efficiency is observed. Overdosing can lead to unnecessary chemical consumption, scavenging of radicals by excess oxidant, formation of unwanted by-products, and ultimately increased operating costs.
- **Catalyst type and dosage:** different catalysts can affect the generation rate and stability of oxidizing radicals. For example, iron-based catalysts are used in Fenton processes to produce $\cdot\text{OH}$ (Ribeiro et al., 2020), while cobalt or cerium-based catalysts might be employed in SR-AOPs (Hu & Long, 2016). The catalyst load must be judiciously selected; a deficiency can lead to insufficient reaction extent and oxidizing radicals production, while an excess can cause potential toxicity of residual catalysts, the formation of unwanted by-products such as sludge, and increased operating costs.
- **Treatment time:** the duration of AOP treatment determines the contact time between oxidizing species and pollutants, thereby influencing treatment efficiency. Longer reaction times may be required for wastewater with high pollutant loads or recalcitrant contaminants, while shorter treatment times may suffice for less complex wastewaters.
- **Energy input:** the most frequent energy burdens associated with AOPs are attributed to the supply of electric current, light, and/or

ultrasounds (US) to the wastewater, besides the energy consumed by auxiliary equipment (e.g., for wastewater stirring). In photochemical AOPs, radiation activates catalyst to produce oxidizing radicals (see [Section 11.3.4](#)). In electrochemical AOPs (eAOPs), electrical current is applied to electrodes to generate oxidizing radicals directly in the wastewater (see [Section 11.3.5](#)). In ultrasonic AOPs, US frequency, intensity, and the presence of acoustic cavitation play critical roles (see [Section 11.3.6](#)).

11.2.2.3 Reactor design and configuration

Easy contact between the reagents and effective mass transfer of oxidizing agents, catalysts, oxidizing radicals, and pollutants are essential for maximizing reaction rates in AOPs ([Umair et al., 2023](#)). Hydrodynamic conditions throughout the reactor dictate mass and heat transfer performance and consequently the distribution and effectiveness of the oxidizing radicals in the wastewater. Therefore the reactor type and design play a key role in the treatment's success. Stirred tanks are suitable for homogeneous AOPs where reactants and catalysts are in the liquid phase, and they are widely used for their simplicity and ability to provide uniform mixing ([Esteves et al., 2018](#); [Ribeiro et al., 2020](#); [Soriano-Molina et al., 2021](#)). Plug flow reactors are suitable for processes with specific reaction kinetics and are particularly efficient for reactions requiring longer contact times; they can be designed for both homogeneous and heterogeneous AOPs ([Liu et al., 2022](#)). Packed bed reactors are suitable for heterogeneous AOPs, allowing for enhanced solid catalyst stability and reusability ([Duarte et al., 2013](#)). The reactor's operation mode also impacts efficiency. Batch reactors typically have lower instrumentation costs, but higher operating costs compared to continuous reactors. Conversely, continuous operation offers higher throughput and consistency for large-scale applications.

For processes relying on external energy input, the reactor design must ensure even distribution of the energy to avoid hotspots or areas of insufficient exposure, which could reduce overall treatment efficiency. For example, in photochemical AOPs, factors such as lamp placement, reactor geometry, and light intensity distribution should be carefully considered to ensure uniform irradiation for efficient treatment. This aspect is particularly relevant in reaction media with high contents of suspended solids, such as PP wastewater. Similarly, in eAOPs, the location and configuration of electrodes (e.g., plates, cylinders) are critical design aspects.

Adequate monitoring of key operating parameters is essential for maintaining optimal reactor performance. Automated control systems, based on Industry 4.0 technologies and enhanced by machine learning algorithms, can monitor and adjust operating conditions in

real time, ensuring consistent treatment efficiency (Kumari & Kumar, 2023). Additionally, special care must be taken with the monitoring of heterogeneous catalysts' activity and the prevention of their deactivation. Regular regeneration or replacement of catalysts may be required. In eAOPs, electrode fouling and passivation can affect performance, so frequent inspection and cleaning of electrodes are necessary.

11.3 Application of AOPs in pulp and paper wastewater treatment

While all AOPs share a common underlying chemical principle, each has its own distinct activation pathways, degradation mechanisms, as well as unique strengths and limitations. The following subsections will explore these characteristics in the context of the most commonly used AOPs for pulp and paper wastewater treatment.

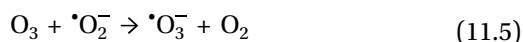
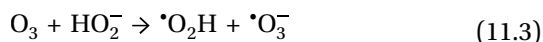
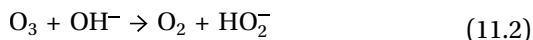
11.3.1 Ozonation

Ozone has been used in the treatment of complex industrial wastewater for many years, due to its very high redox potential ($E=+2.07$ V), effectiveness, and environmental friendliness when compared to other options (He et al., 2016). Ozone can break large molecules, producing more easily biodegradable compounds, making it suitable for coupling with biological treatment for optimal treatment efficiency (Mainardis et al., 2020; Martins & Quinta-Ferreira, 2014). Its preferential oxidation of electron-rich molecules containing carbon-carbon double bonds makes ozonation suitable to treat AOX and lignin-enriched wastewaters, as found in PP (Esmaeeli et al., 2023). Ozone is usually supplied to the wastewater via ozone generators, which dissociate molecular oxygen through electrical or photochemical methods, with the former often being more efficient (Feijoo et al., 2023). Owing to ozone's short half-life, its generation must be continuous (Esmaeeli et al., 2023).

Pollutant degradation by ozonation follows two pathways: direct and indirect. In the direct pathway, molecular ozone directly attacks specific contaminants through highly selective oxidation (Eq. 11.1) (Mainardis et al., 2020). This route is characterized by first-order kinetics and rate constants ranging between 10^{-3} and 10^9 $\text{M}^{-1}\cdot\text{s}^{-1}$ (Feijoo et al., 2023). Ozone oxidation of pollutants occurs through three main mechanisms: cycloaddition, electrophilic reaction, and nucleophilic mechanism. Rapid reaction between O_3 and the unsaturated bond of the organic compound results in bond cleavage (Saravanan et al., 2021). In aqueous media, ozone degrades into free

radicals which drive the indirect ozonation pathway (Eq. 11.2–11.8), characterized by low selectivity and fast reaction rates ranging from 10^9 to $10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$ (Feijoo et al., 2023).

The highly unstable unpaired electron in $\cdot\text{OH}$ makes it extremely reactive toward other molecules. $\cdot\text{OH}$ is a stronger oxidant than O_3 , which nonselectively attacks organic pollutants in the wastewater (Munir et al., 2022; Ribeiro et al., 2022a). Radical-driven indirect ozonation follows three steps: initiation reaction forming hydroperoxide anion from the decomposition of O_3 (Eq. 11.2); chain reactions where hydroperoxide anion and ozone react to form ozonide anion and hydroperoxyl radical ($\cdot\text{O}_2\text{H}$) (Eq. 11.3), leading to the subsequent formation of $\cdot\text{OH}$ (Eqs. 11.4–11.7); termination reactions, in which $\cdot\text{OH}$ react with organic pollutants (R) (Eq. 11.8) (Saravanan et al., 2021).

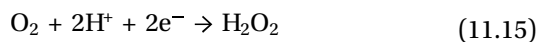
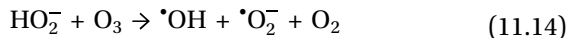
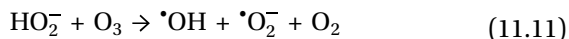
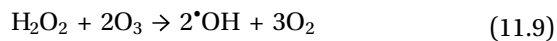


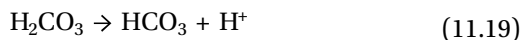
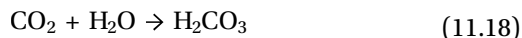
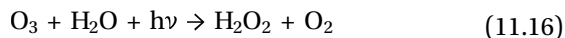
Besides the type and concentration of pollutants to degrade, two major operating conditions rule the efficiency of ozonation: ozone dosage and pH (Esmaeeli et al., 2023). Increasing ozone dosage directly favors pollutant oxidation (Eq. 11.1) and allows increased formation of radicals to break down the pollutant's chemical structure. Munir et al. (2019) studied the removal of COD and color from kraft pulping black liquor, finding that increasing the ozone dosage from 0.1 to $0.3 \text{ g}\cdot\text{L}^{-1}$ improved COD and color removals from 52% and 59% to 59% and 72%, respectively, after 180 minutes of treatment. Conversely, pH dictates the degradation pathway. In opposition to what is usually seen in H_2O_2 -dependent AOP, such as Fenton processes, ozonation performs well over a broader pH range. At acidic media ($\text{pH} < 4$), the direct ozonation route prevails, reacting selectively with compounds of high electronic density sites such as chromophore groups and unsaturated bonds (Martins & Quinta-Ferreira, 2014). For alkaline conditions, the radical-driven indirect ozonation route dominates, boosting reaction (Eq. 11.2) and leveraging chain reactions (Eqs. 11.2–11.7). Under such conditions,

the higher oxidation power and non-selectivity of $\cdot\text{OH}$ improve pollutant oxidation, making ozonation potentially more effective at alkaline conditions (Mainardis et al., 2020; Martins & Quinta-Ferreira, 2014; Munir et al., 2019).

Besides working at wide pH and temperature ranges and being highly effective in degrading organic and inorganic pollutants, ozonation offers other advantages such as avoiding external chemical input and sludge formation, providing strong germicidal activity, having minimal installation cost, and not increasing treated wastewater volume (Manna & Sen, 2023; Saravanan et al., 2021). However, ozonation presents a set of disadvantages that often hinder its full-scale applicability. One is the low mineralization achieved by this AOP, owing to the slow reaction and high selectivity of O_3 toward saturated carboxylic acid or nonactive aromatic organic contaminants, failing to degrade other biorefractory contaminants (Manna & Sen, 2023; Munir et al., 2022). Moreover, low molecular weight carboxylic acids generated as transformation products are usually refractory to further ozone oxidation (Martins & Quinta-Ferreira, 2014). Other drawbacks include high electricity demand, high operating costs, the need for adequate mixing due to ozone's instability and low solubility, and the requirement for adequate technology to deal with off-gases (Feijoo et al., 2023; Mainardis et al., 2020; Manna & Sen, 2023; Saravanan et al., 2021).

Several solutions have been explored to address ozonation's main challenges. One is the combination of O_3 with H_2O_2 , which can improve overall efficiency through enhanced $\cdot\text{OH}$ generation (Eq. 11.9) ($k = 150\text{--}4800 \text{ M}^{-1}\cdot\text{s}^{-1}$ at pH 7.0–8.5). Alternatively, H_2O_2 can dissociate into hydroperoxide anion (Eq. 11.10), which reacts with O_3 to yield $\cdot\text{OH}$ (Eq. 11.11) ($k = 9.6 \times 10^6 \text{ M}^{-1}\cdot\text{s}^{-1}$). Radical-driven reactions then attack refractory pollutants (k up to $10^6\text{--}10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$), aiming at complete mineralization into CO_2 and H_2O (Eq. 11.12–11.14) (Manna & Sen, 2023). Further $\cdot\text{OH}$ generation can be achieved by *in situ* electrochemical production of H_2O_2 from O_2 (Eq. 11.15), or ultraviolet (UV) irradiation (Eq. 11.16–11.17).





Munir et al. (2019) observed higher removal of COD and color (from 52% and 70% to 55% and 72%, respectively) from black liquor under O_3/UV combination at alkaline pH, compared to single ozonation, owing to increased $^\bullet\text{OH}$ generation and faster reaction between pollutants and radical species. The authors highlighted the variations in wastewater pH during treatment, due to the formation and dissolution of CO_2 during ozonation, leading to pH decay (Eq. 11.18–11.20). Conversely, the expected decomposition of H_2O_2 into H_2O and O_2 at alkaline conditions may have prevented a higher performance improvement. Therefore pH tuning is crucial to maximize efficiency gains from electro- or photo-ozonation.

The most cited technique to intensify ozonation is based on the addition of solid catalysts. Catalytic ozonation allows for better ozone utilization, higher mineralization degree, and fewer concerns regarding toxicity of the treated wastewater (Munir et al., 2022). Common catalysts consist of metal oxides such as Al_2O_3 , MnO_2 , TiO_2 , FeOOH , and bimetallic oxides (Manna & Sen, 2023). However, other materials such as activated carbon (AC), sand, zeolites, red mud, among others, have been successfully used as heterogeneous ozonation catalysts (Wang et al., 2019). A major advantage of using heterogeneous catalysts is that, unlike homogeneous ones, easy recovery from the wastewater can be performed, which is crucial in full-scale operations. A good catalyst must be resilient to premature deactivation, which is defined as the loss of activity and/or selectivity and is primarily caused by the leaching of active metal from the catalytic structure and by the deposition of carbonaceous impurities poisoning catalyst pores (Munir et al., 2022).

He et al. (2016) studied the treatment of biologically treated pulp and paper wastewater by ozonation catalysed by $0.2 \text{ g}\cdot\text{L}^{-1}$ of AC impregnated with iron. The authors observed significantly higher removal rates of COD and color (56% and 96%, respectively), compared with simple ozonation (35% and 87%, respectively) under similar operating conditions: $3 \text{ g}\cdot\text{h}^{-1}$ of ozone, 60 minutes of treatment, at 25°C and $\text{pH}=7.3$. Furthermore, the COD removal rate constant for $\text{Fe@AC}/\text{O}_3$ was approximately 1.6 times higher than for AC/O_3 and around 2.1 times higher for O_3 alone. This enhancement in performance was attributed to the increased generation of $^\bullet\text{OH}$

from ozone in the presence of Fe. Some intermediates such as carboxylic acid, oxalic acid, and formic acid, formed upon the degradation of aromatics can resist oxidation by ozone but not by $\cdot\text{OH}$ (Hermosilla et al., 2015).

Mo et al. (2020) also studied biologically treated wastewater and observed remarkable removal rates of 88.2% AOX, 80.2% COD, and 77.1% TOC (total organic carbon) after 25 minutes of treatment with $15 \text{ mg}\cdot\text{L}^{-1}$ of O_3 and $10 \text{ g}\cdot\text{L}^{-1}$ of $\text{La-TiO}_2/\text{Al}_2\text{O}_3$ catalyst, at $\text{pH}=8.0$ and room temperature. In comparison, single ozonation removed only 57.3% of AOX under the same operating conditions. The produced catalyst maintained its activity during three treatment cycles without regeneration, and calcination at 500°C increased its stability to another three cycles.

He et al. (2018) tested various catalysts in the treatment of PP wastewater. $\text{Cu-Ce}/\text{Al}_2\text{O}_3$ catalyst, prepared by an incipient impregnation method, offered the best performance, allowing for 61.5% TOC removal within 60 minutes of treatment with $0.3 \text{ g}\cdot\text{h}^{-1}$ of ozone and $2.0 \text{ g}\cdot\text{L}^{-1}$ of catalyst, at $\text{pH}=7.9$ and 25°C . Catalysts $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$ achieved 52.0% and 55.0% removal, while single ozonation yielded just 26.0%. This demonstrates the superiority of the radical pathway compared to direct ozonation at alkaline pH. In fact, wastewater pH (7.9) was close to the pH_{pzc} value of $\text{Cu-Ce}/\text{Al}_2\text{O}_3$ (8.15), where the hydroxyl groups at the surface of the catalysts are in a neutral state, favouring $\cdot\text{OH}$ generation and leading to the highest TOC removal. At lower pH, pollutant degradation relied mainly on O_3 oxidation, while at higher pH, repulsive electrostatic interactions between the negatively charged catalyst and the pollutants decreased overall performance. More results regarding the treatment of PP wastewater by ozonation are compiled in Table 11.1.

11.3.2 Fenton and Fenton-like processes

The Fenton process is based on the Fe^{2+} -catalysed dissociation of H_2O_2 into species of higher oxidative power, especially $\cdot\text{OH}$ (Eq. 11.21). Hydroxyl radicals show high nonselectivity and fast degradation of most organic pollutants ($k = 10^8\text{--}10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$) (Bokare & Choi, 2014; Feijoo et al., 2023). These properties make them suitable to degrade recalcitrant compounds found in PP wastewater, such as lignin or phenolic-derived compounds (Brink et al., 2017; Esmaeeli et al., 2023). The Fe^{3+} -catalysed reaction is often named the Fenton-like process (Eq. 11.22) and has also received much attention, despite being considerably slower than the Fe^{2+} -catalyzed Fenton due to the rate-limiting step of the reductive generation of Fe^{2+} from Fe^{3+} (Bolobajev et al., 2016a; Lal & Garg, 2017).

Table 11.1 Compilation of results reported on the application of ozonation process to real pulp and paper industry wastewater treatment.

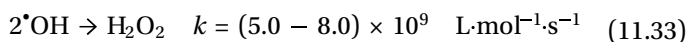
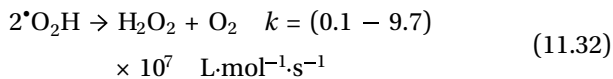
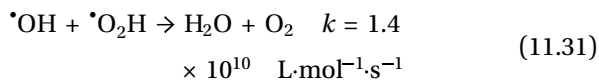
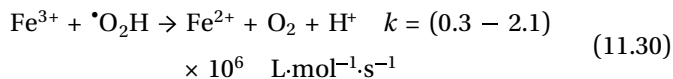
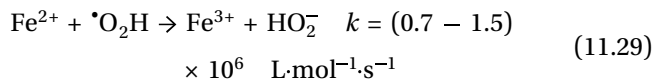
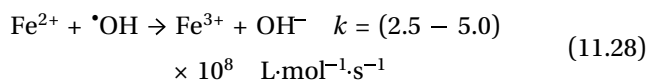
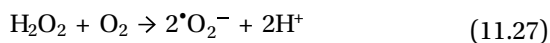
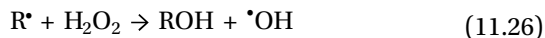
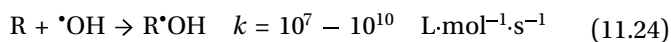
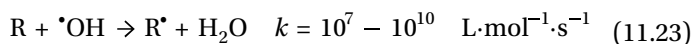
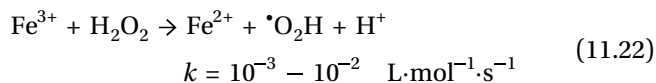
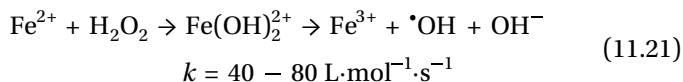
Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
$qO_3=0.14 \text{ g}\cdot\text{h}^{-1}$; $t=180 \text{ min}$; $\text{pH}=9.8$; $T=25^\circ\text{C}$	Black liquor	COD	52.0	Munir et al. (2019)	Ozonation
		Color	70.0		
$[O_3]=0.60 \text{ g}\cdot\text{L}^{-1}$; $t=360 \text{ min}$; $\text{pH}=6.8$; Room T	Pulp bleaching wastewater	COD	28.0	Mainardis et al. (2020)	Ozonation
		BOD	43.0		
$[O_3]=0.60 \text{ g}\cdot\text{L}^{-1}$; $t=360 \text{ min}$; $\text{pH}=7.1$; Room T	Paper desiccation wastewater	COD	64.1	Mainardis et al. (2020)	Ozonation
		BOD	74.0		
O_3 : $0.60 \text{ g}\cdot\text{L}^{-1}$; $t=360 \text{ min}$; $\text{pH}=6.9$; Room T	Mixed streams	COD	46.0	Mainardis et al. (2020)	Ozonation
		BOD	46.0		
$qO_3=3.0 \text{ g}\cdot\text{h}^{-1}$; $t=60 \text{ min}$; $\text{pH}=7.3$; $T=25^\circ\text{C}$	Biologically treated wastewater	COD	35.0	He et al. (2016)	Ozonation
		Color	87.0		
$qO_3=0.3 \text{ g}\cdot\text{h}^{-1}$; $t=60 \text{ min}$; $\text{pH}=7.9$; $T=25^\circ\text{C}$	Biologically treated wastewater	TOC	26.0	He et al. (2018)	Ozonation
$[O_3]=0.26 \text{ g}\cdot\text{L}^{-1}$; $t=8 \text{ min}$; $\text{pH}=9.0$; $T=50^\circ\text{C}$	Biologically treated wastewater	COD	6.4	Tang et al. (2020)	Ozonation
		BOD/COD	48.1%		
			increase		
$[O_3]=0.60 \text{ g}\cdot\text{L}^{-1}$; $t=360 \text{ min}$; $\text{pH}=6.9$; Room T	Biologically treated wastewater	Color	44.5	Mainardis et al. (2020)	Ozonation
		COD	81.0		
		BOD	63.0		
$qO_3=0.14 \text{ g}\cdot\text{h}^{-1}$; $t=180 \text{ min}$; $\text{pH}=9.8$; $T=25^\circ\text{C}$; UV-C lamp $12 \text{ W}\cdot\text{m}^{-2}$	Black liquor	COD	55.0	Munir et al. (2019)	Catalytic ozonation
		Color	72.0		
$[O_3]=0.30 \text{ g}\cdot\text{L}^{-1}$; $t=120 \text{ min}$; $\text{pH}=6.8$; Room T; Catalyst: Fe-impregnated natural zeolite= $10.0 \text{ g}\cdot\text{L}^{-1}$	Black liquor	COD	71.0	Munir et al. (2022)	Catalytic ozonation
		Color	89.0		

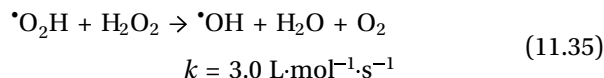
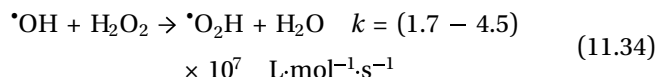
(Continued)

Table 11.1 (Continued)

Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
$q_{O_3}=3.0 \text{ g}\cdot\text{h}^{-1}$; $t=60 \text{ min}$; $\text{pH}=7.3$; $T=25^\circ\text{C}$; Catalyst: Fe-impregnated activated carbon= $0.2 \text{ g}\cdot\text{L}^{-1}$	Biologically treated wastewater	COD Color	56.0 96.0	He et al. (2016)	Catalytic ozonation
$q_{O_3}=0.3 \text{ g}\cdot\text{h}^{-1}$; $t=60 \text{ min}$; $\text{pH}=7.9$; $T=25^\circ\text{C}$; Catalyst: Cu- $\text{Al}_2\text{O}_3=5.0 \text{ g}\cdot\text{L}^{-1}$	Biologically treated wastewater	TOC	52.0	He et al. (2018)	Catalytic ozonation
$q_{O_3}=0.3 \text{ g}\cdot\text{h}^{-1}$; $t=60 \text{ min}$; $\text{pH}=7.9$; $T=25^\circ\text{C}$; Catalyst: Ce- $\text{Al}_2\text{O}_3=2.0 \text{ g}\cdot\text{L}^{-1}$	Biologically treated wastewater	TOC	55.0	He et al. (2018)	Catalytic ozonation
$q_{O_3}=0.3 \text{ g}\cdot\text{h}^{-1}$; $t=60 \text{ min}$; $\text{pH}=7.9$; $T=25^\circ\text{C}$; Catalyst: Cu-Ce/ $\text{Al}_2\text{O}_3=2.0 \text{ g}\cdot\text{L}^{-1}$	Biologically treated wastewater	TOC	61.5	He et al. (2018)	Catalytic ozonation
$[\text{O}_3]=0.02 \text{ g}\cdot\text{L}^{-1}$; $t=25 \text{ min}$; $\text{pH}=8$; Room T; Catalyst: La- $\text{TiO}_2/\text{Al}_2\text{O}_3=10 \text{ g}\cdot\text{L}^{-1}$	Biologically treated wastewater	AOX TOC	88.6 77.1	Mo et al. (2020)	Catalytic ozonation
$[\text{O}_3]=0.02 \text{ g}\cdot\text{L}^{-1}$; $t=8 \text{ min}$; $\text{pH}=9.0$; $T=25^\circ\text{C}$; Catalyst: TiO_2 fixed in a sponge carrier= 7.5% of the wastewater volume	Biologically treated wastewater	COD BOD/COD Color Solids	80.2 52.0 42.3% increase 95.6 65.2	Zhou et al. (2023)	Catalytic ozonation

Overall homogeneous Fenton chemistry can be described by Eq. 11.21–11.36 (Ribeiro & Nunes, 2021). The degradation of organic pollutants (R) by $\cdot\text{OH}$ is governed by hydrogen abstraction (Eq. 11.23); hydroxylation (Eq. 11.24); radical interaction (Eq. 11.31–11.36); and electron transfer, which is also driven by high-valence iron intermediates generated through the absorption of visible light by the complex $\text{Fe}(\text{OH})_2^{2+}$ (ferryl species $\text{Fe}(\text{IV})$) (Feijoo et al., 2023; Lal & Garg, 2017; Ribeiro & Nunes, 2021; Ribeiro et al., 2020). Fenton degradation pathways lead to the formation of lower molecular weight compounds, including short-linear aliphatic carboxylic and dicarboxylic acids, which can ultimately be mineralized to CO_2 (Garcia-Segura et al., 2016; Munoz et al., 2014).





Besides $\cdot\text{OH}$, other oxidative species of lower redox potential may arise from Fenton chain reactions, such as hydroperoxyl radical $\cdot\text{O}_2\text{H}$ ($E=+1.48$ V) or superoxide radical $\cdot\text{O}_2^-$ ($E=+0.59$ V) (Eqs. 11.22, 11.27, and 11.34). Lal and Garg (2017) investigated the contributions of different radicals during the Fenton treatment of pulping effluent, observing an 83.3% decrease in TOC removal upon the addition of an $\cdot\text{OH}$ scavenger (tert-butyl alcohol), and a 93.8% decrease when an $\cdot\text{O}_2\text{H}$ and $\cdot\text{O}_2^-$ scavenger was also added (chloroform). These results highlight the predominance of $\cdot\text{OH}$ as the Fenton process main oxidant species. Furthermore, coagulation by ferric hydroxo-complexes may also contribute to the overall Fenton performance (Esmaeeli et al., 2023). It is expected that oxidation rules the process at higher $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios, while coagulation may add a significant contribution at lower $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios (Feng et al., 2010; Umar et al., 2010).

The efficiency of Fenton processes is mainly ruled by the operating conditions, namely oxidant and catalyst concentrations, pH, temperature, and treatment time (e.g., Zhang et al. (2019)). Generally, it may be stated that higher H_2O_2 and Fe loads allow for improved performance owing to increased $\cdot\text{OH}$ generation (Brink et al., 2017; Ribeiro & Nunes, 2021). However, excessive loads can have a counterproductive effect, due to the scavenging of $\cdot\text{OH}$ by H_2O_2 , Fe, or other ROS through Eq. 11.28–11.35 (Brink et al., 2017; Guo et al., 2018; He & Zhou, 2017; Ramos et al., 2019). One way to prevent this is the staged addition of H_2O_2 during treatment, which alleviates the sharp increase in H_2O_2 concentration and subsequent $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ formation during the initial oxidation stages, thus avoiding scavenging side reactions (Munoz et al., 2014; Wang et al., 2016). Excess iron also increases ferric sludge formation, a potentially toxic by-product that is usually landfilled, incinerated, or used in cement solidification, resulting in high disposal costs and the possibility of secondary pollution (Yu et al., 2022; Zhang et al., 2017). Both Abedinzadeh et al. (2018) and Brink et al. (2018) described the treatment of biologically pre-treated PP wastewater by the Fenton process and observed a decrease in COD reduction above a certain optimal threshold of H_2O_2 and Fe^{2+} concentration, owing to radical scavenging.

Fenton process shows maximum efficiency at acidic pH ranging 2.5–4.2 (Brink et al., 2018; Guo et al., 2018; Hermosilla et al., 2015). Lower pH will favor the generation of complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, which reacts more slowly with H_2O_2 (Babuponnusami & Muthukumar, 2014). Moreover, excessive H^+ will scavenge $\cdot\text{OH}$ (yielding water) and stabilize H_2O_2 to H_3O_2^+ , inhibiting the regeneration of Fe^{2+} (Brink et al., 2018; Guo et al., 2018). Conversely, at alkaline pH, catalytic performance is hindered through iron precipitation as $\text{Fe}(\text{OH})_3$, and H_2O_2 decomposition into O_2 and H_2O is favored (Brink et al., 2018; Ribeiro & Nunes, 2021). A decrease in wastewater pH is often observed during Fenton treatment, explained by the degradation of aromatics by hydroxylation of the aromatic ring and subsequent formation of short-chain carboxylic acids, including maleic acid, fumaric acid, oxalic acid, acetic acid, and formic acid (Brink et al., 2017).

Although higher temperature increases process kinetics, the decomposition of H_2O_2 into O_2 and H_2O increases approximately 2.2 times for every 10°C in the range of 20°C – 100°C (Bautista et al., 2008; Lucas & Peres, 2009; Wang et al., 2010). Lal and Garg (2017) reported over 90% H_2O_2 degradation at 40°C – 60°C , compared to approximately 70% degradation at 30°C . Finally, longer treatment times may allow for higher removal of pollutants, but require larger reactor volumes, which can be problematic for industries generating large amounts of wastewater, such as PP.

The ongoing interest in the Fenton process is justified not only by its recognized efficacy in treating recalcitrant pollutants (M'Arimi et al., 2020; Miklos et al., 2018), but also by several advantages making it attractive for full-scale application, including effectiveness under ambient conditions, relying on readily available and easy-to-handle chemicals, low capital costs, and short reaction time (Abedinzadeh et al., 2018; Anotai et al., 2018; Ochando-Pulido et al., 2017). However, two major drawbacks are often cited: (1) the high demand for chemicals, resulting in high operating costs (Belalcázar-Saldarriaga et al., 2018; Gümüş & Akbal, 2016); (2) the generation of large amounts of ferric sludge, which requires adequate management (Anotai et al., 2018; Ochando-Pulido et al., 2017).

Several upgrades were proposed to the classical Fenton process to address its drawbacks. Although iron is advantageous due to its abundance and low toxicity, the consumption of Fe^{2+} (Eq. 11.21) has a kinetic rate constant over 300-fold higher than its regeneration from Fe^{3+} (Eq. 11.22). Other metallic species have been proposed to replace Fe in Fenton-like processes. For instance, Cu, Co, and Mn were tested by Ribeiro et al. (2022a) as Fenton co-catalysts. Up to 25% of Fe^{2+} was successfully replaced by those metals, allowing for 85%–90% AOX removal from pulp bleaching wastewater within 10 minutes of treatment.

A viable strategy to widen the working pH range is the use of chelating agents, which form complexes with iron ions or participate in redox reactions, resulting in the autocatalytic transformation of iron. These organic ligands (L) may contribute to the: (1) photolysis of Fe^{3+} -L complexes; (2) formation of high-valent iron complexes which are stabilised by L; (3) reduction of Fe^{3+} by neutral organic molecules; (4) oxidation of Fe^{2+} by organic radicals or carbo-cations (Bolobajev et al., 2016b). Huang et al. (2021) studied the interaction between ethylenediamine-*N,N'*-disuccinic acid and Fe^{3+} in the treatment of PP wastewater. The authors observed a 38.5% degradation of 2,4-dichlorophenol after 120 minutes of the modified Fenton-like process at pH=7. Bolobajev et al. (2016b) successfully included tannic acid in the removal of 2,4,6-trichlorophenol from wastewater by Fenton-like process. By reducing Fe^{3+} to Fe^{2+} , tannic acid enhanced the activation of H_2O_2 , leading to 78% dichlorination within 120 minutes of treatment, compared to only 2% with $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. Moreover, tannic acid favored the reduction of Fe^{3+} dissolved from the ferric sludge at acidic pH, which can allow its valorization as Fenton catalyst.

In the last years, increasing research efforts have been dedicated to heterogeneous Fenton catalysis, which allows the operation at milder pH conditions, minimize ferric sludge formation, and enables easy recovery of the catalyst after treatment (Ganiyu et al., 2018; Thomas et al., 2021). The heterogeneous Fenton process relies on the production of $\cdot\text{OH}$ through Fe present both on the catalyst surface and in the bulk solution (Ribeiro & Nunes, 2021; Vorontsov, 2019). Adsorption of pollutant molecules at the active sites of the catalyst surface may also contribute to the overall degradation (Kakavandi & Ahmadi, 2019; Sruthi et al., 2018). However, heterogeneous Fenton is not free of challenges and has been associated with higher demand of H_2O_2 ; lower kinetics limited by mass transfer of H_2O_2 to the active sites on the catalyst surface and by the lower reaction between H_2O_2 and Fe^{3+} ; potential formation of catalyst agglomerates, which reduces free surface availability (Garcia-Segura et al., 2016; Ribeiro et al., 2022b; Wang et al., 2016).

Seesuriyachan et al. (2015) used iron powder as a Fenton catalyst in the treatment of Kraft lignin, observing optimal efficiency using a combination of 0.14 mM of Fe^0 , 0.78 mM of Fe^{2+} , and 0.26 mM of Fe^{3+} . Adding 11.1 mM of H_2O_2 , the authors achieved complete COD elimination and 98.5% lignin degradation within 4 hours. The application of residual iron dust from metallurgical industry as a heterogeneous Fenton catalyst was described in (Ribeiro et al. (2022b)). In that work, similar AOX removal was achieved compared with homogeneous Fenton: around 66% within 10 minutes of treatment using 100 mM of H_2O_2 . That solution allowed for up to

11% savings in the operating cost of treatment and maintained catalytic stability for two consecutive treatment cycles. Afterwards, catalyst deactivation occurred, and efficiency decayed. [Dos Santos et al. \(2021\)](#) reported similar results upon catalysis of the Fenton process with steel nails, reporting decreased efficacy after the first cycle of surface water treatment. The authors attributed that result to the formation of a passive oxide layer on the catalyst surface, reducing the concentration of available reactive Fe sites.

[Table 11.2](#) shows a compilation of relevant research on the application of Fenton and Fenton-like processes to real PP wastewater treatment over the last decade.

11.3.3 Sulfate radical-based processes

SR-AOPs are based on the generation of sulfate radicals ($\text{SO}_4^{\bullet-}$), with E ranging between +2.43 and +3.10 V, depending on pH ([Feijoo et al., 2023](#)). These processes have recently been studied for degrading both biodegradable and nonbiodegradable organic compounds in water and wastewater ([Giannakis et al., 2021](#); [Lin et al., 2022](#); [Wacławek et al., 2017](#)). To generate $\text{SO}_4^{\bullet-}$, a precursor such as peroxymonosulphate (PMS, SO_5^{2-}) or peroxydisulphate (PDS or PS, $\text{S}_2\text{O}_8^{2-}$) must be supplied externally and activated ([Lee et al., 2020](#)). Conventional activation methods include thermal activation, solar radiation, ultrasonic radiation, and electricity ([Eq. 11.37–11.38](#)). Additionally, carbon materials and low-valent transition metals (M) have also been extensively studied as activation methods, including Fe^{2+} , Cu^{2+} , or Ag^+ ([Eq. 11.39–11.40](#)) ([Feijoo et al., 2023](#); [Lee et al., 2020](#); [Li et al., 2022](#); [Wacławek et al., 2017](#)). Regardless of the activation method, precursors are always activated by breaking the peroxide bond (O-O bond) in the peroxydisulfate anion.

Special emphasis was given to thermal, solar, and US activation of PDS, to maximize the generation of $\text{SO}_4^{\bullet-}$ (two moles per mole of precursor, according to [Eq. 11.37](#)) in an economical and environmentally friendly way. Another major difference between the two precursors is that PDS only generates $\text{SO}_4^{\bullet-}$ radicals, while PMS also generates $\bullet\text{OH}$ radicals, according to [Eq. 11.37–11.40](#) ([Wacławek et al., 2017](#)). Although both radical species are highly oxidative, $\text{SO}_4^{\bullet-}$ presents a much longer half-life (30–40 μs), compared to $\bullet\text{OH}$ (20 ns) ([Giannakis et al., 2021](#)). While $\bullet\text{OH}$ contributes to electron transfer, hydroxylation, and hydrogen abstraction reactions, $\text{SO}_4^{\bullet-}$ mainly contributes to electron transfer reactions, explaining its longer half-life compared to $\bullet\text{OH}$ ([Varank et al., 2020](#)).

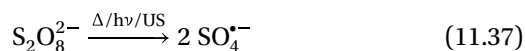
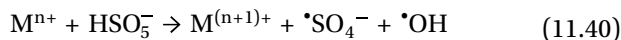
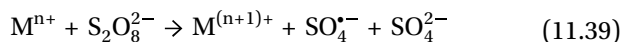
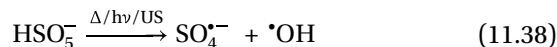


Table 11.2 Compilation of results reported on the application of Fenton and Fenton-like process to real pulp and paper industry wastewater treatment.

Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
[H ₂ O ₂]=235.2 mM; [Fe ²⁺]=21.5 mM (as FeSO ₄ ·7H ₂ O); t=50 min; pH=4.0; T=20°C	Raw PP wastewater	COD	53.8	Olabi (2023)	Fenton
[H ₂ O ₂]=29.4 mM; [Fe ²⁺]=22.4 mM (as FeSO ₄ ·7H ₂ O); t=60 min; pH=7.3; T=24°C	Pulp bleaching wastewater	COD	62.4	Sevimli et al. (2014)	Fenton
[H ₂ O ₂]=22.5 mM; [Fe ²⁺]=0.35 mM (as FeSO ₄ ·7H ₂ O); t=120 min; pH=2.6; Room T	Pulp bleaching wastewater	COD	50.0	Singh and Garg (2019)	Fenton
[H ₂ O ₂]=169.0 mM; [Fe ²⁺]=12.5 mM (as FeSO ₄ ·7H ₂ O); t=10 min; pH=2.0; T=60°C	Pulp bleaching wastewater	AOX	82.2	Ribeiro et al. (2020)	Fenton
		COD	8.0		
		BOD/COD	80% increase		
[H ₂ O ₂]=139.0 mM; [Fe ²⁺]=6.0 mM (as FeSO ₄ ·7H ₂ O); t=10 min; pH=2.8; T=60°C	Pulp bleaching wastewater	AOX	82.0	Ribeiro et al. (2022a)	Fenton
		COD	63.8		
[H ₂ O ₂]=489.0 mM; [Fe ²⁺]=9.3 mM (as FeSO ₄ ·7H ₂ O); t=49 min; pH=3.0; Room T	Pulp bleaching wastewater (after biological treatment)	AOX	82.7	Morim et al. (2024)	Fenton
		COD	68.9		
[H ₂ O ₂]=9.0 mM; [Fe ²⁺]=3.0 mM (as FeSO ₄ ·7H ₂ O); t=30 min; pH=3.0; T=25°C	Biologically treated (SBR) wastewater	COD	92.1	Abedinzadeh et al. (2018)	Fenton
		Color	90.3		
[H ₂ O ₂]=13.2 mM; [Fe ²⁺]=3.6 mM (as FeSO ₄ ·7H ₂ O); t=60 min; pH=3.8; T=25°C	Biologically treated (MBBR) recycle mill wastewater	COD	63.0	Brink et al. (2017)	Fenton
		Phenol	> 85.0		
[H ₂ O ₂]=92.7 mM; [Fe ²⁺]=3.6 mM (as FeSO ₄ ·7H ₂ O); t=60 min; pH=3.8; T=25°C	Biologically treated (MBBR) neutral sulfite semi chemical	COD	44.0	Brink et al. (2017)	Fenton
		Phenol	> 85.0		

[H ₂ O ₂]=139.0 mM; [Fe ²⁺]=4.5 mM (as FeSO ₄ ·7H ₂ O); [Co ²⁺]=1.5 mM (as CoSO ₄ ·7H ₂ O); <i>t</i> =10 min; pH=2.8; <i>T</i> =60°C	Pulp bleaching wastewater	AOX COD	85.2 62.9	Ribeiro et al. (2022a)	Fenton-like
[H ₂ O ₂]=139.0 mM; [Fe ²⁺]=4.5 mM (as FeSO ₄ ·7H ₂ O); [Cu ²⁺]=1.5 mM (as CuSO ₄ ·5H ₂ O); <i>t</i> =10 min; pH=2.8; <i>T</i> =60°C	Pulp bleaching wastewater	AOX COD	88.1 63.3	Ribeiro et al. (2022a)	Fenton-like
[H ₂ O ₂]=139.0 mM; [Fe ²⁺]=4.5 mM (as FeSO ₄ ·7H ₂ O); [Mn ²⁺]=1.5 mM (as MnSO ₄ ·H ₂ O); <i>t</i> =10 min; pH=2.8; <i>T</i> =60°C	Pulp bleaching wastewater	AOX COD	86.7 54.3	Ribeiro et al. (2022a)	Fenton-like
[H ₂ O ₂]=98.0 mM; [Fe ^{2/3+}]=4.9 mM (dissolved after coagulation); <i>t</i> =30 min; pH=4.0; <i>T</i> =30°C	After coagulation with FeCl ₃	TOC Lignin	48.0 85.0	Lal and Garg (2017)	Fenton-like
[H ₂ O ₂]=14.6 mM; [Fe ³⁺]=4.1 mM (as Fe ₂ (SO ₄) ₃ ·3H ₂ O); <i>t</i> =60 min; pH=3.3; <i>T</i> =25°C	Biologically treated (MBBR) recycle mill wastewater	COD	53.7	Brink et al. (2018)	Fenton-like
[H ₂ O ₂]=30.0 mM; [Fe ²⁺]=1.0 mM (as FeSO ₄ ·7H ₂ O); <i>t</i> =180 min; pH=3.0; <i>T</i> =25°C; 308 g·L ⁻¹ of construction sand bed	Biologically treated (activated sludge)	COD Color	56.3 74.8	Anotai et al. (2018)	Fluidised bed Fenton
[H ₂ O ₂]=235.2 mM; Fe ⁰ =1.0 g·L ⁻¹ ; <i>t</i> =50 min; pH=4.0; <i>T</i> =20°C	Raw wastewater	COD	53.8	Olabi (2023)	Heterogeneous Fenton
[H ₂ O ₂]=11.1 mM; [Fe ⁰]=0.136 mM (as iron powder); [Fe ²⁺]=0.78 mM (as FeSO ₄ ·7H ₂ O); Fe ³⁺ =0.26 mM (as Fe ₂ (SO ₄) ₃); <i>t</i> =240 min; pH=3.0; <i>T</i> =35°C	Kraft Lignin	COD Aromatics Lignin	100 82.6 98.5	Seesuriyachan et al. (2015)	Heterogeneous Fenton
[H ₂ O ₂]=29.4 mM; [Fe ⁰]=8.9 mM; <i>t</i> =120 min; pH=3.0; <i>T</i> =24°C	Pulp bleaching wastewater	COD	58.4	Sevimli et al. (2014)	Heterogeneous Fenton
[H ₂ O ₂]=76.0 mM; Fe ⁰ =2.0 g·L ⁻¹ ; <i>t</i> =60 min; pH=2.7; <i>T</i> =60°C	Pulp bleaching wastewater	AOX	85.0	Erhardt et al. (2021)	Heterogeneous Fenton
[H ₂ O ₂]=100.0 mM; Residual iron dust=5.0 g·L ⁻¹ ; <i>t</i> =40 min; pH=2.2; <i>T</i> =60°C	Pulp bleaching wastewater	AOX COD	66.2 34.6	Ribeiro et al. (2022b)	Heterogeneous Fenton
[H ₂ O ₂]=7.1 mM; Cu ₂ O powder=2.0 g·L ⁻¹ ; <i>t</i> =60 min; pH=7.0; <i>T</i> =30°C	Biologically treated	COD	77.0	Zhou et al. (2018)	Heterogeneous Fenton-like



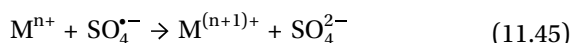
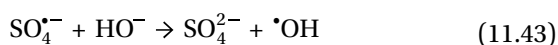
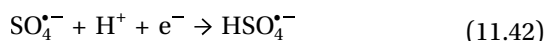
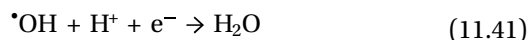
PDS is available as sodium, potassium, and ammonium salts with low solubility, characterized by a bond length of 1.497 Å and a bond dissociation energy of 140 kJ·mol⁻¹ (Wang et al., 2022). Among these, sodium persulphate (Na₂S₂O₈) is often preferred for *in situ* chemical oxidation due to its high water solubility (730 g·kg⁻¹ at 25°C). PMS, derived from Caro's acid (H₂SO₅), is typically found in a stable white triple salt (2KHSO₅·KHSO₄·K₂SO₄) commercialized as Oxone. Despite its higher cost, PMS is highly water-soluble, safe to handle, and versatile. It has a shorter bond length (1.463 Å) and a higher bond dissociation energy (377 kJ·mol⁻¹) compared to PDS, indicating it requires more energy for radical production (Feijoo et al., 2023; Giannakis et al., 2021; Wacławek et al., 2017).

SR-AOPs offer several advantages including: (1) high oxidation potential; (2) longer radical lifetime; (3) high reactivity across a wide pH range (2–8); (4) fast reaction rates; (5) fewer transportation issues; and (6) reduced environmental impact, since it relies on chemicals not classified as pollutants (Gholami et al., 2017a; Lin et al., 2022). Conversely, the main limitations associated with SR-AOPs are: (1) higher demand for PMS/PDS compared to H₂O₂ in Fenton process; (2) probability of toxic by-products formation in the presence of halogenated compounds; (3) enrichment of the wastewater with residual cations, needing further treatment; and (4) the higher cost of PDS compared to, for instance, H₂O₂ (Feijoo et al., 2023; Wacławek et al., 2017).

The key factor determining the efficiency of SR-AOPs is the activation method (Guvenc et al., 2022; Wang et al., 2022). Fe²⁺ is the most used metal for homogeneous chemical activation (Wacławek et al., 2017). Can-Güven et al. (2021) and Guvenc et al. (2022) compared the effectiveness of Fe²⁺-activated PDS with heat-activated PDS for treating PP wastewater, reaching contrasting results. Can-Güven et al. (2021) achieved higher removal efficiencies with Fe²⁺-activated persulphate, while Guvenc et al. (2022) reported better results with heat-activated PDS, even at a lower temperature. Higher temperatures are expected to promote the formation of more SO₄^{•-}, but this does not necessarily mean higher removal efficiency; in fact, excessive temperatures can lead to the self-destruction of SO₄^{•-} (Guvenc et al., 2022). One possible explanation for such conflicting observations may lie in pH, which controls free radical activity and key catalytic functions, including the speciation of iron

catalysts. While [Guven et al. \(2022\)](#) performed their work at pH=5, [Can-Güven et al. \(2021\)](#) adopted pH=3, which is more favorable to Fe^{2+} availability and ROS catalytic generation. The effects of pH on $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ are further described by [Eq. 11.41–11.44](#), including the dual radical generation of PMS: $\text{SO}_4^{\bullet-}$ in acidic medium, and $\bullet\text{OH}$ in alkaline medium.

Despite the good results, using heat to activate PMS has drawbacks, including high energy consumption and lengthy, uncontrollable processing times. Similarly, Fe^{2+} activation produces substantial iron sludge requiring further processing. Moreover, excessive activator dose may lead to radical scavenging, as described in [Eq. 11.45](#).



Activation through UV radiation has the advantage of providing the necessary energy without generating secondary pollutants ([Feijoo et al., 2023](#); [Wang et al., 2018, 2022](#)). [Wang et al. \(2022\)](#) studied the use of UV irradiation to activate PMS and H_2O_2 for removing COD from post-biological PP wastewater. The UV/PMS process achieved higher removal efficiency (64.3%) than UV/ H_2O_2 (48.2%), resulting in higher quality effluent. These results were attributed to the lower peroxide binding energy of PMS (1.463 Å), which made it easier to activate with UV irradiation compared to H_2O_2 (1.458 Å). Additionally, the intensity of UV irradiation played a significant role by providing enough energy to break the peroxide bonds. Specifically, the energy required to break the peroxide bond was estimated to be $140.2 \text{ kJ}\cdot\text{mol}^{-1}$ in PMS and $213.4 \text{ kJ}\cdot\text{mol}^{-1}$ in H_2O_2 , suggesting that PMS can be decomposed more easily than H_2O_2 .

Another strategy to increase the efficiency of SR-AOPs is the addition of other intensifying agents or combining SR-AOPs with other technologies. For example, [Jaafarzadeh et al. \(2016\)](#) combined electrocoagulation (EC) with UV-SR-AOPs using PMS and PDS precursors. Under optimal conditions, they achieved approximately 40% COD removal with UV/PDS and 51% COD removal with UV/PMS. When EC was applied upstream of the UV-SR-AOPs, removal increased to 77% for EC+UV/PDS and 81% for EC+UV/PMS. In another study, [Jaafarzadeh et al. \(2017a\)](#) combined permanganate,

electro-Fenton (EF), and $\text{Co}_3\text{O}_4/\text{PMS}/\text{UV}$ —SR processes. UV and Co_3O_4 were used as activators to enhance reactive radical generation, particularly effective at high PMS concentrations. The SR-AOPs achieved 67.2% COD removal when used alone, while their combination with permanganate and EF increased the overall COD removal to 95.7%.

A compilation of relevant research works on the application of SR-AOPs to PP real wastewater treatment is presented in [Table 11.3](#).

11.3.4 Photochemical processes

Photochemical AOPs received increased attention over recent decades, due to their high performance and potential for use on solar radiation. The primary photochemical processes studied are photocatalysis and photo-Fenton, both of which combine photochemistry and catalysis, requiring light and a catalyst to facilitate or accelerate chemical transformations ([Lee et al., 2016](#); [Nogueira et al., 2018](#)).

Photocatalysis operates by irradiating a semiconductor, causing the excitation of an electron from the valence band (VB) to the conduction band (CB), resulting in charge separation and the formation of an electron-hole pair ([Marques et al., 2017](#)). The photo-induced positive holes (h^+) drive oxidation reactions, while the photo-induced negative electrons (e^-) drive reduction reactions, both contributing to the degradation of organic pollutants ([Lee et al., 2016](#); [Marques et al., 2017](#)).

Many catalysts have been employed over the years, including ZnO , Fe_2O_3 , ZrO_2 , V_2O_5 , and Nb_2O_5 , among others ([Chu & Bach, 2023](#); [Lee et al., 2016](#)). However, titanium dioxide (TiO_2) remains the most widely used due to its excellent properties of high redox potential, chemical inertness, high photoactivity, cost-effectiveness, low toxicity, long life span, etc. ([Chu & Bach, 2023](#); [Mo et al., 2020](#); [Subramonian et al., 2017](#)). The mechanism of TiO_2 -driven photocatalysis, which can be extrapolated to other photocatalysts, is described by [Eq. 11.46–11.53](#) ([Chu & Bach, 2023](#); [Feijoo et al., 2023](#)).

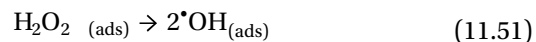
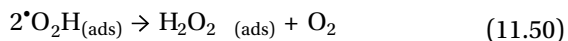
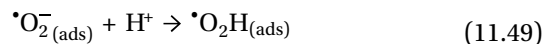
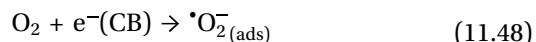
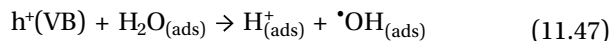
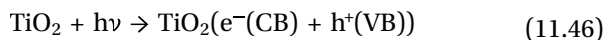


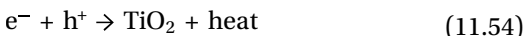
Table 11.3 Compilation of results reported on the application of sulfate radical-based process to real pulp and paper industry wastewater treatment.

Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
PDS/COD mass ratio=8.9; Fe ²⁺ =100 mM; t=93 min; pH=3.0	Paper mill wastewater	COD	72.7	Can-Güven et al. (2021)	PDS activated by Fe ²⁺
PDS=7 mM; Fe ²⁺ =2 mM; pH=3.0	After membrane filtration	COD	84.0	Gholami et al. (2017a)	PDS activated by Fe ²⁺
PDS/COD mass ratio=7; Fe ²⁺ =80 mM; t=95 min; pH=5.0	Recycle mill wastewater	UV ₂₅₄	84.2	Guvenc et al. (2022)	PDS activated by Fe ²⁺
		Phenol	92.6		
		Calcium	85.7		
PDS/COD mass ratio=1; Heat activation at 70°C; t=71 min; pH=6.0	Paper mill wastewater	COD	59.2	Can-Güven et al. (2021)	PDS activated by heat
PDS/COD mass ratio=6; Heat activation at 60°C; t=95 min; pH=5.0	Recycle mill wastewater	UV ₂₅₄	96.4	Guvenc et al. (2022)	PDS activated by heat
		Phenol	96.3		
		Calcium	81.8		
PMS=50 mM; UV _{power} =150 W; t=60 min; pH=7.0	Biologically treated	COD	64.3	Wang et al. (2022)	UV/PMS
PDS=20 mM; UV _{power} =12 W; t=120 min; pH=8.0	After electrocoagulation treatment	COD	40.0	Jaafarzadeh et al. (2016)	UV/PDS
PMS=15 mM; UV _{power} =12 W; t=120 min; pH=4	After electrocoagulation treatment	COD	51.0	Jaafarzadeh et al. (2016)	UV/PMS
PMS=2 mM; UV _{power} =4 W; t=60 min; pH=7	After electro-Fenton treatment	COD	67.2	Jaafarzadeh et al. (2017a)	Co ₃ O ₄ /UV/PMS



Following the photoelectron excitation from VB to CB and electron-hole pairs production (Eq. 11.46), the reaction between h^+ in the VB and water yields $\cdot OH$ (Eq. 11.47), the main oxidant species in this process (Eq. 11.52–11.53). Simultaneously, the excited electron in CB reacts with oxygen, initiating a series of radical-driven reactions involving other ROS such as $\cdot O_2H$, $\cdot O_2^-$, O_2 , and H_2O_2 (Eq. 11.48–11.51), ultimately leading to the attack of organics, primarily by $\cdot OH$.

Despite its many advantages, TiO_2 has some drawbacks including a wide electronic bandgap requiring UV or sunlight radiation in the wavelength range of 280–380 nm, and a high recombination rate of photogenerated electron-hole pairs (Chu & Bach, 2023; Subramonian et al., 2017). Electron-hole recombination, which can occur either with unreacted positive holes (Eq. 11.54) or with adsorbed $\cdot OH$ radicals (Eq. 11.55), results in low quantum yield, making it the major energy-wasting step in photocatalysis (Feijoo et al., 2023; Lee et al., 2016). Doping with rare earth and alkaline-earth metals can widen the absorption band, allowing for visible light utilization, and improving the separation of electron hole pairs, thereby yielding more $\cdot OH$ (Mo et al., 2020).



Using mixed elements as photocatalysts has often been cited as a solution to improve treatment performance. Subramonian et al. (2017) used a mixed Fe_2O_3/TiO_2 catalyst ($1.3 \text{ g}\cdot\text{L}^{-1}$) to treat pulp mill wastewater, achieving 80.6% COD removal after 180 minutes of artificial UV light irradiation at pH=3.9. The addition of other reactive species (H_2O_2 , BrO_3^- , and $HOCl$) enhanced treatment efficiency, raising COD removal to a maximum of 93.0% upon the addition of 0.625 mM of $HOCl$, owing to the generation of $\cdot OH$ from the direct photolysis of $HOCl$. The positive effect of inorganic oxidants is attributed to: (1) increased number of trapped electrons to avoid recombination of electron-hole pairs; (2) higher radical generation; and (3) avoidance of problems caused by low oxygen concentration (Lee et al., 2016).

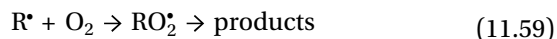
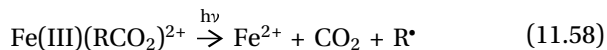
Marques et al. (2017) studied the degradation of COD from biologically treated PP wastewater using Ag_2O - and Fe_2O_3 -doped ZnO and Nb_2O_5 photocatalysts. Ag_2O/ZnO showed the highest photocatalytic performance under visible radiation, allowing for 66% COD reduction within 360 minutes owing to the reduction in

ZnO band gap energy by Ag, which slowed excitation in the visible range. Under equal catalyst dose ($1.0 \text{ g}\cdot\text{L}^{-1}$) and only 120 minutes of treatment, [Nogueira et al. \(2018\)](#) observed 62.6% COD and 87.2% color removal from biologically treated wastewater using nano-TiO₂ as the photocatalyst. The high catalytic performance was associated with the higher surface area and availability of active sites of nanosized materials.

Although the properties of the chosen catalyst play a major role in determining process performance, other factors are crucial for optimizing photocatalysis. Higher catalyst load allows for more available active sites and consequently more $\cdot\text{OH}$ generation. However, excess catalyst fosters aggregation and reduces the available active surface and light penetration ([Nogueira et al., 2018](#)). Wastewater pH affects the electrostatic interaction between the catalyst surface, charged radicals formed during photocatalysis, and target pollutants. At pH above the pH_{pzc} , that is, the pH at which the surface charge is neutral, the catalyst surface is negatively charged; below the pH_{pzc} , the catalyst surface is positively charged. Photogenerated holes (h^+) are the predominant oxidizing species at low pH, while $\cdot\text{OH}$ governs the degradation of organics in neutral or alkaline media ([Esmaeeli et al., 2023](#); [Lee et al., 2016](#); [Nogueira et al., 2018](#)). [Lee et al. \(2016\)](#) observed a sharp decrease in COD removal with increasing pH owing to electrostatic repulsion between the negatively charged Fe₂O₃-TiO₂ photocatalyst surface and the negatively charged organic pollutants at pH above the pH_{pzc} of the catalyst. Finally, radiation intensity also plays a major role in the treatment performance since reaction rates depend on the light absorption by the photocatalyst. Stronger radiation is expected to lead to increased $\cdot\text{OH}$ generation and boost the formation of electron-hole pairs, thereby favouring higher reaction rates ([Shafaei et al., 2010](#)).

The photo-Fenton process is another photocatalytic AOP that has historically received significant attention. Compared to the conventional Fenton process, photo-Fenton is associated with higher organic removal rates, less sludge generation, and shorter reaction times, among other advantages ([Esmaeeli et al., 2023](#); [Hermosilla et al., 2015](#); [Ribeiro & Nunes, 2021](#)). Moreover, photo-Fenton can be carried out at wavelengths ranging between 240 and 600 nm, allowing for the use of solar radiation ([Feijoo et al., 2023](#); [Garcia-Segura et al., 2016](#); [Zhang et al., 2019](#)). Adding UV irradiation to the classical Fenton chemistry increases performance by: (1) photo-reduction of Fe^{3+} to Fe^{2+} , promoting catalyst regeneration ([Eq. 11.56](#)) ([Zhang et al., 2019](#)); (2) generation of extra $\cdot\text{OH}$ through direct photolysis of H_2O_2 ([Eq. 11.57](#)) ([Xu et al., 2007](#); [Zhang et al., 2019](#)); and (3) photo-decarboxylation of ferric carboxylates through charge

transfer in the complexes formed between Fe^{3+} and the carboxylic acid moiety (Eqs. 11.58 and 11.59) (Feijoo et al., 2023; Garcia-Segura et al., 2016; Hermosilla et al., 2015).



Gopalakrishnan et al. (2019) reported similar outcomes from treating PP wastewater by TiO_2 photocatalysis and photo-Fenton, achieving 69%–70% COD removal and 76%–78% color removal within 60 minutes of treatment. Photocatalysis relied on a higher catalyst dose ($250 \text{ mg}\cdot\text{L}^{-1}$ of TiO_2 compared to $240 \text{ mg}\cdot\text{L}^{-1}$ of Fe^{2+}), but a lower H_2O_2 dose (26.5 mM added to the photocatalytic reactor, compared to 35.3 mM used in photo-Fenton). Photo-Fenton is usually associated with sludge formation, a narrow pH range, and difficulty in catalyst recovery, compared to heterogeneous photocatalysis (Puri & Verma, 2022).

Ribeiro et al. (2020) compared photo-Fenton and conventional Fenton processes, finding that the former allowed for higher AOX removal from kraft pulp bleaching wastewater (90% against 80%) with lower chemical consumption: 178 mM of H_2O_2 and 1.0 mM of Fe^{2+} in photo-Fenton, compared to 169 mM of H_2O_2 and 12.5 mM of Fe^{2+} with conventional Fenton. Moreover, photo-Fenton achieved 33.6% savings in operating costs. In another work, photo-Fenton was also linked with significant reductions in treated wastewater toxicity, showing up to a 631.4% improvement in germination index, the most used phytotoxicity index (Neves et al., 2020).

More results regarding wastewater treatment by photochemical AOPs applied to PP wastewater treatment can be found in Table 11.4.

11.3.5 Electrochemical processes

Over the past decades, electrochemical processes have gained considerable attention due to their easy implementation, high effectiveness, low chemical usage, and reduced sludge generation (Guven et al., 2017; Liu et al., 2019). eAOPs employ electrodes to initiate reactions that ultimately lead to the breakdown of organic pollutants (Klidi et al., 2018; Kumar et al., 2021). Oxidation increases at the anode as charge is transferred from the organics to the electrode, while at the cathode, oxidation decreases as charge is transferred from the

Table 11.4 Compilation of results reported on the application of photochemical process to real pulp and paper industry wastewater treatment.

Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
Catalyst [TiO ₂]=0.7 g·L ⁻¹ ; t=120 min; pH=6.3; T=25°C; 400 W UV lamp (280–400 nm)	Unspecified stream	COD BOD Solids	79.0 80.0 11.0	Ejraei et al. (2019)	Photocatalysis
Catalyst [TiO ₂]=0.5 g·L ⁻¹ ; t=180 min; pH=7.0; Room T; UV lamp 200–390 nm	Pulp bleaching wastewater	TOC	14.0	Oke et al. (2017)	Photocatalysis
Catalyst [TiO ₂]=0.5 g·L ⁻¹ ; [H ₂ O ₂]=50 mM; t=180 min; pH=3.7; Room T; UV lamp 200–390 nm	Pulp bleaching wastewater	TOC BOD/COD	16.0 13.7% increase	Oke et al. (2017)	Photocatalysis
Catalyst [TiO ₂]=0.5 g·L ⁻¹ ; [Fe ²⁺]=2 mM; [H ₂ O ₂]=200 mM; t=120 min; pH=3.0; Room T; UV lamp 200–390 nm	Pulp bleaching wastewater	TOC COD BOD/COD	78.5 76.8 58.6% increase	Oke et al. (2017)	Photocatalysis
Catalyst [Fe ₂ O ₃ -TiO ₂]=1.3 g·L ⁻¹ ; t=180 min; pH=3.9; Room T; UV light 400 W Lamp; Air flowrate=2.3 L·min ⁻¹	After coagulation	COD	80.6	Subramonian et al. (2017)	Photocatalysis
Catalyst [Fe ₂ O ₃ -TiO ₂]=1.3 g·L ⁻¹ ; [HOCl]=0.63 mM; t=180 min; pH=3.9; Room T; UV light 400 W Lamp; Air flowrate=2.3 L·min ⁻¹	After coagulation	COD	90.3	Subramonian et al. (2017)	Photocatalysis
Catalyst [Nb ₂ O ₅]=1.0 g·L ⁻¹ ; t=360 min; pH=6.8; Room T; 205 W UV lamp	Biologically treated wastewater	COD Color	36.0 43.0	Marques et al. (2017)	Photocatalysis
Catalyst [Ag ₂ O/Nb ₂ O ₅]=1.0 g·L ⁻¹ ; t=360 min; pH=6.8; Room T; 205 W Vis lamp	Biologically treated wastewater	COD Color	44.0 50.0	Marques et al. (2017)	Photocatalysis
Catalyst [Fe ₂ O ₃ /Nb ₂ O ₅]=1.0 g·L ⁻¹ ; t=360 min; pH=6.8; Room T; 205 W Vis lamp	Biologically treated wastewater	COD Color	29.0 32.0	Marques et al. (2017)	Photocatalysis

(Continued)

Table 11.4 (Continued)

Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
Catalyst [ZnO]=1.0 g·L ⁻¹ ; t=360 min; pH=6.8; Room T; 205 W Vis lamp	Biologically treated wastewater	COD Color	59.0 37.0	Marques et al. (2017)	Photocatalysis
Catalyst [Ag ₂ O/ZnO]=1.0 g·L ⁻¹ ; t=360 min; pH=6.8; Room T; 205 W Vis lamp	Biologically treated wastewater	COD Color	66.0 41.0	Marques et al. (2017)	Photocatalysis
Catalyst [Fe ₂ O ₃ /ZnO]=1.0 g·L ⁻¹ ; t=360 min; pH=6.8; Room T; 205 W Vis lamp	Biologically treated wastewater	COD Color	41.0 30.0	Marques et al. (2017)	Photocatalysis
Catalyst [nano-TiO ₂]=1.0 g·L ⁻¹ ; t=120 min; pH=3.0; T=20°C; UV lamp	Biologically treated wastewater	COD Color Aromatics	62.6 87.2 59.7	Nogueira et al. (2018)	Photocatalysis
Catalyst [nano-Fe ₂ O ₃]=0.75 g·L ⁻¹ ; t=120 min; pH=3.0; T=20°C; UV lamp	Biologically treated wastewater	COD Color Aromatics	42.5 43.3 21.8	Nogueira et al. (2018)	Photocatalysis
Catalyst [nano-TiO ₂]=0.75 g·L ⁻¹ ; [H ₂ O ₂]=10 mM; t=120 min; pH=3.0; T=20°C; UV lamp	Biologically treated wastewater	COD Color Aromatics	78.0 93.3 55.0	Nogueira et al. (2018)	Photocatalysis
Catalyst [nano-Fe ₂ O ₃]=0.75 g·L ⁻¹ ; [H ₂ O ₂]=10 mM; t=120 min; pH=3.0; T=20°C; UV lamp	Biologically treated wastewater	COD Color Aromatics	70.0 92.9 68.4	Nogueira et al. (2018)	Photocatalysis
Catalyst [Fe ₃ O ₄ /MnO ₂ /KMnO ₄] nanocomposites=1.75 g·L ⁻¹ ; t=180 min; pH=3.0; T=25°C; 200 W UV lamp (350–450 nm)	Biologically treated wastewater	COD	57.6	Du et al. (2019)	Photocatalysis
Catalyst [TiO ₂]=0.25 g·L ⁻¹ ; [H ₂ O ₂]=26.5 mM; t=60 min; pH=6.0; Room T; Solar radiation 103 W·m ⁻²	Unspecified stream	COD BOD/COD Color	69.0 45% increase 48.0	Gopalakrishnan et al. (2019)	Solar photocatalysis

Catalyst [TiO ₂]=0.83 g·L ⁻¹ ; [H ₂ O ₂]=21.2 mM; $t=196$ min; pH=8.1; Room T; Solar radiation	Unspecified stream	COD	82.0	Chu and Bach (2023) Puri and Verma (2022)	Solar photocatalysis
Catalyst fixed-bed of TiO ₂ -coated composites made of clay, foundry sand, and furnace blast sand=80 beads (12 mm diameter each); $t=60$ min; pH=4.5; Room T; Solar radiation (553 W·m ⁻²)	Biologically treated wastewater	Color	53.8		
Catalyst fixed-bed of TiO ₂ -coated composites made of clay, foundry sand, and furnace blast sand=80 beads (12 mm diameter each); [H ₂ O ₂]=15.44 mM; $t=60$ min; pH=4.5; Room T; Solar radiation (553 W·m ⁻²)	Biologically treated wastewater	Color	91.6	Puri and Verma (2022)	Solar photocatalysis
[H ₂ O ₂]=7.94 mM; Catalyst Fe ²⁺ /chitosan=2.0 g·L ⁻¹ ; $t=20$ min; pH=7.0; T=35°C; 125 W UV lamp (2.38×10 ⁻⁷ Einstein·s ⁻¹)	Unspecified stream	COD	86.0	Lopes et al. (2020)	Photo-Fenton
		BOD	100.0		
		Color	96.0		
[H ₂ O ₂]=235.2 mM; Fe ²⁺ =21.5 mM (as FeSO ₄ ·7H ₂ O); $t=50$ min; pH=4.0; T=20°C– 22°C; UV-C lamp (256 nm)	Raw PP wastewater	COD	82.2	Olabi (2023)	Photo-Fenton
[H ₂ O ₂]=235.2 mM; Fe ⁰ =1 g·L ⁻¹ ; $t=50$ min; pH=4.0; T=20°C– 22°C; UV-C lamp (256 nm)	Raw PP wastewater	COD	84.2	Olabi (2023)	Photo-Fenton
[H ₂ O ₂]=200 mM; [Fe ²⁺]=2 mM; $t=120$ min; pH=3.0; Room T; UV lamp (200–390 nm)	Pulp bleaching wastewater	TOC	67.0	Oke et al. (2017)	Photo-Fenton
		COD	63.0		
		BOD/COD	48.3% increase		
[H ₂ O ₂]=22.5 mM; [Fe ²⁺]=0.35 mM; $t=120$ min; pH=2.6; Room T; 250 W UV lamp (200–390 nm)	Pulp bleaching wastewater	TOC	78.0	Singh and Garg (2019)	Photo-Fenton
[H ₂ O ₂]=178 mM; [Fe ²⁺]=1.0 mM; $t=10$ min; pH=2.0; T=60°C; 150 W UV lamp	Pulp bleaching wastewater	AOX	89.4	Ribeiro et al. (2020)	Photo-Fenton
		COD	20.0		
		BOD/COD	80% increase		
		Color	76.0		
[H ₂ O ₂]=139.0 mM; [Fe ²⁺]=6.0 mM (as FeSO ₄ ·7H ₂ O); $t=10$ min; pH=2.8; T=60°C; 150 W UV lamp	Pulp bleaching wastewater	AOX	81.7	Ribeiro et al. (2022a)	Photo-Fenton
		COD	51.3		
[H ₂ O ₂]=5.9 mM; [Fe ²⁺]=0.1 mM (as FeSO ₄ ·7H ₂ O); $t=90$ min; pH=8.0; Room T; 125 W UV lamp	Biologically treated wastewater	COD	90.4	Neves et al. (2020)	Photo-Fenton
		Color	93.4		
		Phenol	88.2		

(Continued)

Table 11.4 (Continued)

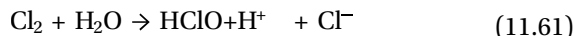
Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
[H ₂ O ₂]=1.0 mM; Fe(III)-EDDS=0.1 mM; <i>t</i> ≈120 min; pH=7.0; Room T; UV Lamp (290–800 nm)	Biologically treated wastewater	Phenol	38.5	Huang et al. (2021)	Photo-Fenton
[H ₂ O ₂]=139.0 mM; [Fe ²⁺]=4.5 mM (as FeSO ₄ ·7H ₂ O); Cu ²⁺ (as CuSO ₄ ·5H ₂ O)=1.5 mM; <i>t</i> ≈10 min; pH=2.8; <i>T</i> =60°C; 150 W UV lamp	Pulp bleaching wastewater	AOX	60.4	Ribeiro et al. (2022a)	Photo-Fenton-like
		COD	45.5		
	Pulp bleaching wastewater	AOX	79.6	Ribeiro et al. (2022a)	Photo-Fenton-like
		COD	39.5		
[H ₂ O ₂]=139.0 mM; [Fe ²⁺]=4.5 mM (as FeSO ₄ ·7H ₂ O); Mn ²⁺ (as MnSO ₄ ·H ₂ O)=1.5 mM; <i>t</i> ≈10 min; pH=2.8; <i>T</i> =60°C; 150 W UV lamp	Pulp bleaching wastewater	AOX	74.1	Ribeiro et al. (2022a)	Photo-Fenton-like
		COD	25.9		
	Unspecified stream	COD	100.0	Ginni et al. (2014)	Solar photo-Fenton
		BOD/COD	400% increase		
[H ₂ O ₂]=35.3 mM; [Fe ²⁺]=4.3 mM (as FeSO ₄ ·7H ₂ O); <i>t</i> ≈60 min; pH=3.0; Room T; Solar irradiation (103 W·m ⁻²)	Unspecified stream	Color	100.0	Gopalakrishnan et al. (2019)	Solar photo-Fenton
		COD	70.0		
		BOD/COD	45% increase		
		Color	76.0		
[H ₂ O ₂]=41 mM; [Fe ²⁺]=0.2 mM (as FeSO ₄ ·7H ₂ O); <i>t</i> ≈360 min; pH=2.8; <i>T</i> =25°C; solar irradiation (19 kJ·L ⁻¹)	Biologically treated wastewater	DOC	90.0	Fernandes et al. (2014)	Solar photo-Fenton
[H ₂ O ₂]=29.4 mM; [Fe ²⁺]=0.2 mM (as FeSO ₄ ·7H ₂ O); <i>t</i> ≈120 min; pH=3.0; Room T; Solar irradiation (475 W·m ⁻²)	Biologically treated wastewater	AOX	19.1	Rabelo et al. (2014)	Solar photo-Fenton
		TOC	24.4		
		COD	61.8		
		BOD	45.8		
		BOD/COD	42.5% increase		

electrode to the organics, changing their chemical properties (Varank et al., 2020). This process can occur in two ways: (1) direct or anodic oxidation, where pollutants adsorbed on the anode surface decompose through electron transfer between the anode surface and pollutants without needing chemical addition; and/or (2) indirect oxidation, where pollutants decompose in the solution through reactions with oxidants such as ozone, chlorine, and hydrogen peroxide, which are either produced *in situ* or externally added (Asha et al., 2014; Doumbi et al., 2022; Liu et al., 2019; Särkkä et al., 2015).

Direct oxidation is a highly effective and straightforward method for the oxidative destruction of organic compounds in wastewater. Pollutants are diffused from the bulk solution and adsorbed on the anode surface, where they are oxidized through direct electron transfer reactions (Guo et al., 2022). Therefore the selection of the electrode material is of utmost relevance. Anodes can be categorized as active (DSA-, IrO_2 , Pt, and doped Ti), and non-active (boron-doped diamond (BDD), SnO_2 , or PbO_2), based on the strength of their interaction with $\cdot\text{OH}$ on their surfaces. Active anodes have strong interactions with $\cdot\text{OH}$ radicals, resulting in lower reactivity, whereas non-active anodes, better suited for organic degradation, have weaker interactions, leading to higher reactivity (Doumbi et al., 2022; Feijoo et al., 2023; Ganiyu et al., 2015).

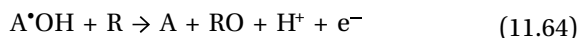
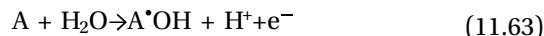
To reduce the energy requirements for eAOPs, NaCl or NaOH is often added to increase conductivity, particularly when dealing with low salinity wastewaters (Feijoo et al., 2023; Guven et al., 2017; Varank et al., 2020).

Asha et al. (2014) studied the treatment of PP wastewater by eAOPs using stainless steel as the cathode and graphite as the anode. The wastewater biodegradability, expressed as BOD/COD ratio, increased from 0.14 to 0.40 after only 35 minutes of treatment. The authors also compared these results with the photo-Fenton process, which needed 150 minutes to reach the same biodegradability index of 0.4. Besides higher efficiency, eAOP also presented the advantage of eliminating the sludge formation. In a similar work, Klidi et al. (2018) used stainless steel cathode, but studied BDD and TiRuSnO_2 as anodes, in the presence of NaCl. These authors observed that higher current intensity improved COD removal only with TiRuSnO_2 anodes, suggesting that this material facilitates oxidation not only on the anode surface but also in the solution bulk, likely through electrogenerated active chlorine from chloride ions. The presence of chloride ions enhances organic compound removal through the synergistic action of hydroxyl radicals and active chlorine, generated and promoted at high currents through the anodic oxidation of chlorides in the solution, according to Eq. 11.60–11.62.



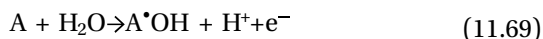
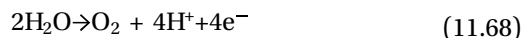
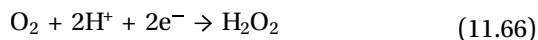
Klidi et al. (2018) also concluded that adding NaCl reduced the time needed to achieve complete COD removal from 240 to 150 minutes with 1 g·L⁻¹ of NaCl, and to 120 minutes with 2 g·L⁻¹ of NaCl. Without NaCl, maximum COD removal was 83%. BDD could be suitable for industrial application when coupled with NaCl addition due to higher oxidation rates, higher current efficiency, no need for pH adjustment, and lower energy consumption. Despite optimistic results, electrode passivation during direct oxidation reduces electrocatalytic activity and affects pollutant mass transfer, particularly at high concentrations. This issue can be mitigated using indirect oxidation methods (Guo et al., 2022).

The indirect oxidation mechanism is driven by the high electrocatalytic activity at the anode, where oxidation is facilitated by a surface mediator continuously generated on the anodic surface. Water is oxidized on the electrode, producing hydroxyl radicals that are then adsorbed on the anode surface, where they indirectly oxidize organic matter, according to Eq. 11.63–11.65, where A is an active site on the anode surface (Feijoo et al., 2023; Ganiyu et al., 2015).



The most intensive research efforts on indirect eAOPs have been directed towards leveraging the Fenton reaction. Hybrid systems integrating various oxidation processes (such as Fenton oxidation, photo-oxidation, electro-oxidation, etc.) within a single electrochemical reactor are commonly employed to enhance the efficiency of electrochemical methods (Altin et al., 2017). The EF process can be implemented in four ways, depending on how the Fenton reagent is added or generated (Feijoo et al., 2023; Ribeiro & Nunes, 2021):

- Externally added Fe²⁺ and *in situ* generated H₂O₂ through cathodic reduction of dissolved oxygen (Eqs. 11.66–11.68);
- Externally added Fe²⁺ and H₂O₂, comprising Fe²⁺ regeneration at the cathode (Eqs. 11.21 and 11.70);
- Electrogenenerated Fe²⁺ and H₂O₂ using a sacrificial anode and an inert cathode (Eq. 11.66–68 and 11.71);
- Externally added H₂O₂ and *in situ* generated Fe²⁺ from a sacrificial iron anode (Eq. 11.71).



Several authors have studied the EF process using iron electrodes, which serve a dual purpose, and externally added oxidants (H_2O_2 , SO_5^{2-} , or $\text{S}_2\text{O}_8^{2-}$) (Altin et al., 2017; Guven et al., 2017; Un et al., 2015). Current density is primarily considered the key factor in generating iron species in the electrochemical process, significantly impacting EF costs and efficiency. Generally, COD removal improves with increasing current density; however, exceeding the optimal value can have counterproductive effects. Higher current density generates more ferrous ions, which may negatively affect SR-eAOPs by scavenging sulfate radicals (Jaafarzadeh et al., 2017b; Altin et al., 2017). Moreover, current density also influences the production rate of bubbles and floc growth, which affect treatment efficiency. As current increases, bubble density increases and bubble size decreases, resulting in faster pollutant removal (Guven et al., 2017).

Klidi et al. (2019) studied the impact of different cathodes (carbon felt, modified carbon felt and gas diffusion electrodes) and anodes ($\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ and BDD) on the removal of TOC from PP wastewater using the EF process. These authors concluded that the most suitable cathodes were modified carbon felt or gas diffusion electrodes, while BDD excelled as anode. Under these conditions, TOC removal reached a maximum of approximately 85% after 5 hours.

Further examples of the treatment of PP wastewater by direct and indirect eAOPs are compiled in Table 11.5.

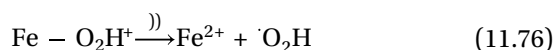
11.3.6 Ultrasonic

Ultrasonic advanced oxidation process (usAOP) combines US waves with conventional AOPs to enhance the degradation of pollutants in wastewater (Eslami et al., 2021). US radiation induces acoustic cavitation, where bubbles form, grow, and collapse (Ribeiro & Nunes, 2021). When US frequencies of 20–1000 kHz are applied, oscillating gas bubbles are generated. As these bubbles grow, gas is drawn inside, and their subsequent collapse results in locally high temperatures exceeding 4000K at the microscale (Hübner et al., 2024). This phenomenon creates transient high-pressure and high-temperature sites, leading to the

Table 11.5 Compilation of results reported on the application of Electrochemical process to real pulp and paper industry wastewater treatment.

Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
Anode: graphite; Cathode: stainless steel; Current density=12.5 mA·cm ⁻¹ ; t=70 min; pH=4.5	Unspecified stream	COD BOD/COD	86.5 69.1% increase	Asha et al. (2014)	Direct eAOP
Anode: BDD; Cathode: stainless steel; t=120 min; Current intensity=0.5 A; pH=6.8; NaCl=2 g·L ⁻¹	Pulp bleaching wastewater	COD	100.0	Klidi et al. (2018)	Direct eAOP
Anode: TiRuSnO ₂ ; Cathode: stainless steel; t=180 min; Current intensity=1.5 A; pH=3.0; NaCl=2 g·L ⁻¹	Pulp bleaching wastewater	COD	92.0	Klidi et al. (2018)	Direct eAOP
Anode: BDD; Cathode: MCF; Fe ²⁺ =0.5 mM; t=200 min; Current density=50 mA·cm ⁻² ; pH=3.0	Pulp bleaching wastewater	TOC	85.0	Klidi et al. (2019)	Direct eAOP
Anode: IrO ₂ -Ta ₂ O ₅ Cathode: carbon felt; [Fe ²⁺]=0.5 mM; t=200 min; Current density=20 mA·cm ⁻² ; pH=3.0	Pulp bleaching wastewater	TOC	13.0	Klidi et al. (2019)	Direct eAOP
Anode: IrO ₂ -Ta ₂ O ₅ ; Cathode: modified carbon felt; [Fe ²⁺]=0.5 mM; t=200 min; Current density=20 mA·cm ⁻² ; pH=3.0	Pulp bleaching wastewater	TOC	29.0	Klidi et al. (2019)	Direct eAOP
Anode: IrO ₂ -Ta ₂ O ₅ ; Cathode=gas diffusion; [Fe ²⁺]=0.5 mM; t=200 min; Current density=20 mA·cm ⁻² ; pH=3.0	Pulp bleaching wastewater	TOC	40.0	Klidi et al. (2019)	Direct eAOP
Anode: iron; Cathode: iron; [H ₂ O ₂]=29.4 mM; t=20 min; Current intensity=1.0 A; pH=2.5	Raw wastewater	COD	91.7	Altin et al. (2017)	Indirect eAOP
Anode: iron; Cathode: iron; [H ₂ O ₂]=747.8 mM; t=60 min; Current density=0.75 mA·cm ⁻² ; pH=2.0	Raw wastewater	COD	74.3	Guven et al. (2017)	Indirect eAOP
Anode: iron; Cathode: iron; [SO ₅ ²⁻]=6 mM; t=60 min; Current density=0.75 mA·cm ⁻² ; pH=4.9	Unspecified stream	COD	53.0	Jaafarzadeh et al. (2017b)	Indirect eAOP
Anode: iron; Cathode: iron; [H ₂ O ₂]=6 mM; t=60 min; Current density=0.75 mA·cm ⁻² ; pH=4.9	Unspecified stream	COD	38.0	Jaafarzadeh et al. (2017b)	Indirect eAOP
Anode: iron; Cathode: iron; [H ₂ O ₂]=1000 mM; t=60 min; Current density=20 mA·cm ⁻² ; pH=2.0	Raw wastewater	COD	80.0	Un et al. (2015)	Indirect eAOP
Anode: iron; Cathode: iron; [S ₂ O ₈ ²⁻]=101.5 mM; t=5 min; Current intensity=4.1 A; pH=6.0	Raw wastewater	COD	63.5	Varank et al. (2020)	Indirect eAOP

according to Eq. 11.72–11.75, where “ $\xrightarrow{\text{US}}$ ” represents US (Pani et al., 2022; Ribeiro & Nunes, 2021).



Ultrasonic processes require minimal to no chemical consumption and offer the advantage of higher synergistic interactions with other AOPs (Feijoo et al., 2023). Thus integrating US with other treatment methods may be more attractive and can support Fenton reactions. Faster degradation and improved catalytic activity are achieved when combining usAOP with other methods such as photo-Fenton, peroxi-coagulation, EC, and EF. This is due to enhanced $\cdot\text{OH}$ generation, improved turbulence allowing for better contact between radicals and pollutants, and enhanced regeneration of ferrous ions (Eq. 11.76) (Eslami et al., 2021; Olabi, 2023). However, the recombination of these radicals can lead to the accumulation of H_2O_2 , which decreases the degradation rate of organic matter (Xu et al., 2020).

Eslami et al. (2021) found that the application of US had a remarkable effect on the performance of EC and peroxi-coagulation processes. In this hybrid approach, more free radicals are available for the reaction, increasing the reaction rate and COD removal efficiency. Conversely, the use of US alone removed only 5% of the organic content. The sono-peroxi-coagulation process exhibited higher COD removal compared to the sono-EF process, with their performance difference reaching nearly 40%. This superior performance of the sono-peroxi-coagulation process can be attributed to the continuous generation of Fe^{2+} ions in the solution, providing a sufficient catalyst for the Fenton reaction and resulting in the production of more $\cdot\text{OH}$ species, thereby enhancing oxidation performance. Additionally, the sono-peroxi-coagulation process benefits from the combination of oxidation and EC processes, leveraging the *in situ* generation of ferric ions and consequently improving removal efficiency. However, the process shows a high dependence on pH. Optimal COD removal (80%) through oxidation occurs in a pH range of 2–4, where the production of $\cdot\text{OH}$ is most efficient. Under pH ranging 5–6, EC becomes the dominant mechanism for COD removal ($\approx 50\%$).

[Olabi \(2023\)](#) also evaluated the synergistic effect of combining Fenton and photo-Fenton processes with US as a promising approach for PP wastewater treatment. Despite significantly enhancing water treatment efficiency, the addition of US increased the relative cost of treatment by around 40% for photo-Fenton/US (COD removal=90.1%) compared to single Fenton process (COD removal=57.8%). The combination of photo-Fenton and US almost eliminated phytotoxicity, and the final effluent also had significant water reuse potential for soil irrigation. Overall, usAOPs represent an innovative approach in wastewater treatment, leveraging US technology to enhance pollutant degradation through the generation of reactive species. However, it is still a process that increases treatment costs compared to others. Despite exhibiting some notable features and advantages, the technology required for the full-scale application of usAOPs is still in an early development stage and is not as well established as other options ([Feijoo et al., 2023](#)). Some results regarding the incorporation of US in PP wastewater treatment are compiled in [Table 11.6](#).

Table 11.6 Compilation of results reported on the application of Ultrasonic process to real pulp and paper industry wastewater treatment.

Operating conditions	Wastewater treated	Parameter	Removal (%)	References	Technology
US power=100 W; Anode=iron; Cathode=carbon felt; Current intensity=140 mA; t =50 min; pH=2.0	Raw wastewater	COD	81.7	Eslami et al. (2021)	Sono-peroxi-coagulation
US power=100 W; Anode=platinum; Cathode=carbon felt; $[\text{Fe}^{2+}]$ =1.0 mM; t =50 min; Current intensity=140 mA; pH=2.0	Raw wastewater	COD	46.7	Eslami et al. (2021)	Sono-EF
US power=100 W; Anode=iron; Cathode=carbon felt; t =50 min; Current intensity=140 mA; pH=2.0	Raw wastewater	COD	60.3	Eslami et al. (2021)	EC/US
$[\text{Fe}^{2+}]$ =21.5 mM; $[\text{H}_2\text{O}_2]$ =235 mM; US power=180 W; t =50 min; pH=4.0	Pulp and paper mill	COD	72.9	Olabi (2023)	Fenton/US
$[\text{Fe}^{2+}]$ =21.5 mM; $[\text{H}_2\text{O}_2]$ =235 mM; US power=180 W; UV=256 nm; t =50 min; pH=4.0	Pulp and paper mill	COD	90.1	Olabi (2023)	Photo-Fenton/US

11.4 Process implementation

Integrating AOPs into the treatment of pulp and paper wastewater requires careful consideration not only of the inherent strengths and limitations of each process but also the challenges associated to full-scale implementation. The following subsections will address these challenges, including the coupling of AOPs with other treatment techniques, implementation costs, environmental impacts, and issues related to scaling-up.

11.4.1 Integration of AOP in wastewater treatment plants: hybrid treatments and coupling with biological treatment

When searching for the most suitable solution to treat industrial wastewater in general, and PP wastewater in particular, one must acknowledge that there is no perfect solution. While all AOPs offer high effectiveness in degrading recalcitrant compounds, none is inherently superior to the others. Each AOP has its own intrinsic strengths and weaknesses, which may make it particularly suited to one type of wastewater but insufficient or inefficient for another. The main advantages and disadvantages of the different AOPs listed in [Table 11.7](#) highlight the need for a case-by-case assessment of advanced wastewater treatment solutions.

The characteristics of the wastewater and the available resources will ultimately dictate the most adequate solution for each case. Moreover, it is often impossible to achieve the desired treatment goals with a single AOP. Combining processes is usually the most efficient route to maximize pollution abatement, owing to increased ROS generation and synergistic effects between processes ([Dewil et al., 2017](#)). These hybrid methods can solve many challenges present in single-stage treatment techniques ([Esmaeeli et al., 2023](#)). For instance, [Martins and Quinta-Ferreira \(2014\)](#) suggested that using sequential schemes of ozonation and hydrogen peroxide and/or UV radiation could address some of the shortcomings of ozonation, such as its higher selectivity. The recombination of the electron-hole pairs, often identified as the main weakness of photocatalytic oxidation, may be suppressed by applying an external electric field ([Chu & Bach, 2023](#); [Subramonian et al., 2017](#)). Another way to intensify photocatalytic oxidation is by using solar, which reduces operating costs and environmental impact. Particularly, combining solar photo-Fenton and solar photocatalysis processes is an attractive option to maximize treatment efficiency ([Gopalakrishnan et al., 2019](#)). Hybrids between photocatalysis and Fenton chemistry have also been proposed. For instance, [Nogueira et al. \(2018\)](#) added H_2O_2 to TiO_2 -photocatalysed

Table 11.7 Main advantages and disadvantages of the Advanced oxidation process (AOPs) applied to the treatment of pulp and paper wastewater.

AOP	Strengths	Weaknesses	References
Ozonation	• Effective at wide pH and T ranges • Minimal installation cost • No external chemical input • No sludge formation	• Low mineralization rate • High selectivity of O₃ • High electricity demand • High operating costs	Feijoo et al. (2023) Mainardis et al. (2020) Manna and Sen (2023) Martins and Quinta-Ferreira (2014) Munir et al. (2022) Saravanan et al. (2021)
Fenton and Fenton-like	• Efficacy at room conditions • Readily available and easy-to-handle chemicals • Minimal installation cost • Short reaction time	• Dependent on acidic pH • High demand of chemicals • Higher sludge formation	Abedinzadeh et al. (2018) Anotai et al. (2018) Belalcázar-Saldarriaga et al. (2018) Gümüş and Akbal (2016) Ochando-Pulido et al. (2017) Ribeiro and Nunes (2021)
Sulfate radical	• Longer radical lifetime • Effective at wide pH range • Fast reaction rates and short reaction time	• High demand of chemicals • High operating cost	Feijoo et al. (2023) Gholami et al. (2017b) Lin et al. (2022) Wacławek et al. (2017)
Photochemical processes	• No sludge generation • No external chemical input • Effective at wide pH and T ranges • Long life span of photocatalysts	• Cost and complexity of process design and layout • High cost of UV reactors • Variability of solar radiation	Belalcázar-Saldarriaga et al. (2018) Chu and Bach (2023) Durán et al. (2012) Mo et al. (2020) Subramonian et al. (2017) Zhang et al. (2019)
Electrochemical processes	• Reduced demand of chemicals • Efficacy at room conditions • Low sludge generation • Versatility • Easy to interrupt and restart	• Continuous electricity demand • High operating costs • Dependence on acidic pH	Brillas (2020) Casado (2019) Serra et al. (2011)
Ultrasonic processes	• High disinfection rate • No external chemical input • No sludge generation	• Continuous electricity demand • High operating cost • Low efficacy when used alone	Kakavandi and Ahmadi (2019) Olabi (2023) Siddique et al. (2014)

oxidation of biologically treated PP wastewater, observing an increase in COD and color removal from 62.6% and 87.2% (with $1.0 \text{ g}\cdot\text{L}^{-1}$ TiO_2 and no H_2O_2) to 78.0% and 93.3% (with $0.75 \text{ g}\cdot\text{L}^{-1}$ TiO_2 and 10 mM of H_2O_2). Similarly, Oke et al. (2017) observed an increase in TOC removal from pulp bleaching wastewater from 14.0% to 78.5% upon adding 200 mM of H_2O_2 and 2 mM of Fe^{2+} to the original $0.5 \text{ g}\cdot\text{L}^{-1}$ TiO_2 .

Combining AOPs with other treatment techniques, such as coagulation–flocculation, adsorption, and membrane filtration, has also been discussed in the literature (Manna & Sen, 2023; Ribeiro et al., 2023; Yadav & Garg, 2017; Zhou et al., 2018). However, for AOPs to be effectively implemented in PP wastewater treatment plants, it is crucial to study their coupling with biological systems. AOPs may be applied before or after the biological reactor. In the former case, they aim to increase wastewater biodegradability, favouring the downstream biological action (Manna & Sen, 2023; Martins & Quinta-Ferreira, 2014). When applied after biological treatment, AOPs serve as a final polishing step, preventing bio-recalcitrant compounds from reaching the environment and causing severe damage to the microecosystems (Liu et al., 2023). Morim et al., 2024 studied the coupling of Fenton process with aerobic biological treatment and observed that implementing the AOP downstream of the biological degradation resulted in the highest COD and AOX removals of 68.9% and 82.7%, respectively, under optimized conditions. Similarly, Du et al. (2019) registered 57.6% COD removal from biologically treated wastewater using $1.75 \text{ g}\cdot\text{L}^{-1}$ of a $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{KMnO}_4$ nanocomposite as a photocatalyst and $350\text{--}450 \text{ nm}$ UV radiation. The innovative petal-shaped nanocomposites maintained their catalytic activity after five consecutive treatment cycles. In another work, 52% COD and 95.6% of color were removed from biologically treated wastewater within only 8 minutes of treatment by catalytic ozonation (Zhou et al., 2023). In that work, only $0.02 \text{ g}\cdot\text{L}^{-1}$ of O_3 was needed due to the high photocatalytic activity of TiO_2 at $\text{pH}=9$. These results demonstrate that the hybridization and/or sequencing of AOPs can significantly improve process performance and effectively address the recalcitrancy of PP wastewater.

11.4.2 Implementation cost and environmental impact of AOPs

The implementation of any treatment technology must rely on more than just technical performance. Implementation costs are equally relevant for assessing process efficiency. Additionally, the environmental impact of implementing an AOP must be considered.

Regarding economic cost, the literature offers a wide range of estimates for different AOPs, showcasing the impact of wastewater characteristics on treatment efficiency. For instance, the cost of Fenton processes is mainly dictated by the chemical input, reaching values as high as $19 \text{ €}\cdot\text{m}^{-3}$ for 50% AOX removal from pulp bleaching wastewater (Ribeiro et al., 2020). Although intensification strategies such as adding electric or UV radiation may reduce the need for H_2O_2 /catalyst, they imply continuous electricity consumption. For instance, Balabanič et al. (2012) spent $36.26 \text{ €}\cdot\text{m}^{-3}$ to remove 96% COD from raw pulp and paper wastewater, while Ribeiro et al. (2020) observed operating costs of $11 \text{ €}\cdot\text{m}^{-3}$ associated with 50% AOX removal from pulp bleaching wastewater. Conversely, the energy consumption for electrochemically generating H_2O_2 in electro-oxidation processes may range between 9.63 and $10.86 \text{ kWh}\cdot\text{kg}_{\text{H}_2\text{O}_2}^{-1}$, translating into a similar cost compared with acquiring H_2O_2 aqueous solution (Manna & Sen, 2023). However, considerable savings in storage, transportation, and handling of H_2O_2 could be achieved. On the other hand, HR-AOPs are estimated to be two orders of magnitude cheaper than SR-AOPs, due to the lower cost of the oxidants (Fernandes et al., 2019).

The development of catalysts is perhaps the most used approach to increasing AOP efficiency and cost-effectiveness. From the array of results published regarding catalytic ozonation, oxalic acid was associated with a cost of around $3.7 \text{ €}\cdot\text{m}^{-3}$ of wastewater treated, while dichloroacetic acid may increase the cost to up to $10.8 \text{ €}\cdot\text{m}^{-3}$. Photocatalytic ozonation was considered the most attractive solution, lowering both costs by around 50%, while significantly increasing removal performance (Mehrijouei et al., 2014). On the other hand, the use of residual iron dust as low-cost Fenton catalyst allowed for up to 11% savings in the cost of removing over 60% AOX from pulp bleaching stream (Ribeiro et al., 2022b). In the field of photocatalytic oxidation, nanocatalysts have received increased attention in recent years. Despite their technical advantages, nanomaterials often increase the cost of treatment due to the need for high-tech synthesis of materials that are not easily available on the market. Handling and recovering nanomaterials also demand adequate industrial facilities. Additionally, there is still a lack of knowledge regarding environmental risks associated with the release of unrecovered nanomaterials.

Besides technical performance and economic requirements, a third factor must be considered before implementing an AOP: its environmental impact. In this regard, ozonation is often considered the reference scenario, with an environmental impact of 0.2–0.3

$\text{kg}_{\text{CO}_2\text{-eq}} \cdot \text{m}^{-3}$ for several wastewaters (Feijoo et al., 2023). Photocatalytic ozonation may reduce the energy requirements of the process by up to 72% and 82% compared to single ozonation and photocatalysis, respectively (Mecha et al., 2017). In fact, the environmental burdens associated with photocatalytic oxidation and eAOPs are primarily attributed to energy consumption. A viable strategy to improve the environmental performance of such AOPs is to rely on renewable energy sources such as solar radiation or green electricity. Energy was also considered the main environmental hotspot in most works dealing with Fenton and Fenton-like processes, followed by the production of chemicals (Ribeiro et al., 2024). Regarding this latter issue, the impacts were attributed not only to the demand for H_2O_2 and Fe, but also to the consumption of auxiliary chemicals to adjust pH. Research efforts are needed to overcome the pH dependence, namely by finding sustainable, low-cost heterogeneous catalysts. Life cycle assessments of nanocatalysts were performed, namely focusing on magnetite nanoparticles coated with ZnO or TiO_2 . Results showed that the normalized environmental impact of those materials might be up to seven times higher than that one of the standard Fenton iron nanocatalyst, owing to the increased complexity and chemical/energy demands of the catalyst synthesis process (Feijoo et al., 2020; Lee et al., 2016). Moreover, Fenton processes may present high sludge formation, which can cause secondary pollution. Furthermore, SR-AOPs are usually associated with generating toxic by-products and excessive levels of PDS and SO_4^{2-} in the treated wastewater (Giannakis et al., 2021). Most studies measure AOP by-products toxicity by conducting standard ecotoxicity test methods, rather than assessing real bacterial populations from industrial biological reactors (Esteves et al., 2016). These are critical issues in AOP implementation that must be thoroughly considered upon scale-up.

11.4.3 Scaling-up and process monitoring and control

The highly complex composition of PP wastewater is a significant challenge to the successful full-scale implementation of AOPs. Most research focuses on synthetic wastewaters or solutions of target contaminants, overlooking the interaction between contaminants and the effect that complex matrices will have on the generation of reactive oxidants and their inefficient consumption throughout the treatment. For instance, moderate concentrations of SO_4^{2-} and Cl^- may improve the degradation of organics through the formation of $\text{SO}_4^{\bullet-}$ and $\text{Cl}^\bullet$. Conversely, above a certain threshold, those ions will hinder the efficacy of AOPs by

scavenging $\cdot\text{OH}$. Moreover, both $\text{SO}_4^{\cdot-}$ and $\text{Cl}^\cdot$ are weaker oxidants than $\cdot\text{OH}$ (Huang et al., 2021). Carbonates are also known $\cdot\text{OH}$ scavengers (Miralles-Cuevas et al., 2014). Nitrates can produce $\cdot\text{OH}$ under irradiation, but their UV shielding effect overcomes this benefit, rendering NO_3^- detrimental to AOPs efficiency (Huang et al., 2021).

Besides the composition of the wastewater, another critical factor in the full-scale implementation of AOPs is the optimization of operating conditions. Determining the optimal dosage of oxidants, catalysts, and other additives is essential for achieving efficient pollutant removal while minimizing chemical consumption and operating costs. Moreover, controlling operating parameters such as pH, temperature, and reaction time is critical for maximizing AOPs efficiency and ensuring consistent treatment performance under varying wastewater conditions. On the other hand, adequate feedback control systems, based on real-time data acquisition and analysis, are of utmost importance. This will allow for dynamic adjustment of operating parameters (e.g., oxidant dosage, pH, temperature) to maintain optimal treatment conditions and respond to fluctuations in wastewater quality and composition.

The implementation of AOPs, either as single treatments or in combination with other techniques, requires the careful assessment of transformation products, which may sometimes be more toxic than the original pollutants. For instance, Pesqueira et al. (2021) highlighted the importance of efficiently dosing and recovering iron in Fenton-treated wastewaters. The authors stated that if over $2 \text{ mg}_{\text{Fe}}\cdot\text{L}^{-1}$ was discharged, the impact of that iron on ecosystems would be higher than that caused by the studied micropollutants. In this framework, scaling-up AOPs from laboratory-scale studies to full-scale implementation requires careful consideration of engineering design, equipment selection, and economic and environmental feasibility. Cost-benefit analyses and life-cycle assessments can help evaluate the economic viability and overall sustainability of AOPs, guiding industries towards their efficient implementation for wastewater treatment.

11.5 Future challenges and research directions

As the PP continues to evolve, so must its approach to wastewater treatment. This chapter explores the potential of AOPs to effectively address the challenges posed by the recalcitrant nature of PP wastewater. Despite their many advantages, AOPs still face several challenges, including the complexity of wastewater matrices, the generation

of potentially toxic by-products, high operating costs, environmental concerns, and scalability issues. To move forward in the full-scale dissemination of AOPs, targeted research is necessary to address these challenges and push the boundaries of current technology.

A thorough characterization of raw wastewater is crucial for selecting the appropriate and designing an effective treatment sequence. While optimizing operating conditions on a case-by-case basis is essential, relying solely on studies of model contaminants may not accurately predict real-world process performance. Therefore there is a need for increased focus on the treatment of actual wastewater samples.

AOP optimization should aim to minimize the consumption of energy and chemicals, as these factors contribute significantly to both economic and environmental burdens. Utilizing renewable energy sources can help reduce the environmental footprint of AOPs, promote investment in green energy, and enhance public awareness and acceptance of these treatment methods. Reducing chemical inputs is challenging but can be addressed by: (1) exploring methods to generate radicals without adding chemical precursors, and/or (2) developing alternative, low-cost, and sustainable catalytic materials. An ideal catalyst should exhibit high activity and stability across a wide range of temperatures and pH levels, low leaching rates, minimal toxicity, and low manufacturing costs. Waste-derived catalysts, aligned with circular economy principles, are a promising yet under-researched alternative. However, attention must be paid to the potential toxicity of waste materials and the challenges of immobilising powdered catalysts. Lifecycle analysis can guide the selection of suitable materials. Additionally, simple and cost-effective techniques for recovering, regenerating, and reusing spent catalysts should be explored, with magnetic separation being a viable option when applicable. In eAOPs, developing novel, cost-efficient electrode materials and configurations could enhance reactive species generation and prevent electrode passivation.

Despite considerable effort, significant gaps remain in understanding the fundamental mechanisms of AOPs, including radical generation, pollutant degradation pathways, and reaction kinetics. Gaining insights into these mechanisms is crucial for optimizing AOP-based treatment systems and predicting their performance under varying conditions. Additionally, evaluating the toxicity of AOP by-products is critical, as they can sometimes be more toxic than the original wastewater.

Comprehensive techno-economic analyses and environmental impact assessments are required for providing decision-makers with the information needed to evaluate AOPs. Such analyses should include considerations of equipment and implementation costs, amortization, and sludge management. The lack of pilot-scale

studies also highlights the need to better understand the continuous operation challenges of AOP-based systems.

Finally, the implementation of AOPs in PP wastewater treatment, like in any industrial sector, should adhere to principles of the circular economy and zero liquid discharge. This approach aligns with current best practices and international priorities. Research should also support industrial decision-makers in integrating AOPs with innovation strategies, particularly in the context of Industry 4.0. The smart, interconnected, and automated systems that characterise the Fourth Industrial Revolution may offer the key to enhancing the efficiency of wastewater treatment through AOPs.

11.6 Conclusions and future trends

The PP plays a crucial role in modern society by providing essential products. However, it also generates significant volumes of wastewater characterized by high organic loads and persistent pollutants. AOPs have emerged as effective solutions for addressing the treatment challenges associated with PP wastewater due to their ability to efficiently degrade both biodegradable and non-biodegradable contaminants.

This chapter has examined the mechanisms, strengths, weaknesses, and practical applications of various AOPs, including ozonation, Fenton and Fenton-like processes, sulfate radical-based processes, photochemical processes, electrochemical processes, and ultrasonic processes. Ozonation is a straightforward technique with widespread use, but it suffers from high electricity consumption and low mineralization rates. Fenton and Fenton-like processes are effective for degrading recalcitrant compounds such as lignin and phenolic substances, with ongoing research focused on enhancing catalyst efficiency and process scalability. Sulfate radical-based processes surpass the pH limitations of Fenton processes and are highly effective in removing amines and phenols, although further advancements in precursor activation are needed. Photochemical processes use light to drive oxidation reactions, showing significant potential, especially when optimized with catalysts and co-oxidants. Electrochemical processes offer a versatile approach by integrating direct and indirect oxidation mechanisms to decompose pollutants. Finally, ultrasonic processes use US to enhance treatment efficiency through synergistic interactions with other AOPs and reduce chemical usage. All these energy-dependent AOPs could benefit from the integration of renewable energy sources.

AOPs can be tailored to fit specific wastewater characteristics and operating conditions, making them adaptable to various industrial

settings. Their ability to generate ROS with high oxidation capacities allows for their use alone or in combination with other AOPs or treatment methods, thus improving overall pollution removal in PP wastewater. Optimal results require careful consideration of factors such as oxidant and catalyst load, pH, energy input, and reactor design. While AOPs offer significant environmental benefits, understanding their reaction mechanisms and potential formation of unwanted by-products, some of which may be more toxic than the original pollutants, is crucial.

Looking ahead, researchers and industry practitioners can leverage the unique capabilities of APOs to develop innovative and sustainable solutions for managing recalcitrant organic pollutants in wastewater. This chapter provides insights that can assist the PP in implementing AOPs more effectively, ensuring regulatory compliance while minimizing environmental impact.

Despite notable progress, several challenges remain that must be addressed before the widespread implementation of AOPs can be achieved. Key areas for future research include:

- 1. Wastewater composition and real-world applications.** More studies using real wastewater samples are needed to better understand the impact of complex water matrices on treatment efficiencies and outcomes.
- 2. Optimization of operational conditions.** Reducing energy and chemical consumption is critical to improving the economic and environmental viability of AOPs. This calls for optimizing variables such as oxidant dose, catalyst type, energy input, among others.
- 3. Mechanisms of pollutant degradation and toxicity of by-products.** A deeper understanding of pollutant degradation mechanisms is required to ensure that AOPs do not increase the toxicity of treated wastewater. Research on the formation and toxicity of the products will help make AOPs safer and more reliable for large-scale applications.

By addressing these challenges, the field can move toward more efficient, cost-effective, and environmentally friendly AOP technologies that will enhance the sustainability of wastewater treatment in the PP.

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List of acronyms

AC	Activated carbon
AOP	Advanced oxidation process
AOX	Adsorbable organic halides
BDD	Boron-doped diamond
BOD	Biochemical oxygen demand
CB	Conduction band
COD	Chemical oxygen demand
DSA	Dimensionally stable anode
eAOPs	Electrochemical AOPs
EC	Electrocoagulation
EDDS	Ethylenediamine- <i>N,N'</i> -disuccinic acid
EF	Electro-Fenton
HR-AOPs	Hydroxyl radical-based AOPs
PDS	Peroxydisulphate
PMS	Peroxymonosulphate
PP	Pulp and paper industry
PZC	Point of zero charge
ROS	Reactive oxygen species
SR-AOPs	Sulfate radical-based AOPs
TOC	Total organic carbon
US	Ultrasound
usAOPs	Ultrasonic AOPs
UV	Ultraviolet radiation
VB	Valence band

List of symbols

Δ	Heat
A	Active site at electrode surface
E	Redox potential
$h\nu$	Light radiation
k	Kinetic rate constant
L	Organic ligands
M	Metal
pH	Potential of hydrogen, expressing the logarithmic measure of the concentration of hydrogen ions in solution
q	Mass flow
R	Organic pollutants
R_{oxid}	Oxidized products
T	Temperature
t	Time

References

- Abedinzadeh, N., Shariat, M., Monavari, S. M., & Pendashteh, A. (2018). Evaluation of color and COD removal by Fenton from biologically (SBR) pre-treated pulp and paper wastewater. *Process Safety and Environmental Protection*, 116, 82–91. <https://doi.org/10.1016/j.psep.2018.01.015>.

- Altin, A., Altin, S., & Yildirimi, O., (2017). Treatment of Kraft pulp and paper mill wastewater by electro- Fenton / electro-coagulation process.
- Anotai, J., Wasukran, N., & Boonrattanakij, N. (2018). Heterogeneous fluidized-bed Fenton process: Factors affecting iron removal and tertiary treatment application. *Chemical Engineering Journal*, 352, 247–254. <https://doi.org/10.1016/j.cej.2018.07.037>.
- Asha, A., Keerthi, Muthukrishnaraj, A., & Balasubramanian, N. (2014). Improvement of biodegradability index through electrocoagulation and advanced oxidation process. *International Journal of Industrial Chemistry*, 5, 1–6. <https://doi.org/10.1007/s40090-014-0004-x>.
- Babuponnusami, A., & Muthukumar, K. (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment. *Journal of Environmental Chemical Engineering*, 2, 557–572. <https://doi.org/10.1016/j.jece.2013.10.011>.
- Balabanić, D., Hermosilla, D., Merayo, N., Klemenčič, A. K., & Blanco, A. (2012). Comparison of different wastewater treatments for removal of selected endocrine-disruptors from paper mill wastewaters. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 47, 1350–1363. <https://doi.org/10.1080/10934529.2012.672301>.
- Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A., & Rodríguez, J. J. (2008). An overview of the application of Fenton oxidation to industrial wastewaters treatment. *Journal of Chemical Technology & Biotechnology*, 83, 1323–1338. <https://doi.org/10.1002/jctb>.
- Belalcázar-Saldarriaga, A., Prato-Garcia, D., & Vasquez-Medrano, R. (2018). Photo-Fenton processes in raceway reactors: Technical, economic, and environmental implications during treatment of colored wastewaters. *Journal of Cleaner Production*, 182, 818–829. <https://doi.org/10.1016/j.jclepro.2018.02.058>.
- Boczka, G., & Fernandes, A. (2017). Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2017.03.084>.
- Bokare, A. D., & Choi, W. (2014). Review of iron-free Fenton-like systems for activating H₂O₂ in advanced oxidation processes. *Journal of Hazardous Materials*, 275, 121–135. <https://doi.org/10.1016/j.jhazmat.2014.04.054>.
- Bolobajev, J., Trapido, M., & Goi, A. (2016a). Effect of iron ion on doxycycline photocatalytic and Fenton-based autocatalytic decomposition. *Chemosphere*, 153, 220–226. <https://doi.org/10.1016/j.chemosphere.2016.03.042>.
- Bolobajev, J., Trapido, M., & Goi, A. (2016b). Interaction of tannic acid with ferric iron to assist 2,4,6-trichlorophenol catalytic decomposition and reuse of ferric sludge as a source of iron catalyst in Fenton-based treatment. *Applied Catalysis B: Environmental*, 187, 75–82. <https://doi.org/10.1016/j.apcatb.2016.01.015>.
- Brillas, E. (2020). A review on the photoelectro-Fenton process as efficient electrochemical advanced oxidation for wastewater remediation. Treatment with UV light, sunlight, and coupling with conventional and other photo-assisted advanced technologies. *Chemosphere*. <https://doi.org/10.1016/j.chemosphere.2020.126198>.
- Brink, A., Sheridan, C., & Harding, K. (2018). Combined biological and advance oxidation processes for paper and pulp effluent treatment. *South African Journal of Chemical Engineering*, 25, 116–122. <https://doi.org/10.1016/j.sajce.2018.04.002>.
- Brink, A., Sheridan, C. M., & Harding, K. G. (2017). The Fenton oxidation of biologically treated paper and pulp mill effluents: A performance and kinetic study. *Process Safety and Environmental Protection*, 107, 206–215. <https://doi.org/10.1016/j.psep.2017.02.011>.

- Can-Güven, E., Guvenc, S. Y., Kavan, N., & Varank, G. (2021). Paper mill wastewater treatment by Fe^{2+} and heat-activated persulfate oxidation: Process modeling and optimization. *Environmental Progress & Sustainable Energy*, 40. <https://doi.org/10.1002/ep.13508>.
- Casado, J. (2019). Towards industrial implementation of electro-Fenton and derived technologies for wastewater treatment: A review. *Journal of Environmental Chemical Engineering*, 7. <https://doi.org/10.1016/j.jece.2018.102823>.
- Chu, Y. M., & Bach, Q. V. (2023). Application of TiO_2 nanoparticle for solar photocatalytic oxidation system. *Applied Nanoscience (Switzerland)*, 13, 1729–1736. <https://doi.org/10.1007/s13204-020-01614-5>.
- Dewil, R., Mantzavinos, D., Poullos, I., & Rodrigo, M. A. (2017). New perspectives for advanced oxidation processes. *Journal of Environmental Management*, 195, 93–99. <https://doi.org/10.1016/j.jenvman.2017.04.010>.
- Dos Santos, N. O., Teixeira, L. A. C., Spadotto, J. C., & Campos, L. C. (2021). A simple ZVI-Fenton pre-oxidation using steel-nails for NOM degradation in water treatment. *Journal of Water Process Engineering*, 43. <https://doi.org/10.1016/j.jwpe.2021.102230>.
- Doumbi, R. T., Bertrand Noumi, G., Ngobtchok, B., & Domga (2022). Tannery wastewater treatment by electro-Fenton and electro-persulfate processes using graphite from used batteries as free-cost electrode materials. *Case Studies in Chemical and Environmental Engineering*, 5, 1–9. <https://doi.org/10.1016/j.cscee.2022.100190>.
- Du, Y., Li, F., Peng, Y., Jia, S., Lan, L., Zhou, J., & Wang, S. (2019). Synthesis of petal-like MnO_2 nanosheets on hollow Fe_3O_4 nanospheres for heterogeneous photocatalysis of biotreated papermaking effluent. *Materials*, 12. <https://doi.org/10.3390/ma12152346>.
- Duarte, F., Morais, V., Maldonado-Hódar, F. J., & Madeira, L. M. (2013). Treatment of textile effluents by the heterogeneous Fenton process in a continuous packed-bed reactor using Fe/activated carbon as catalyst. *Chemical Engineering Journal*, 232, 34–41. <https://doi.org/10.1016/j.cej.2013.07.061>.
- Durán, A., Monteagudo, J. M., & San Martín, I. (2012). Photocatalytic treatment of an industrial effluent using artificial and solar UV radiation: An operational cost study on a pilot plant scale. *Journal of Environmental Management*, 98, 1–4. <https://doi.org/10.1016/j.jenvman.2011.12.007>.
- Ejraei, A., Aroon, M. A., & Ziarati Saravani, A. (2019). Wastewater treatment using a hybrid system combining adsorption, photocatalytic degradation and membrane filtration processes. *Journal of Water Process Engineering*, 28, 45–53. <https://doi.org/10.1016/j.jwpe.2019.01.003>.
- Erhardt, C. S., Basegio, T. M., Capela, I., Rodríguez, A. L., Machado, Ê. L., López, D., Tarelho, L., & Bergmann, C. P. (2021). AOX degradation of the pulp and paper industry bleaching wastewater using nZVI in two different agitation processes. *Environmental Technology & Innovation*, 22, 101420. <https://doi.org/10.1016/j.eti.2021.101420>.
- Eslami, A., Khavari Kashani, M. R., Khodadadi, A., Varank, G., Kadier, A., Ma, P. C., Madihi-Bidgoli, S., & Ghanbari, F. (2021). Sono-peroxi-coagulation (SPC) as an effective treatment for pulp and paper wastewater: Focus on pH effect, biodegradability, and toxicity. *Journal of Water Process Engineering*, 44, 102330. <https://doi.org/10.1016/j.jwpe.2021.102330>.
- Esmaeeli, A., Sarrafzadeh, M., Zeighami, S., Kalantar, M., Bariki, S. G., Fallahi, A., Asgharnejad, H., & Ghaffari, S. (2023). A comprehensive review on pulp and paper industries wastewater treatment advances. *Industrial & Engineering Chemistry Research*, 63. <https://doi.org/10.1021/acs.iecr.2c04393>.

- Esteves, B. M., Rodrigues, C. S. D., Boaventura, R. A. R., Maldonado-Hódar, F. J., & Madeira, L. M. (2016). Coupling of acrylic dyeing wastewater treatment by heterogeneous Fenton oxidation in a continuous stirred tank reactor with biological degradation in a sequential batch reactor. *Journal of Environmental Management*, 166, 193–203. <https://doi.org/10.1016/j.jenvman.2015.10.008>.
- Esteves, B. M., Rodrigues, C. S. D., & Madeira, L. M., (2018). Synthetic olive mill wastewater treatment by Fenton's process in batch and continuous reactors operation (pp. 34826–34838).
- Feijoo, S., González-Rodríguez, J., Fernández, L., Vázquez-Vázquez, C., Feijoo, G., & Moreira, M. T. (2020). Fenton and photo-Fenton nanocatalysts revisited from the perspective of life cycle assessment. *Catalysts*, 10. <https://doi.org/10.3390/catal10010023>.
- Feijoo, S., Yu, X., Kamali, M., Appels, L., & Dewil, R. (2023). Generation of oxidative radicals by advanced oxidation processes (AOPs) in wastewater treatment: A mechanistic, environmental and economic review. *Reviews in Environmental Science and Biotechnology*. <https://doi.org/10.1007/s11157-023-09645-4> Springer Netherlands.
- Feng, F., Xu, Z., Li, X., You, W., & Zhen, Y. (2010). Advanced treatment of dyeing wastewater towards reuse by the combined Fenton oxidation and membrane bioreactor process. *Journal of Environmental Sciences*, 22, 1657–1665. [https://doi.org/10.1016/S1001-0742\(09\)60303-X](https://doi.org/10.1016/S1001-0742(09)60303-X).
- Fernandes, A., Makoš, P., Khan, J. A., & Boczkaj, G. (2019). Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based advanced oxidation processes. *Journal of Cleaner Production*, 208, 54–64. <https://doi.org/10.1016/j.jclepro.2018.10.081>.
- Fernandes, L., Lucas, M. S., Maldonado, M. I., Oller, I., & Sampaio, A. (2014). Treatment of pulp mill wastewater by *Cryptococcus podzolicus* and solar photo-Fenton: A case study. *Chemical Engineering Journal*, 245, 158–165. <https://doi.org/10.1016/j.cej.2014.02.043>.
- Ganiyu, S. O., Van Hullebusch, E. D., Cretin, M., Esposito, G., & Oturan, M. A. (2015). Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: A critical review. *Separation and Purification Technology*, 156, 891–914. <https://doi.org/10.1016/j.seppur.2015.09.059>.
- Ganiyu, S. O., Zhou, M., & Martínez-Huitle, C. A. (2018). Heterogeneous electro-Fenton and photoelectro-Fenton processes: A critical review of fundamental principles and application for water/wastewater treatment. *Applied Catalysis B: Environmental*, 235, 103–129. <https://doi.org/10.1016/j.apcatb.2018.04.044>.
- García-Segura, S., Bellotindos, L. M., Huang, Y.-H., Brillas, E., & Lu, M.-C. (2016). Fluidized-bed Fenton process as alternative wastewater treatment technology - A review. *Journal of the Taiwan Institute of Chemical Engineers*, 67, 211–225. <https://doi.org/10.1016/j.jtice.2016.07.021>.
- Gholami, M., Abbasi Souraki, B., Pendashteh, A., & Bagherian Marzouni, M. (2017a). Efficiency evaluation of the membrane/AOPs for paper mill wastewater treatment. *Environmental Technology (United Kingdom)*, 38, 1127–1138. <https://doi.org/10.1080/09593330.2016.1218553>.
- Gholami, M., Souraki, B. A., Pendashteh, A., Mozhdehi, S. P., & Marzouni, M. B. (2017b). Treatment of pulp and paper wastewater by lab-scale coagulation/SR-AOPs/ ultrafiltration process: Optimization by taguchi. *Desalination Water Treat*, 95, 96–108. <https://doi.org/10.5004/dwt.2017.21530>.
- Giannakis, S., Lin, K. Y. A., & Ghanbari, F. (2021). A review of the recent advances on the treatment of industrial wastewaters by sulfate radical-based advanced oxidation processes (SR-AOPs). *Chemical Engineering Journal*, 406, 127083. <https://doi.org/10.1016/j.cej.2020.127083>.

- Ginni, G., Adishkumar, S., Rajesh Banu, J., & Yogalakshmi, N. (2014). Treatment of pulp and paper mill wastewater by solar photo-Fenton process. *Desalination Water Treat*, 52, 2457–2464. <https://doi.org/10.1080/19443994.2013.794114>.
- Gopalakrishnan, G., Somanathan, A., & Jeyakumar, R. B. (2019). Combination of solar advanced oxidation processes and biological treatment strategy for the decolourization and degradation of pulp and paper mill wastewater. *Desalination Water Treat*, 158, 87–96. <https://doi.org/10.5004/dwt.2019.24180>.
- Guerra-Rodríguez, S., Rodríguez, E., Singh, D. N., & Rodríguez-Chueca, J. (2018). Assessment of sulfate radical-based advanced oxidation processes for water and wastewater treatment: A review. *Water (Switzerland)*. <https://doi.org/10.3390/w10121828>.
- Gümüş, D., & Akbal, F. (2016). Comparison of Fenton and electro-Fenton processes for oxidation of phenol. *Process Safety and Environmental Protection*, 103, 252–258. <https://doi.org/10.1016/j.psep.2016.07.008>.
- Guo, Y., Xue, Q., Zhang, H., Wang, N., Chang, S., Wang, H., Pang, H., & Chen, H. (2018). Treatment of real benzene dye intermediates wastewater by the Fenton method: Characteristics and multi-response optimization. *RSC Advances*, 8, 80–90. <https://doi.org/10.1039/c7ra09404c>.
- Guo, Z., Zhang, Y., Jia, H., Guo, J., Meng, X., & Wang, J. (2022). Electrochemical methods for landfill leachate treatment: A review on electrocoagulation and electrooxidation. *Science of the Total Environment*, 806, 1–19. <https://doi.org/10.1016/j.scitotenv.2021.150529>.
- Güven, S. Y., Erkan, H. S., Varank, G., Bilgili, M. S., & Engin, G. O., (2017). Optimization of paper mill industry wastewater treatment by electrocoagulation and electro-Fenton processes using response surface methodology (pp. 2015–2031). <https://doi.org/10.2166/wst.2017.327>
- Güvenç, Y. S., Can-Güven, E., & Varank, G. (2022). Recalcitrant pollutants removal from paper mill wastewater by ferrous ion- and heat- activated persulfate oxidation processes using response surface methodology: A comparison study. *Separation Science and Technology (Philadelphia)*, 57, 1151–1166. <https://doi.org/10.1080/01496395.2021.1967393>.
- Hassan, A. A., Gheni, S. A., Ahmed, S. M. R., Abdullah, G. H., & Harvey, A. (2022). Aromatic free Fenton process for rapid removal of phenol from refinery wastewater in an oscillatory baffled reactor. *Arabian Journal of Chemistry*, 15. <https://doi.org/10.1016/j.arabjc.2021.103635>.
- He, H., & Zhou, Z. (2017). Electro-fenton process for water and wastewater treatment. *Critical Reviews in Environmental Science and Technology*, 47, 2100–2131. <https://doi.org/10.1080/10643389.2017.1405673>.
- He, S., Li, J., Xu, J., & Mo, L. (2016). Enhanced removal of COD and color in paper-making wastewater by ozonation catalyzed by Fe supported on activated carbon. *Bioresources*, 11, 8396–8408. <https://doi.org/10.15376/biores.11.4.8396-8408>.
- He, S., Luan, P., Mo, L., Xu, J., Li, J., Zhu, L., & Zeng, J. (2018). Mineralization of recalcitrant organic pollutants in pulp and paper mill wastewaters through ozonation catalyzed by Cu-Ce supported on Al₂O₃. *Bioresources*, 13, 3686–3703. <https://doi.org/10.15376/biores.13.2.3686-3703>.
- Hermosilla, D., Merayo, N., Gascó, A., & Blanco, Á. (2015). The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: A review. *Environmental Science and Pollution Research*, 22, 168–191. <https://doi.org/10.1007/s11356-014-3516-1>.
- Hu, P., & Long, M. (2016). Cobalt-catalyzed sulfate radical-based advanced oxidation: A review on heterogeneous catalysts and applications. *Applied Catalysis B: Environmental*. <https://doi.org/10.1016/j.apcatb.2015.07.024>.

- Huang, W., Huang, Y., Wang, S., Lin, H., & Mailhot, G. (2021). Degradation of 2,4-dichlorophenol by ethylenediamine-N,N'-disuccinic acid-modified photo-Fenton system: Effects of chemical compounds present in natural waters. *Processes*, 9. <https://doi.org/10.3390/pr9010029>.
- Hübner, U., Spahr, S., Lutze, H., Wieland, A., Rüting, S., Gernjak, W., & Wenk, J. (2024). Advanced oxidation processes for water and wastewater treatment – Guidance for systematic future research. *Heliyon*. <https://doi.org/10.1016/j.heliyon.2024.e30402>.
- Jaafarzadeh, N., Ghanbari, F., Ahmadi, M., & Omidinasab, M. (2017a). Efficient integrated processes for pulp and paper wastewater treatment and phytotoxicity reduction: Permanganate, electro-Fenton and $\text{CO}_3\text{O}_4/\text{UV}$ /peroxymonosulfate. *Chemical Engineering Journal*, 308, 142–150. <https://doi.org/10.1016/j.cej.2016.09.015>.
- Jaafarzadeh, N., Ghanbari, F., & Alvandi, M. (2017b). Integration of coagulation and electro-activated HSO_5^- to treat pulp and paper wastewater. *Sustainable Environment Research*, 27, 223–229. <https://doi.org/10.1016/j.serj.2017.06.001>.
- Jaafarzadeh, N., Omidinasab, M., & Ghanbari, F. (2016). Combined electrocoagulation and UV-based sulfate radical oxidation processes for treatment of pulp and paper wastewater. *Process Safety and Environmental Protection*, 102, 462–472. <https://doi.org/10.1016/j.psep.2016.04.019>.
- Jiang, Z., Abdoulaye, M. G., Wei, T., Xiao, X., Liang, Y., Xiong, J., Chen, G., & Chen, Y. (2023). Treatment of Eucalyptus chemical-mechanical pulp wastewater by coupling system of advanced catalytic oxidation and biodegradation: Synergistic effect of ozonation photocatalytic-microbial. *Journal of Water Process Engineering*, 55, 104071. <https://doi.org/10.1016/j.jwpe.2023.104071>.
- Kakavandi, B., & Ahmadi, M. (2019). Efficient treatment of saline recalcitrant petrochemical wastewater using heterogeneous UV-assisted sono-Fenton process. *Ultrason Sonochem*, 56, 25–36. <https://doi.org/10.1016/j.ultsonch.2019.03.005>.
- Klidi, N., Clematis, D., Delucchi, M., Gadri, A., Ammar, S., & Panizza, M. (2018). Applicability of electrochemical methods to paper mill wastewater for reuse. Anodic oxidation with BDD and TiRuSnO_2 anodes. *Journal of Electroanalytical Chemistry*, 815, 16–23. <https://doi.org/10.1016/j.jelechem.2018.02.063>.
- Klidi, N., Proietto, F., Vicari, F., Galia, A., & Ammar, S., (2019). Electrochemical treatment of paper mill wastewater by electro-Fenton process, 841, (pp. 166–171). <https://doi.org/10.1016/j.jelechem.2019.04.022>
- Kumar, A., Srivastava, N. K., & Gera, P. (2021). Removal of color from pulp and paper mill wastewater- methods and techniques- A review. *Journal of Environmental Management*, 298, 113527. <https://doi.org/10.1016/j.jenvman.2021.113527>.
- Kumar, V., & Verma, P. (2023). A critical review on environmental risk and toxic hazards of refractory pollutants discharged in chlorolignin waste of pulp and paper mills and their remediation approaches for environmental safety. *Environmental Research*. <https://doi.org/10.1016/j.envres.2023.116728>.
- Kumari, P., & Kumar, A. (2023). Advanced oxidation process: A remediation technique for organic and non-biodegradable pollutant. *Results in Surfaces and Interfaces*. <https://doi.org/10.1016/j.rsufi.2023.100122>.
- Lal, K., & Garg, A. (2017). Utilization of dissolved iron as catalyst during Fenton-like oxidation of pretreated pulping effluent. *Process Safety and Environmental Protection*, 111, 766–774. <https://doi.org/10.1016/j.psep.2017.09.005>.
- Lee, J., Von Gunten, U., & Kim, J. H. (2020). Persulfate-based advanced oxidation: Critical assessment of opportunities and roadblocks. *Environmental Science & Technology*, 54, 3064–3081. <https://doi.org/10.1021/acs.est.9b07082>.

- Lee, K. M., Lai, C. W., Ngai, K. S., & Juan, J. C. (2016). Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Research*, 88, 428–448. <https://doi.org/10.1016/j.watres.2015.09.045>.
- Li, J., Li, Y., Xiong, Z., Yao, G., & Lai, B. (2019). The electrochemical advanced oxidation processes coupling of oxidants for organic pollutants degradation: A mini-review. *Chinese Chemical Letters*, 30, 2139–2146. <https://doi.org/10.1016/j.cclet.2019.04.057>.
- Li, Y., Chen, J., Zhong, J., Yang, B., Yang, Z., Shih, K., & Feng, Y. (2022). Acceleration of traces of Fe₃₊-activated peroxymonosulfate by natural pyrite: A novel cocatalyst for improving Fenton-like processes. *Chemical Engineering Journal*, 435. <https://doi.org/10.1016/j.cej.2022.134893>.
- Lin, D., Fu, Y., Li, X., Wang, L., Hou, M., Hu, D., Li, Q., Zhang, Z., Xu, C., Qiu, S., Wang, Z., & Boczkaj, G. (2022). Application of persulfate-based oxidation processes to address diverse sustainability challenges : A critical review, 440. <https://doi.org/10.1016/j.jhazmat.2022.129722>
- Lindholm-Lehto, P. C., Knuutinen, J. S., Ahkola, H. S. J., & Herve, S. H. (2015). Refractory organic pollutants and toxicity in pulp and paper mill wastewaters. *Environmental Science and Pollution Research*. <https://doi.org/10.1007/s11356-015-4163-x>.
- Liu, J., Ren, N., Qu, C., Lu, S., Xiang, Y., & Liang, D. (2022). Recent advances in the reactor design for industrial wastewater treatment by electro-oxidation process. *Water (Switzerland)*. <https://doi.org/10.3390/w14223711>.
- Liu, X., Yang, Z., Peng, J., Chen, L., Yang, Y., Li, H., & Yang, L. (2023). Advanced treatment of secondary effluent by the integration of heterogeneous catalytic ozonation and biological aerated filter. *Water Science and Technology*, 87, 1893–1906. <https://doi.org/10.2166/wst.2023.099>.
- Liu, Y., Hu, C., & Lo, S. (2019). Direct and indirect electrochemical oxidation of amine-containing pharmaceuticals using graphite electrodes. *Journal of Hazardous Materials*, 366, 592–605. <https://doi.org/10.1016/j.jhazmat.2018.12.037>.
- Lopes, E.de O., Dallabona, I. D., Weinschutz, R., & Jorge, R. M. M. (2020). Fe/polymer-based photocatalyst synthesized by sono-sorption method applied to wastewater treatment. *Journal of Photochemistry and Photobiology A: Chemistry*, 396, 112545. <https://doi.org/10.1016/j.jphotochem.2020.112545>.
- Lucas, M. S., & Peres, J. A. (2009). Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study. *Journal of Hazardous Materials*, 168, 1253–1259. <https://doi.org/10.1016/j.jhazmat.2009.03.002>.
- Luo, S., Wei, Z., Dionysiou, D. D., Spinney, R., Hu, W. P., Chai, L., Yang, Z., Ye, T., & Xiao, R. (2017). Mechanistic insight into reactivity of sulfate radical with aromatic contaminants through single-electron transfer pathway. *Chemical Engineering Journal*, 327, 1056–1065. <https://doi.org/10.1016/j.cej.2017.06.179>.
- M'Arimi, M. M., Mecha, C. A., Kiprop, A. K., & Ramkat, R. (2020). Recent trends in applications of advanced oxidation processes (AOPs) in bioenergy production: Review. *Renewable and Sustainable Energy Reviews*, 121, 109669. <https://doi.org/10.1016/j.rser.2019.109669>.
- Mainardis, M., Buttazzoni, M., De Bortoli, N., Mion, M., & Goi, D. (2020). Evaluation of ozonation applicability to pulp and paper streams for a sustainable wastewater treatment. *Journal of Cleaner Production*, 258, 120781. <https://doi.org/10.1016/j.jclepro.2020.120781>.
- Manna, M., & Sen, S. (2023). Advanced oxidation process: A sustainable technology for treating refractory organic compounds present in industrial wastewater. *Environmental Science and Pollution Research*, 30, 25477–25505. <https://doi.org/10.1007/s11356-022-19435-0>.

- Marques, R. G., Ferrari-Lima, A. M., Slusarski-Santana, V., & Fernandes-Machado, N. R. C. (2017). Ag₂O and Fe₂O₃ modified oxides on the photocatalytic treatment of pulp and paper wastewater. *Journal of Environmental Management*, 195, 242–248. <https://doi.org/10.1016/j.jenvman.2016.08.034>.
- Martins, R. C., & Quinta-Ferreira, R. M. (2014). A Review on the applications of ozonation for the treatment of real agro-industrial wastewaters. *Ozone: Science & Engineering*, 36, 3–35. <https://doi.org/10.1080/01919512.2013.842158>.
- Mecha, A. C., Onyango, M. S., Ochieng, A., & Momba, M. N. B. (2017). Ultraviolet and solar photocatalytic ozonation of municipal wastewater: Catalyst reuse, energy requirements and toxicity assessment. *Chemosphere*, 186, 669–676. <https://doi.org/10.1016/j.chemosphere.2017.08.041>.
- Mehrjouei, M., Müller, S., & Möller, D. (2014). Energy consumption of three different advanced oxidation methods for water treatment: A cost-effectiveness study. *Journal of Cleaner Production*, 65, 178–183. <https://doi.org/10.1016/j.jclepro.2013.07.036>.
- Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., & Hübner, U. (2018). Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review. *Water Research*, 139, 118–131. <https://doi.org/10.1016/j.watres.2018.03.042>.
- Miralles-Cuevas, S., Audino, F., Oller, I., Sánchez-Moreno, R., Sánchez Pérez, J. A., & Malato, S. (2014). Pharmaceuticals removal from natural water by nanofiltration combined with advanced tertiary treatments (solar photo-Fenton, photo-Fenton-like Fe(III)-EDDS complex and ozonation). *Separation and Purification Technology*, 122, 515–522. <https://doi.org/10.1016/j.seppur.2013.12.006>.
- Mo, L., Lyu, P., Yang, Z., Gong, J., Liu, K., & Li, J. (2020). Photocatalytic degradation of bagasse pulp wastewater with La-TiO₂/Al₂O₃ as a catalyst. *Desalination Water Treat*, 187, 256–265. <https://doi.org/10.5004/dwt.2020.25408>.
- Morim, C., Ribeiro, J. P., Silva, F. C., & Nunes, M. I. (2024). Two-stage treatment of pulp bleaching wastewater by Fenton and biological processes to remove recalcitrant pollutants. *Journal of Water Process Engineering*, 63. <https://doi.org/10.1016/j.jwpe.2024.105451>.
- Munir, H. M. S., Feroze, N., Ikhlaq, A., Kazmi, M., Javed, F., & Mukhtar, H. (2019). Removal of colour and COD from paper and pulp industry wastewater by ozone and combined ozone/UV process. *Desalination Water Treatment*, 137, 154–161. <https://doi.org/10.5004/dwt.2019.23186>.
- Munir, H. M. S., Feroze, N., Ramzan, N., Sagir, M., Babar, M., Tahir, M. S., Shamshad, J., Mubashir, M., & Khoo, K. S. (2022). Fe-zeolite catalyst for ozonation of pulp and paper wastewater for sustainable water resources. *Chemosphere*, 297, 134031. <https://doi.org/10.1016/j.chemosphere.2022.134031>.
- Munoz, M., Pliego, G., Pedro, Z. M., Casas, J. A., & Rodriguez, J. J. (2014). Application of intensified Fenton oxidation to the treatment of sawmill wastewater. *Chemosphere*, 109, 34–41. <https://doi.org/10.1016/j.chemosphere.2014.02.062>.
- Neves, L. C., Souza, J. B. de, Vidal, C. M. de S., Herbert, L. T., de Souza, K. V., Martins, K. G., & Young, B. J. (2020). Phytotoxicity indexes and removal of color, COD, phenols and ISA from pulp and paper mill wastewater post-treated by UV/H₂O₂ and photo-Fenton. *Ecotoxicology and Environmental Safety*, 202, 110939. <https://doi.org/10.1016/j.ecoenv.2020.110939>.
- Nogueira, V., Lopes, I., Rocha-Santos, T. A. P., Gonçalves, F., & Pereira, R. (2018). Treatment of real industrial wastewaters through nano-TiO₂ and nano-Fe₂O₃ photocatalysis: Case study of mining and kraft pulp mill effluents. *Environmental Technology (United Kingdom)*, 39, 1586–1596. <https://doi.org/10.1080/09593330.2017.1334093>.
- Ochando-Pulido, J. M., Pimentel-Moral, S., Verardo, V., & Martinez-Ferez, A. (2017). A focus on advanced physico-chemical processes for olive mill wastewater

- treatment. *Separation and Purification Technology*, 179, 161–174. <https://doi.org/10.1016/j.seppur.2017.02.004>.
- Oke, N., Singh, S., & Garg, A. (2017). A comparative treatment of bleaching wastewater by physicochemical processes. *Water Science and Technology*, 76, 2367–2379. <https://doi.org/10.2166/wst.2017.355>.
- Olabi, A. (2023). Ultrasound-assisted photo-Fenton process for treatment of pulp and paper mill wastewater and reduction of phytotoxicity. *Water and Environment Journal*, 37, 339–350. <https://doi.org/10.1111/wej.12841>.
- Pani, N., Singh, A. T. S., Menon, P. M., Boruah, S., Patel, B., & Kaul, D. S. (2022). Electrocoagulation followed by sound agitation for removal of nitrogen and carbon-based pollutants from industrial wastewater. *Water Science and Technology*, 86, 2861–2877. <https://doi.org/10.2166/wst.2022.364>.
- Pesqueira, J. F. J. R., Pereira, M. F. R., & Silva, A. M. T. (2021). A life cycle assessment of solar-based treatments (H_2O_2 , TiO_2 photocatalysis, circumneutral photo-Fenton) for the removal of organic micropollutants. *Science of the Total Environment*, 761, 143258. <https://doi.org/10.1016/j.scitotenv.2020.143258>.
- Phaniendra, A., Jestadi, D. B., & Periyasamy, L. (2015). Free radicals: Properties, sources, targets, and their implication in various diseases. *Indian Journal of Clinical Biochemistry*. <https://doi.org/10.1007/s12291-014-0446-0>.
- Puri, S., & Verma, A. (2022). Color removal from secondary treated pulp & paper industry effluent using waste driven Fe- TiO_2 composite. *Chemosphere*, 303, 135143. <https://doi.org/10.1016/j.chemosphere.2022.135143>.
- Qiu, H. B., Guo, P. C., Yuan, L., & Sheng, G. P. (2020). Different non-radical oxidation processes of persulfate and peroxymonosulfate activation by nitrogen-doped mesoporous carbon. *Chinese Chemical Letters*, 31, 2614–2618. <https://doi.org/10.1016/j.cclet.2020.08.014>.
- Rabelo, M. D., Bellato, C. R., Silva, C. M., Ruy, R. B., Silva, C. A. B., & da, Nunes, W. G. (2014). Application of photo-Fenton process for the treatment of Kraft pulp mill effluent. *Advances in Chemical Engineering and Science*, 4, 483–490. <https://doi.org/10.4236/aces.2014.44050>.
- Ramos, J. M. P., Pereira-Queiroz, N. M., Santos, D. H. S., Nascimento, J. R., Carvalho, C. M., Tonholo, J., & Zanta, C. L. P. S. (2019). Printing ink effluent remediation: A comparison between electrochemical and Fenton treatments. *Journal of Water Process Engineering*, 31, 100803. <https://doi.org/10.1016/j.jwpe.2019.100803>.
- Razumovskii, S. D., & Zaikov, G. E. (1980). Kinetics and mechanism of the reaction of ozone with double bonds (Translated from *Uspekhi Khimii*).
- Ribeiro, J. P., Cruz, N. C., Neves, M. C., Rodrigues, S. M., Tarelho, L. A. C., & Nunes, M. I. (2023). Granulated biomass fly ash coupled with Fenton process for pulp and paper wastewater treatment. *Environmental Pollution*, 317. <https://doi.org/10.1016/j.envpol.2022.120777>.
- Ribeiro, J. P., Gomes, H. G. M. F., Sarinho, L., Marques, C. C., & Nunes, M. I. (2022a). Synergies of metallic catalysts in the Fenton and photo-Fenton processes applied to the treatment of pulp bleaching wastewater. *Chemical Engineering and Processing - Process Intensification*, 181. <https://doi.org/10.1016/j.cep.2022.109159>.
- Ribeiro, J. P., Marques, C. C., Portugal, I., & Nunes, M. I. (2020). Fenton processes for AOX removal from a kraft pulp bleaching industrial wastewater: Optimisation of operating conditions and cost assessment. *Journal of Environmental Chemical Engineering*, 8, 10. <https://doi.org/10.1016/j.jece.2020.104032>.
- Ribeiro, J. P., & Nunes, M. I. (2021). Recent trends and developments in Fenton processes for industrial wastewater treatment – A critical review. *Environmental Research*. <https://doi.org/10.1016/j.envres.2021.110957>.

- Ribeiro, J. P., Sarinho, L., Neves, M. C., & Nunes, M. I. (2022b). Valorisation of residual iron dust as Fenton catalyst for pulp and paper wastewater treatment. *Environmental Pollution*, 310. <https://doi.org/10.1016/j.envpol.2022.119850>.
- Ribeiro, J. P., Sarinho, L., & Nunes, M. I. (2024). Application of life cycle assessment to Fenton processes in wastewater treatment – A review. *Journal of Water Process Engineering*, 57. <https://doi.org/10.1016/j.jwpe.2023.104692>.
- Roslan, N. N., Lau, H. L. H., Suhaimi, N. A. A., Shahri, N. N. M., Verinda, S. B., Nur, M., Lim, J. W., & Usman, A. (2024). Recent advances in advanced oxidation processes for degrading pharmaceuticals in wastewater—A review. *Catalysts*. <https://doi.org/10.3390/catal14030189>.
- Saravanan, A., Senthil Kumar, P., Jeevanantham, S., Karishma, S., Tajsabreen, B., Yaashikaa, P. R., & Reshma, B. (2021). Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development. *Chemosphere*, 280, 130595. <https://doi.org/10.1016/j.chemosphere.2021.130595>.
- Särkkä, H., Bhatnagar, A., & Sillanpää, M. (2015). Recent developments of electro-oxidation in water treatment—A review. *JEAC*, 754, 46–56. <https://doi.org/10.1016/j.jelechem.2015.06.016>.
- Seesuriyachan, P., Kuntiya, A., Kawee-ai, A., Techapun, C., Chaiyaso, T., & Leksawasdi, N. (2015). Improvement in efficiency of lignin degradation by Fenton reaction using synergistic catalytic action. *Ecological Engineering*, 85, 283–287. <https://doi.org/10.1016/j.ecoleng.2015.10.013>.
- Serra, A., Domènech, X., Brillas, E., & Peral, J. (2011). Life cycle assessment of solar photo-Fenton and solar photoelectro-Fenton processes used for the degradation of aqueous α -methylphenylglycine. *Journal of Environmental Monitoring*, 13, 167–174. <https://doi.org/10.1039/c0em00552e>.
- Sevimli, M. F., Deliktaş, E., Şahinkaya, S., & Güçlü, D. (2014). A comparative study for treatment of white liquor by different applications of Fenton process. *Arabian Journal of Chemistry*, 7, 1116–1123. <https://doi.org/10.1016/j.arabjc.2012.12.015>.
- Shafaei, A., Nikazar, M., & Arami, M. (2010). Photocatalytic degradation of terephthalic acid using titania and zinc oxide photocatalysts: Comparative study. *Desalination*, 252, 8–16. <https://doi.org/10.1016/j.desal.2009.11.008>.
- Shafeeyan, M. S. (2024). Application of photocatalytic and fenton processes for the degradation of toxic pollutants from pulp and paper industry effluents. *Water Resources and Industry*, 32. <https://doi.org/10.1016/j.wri.2024.100260>.
- Sharma, P., Iqbal, H. M. N., & Chandra, R. (2022). Evaluation of pollution parameters and toxic elements in wastewater of pulp and paper industries in India: A case study. *Case Studies in Chemical and Environmental Engineering*, 5. <https://doi.org/10.1016/j.cscee.2021.100163>.
- Siddique, M., Farooq, R., & Price, G. J. (2014). Synergistic effects of combining ultrasound with the Fenton process in the degradation of Reactive Blue 19. *Ultrasonics Sonochemistry*, 21, 1206–1212. <https://doi.org/10.1016/j.ultsonch.2013.12.016>.
- Singh, S., & Garg, A. (2019). Performance of photo-catalytic oxidation for degradation of chlorophenols: Optimization of reaction parameters and quantification of transformed oxidized products. *Journal of Hazardous Materials*, 361, 73–84. <https://doi.org/10.1016/j.jhazmat.2018.08.055>.
- Soriano-Molina, P., De la Obra, I., Miralles-Cuevas, S., Gualda-Alonso, E., Casas López, J. L., & Sánchez Pérez, J. A. (2021). Assessment of different iron sources for continuous flow solar photo-Fenton at neutral pH for sulfamethoxazole removal in actual MWWTP effluents. *Journal of Water Process Engineering*, 42. <https://doi.org/10.1016/j.jwpe.2021.102109>.

- Sruthi, T., Gandhimathi, R., Ramesh, S. T., & Nidheesh, P. V. (2018). Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes. *Chemosphere*, 210, 38–43. <https://doi.org/10.1016/j.chemosphere.2018.06.172>.
- Subramonian, W., Wu, T. Y., & Chai, S. P. (2017). Photocatalytic degradation of industrial pulp and paper mill effluent using synthesized magnetic $\text{Fe}_2\text{O}_3\text{-TiO}_2$: Treatment efficiency and characterizations of reused photocatalyst. *Journal of Environmental Management*, 187, 298–310. <https://doi.org/10.1016/j.jenvman.2016.10.024>.
- Tang, Z., Lin, Z., Wang, Y., Zhao, P., Kuang, F., & Zhou, J. (2020). Coupling of thermophilic biofilm-based systems and ozonation for enhanced organics removal from high-temperature pulping wastewater: Performance, microbial communities, and pollutant transformations. *Science of the Total Environment*, 714, 136802. <https://doi.org/10.1016/j.scitotenv.2020.136802>.
- Thomas, N., Dionysiou, D. D., & Pillai, S. C. (2021). Heterogeneous Fenton catalysts: A review of recent advances. *Journal of Hazardous Materials*, 404, 124082. <https://doi.org/10.1016/j.jhazmat.2020.124082>.
- Trapido, M., Tenno, T., Goi, A., Dulova, N., Kattel, E., Klauson, D., Klein, K., Tenno, T., & Viisimaa, M. (2017). Bio-recalcitrant pollutants removal from wastewater with combination of the Fenton treatment and biological oxidation. *Journal of Water Process Engineering*, 16, 277–282. <https://doi.org/10.1016/j.jwpe.2017.02.007>.
- Umair, M., Kanwal, T., Loddo, V., Palmisano, L., & Bellardita, M. (2023). Review on recent advances in the removal of organic drugs by advanced oxidation processes. *Catalysts*. <https://doi.org/10.3390/catal13111440>.
- Umar, M., Aziz, H. A., & Yusoff, M. S. (2010). Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. *Waste Management*, 30, 2113–2121. <https://doi.org/10.1016/j.wasman.2010.07.003>.
- Un, U. T., Topal, S., Oduncu, E., & Ogutveren, U. B. (2015). Treatment of tissue paper wastewater : Application of electro-Fenton method 6, (pp. 415–418). <https://doi.org/10.7763/IJESD.2015.V6.628>
- Varank, G., Guvenc, S. Y., Demir, A., Kavan, N., Donmez, N., & Onen, Z. T. (2020). Modeling and optimizing electro-persulfate processes using Fe and Al electrodes for paper industry wastewater treatment. *Water Science and Technology*, 81, 345–357. <https://doi.org/10.2166/wst.2020.115>.
- Vorontsov, A. V. (2019). Advancing Fenton and photo-Fenton water treatment through the catalyst design. *Journal of Hazardous Materials*, 372, 103–112. <https://doi.org/10.1016/j.jhazmat.2018.04.033>.
- Waclawek, S., Lutze, H. V., Grübel, K., Padil, V. V. T., Černík, M., & Dionysiou, D. D. (2017). Chemistry of persulfates in water and wastewater treatment: A review. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2017.07.132>.
- Wang, B., Zhang, H., Wang, F., Xiong, X., Tian, K., Sun, Y., & Yu, T. (2019). Application of heterogeneous catalytic ozonation for refractory organics in wastewater. *Catalysts*, 9. <https://doi.org/10.3390/catal9030241>.
- Wang, C.-T., Chou, W.-L., Chung, M.-H., & Kuo, Y.-M. (2010). COD removal from real dyeing wastewater by electro-Fenton technology using an activated carbon fiber cathode. *Desalination*, 253, 129–134. <https://doi.org/10.1016/j.desal.2009.11.020>.
- Wang, L., Fei, Y., Gong, C., Shan, Y., Zhang, Z., & Zhang, F. (2022). Comparative study of UV / H_2O_2 and UV/PMS processes for treating pulp and paper. *wastewater*, 86, 2032–2044. <https://doi.org/10.2166/wst.2022.326>.
- Wang, N., Zheng, T., Zhang, G., & Wang, P. (2016). A review on Fenton-like processes for organic wastewater treatment. *Journal of Environmental Chemical Engineering*, 4, 762–787. <https://doi.org/10.1016/j.jece.2015.12.016>.

- Wang, Y., Shia, S., Wang, C., & Fanga, S. (2018). Degradation of pulp mill wastewater by a heterogeneous Fenton-like catalyst Fe/Mn supported on zeolite. *Environment Protection Engineering*, 44, 131–145. <https://doi.org/10.37190/EPE180209>.
- Xu, L., Zhang, X., Han, J., Gong, H., Meng, L., Mei, X., Sun, Y., Qi, L., & Gan, L. (2020). Degradation of emerging contaminants by sono-Fenton process with in situ generated H_2O_2 and the improvement by P25-mediated visible light irradiation. *Journal of Hazardous Materials*, 391, 122229. <https://doi.org/10.1016/j.jhazmat.2020.122229>.
- Xu, M., Wang, Q., & Hao, Y. (2007). Removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process. *Journal of Hazardous Materials*, 148, 103–109. <https://doi.org/10.1016/j.jhazmat.2007.02.015>.
- Yadav, B. R., & Garg, A. (2017). Performance assessment of activated carbon supported catalyst during catalytic wet oxidation of simulated pulping effluents generated from wood and bagasse based pulp and paper mills. *RSC Advances*, 7, 9754–9763. <https://doi.org/10.1039/c6ra25695c>.
- Yu, Z., Zhao, G., Yu, H., Liu, Q., Zhang, Z., Sun, R., Wang, L., Geng, W., & Yuan, D. (2022). Application of Fenton sludge coupled selective acid leaching in selective catalytic reduction of NOx: Performance and mechanisms. *Fuel*, 326, 125058. <https://doi.org/10.1016/j.fuel.2022.125058>.
- Zhang, H., Liu, J., Ou, C., Faheem, Shen, J., Yu, H., Jiao, Z., Han, W., Sun, X., Li, J., & Wang, L. (2017). Reuse of Fenton sludge as an iron source for $NiFe_2O_4$ synthesis and its application in the Fenton-based process. *Journal of Environmental Sciences*, 53, 1–8. <https://doi.org/10.1016/j.jes.2016.05.010>.
- Zhang, M. H., Dong, H., Zhao, L., Wang, D.xi, & Meng, D. (2019). A review on Fenton process for organic wastewater treatment based on optimization perspective. *Science of the Total Environment*, 670, 110–121. <https://doi.org/10.1016/j.scitotenv.2019.03.180>.
- Zhou, C., Zhang, J., Cai, Y., & Xiong, J. (2023). Catalytic ozonation for pulp and paper mill wastewater treatment: COD reduction and organic matter degradation mechanism. *Separations*, 10. <https://doi.org/10.3390/separations10030148>.
- Zhou, H., Kang, L., Zhou, M., Zhong, Z., & Xing, W. (2018). Membrane enhanced COD degradation of pulp wastewater using Cu_2O/H_2O_2 heterogeneous Fenton process. *Chinese Journal of Chemical Engineering*, 26, 1896–1903. <https://doi.org/10.1016/j.cjche.2018.01.007>.

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Microbial fuel cells' application for pulp and paper industries' wastewater treatment

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12.1 Introduction

In today's world the energy requirement is high, and it has increased tremendously within the last few years. On the contrary, we are also witnessing a rise in pollution rates. It is clear that our world needs clean energy to survive and thrive. What if we could use waste to generate energy? We have a lot of nonrenewable energy sources, like nuclear power and fossil fuels. We have made remarkable efforts to focus more on renewable energy sources such as wind, water, and solar energy with the aim of finding a viable solution to the energy crisis. The significance of developing a sustainable energy sector in light of worldwide issues like pollution and climate change is more than evident. It is difficult to create a sustainable system (Lior, 2008). Waste to energy (WtE) or energy from waste represents typical solutions to these problems! They reduce landfills, generate energy, aid in waste management (WM), fight against global warming, and contribute to the circular economy (El Hanandeh & El-Zein, 2009).

The two main obstacles defining the future growth of energy systems are the reliability of the energy supply and the threat posed by climate change. The issue of supply security arises after problems with waste production, import dependency, and shortages of materials and energy. The circular economy and "closing the loop" strategy are two of its foundations. By employing waste energy to power the entire WM and recovery chain an integrated WM system may close the loop both materially and energetically. This method is an environmentally friendly and sustainable solution to conserve our resources (Tomić & Schneider, 2018). Traditional methods for cooking, such as incineration or biogas, are simply WtE methods. Biochemical (anaerobic digestion, alcoholic

fermentation, and photobiological hydrogen production) and thermochemical (gasification, liquefaction, and pyrolysis) approaches have made a lot of progress in the last few years. Transesterification seems to be the most straightforward and cost-effective way to make biodiesel in large quantities. Methods for directly converting trash and biomass leftovers into bioelectricity include the utilization of microbial fuel cells (MFCs) and burning ([Lee et al., 2019](#)).

In recent years, there has been growing interest in using MFCs as a method of producing power from organic waste material (OWM), such as lignocellulosic biomass and low-strength wastewater (WW). Since MFCs allow the extraction of electric current from a variety of soluble or dissolved complex organic waste and renewable biomass, microbial electricity production could become a significant source of bioenergy in the future. Researchers have investigated a wide variety of substrates, including lignocellulosic biomass and a variety of synthetic and actual WW ([Pant et al., 2010](#)).

An anode chamber (AC), a cathode chamber (CC), and a separator connecting the two chambers make up the main components of an MFC's instrumentation. Microorganisms, most commonly bacteria, populate the AC. The electrogenic bacteria in the AC oxidize the OWM, also known as the substrate in WW. The bacteria break down the OWM, releasing protons and electrons in the process. MFC's ability to produce current is significantly dependent on the bacteria's ability to oxidize a substrate and transmit the resulting electrons to the anode electrode. The MFC's anode electrode receives the freed electrons from the oxidation process (electron transfer). Typically, a conductive substance that accepts electrons, such as graphite or carbon cloth, composes the anode electrode. Protons (H^+) produced concurrently with the oxidation process go to the CC via a separator or proton exchange membrane (PEM) (proton migration). This membrane lets protons pass, but prevents AC and CC mixing. The CC receives oxygen from either the surrounding air or an external source. A cathode electrode, usually composed of carbon or platinum, is present in the CC. Oxygen takes electrons from the AC and mixes with protons at the cathode electrode to create water. We refer to this procedure as oxygen reduction. Electrons move from the anode to the cathode via an external circuit, producing an electric current. This current can be used to power devices or store them for later use. In an MFC the creation of water and electricity is the outcome of the oxidation of OWM at the anode, and the reduction of oxygen at the cathode produces water and electricity ([Roy et al., 2017](#)).

Improving MFC performance for both making electricity and cleaning sewage by adding nanomaterials like gold and iron oxide nanoparticles to the electrodes or using pretreatment methods like sonication and autoclave sterilization has shown promising results.

Researchers have studied MFC technology in relation to the elimination of various heavy metals and toxic elements, as well as the identification of hazardous element contamination in WW. Moreover, we can modify the MFCs to act as microbial electrolysis cells, generating hydrogen energy from a range of OWMs (Kumar et al., 2018).

MFC's instrumentation usually consists of multiple parts. The data acquisition system gathers and records measurements from a variety of sensors and devices. These tools are crucial for deciphering the MFC's behavior, maximizing its performance, and researching the variables that affect it. The galvanostat is the first essential tool in an MFC's instrumentation. The galvanostat regulates the voltage or current supply to the MFC. The reference electrode measures the potential difference between the anode and cathode, and the pH meter monitors the acidity or alkalinity of the electrolyte solution. The temperature sensor helps to keep track of and regulate the MFC's internal temperature. We use gas sensors to measure the levels of oxygen and carbon dioxide in AC and CC. Flowmeters determine the influent and effluent flow rates of the MFC, while current meters calculate how much electricity the MFC produces (Roy et al., 2017).

Environmental monitoring, bioremediation, decentralized WW treatment, and renewable energy harvesting can all use MFCs. It is important to keep in mind that an MFC's efficiency and power production are dependent on a number of variables, such as the type of microorganisms used, the composition of the OWM, the MFC's design, and the operating environment. The WW treatment covers effluents from a variety of industrial sectors, including food and food processing, beverages, dairy, agricultural processing, refinery, mining, textiles, paper and pulp, pharmaceuticals, petrochemicals, and domestic and municipal systems (Pandey et al., 2016).

Compared to traditional bioenergy manufacturing methods, MFCs offer a number of distinct benefits. Firstly, compared to other energy carriers, electricity is more convenient to use and transmit. Additionally, they produce electricity directly from the substrate energy, allowing for excellent conversion efficiency. MFCs can function effectively in ambient and even low temperatures, eliminating the need for additional energy and enabling their use in isolated areas without access to electricity (Li & Yu, 2011).

12.2 Substrates in microbial fuel cell

The MFC method may generate energy from a variety of substrates, including complex mixtures of organic compounds found in WW or pure chemicals. The primary goal of all treatment procedures is to reduce the number of organic contaminants in water so that it is

harmless for use and the environment (ElMekawy et al., 2015). Among these organics, undoubtedly the most prevalent group is carbohydrates. Lignocellulosic biomass, including woody matter and farm waste, has garnered a lot of interest as a fuel and energy resource due to its accessibility and abundance (Petrus & Noordermeer, 2006).

Generally, the substrates or feeds used in MFC can be classified as carbon-based, nitrogen-based, and others. Carbon-based substrates include the following: acetates; hexoses like glucose, galactose, fructose, fucose, rhamnose, and mannose; pentoses like xylose, arabinose, and ribose; and sugar derivatives like galacturonic acid and glucuronic acid. A mixed bacterial culture successfully tested these substrates (Catal, Li, et al., 2008). Polyalcohols like xylitol, arabitol, ribitol, galactitol, mannitol, and sorbitol were also administered in MFC (Catal, Xu, et al., 2008). The majority of MFC research conducted so far has used acetate as the common substrate for energy production. When used as a carbon source to activate electroactive bacteria, acetate served as a simple substrate. Due to its inert behavior, acetate is frequently considered a feed for microbial conversions such as methanogenesis and fermentation at normal temperatures. This makes it an excellent example for novel MFC constituents, functioning circumstances, or device prototypes (Fadzli et al., 2021).

The major class of nitrogen-containing substrates is azodyes, followed by proteins. They cause major issues, such as obstructing the entry of light and oxygen into the water, and adversely affect water life. Some reports indicate that the use of confection and glucose effluent as cosubstrates in MFC led to the rapid elimination of a model azo dye, ABRX3, also known as active brilliant red X-3B. Nevertheless, dye at high concentrations of up to 1500 mg/L did not exhibit decolorization; yet, an elevated concentration of more than 300 mg/L ABRX3 is required to produce energy from glucose. The competition between the anode and azo dye for electrons from organic compounds influenced this outcome. Consequently, merging two distinct sewer water streams in MFC allows for simultaneous treatment of WW with azo dye and effluent with instantly biodegradable OWM, thereby reducing costs and increasing energy efficiency. The drawback is that much work still has to be done to identify a dense bacterial population that can apply dyes together with basic carbon sources to produce a workable MFC treatment for this effluent (Fadzli et al., 2021; Pandey et al., 2016).

12.3 Microbial fuel cell in paper and pulp industry

Paper industry effluent contains particle debris, including cellulose and soluble organics, that are unsuitable for treatment with conventional WW methods. We devise a vast range of MFC

configurations to enhance functioning by reducing systemic losses for specific applications. A few noteworthy instances are the membrane electrode assembly MFCs, stacked MFCs, air cathode single-chamber MFCs, flat-plate MFCs, up-flow MFCs, tubular MFCs, and separator electrode assembly MFCs. However, the two-chambered, "H-shaped" MFCs are the most frequently registered because they have proven to be the most practical ones for characterizing operating conditions and improving the performance of new components despite their modest current output.

12.3.1 Single-chamber-based microbial fuel cells

Velasquez-Orta et al. (2011) conducted a study on MFC using different industrial WW sources, such as dairy, paper, bakery, and brewery. They collected samples from a variety of industries in the United Kingdom and North East England. Specifically, they collected paper WW from a paper recycling mill, which had removed fiber and other solid materials in the primary sedimentation tank. Typically, paper effluents contain hemicellulose, lignosulphonates, organic soluble fatty acids, and low quantities of bleaching particles. Kloch and Toczyłowska-Maminska (2020) used a single chamber based microbial fuel cell (Fig. 12.1) to make an anaerobic chamber. It was achieved by covering polyacrylate tubes with plates. They placed a carbon cloth anode on one side of the chamber, attached to a stainless-steel wire, and an air cathode made of 20% wet-proof Toray carbon paper on the opposite side's orifice. MFC fed with paper sewage produced the maximum current density ($125 \pm 2 \text{ mA/m}^2$), which was five times greater than other effluents. Such increased power generation was independent of substrate degradability. The microbes in the biofilms on the anodes changed depending on the type of WW that was used. Only MFC anodes that were fed with paper WW showed redox activity at $-134 \pm 5 \text{ mV}$ compared to the normal hydrogen electrode. To figure out the properties of current electroactive factors, more work needs to be done to separate electroactive microbes and show how their redox-active cell materials work.

Huang et al. (2009) put forward a technique for treating sewage from paper recycling factories with the help of MFCs. The aim of this work was to check the removal of chemical oxygen demand (COD) under the continuous flow environment to assess the effect of hydraulic retention time (HRT) on COD shifting and electricity triggering. They designed a more improvised type of MFC, distinct from previous tests, to enhance power generation and decrease treatment time. Specifically, they assembled MFCs on an efficient air cathode plan, which included a liquid chamber measuring 4 cm in

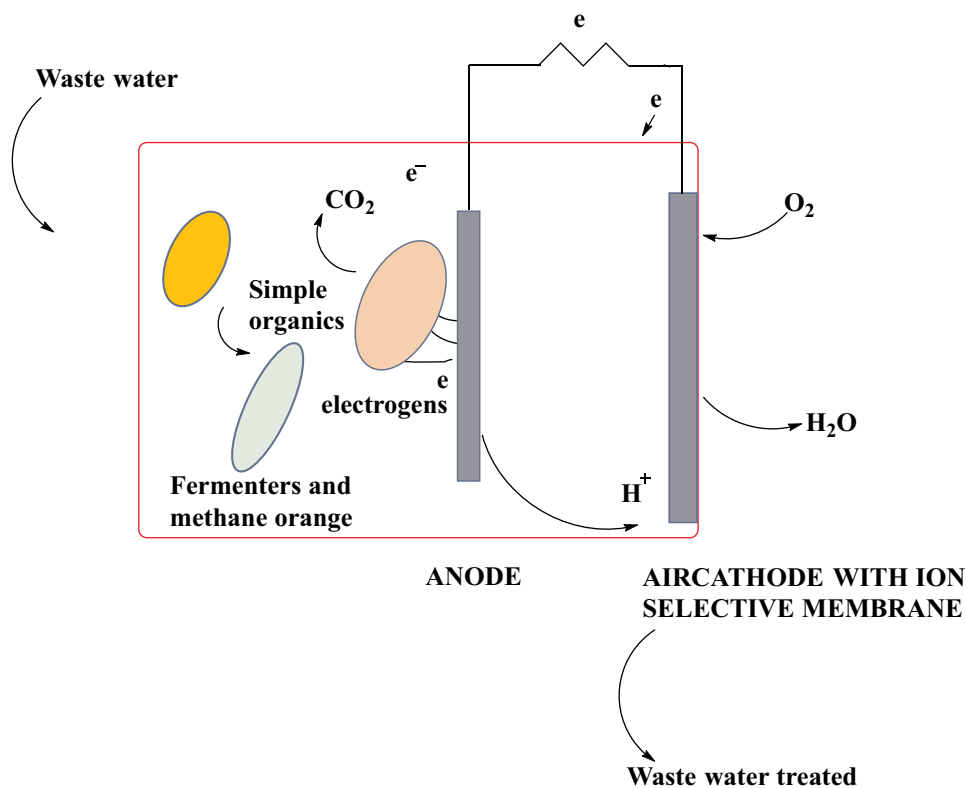


Figure 12.1 Diagrammatic representation of a single-chamber-based microbial fuel cell (Kloch & Toczylowska-Maminska, 2020).

length and 3 cm in diameter. They constructed the anode using an ammonia gas based carbon brush (Logan et al., 2007). The experiment was conducted exclusively with microbes present in the paper mill WW. Once the reaction reached a stable power output of at least 4–5 HRTs, they took all the measurements. They conducted all experiments at a temperature of 22°C–26°C. The result indicated that the COD in sewage from a paper plant could be decreased by $26\% \pm 2\%$ with an HRT of 6 hours and a power density of $5.9 \pm 0.2 \text{ W/m}^3$. Other authors investigated the treatment of carbon cloth anodes and ion exchange membrane cathodes to enhance the power generation of MFCs (Cheng & Logan, 2007; Zuo et al., 2007; Zuo et al., 2008). Additional works may lead to a more effective and economic reactor design, which could contribute to the power generation from paper WW.

12.3.2 Power generation in mediator-less microbial fuel cells

Huang and Logan (2008) proposed a paper recycling sewage treatment with MFC, with simultaneous electricity production. They conducted the study on an unamended paper recycling wastewater (PRW) system and then improved the solution conductivity with a phosphate buffer solution (PBS). They also looked at the power yield based on the strength of the WW and reported the treatment efficiency in terms of cellulose removal, total COD, and soluble COD. This MFC was a single chamber with a graphite fiber brush as an anode. The anode brush was made of carbon fibers with an approximate 7.2 μm diameter. They treated the anodes with ammonia gas at a high temperature and connected the circuit with titanium wires. Cathodes were achieved using 30% wet proof carbon cloth, a platinum catalyst, and four diffusion sheets. The chamber had a working capacity of 300 mL. With the exception of liquid sampling time, the reacting system operated in fed batch mode at room temperature without mixing. Results showed that solution conductivity and buffer action capacity were the main factors reducing effluent power. The addition of phosphate buffer was able to carry off $672 \pm 27 \text{ mM/m}^2$ in a normalized environment, but in the presence of unamended sewage, the energy output was at least $144 \pm 7 \text{ mM/m}^2$ to account for a major part of the small solution conductivity (0.8 mS/cm). When the effluent's pH falls below 5.9, it increases the capacity to remove COD. In this case the percentage of total COD removal capacity was $73\% \pm 1\%$ in standard conditions like 100 mM PBS. According to the observations the inclusion of PBS improved the treatment process. However, the authors did not suggest adding PBS to the sewage to boost energy production, as it would not be cost effective, and adding phosphate to an industrial area's effluents would not be suitable. However, the inputs suggest that a lack of solution potential and buffer capacity could significantly impact energy consumption and efficiency. It has been suggested that in the future, the MFC treatment should incorporate the data related solution, such as the conductivity of the treated water. In previous works, they did not take into account the solution conductivity, except in cases where salinity was extremely high and microbial activity was prohibited. In normal situations, cellulose transfer was very effective, with $85\% \pm 2\%$ removal. An enzyme known as a cellulosome is associated with the rate of cellulose degradation. Typically, the cellulose disintegration process involves two steps: (1) the hydrolysis of cellulose and (2) the fermentation of sugar, which results in the loss of the fermentation final byproduct to the solution. The process of cellulose transformation in MFC

requires the distribution of microbes in the solution to bind the cellulose. Exoelectrogenic microbes on the anode can utilize the finished product, released into solution after fermentation, to generate electricity. However, in this scenario, no known microorganism possesses the capacity to simultaneously hydrolyze cellulose and generate current. As a result, two different paces were required for tiny bits; the process of cellulose decay in MFCs is more tedious than the disintegration of dissolved materials. However, this study demonstrates that it was possible to achieve both of these stages in a similar reactor. To better understand and enhance the performance, we need to conduct further research on the microbe community in MFC-degenerating PRW and continuous flow systems.

Kassongo and Togo (2011) introduced a method for energy production in mediator-less MFC from full-strength paper mill WW. This work focused on minimizing any energy input to enable practical estimation in future advanced studies. Additionally, they employed molecular monitoring of the electrodes to identify the anodophilic microorganisms. Several studies have documented the feasibility of producing electricity from full strength paper mill sewage, leading to significant improvements in H-type MFCs. Nambiar et al. (2009) investigated the application of multiwalled carbon nanotubes to enhance the anodic performance of an *Enterobacter cloacae* based fuel cell. They used paper mill WW as an anolyte and potassium ferricyanide in sodium phosphate buffer as a catalyst. The reaction temperature of MFC was kept at standard conditions $22^{\circ}\text{C} \pm 3^{\circ}\text{C}$. They accumulated each MFC unit for 10–14 days and used a multimeter to record the output voltage every 2 hours. Total COD and solid pollution were assessed at the beginning and end of each MFC cycle. The power value, substrate degradation level, and coulombic efficiency were also computed, and scanning electron microscopy was used to assess the density of the bacterial population on the anode surface. The microbe's diversity was also studied by using molecular techniques such as DNA extraction, polymerase chain reaction, denaturing gradient gel electrophoresis, and ordering.

The sampler's pH of WW was 6.61 ± 0.1 , with a potential of 4.5 Ms/cm. At first, solids and total COD were 584 ± 0.2 mg/L and 43.7 ± 0.3 g/L, respectively. The sugar content was between 1.4 and 0.02 g/L. These values were nearly constant in storage. From different observations using various added bacteria and only effluents, it was shown that sewage from mills with no added microbes generated a maximum power of 24 ± 3 mW/m². *E. cloacae* degraded paper mill effluent with inherent waste microbes, resulting in pollutants and reduced sludge (up to 98.8% settleable solids

removal efficiency). However, the drop-in glucose removal (44.1%) may indicate a lack of synergy with the exogenous culture (Rezaei et al., 2009). Two methods could be used to describe this lack of collaboration among microbes. Microbes have the ability to reduce glucose and utilize excess electrons, typically stored by the anode, to their advantage. Alternatively, *E. cloacae* might be consuming or suppressing microbes, potentially serving as a precursor for power generation by diverse bacterial consortia in sewage. This study acknowledges that both carbon and energy resources can break down and utilize full-strength paper mill sewage, enabling endogenous bacteria to generate noticeable power in MFCs.

12.3.3 Energy creation by constructed wetland coupled with microbial fuel cell

Narayan et al. (2018) used a specific method for electricity generation from paper waste effluent by wetland coupled with MFC (CW-MFC). The CW-MFC is a novel tool that seamlessly integrates a synthetic ecosystem (manufactured wetlands) with the bioelectrochemical method (MFC). The CW-MFC initiates current production through the rhizosphere effect of wetland plants (Liu et al., 2013; Villaseñor et al., 2013) and eliminates pollutants from the effluents by combining the output from both units (Fang et al., 2013; Yadav et al., 2012). This system contains both aerobic and anaerobic sections, where redox operations take place; these similarities served as the foundation for the union of the two units. The primary goal of this method was to examine the viability and efficiency of MFC in conjunction with CW. The production of savage treatments like COD and BOD transfer in the hybrid system was determined, and the current production was calculated. The CW-MFC reaction chamber was designed and constructed using a cylindrical polyacrylic plastic chamber, measuring 100 cm in height and 18 cm in diameter. Carbon electrodes make up the cathode and anode, and copper wire was used to connect the electrodes. The authorities experimented with the CW-MFC's capacity to analyze WW, focusing on the shifting effectiveness of BOD, COD, chlorine, sodium, potassium, sulfates, and total nitrogen. The observations indicated that Ohm's Law could calculate the generated current. The influence of HRT on the COD cluster, the current production of CW-MFC, and the destruction properties of pulp and paper (P and P) sewage were evaluated. The system underwent various stages of development. In step 2 the highest deterioration for BOD at 97.86%, COD at 89.09%, and chloride at 88.54% was assessed. In step 3 a voltage of 26.33 mV and a current of 29 mA were obtained. This methodology clearly demonstrates that the combination of MFC and

CW increased the treatment interpretation. This study was suitable for long-term operations and allowed for better adaptability to various water qualities. The cathode played a main role in electricity production. The combination of CW and MFC techniques significantly enhanced their specific benefits.

12.3.4 Electrode combinations in electricity generation in microbial fuel cells

Iqbal et al. (2022) proposed a variety of electrode combinations for electricity production from P and P industrial effluents. They studied WW specimens from the P and P industries using MFCs with different sets of electrodes (Table 12.1) (Iqbal et al., 2022). They examined the anodes and cathodes' efficacy in generating current and eliminating pollutants, as well as rectifying various sample water variations. Field emission scanning electron microscopy (FESEM) on microbial biofilms was implemented to examine their adhesion characteristics.

In this work, various types of metal electrodes with carbon sheets to generate bioelectricity were examined. Carbon and metals were used as electrodes to measure efficiency. Six groups of electrodes were investigated. The authors used a total of 1.0 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1.0 M $\text{Fe}_2(\text{SO}_4)_3$ mediators in MFC-5 and MFC-6, respectively.

Observations in different MFCs revealed that MFC-5, with its metal electrodes of zinc and copper, had the highest power density at 939 mW/m^2 . The sewage showed an opening BOD of 9386 ppm; the investigations revealed that MFC-5 had the highest BOD depletion, with a reduction of 93%. Total suspended solids (TSSs), total dissolved solids (TDSs), and turbidity also showed the same trend. This work used inexpensive and readily available metal electrodes. The highest power density was achieved by combining zinc and copper electrodes with a copper sulfate solution as a catalyst. Finally, FESEM considered the microbial morphology, and the findings revealed that microbial growth is highly dependent on the nature of electrode materials. This study offers a fresh perspective on diverse electrode materials and how varying bacterial development and origins lead to significant differences in water treatment.

12.3.5 Energy production from paper industry wastewater using electrocoagulation and microbial fuel cell

Shankar et al. (2016) treated and simultaneously produced power from paper industry wastewater (PIW) with electrocoagulation (EC) and MFC. EC first treated the PIW, increasing its biodegradability

Table 12.1 MFC IDs and associated electrode materials (Iqbal et al., 2022).

MFC ID	Anode materials	Cathode materials	Cathode electrolyte
MFC -1	Zn plate	Cu plate	—
MFC -2	Zn mesh	Carbon plate	—
MFC -3	Al mesh	Carbon plate	
MFC -4	Carbon plate	Carbon plate	
MFC -5	Zn plate	Cu plate	CuSO ₄ ·5H ₂ O
MFC -6	Carbon plate	Carbon plate	Fe ₂ (SO ₄) ₃

MFC, Microbial fuel cell.

index, and then used it as a raw material for the MFC reactor. Observations showed that EC, MFC, and MFC individually can treat PIW with initial organic fill-ups of 2400, 750, and 5600 mg/L, reducing the sewage parameters below the permitted limit. In an investigational scenario the residue could produce approximately 1.29 and 8.62 KJ/g of energy during the EC process, while an uninterrupted MFC process could produce approximately 56 mV voltage and 0.02 mA current.

12.3.6 Dual-chambered microbial fuel cell-based bioelectrochemical treatment

Sakdaronnarong et al. (2015) first studied the possibility of using lignin waste from the P and P industry as a stabilizer to test ethanol stillage WW in MFCs in 2015 (Fig. 12.2). Two different arrangements of MFCs were investigated using a salt bridge and a PEM. They tested lignin and KMnO₄ as conciliators in PEM MFCs. Graphite plates were used as electrodes for the salt-bridge MFC, while the cathode and anode in the PEM MFC were substituted with carbon cloth and graphite. Both designs had an exterior resistance of 550 ± 50 U. According to the results, PEM MFC obtained a large amount of bioelectric power with adequate analysis. Simultaneously, lignin was incorporated as an arbiter into PEM MFC, resulting in an increase in power density to 93 W/m² and a COD transfer capacity of up to 81% over a 6-day period. KMnO₄ was proven to be extremely efficient in improving MFCs' energy output, outperforming almost all cathode electron receptors examined (Guerrero-Rangel et al., 2010). Furthermore, researchers added conciliars such as AQDS, safranin O, resazurin, methylene blue, and humic acids to AC (Scott & Murano, 2007) to improve electron flow between the

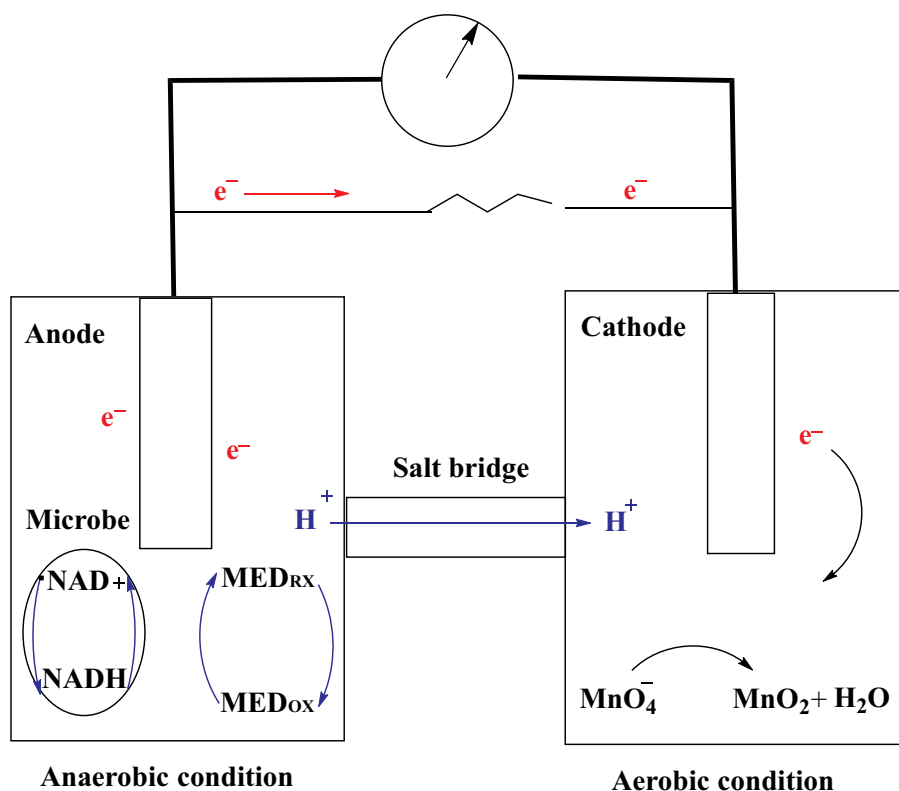


Figure 12.2 Schematic representation of a two-compartment salt-bridge microbial fuel cell (Sakdaronnarong et al., 2015).

exoelectrogens and the anode's exterior. People believe that a single chamber MFC performs better than a double chamber MFC. Two-chamber MFCs need a valuable metal coating, like platinum, on the outside of the cathode to improve electron receiving treatments at temperatures that are more like room temperature (Di Lorenzo et al., 2009). Moreover, the strategy of covering a carbon cathode with a metal catalyst is relatively complex, and its effectiveness has a limited duration (Oh et al., 2004). Dual chamber MFCs enable electron receivers to prioritize electron-acquiring reactions, thereby preventing the accumulation of expensive metals. Moreover, dual chamber MFCs have the ability to operate in batch or continuous modes. Due to the high cost of specific PEMs used in MFC construction, their use was limited to laboratory based investigations. Researchers conducted numerous trials to assess the effects of various MFC methods on their execution. To make the developed MFCs look better, they looked into different ways to set up the

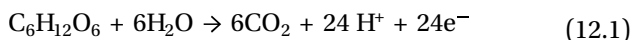
reactors, including tubular, stacked, fixed-bed, and fluidised beds. They also looked into different proton transmission systems, as well as types of cathodes and anodes (Logan et al., 2006; Logan, 2008). In terms of power density and moving about the same amount of COD from ethyl alcohol stillage effluent the PEM MFC did a better job than the salt-bridge MFC. The PEM MFC sewage treatment system found that lignin, a fine mediator with lower pathogenicity than methylene blue and KMnO_4 , increased power generation. Therefore PEM MFC was an advanced system designed for the treatment of pulping wastewater (PW) and paper mills, as well as other similar activities such as the examination of unmanageable dyes. However, factors such as microbial strains, external resistance, and electrodes to ensure the optimal performance of a specific MFC design need to be adjusted. This involved comparing the performance of individual lignin waste and ethyl alcohol distillate effluent combined MFCs, with the ultimate goal of producing electric power.

Elakkiya and Niju (2021) proposed a bioelectrochemical solution for the treatment of bagasse based paper mill WW. They implemented the bioelectrochemical method in a dual chambered MFC, using ordinary graphite sheets as electrodes. These sections produce two different WW streams: (1) bagasse wash water (BWW) from the sugarcane bagasse bin and (2) the washing chamber of mill and PW from the pulping and belching units. In this study the authors aimed to incorporating lignin rich PW into MFC operations alongside biorich BWW to enhance the energy retrieval capability. They stored the WW at 4°C to prevent microbial growth and then used it as an unfrozen primary. The pH and COD of BWW were 5.4 and 8000–8800 mg/L, respectively; however, PW had a lower COD, ranging from 3200 to 3400 mg/L at pH 4.44. Authors examined the feasibility of treating the same waste source (BWW from paper mills) in a dual chambered MFC. They looked at what would happen if they mixed BWW and PW in different amounts to see what kind of results they could get and how well the combined effluent treatment would work. The researchers executed mixed wastewater management of BWW and PW by blending PW and BWW at various percentages. PW at 10%, 20% and 30% (PW10, PW20, and PW30), respectively, are specified MFC performing with BWW and PW v/v proportions of 9:1, 8:2, and 7:3, each. MFC could profitably handle only BWW treatment, with a significant COD removal rate of 85%, but the energy recovery capacity was only 6%. As anticipated the sewage from P and P plants, which is rich in lignin and inorganic salts, was not profitably treated in MFC, and only 62.5% of the COD could be shifted with minimal power generation. Another option is the mixed savage usage of bagasse sponge water, pulp, and bleach plant effluent in proportion 9:1 each, which could result in the coulombic ability to 18% without influencing

the COD shift capacity. Eighteen percent of faradaic effectiveness is still not enough for real-world use. To improve power conversion the microbial body of the anode slush had to be studied to find the most powerful metabolic unit scavenging electrons from the current generation. More accurate estimations should be made to improve the energy recovery capacity.

Singh and Srivastava (2017) presented an efficient method for generating electricity through the MFC technique, utilizing three sewage materials: P and P mill effluent, water vermicompost, and *Escherichia coli*. The first two utilized an effective substrate rich in organic components, while the latter one operated under anaerobic conditions in MFC. The study found that P and P mill effluent can generate more electricity than vermicompost and *E. coli* in MFCs. They chose an anode consisting of a 140 cm² aluminum plate with 0.1 cm diameter pores. For bacterial growth, aluminum plates were held with a graphite rod generated from pencil rods. They selected an aluminum plate cathode, featuring pores measuring 70 cm². A salt bridge to balance the high concentration of NaCl was used, and the experiments were conducted at different time intervals. The multimeter observed the potential drop along the resistor after a specific time interval. To enhance bacterial growth in P and P mill effluent cases, a sugar solution was used.

Different variables such as pH, total solids, TSS, TDS, COD, and BOD can be monitored in paper industry effluents. When these effluents are used in MFC construction, glucose is the best food for microbial growth. The degeneration of glucose into CO₂ produces protons and electrons, as reported in Eq. (12.1):



The rate of oxygen flow (OFR) is one of the factors influencing efficient production, and the observations from the trials showed an improvement in voltage generation. The OFR increased, reaching an optimum of nearly 2.52 V at 45 psi, before subsequently declining. An increased rate of OFR disperses down the air near the anode, likely causing the anode surface to diffuse more widely. pH is another factor that influences microbe activity. Researchers discovered that the optimal pH level for electricity production maximizes microbe growth and increment. Studies revealed that the top-level voltage output peaked at pH 8.5. At pH levels below 6 the activity of microbes decreased as the acidic nature neutralized their active sites and proteins. Another important factor is the concentration of the substrate; initially, an increase in concentration led to a rise in power generation, but after a concentration of 7%, the rate of power production decreased. This means that microbe activity is dependent on pH. Increased substrate concentration also affects the anode's effective performance. It results in a decrease in power formation. Using MFC with WW led to a little

increase in waste pH. Additionally, MFC treatment of WW resulted in a significant reduction in TSS levels. Table 12.2 illustrates the impact of the MFC using P and P mill water (Singh & Srivastava, 2017).

The improvement in TDS values indicates an increase in microorganisms during MFC operations. After 60 hours of operation the MFC had removed 99% COD, 99.2% BOD, and 96% TSS. In this work the authors attempt to prove that the P and P mill sewages showed better potential for generating electricity than vermicompost and *Escherichia coli* in MFC mode. For this method the optimum temperature is around 35°C. By optimizing certain parameters the treatment mode for WW management can be implemented at an industrial level, producing energy and reducing pollution.

From the observations, any single method will not be efficient or only remedy collection of technologies should have introduced and employed to address the demanding energy usage and CO₂ emission for P and P industry. Although boost drying and microwave drying technology can increase multicylinder drying efficiency, they cannot entirely replace them in paper machine dryers. Biological technology, which includes pretreatment, black liquor, biomass gasification, and biorefineries, is a promising emerging technology. It is eco-friendly and increases energy efficiency in the P and P business (Kong et al., 2016).

12.4 The limitations of microbial fuel cell methods pulp and paper wastewater treatments

Conventional methods and current technologies, such as MFC systems for P and P sewage treatment, have limitations. The

Table 12.2 Effects of MFC using P and P wastewater on pollution load (Singh & Srivastava, 2017).

Parameters	Pollution load	
	Before treatment	After treatment
BOD	32,000	268
COD	45,000	450
TSS	9566.66	567
TDS	17,686.66	120,789

BOD, Biological oxygen demand; *COD*, chemical oxygen demand; *MFC*, microbial fuel cell; *P and P*, pulp and paper; *TSS*, total suspended solid; *TDS*, total dissolved solid.

traditional P and P effluent treatments are physicochemical and biological procedures. Among the various physicochemical techniques, coagulation/flocculation was the most commonly used separation method for transferring dissolved and suspended OWM and solids from WW. Using inorganic coagulants like aluminum sulfate, ferric chloride, or polyelectrolytes can result in various ecological problems, including the formation of metal hydroxide rich sludge, which can cause serious disposal issues and increase metal concentrations. Moreover, nearly all physicochemical methods produce greenhouse gases, which vary depending on the specific system. Other limitations of these techniques include their sensitivity to pH variations, their limited effectiveness when dealing with tiny particles, and their low output in cold water. Polymeric coagulants, introduced to address these issues, offer some advantages. However, due to their cost-effectiveness and environmental concerns, they are unsuitable for industrial WW treatment. Unreacted monomers, such as acrylamides, are highly toxic carcinogens. Natural materials like chitosan, tannins, and cellulose can be used instead of chemical coagulants to prevent secondary pollution. Despite their eco-friendly nature, these materials have a low biodegradability and a short life span for hydrolysis. Membrane processes, including membrane filtration, nanofiltration, and membrane bioreactors, are also promising approaches for the treatment of paper mill wastewaters. However, these processes are limited by membrane fouling phenomena, which reduce permeate flux and membrane lifetime. Other processes, such as electrochemical methods and advanced oxidation techniques, are similar to ozonation and Fenton processes, but their main disadvantage is that they are not cost effective and need a substantial energy input. The use of live microbes like bacteria, fungi, and algae for sewage treatment is another potential approach to meet environmental concerns and avoid secondary sewage pollution. The biomethods commonly used in paper wastewater treatment are either aerobic or anaerobic. In the aerobic method, OWM are converted into CO_2 , H_2O , and inorganic compounds by selected microorganisms. This activated slurry technique needs the constant performance of oxygen blowers and sludge pumps. Similarly, an aerated lagoon functions as a reaction pond, actively aerating the effluent to boost biological oxidation. The highest demerit of all the aerobic treatment techniques is the need for an always high-energy supply. Anaerobic treatment is the technique that holds the most promise. However, it has some drawbacks, such as producing air pollutants like nitrous oxides. In this case the input energy required is nearly negligible, but the output is superior. If a method is sustainable, it should be eco-friendly, have no input energy, and output reasonably high (Toczyłowska-Mamińska, 2017).

12.5 Conclusions and future trends

The P and P industry, one of the main drivers of the world's economy, faces significant WW management challenges. The pulping, bleaching, and papermaking processes release large volumes of lignin, organic debris, and other contaminants into the effluent. Despite their effectiveness, traditional WW treatment (physical, chemical, and biological) techniques have drawbacks in terms of cost, energy usage, and the production of secondary pollutants.

MFCs provide energy generation in conjunction with WM. They produce electrical energy by exploiting the metabolism of microorganisms. Microbes oxidize OWM at the anode, releasing electrons, whereas in the cathode, these electrons combine with oxygen to produce water. The produced electrical energy can be stored or used directly. The system also fights pollution by breaking down the OWM into simpler forms. WW from the paper industry contains redox chemicals that can mediate electron transfer to the anode, resulting in an energy gain. Compared to anaerobic treatments, MFC has greater COD removal rates.

The process's challenges include ensuring stable microbial communities and preventing contamination while scaling up. At various levels, we should employ more collaborative efforts and pilot projects to ensure industrial feasibility.

List of acronyms

AC	Anode chamber
AQDS	9,10-anthraquinone-2,6- disulfonic acid disodium salt
BI	Biodegradability index
BOD	Biological oxygen demand
BWW	Bagasse wash water
CC	Cathode chamber
COD	Chemical oxygen demand
CW-MFC	Wetland coupled with MFC
DGGE	Denaturing gradient gel electrophoresis
EC	Electrocoagulation
EFW	Energy from waste
FESEM	Field emission scanning electron microscopy
HRT	Hydraulic retention time
MFC	Microbial fuel cell
NHE	Normal hydrogen electrode
OFR	Rate of oxygen flow
OWM	Organic waste material
PCR	Polymerase chain reaction
PEM	Proton exchange membrane
P and P	Pulp and paper
PRS	Phosphate buffer solution
PW	Pulping wastewater
PIW	Paper industry wastewater

PRW	Paper recycling wastewater
SCMFCs	Single-chambered microbial fuel cells
TDS	Total dissolved solid
TS	Total solid
TSS	Total suspended solid
WM	Waste management
WtE	Waste to energy
WW	Wastewater

References

- Catal, T., Li, K., Bermek, H., & Liu, H. (2008). Electricity production from twelve monosaccharides using microbial fuel cells. *Journal of Power Sources*, 175(1), 196–200. <https://doi.org/10.1016/j.jpowsour.2007.09.083>.
- Catal, T., Xu, S., Li, K., Bermek, H., & Liu, H. (2008). Electricity generation from polyalcohols in single-chamber microbial fuel cells. *Biosensors and Bioelectronics*, 24(4), 849–854. <https://doi.org/10.1016/j.bios.2008.07.015>.
- Cheng, S., & Logan, B. E. (2007). Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells. *Electrochemistry Communications*, 9(3), 492–496. <https://doi.org/10.1016/j.elecom.2006.10.023>.
- Di Lorenzo, M., Curtis, T. P., Head, I. M., & Scott, K. (2009). A single-chamber microbial fuel cell as a biosensor for wastewaters. *Water Research*, 43(13), 3145–3154. <https://doi.org/10.1016/j.watres.2009.01.005>, <https://www.sciencedirect.com/science/journal/00431354>.
- El Hanandeh, A., & El-Zein, A. (2009). Strategies for the municipal waste management system to take advantage of carbon trading under competing policies: The role of energy from waste in Sydney. *Waste Management*, 29(7), 2188–2194. <https://doi.org/10.1016/j.wasman.2009.03.002>.
- Elakkiya, E., & Niju, S. (2021). Bioelectrochemical treatment of real-field bagasse-based paper mill wastewater in dual-chambered microbial fuel cell. *3 Biotech*, 11(2). <https://doi.org/10.1007/s13205-020-02606-6>.
- ElMekawy, A., Srikanth, S., Bajracharya, S., Hegab, H. M., Nigam, P. S., Singh, A., Mohan, S. V., & Pant, D. (2015). Food and agricultural wastes as substrates for bioelectrochemical system (BES): The synchronized recovery of sustainable energy and waste treatment. *Food Research International*, 73, 213–225. <https://doi.org/10.1016/j.foodres.2014.11.045>, www.elsevier.com/inca/publications/store/4/2/2/9/7/0.
- Fadzli, F. S., Bhawani, S. A., & Mohammad, R. E. A. (2021). Microbial fuel cell: Recent developments in organic substrate use and bacterial electrode interaction. *Journal of Chemistry*, 2021. <https://doi.org/10.1155/2021/4570388>, <http://www.hindawi.com/journals/chem/contents/>.
- Fang, Z., Song, H. L., Cang, N., & Li, X. N. (2013). Performance of microbial fuel cell coupled constructed wetland system for decolorization of azo dye and bioelectricity generation. *Bioresource Technology*, 144, 165–171. <https://doi.org/10.1016/j.biortech.2013.06.073>, www.elsevier.com/locate/biortech.
- Guerrero-Rangel, N., Rodriguez-de la Garza, J. A., Garza-Garc, Y., Rios-Gonza, L. J., Sosa-Santi, G. J., de la Garza-Rodriguez, I. M., Martinez-Amador, S. Y., Rodriguez-Garza, M. M., & Rodriguez, J. (2010). Comparative study of three cathodic electron acceptors on the performance of mediatorless microbial fuel cell. *International Journal of Electrical and Power Engineering*, 4(1), 27–31. <https://doi.org/10.3923/ijepe.2010.27.31>.

- Huang, L., Cheng, S., Rezaei, F., & Logan, B. E. (2009). Reducing organic loads in wastewater effluents from paper recycling plants using microbial fuel cells. *Environmental Technology*, 30(5), 499–504. <https://doi.org/10.1080/09593330902788244>, <http://www.tandf.co.uk/journals/titles/09593330.asp>.
- Huang, L., & Logan, B. E. (2008). Electricity generation and treatment of paper recycling wastewater using a microbial fuel cell. *Applied Microbiology and Biotechnology*, 80(2), 349–355. <https://doi.org/10.1007/s00253-008-1546-7>.
- Iqbal, H., Bhowmik, A., Yasmin, S., Aziz, S., Islam, D., Jamal, M. S., & Hossain M. (2022). Investigation of electrode combinations in electricity generation from the pulp and paper industry wastewater. Research Square, Bangladesh Research Square. <https://www.researchsquare.com/browse>. <https://doi.org/10.21203/rs.3.rs-2167210/v1>.
- Kassongo, J., & Togo, C. A. (2011). Evaluation of full-strength paper mill effluent for electricity generation in mediator-less microbial fuel cells. *African Journal of Biotechnology*, 10(69), 15564–15570. <https://doi.org/10.5897/AJB11.146>, <http://www.academicjournals.org/AJB/PDF/pdf2011/7Nov/Kassongo%20and%20Togo.pdf>.
- Kloch, M., & Toczylowska-Maminska, R. (2020). Toward optimization of wood industry wastewater treatment in microbial fuel cells-mixed wastewaters approach. *Energies*, 13(1). <https://doi.org/10.3390/en13010263>, <https://www.mdpi.com/1996-1073/13/1>.
- Kong, L., Hasanbeigi, A., & Price, L. (2016). Assessment of emerging energy-efficiency technologies for the pulp and paper industry: A technical review. *Journal of Cleaner Production*, 122, 5–28. <https://doi.org/10.1016/j.jclepro.2015.12.116>.
- Kumar, R., Singh, L., Zularisam, A. W., & Hai, F. I. (2018). Microbial fuel cell is emerging as a versatile technology: A review on its possible applications, challenges and strategies to improve the performances. *International Journal of Energy Research*, 42(2), 369–394. <https://doi.org/10.1002/er.3780>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1099-114X](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1099-114X).
- Lee, S. Y., Sankaran, R., Chew, K. W., Tan, C. H., Krishnamoorthy, R., Chu, D.-T., & Show, P.-L. (2019). Waste to bioenergy: A review on the recent conversion technologies. *BMC Energy*, 1(1). <https://doi.org/10.1186/s42500-019-0004-7>.
- Li, W. W., & Yu, H. Q. (2011). From wastewater to bioenergy and biochemicals via two-stage bioconversion processes: A future paradigm. *Biotechnology Advances*, 29(6), 972–982. <https://doi.org/10.1016/j.biotechadv.2011.08.012>.
- Lior, N. (2008). Energy resources and use: The present situation and possible paths to the future. *Energy*, 33(6), 842–857. <https://doi.org/10.1016/j.energy.2007.09.009>, www.elsevier.com/inca/publications/store/4/8/3/.
- Liu, S., Song, H., Li, X., & Yang, F. (2013). Power generation enhancement by utilizing plant photosynthate in microbial fuel cell coupled constructed wetland system. *International Journal of Photoenergy*, 2013, 1–10. <https://doi.org/10.1155/2013/172010>.
- Logan, B. E. (2008). *Microbial fuel cells*. Wiley. <https://doi.org/10.1002/9780470258590>.
- Logan, B., Cheng, S., Watson, V., & Estadt, G. (2007). Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environmental Science & Technology*, 41(9), 3341–3346. <https://doi.org/10.1021/es062644y>.
- Logan, B. E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., & Rabaey, K. (2006). Microbial fuel cells: Methodology and technology. *Environmental Science and Technology*, 40(17), 5181–5192. <https://doi.org/10.1021/es0605016>.
- Nambiar, S., Togo, C. A., & Limson, J. L. (2009). Application of multi-walled carbon nanotubes to enhance anodic performance of an *Enterobacter cloacae*-based fuel cell. *African Journal of Biotechnology*, 8(24), 6927–6932. <http://www.academicjournals.org/AJB/PDF/pdf2009/15Dec/Nambiar%20et%20al.pdf>.

- Narayan, M., Solanki, P., Rabha, A. K., & Srivastava, R. K. (2018). Treatment of pulp and paper industry effluent and electricity generation by constructed wetland coupled with microbial fuel cell (CW-MFC). *Journal of Pharmacognosy and Phytochemistry*, 7, 493–498.
- Oh, S., Min, B., & Logan, B. E. (2004). Cathode performance as a factor in electricity generation in microbial fuel cells. *Environmental Science and Technology*, 38(18), 4900–4904. <https://doi.org/10.1021/es049422p>.
- Pandey, P., Shinde, V. N., Deopurkar, R. L., Kale, S. P., Patil, S. A., & Pant, D. (2016). Recent advances in the use of different substrates in microbial fuel cells toward wastewater treatment and simultaneous energy recovery. *Applied Energy*, 168, 706–723. <https://doi.org/10.1016/j.apenergy.2016.01.056>, <http://www.elsevier.com/inca/publications/store/4/0/5/8/9/1/index.htm>.
- Pant, D., Van Bogaert, G., Diels, L., & Vanbroekhoven, K. (2010). A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. *Bioresource Technology*, 101(6), 1533–1543. <https://doi.org/10.1016/j.biortech.2009.10.017>.
- Petrus, L., & Noordermeer, M. A. (2006). Biomass to biofuels, a chemical perspective. *Green Chemistry*, 8(10), 861–867. <https://doi.org/10.1039/b605036k>.
- Rezaei, F., Xing, D., Wagner, R., Regan, J. M., Richard, T. L., & Logan, B. E. (2009). Simultaneous cellulose degradation and electricity production by *Enterobacter cloacae* in a microbial fuel cell. *Applied and Environmental Microbiology*, 75(11), 3673–3678. <https://doi.org/10.1128/aem.02600-08>.
- Roy, S., Marzorati, S., Schievano, A., & Pant, D. (2017). Microbial fuel cells. In *Encyclopedia of sustainable technologies*. India: Elsevier, 245–259. <https://doi.org/10.1016/B978-0-12-409548-9.10122-8>, <http://www.sciencedirect.com/science/book/9780128047927>.
- Sakdaronnarong, C., Ittitanakam, A., Tanubumrungsuk, W., Chaithong, S., Thanosawan, S., Sinbuathong, N., & Jeraputra, C. (2015). Potential of lignin as a mediator in combined systems for biomethane and electricity production from ethanol stillage wastewater. *Renewable Energy*, 76, 242–248. <https://doi.org/10.1016/j.renene.2014.11.009>.
- Scott, K., & Murano, C. (2007). Microbial fuel cells utilising carbohydrates. *Journal of Chemical Technology & Biotechnology*, 82(1), 92–100. <https://doi.org/10.1002/jctb.1641>.
- Shankar, R., Varma, A. K., Mondal, P., & Chand, S. (2016). Simultaneous treatment and energy production from PIW using electro coagulation & microbial fuel cell. *Journal of Environmental Chemical Engineering*, 4(4), 4612–4618. <https://doi.org/10.1016/j.jece.2016.10.021>, <http://www.journals.elsevier.com/journal-of-environmental-chemical-engineering/>.
- Singh, P., & Srivastava, A. S. N. (2017). Electricity generation by microbial fuel cell using pulp and paper mill wastewater, vermicompost and *Escherichia coli*. *Indian Journal of Biotechnology*, 16(2), 211–215. <http://nopr.niscair.res.in/bitstream/123456789/42921/1/IJBT%2016%282%29%20211-215.pdf>.
- Toczyłowska-Mamińska, R. (2017). Limits and perspectives of pulp and paper industry wastewater treatment – A review. *Renewable and Sustainable Energy Reviews*, 78, 764–772. <https://doi.org/10.1016/j.rser.2017.05.021>.
- Tomić, T., & Schneider, D. R. (2018). The role of energy from waste in circular economy and closing the loop concept–Energy analysis approach. *Renewable and Sustainable Energy Reviews*, 98, 268–287. <https://doi.org/10.1016/j.rser.2018.09.029>, <https://www.journals.elsevier.com/renewable-and-sustainable-energy-reviews>.
- Velasquez-Orta, S. B., Head, I. M., Curtis, T. P., & Scott, K. (2011). Factors affecting current production in microbial fuel cells using different industrial wastewaters. *Bioresource Technology*, 102(8), 5105–5112. <https://doi.org/10.1016/j.biortech.2011.01.059>.

- Villaseñor, J., Capilla, P., Rodrigo, M. A., Cañizares, P., & Fernández, F. J. (2013). Operation of a horizontal subsurface flow constructed wetland – Microbial fuel cell treating wastewater under different organic loading rates. *Water Research*, 47(17), 6731–6738. <https://doi.org/10.1016/j.watres.2013.09.005>.
- Yadav, A. K., Dash, P., Mohanty, A., Abbassi, R., & Mishra, B. K. (2012). Performance assessment of innovative constructed wetland-microbial fuel cell for electricity production and dye removal. *Ecological Engineering*, 47, 126–131. <https://doi.org/10.1016/j.ecoleng.2012.06.029>.
- Zuo, Y., Cheng, S., Call, D., & Logan, B. E. (2007). Tubular membrane cathodes for scalable power generation in microbial fuel cells. *Environmental Science and Technology*, 41(9), 3347–3353. <https://doi.org/10.1021/es0627601>.
- Zuo, Y., Cheng, S., & Logan, B. E. (2008). Ion exchange membrane cathodes for scalable microbial fuel cells. *Environmental Science and Technology*, 42(18), 6967–6972. <https://doi.org/10.1021/es801055r>.

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Pulp and paper wastewater treatment using agricultural and bio-based materials

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13.1 Introduction

The necessity for innovative wastewater treatment methods has arisen as a result of the proliferation of industrial activity, population development, and escalating environmental concerns (Obaideen et al., 2022). The pulp and paper industry is widely recognized as a significant sector on a global scale, as evidenced by its substantial consumption of paper and paperboard products, which amounted to 250 million metric tons in the year 2020 (Haile et al., 2021). Nevertheless, the sector produces a substantial volume of wastewater as a result of chemical-intensive operations, including pulping, bleaching, and washing (Chauhan & Meena, 2021). This wastewater is found to include many contaminants, including lignin, lead, sulfate, and phenolic compounds (Kumar et al., 2020, 2023). Failure to remove these compounds may result in severe environmental problems like water pollution, increased soil salinity, and disruption of aquatic life (Hossain & Ismail, 2015). Hence, adequate treatment of the generated wastewater is crucial.

Either physicochemical or biological methods typically treat pulp and paper wastewater. Physicochemical treatment techniques include sedimentation, adsorption, coagulation and precipitation, membrane filtration, and chemical oxidation (Toczyłowska-Mamińska, 2017), among which coagulation and flocculation by the use of metal salts as a coagulant are most widely used (Alengebawy et al., 2021). However, this approach results in the production of toxic metal hydroxide sludge and high concentrations of metal in treated wastewater (Toczyłowska-Mamińska, 2017).

Biological methods, unlike physicochemical methods, are eco-friendly processes for wastewater treatment. Microbes break down organic compounds in the presence of oxygen in the activated sludge process. Nevertheless, it requires energy-intensive aeration (about 880–1000 kWh) to remove one ton of chemical oxygen demand (COD), which is roughly 50%–90% of the total electricity demand of the treatment plant (Drewnowski et al., 2019; Mininni et al., 2015). Several advanced water treatment methods, such as microbial fuel cells (Srivastava et al., 2023), membrane bioreactors (Qu et al., 2012), and moving bed biofilm reactors (Vaidhegi, 2013), have shown better energy efficiency and environmental benefits. However, these methods are complex, with high manufacturing costs (Wu et al., 2022). Hence, low-energy, cost-efficient, and nontoxic water treatment methods with abundant raw materials are needed to make pulp and paper wastewater treatment sustainable. In this scenario, agricultural and biobased materials can be energy and cost-efficient, accessible, and clean alternatives.

Agricultural and biobased materials are products derived from renewable resources, such as agricultural residues, animal by-products, and microorganisms. They are suitable for pulp and paper wastewater treatment due to their superior versatility, renewability, abundance, affordability, energy effectiveness, and environmental friendliness (Wu et al., 2022). The major agricultural and biobased materials to treat pulp and paper wastewater include biosorbents, biomembranes, and bioflocculants.

13.2 Pulp and paper wastewater

The pulp and paper industry plays a crucial role in numerous economies by facilitating the manufacturing of paper products that are ubiquitous in our daily lives. Nevertheless, the manufacturing procedures utilized within this sector produce significant quantities of effluent that require meticulous control. The following sections explore the origins and properties of effluent from the paper and pulp industry (Section 13.2.1), in addition to its extensive ecological

consequences and related toxicity (Section 13.2.2). It is imperative to comprehend the composition and potential risks associated with this effluent to formulate efficacious treatment approaches and alleviate its environmental impacts.

13.2.1 Sources and characteristics

Major pulp and paper manufacturing operations are raw material preparation, pulping, chemical recovery, bleaching, stock preparation, and papermaking (Bajpai, 2015). Each process generates wastewater with different characteristics. Raw material preparation, pulping (e.g., wood digestion), and bleaching generate the largest amount of wastewater (Ashrafi et al., 2015). Wood is the most prominent raw material prepared for pulping by debarking, chipping, and chip-screening (Bajpai, 2018). The wastewater generated in this operation contains dirt, fibers, COD, and suspended solids (SS) (Ashrafi et al., 2015). Screened chips are then pulped to remove lignin from the chips and separate fibers.

Chemical pulping is the most prominent pulping process, as it improves the strength and durability of paper (Mboowa, 2024). In chemical pulping, kraft pulping is the most practiced process. It generates a lot of toxic kraft lignin in wastewater (Li et al., 2021). Sulfite pulping, the next common process, also generates a large amount of sulfite lignin (Kumar et al., 2023). In either process, black liquor, fatty acids, tannins, and chlorophenols are also present in wastewater (Ashrafi et al., 2015). Bleaching is also done using chlorine to brighten pulp, which generates the most toxic compounds (Kulshreshtha et al., 2012), such as lignin, chloride, dioxin, chlorate, adsorbable organic halide (AOX), furans, and volatile organic compounds (VOCs) (Ashrafi et al., 2015). As a result a high concentration of SS, COD, and color needs to be removed during the treatment of pulping wastewater. Moreover, the low pH of the wastewater makes the treatment challenging. Dyes, nitrate, lead, acetone, sulfate, and chromium are the pollutants generated in the rest of the operations (Ashrafi et al., 2015; Kumar et al., 2020) (Table 13.1).

13.2.2 Environmental impacts and ecotoxicity

Lignin is the largest constituent of pulp and paper wastewater. Kraft lignin is generated from the kraft pulping process, which is insoluble in water and responsible for its dark brown or black color (Verma & Ekka, 2018). It is considered the most toxic lignin type, as it does not undergo chemical or biological degradation and accumulates in water bodies due to its complex three-dimensional structure (Singh et al., 2019). This accumulation leads to a larger lignin load, and water becomes susceptible to eutrophication. Eutrophication leads to algal blooms and threatens aquatic flora

Table 13.1 Wastewater characteristics of pulp and paper manufacturing (Kumar et al., 2020).

Parameters	Value (mg/L)	Permissible limits (mg/L) ^a
Lignin	578 ± 0.13	0.05
Total phenol	13.195 ± 0.52	0.5
Sulfate	713.1 ± 1.11	250
Nitrate	210.08 ± 2.32	50
Lead	0.2550 ± 0.12	0.05
Chromium	0.3058 ± 0.01	0.05
Copper	1.3814 ± 0.16	0.5
Cadmium	0.08632 ± 0.13	0.01
Chloride	2350 ± 1.14	1500
BOD	225 ± 2.24	40
COD	543.04 ± 1.22	120
Total solids	3280 ± 1.32	300
Color	1275 ± 3.11 (Unit: Pt-Co)	Colorless

BOD, Biochemical oxygen demand; *COD*, chemical oxygen demand.

^a The permissible limits are listed as provided by the Environmental Protection Agency (EPA).

and fauna, especially when caused by phosphorus (Elgarhy et al., 2022). Similarly, sulfite pulping generates lignosulfonate. Water bodies with excess lignosulfonate have a decreased sunlight transmission capability, which hinders the growth of phototrophic plants and algae (Verma et al., 2020).

Phenolic compounds are other major pollutants. In pulp and paper wastewater, lignin can transform into phenolic compounds through hydroxyalkylation (Haq & Raj, 2019). Toxic phenolic compounds like dichlorophenol, trichlorophenol, dichloroguicol, tetrachloroguicol, and pentachlorophenol are also generated in pulp and paper manufacturing (Ragunathan & Swaminathan, 2004). These compounds damage red blood cells and the liver and are mutagenic and carcinogenic even at low concentrations (Barik et al., 2021). They can also interact with microbes and inorganic and organic compounds to produce other toxic moieties (Haq & Raj, 2019). As these compounds are acidic, even a small amount in drinking water gives an offensive odor and taste (Panigrahy et al., 2022).

Heavy metals, such as lead, chromium, copper, and cadmium, are also generated in pulp and paper manufacturing. They are major environmental pollutants owing to their toxicity, longevity, and bioaccumulative nature (Mitra et al., 2022). Irrigation with industrial

effluents that contain high levels of heavy metals causes adverse effects on human health, plants, and soil (Haq & Raj, 2019). Lead is the most toxic heavy metal, causing oxidative stress in organisms by spreading and interfering with every biochemical process by binding with sulfhydryl (Ghosh et al., 2018). Oxidative stress triggers neurotoxicity and immune responses (Lee et al., 2019). Lead also interrupts physiological functions, causes pulmonary, cardiovascular, and kidney diseases, and is identified as a carcinogen (Li et al., 2016; Raj & Das, 2023).

High sulfate load in water causes laxative effects and digestive problems. It affects phosphorus, carbon, and nitrogen cycles (Zak et al., 2021). Nitrate causes eutrophication and damages oxygen-carrying pigments (Singh et al., 2022). Water with nitrite may leak into aquifers and cause chemolithoautotrophic pyrite oxidation, deteriorating groundwater quality by releasing toxic compounds, such as sulfuric acid and arsenic (Sanz et al., 2021). If ingested, nitrate-contaminated water increases the risk of colorectal cancer, thyroid disease, and congenital disabilities. Similarly, a large amount of chloride in water increases corrosiveness and affects the osmoregulation of aquatic animals, which hinders their growth, survival, and reproduction (Supratim & Kaushik, 2017). The most common wastewater constituents and their relevant impacts are summarized in Table 13.2.

The pulp and paper industry also generates large amounts of sludge each year, which needs proper disposal. High water content hinders its effective disposal (e.g., landfilling and incineration) (Hu et al., 2022). Therefore sludge management is also an environmental concern in the pulp and paper industries and needs to be considered.

13.3 Agricultural and biobased materials for pulp and paper wastewater treatment

The utilization of agricultural and biobased materials has emerged as a promising material for sustainable solutions to the challenges posed by pulp and paper effluent. Biosorbents, predominantly composed of substances obtained from natural and agricultural materials, are the subject of discussion in Section 13.3.1. These substances demonstrate an outstanding ability to absorb and eliminate impurities from effluent generated by the processing of pulp and paper. Also, the investigation of biomembranes as a means of treating effluent is detailed in Section 13.3.2. By functioning as selective barriers that permit the flow of treated water while efficiently eliminating contaminants, biomembranes are frequently

Table 13.2 Wastewater-containing components and their environmental impacts.

Categories	Components	Impacts	References
Micropollutants	Pharmaceuticals, chemicals, pesticides, hormones, cyanotoxins, detergents, and personal care products	Endocrine conduit disturbance in aquatic organisms, brain damage, convulsion, carcinogenic diseases, reproductive behavioral disorder, cardiovascular disease, liver damage, and lung defects, as well as disturbances in gene expression leading to feminization of aquatic organisms	Bhatt et al. (2022) and Priya et al. (2022)
Microorganisms	Bacteria, fungi, protozoa, viruses, and worms	Modification of water properties, posing a threat to human health, and utilization of available oxygen to accept electrons, leading to the oxidation of organic matter into more stable substances	Koul et al. (2022)
Metals	Lead, copper, nickel, zinc, chromium, cadmium, and mercury	Reducing seed germination and lipid content due to cadmium and nickel accumulation, hindering enzyme activity and plant growth caused by chromium, impeding photosynthesis by copper and mercury, decreasing chlorophyll production and plant growth due to lead, and animals may suffer from stunted growth and development, cancer, organ damage, nervous system damage, and in severe cases, death	Akor (2014)
Nutrients	Nitrogen and phosphorus	Overgrowth of aquatic plants like hyacinths and the formation of algal blooms, a decline in dissolved oxygen levels in rivers, lakes, and coastal regions due to nitrogen-rich fertilizers, which can have detrimental consequences on marine life	Akinlawo (2023)
Biodegradable organic materials	Protein, organic carbon, ammonia, and sugars	Eutrophication, toxic algal blooms, hypoxic dead zones, unsafe drinking water supplies, membrane fouling, corrosion issues, and repercussions for human health, environment, and economies. In addition to inhibition of natural nitrification due to ammonia, causing water hypoxia, resulting in fish poisoning, it decreases the water purification capacity and harms the water environment	(Fernández-Dacosta et al., 2015) and (Luo et al., 2015)

Other organic materials	Detergents, oil, fat, phenols, grease, and solvents	Carcinogenic and mutagenic properties of treated oily wastewater impede plant growth, elevate BOD and COD of water bodies, and reduce sunlight penetration into the water by forming a layer on the water surface, which can disrupt the aquatic ecosystem. In addition to the hazardous impacts of many phenolic compounds due to their toxic, carcinogenic, and dangerous nature when exposed to animals and humans	Yashas et al. (2018)
Inorganic materials	Phosphates, soaps, and heavy metals	Corrosion in wastewater appliances, fouling issues, odors, lethal fumes, and the production of corrosive acids	Wu et al. (2013)

BOD, Biochemical oxygen demand; *COD*, chemical oxygen demand.

derived from biobased materials. Moreover, bioflocculants, composed of natural materials, aggregate and settle wastewater particles. [Section 13.3.3](#) examines the role of bioflocculants in increasing pulp and paper wastewater treatment efficiency and sustainability.

13.3.1 Biosorbents

Materials, such as lignin, biochar, chitin/chitosan, and cellulose, exhibit excellent adsorption capacities for various contaminants in paper mill effluent. Lignin can adsorb residual dyes and aromatics, while biochar removes chlorophenols, heavy metals, and toxins ([Karić et al., 2022](#)). The abundant surface functional groups and high surface area of these biomaterials enable adsorptive removal through mechanisms like electrostatic attraction, cation exchange, and adsorption interactions ([Vasić et al., 2023](#)), as shown in [Fig. 13.1](#). The following subtitles present the most commonly used biosorbents for wastewater treatment, including biochar, zeolites, and lignin.

13.3.1.1 Biochar

Biochar is a carbon-rich porous material with functional groups, such as hydroxyl, carbonyl, and carboxyl, and a large specific surface area ([Xiang et al., 2020](#)). Thermochemical decomposition, such as pyrolysis, gasification, torrefaction, hydrothermal carbonization, and microwave heating of biomass, produces biochar. Various biomasses, such as agricultural and forest residues, algae, municipal solid waste, wood chips, and sewage sludge, can be used as biomass feedstock.

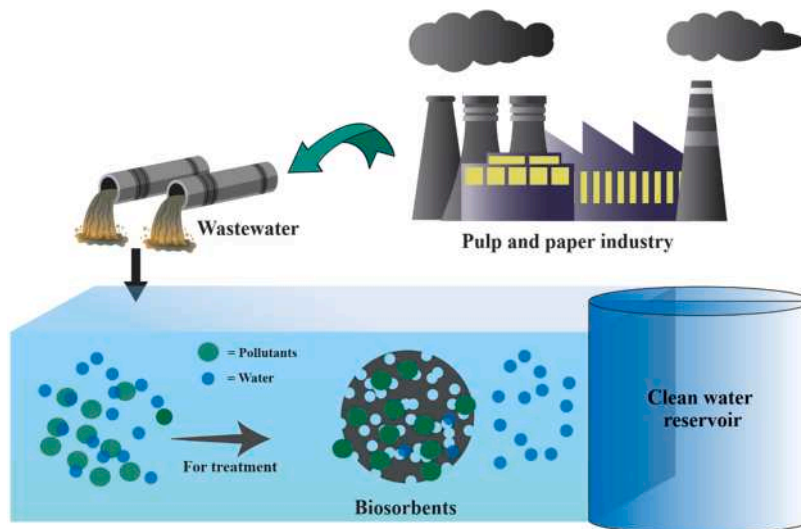


Figure 13.1 Adsorption mechanism of pulp and paper industry wastewater pollutants.

Pyrolysis is the most common thermochemical method to produce biochar. Variations in operating temperature and duration of thermal decomposition give different quantities of solid (biochar), liquid (biooil), and gaseous (syngas/pyro-gas) products (Ghimire et al., 2021). Biochar production is favored by low operating temperature and high residence time, often known as slow pyrolysis. Operating parameters also affect the physical and chemical properties of biochar significantly (Yu et al., 2019). Physical and chemical pretreatment and posttreatment, and biological pretreatment also affect biochar properties (Xiang et al., 2020).

Biochar has been considered mostly for carbon sequestration and adsorption of pollutants, thus solving some global pollution (Creamer & Gao, 2016). Interest in biochar is increasing among researchers as it is cheap, environment-friendly, and effectively removes pollutants from wastewater by adsorption by means of rice straw-derived biochar (Ma et al., 2023). Wastewater from the pulp and paper industry contains toxic and nonbiodegradable substances, making conventional biological treatments, such as activated sludge and anaerobic digestion, unstable (Kamali et al., 2020). As lignin and its derivatives, responsible for COD and color in pulp and paper wastewater treatment, are difficult to degrade in biological treatments, adsorption by biochar is considered to be a better option. Ciputra et al. (2010) found 76% removal of dissolved organic carbon while using granular activated carbon (similar to biochar) in pulp and paper wastewater treatment.

Biochar engineering has recently gained momentum as pristine biochar has a lower adsorption capacity. Different engineering techniques, such as biological modification, ball milling, and microwave modification, have been in use to enhance the effective adsorption of biochar (Wang et al., 2017). Engineered biochar is found to have improved functional groups, surface active sites, pore properties, and ease of separation from wastewater (Tan et al., 2016). Biochar is also modified to enhance the adsorption capacity of phosphate (anionic compound) by reacting with metals and metal oxides (Zhang, Lin, et al., 2022). Kapatel et al. (2022) activated biochar using phosphoric acid and observed color and COD removal by 98.03% and 84.61%, respectively, a significant improvement compared to nonactivated biochar.

Pulp and paper wastewater treatment by biochar involves mixing biochar with the wastewater, allowing sufficient contact time for adsorption and microbial activity, and then separating the treated water from biochar using physical methods like filtering or settling (Osman et al., 2023). Biochar has also been used extensively in pulp and paper wastewater treatment to remove dyes by adsorption. Biochar has the capacity to effectively mitigate the acidic nature of pulp and paper wastewater, which is mostly attributed to the presence of lignin and other organic substances (Jaiswal et al., 2021). Given the current emphasis of the pulp and paper industry on enhancing production processes and environmental sustainability, the utilization of biochar as an economical and eco-friendly adsorbent for wastewater treatment is a viable alternative (Osman et al., 2023). Additionally, this approach aids in adhering to rigorous environmental requirements while still maintaining treatment costs under the industry's profitable threshold.

13.3.1.2 Zeolite

Zeolites are microporous and crystalline minerals used for their ion-exchange properties. They are naturally occurring and synthesized with microporous cavities and channels (Khaleque et al., 2020). When environmental consciousness peaked, they were also used in environmental sectors, such as water and wastewater treatment, due to their adsorption and ion-exchange properties (Roshanfekr Rad & Anbia, 2021). Natural clay minerals, such as zeolite, bentonite, and kaolinite, are currently receiving significant attention for their potential to effectively remove various contaminants, including phosphors, cations, and anions, from wastewater (Elgarhy et al., 2022). Recently, they have been used in various

industries, including detergents, gas separation, nuclear waste remediation, agriculture, and construction.

Natural zeolite is found in pores and fractures of volcanic rocks. However, kaolinite, feldspar, volcanic glass, and kaolinite can form zeolite in the presence of favorable temperature, pressure, and mineralizing fluid (Hay & Sheppard, 2001). Natural zeolite has a heterogeneous chemical composition, and its application is restrained in case of homogeneous property requirements for higher efficiency. However, lower cost than synthetic zeolite provides wider application for natural zeolite (De Magalhães et al., 2022). On the contrary, synthetic zeolite can be prepared using two different approaches depending on chemical reactions in the solid or liquid state. The uniform pore size in synthetic zeolite gives wider applications that require superior product quality compared to natural zeolite. Modification of physiochemical and structural properties of zeolite is very common nowadays to improve the effectiveness of the different processes (Khaleque et al., 2020).

Zeolite has great potential in wastewater treatment owing to its unique characteristics. It is used in wastewater treatment to adsorb contaminants, such as organic pollutants and dyes, as zeolite's microporous structure provides a large surface area for effective adsorption (Ayar et al., 2015). Heavy metals, such as lead, cadmium, and mercury, are also removed by zeolite from the wastewater due to their affinity to the metals (Dal Bosco et al., 2005). Zeolite also has a good removal capacity for ammonia (Liu, Peng, et al., 2013), nutrients like phosphorus (Safie & Zahrim, 2021), and oil. It can also be used in ion-exchange processes to remove unwanted ions with beneficial ions, as in the water softening process. Moreover, it can buffer pH in wastewater and help reduce moisture content to improve sludge handling and disposal properties (Roshanfekr Rad & Anbia, 2021). Recently, zeolite has been getting much research interest due to its ability to handle emerging contaminants that are difficult to stabilize in conventional treatment processes.

The use of zeolite is limited in pulp and paper wastewater treatment. Munir et al. (2022) impregnated natural zeolite with iron and observed 71% and 89% COD and color removal, respectively, in pulp and paper wastewater, significantly higher than the removal rate by single ozonation process (SOP) and catalytic ozonation process (COP). Owing to the economic and environmental benefits of zeolite, more application is expected in the future in pulp and paper wastewater treatment, as conventional treatment is often inadequate to meet stringent government regulations.

13.3.1.3 Lignin

Lignin is a phenolic polymer found abundantly on Earth (Righi et al., 2016). It has gained attention for various environmental applications as a potential bioadsorbent due to its abundance, renewability, and adsorbent properties. As lignin is a by-product of various industrial processes and must be removed from wastewater before disposal, its use as a bioadsorbent adds economic value. It has a high surface area and different functional groups (e.g., phenolic group, hydroxyl, and carboxyl) capable of interacting with various pollutants, such as organic pollutants, heavy metals, nutrients, and dyes (Ruthran et al., 2022). It can also be engineered by modifying its functional group or structure to support the adsorption of selective pollutants from a complex mixture (Wang et al., 2022). Both chemical and physical treatments can be applied for surface modification and can also be regenerated and reused for multiple adsorption cycles (Li et al., 2019). Modifying lignin adsorbent includes containing oxygen, nitrogen, and sulfur functional groups and other methods, such as Cu (II) codoped with the nitrogen source (Wang et al., 2022). Adsorption can also be enhanced in lignin by forming lignin and its derivatives with inorganic and organic materials, such as composites of lignin and graphene, lignin and nanoparticles, lignin and chitosan, and lignin and carbon nanotubes (Wang et al., 2022).

Lignin is extracted from lignin-rich biomass, such as agricultural residues, including cotton residue, sugarcane bagasse, corncob, and other lignocellulosic biomasses (Ghimire et al., 2021). Sometimes, it can also be extracted from industrial waste streams, such as pulp and paper wastewater. However, pretreatments, such as hot water extraction, steam explosion, and enzymatic hydrolysis, are necessary to extract lignin from lignocellulosic biomass (Ghimire et al., 2021). These pretreatments can be costly economically and environmentally, especially if chemical pretreatments are preferred over physical or biological pretreatments (Alonso et al., 2013). Although physical and biological pretreatments are cheaper and environmentally friendly, the extraction process is slower.

Similar to biochar and zeolite, lignin has various applications in wastewater treatment. Heavy metals from wastewater streams form complexes with functional groups of lignin to remove the metals from the wastewater. Lignin can also be used in removing dyes from wastewater released from the textile industry. Similarly, lignin is used to remove organic pollutants, recover nutrients, such as phosphorus and nitrogen, from wastewater to support resource recovery, purify drinking water, and treat landfill leachate (Mohan et al., 2006). Although the specific application of lignin-based bioadsorption in pulp and paper wastewater is limited, different metal cations, inorganic anions, organic dyes, drugs, and other

pollutants, such as humic acid, benzene, crude oil, 2,4-dichlorophenoxyacetic acid, and persistent organic pollutants, have been removed efficiently using the bioadsorption (Wang et al., 2022).

As an economical and clean alternative, lignin-based bioadsorbent research will continue to grow in the coming years. To improve the overall efficiency of the adsorption of lignin, more research on extraction methods, lignin engineering, and lignin's structure-function relationship needs to be understood well. This improvement will help in sustainable wastewater treatment, focusing on the circular economy.

13.3.2 Biomembranes

In contrast to traditional materials, biomembranes can be used sustainably in separation processes. Various materials, including cellulose, chitosan, lignin, and alginate, have the potential to undergo processing for the production of specialized membranes, such as ultrafiltration (UF), nanofiltration (NF), and forward osmosis membranes (Ehsani et al., 2022). Biopolymer membranes possess several advantageous characteristics in comparison with typical synthetic membranes, including but not limited to enhanced selectivity, biodegradability, and resistance to fouling (Morales-Jiménez et al., 2023). The selective permeability of these substances allows for the separation of effluent streams, facilitating the recovery of compounds with added value or producing higher-quality water suitable for recycling and reuse (Zhang, 2022). The following subtitles present the most commonly used biomembranes for wastewater treatment, including cellulose-based, chitosan-based, and polymeric membranes.

13.3.2.1 Cellulose-based membranes

The wide use of membranes in wastewater treatment has invited researchers to focus on sustainable and environment-friendly alternatives to conventional materials, such as polymers, ceramics, and metals. Cellulose is a long chain of polymer with amorphous and crystalline regions. A feasible source of cellulose can be found in agricultural biomass, such as maize stalks, wheat straws, rice straws, and soy stalks. They can be used to make sustainable cellulose nanomaterials, such as cellulose nanocrystals (CNCs) and cellulose nanofibers (CNF) (Sadare et al., 2022). Nanocellulose has a diameter ranging from 10 to 100 nm and a high surface area (Shak et al., 2018). Using lignocellulosic biomass has gained significant attention in line with the circular economy to obtain zero waste. Existing nanomaterials, such as titanium oxide, carbon nanotubes, graphene oxide, and silica used in nanocomposite membranes, have environmental and health hazards, making cellulose nanomaterials a lucrative alternative (Carpenter et al., 2015). Among these, CNCs

are considered more strong, biodegradable, crystalline, reactive, easily separated, and better adsorbent due to their large specific surface area (Trache et al., 2017).

Lignocellulosic biomass, including a diverse range of agricultural residues, including deciduous and coniferous forests, crop residues, and energy crops, needs to be pretreated before the isolation of CNCs. Pretreatment of lignocellulosic biomass to extract cellulose includes alkaline treatment, solvent extraction, and steam explosion. Isolation of cellulose nanocrystals involves physical, chemical, and enzymatic processes. Grinding, hot water extraction, high-intensity ultrasonic treatment, and microfluidization technology are the physical treatments (Li et al., 2012). However, these processes consume energy, and the final product is unsatisfactory. The enzymatic process takes a longer time and needs to be repeated several times to achieve uniform small particles (Rovera et al., 2018). The chemical process is often the best option to obtain high-quality CNCs. Sulfuric acid hydrolysis is one of the frequently used chemical processes. Acid strength, contact time, temperature, and acid/pulp are important in hydrolysis (Jonooobi et al., 2015). Alkaline bleaching and chlorination are other common chemical processes to obtain CNCs.

Cellulose-based membrane removes dyes, organic and inorganic pollutants, heavy metals, pesticides, and pharmaceuticals from the wastewater. The surface of cellulose nanocrystals can be modified to efficiently remove organic pollutants from wastewater. NF membrane based on CNC effectively removed 98% and 96% of NaSO_4 and Mg_2SO_4 , respectively (Huang et al., 2019). Similarly, 90% of copper ions were found to be removed by polyethersulfone (PES)/1% modified CNC (Rafieian et al., 2019). Bovine serum albumin was removed 93% by CNC/PES (Zhang et al., 2018).

Although the use of cellulose-based membranes in the pulp and paper industry is still in the early stages, their use is expected to increase in the coming years due to the above-mentioned inherent advantages. This will help to revolutionize wastewater treatment in the pulp and paper industry. As conventional wastewater treatment plants cannot treat some emerging contaminants efficiently, membrane-based wastewater treatment helps to capture most of the contaminants. This will also allow water to be recycled for further use. Moreover, unlike other commercial membranes, the biodegradable nature of the cellulose-based membrane allows disposal without any further environmental concerns.

13.3.2.2 Chitosan-based membranes

Chitosan is a biopolymer derived from chitin found in the shells of crustaceans like lobsters, shrimp, and crabs, and in the cell walls

of fungi. It consists of β -(1 $\rightarrow$ 4) linkages of D-glucosamine and N-acetyl-D-glucosamine (Goswami et al., 2021). Chitosan has versatile properties due to the presence of hydroxyl (-OH) groups and amino (-NH₂) groups, which are very active (Wu et al., 2001). It is a nontoxic, polycationic, and biodegradable polymer. It has various uses, such as food, agriculture, medicine, and wastewater treatment. It has gained notable attention in recent years due to its various characteristics. It is biocompatible, biodegradable, highly resistant to microbial degradation, and can be used effectively in biological wastewater treatment. It also has a good adsorption capacity for dyes, heavy metals, and organic pollutants, making it a suitable candidate for wastewater treatment. Moreover, agents like isocyanates, glutaraldehyde, formaldehyde, and glyoxal can be cross-linked to improve their metal binding capacity (Zhou et al., 2007). The chelation process involves the formation of stable and robust coordination complexes between metal ions and a compound referred to as a chelating agent or chelator. As an inhibitor of scale and deposit formation during wastewater treatment, chelating agents are utilized to regulate the concentration of metal ions in water (Gulcin & Alwasel, 2022).

Usually, alkaline N-deacetylation is done on chitin to form this polyaminosaccharide. During deacetylation, acetyl groups are removed from the chitin molecule. Usually, sodium hydroxide (NaOH) is treated with chitin at elevated temperatures. The properties of chitosan are determined by the degree of deacetylation. However, the source of chitin, its intended use, and the final product determine the production process.

As a 100% biodegradable, it is an efficient flocculant with the benefits of fast settling times, backwashing, and filtration (Lichtfouse et al., 2019). Chitosan can form composites with poly (vinyl alcohol), montmorillonite, clay, perlite, polyvinyl chloride, and bentonite, and different composites can be used for different purposes in wastewater (Liu, Wang, et al., 2013). Chitosan/nanocellulose composite membrane can also be formed by solution casting. It was found to remove chromium ions from aqueous solution up to 87% (Goswami et al., 2021). Similarly, the chitosan/coconut fiber membrane showed around 90% Cu (II) and Pb (II) removal of heavy metals (Trang & Takaomi, 2021).

Chitosan is found to be a low-cost, efficient, and environment-friendly adsorbent with broader use in pulp and paper wastewater treatment. It is certain to gain more research interest in the coming years, as the world is searching for sustainable, green, and renewable wastewater treatment solutions.

13.3.2.3 Polymeric membranes

Polymeric membranes are usually made from synthetic or natural polymers and are thin, allowing selective substances to pass depending on charge, size, and solubility (Manetti & Tomei, 2022). These biobased polymers have been successfully produced using agricultural-based materials, such as plant-derived substrates that consist of lignocellulose fibers, cellulose esters, polylactic acid, and polyhydroxyalkanoates (PHA) (Maraveas, 2020). Municipal and industrial wastewater treatment is mostly based on biological treatment in direct contact with biomass. However, the concentration of xenobiotics, organic compounds not usually occurring in nature and toxic to biomass that are discarded in the wastewater, is increasing over time. Pharmaceutical and beauty product industries are mostly responsible for discarding xenobiotics with low threshold values and highly toxic to biomass (Daugulis et al., 2011). Similarly, recalcitrant materials, metals, salts, and nonneutral pH also hamper the biomass, affecting the overall biological treatment process (Metcalf et al., 2002). Physiochemical process is usually done before the biological process to overcome this process, but it is not cost-effective and environmentally friendly. Although microorganisms have an inherent capability to acclimatize to xenobiotics, it is a slow process and not applicable during the shock concentration. In such cases, polymeric membranes can act as barriers to xenobiotics, avoiding direct exposure to biomass. Slow release of adsorbed xenobiotics into the wastewater-containing biomass and acclimatized microorganisms to salts, inorganic materials, and metals makes membrane bioreactor a lucrative alternative to conventional wastewater treatment (Metcalf et al., 2002).

Polymeric membranes have several benefits, such as low-energy consumption, ease of operation, ability to separate contaminants to give higher purity treated water, recyclability of the membrane, and use at elevated temperatures (Rather et al., 2022). They are categorized into reverse osmosis (RO), NF, UF, and microfiltration (MF) based on their pore size, specific separation, characteristics, and performance (Rather et al., 2022). The use of polymeric membranes to treat industrial wastewater is fairly recent. 4-Chlorophenol was removed up to 99% for lower organic loading when a Hytrel 8206 membrane of 1 mm thickness was used in a submerged extractive membrane bioreactor (Tomei et al., 2016). Similarly, 98% of 4-chlorophenol and 100% of Cr (IV) were removed while treating synthetic wastewater in a bioreactor with hydraulic retention time as low as 3 hours (Angelucci et al., 2022). Polymer membranes have recently been considered for treating wastewater to produce potable water, as the source of drinking water is dwindling due to climate change, as seen in different parts of

the world (Brandt & Kwan, 2013). However, several challenges need to be overcome before this can be turned into reality. The major challenge is changing human perception, including other common problems of membranes (Warsinger et al., 2018).

Polymeric membranes have been gaining ample attention recently and are evolving continually due to extensive research and development to make them more efficient, durable, and selective. Polymeric membranes have already increased its scope of application and are likely to take up more applications in the coming years with improved demerits, such as membrane fouling, limited thermal and chemical stability, and nonconsistent performances under different conditions.

13.3.3 Biofloculants

Biofloculants can efficiently agglomerate suspended particles and destabilize emulsions and colloids through bridging, charge neutralization, and interparticle interactions (Maćczak et al., 2020). Chitosan, cellulose, starch, and biofloculants generated from plants have demonstrated remarkable capacities in coagulating and flocculating paper mill effluent throughout the treatment process (Mnif & Ben Rebah, 2023). Biofloculants offer several benefits, including their capacity to biodegrade, lack of toxicity, and prevention of secondary contamination. Nevertheless, it is imperative to tackle the obstacles associated with developing economically viable production methods and maintaining consistent performance (El-Gaayda et al., 2021). The following subtitles present the most commonly used biofloculants for wastewater treatment, including chitosan, polymeric, and plant-derived biofloculants.

13.3.3.1 Chitosan biofloculants

Chitosan biofloculant is a nontoxic, biocompatible, and biodegradable substitute to toxic inorganic coagulants and flocculants, which can reduce oxygen demand, total solids, and color of pulp and paper wastewater. Classified as a green product, it also has a quick deposition time (Hadiyanto et al., 2022). Chitosan is a linear aminopolysaccharide with 1,4- β -glycosidic bonds (Manek & Petroianu, 2021). Under acidic conditions the amino group protonates and destabilizes the anionic insoluble and dissolved colloidal and suspended particles into microflocs (Lichtfouse et al., 2019; Tang et al., 2020). Destabilization is driven by either charge neutralization or bridging of the chitosan chain, which eliminates the requirement of a preceding coagulation step (Lichtfouse et al., 2019). Microflocs aggregate and clump into a larger solid when agitated. Aggregated solid is removed in the subsequent sedimentation or filtration step (Morin-Crini et al., 2019; Vidal & Moraes, 2019).

Chitosan production involves the extraction of chitin and its deacetylation, which means removing the acetyl group in chitin to expose the amine group (Aranaz et al., 2021). Chitin is one of the most abundant biopolymers, which is attached to other biopolymers in organisms. Common sources of commercial chitin are the exoskeletons of crustaceans (shrimps, lobsters, crabs), mollusks (snails, oysters), and cuticles of insects (cockroaches, spiders) (Joseph et al., 2021). Production steps of chitosan from chitin-based sources are presented in Fig. 13.2.

Chitin may be covalently or noncovalently bonded with the exoskeleton or proteins of these sources while being affected by external conditions (Elieh-Ali-Komi & Hamblin, 2016). These variations, along with environmental and economic considerations, demand variations in production approaches. For instance, chitin from crustacean shells, the largest source of commercial chitosan, has many minerals that need

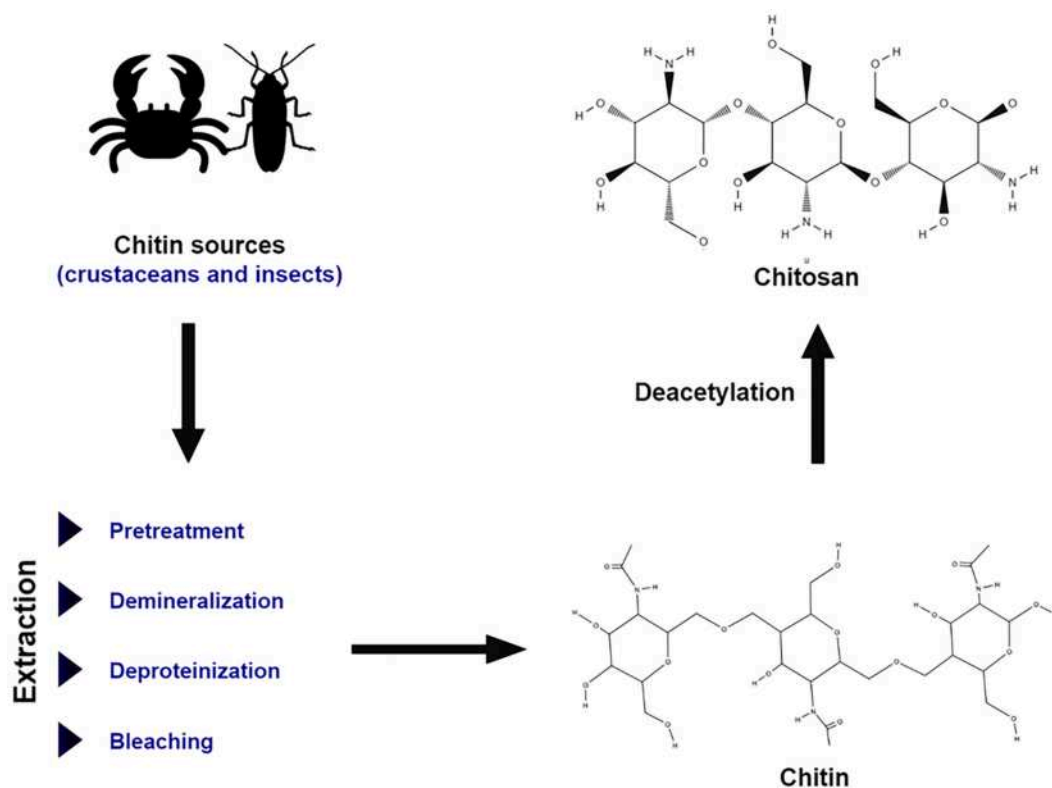


Figure 13.2 Chitin purification and chitosan production processes.

demineralization (Pellis et al., 2022). As a result, chemical extraction and deacetylation are preferred, as demineralization by hydrochloric acid has been shown to produce high-quality chitin in insects (Mohan et al., 2020). Hence, the chemical approach is also the most prominent production technique in industries. However, the method generates a large quantity of toxic waste and a high concentration of calcium carbonate in wastewater (Joseph et al., 2021).

Cleaner techniques, such as biological extraction of chitin followed by enzymatic deacetylation (using proteinases and deacetylases), ultrasound or microwave-assisted extraction coupled with enzymatic deacetylation, and deep eutectic solvents or ionic liquid-based techniques, have emerged in recent years (Hou et al., 2020; Pellis et al., 2022). However, these approaches have not been upscaled to industries due to shortcomings, such as slower process (bioenzymatic technique), toxicity (deep eutectic solvents and ionic liquids), and low yield and purity (ultrasound) (Joseph et al., 2021; Pellis et al., 2022).

Often used to flocculate algal cells in algae harvesting, chitosan can also be used to flocculate algae generated by the eutrophication of lignin in pulp and paper wastewater. Chitosan significantly reduced *Spirulina*, *Oscillatoria*, *Chlorella*, and *Synechocystis* content in water at a maximum pH of 7 (Divakaran & Pillai, 2002). It has shown remarkable *Chlorella* sp. removal at low concentrations (Ahmad et al., 2011). However, high chitosan concentration impedes flocculation by restabilizing algae cells (Yang et al., 2016). Conventionally, a series of deacetylation reactions under alkaline conditions is used to solve this problem (Moura et al., 2011). One emerging technique to facilitate flocculation even at higher chitosan concentrations is the deacylation of chitosan by electrolysis, which enhances charge neutralization in algae cells and improves flocculation (Zhu et al., 2021). Cobioflocculants, such as walnut protein extract and other seed-based proteins, have also been used with chitosan in recent years to offset the shortcomings (Xu et al., 2021).

The bioflocculant has also shown excellent dye removal capability. Out of chitosan, starch, and dialdehyde derivatives, unmodified chitosan showed superior turbidity removal, which was comparable to the levels of commercial polyacrylamide (PAM) flocculants (Maćczak et al., 2022). Chitosan bioflocculant dissolved in acetic acid also enabled 99.7% turbidity and 78% color removal of wastewater contaminated with 5 mg/L acid blue dye (Abdullah & Jael, 2019). However, chitosan has shown reduced performance in dye flocculation at higher pH due to charge restabilization (Abdullah & Jael, 2019; Hadiyanto et al., 2022).

Heavy metal removal capacity of chitosan bioflocculant has been largely unexplored, although one study has found that it can remove iron

concentration comparable to commercial PAM flocculant (Maćczak et al., 2022). By contrast, chitosan-based coflocculants, such as sulfonated chitosan and chitosan-based magnetic composites, have shown good results in heavy metal removal (Tang et al., 2020; Xiao et al., 2021).

13.3.3.2 Polymeric bioflocculants

Besides Chitosan, other natural polymers can also be used as bioflocculants (Ishak et al., 2020). These polymers are also nontoxic, biodegradable, and easily available and can be produced from agricultural-based materials, such as plant-derived substrates (Maraveas, 2020). They work in a wide pH range with low doses, generate less sludge, are shear resistant, and can be tailored extensively according to requirements (Liu et al., 2020). The extraction process of natural polymers depends upon the characteristics of the polymer in question and its source. For example, acids are usually used to extract gelatin from pig and fish skins, but alkalis are used if the animals are old (Mariod, 2015). Overall, extraction techniques used for chitosan (chemical, bioenzymatic, ionic liquid, ultrasound-assisted, microwave-assisted) are also used for other natural polymers, such as gelatin, lignin, starch, and pectin (Hameed et al., 2020; Karbuz & Tugrul, 2021; Pu et al., 2007).

A major disadvantage of these bioflocculants is their low shelf life due to quick biodegradation time (Kolya & Kang, 2023). Graft copolymerization of organic polymers in biopolymers is a cheap, effective, and widespread modification technique to mitigate this shortcoming. Additionally, this modification also increases the flocculation efficiency or flocculant multifunctionality (Du et al., 2018; Yang et al., 2016). For pulp and paper wastewater treatment, some of the organic polymers used in the copolymerization include polymethyl methacrylate (PMMA), peracetic acid (PAA), and PAM (Kolya et al., 2017; Sarkar et al., 2014). Monomers of these compounds are grafted as branches in the active sites of the natural polymer backbone via a coupling reaction (Purohit et al., 2023). The active sites can be generated by swelling the backbone using solvents, chemical activation (free radical or ionic mechanism), or radiation (Sand & Vyas, 2020).

Several studies have reported the color removal capacity of natural graft polymers. Sasmal et al. (2015) reported that poly (acrylamide-co-N-methylacrylamide)-grafted amylopectin [AP-g-poly(AM-co-NMA)] and PAM-grafted amylopectin (AP-g-PAM) removed the color of machining wastewater with 99.1% and 82.3% efficiency, respectively. Hydrolyzed PAM-grafted carboxymethyl starch (Hyd. CMS-g-PAM) removed the color from textile wastewater more efficiently than pure starch flocculant (Sen et al., 2011). Similarly, the polymers have also shown excellent solid and organic materials removal capability. Polyethylenimine-grafted cellulose

removed 96.2%, 79.9%, and 93.5% of total SS (TSS), COD, and turbidity, respectively, in machining wastewater (Zhang et al., 2018). The flocculant also showed excellent iron, phosphorus, and ammonia nitrogen removal capacity (Zhang et al., 2018). Poly (N,N-dimethylacrylamide) and acrylic acid copolymer graft on the family of starch (starch, amylopectin, hydroxyethyl starch) and acrylic acid graft on amylopectin (AP-g-AA) exhibited better flocculation activity than commercial inorganic flocculants when tested for pulp and paper wastewater (Du et al., 2018).

Although graft copolymers are cleaner alternatives to inorganic flocculants, the organic polymer grafts can cause environmental problems in water due to their long degradation time and the possibility of toxic monomer release. Owing to this, microbial bioflocculants have garnered interest over the years. Microbes can be used as bioflocculants if they can produce extracellular polysaccharides (EPSs). The EPSs are natural adhesives that flocculate the solid in wastewater (Nakata & Kurane, 1999). Microbes that can produce EPSs are called bioflocculant-producing bacteria. There are five major steps to produce bioflocculant from bioflocculant-producing bacteria: (1) isolation and identification of bioflocculant-producing bacteria strain using polymerase chain reaction (PCR), (2) growth and fermentation of selected bioflocculant-producing bacteria in suitable cultivation medium, (3) determination of flocculation activity, (4) extraction of bioflocculant, and (5) purification of bioflocculant (Bakar et al., 2021). Extraction can be done by physical methods, such as centrifugation, sonication, and heating, or by chemical methods, such as solvent extraction, acid/base treatment, EDTA, and enzyme-assisted extraction (Bakar et al., 2021).

Plethora of microbes, such as *Aspergillus parasiticus*, *Phormidium* sp., *Bacillus mojavensis*, *Microcoleus* sp., *Bacillus salmalaya*, *Acidithiobacillus ferrooxidans*, *Klebsiella* sp., and *Pseudomonas koreensis*, have been investigated as bioflocculants (Chen et al., 2011; Kolya et al., 2017; Kurade et al., 2016; Liu et al., 2014; Tawila et al., 2018). Ben Rebah et al. (2018) have reported that microbial bioflocculants are capable of reducing TSS, turbidity, COD, dye, and heavy metal concentration significantly (up to 90% depending on wastewater characteristics), which are the usual pollutants in pulp and paper wastewater. Bioflocculant from *Paenibacillus mucilaginosus* removed 70%–75.2% COD and 81.5%–88% SS from paper mill wastewater (Tang et al., 2014). *Pichia membranifaciens* and *Bacillus cereus* also decreased COD, turbidity, color, and SS of printing and dyeing wastewater (Zhang et al., 2015).

13.3.3.3 Plant-derived bioflocculants

Plant-derived bioflocculants are another biodegradable, non-toxic, and cost-effective alternative to inorganic flocculants. Additionally, they are healthy for animals and humans and do not cause secondary contamination (Das et al., 2021). These bioflocculants are mucilaginous polysaccharides extracted from plant-based sources, such as aloe, okra, guar gum, orange peel, moringa, acorn, cactus, and hyacinth bean peel (Benalia et al., 2019; de Barros et al., 2018; Hendrawati et al., 2016; Jain et al., 2017; Jaouadi et al., 2020; Shende & Das, 2021; Shilpa et al., 2012). The mechanisms proposed for these flocculants are electrostatic attraction, polymer bridging, hydrogen bonding, sweep flocculation, and charge neutralization, among which polymer bridging is most widely accepted (Das et al., 2021; Shende & Chidambaram, 2023).

Extraction of flocculants from plants is usually done by solvent extraction and drying coupled with grinding (Das et al., 2021). Drying and grinding are prevalent extraction techniques (Jaouadi et al., 2020; Wai et al., 2009). However, bioflocculants produced from this approach exhibit lower flocculating activity than solvent extraction (Yusoff et al., 2019). Solvents used for extraction of bioflocculant from plant sources are salt solutions (sodium chloride, metabisulfite) and a mixture of water and organic solvents (acetone, ethanol, and methanol) (Betatache et al., 2014; Shende & Das, 2021). Pure water solvent is also used due to its easy availability and nontoxicity (Le et al., 2020). However, water has limitations, such as high energy requirement, low solubility of apolar compounds, long extraction time, large quantity requirement, and low yield. Therefore water is instead used as a solvent in techniques, such as hydrothermal, microwave, and ultrasound (Flórez et al., 2015; Siah, 2017). Supercritical fluids are emerging solvents to extract plant flocculants (Chen et al., 2022; Yusoff et al., 2019). Yusoff et al. (2019) reported that supercritical fluid extraction produced 42% more bioflocculant than conventional solvent extraction in a shorter time (7 hours less) and lower cost (USD 30 less per kg).

Plant-derived flocculants have been shown to decrease COD, SS, and turbidity in pulp and paper wastewater. Pomegranate seed-based bioflocculant achieved 60% COD and 87% turbidity removal efficiency in pulp and paper wastewater (Shabanizadeh & Taghavijeloudar, 2023). However, coflocculation using alum with pomegranate seeds showed significantly superior performance (81% COD and 98% turbidity removal) (Shabanizadeh & Taghavijeloudar, 2023). Similarly, only *Cassia obtusifolia* gum seeds exhibited comparable TSS (36.2%) and COD (86.9%) removal capacity to alum among tannic acid, xanthan gum, acacia, and guar gum

(Subramonian et al., 2014). Similar pulp and paper wastewater-specific studies are limited. However, flocculants derived from moringa, acron, and cocoyam powder have been reported to efficiently remove bacterial population, heavy metals, turbidity, total solid, oxygen demand, dye, sulfate, and nitrate (Al-Hamadani et al., 2011; Benalia et al., 2019; Shende & Chidambaram, 2023).

Okra, cactus, moringa, and aloe vera have also been investigated as flocculants for sludge dewatering, a technique to enhance sludge disposal (Mnif & Ben Rebah, 2023). Microwave-extracted okra bioflocculant removed a larger amount of SS ($\geq 99\%$) and exhibited better water recovery ($\geq 75\%$) than conventional PAM flocculant (Lee et al., 2018). Similarly, bioflocculant extracted from cactus showed better specific resistance of filtration reduction than alum, ferrous chloride, and PAM flocculants (Betatache et al., 2014). Moringa-derived bioflocculant exhibited comparable dewatering performance to alum (Ghebremichael & Hultman, 2004). Additionally, dry moringa powder and commercial Zetag 7653 flocculant reduced specific resistance to sludge filtration by about 2.5 times (Wai et al., 2009). However, the concentration of moringa bioflocculant was 40 times higher than Zetag 7653 (Wai et al., 2009). Scaling up of these bioflocculants for sludge dewatering demands further study on their rheological characteristics, variation, and interaction of EPS components in the flocculation process, mechanism of flocculation, and techno-economic analysis of the bioflocculants (Hadj Mansour et al., 2023).

13.3.4 Outline and recent advances

Agricultural and biobased materials have shown great potential in addressing the challenges associated with treating pulp and paper wastewater. In summary the materials encompassed in this category consist of biosorbents, biomembranes, and bioflocculants. Table 13.3 provides a comprehensive overview of the utilization of different agricultural and biobased materials for the treatment of wastewater produced from the pulp and paper industry. The table shown herein offers a detailed review of the various applications, techniques, benefits, and concerns associated with diverse materials. Additionally, it provides significant insights into the possible contributions of certain materials in addressing the specific difficulties posed by effluents from the pulp and paper industry.

The incorporation of agricultural and biobased materials has played a pivotal role in facilitating notable progress in the treatment of pulp and paper wastewater, offering environmentally friendly and effective remedies. The utilization of agricultural and biobased

Table 13.3 A comparison between biobased and chemical materials for wastewater treatment.

Materials	Examples	Application purpose	Mechanism	Advantages	Challenges	References
Biosorbents	Biochar Zeolites Lignin	Adsorption of organics, dyes, and removal of metals	Adsorption, ion-exchange, and selective removal of target pollutants	Low-cost, high surface area, and reduction of color and aromaticity	Slow kinetics, production, sourcing, and disposal challenges	Chong et al. (2023) , Karić et al. (2022) , and Osman et al. (2023)
Biomembranes	Cellulose Chitosan Polymeric membranes	Selective separation and concentration of target compounds	Size-based separation, sorption, and diffusion	High selectivity and reusability, and efficient removal of suspended solids	Fouling and high cost for large-scale and real wastewater	Ehsani et al. (2022) , Kaushal and Singh (2023) , and Morales-Jiménez et al. (2023)
Biofloculants	Chitosan Polymeric Plant-derived biofloculants	Coagulation/flocculation, solid–liquid separation, and sludge reduction	Bridging, sedimentation, and charge neutralization	Biodegradability, nontoxicity, and reduced sediment volume and settling time	Dosage variability, scaling up, and potential for residual chemicals	Badawi et al. (2023) , Das et al. (2021) , and Maćczak et al. (2020)
Conventional chemical materials	Oxidants Coagulants Flocculants	Chemical oxidation of organics and inorganics for reduction of pollutants	Chemical reactions based on catalyst properties, in addition to solid–liquid separation via coagulation/flocculation	Established and known reactions, wide availability, and cost-effective processes	Sludge generation, secondary pollution, high chemical consumption, and limited selectivity and specificity	El Bouaidi et al. (2022) and Suresh et al. (2023)

materials has demonstrated significant promise in effectively tackling the various issues linked to the treatment of wastewater generated from pulp and paper industries. Biosorbents, such as biochar, zeolites, and lignin, have demonstrated effective utilization in the adsorption and subsequent elimination of diverse contaminants present in wastewater streams. Biomembranes composed of cellulose, chitosan, and polymeric materials have demonstrated discerning separation characteristics, facilitating the effective elimination of impurities. Various types of biofloculants, such as chitosan, polymeric biofloculants, and biofloculants generated from plants, have exhibited notable improvements in the processes of coagulation and solid-liquid separation. Consequently, these advancements have resulted in higher efficiency in the treatment of wastewater. The recent advancements in agricultural and biobased materials present a viable and ecologically conscious method for treating pulp and paper wastewater. This development can potentially enhance efficiency and cleanliness in the industry's processes.

13.4 Conclusions and future trends

The treatment of pulp and paper effluent has seen a significant transformation due to recent advancements in agricultural and biobased materials, presenting sustainable and highly effective remedies. Biosorbents, biomembranes, and biofloculants have exhibited considerable promise in pollutant elimination, selective partitioning, improved coagulation, and catalytic decomposition. These technological breakthroughs facilitate the adoption of an ecologically conscious approach to tackle the issues related to wastewater in the pulp and paper industry. Through continuous research and development, there are excellent prospects for enhancing the optimization of agricultural and biobased materials in the treatment of pulp and paper effluent.

The prospects of wastewater treatment for the pulp and paper industry are reliant on the ongoing advancement and application of agricultural and biobased materials. These materials possess significant promise in enhancing the efficiency and sustainability of wastewater treatment operations within the industry. Future research and innovation may prioritize the enhancement of biosorbents, biomembranes, and biofloculants to achieve greater efficiency in treating pulp and paper effluent. These advancements would involve tailoring these materials specifically for this purpose. This encompasses the augmentation of the adsorption capacity and selectivity of biosorbents, the enhancement of the durability and separation efficiency of biomembranes, and the innovation of biofloculants with exceptional coagulation properties.

Furthermore, incorporating agricultural and biobased materials into hybrid or mixed treatment systems, in conjunction with developing technologies such as membrane bioreactors and sophisticated oxidation processes, exhibits potential for advancing pulp and paper wastewater treatment in the future. By leveraging the capabilities of agricultural and biobased materials and pushing the limits of innovation, the industrial sector can attain enhanced sustainability, cost-efficiency, and environmental friendliness in their methods of treating effluent from pulp and paper production.

List of acronyms

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
COP	Catalytic ozonation process
CNCs	Cellulose nanocrystals
CNF	Cellulose nanofiber
EPS	Extracellular polysaccharides
MF	Microfiltration
NF	Nanofiltration
PAA	Peracetic acid
PAM	Polyacrylamide
PES	Polyethersulfone
PHA	Polyhydroxyalkanoates
PCR	Polymerase chain reaction
PMMA	Polymethyl methacrylate
RO	Reverse osmosis
SOP	Single ozonation process
SS	Suspended solids
TSS	Total suspended solids
UF	Ultrafiltration
VOCs	Volatile organic compounds

References

- Abdullah, H. A., & Jaeel, A. J. (2019). Chitosan as a widely used coagulant to reduce turbidity and color of model textile wastewater containing an anionic dye (acid blue). *IOP Conference Series: Materials Science and Engineering*, 584. <https://doi.org/10.1088/1757-899X/584/1/012036>, <https://iopscience.iop.org/journal/1757-899X>.
- Ahmad, A. L., Mat Yasin, N. H., Derek, C. J. C., & Lim, J. K. (2011). Optimization of microalgae coagulation process using chitosan. *Chemical Engineering Journal*, 173(3), 879–882. <https://doi.org/10.1016/j.cej.2011.07.070>.
- Akinnawo, S. O. (2023). Eutrophication: Causes, consequences, physical, chemical and biological techniques for mitigation strategies. *Environmental Challenges*, 12, 100733. <https://doi.org/10.1016/j.envc.2023.100733>.
- Akpor, O. B. (2014). Heavy metal pollutants in wastewater effluents: Sources, effects and remediation. *Advances in Bioscience and Bioengineering*, 2(4), 37. <https://doi.org/10.11648/j.abb.20140204.11>.

- Al-Hamadani, Y. A. J., Yusoff, M. S., Umar, M., Bashir, M. J. K., & Adlan, M. N. (2011). Application of psyllium husk as coagulant and coagulant aid in semi-aerobic landfill leachate treatment. *Journal of Hazardous Materials*, 190(1-3), 582-587. <https://doi.org/10.1016/j.jhazmat.2011.03.087>.
- Alengebaw, A., Jin, K., Ran, Y., Peng, J., Zhang, X., & Ai, P. (2021). Advanced pre-treatment of stripped biogas slurry by polyaluminum chloride coagulation and biochar adsorption coupled with ceramic membrane filtration. *Chemosphere*, 267, 129197. <https://doi.org/10.1016/j.chemosphere.2020.129197>.
- Alonso, D. M., Wettstein, S. G., Mellmer, M. A., Gurbuz, E. I., & Dumesic, J. A. (2013). Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass. *Energy & Environmental Science*, 6(1), 76-80. <https://doi.org/10.1039/c2ee23617f>.
- Angelucci, D. M., Donati, E., & Tomei, M. C. (2022). Extractive membrane bioreactor to detoxify industrial/hazardous landfill leachate and facilitate resource recovery. *Science of the Total Environment*, 806, 150892. <https://doi.org/10.1016/j.scitotenv.2021.150892>.
- Aranaz, I., Alcántara, A. R., Civera, M. C., Arias, C., Elorza, B., Caballero, A. H., & Acosta, N. (2021). Chitosan: An overview of its properties and applications. *Polymers*, 13(19), 20734360. <https://doi.org/10.3390/polym13193256>, <https://www.mdpi.com/2073-4360/13/19/3256/pdf>.
- Ashrafi, O., Yerushalmi, L., & Haghighat, F. (2015). Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management*, 158, 146-157. <https://doi.org/10.1016/j.jenvman.2015.05.010>, <https://www.sciencedirect.com/journal/journal-of-environmental-management>.
- Ayar, N., Keçeli, G., Kurtoglu, A. E., & Atun, G. (2015). Cationic dye adsorption onto natural and synthetic zeolites in the presence of Cs⁺ and Sr²⁺ ions. *Toxicological and Environmental Chemistry*, 97(1), 11-21. <https://doi.org/10.1080/02772248.2014.949264>, <http://www.tandfonline.com/loi/gtec20>.
- Badawi, A. K., Salama, R. S., & Mostafa, M. M. M. (2023). Natural-based coagulants/flocculants as sustainable market-valued products for industrial wastewater treatment: A review of recent developments. *RSC Advances*, 13(28), 19335-19355. <https://doi.org/10.1039/d3ra01999c>, <http://pubs.rsc.org/en/journals/journal/ra>.
- Bajpai, P. (2015). *Basic overview of pulp and paper manufacturing process*. Springer Science and Business Media LLC, 11-39. https://doi.org/10.1007/978-3-319-18744-0_2.
- Bajpai, P. (2018). *Brief description of the pulp and papermaking process*. Springer Science and Business Media LLC, 9-26. https://doi.org/10.1007/978-981-10-7853-8_2.
- Bakar, S. N. H. A., Hasan, H. A., Abdullah, S. R. S., Kasan, N. A., Muhamad, M. H., & Kurniawan, S. B. (2021). A review of the production process of bacteria-based polymeric flocculants. *Journal of Water Process Engineering*, 40. <http://www.journals.elsevier.com/journal-of-water-process-engineering/>, <https://doi.org/10.1016/j.jwpe.2021.101915>, <http://www.journals.elsevier.com/journal-of-water-process-engineering/>.
- Barik, M., Das, C. P., Verma, A. K., Sahoo, S., & Sahoo, N. K. (2021). Metabolic profiling of phenol biodegradation by an indigenous *Rhodococcus pyridinivorans* strain PDB9T N-1 isolated from paper pulp wastewater. *International Biodeterioration and Biodegradation*, 158. <https://doi.org/10.1016/j.ibiod.2020.105168>, <http://www.elsevier.com/inca/publications/store/4/0/5/8/9/9>.
- Ben Rebah, F., Mnif, W., & Siddeeg, S. M. (2018). Microbial flocculants as an alternative to synthetic polymers for wastewater treatment: A review. *Symmetry*, 10(11), 556. <https://doi.org/10.3390/sym10110556>.
- Benalia, A., Derbal, K., Panico, A., & Pirozzi, F. (2019). Use of acorn leaves as a natural coagulant in a drinking water treatment plant. *Water*, 11(1), 57. <https://doi.org/10.3390/w11010057>.

- Betatache, H., Aouabed, A., Drouiche, N., & Lounici, H. (2014). Conditioning of sewage sludge by prickly pear cactus (*Opuntia ficus Indica*) juice. *Ecological Engineering*, 70, 465–469. <https://doi.org/10.1016/j.ecoleng.2014.06.031>.
- Bhatt, P., Bhandari, G., & Bilal, M. (2022). Occurrence, toxicity impacts and mitigation of emerging micropollutants in the aquatic environments: Recent tendencies and perspectives. *Journal of Environmental Chemical Engineering*, 10(3), 107598. <https://doi.org/10.1016/j.jece.2022.107598>.
- Brandt, J., & Kwan, P. (2013). *State-of-the-science review of membrane fouling: Organic, inorganic, and biological*. WateReuse Research Foundation.
- Carpenter, A. W., De Lannoy, C. F., & Wiesner, M. R. (2015). Cellulose nanomaterials in water treatment technologies. *Environmental Science and Technology*, 49(9), 5277–5287. <https://doi.org/10.1021/es506351r>, <http://pubs.acs.org/journal/esthag>.
- Chauhan, S., & Meena, B. L. (2021). Introduction to pulp and paper industry: Global scenario. In *Green pulp and paper industry: Biotechnology for ecofriendly processing*. India: De Gruyter, 1–30. <https://www.degruyter.com/document/doi/10.1515/9783110592412/html>, <https://doi.org/10.1515/9783110592412-001>.
- Chen, L., Li, T., Guan, L., Zhou, Y., & Li, P. (2011). Flocculating activities of polysaccharides released from the marine mat-forming cyanobacteria *Microcoleus* and *Lyngbya*. *Aquatic Biology*, 11(3), 243–248. <https://doi.org/10.3354/ab00309>.
- Chen, X., Li, Z., Smith, S. A., Chen, M., Liu, H., Zhang, J., Tang, L., Li, J., Liu, Q., & Wu, X. (2022). Optimization of supercritical CO₂ extraction of moringa oleifera seed oil using response surface methodological approach and its antioxidant activity. *Frontiers in Nutrition*, 8. <https://doi.org/10.3389/fnut.2021.829146>, [journal.frontiersin.org/journal/nutrition](https://www.frontiersin.org/journal/nutrition).
- Chong, Z. T., Soh, L. S., & Yong, W. F. (2023). Valorization of agriculture wastes as biosorbents for adsorption of emerging pollutants: Modification, remediation and industry application. *Results in Engineering*, 17. <https://doi.org/10.1016/j.rineng.2023.100960>, <https://www.journals.elsevier.com/results-in-engineering>.
- Ciputra, S., Antony, A., Phillips, R., Richardson, D., & Leslie, G. (2010). Comparison of treatment options for removal of recalcitrant dissolved organic matter from paper mill effluent. *Chemosphere*, 81(1), 86–91. <https://doi.org/10.1016/j.chemosphere.2010.06.060>.
- Creamer, A. E., & Gao, B. (2016). Carbon-based adsorbents for postcombustion CO₂ capture: A critical review. *Environmental Science and Technology*, 50(14), 7276–7289. <https://doi.org/10.1021/acs.est.6b00627>, <http://pubs.acs.org/journal/esthag>.
- Dal Bosco, S. M., Jimenez, R. S., & Carvalho, W. A. (2005). Removal of toxic metals from wastewater by *Brazilian* natural scolécite. *Journal of Colloid and Interface Science*, 281(2), 424–431. <https://doi.org/10.1016/j.jcis.2004.08.060>.
- Das, N., Ojha, N., & Mandal, S. K. (2021). Wastewater treatment using plant-derived bioflocculants: Green chemistry approach for safe environment. *Water Science and Technology*, 83(8), 1797–1812. <https://doi.org/10.2166/wst.2021.100>, <https://watermark.silverchair.com/wst083081797.pdf?>.
- Daugulis, A. J., Tomei, M. C., & Guieysse, B. (2011). Overcoming substrate inhibition during biological treatment of monoaromatics: Recent advances in bioprocess design. *Applied Microbiology and Biotechnology*, 90(5), 1589–1608. <https://doi.org/10.1007/s00253-011-3229-z>.
- de Barros, C. H. N., Cruz, G. C. F., Mayrink, W., & Tasic, L. (2018). Bio-based synthesis of silver nanoparticles from orange waste: Effects of distinct biomolecule coatings on size, morphology, and antimicrobial activity. *Nanotechnology, Science and Applications*, 11, 1–14. <https://doi.org/10.2147/NSA.S156115>, <https://www.dovepress.com/getfile.php?fileID=41188>.
- De Magalhães, L. F., Da Silva, G. R., & Peres, A. E. C. (2022). Zeolite application in wastewater treatment. *Adsorption Science and Technology*, 2022, 20484038. <https://doi.org/10.1155/2022/4544104>, <https://journals.sagepub.com/home/ADT>.

- Divakaran, R., & Pillai, V. N. S. (2002). Flocculation of algae using chitosan. *Journal of Applied Phycology*, 14(5), 419–422. <https://doi.org/10.1023/A:1022137023257>.
- Drewnowski, J., Remiszewska-Skwarek, A., Duda, S., & Łagód, G. (2019). Aeration process in bioreactors as the main energy consumer in a wastewater treatment plant. Review of solutions and methods of process optimization. *Processes*, 7(5). <https://doi.org/10.3390/pr7050311>, https://res.mdpi.com/processes/processes-07-00311/article_deploy/processes-07-00311-v2.pdf?filename=&attachment=1.
- Du, Q., Wang, Y., Li, A., & Yang, H. (2018). Scale-inhibition and flocculation dual-functionality of poly(acrylic acid) grafted starch. *Journal of Environmental Management*, 210, 273–279. <https://doi.org/10.1016/j.jenvman.2018.01.016>, <https://www.sciencedirect.com/journal/journal-of-environmental-management>.
- Ehsani, M., Kalugin, D., Doan, H., Lohi, A., & Abdelrasoul, A. (2022). Bio-sourced and biodegradable membranes. *Applied Sciences*, 12(24), 12837. <https://doi.org/10.3390/app122412837>.
- El Bouaidi, W., Libralato, G., Douma, M., Ounas, A., Yaacoubi, A., Lofrano, G., Albarano, L., Guida, M., & Loudiki, M. (2022). A review of plant-based coagulants for turbidity and cyanobacteria blooms removal. *Environmental Science and Pollution Research*, 29(28), 42601–42615. <https://doi.org/10.1007/s11356-022-20036-0>, <https://link.springer.com/journal/11356>.
- El-Gaayda, J., Titchou, F. E., Oukhrib, R., Yap, P. S., Liu, T., Hamdani, M., & Akbour, R. A. (2021). Natural flocculants for the treatment of wastewaters containing dyes or heavy metals: A state-of-the-art review. *Journal of Environmental Chemical Engineering*, 9(5). <https://doi.org/10.1016/j.jece.2021.106060>, <http://www.journals.elsevier.com/journal-of-environmental-chemical-engineering/>.
- Elgarhy, A. H., Mahran, B. N. A., Liu, G., Salem, T. A., ElSayed, E. S. E. B., & Ibrahim, L. A. (2022). Comparative study for removal of phosphorus from aqueous solution by natural and activated bentonite. *Nature Research, Egypt Scientific Reports*, 12(1). <https://doi.org/10.1038/s41598-022-23178-w>, <https://www.nature.com/srep/>.
- Elieh-Ali-Komi, D., & Hamblin, M. R. (2016). Chitin and chitosan: Production and application of versatile biomedical nanomaterials. *International Journal of Advanced Research*, 4, 411–427.
- Fernández-Dacosta, C., Posada, J. A., Kleerebezem, R., Cuellar, M. C., & Ramirez, A. (2015). Microbial community-based polyhydroxyalkanoates (PHAs) production from wastewater: Techno-economic analysis and ex-ante environmental assessment. *Bioresource Technology*, 185, 368–377. <https://doi.org/10.1016/j.biortech.2015.03.025>, <http://www.elsevier.com/locate/biortech>.
- Flórez, N., Conde, E., & Domínguez, H. (2015). Microwave assisted water extraction of plant compounds. *Journal of Chemical Technology and Biotechnology*, 90(4), 590–607. <https://doi.org/10.1002/jctb.4519>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1097-4660](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1097-4660).
- Ghebremichael, K. A., & Hultman, B. (2004). Alum sludge dewatering using Moringa oleifera as a conditioner. *Water, Air, and Soil Pollution*, 158(1), 153–167. <https://doi.org/10.1023/B:WATE.0000044852.23764.9c>.
- Ghimire, N., Bakke, R., & Bergland, W. H. (2021). Liquefaction of lignocellulosic biomass for methane production: A review. *Bioresource Technology*, 332, 125068. <https://doi.org/10.1016/j.biortech.2021.125068>.
- Ghosh, S., Kumar, M. S., Bal, B., & Das, A. P. (2018). Application of bioengineering in revamping human health. In *Synthetic biology: Omics tools and their applications*. India: Springer Singapore, 21–37. <http://www.springer.com/in/book/9789811086922>, https://doi.org/10.1007/978-981-10-8693-9_2.
- Goswami, R., Mishra, A., Bhatt, N., Mishra, A., & Naithani, P. (2021). Potential of chitosan/nanocellulose based composite membrane for the removal of heavy metal (chromium

- ion). *Materials Today: Proceedings*, 46, 10954–11959. <https://doi.org/10.1016/j.matpr.2021.02.036>, <https://www.sciencedirect.com/journal/materials-today-proceedings>.
- Gulcin, İ., & Alwasel, S. H. (2022). Metal ions, metal chelators and metal chelating assay as antioxidant method. *Processes*, 10(1). <https://doi.org/10.3390/pr10010132>, <https://www.mdpi.com/2227-9717/10/1/132/pdf>.
- Hadiyanto, H., Widayat, W., Christwardana, M., & Pratiwi, M. E. (2022). The flocculation process of *Chlorella* sp. using chitosan as a bio-flocculant: Optimization of operating conditions by response surface methodology. *Current Research in Green and Sustainable Chemistry*, 5, 100291. <https://doi.org/10.1016/j.crgsc.2022.100291>.
- Hadj Mansour, Y., Othmani, B., Ben Rebah, F., Mnif, W., Saoudi, M., & Khadhraoui, M. (2023). Could plant-based flocculants substitute the conventional synthetic chemicals in the sludge dewatering process? *Water*, 15(14), 2602. <https://doi.org/10.3390/w15142602>.
- Haile, A., Gelebo, G. G., Tesfaye, T., Mengie, W., Mebrate, M. A., Abuhay, A., & Limeneh, D. Y. (2021). Pulp and paper mill wastes: Utilizations and prospects for high value-added biomaterials. *Bioresources and Bioprocessing*, 8(1). <https://doi.org/10.1186/s40643-021-00385-3>, <https://bioresourcesbioprocessing.springeropen.com>.
- Hameed, M., Ahmad, S. W., Ahmad, S., Qutab, H. G., Dasih, M., & Imran, M. (2020). Enzymatic extraction of potato starch: A parametric optimization study using response surface methodology. *Scienco, Pakistan Polish Journal of Chemical Technology*, 22(3), 48–54. <https://doi.org/10.2478/pjct-2020-0027>, <http://www.degruyter.com/view/j/pjct>.
- Haq, I., & Raj, A. (2019). *Pulp and paper mill wastewater: Ecotoxicological effects and bioremediation approaches for environmental safety*. Springer Science and Business Media LLC, 333–356. https://doi.org/10.1007/978-981-13-3426-9_14.
- Hay, R. L., & Sheppard, R. A. (2001). Occurrence of zeolites in sedimentary rocks: An overview. *Reviews in Mineralogy and Geochemistry*, 45(1), 217–234. <https://doi.org/10.2138/rmg.2001.45.6>.
- Hendrawati, H., Yulianti, I. R., Rohaeti, E. N., Effendi, H., & Darusman, L. K. (2016). The use of moringa oleifera seed powder as coagulant to improve the quality of wastewater and ground water. *IOP Conference Series: Earth and Environmental Science*, 31. <https://doi.org/10.1088/1755-1315/31/1/012033>, <http://www.iop.org/EJ/volume/1755-1315>.
- Hossain, K., & Ismail, N. (2015). Bioremediation and detoxification of pulp and paper mill effluent: A review. *Research Journal of Environmental Toxicology*, 9(3), 113–134. <https://doi.org/10.3923/rjet.2015.113.134>, <http://docsdrive.com/pdfs/academicjournals/rjet/2015/113-134.pdf>.
- Hou, F., Ma, X., Fan, L., Wang, D., Ding, T., Ye, X., & Liu, D. (2020). Enhancement of chitin suspension hydrolysis by a combination of ultrasound and chitinase. *Carbohydrate Polymers*, 231, 115669. <https://doi.org/10.1016/j.carbpol.2019.115669>.
- Hu, X., Shen, Y., Zhang, H., Xia, J., Kong, F., & Zhang, W.-H. (2022). Insight into the effect of calcium carbonate filler on the dewatering performance of simulated pulp & paper mill sludge. *Journal of Environmental Chemical Engineering*, 10(6), 108863. <https://doi.org/10.1016/j.jece.2022.108863>.
- Huang, S., Wu, M. B., Zhu, C. Y., Ma, M. Q., Yang, J., Wu, J., & Xu, Z. K. (2019). Polyamide nanofiltration membranes incorporated with cellulose nanocrystals for enhanced water flux and chlorine resistance. *ACS Sustainable Chemistry and Engineering*, 7(14), 12315–12322. <https://doi.org/10.1021/acssuschemeng.9b01651>, <http://pubs.acs.org/journal/ascecg>.
- Ishak, S. A., Murshed, M. F., Akil, H. M., Ismail, N., Md Rasib, S. Z., & Al-Gheethi, A. A. S. (2020). The application of modified natural polymers in toxicant dye compounds wastewater: A review. *Water (Switzerland)*, 12(7), 2073441. <https://doi.org/10.3390/w12072032>, https://res.mdpi.com/d_attachment/water/water-12-02032/article_deploy/water-12-02032.pdf.

- Jain, V., Tammishetti, V., Joshi, K., Kumar, D., Pradip, & Rai, B. (2017). Guar gum as a selective flocculant for the beneficiation of alumina rich iron ore slimes: Density functional theory and experimental studies. *Minerals Engineering*, 109, 144–152. <https://doi.org/10.1016/j.mineng.2017.03.007>, <http://www.journals.elsevier.com/minerals-engineering/>.
- Jaiswal, S., Gupta, G. K., Panchal, K., Mandeep, & Shukla, P. (2021). Synthetic organic compounds from paper industry wastes: Integrated biotechnological interventions. *Frontiers in Bioengineering and Biotechnology*, 8. <https://doi.org/10.3389/fbioe.2020.592939>, <http://journal.frontiersin.org/journal/bioengineering-and-biotechnology#archive>.
- Jaouadi, T., Hajji, M., Kasmi, M., Kallel, A., Chatti, A., Hamzaoui, H., Mnif, A., Tizaoui, C., & Trabelsi, I. (2020). Aloe sp. leaf gel and water glass for municipal wastewater sludge treatment and odour removal. *Water Science and Technology*, 81(3), 479–490. <https://doi.org/10.2166/WST.2020.123>, <https://iwaponline.com/wst/article/doi/10.2166/wst.2020.123/73102/Aloe-sp-leaf-gel-and-water-glass-for-municipal>.
- Jonoobi, M., Oladi, R., Davoudpour, Y., Oksman, K., Dufresne, A., Hamzeh, Y., & Davoodi, R. (2015). Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: A review. *Cellulose*, 22(2), 935–969. <https://doi.org/10.1007/s10570-015-0551-0>, <https://www.springer.com/journal/10570>.
- Joseph, S. M., Krishnamoorthy, S., Paranthaman, R., Moses, J. A., & Anandharamakrishnan, C. (2021). A review on source-specific chemistry, functionality, and applications of chitin and chitosan. *Carbohydrate Polymer Technologies and Applications*, 2, 100036. <https://doi.org/10.1016/j.carpta.2021.100036>.
- Kamali, M., Khalaj, M., Costa, M. E. V., Capela, I., & Aminabhavi, T. M. (2020). Optimization of kraft black liquor treatment using ultrasonically synthesized mesoporous tenorite nanomaterials assisted by Taguchi design. *Chemical Engineering Journal*, 401. <https://doi.org/10.1016/j.cej.2020.126040>, <http://www.elsevier.com/inca/publications/store/6/0/1/2/7/3/index.htm>.
- Kapatel, D. V., Rotliwala, Y. C., & Patel, H. J. (2022). Co-pyrolysis based activated bio-char: Characterization and its utilization for secondary treated pulp and paper industry wastewater. *Materials Today: Proceedings*, 57, 1724–1729. <https://doi.org/10.1016/j.matpr.2021.12.361>, <https://www.sciencedirect.com/journal/materials-today-proceedings>.
- Karbuz, P., & Tugrul, N. (2021). Microwave and ultrasound assisted extraction of pectin from various fruits peel. *Journal of Food Science and Technology*, 58(2), 641–650. <https://doi.org/10.1007/s13197-020-04578-0>, <http://www.springerlink.com/content/121580/>.
- Karić, N., Maia, A. S., Teodorović, A., Atanasova, N., Langergraber, G., Crini, G., Ribeiro, A. R. L., & Đolić, M. (2022). Bio-waste valorisation: Agricultural wastes as biosorbents for removal of (in)organic pollutants in wastewater treatment. *Chemical Engineering Journal Advances*, 9. <https://doi.org/10.1016/j.cej.2021.100239>, <https://www.journals.elsevier.com/chemical-engineering-journal-advances>.
- Kaushal, N., & Singh, A. K. (2023). Advancement in utilization of bio-based materials including cellulose, lignin, chitosan for bio-inspired surface coatings with special wetting behavior: A review on fabrication and applications. *International Journal of Biological Macromolecules*, 246, 125709. <https://doi.org/10.1016/j.ijbiomac.2023.125709>.
- Khaleque, A., Alam, M. M., Hoque, M., Mondal, S., Haider, J. B., Xu, B., Johir, M. A. H., Karmakar, A. K., Zhou, J. L., Ahmed, M. B., & Moni, M. A. (2020). Zeolite synthesis from low-cost materials and environmental applications: A review. *Environmental Advances*, 2. <https://doi.org/10.1016/j.envadv.2020.100019>, <http://www.journals.elsevier.com/environmental-advances>.

- Kolya, H., & Kang, C.-W. (2023). Bio-based polymeric flocculants and adsorbents for wastewater treatment. *Sustainability*, 15(12), 9844. <https://doi.org/10.3390/su15129844>.
- Kolya, H., Sasmal, D., & Tripathy, T. (2017). Novel biodegradable flocculating agents based on grafted starch family for the industrial effluent treatment. *Journal of Polymers and the Environment*, 25(2), 408–418. <https://doi.org/10.1007/s10924-016-0825-0>, <http://www.kluweronline.com/issn/1566-2543/>.
- Koul, B., Yadav, D., Singh, S., Kumar, M., & Song, M. (2022). Insights into the domestic wastewater treatment (DWWT) regimes: A review. *Water*, 14(21), 3542. <https://doi.org/10.3390/w14213542>.
- Kulshreshtha, S., Mathur, N., & Bhatnagar, P. (2012). *Mycoremediation of paper, pulp and cardboard industrial wastes and pollutants*. Springer Science and Business Media LLC, 77–116. https://doi.org/10.1007/978-3-642-33811-3_4.
- Kumar, A., Singh, A. K., & Chandra, R. (2020). Comparative analysis of residual organic pollutants from bleached and unbleached paper mill wastewater and their toxicity on *Phaseolus aureus* and *Tubifex tubifex*. *Urban Water Journal*, 17(10), 860–870. <https://doi.org/10.1080/1573062X.2020.1836238>, <http://www.tandf.co.uk/journals/titles/1573062X.asp>.
- Kumar, R., Maurya, A., & Raj, A. (2023). Emerging technological solutions for the management of paper mill wastewater: Treatment, nutrient recovery and fourth industrial revolution (IR 4.0). *Journal of Water Process Engineering*, 53, 103715. <https://doi.org/10.1016/j.jwpe.2023.103715>.
- Kurade, M. B., Murugesan, K., Selvam, A., Yu, S. M., & Wong, J. W. C. (2016). Sludge conditioning using biogenic flocculant produced by *Acidithiobacillus ferrooxidans* for enhancement in dewaterability. *Bioresource Technology*, 217, 179–185. <https://doi.org/10.1016/j.biortech.2016.02.113>, <http://www.elsevier.com/locate/biortech>.
- Le, O. T. H., Tran, L. N., Doan, V. T., Pham, Q. V., Ngo, A. V., & Nguyen, H. H. (2020). Mucilage extracted from dragon fruit peel (*Hylocereus undatus*) as flocculant for treatment of dye wastewater by coagulation and flocculation process. *International Journal of Polymer Science*, 2020. <https://doi.org/10.1155/2020/7468343>, <http://www.hindawi.com/journals/ijps/>.
- Lee, C. S., Chong, M. F., Binner, E., Gomes, R., & Robinson, J. (2018). Techno-economic assessment of scale-up of bio-flocculant extraction and production by using okra as biomass feedstock. *Chemical Engineering Research and Design*, 132, 358–369. <https://doi.org/10.1016/j.cherd.2018.01.050>, http://www.elsevier.com/wps/find/journaldescription.cws_home/713871/description#description.
- Lee, J. W., Choi, H., Hwang, U. K., Kang, J. C., Kang, Y. J., Kim, K. I., & Kim, J. H. (2019). Toxic effects of lead exposure on bioaccumulation, oxidative stress, neurotoxicity, and immune responses in fish: A review. *Environmental Toxicology and Pharmacology*, 68, 101–108. <https://doi.org/10.1016/j.etap.2019.03.010>, <http://www.elsevier.com/locate/etap>.
- Li, T., Tong, Z., Meng, S., Li, Y. C., Gao, B., & Bayabil, H. K. (2021). Characterization of residues from non-woody pulping process and its function as fertilizer. *Chemosphere*, 262. <https://doi.org/10.1016/j.chemosphere.2020.127906>, <http://www.elsevier.com/locate/chemosphere>.
- Li, W., Yue, J., & Liu, S. (2012). Preparation of nanocrystalline cellulose via ultrasound and its reinforcement capability for poly(vinyl alcohol) composites. *Ultrasonics Sonochemistry*, 19(3), 479–485. <https://doi.org/10.1016/j.ultsonch.2011.11.007>, <http://www.elsevier.com/inca/publications/store/5/2/5/4/5/1>.
- Li, X., Peng, W., Jia, Y., Lu, L., & Fan, W. (2016). Bioremediation of lead contaminated soil with *Rhodobacter sphaeroides*. *Chemosphere*, 156, 228–235. <https://doi.org/10.1016/j.chemosphere.2016.04.098>, <http://www.elsevier.com/locate/chemosphere>.
- Li, Z., Ge, Y., Zhang, J., Xiao, D., & Wu, Z. (2019). Chemical modification of lignin and its environmental application. In *Sustainable polymer composites and*

- nanocomposites*. China: Springer International Publishing, 1345–1364. <https://doi.org/10.1007/978-3-030-05399-4>, https://doi.org/10.1007/978-3-030-05399-4_45.
- Lichtfouse, E., Morin-Crini, N., Fourmentin, M., Zemmouri, H., do Carmo Nascimento, I. O., Queiroz, L. M., Tadza, M. Y. M., Picos-Corrales, L. A., Pei, H., Wilson, L. D., & Crini, G. (2019). Chitosan for direct bioflocculation of wastewater. *Environmental Chemistry Letters*, 17(4), 1603–1621. <https://doi.org/10.1007/s10311-019-00900-1>, <https://www.springer.com/journal/10311>.
- Liu, B., Wang, D., Yu, G., & Meng, X. (2013). Adsorption of heavy metal ions, dyes and proteins by chitosan composites and derivatives – A review. *Journal of Ocean University of China*, 12(3), 500–508. <https://doi.org/10.1007/s11802-013-2113-0>.
- Liu, H., Peng, S., Shu, L., Chen, T., Bao, T., & Frost, R. L. (2013). Effect of Fe₃O₄ addition on removal of ammonium by zeolite NaA. *Journal of Colloid and Interface Science*, 390(1), 204–210. <https://doi.org/10.1016/j.jcis.2012.09.010>.
- Liu, J., Ma, J., Liu, Y., Yang, Y., Yue, D., & Wang, H. (2014). Optimized production of a novel bioflocculant M-C11 by *Klebsiella* sp. and its application in sludge dewatering. *Journal of Environmental Sciences (China)*, 26(10), 2076–2083. <https://doi.org/10.1016/j.jes.2014.08.007>, <http://www.journals.elsevier.com/journal-of-environmental-sciences/>.
- Liu, Y., Zheng, H., Sun, Y., Ren, J., Zheng, X., Sun, Q., Jiang, S., & Ding, W. (2020). Synthesis of novel chitosan-based flocculants with amphiphilic structure and its application in sludge dewatering: Role of hydrophobic groups. *Journal of Cleaner Production*, 249, 119350. <https://doi.org/10.1016/j.jclepro.2019.119350>.
- Luo, X., Yan, Q., Wang, C., Luo, C., Zhou, N., & Jian, C. (2015). Treatment of ammonia nitrogen wastewater in low concentration by two-stage ozonization. *International Journal of Environmental Research and Public Health*, 12(9), 11975–11987. <https://doi.org/10.3390/ijerph120911975>, <http://www.mdpi.com/1660-4601/12/9/11975/pdf>.
- Ma, Y., Meng, H., Shen, Y., Zhou, H., Zhu, M., Geng, J., Alengebawy, A., Ding, J., & Zhang, D. (2023). Optimisation of phosphorus recovery process from biogas slurry using straw-derived biochar coupled with Mg/La oxide as an adsorbent. *Chemical Engineering Research and Design*, 191, 249–260. <https://doi.org/10.1016/j.cherd.2023.01.011>, http://www.elsevier.com/wps/find/journaldescription.cws_home/713871/description#description.
- Maćczak, P., Kaczmarek, H., & Ziegler-Borowska, M. (2020). Recent achievements in polymer bio-based flocculants for water treatment. *Materials*, 13(18), 3951. <https://doi.org/10.3390/ma13183951>.
- Maćczak, P., Kaczmarek, H., Ziegler-Borowska, M., Węgrzynowska-Drzymalska, K., & Burkowska-But, A. (2022). The use of chitosan and starch-based flocculants for filter backwash water treatment. *Materials*, 15(3). <https://doi.org/10.3390/ma15031056>, <https://www.mdpi.com/1996-1944/15/3/1056/pdf>.
- Manek, E., & Petroianu, G. (2021). Chitosan-based nanoparticles in Alzheimer's disease: Messenger or message? *Neural Regeneration Research*, 16(11), 2204–2205. <https://doi.org/10.4103/1673-5374.310685>, <http://www.nrronline.org/>.
- Manetti, M., & Tomei, M. C. (2022). Extractive polymeric membrane bioreactors for industrial wastewater treatment: Theory and practice. *Process Safety and Environmental Protection*, 162, 169–186. <https://doi.org/10.1016/j.psep.2022.03.063>, http://www.elsevier.com/wps/find/journaldescription.cws_home/713889/description#description.
- Maraveas, C. (2020). Production of sustainable and biodegradable polymers from agricultural waste. *Polymers*, 12(5), 1127. <https://doi.org/10.3390/polym12051127>.
- Mariod, A. A. (2015). Extraction, purification, and modification of natural polymers. In *Natural polymers: Industry techniques and applications*. Saudi Arabia: Springer International Publishing, 63–91. <https://doi.org/10.1007/978-3-319-26414-1>, https://doi.org/10.1007/978-3-319-26414-1_3.

- Mboowa, D. (2024). A review of the traditional pulping methods and the recent improvements in the pulping processes. *Biomass Conversion and Biorefinery*, 14(1), 1–12. <https://doi.org/10.1007/s13399-020-01243-6>, <https://www.springer.com/journal/13399>.
- Metcalf, L., Eddy, H. P., & Tchobanoglous, G. (2002). *Wastewater engineering: Treatment and reuse*. McGraw-Hill Science/Engineering/Math.
- Mininni, G., Laera, G., Bertanza, G., Canato, M., & Sbrilli, A. (2015). Mass and energy balances of sludge processing in reference and upgraded wastewater treatment plants. *Environmental Science and Pollution Research*, 22(10), 7203–7215. <https://doi.org/10.1007/s11356-014-4013-2>.
- Mitra, S., Chakraborty, A. J., Tareq, A. M., Emran, T. B., Nainu, F., Khushro, A., Idris, A. M., Khandaker, M. U., Osman, H., Alhumaydhi, F. A., & Simal-Gandara, J. (2022). Impact of heavy metals on the environment and human health: Novel therapeutic insights to counter the toxicity. *Elsevier BJournal of King Saud University - Science*, 34(3). <https://doi.org/10.1016/j.jksus.2022.101865>, <http://www.sciencedirect.com/science/journal/10183647>.
- Mnif, W., & Ben Rebah, F. (2023). Biofloculants as alternative to synthetic polymers to enhance wastewater sludge dewaterability: A review. *Energies*, 16(8), 3392. <https://doi.org/10.3390/en16083392>.
- Mohan, D., Pittman, C. U., & Steele, P. H. (2006). Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin-a biosorbent. *Journal of Colloid and Interface Science*, 297(2), 489–504. <https://doi.org/10.1016/j.jcis.2005.11.023>.
- Mohan, K., Ganesan, A. R., Muralisankar, T., Jayakumar, R., Sathishkumar, P., Uthayakumar, V., Chandrasekar, R., & Revathi, N. (2020). Recent insights into the extraction, characterization, and bioactivities of chitin and chitosan from insects. *Trends in Food Science and Technology*, 105, 17–42. <https://doi.org/10.1016/j.tifs.2020.08.016>, http://www.elsevier.com/wps/find/journaldescription.cws_home/601278/description#description.
- Morales-Jiménez, M., Palacio, D. A., Palencia, M., Meléndrez, M. F., & Rivas, B. L. (2023). Bio-based polymeric membranes: Development and environmental applications. *Membranes*, 13(7). <https://doi.org/10.3390/membranes13070625>, <http://www.mdpi.com/journal/membranes>.
- Morin-Crini, N., Lichtfouse, E., Torri, G., & Crini, G. (2019). *Fundamentals and applications of chitosan*. Springer Science and Business Media LLC, 49–123. https://doi.org/10.1007/978-3-030-16538-3_2.
- Moura, C. Md, Moura, J. Md, Soares, N. M., & Pinto, L. Ad. A. (2011). Evaluation of molar weight and deacetylation degree of chitosan during chitin deacetylation reaction: Used to produce biofilm. *Chemical Engineering and Processing: Process Intensification*, 50(4), 351–355. <https://doi.org/10.1016/j.cep.2011.03.003>.
- Munir, H. M. S., Feroze, N., Ramzan, N., Sagir, M., Babar, M., Tahir, M. S., Shamshad, J., Mubashir, M., & Khoo, K. S. (2022). Fe-zeolite catalyst for ozonation of pulp and paper wastewater for sustainable water resources. *Chemosphere*, 297. <https://doi.org/10.1016/j.chemosphere.2022.134031>, <http://www.elsevier.com/locate/chemosphere>.
- Nakata, K., & Kurane, R. (1999). Production of an extracellular polysaccharide biofloculant by *Klebsiell*. *Bioscience, Biotechnology, and Biochemistry*, 63(12), 2064–2068. <https://doi.org/10.1271/bbb.63.2064>.
- Obaideen, K., Shehata, N., Sayed, E. T., Abdelkareem, M. A., Mahmoud, M. S., & Olabi, A. G. (2022). The role of wastewater treatment in achieving sustainable development goals (SDGs) and sustainability guideline. *Energy Nexus*, 7. <https://doi.org/10.1016/j.nexus.2022.100112>, <https://www.journals.elsevier.com/energy-nexus>.
- Osman, A. I., El-Monaem, E. M. A., Elgarahy, A. M., Aniagor, C. O., Hosny, M., Farghali, M., Rashad, E., Ejimofor, M. I., López-Maldonado, E. A., Ihara, I., Yap, P.

- S., Rooney, D. W., & Eltaweil, A. S. (2023). Methods to prepare biosorbents and magnetic sorbents for water treatment: A review. *Environmental Chemistry Letters*, 21(4), 2337–2398. <https://doi.org/10.1007/s10311-023-01603-4>, <https://www.springer.com/journal/10311>.
- Panigrahy, N., Priyadarshini, A., Sahoo, M. M., Verma, A. K., Daverey, A., & Sahoo, N. K. (2022). A comprehensive review on eco-toxicity and biodegradation of phenolics: Recent progress and future outlook. *Environmental Technology and Innovation*, 27. <https://doi.org/10.1016/j.eti.2022.102423>, <http://www.journals.elsevier.com/environmental-technology-and-innovation/>.
- Pellis, A., Guebitz, G. M., & Nyanhongo, G. S. (2022). Chitosan: Sources, processing and modification techniques. *Gels*, 8(7). <https://doi.org/10.3390/gels8070393>, <https://www.mdpi.com/2310-2861/8/7/393/pdf?version=1655817695>.
- Priya, A. K., Gnanasekaran, L., Rajendran, S., Qin, J., & Vasseghian, Y. (2022). Occurrences and removal of pharmaceutical and personal care products from aquatic systems using advanced treatment – A review. *Environmental Research*, 204, 112298. <https://doi.org/10.1016/j.envres.2021.112298>.
- Pu, Y., Jiang, N., & Ragauskas, A. J. (2007). Ionic liquid as a green solvent for lignin. *Journal of Wood Chemistry and Technology*, 27(1), 23–33. <https://doi.org/10.1080/02773810701282330>.
- Purohit, P., Bhatt, A., Mittal, R. K., Abdellattif, M. H., & Farghaly, T. A. (2023). Polymer Grafting and its chemical reactions. *Frontiers in Bioengineering and Biotechnology*, 10. <https://doi.org/10.3389/fbioe.2022.1044927>, <http://journal.frontiersin.org/journal/bioengineering-and-biotechnology#archive>.
- Qu, X., Gao, W. J., Han, M. N., Chen, A., & Liao, B. Q. (2012). Integrated thermophilic submerged aerobic membrane bioreactor and electrochemical oxidation for pulp and paper effluent treatment – Towards system closure. *Bioresource Technology*, 116, 1–8. <https://doi.org/10.1016/j.biortech.2012.04.045>.
- Rafieian, F., Jonoobi, M., & Yu, Q. (2019). A novel nanocomposite membrane containing modified cellulose nanocrystals for copper ion removal and dye adsorption from water. *Cellulose*, 26(5), 3359–3373. <https://doi.org/10.1007/s10570-019-02320-4>.
- Ragunathan, R., & Swaminathan, K. (2004). Biological treatment of a pulp and paper industry effluent by *Pleurotus* spp. *World Journal of Microbiology and Biotechnology*, 20(4), 389–393. <https://doi.org/10.1023/B:WIBL.0000033064.63031.1c>.
- Raj, K., & Das, A. P. (2023). Lead pollution: Impact on environment and human health and approach for a sustainable solution. *Environmental Chemistry and Ecotoxicology*, 5, 79–85. <https://doi.org/10.1016/j.enceco.2023.02.001>, <https://www.sciencedirect.com/journal/environmental-chemistry-and-ecotoxicology>.
- Rather, A. M., Xu, Y., Dupont, R. L., & Wang, X. (2022). Polymeric membranes in wastewater treatment. In *Nanoscale engineering of biomaterials: Properties and applications*. United States: Springer Nature, 487–515. <https://link.springer.com/book/10.1007/978-981-16-3667-7>, https://doi.org/10.1007/978-981-16-3667-7_17.
- Righi, S., Bandini, V., Marazza, D., Baioli, F., Torri, C., & Contin, A. (2016). Life Cycle Assessment of high ligno-cellulosic biomass pyrolysis coupled with anaerobic digestion. *Bioresource Technology*, 212, 245–253. <https://doi.org/10.1016/j.biortech.2016.04.052>, <http://www.elsevier.com/locate/biortech>.
- Roshanfekr Rad, L. R., & Anbia, M. (2021). Zeolite-based composites for the adsorption of toxic matters from water: A review. *Journal of Environmental Chemical Engineering*, 9(5), 106088. <https://doi.org/10.1016/j.jece.2021.106088>.
- Rovera, C., Ghaani, M., Santo, N., Trabattini, S., Olsson, R. T., Romano, D., & Farris, S. (2018). Enzymatic hydrolysis in the green production of bacterial cellulose nanocrystals. *ACS Sustainable Chemistry and Engineering*, 6(6), 7725–7734. <https://doi.org/10.1021/acssuschemeng.8b00600>, <http://pubs.acs.org/journal/ascecg>.

- Ruthran, R. V., Barman, P., Kadam, R., & Kumar, A. (2022). Lignin-based adsorbent for effective removal of toxic heavy metals from wastewater. *Emergent Materials*, 5(3), 923–943. <https://doi.org/10.1007/s42247-021-00311-5>.
- Sadare, O. O., Yoro, K. O., Moothi, K., & Daramola, M. O. (2022). Lignocellulosic biomass-derived nanocellulose crystals as fillers in membranes for water and wastewater treatment: A review. *Membranes*, 12(3). <https://doi.org/10.3390/membranes12030320>, <https://www.mdpi.com/2077-0375/12/3/320/pdf>.
- Safie, N. N., & Zahrim, A. Y. (2021). Recovery of nutrients from sewage using zeolite-chitosan-biochar adsorbent: Current practices and perspectives. *Journal of Water Process Engineering*, 40, 101845. <https://doi.org/10.1016/j.jwpe.2020.101845>.
- Sand, A., & Vyas, A. (2020). *Introductory chapter: Organic polymer – Graft copolymers*. IntechOpen. <https://doi.org/10.5772/intechopen.88037>.
- Sanz, E., Bezares, C., Pascual, C., Menéndez Pidal, I., & Fonolla, C. (2021). Hydrogeochemical evolution of an aquifer regulated by pyrite oxidation and organic sediments. *Water*, 13(17), 2444. <https://doi.org/10.3390/w13172444>.
- Sarkar, A. K., Ghorai, S., Patra, A. S., Mishra, B. K., Mandre, N. R., & Pal, S. (2014). Modified amylopectin based flocculant for the treatment of synthetic effluent and industrial wastewaters. *International Journal of Biological Macromolecules*, 72, 356–363. <https://doi.org/10.1016/j.ijbiomac.2014.08.019>, <http://www.elsevier.com/locate/ijbiomac>.
- Sasmal, D., Singh, R. P., & Tripathy, T. (2015). Synthesis and flocculation characteristics of a novel biodegradable flocculating agent amylopectin-g-poly (acrylamide-co-N-methylacrylamide). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 482, 575–584. <https://doi.org/10.1016/j.colsurfa.2015.07.017>, <http://www.elsevier.com/locate/colsurfa>.
- Sen, G., Ghosh, S., Jha, U., & Pal, S. (2011). RETRACTED: Hydrolyzed polyacrylamide grafted carboxymethylstarch (Hyd. CMS-g-PAM): An efficient flocculant for the treatment of textile industry wastewater. *Chemical Engineering Journal*, 171(2), 495–501. <https://doi.org/10.1016/j.cej.2011.04.016>.
- Shabanizadeh, H., & Taghavijeloudar, M. (2023). Potential of pomegranate seed powder as a novel natural flocculant for pulp and paper wastewater treatment: Characterization, comparison and combination with alum. *Process Safety and Environmental Protection*, 170, 1217–1227. <https://doi.org/10.1016/j.psep.2023.01.004>, http://www.elsevier.com/wps/find/journaldescription.cws_home/713889/description#description.
- Shak, K. P. Y., Pang, Y. L., & Mah, S. K. (2018). Nanocellulose: Recent advances and its prospects in environmental remediation. *Beilstein Journal of Nanotechnology*, 9(1), 2479–2498. <https://doi.org/10.3762/bjnano.9.232>, <https://www.beilstein-journals.org/bjnano/content/pdf/2190-4286-9-232.pdf>.
- Shende, A. P., & Chidambaram, R. (2023). Cocoyam powder extracted from Colocasia antiquorum as a novel plant-based bioflocculant for industrial wastewater treatment: Flocculation performance and mechanism. *Heliyon*, 9(4). <https://doi.org/10.1016/j.heliyon.2023.e15228>, <http://www.journals.elsevier.com/heliyon/>.
- Shende, A. P., & Das, N. (2021). Green synthesis of iron nanoparticles using bioflocculant extracted from okra (*Abelmoschus esculentus* (L) moench) and its application towards elimination of toxic metals from wastewater: A statistical approach. *Journal of Water and Environmental Nanotechnology*, 6(4), 338–355. <https://doi.org/10.22090/jwent.2021.04.005>, <http://www.jwent.net>.
- Shilpa, B. S., Akanksha, P., & Kavita, G. (2012). Evaluation of cactus and hyacinth bean peels as natural coagulants. *International Journal of Chemical and Environmental Engineering*, 3, 187–191.
- Siah, C. (2017). *Extraction of Bio-Flocculant from Okra Using Hydrothermal and Microwave Extraction Methods Combined with a Techno-Economic Assessment*.
- Singh, A. K., Yadav, P., Bharagava, R. N., Saratale, G. D., & Raj, A. (2019). Biotransformation and cytotoxicity evaluation of kraft lignin degraded by

- ligninolytic *Serratia liquefaciens*. *Frontiers in Microbiology*, 10. <https://doi.org/10.3389/fmicb.2019.02364>, <https://www.frontiersin.org/journals/microbiology#>.
- Singh, S., Anil, A. G., Kumar, V., Kapoor, D., Subramanian, S., Singh, J., & Ramamurthy, P. C. (2022). Nitrates in the environment: A critical review of their distribution, sensing techniques, ecological effects and remediation. *Chemosphere*, 287. <https://doi.org/10.1016/j.chemosphere.2021.131996>, <http://www.elsevier.com/locate/chemosphere>.
- Srivastava, A., Singh, P., Srivastava, S., & Singh, S. (2023). Reclamation and characterization of value-added products from pulp and paper mill effluent using microbial fuel cell. *Materials Today: Proceedings*. <https://doi.org/10.1016/j.matpr.2023.02.415>, <https://www.sciencedirect.com/journal/materials-today-proceedings>.
- Subramonian, W., Wu, T. Y., & Chai, S. P. (2014). A comprehensive study on coagulant performance and floc characterization of natural Cassia obtusifolia seed gum in treatment of raw pulp and paper mill effluent. *Industrial Crops and Products*, 61, 317–324. <https://doi.org/10.1016/j.indcrop.2014.06.055>, <http://www.elsevier.com/inca/publications/store/5/2/2/8/2/5>.
- Supratim, P., & Kaushik, C. (2017). Different aspects of chloride in freshwater: A review. *International Journal of Current Trends in Science and Technology*, 7, 20295–20303.
- Suresh, R., Subramaniyan, R., Kumar, K. S., Kumar, N., & Chenniappan, M. (2023). Sustainable technologies for treatment of industrial wastewater and its potential for reuse. In *Microbial technologies in industrial wastewater treatment*. India: Springer Nature, 143–168. <https://link.springer.com/book/10.1007/978-981-99-2435-6>, https://doi.org/10.1007/978-981-99-2435-6_9.
- Tan, X.-F, Liu, Y.-G, Gu, Y.-L, Xu, Y., Zeng, G.-M, Hu, X.-J, Liu, S.-B, Wang, X., Liu, S.-M, & Li, J. (2016). Biochar-based nano-composites for the decontamination of wastewater: A review. *Bioresource Technology*, 212, 318–333. <https://doi.org/10.1016/j.biortech.2016.04.093>.
- Tang, W., Song, L., Li, D., Qiao, J., Zhao, T., & Zhao, H. (2014). Production, characterization, and flocculation mechanism of cation independent, pH tolerant, and thermally stable bioflocculant from *Enterobacter* sp. ETH-2. *PLoS ONE*, 9(12), 19326203. <https://doi.org/10.1371/journal.pone.0114591>, <http://www.plosone.org/article/fetchObject.action?uri=info%3Adoi%2F10.1371%2Fjournal.pone.0114591&representation=PDF>.
- Tang, X., Huang, T., Zhang, S., Wang, W., & Zheng, H. (2020). The role of sulfonated chitosan-based flocculant in the treatment of hematite wastewater containing heavy metals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 585, 124070. <https://doi.org/10.1016/j.colsurfa.2019.124070>.
- Tawila, Z. M. A., Ismail, S., Dadrasnia, A., & Usman, M. M. (2018). Production and characterization of a bioflocculant produced by *Bacillus salmalaya* 139si-7 and its applications in wastewater treatment. *Molecules*, 23(10), 14203049. <https://doi.org/10.3390/molecules23102689>, <https://www.mdpi.com/1420-3049/23/10/2689/pdf>.
- Toczyłowska-Mamińska, R. (2017). Limits and perspectives of pulp and paper industry wastewater treatment – A review. *Renewable and Sustainable Energy Reviews*, 78, 764–772. <https://doi.org/10.1016/j.rser.2017.05.021>, <https://www.journals.elsevier.com/renewable-and-sustainable-energy-reviews>.
- Tomei, M. C., Angelucci, D. M., & Daugulis, A. J. (2016). Towards a continuous two-phase partitioning bioreactor for xenobiotic removal. *Journal of Hazardous Materials*, 317, 403–415. <https://doi.org/10.1016/j.jhazmat.2016.05.092>, <http://www.elsevier.com/locate/jhazmat>.
- Trache, D., Hussin, M. H., Haafiz, M. K. M., & Thakur, V. K. (2017). Recent progress in cellulose nanocrystals: Sources and production. *Nanoscale*, 9(5), 1763–1786. <https://doi.org/10.1039/c6nr09494e>, <http://pubs.rsc.org/en/journals/journal/nr>.

- Trang, T. T. C., & Takaomi, K. (2021). Chitosan and its biomass composites in application for water treatment. *Current Opinion in Green and Sustainable Chemistry*, 29, 100429. <https://doi.org/10.1016/j.cogsc.2020.100429>.
- Vaidhegi, K. (2013). Treatment of bagasse based pulp and paper industry effluent using moving bed biofilm reactor. *International Journal of ChemTech Research*, 5(3), 1313–1319. http://www.sphinxssai.com/2013/vol_5_3/pdf/CT=29%281313-1319%29IPACT.pdf.
- Vasić, V., Kukić, D., Šćiban, M., Đurišić-Mladenović, N., Velić, N., Pajin, B., Crespo, J., Farre, M., & Šereš, Z. (2023). Lignocellulose-based biosorbents for the removal of contaminants of emerging concern (CECs) from water: A review. *Water*, 15(10), 1853. <https://doi.org/10.3390/w15101853>.
- Verma, M., & Ekka, A. (2018). Decolorization and degradation of kraft lignin discharged from pulp and paper mill industry by axenic and co-culture of *Bacillus* sp. *Research Journal of Pharmacy and Technology, India*, 11(10), 4386–4392. <https://doi.org/10.5958/0974-360X.2018.00802.8>, <http://www.rjptonline.org/>.
- Verma, M., Ekka, A., Mohapatra, T., & Ghosh, P. (2020). Optimization of kraft lignin decolorization and degradation by bacterial strain *Bacillus velezensis* using response surface methodology. *Journal of Environmental Chemical Engineering*, 8(5), 104270. <https://doi.org/10.1016/j.jece.2020.104270>.
- Vidal, R. R. L., & Moraes, J. S. (2019). Removal of organic pollutants from wastewater using chitosan: A literature review. *International Journal of Environmental Science and Technology*, 16(3), 1741–1754. <https://doi.org/10.1007/s13762-018-2061-8>.
- Wai, K. T., Idris, A., Johari, M. M. N. M., Mohammad, T. A., Ghazali, A. H., & Muyibi, S. A. (2009). Evaluation on different forms of *Moringa oleifera* seeds dosing on sewage sludge conditioning. *Desalination and Water Treatment*, 10(1-3), 87–94. <https://doi.org/10.5004/dwt.2009.783>.
- Wang, B., Gao, B., & Fang, J. (2017). Recent advances in engineered biochar productions and application. *Critical Reviews in Environmental Science and Technology*, 47(22), 2158–2207. <https://doi.org/10.1080/10643389.2017.1418580>, <http://www.tandf.co.uk/journals/titles/10643389.asp>.
- Wang, T., Jiang, M., Yu, X., Niu, N., & Chen, L. (2022). Application of lignin adsorbent in wastewater treatment: A review. *Separation and Purification Technology*, 302, 122116. <https://doi.org/10.1016/j.seppur.2022.122116>.
- Warsinger, D. M., Chakraborty, S., Tow, E. W., Plumlee, M. H., Bellona, C., Loutatidou, S., Karimi, L., Mikelonis, A. M., Achilli, A., Ghassemi, A., Padhye, L. P., Snyder, S. A., Curcio, S., Vecitis, C. D., Arafat, H. A., & Lienhard, J. H. (2018). A review of polymeric membranes and processes for potable water reuse. *Progress in Polymer Science*, 81, 209–237. <https://doi.org/10.1016/j.progpolymsci.2018.01.004>, <http://www.sciencedirect.com/science/journal/00796700>.
- Wu, F. C., Tseng, R. L., & Juang, R. S. (2001). Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization. *Journal of Hazardous Materials*, 81(1-2), 167–177. [https://doi.org/10.1016/S0304-3894\(00\)00340-X](https://doi.org/10.1016/S0304-3894(00)00340-X).
- Wu, S., Shi, W., Li, K., Cai, J., & Chen, L. (2022). Recent advances on sustainable bio-based materials for water treatment: Fabrication, modification and application. *Journal of Environmental Chemical Engineering*, 10(6), 108921. <https://doi.org/10.1016/j.jece.2022.108921>.
- Wu, X., Li, H., Kan, Y., & Yin, B. (2013). A regeneratable and highly selective fluorescent probe for sulfide detection in aqueous solution. *Dalton Transactions*, 42(46), 16302. <https://doi.org/10.1039/c3dt51953h>.
- Xiang, W., Zhang, X., Chen, J., Zou, W., He, F., Hu, X., Tsang, D. C. W., Ok, Y. S., & Gao, B. (2020). Biochar technology in wastewater treatment: A critical review. *Chemosphere*, 252, 18791298. <https://doi.org/10.1016/j.chemosphere.2020.126539>, <http://www.elsevier.com/locate/chemosphere>.

- Xiao, X., Yu, Y., Sun, Y., Zheng, X., & Chen, A. (2021). Heavy metal removal from aqueous solutions by chitosan-based magnetic composite flocculants. *Journal of Environmental Sciences (China)*, 108, 22–32. <https://doi.org/10.1016/j.jes.2021.02.014>, <http://www.journals.elsevier.com/journal-of-environmental-sciences/>.
- Xu, K., Zou, X., Mouradov, A., Spangenberg, G., Chang, W., & Li, Y. (2021). Efficient bioflocculation of *Chlorella vulgaris* with a chitosan and walnut protein extract. *Biology*, 10(5). <https://doi.org/10.3390/biology10050352>, <https://www.mdpi.com/2079-7737/10/5/352/pdf>.
- Yang, R., Li, H., Huang, M., Yang, H., & Li, A. (2016). A review on chitosan-based flocculants and their applications in water treatment. *Water Research*, 95, 59–89. <https://doi.org/10.1016/j.watres.2016.02.068>, <http://www.elsevier.com/locate/watres>.
- Yashas, S. R., Shivakumara, B. P., Udayashankara, T. H., & Krishna, B. M. (2018). Laccase biosensor: Green technique for quantification of phenols in wastewater. *Oriental Journal of Chemistry*, 34(2), 631–637. <https://doi.org/10.13005/ojc/340204>.
- Yu, H., Zou, W., Chen, J., Chen, H., Yu, Z., Huang, J., Tang, H., Wei, X., & Gao, B. (2019). Biochar amendment improves crop production in problem soils: A review. *Journal of Environmental Management*, 232, 8–21. <https://doi.org/10.1016/j.jenvman.2018.10.117>, <https://www.sciencedirect.com/journal/journal-of-environmental-management>.
- Yusoff, M. A. M., Lee, C. W., & Bong, C. W. (2019). Analysis of water treatment by Moringa oleifera bioflocculant prepared via supercritical fluid extraction. *Polish Journal of Environmental Studies*, 28(4), 2995–3002. <https://doi.org/10.15244/pjoes/92119>, <http://www.pjoes.com/pdf-92119-37093?filename=Analysis%20of%20Water.pdf>.
- Zak, D., Hupfer, M., Cabezas, A., Jurasinski, G., Audet, J., Kleberg, A., McInnes, R., Kristiansen, S. M., Petersen, R. J., Liu, H., & Goldammer, T. (2021). Sulphate in freshwater ecosystems: A review of sources, biogeochemical cycles, ecotoxicological effects and bioremediation. *Earth-Science Reviews*, 212. <https://doi.org/10.1016/j.earscirev.2020.103446>, <http://www.sciencedirect.com/science/journal/00128252>.
- Zhang, D., Karkooti, A., Liu, L., Sadrzadeh, M., Thundat, T., Liu, Y., & Narain, R. (2018). Fabrication of antifouling and antibacterial polyethersulfone (PES)/cellulose nanocrystals (CNC) nanocomposite membranes. *Journal of Membrane Science*, 549, 350–356. <https://doi.org/10.1016/j.memsci.2017.12.034>, <http://www.elsevier.com/locate/memsci>.
- Zhang, F., Jiang, W., Wang, X., Ji, X., Wang, Y., Zhang, W., & Chen, J. (2015). Culture condition effect on bioflocculant production and actual wastewater treatment application by different types of bioflocculants. InTech. <https://doi.org/10.5772/62114>.
- Zhang, L. W., Hua, J. R., Zhu, W. J., Liu, L., Du, X. L., Meng, R. J., & Yao, J. M. (2018). Flocculation performance of hyperbranched polyethylenimine-grafted cellulose in wastewater treatment. *ACS Sustainable Chemistry and Engineering*, 6(2), 1592–1601. <https://doi.org/10.1021/acssuschemeng.7b02343>, <http://pubs.acs.org/journal/ascecg>.
- Zhang, M., Lin, K., Li, X., Wu, L., Yu, J., Cao, S., Zhang, D., Xu, L., Parikh, S. J., & Ok, Y. S. (2022). Removal of phosphate from water by paper mill sludge biochar. *Environmental Pollution*, 293. <https://doi.org/10.1016/j.envpol.2021.118521>, <https://www.journals.elsevier.com/environmental-pollution>.
- Zhang, X. (2022). Selective separation membranes for fractionating organics and salts for industrial wastewater treatment: Design strategies and process assessment. *Journal of Membrane Science*, 643, 120052. <https://doi.org/10.1016/j.memsci.2021.120052>.
- Zhou, J., Chang, C., Zhang, R., & Zhang, L. (2007). Hydrogels prepared from unsubstituted cellulose in NaOH/urea aqueous solution. *Macromolecular bioscience*, 7(6), 804–809. <https://doi.org/10.1002/mabi.200700007>.

Zhu, L., Pan, G., Xu, H., Kong, L., Guo, W., Yu, J., Mortimer, R. J. G., & Shi, W. (2021). Enhanced chitosan flocculation for microalgae harvesting using electrolysis. *Algal Research*, 55. <https://doi.org/10.1016/j.algal.2021.102268>, <http://www.sciencedirect.com/science/journal/aip/22119264>.

Further reading

USEPA (U.S. Environmental Protection Agency). (2012). Endocrine Disruptor Screening Program, Universe of Chemicals for Potential Endocrine Disruptor Screening and Testing report. In *Jointly developed by the Office of Chemical Safety & Pollution Prevention, the Office of Water and the Office of Research and Development*, 1–176.

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Advanced Technologies in Wastewater Treatment Pulp and Paper Industry

Edited by **Mohammad Reza Rahimpour, Angelo Basile, Alfredo Cassano, Parvin Kiani**

Pulp and Paper Industry provides detailed discussion on the characteristics, environmental hazards, and human health effects of pulp and paper industries' wastewater. This book discusses their different treatment methods and related challenges. These techniques start from physical methods such as sedimentation and froth flotation, followed by physiochemical treatments including activated carbon filtration and chemical precipitation, as well as biological techniques like aerobic and anaerobic processes. This book also covers application of advanced and novel wastewater treatment techniques in pulp and paper industries, such as ozonation, photocatalysis, advanced oxidation process, electrolysis, microbial fuel cells, etc., as well as challenges of industries, economic assessments, and future perspectives of pulp and paper industries' wastewater treatments.

Key features

- Introduces pulp and paper industries' wastewater and pollutant characteristics, challenges, and utilization
- Includes physical, physiochemical, and biological methods for pulp and paper industries' wastewater treatment
- Describes novel and innovative methods for pulp and paper industries' wastewater treatment

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