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Engineered Biopolymer Architectures for Selective Metal Ions Extraction

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ABSTRACT

The separation and recovery of metal ions from industrial and municipal wastewaters and leachates is essential for environmental sustainability and resource conservation. Bio-based polysaccharides, such as cellulose and chitin; proteins, such as keratin; and other biomacromolecules, such as lignin, offer a promising, sustainable alternative to conventional adsorbents due to their abundance, renewability, and inherent presence of metal-binding functional groups. This review explores strategies to engineer these materials and enhance their metal interaction capabilities. These include chemical modifications (e.g., introduction of charged groups and metal-specific ligands), physical treatments (e.g., particle size reduction and porosity control), and the development of composite materials and advanced architectures, such as activated carbons, membranes, fibers, and 3D-printed structures. Despite their potential, challenges such as natural variability, lower durability compared to synthetic materials, and economic considerations remain. Through targeted research and development, biopolymers could become viable, eco-friendly solutions for hydrometallurgical metal recovery processes, aligning with circular economy principles. This review provides a comprehensive, mechanism-oriented synthesis that integrates material classes, functionalization strategies, and adsorption selectivity trends relevant to metal recovery under hydrometallurgical conditions and outlines future directions to overcome existing barriers.

1 | Introduction

Growing emphasis on sustainable resource management and circular economy principles has accelerated the shift toward environmentally friendly metal recovery from secondary sources. In this context, hydrometallurgical methods have emerged as a more sustainable alternative to traditional pyrometallurgical processes. Unlike pyrometallurgy, which requires high temperatures and substantial energy input, hydrometallurgy offers several advantages as it operates under milder thermal and pressure conditions, consumes less energy, and provides higher selectivity for targeted metal recovery [1–3]. Hydrometallurgical techniques typically begin with a leaching step, in which metals are solubilized from solid matrices. This is commonly achieved through chemical leaching, using mineral acids (e.g., HCl, H_2SO_4) or complexing agents, although biological leaching (bioleaching) using microorganisms has also been explored. These leaching processes are widely applied to a variety of metal-rich secondary resources, including end-of-life batteries, spent automotive catalytic converters, electronic waste, and photovoltaic panels [3]. The leachates obtained from these processes, as well as from metal-containing wastewaters generated by industries such as mining, electroplating, and battery manufacturing, are subjected to selective separation steps for preferential binding of a target metal ion in the presence of competing species. These steps conventionally involve precipitation, solvent extraction, or ion

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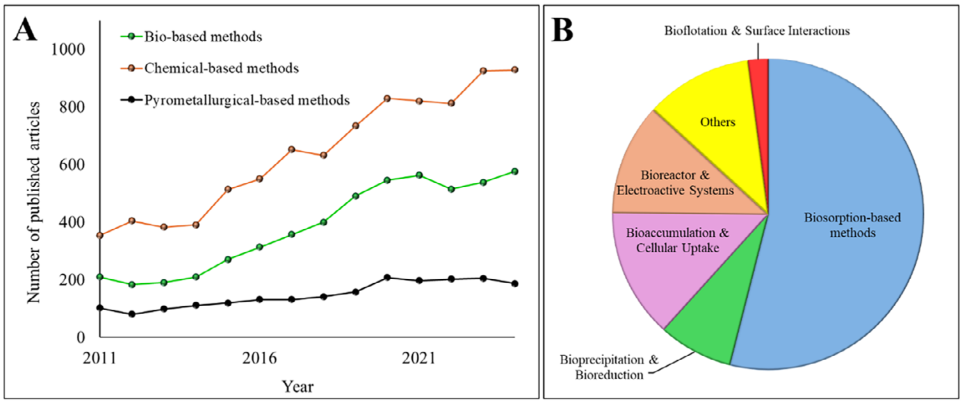


FIGURE 1 | (A) Number of published articles using pyrometallurgical, chemical-, and bio-based methods for metal separation and recovery from different matrices between 2011 and 2024 (Source: Scopus, accessed October 2025). (B) Distribution of bio-based methods used for metal separation and recovery.

exchange using chemical reagents. However, they often require substantial reagent consumption and generate secondary waste streams that pose challenges for treatment, disposal, and environmental safety [4]. As a result, there is a growing interest in developing more sustainable and lower-impact metal recovery alternatives based on biomaterials. These materials, derived from renewable resources or waste biomass, are being investigated for their potential to reduce chemical usage, minimize waste generation, and provide selective recovery of valuable metals in an eco-friendly manner [5].

To have a better insight into the trend of studies focusing on metal separation and recovery methods, an assessment was conducted by searching Scopus for publications on pyro and hydrometallurgical (with a focus on bio-based and chemical metal recovery methods) methods from 2011 to 2024. As illustrated in Figure 1A, the number of publications on bio-based methods for metal separation and recovery has been increasing steadily since 2011 [6], significantly outpacing pyrometallurgical approaches, though still lagging behind chemical-based hydrometallurgical methods. This trend reflects the increasing recognition of bio-based materials' potential as solutions for addressing global challenges in resource management and environmental remediation. Hydrometallurgical systems leveraging metal–biomaterial interactions represent a pathway toward more sustainable metal recovery within a circular economy framework [6, 7]. Chemical-based hydrometallurgical methods continue to dominate research due to their maturity, resulting in a persistent focus on chemical approaches over bio-based materials in metal separation and/or recovery studies [3, 8].

The literature research also revealed that the most common bio-based metal recovery methods are biosorption, bioaccumulation, bioreactor and electroactive systems, bioprecipitation, and bioflotation. Biosorption, accounting for more than half of published studies (Figure 1B), involves passive binding of metals to functional groups on bio-based materials. The next most widely studied method is bioaccumulation, which is an active process where living organisms (microbes or plants) take up metal species through metabolic activity and store them within cellular compartments. In bioprecipitation, metals are reduced or react with bio-based materials (usually obtained from plants or microbes) [9, 10]. Bioreactors, electroactive systems, and bioflotation are metal recovery methods based on bacterial activity, utilizing microbial metabolism or electrochemical interactions. Most biopolymer-based methods for metal recovery rely on metal sorption or bioprecipitation, where metal ions are adsorbed to the functional groups of biopolymers, or interact with bio-based molecules in the solution and precipitate.

Biopolymers are renewable, environmentally friendly, and, in many cases, abundant, making them ideal for sustainable applications. The most abundant biopolymer is cellulose, a widely available plant-based polysaccharide, and chitin, derived from marine organisms and fungi. Additionally, lignin, an abundant aromatic biopolymer that is a byproduct of the pulp and paper and bioethanol industries, must also be cited. Other examples include keratin, sourced from animal byproducts such as wool and feathers, and alginates, extracted from marine algae. Biopolymers, derived from renewable biological sources, contain diverse functional groups, which enable them to interact with metal ions through electrostatic interactions, chelation, ion exchange, adsorption, and coordination bonding. These features also enable further modification to improve their application potential in various sectors, including metal separation and recovery from different wastewaters and leachates.

Despite the growing body of literature on biopolymer-based materials for metal recovery, the existing reviews often adopt a fragmented perspective, emphasizing a single target metal, a limited subset of biopolymers, or a specific functionalization route, and frequently drawing conclusions from studies performed under idealized aqueous conditions [11–14]. In contrast, this review links material chemistry and structural design with solution chemistry. It analyzes how these factors control adsorption capacity and selectivity under acidic, multicomponent conditions typical of hydrometallurgical leachates. This review systematically connects (i) material chemistry, (ii) engineering strategies, and (iii) process-relevant variables (acid concentration, competing ions, and metal speciation) to rationalize observed selectivity and guide material design for metal recovery and separation. The following sections therefore provide a unified, mechanism-oriented framework that maps key material classes and modification strategies to selective metal capture, offering practical insights for deploying sustainable adsorbents in hydrometallurgical recycling and related metal recovery applications.

2 | Classes of Biopolymers and Their Metal-Interacting Functional Groups

Biopolymers, classified by their biological origin and macromolecular composition (Table 1), include: (1) polysaccharide-based materials, derived from plants (e.g., cellulose, starch, pectin), algae (e.g., alginate), and microorganisms (e.g., microbial exopolymers like xanthan gum, levan, and bacterial cellulose), as well as exoskeletons of arthropods and the cell walls of fungi (e.g., chitin); (2) protein- and peptide-based materials, from both plant and animal sources, such as zein, soy protein, keratin, collagen, and casein; (3) polyphenolic and lignin-rich materials, primarily plant-derived, including lignin, tannins, and other polyphenolic compounds.

These materials possess a wide range of functional groups, such as hydroxyl, carboxyl, amino, thiol, phenolic, phosphate, and sulfate, that are key to their reactivity, particularly in interactions with metal ions through various mechanisms. These mechanisms include adsorption, chelation, electrostatic interactions, ion exchange, complexation, hydrogen bonding, and reduction, each governed by the nature and ionization state of their functional groups. For instance, hydroxyl, carboxyl, and phenolic moieties can ionically bind, or chelate metal species once deprotonated, whereas amine, thiol, and imidazole groups can coordinate metals under protonated or neutral conditions [6, 15]. Hydrogen bonding and coordinate bonds further stabilize these interactions, while ion exchange becomes prominent when functional groups such as carboxylates or sulfonates replace metal counter-ions [6, 7]. Precipitation and co-precipitation can also occur, especially in the presence of multifunctional biopolymers that alter local pH or redox conditions, driving metals to form insoluble complexes [16]. Table 1 summarizes key biopolymers by origin, natural sources, their estimated global production, and their primary functional groups.

Polysaccharide-based materials offer hydroxyl-, carboxyl-, and amino-rich frameworks ideal for capturing metals from aqueous environments. Cellulose, the most abundant polysaccharide (Table 1), can interact with metal species mainly via surface hydroxyl groups through hydrogen bonding, weak coordination, and pH-dependent electrostatic interactions [30] (Figure 2A). Pectin, rich in galacturonic acid residues, exhibits a strong affinity for divalent and trivalent metals through their carboxyl groups (Figure 2B), making them highly effective for recovering metals from industrial effluents [31]. Chitosan, a derivative of chitin, is a particularly effective material with amino and hydroxyl groups that, based on its isoelectric point (pI), can bind to both positively and negatively charged metal complexes from alkaline or acidic matrices, respectively [32] (Figure 2C). Similarly, marine polysaccharides such as alginates act as polyanionic ligands, where carboxylate groups enable strong coordination with divalent metal ions such as calcium and magnesium, leading to metal stabilization and network formation in diverse matrices [33].

Proteins and peptides, with groups such as carboxyl, amino, thiol, disulfide, and imidazole, offer selective metal-binding capabilities critical for recovering valuable or toxic metals. Peptides containing histidine (e.g., collagen), cysteine, and arginine-rich proteins (e.g., keratin) demonstrate potential for sequestering a wide range of metals, including heavy and precious metals like gold and silver. Their binding capabilities primarily arise from imidazole rings in histidine [34], thiol, disulfide, and amine groups in cysteine [35, 36], which facilitate metal interactions through coordination, chelation, or electrostatic mechanisms (Figure 2D–F). This flexibility enables adsorption of both cationic metals and anionic metal complexes, depending on pH and solution conditions, supporting applications in metal recovery and environmental remediation.

Polyphenolic [37] and lignin-based [38] materials combine aromatic structures and phenolic hydroxyl groups, enabling strong metal coordination through hydrogen bonding, electrostatic interactions, and chelation. Lignin, a highly abundant biopolymer, contains diverse functional groups (phenolic, methoxyl, carboxyl, and hydroxyl) that enhance metal selectivity, making it effective in Fenton-like oxidation and other advanced oxidation processes [38–40]. Similarly, polyphenolic compounds, including tannins, feature high-density chelating sites (Figure 2G–I), further supporting metal recovery [37, 41].

Evidence for these interaction mechanisms is typically derived from adsorption studies combined with spectroscopic and surface-sensitive characterization techniques. Vibrational spectroscopies such as Fourier Transform Infrared (FTIR) and Raman spectroscopy are widely used to probe these interactions by monitoring shifts in the characteristic vibrational bands of functional groups after metal uptake. Coordination of a metal ion alters the electron density and bond strength of donor atoms (e.g., O, N, or S), resulting in measurable changes in the stretching frequencies of groups such as $-OH$, $-NH_2$, $-COO^-$, or $-SH$ [33, 41, 49]. Surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS) provide complementary evidence by detecting changes in the binding energies of heteroatoms involved in coordination and by revealing the appearance of metal-specific core-level signals, confirming the formation of metal–ligand bonds at the sorbent surface [41, 50]. In addition, density functional theory (DFT) calculations are increasingly used to model metal–ligand coordination environments and adsorption energies, enabling interpretation of spectroscopic shifts and helping to identify the most favorable binding configurations within the biopolymer matrix [51].

This natural diversity of functional groups across biopolymers provides a foundation for advancing metal recovery technologies. Despite these advantages, the native properties of these materials can limit efficiency, selectivity, and stability under demanding conditions. Introducing additional functional groups, improving structural integrity, and tailoring porosity can enhance metal-binding capacity and selectivity toward specific ions. In this review, adsorption capacity (q) refers to the total amount of metal taken up under defined conditions, whereas selectivity denotes preferential binding of a given ion (M_i) in the presence of a competing species ($\mathrm{M_n}$) ($S = q_{Mi}/q_{Mn}$). The following sections examine modification strategies to enhance metal interaction and separation selectivity.

TABLE 1 | Classification of abundant natural polymers based on origin and type.

General classification	Origin	Name	Natural source	Functional group	Total global production (kilotons)
Polysaccharides	Plants	Cellulose	Wood, cotton, and agricultural residues	Hydroxyl	1.5×10^8 [17]
		Starch	Agricultural processing residues	Hydroxyl	88 000–97 000 [18]
		Pectin	Juice industry waste (e.g., Citrus peel waste)	Hydroxyl, carboxyl	100 [19]
	Algae	Alginate	Seaweed processing waste	Hydroxyl, carboxyl	30 [20]
	Microorganisms	Xanthan gum	Fermentation residues from xanthan and levan production	Hydroxyl, carboxyl, pyruvyl, ketone	205 [21]
		Levan		Hydroxyl, ether	—
	Arthropods and fungi	Chitosan	Crustacean shell waste (shrimp, crab shell waste from seafood industry)	Hydroxyl, amine	200 [22]
Proteins and peptides	Plants	Zein	Corn gluten meal (byproduct of corn wet milling)	Hydroxyl, carboxyl, amine, amide, phenol, thiol	0.5 [23, 24]
		Soy protein	Soybean meal or okara (waste from tofu or soymilk production)	Hydroxyl, carboxyl, amine, amide, phenol, thiol, guanidino, indole	153 000 [25]
	Animals	Keratin	Poultry feather waste, wool waste	Hydroxyl, carboxyl, amine, amide, phenol, thiol, disulfide, guanidino, indole, imidazole	40 000 [26]
		Collagen	Slaughterhouse byproducts (e.g., animal skin, tendon, and bone waste)	Hydroxyl, carboxyl, amine, amide, phenol, thiol, disulfide, guanidino, imidazole	—
		Casein	Dairy industry waste (e.g., cheese whey)	Hydroxyl, carboxyl, amine, amide, phenol, thiol, guanidino, imidazole, phosphate ester	427 [27]
Polyphenolics and lignin-rich materials	Plants	Lignin	Pulp and paper industry waste (black liquor), lignocellulosic biomass residues	Hydroxyl, carboxyl, methoxy, carbonyl, ether, aromatic rings (phenyl groups)	$(0.5\text{–}3.6) \times 10^7$ [28]
		Tannin	Bark waste from wood industry, grape pomace (wine industry), spent tea leaves	Hydroxyl, carboxyl, carbonyl, ether, phenolic hydroxyl, aromatic rings (phenyl groups)	1100 [29]

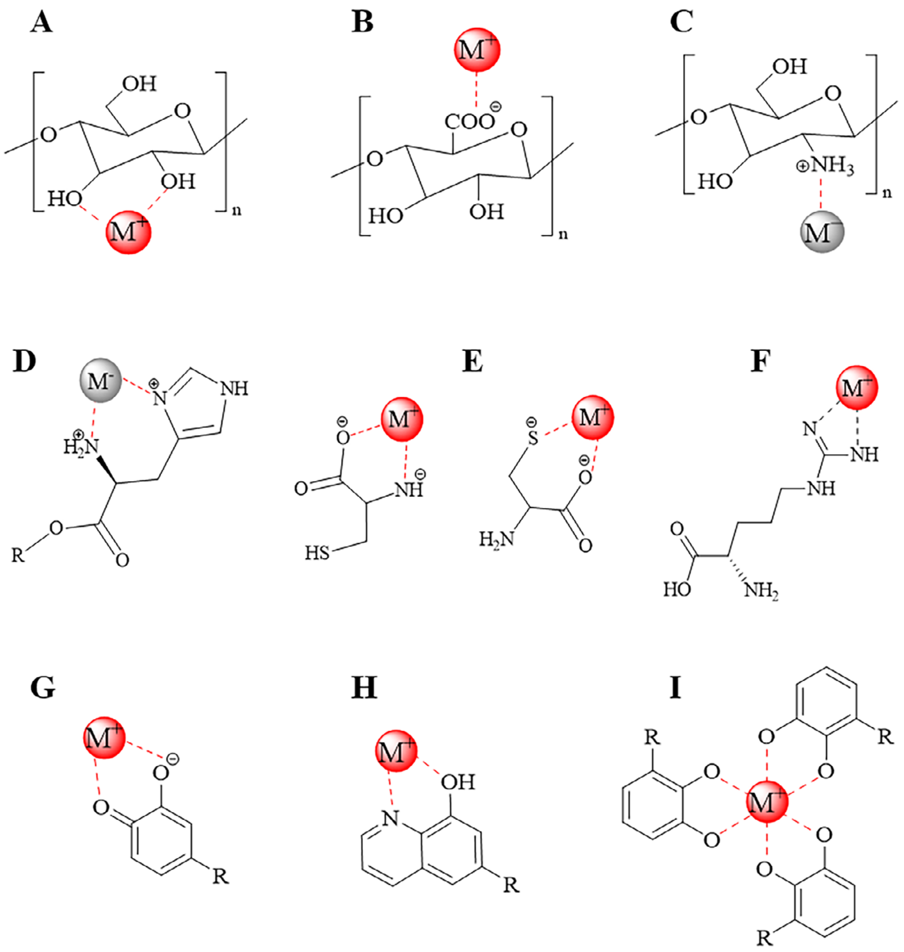


FIGURE 2 | Interaction mechanisms of (A) cellulose through hydrogen bond formation [42], (B) pectin through deprotonated carboxyl groups at pH > carboxyl pKa (~4.0) [43], (C) chitosan through protonated amino group at pH < pI (~6.5) [44], (D) histidine at pH ˂ pI (~7.6) [45], (E) cysteine through thiolate and carboxylate donor groups at pH > relevant pKa values [46], (F) arginine through N-donor chelation [47], and (G–I) phenolic compounds [37, 48] with metal ions or complexes (M^+: $[M(X)_x.mH_2O]^{n+}$; M^-: $[MX_y]^{n-}$ or $[MO_y]^{n-}$; M: metal ion and X: anion like Cl^-, NO_3^-, SO_4^{2-}, OH^-).

3 | Chemical Modifications and Functionalization of Biopolymers

Chemical modification and functionalization of biopolymers enhance metal-binding capacity, selectivity, and structural performance. These processes can be applied in different ways: directly on native biopolymers in their solid state, after solubilization when internal reactive sites are exposed, or on pre-formed materials such as membranes, beads, and composites. This section presents key functionalization approaches, including solubilization techniques, cross-linking strategies, and the introduction of reactive or metal-specific ligands, offering a comprehensive foundation for designing efficient biopolymers for metal separation and environmental applications (Figure 3).

3.1 | Solubilization of Biopolymers

Solubilizing biopolymers is a critical step to enhance their chemical functionalization and facilitate the formation of tailored structures. In their native states, these materials often exhibit extensive hydrogen bonding and rigid supramolecular structures, limiting accessibility to reactive sites [52, 53]. Solubilization disrupts these interactions and exposes previously unavailable functional groups. This enhances the reactivity of biopolymers by enabling the introduction of new chemical groups into their structure (Sections 3.2–3.4). Once the desired modifications are made, the biopolymer can be regenerated into structured forms with tailored properties by re-establishing interactions such as hydrogen bonding and hydrophobic forces.

Table 2 demonstrates some common solubilization methods for cellulose, chitosan, keratin, collagen, and lignin. Cellulose is commonly dissolved in ionic liquids (ILs) [54–56] or deep eutectic solvents (DES) [57] to disrupt hydrogen bonds and crystalline regions, making hydroxyl groups (—OH) more accessible for functionalization processes. Lignin, with its complex aromatic structure, is often solubilized using alkaline solutions (e.g., NaOH) [58], DESs [59], or organic solvents [60]. This treatment exposes phenolic and aliphatic hydroxyl groups, enabling subsequent chemical modifications. A fibrous, rigid protein like keratin, by disulfide bonds and hydrophobic interactions, is insoluble in water, and neutral solvents, but can be solubilized using ILs, such as cholinium acetate [61], reducing agents (e.g., dithiothreitol) [62], alkaline hydrolysis [63], or other methods

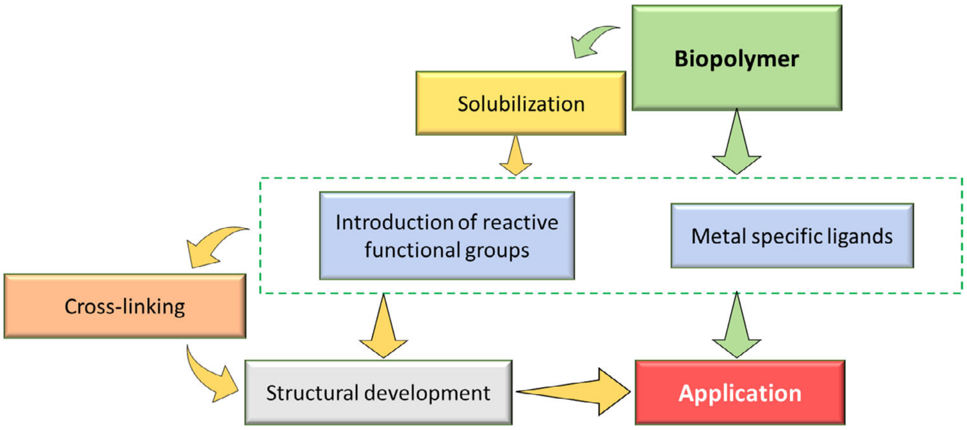


FIGURE 3 | Schematic overview of chemical modification strategies discussed in Section 3.

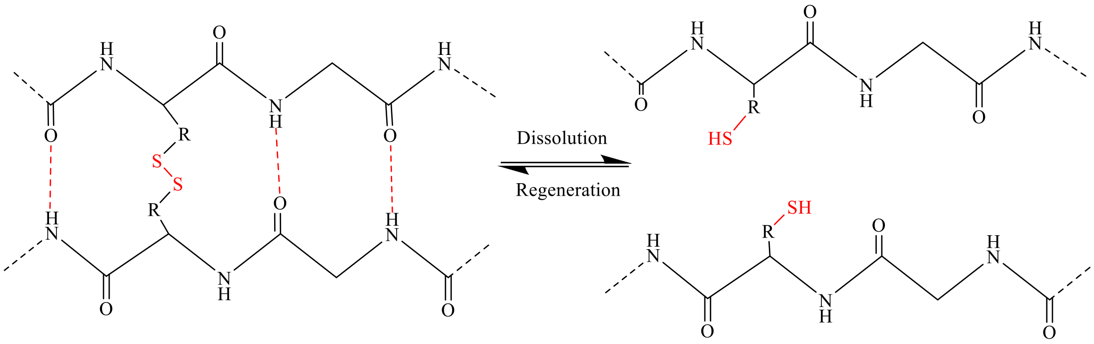


FIGURE 4 | Reductive cleavage of S—S cystine bonds in keratin dissolution, adapted from Fitz-Binder et al. [36].

(Table 2). Solubilization of keratin exposes thiol groups (—SH), as well as previously inaccessible amine (—NH_2) groups, enabling its use in functionalized biomaterials (Figure 4) [36].

Among the available solubilization strategies, ILs and DESs are favored because they disrupt hydrogen bonding and secondary interactions through specific ion–polymer interactions rather than indiscriminate chemical attack, thereby preserving polymer backbone integrity, molecular weight, and reactive functional groups. In addition, certain ILs and DESs, particularly those derived from inexpensive and benign components (e.g., cholinium-based systems such as cholinium acetate [61]), are non-volatile and recyclable, enabling controlled dissolution–regeneration cycles that are difficult to achieve using strong alkaline or hydrolytic treatments.

3.2 | Cross-Linking and Stabilization

A cross-linking agent is a compound that facilitates the formation of covalent or ionic bonds between polymer chains, creating a three-dimensional network, thereby enhancing the material's mechanical, thermal, and chemical properties by altering its structure, while preserving or enhancing metal binding sites [118]. Cross-linking can also modulate porosity and chemical stability, making the material more robust under operational conditions [119]. Table 3 presents examples of cross-linking agents from the different groups of cross-linking agents used in biopolymers.

The selection of a cross-linking agent largely depends on the reactive sites present on the biopolymer and whether these sites should remain available or be incorporated into the cross-linked structure. In the case of chitosan, for example, glutaraldehyde or epichlorohydrin can be chosen to cross-link the biopolymer through amine or hydroxyl groups [128]. As shown in Figure 5, glutaraldehyde primarily reacts with amine groups, forming imine (Schiff base) linkages, thereby preserving hydroxyl groups for subsequent functionalization or application. Conversely, epichlorohydrin predominantly targets hydroxyl groups under alkaline conditions, forming ether bonds and leaving amine groups free (Figure 5).

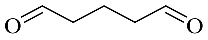
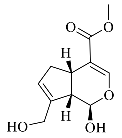
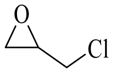
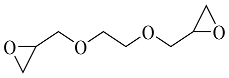
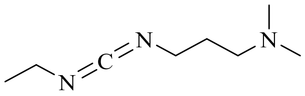
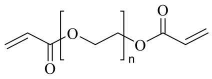
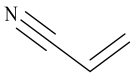
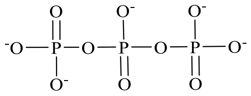
Beyond the impact of cross-linking agents, they may also play an important role on metals interaction affinity of biopolymers. Glutaraldehyde-cross-linked chitosan chelates first-row transition metals (Cr, Mn, Fe, Co, Ni, Cu, and Zn), showing especially strong affinities for Cu^{2+} and Ni^{2+} [129]. Conversely, epichlorohydrin-cross-linked chitosan preserves virtually all primary amines, enabling broad uptake of hard divalent cations. Reported Langmuir capacities reach ~131 mg g^{-1} for Cu^{2+} and ~84 mg g^{-1} for Cd^{2+}, with selectivity in the order $Cu^{2+} > Cd^{2+} > Pb^{2+} \approx Zn^{2+}$, driven by electrostatic attraction and amine chelation, further aided by the material's swelling [130].

Moreover, certain cross-linking agents can play a dual role, reinforcing the polymer network while selectively binding metal

TABLE 2 | Common solubilization methods for cellulose, chitosan, keratin, collagen, and lignin.

	Solubilization methods							
Biopolymer	**Acidic solutions**	**Alkaline solutions**	**Ionic liquids**	**Deep eutectic solvents**	**Organic solvents/co-solvents**	**Reductive/ oxidative methods**	**Derivatization/ chemical modification**	**Other methods**
Cellulose	Concentrated H_3PO_4 or mixed acidic systems like H_2SO_4—glycerol [64]	Alkali + urea [65]	Imidazolium- [66, 67], pyridinium-, ammonium- [68], and phosphonium-based [69] ILs	Choline chloride–oxalic or –lactic acid systems [70], metal-salt DESs like $ZnCl_2 \cdot H_2O/H_3PO_4$ [71]	N-methylmorpholine N-oxide [72], N,N-Dimethylacetamide with LiCl [73]	—	Esterification/ xanthation (converts cellulose to soluble derivatives) [74]	Schweizer's reagent, and similar materials like Cd ethylene-diamine [75]
Chitosan	Dilute organic and inorganic acids [76]	Alkali + urea [77]	Imidazolium- [78], pyridinium- [68], ammonium- [79], and amino acid-based [80] ILs	Choline chloride-, betaine-, ammonium Salt-, and organic acid-based DES [81]	—	Mild oxidative depolymerization	Quaternization [82], car-boxymethylation [83]	Enzymatic solubilization [84]
Keratin	Concentrated organic acids such as formic acid [85]	Alkaline + reducer [86]	Imidazolium- [87], cholinium- [61], protic-based [88], and others [89, 90]	Choline chloride-based DES [91]	Polar organic co-solvents (see acidic)	Reductive (e.g., thiols in urea/SDS(sodium dodecyl sulfate)) [92], sulfitolysis, and oxidative (performic acid) [91]	—	Shindai [92] and enzymatic [93] methods
Collagen	Mild acidic solutions [94]	Alkaline + heat [95, 96]	Imidazolium- and cholinium-based ILs [97, 98]	Choline chloride-based DES (with urea, lactic acid, or glycerol) [99], urea–lactic acid or citric acid–xylitol [100]	Soluble in hexafluoro-2-propanol [101], 2,2,2-trifluoroethanol [102] or in ethanol–, glycerol– or dimethyl sulfoxide– as co-solvents in water [103]	—	Chemical derivatizations like succinylated collagen (introduction of carboxyls) [104]	Enzymatic methods like Pepsin-solubilized collagen [105]
Lignin	Organic acids, e.g., levulinic acid [106]	Alkaline + heat [107]	Imidazolium-, pyridinium- [108], tetraalkyl ammonium- and tetraalkyl-phosphonium- [109], and Protic- [110] based ILs	Choline chloride- [111], amino acid- [112], benzyltriethylammonium chloride- [113] based DES, ternary DESs with acidic or aromatic components [114]	Partially soluble in DMSO (dimethyl sulfoxide), ethanol with water or acid, formic acid, and acetone [115, 116]	Oxidative dissolution, e.g., by acetic acid and hydrogen peroxide mixture [117]	Sulfonation [107], alkoxylation (ethylene oxide propoxylation) [115]	—

TABLE 3 | Examples of common cross-linking agents used in biopolymers to enhance stability and functionality.

Group	Example	Structure	Refs.
Aldehyde-based	Glutaraldehyde		[120]
Natural cross-linkers	Genipin		[121]
Epoxy-based cross-linkers	Epichlorohydrin		[122]
	EGDE (Ethylene glycol diglycidyl ether)		[123]
Carbodiimides	EDC (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide)		[124]
Vinyl-based cross-linkers	PEGDA (polyethylene glycol diacrylate)		[125]
	Acrylonitrile		[126]
Ionic cross-linkers	Tripolyphosphate		[127]

ions. Zhao et al. [131], for example, cross-linked chitosan with cystamine, a disulfide-bearing molecule, and obtained a composite that adsorbed $[AuCl_4]^-$ at an impressive 478 mg g^{-1}. This uptake, driven chiefly by chelation and supplemented by ion-exchange interactions, demonstrates how multifunctional cross-linkers can endow biopolymer adsorbents with both mechanical robustness and metal specificity (Figure 6).

3.3 | Introduction of Charged and Reactive Functional Groups

The strategies outlined in Sections 3.3 and 3.4 for introducing specific or non-specific functional groups into bio-based polymers are well-founded, as biopolymers possess abundant reactive sites whose efficiency and selectivity can be refined through targeted functionalization.

Functional groups such as carboxylates (—COOH), sulfonates (—SO_3H), phosphonates (—PO_3H_2), amines (—NH_2), thiols (—SH), and hydroxyls (—OH) impart unique chemical properties that enable diverse modes of metal ion binding, including electrostatic interactions, coordination bonds, chelation, hydrogen bonding, redox interactions, and π interactions, depending on the specific chemistry of the metal ion and functional group [132–134]. This section details the functionalization of biopolymers with such groups, exploring their chemical modification and impact on metal binding. Additionally, a literature overview, drawn from Scopus data, analyzes the prevalence of functionalization methods applied to biopolymers, identifying key trends and dominant strategies in the field, as illustrated in Figure 7.

The introduction of these groups into biopolymers can be achieved either directly on the biopolymer, on the dissolved biopolymer (Section 3.1), or through a two-step process, depending on the availability of reactive sites within the material. In materials with limited reactive sites, such as cellulose, preliminary functionalization is critical for creating a foundation to support further chemical modifications. Commonly, this step involves oxidation reactions to introduce hydroxyl or aldehyde groups, which serve as highly reactive intermediates [135]. Newly formed hydroxyl groups, for example, can undergo esterification to incorporate additional functionalities or be further oxidized to carboxylic acids, thereby enhancing the substrate's reactivity [135, 136]. In cases where the material already possesses adequate reactive groups, or after these groups have been introduced, desired functional groups can be grafted on through standard chemical reactions.

Esterification, which links hydroxyl-rich biopolymers such as cellulose, chitosan, lignin, collagen/gelatin, and alginate with carboxylic acid-containing functional ligands, is a prominent reaction in this context. This reaction forms ester bonds that enhance the mechanical and chemical stability of the material

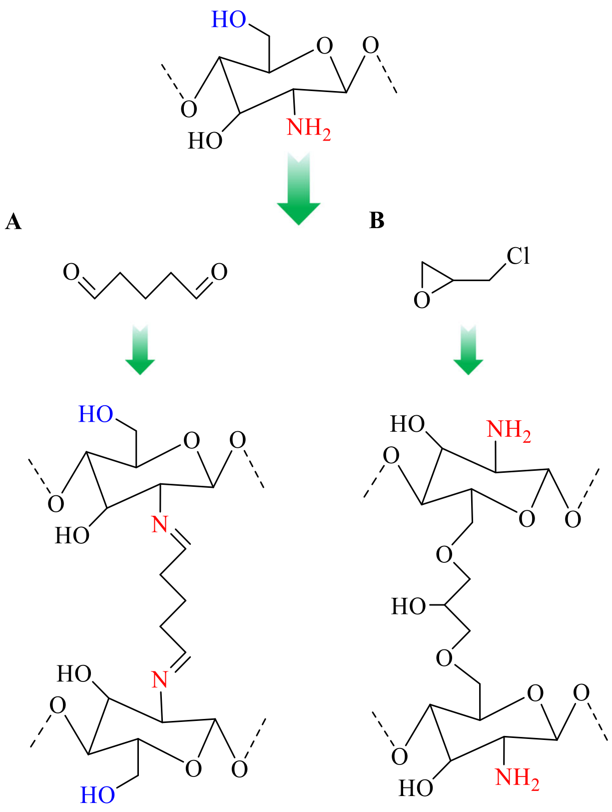


FIGURE 5 | Chitosan cross-linking scheme with (A) glutaraldehyde and (B) epichlorohydrin adapted from Filipkowska and Jóźwiak [128].

while introducing new coordination sites for metal binding (Reaction 1) [137].

$$R_1 - OH + R_2 - COOH \rightarrow R_1 - (CO) - O - R_2 + H_2O \quad (1)$$

Esterification of cellulose or chitosan with phosphonate or thiol-containing compounds, for example, has been shown to enhance their adsorption performance toward multivalent metals, enabling efficient removal and recovery from wastewater [138]. Moreover, introducing carboxylic acid groups to cellulose via esterification with octenyl succinic anhydride has been shown to enhance its affinity for Cu^{2+} ions [139]. Similarly, Li et al. [140] modified spent grain, a lignocellulosic biopolymer, with citric acid, improving its adsorption capacity for Pb^{2+}, Cd^{2+}, and Zn^{2+}.

As shown in Figure 7, esterification is the most widely employed biopolymer functionalization technique, with cellulose being the primary target (Figure 7C). This is due to the abundance of cellulose and its plentiful hydroxyls, allowing straightforward synthesis of cellulose esters and making it the widely studied candidate for esterification [141]. Furthermore, native cellulose is water-insoluble; converting it into esters can tailor key properties such as solubility and thermoplasticity, thus enabling a broad range of applications [141]. By contrast, other biopolymers have fewer or less-accessible hydroxyls and often different primary functional groups, making direct esterification less prevalent (Figure 7C). In proteins like collagen and keratin, there is also a risk of structural disruption if esterified, so they are more often cross-linked or amidated rather than esterified.

Grafting is the second most prevalent method, notably applied to cellulose and chitosan due to their numerous reactive sites and robust backbones for hybrid materials (Figure 7). It involves the covalent attachment of large polymer chains or networks, such as polyacrylic acid, onto bio-based backbones to create synthetic–biological hybrid materials [142]. This process can be achieved through various mechanisms, such as grafting-to, where pre-synthesized polymers are covalently bound to the material; grafting-from, where polymer chains are grown directly from the surface via polymerization; or grafting-through, where polymerizable units on the bio-based material are incorporated into a copolymerization reaction (Reactions 2–4) [143–145]. These hybrids combine the structural advantages of natural materials, such as biocompatibility and biodegradability, with the functional versatility of synthetic polymers, enabling the creation of a robust matrix with enhanced chelating capacity and mechanical properties [146, 147]. Free-radical or chemical initiators generate active sites on these biopolymers, enabling vinyl monomers or other polymers to branch off. Cellulose is especially attractive for grafting (Figure 7E) due to its abundance, high molecular weight, thermal stability, and multiple —OH groups [148], often yielding improved water absorbency or ion-exchange capacity while preserving mechanical integrity [149]. Likewise, chitosan's —NH_2 and —OH functionalities facilitate radical formation and easy chemical modification [83, 150]. Other biopolymers are grafted less often due to structural complexity and vulnerability to denaturation, thus making blending, cross-linking, or simpler modifications more practical.

Grafting to

$$R_1 - X + R_2 - Y R_1 - Y - R_2 \quad (2)$$

Grafting from

$$R_1 - \text{initiator} + \text{Monomer} \xrightarrow{Polymerization} R_1 - \text{polymerchain} \quad (3)$$

Grafting through

$$R - \text{polymerizableunit} + \text{Monomer} \xrightarrow{Copolymerization} R - \text{Copolymerchain} \quad (4)$$

Different studies performed grafting for the improvement of the metal interaction potential of biopolymers. For example, grafting poly(acrylic acid) onto cellulose enhanced its metal ion sorption capacity and mechanical stability, making it suitable for water purification and heavy metal recovery applications as shown by Kumar et al. [147]. In another study, Zhou et al. [151] conducted grafting to by copolymerizing acrylic acid onto a chitosan–cellulose hybrid using ammonium persulfate as an initiator, resulting in a superabsorbent graft copolymer with highly available carboxyl and amino groups and enhanced Ca^{2+}, Mg^{2+}, and Na^{+} ion removal efficiency for water softening applications.

Etherification is often employed to modify polysaccharides such as dextran [152] and carrageenan [153] by attaching alkyl or aryl groups through alkylation reactions (Reaction 5). Etherification

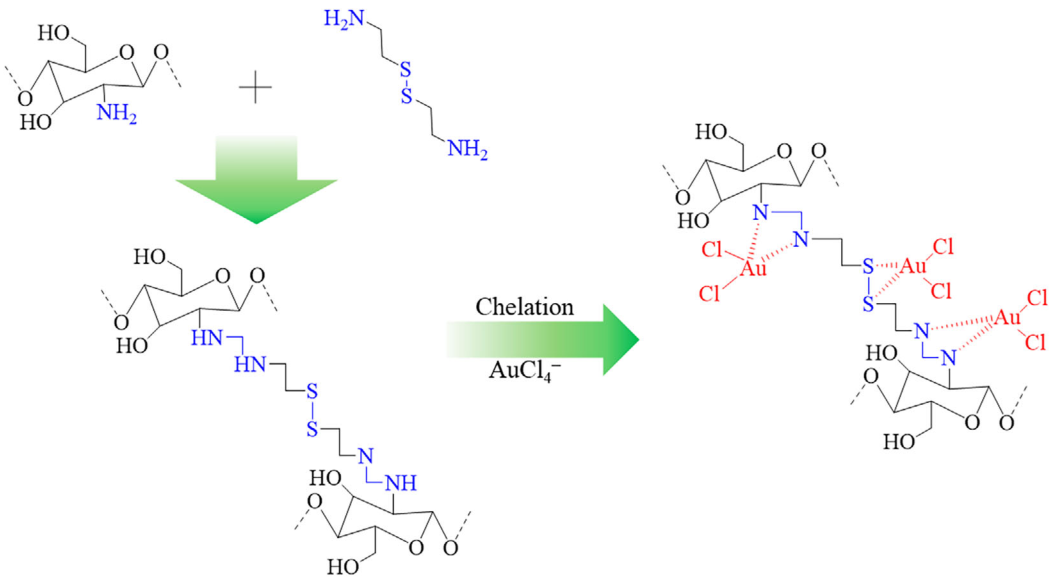


FIGURE 6 | Adsorption of $[AuCl_4]^-$ by chitosan cross-linked with cystamine composites adapted from Zhao et al. [131].

not only improves the chelating properties of biopolymers but also contributes to their structural integrity, ensuring durability in challenging environments such as acidic or alkaline solutions [154].

$$R_1 - OH + R_2 - OH \rightarrow R_1 - O - R_2 + H_2O \quad (5)$$

For chitosan, etherification has been studied more extensively (Figure 7F) because the native polymer has limited solubility and restricted reactivity. A widely explored route is carboxymethylation, typically achieved by reacting chitosan with chloroacetic acid to form O-carboxymethyl chitosan (and some N-carboxymethylation) [83]. This derivative is amphoteric and contains carboxylate groups that substantially increase water solubility over a broad pH range while also improving hydrophilicity and flexibility [83]. This enables applications in pharmaceuticals and environmental fields where pristine (unmodified) chitosan was unsuitable. In a study by Li et al., a carboxymethyl-inulin-modified chitosan (CMI-CS) adsorbent was synthesized through a three-step alkalization–etherification of inulin. The CMI-CS displayed a good Cu^{2+} uptake capacity (~49 mg g^{-1}), while retaining >80% removal efficiency across pH 3.5–6, revealing the efficiency of etherification in creating robust, bio-based adsorbents for wastewater treatment. Other biopolymers are less commonly etherified; lignin methylation is more niche, and alginate or proteins typically focus on different modifications.

Amidation is also a widely used reaction for introducing nitrogen-containing groups into bio-based materials. It is a process where the amine group of one molecule bonds to the carboxylic acid group of another, forming a stable amide bond (Reaction 6) [155, 156]. Amidation is particularly effective for grafting functional ligands, such as ethylenediamine or polyethyleneimine, which provide high-affinity binding sites for metal ions [157]. By enhancing the stability of the material and improving its metal adsorption capacity, amidation has become a preferred method in applications targeting heavy metals and precious metal recovery [157].

$$R_1 - COOH + NH_2 - R_2 \rightarrow R_1 - CONH - R_2 + H_2O \quad (6)$$

Amidation is a key technique for functionalizing biopolymers, particularly cellulose and chitosan, by forming stable amide bonds between carboxyl and amine groups (Figure 7). Chitosan, with its natural amine groups, is easily modified through amidation, attaching small molecules or polymers to create stable conjugates resistant to hydrolysis [158]. This process also allows cross-linking of chitosan with dicarboxylic acids, forming hydrogels with adjustable properties [83]. Cellulose, lacking amine or carboxyl groups, requires activation, typically via oxidation (e.g., TEMPO oxidation) to introduce carboxyl groups, especially in nano-forms like cellulose nanocrystals (CNC) [159]. These carboxylated celluloses can then be amidated with amines to graft functional moieties, enhancing their utility under mild conditions like EDC-mediated coupling, which preserves cellulose's structure [159]. While amidation is widely applied to cellulose and chitosan, it is less common for other biopolymers like alginate, collagen, lignin, and keratin (Figure 7B).

As a representative amidation case, Zhou et al. [160] repeatedly amidated methyl-acrylate-activated cellulose nanofibrils with ethylenediamine, growing poly(amidoamine) dendrimers on the surface. The resulting material showed high adsorption capacity for Cr^{6+} and even reduced part of it to Cr^{3+}. Zhu et al. [161] functionalized bis-carboxylated chitosan cryogels with L-proline using TCFH/NMI-mediated amidation. The product exhibited strong selectivity and high U^{6+} uptake (~463 mg g^{-1}), maintaining over 80% efficiency after multiple reuse cycles.

Sulfonation (Reaction 7) and phosphorylation (Reaction 8) reactions introduce sulfonate ($—SO_3^-$) and phosphate ($—PO_3^{2-}$) groups, respectively, which are highly effective in binding divalent and trivalent metal ions [162, 163]. These reactions are typically carried out using chlorosulfonic acid, sulfur trioxide, or phosphorylating agents like phosphoric acid derivatives [164]. These negatively charged functional groups enhance the

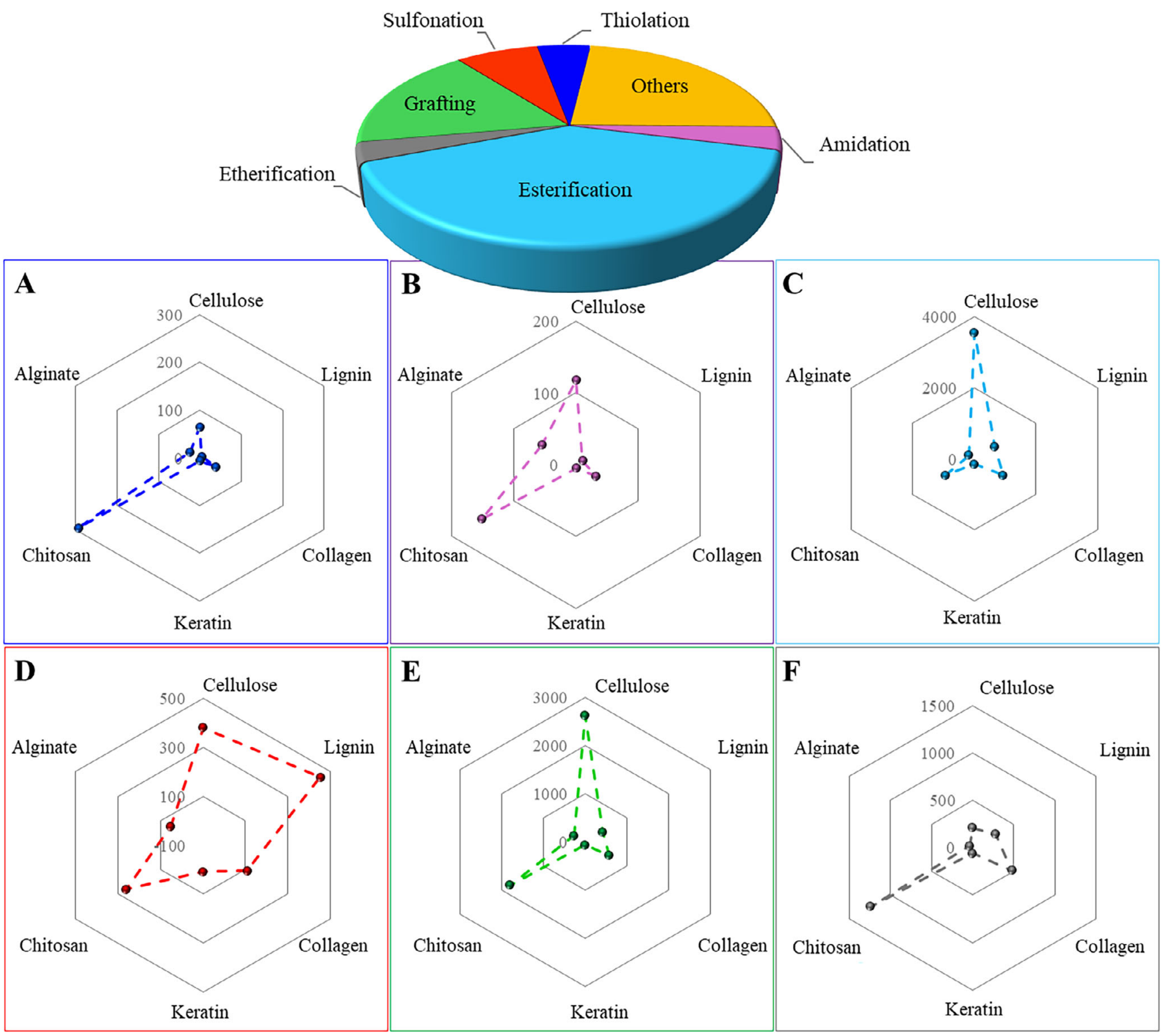


FIGURE 7 | Distribution of published works on biopolymer functionalization methods across general polymer applications between 1990 and 2024. The pie graph illustrates the prevalence of different functionalization methods applied to biopolymers. Radar plots represent the distribution of published articles for each functionalization method: (A) thiolation; (B) amidation; (C) esterification; (D) sulfonation; (E) grafting; (F) etherification, across various biopolymers (cellulose, lignin, collagen, keratin, chitosan, and alginate). (Source: Scopus, accessed October 2025).

material's affinity for metals like Cd^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, Fe^{3+}, and Al^{3+}, making them highly effective candidates for environmental remediation [13, 165, 166].

$$R - OH + SO_3 \rightarrow R - SO_3H \tag{7}$$

$$R - OH + H_3PO_4 \rightarrow R - OPO_3H_2 \tag{8}$$

Sulfonation spans lignin, cellulose, chitosan, collagen, keratin, and alginate, with particular emphasis on lignin, cellulose, chitosan, and collagen (Figure 7D). The versatility of sulfonation comes from the fact that many biopolymers have sites that can be sulfated or sulfonated (e.g., —OH or —NH groups), and introducing sulfonic acid groups often dramatically changes polymer properties in useful ways. A primary motive is to increase water solubility and charge. For example, lignin, becomes water-soluble after sulfonation; lignosulfonates carry sulfonate anions that make them useful as dispersants, binders, and emulsifiers [167]. Indeed, sulfonation is the most effective way to improve the water solubility of alkali lignin and thus broaden its applications [167]. Sulfated cellulose gains strong electronegativity, good solution stability, and film-forming ability with various applications [168]. Sulfonated chitosan becomes amphoteric or anionic, improving solubility at neutral pH and conferring ionic conductivity [169]. Keratin can undergo S-sulfonation (breaking disulfide bonds and adding $—SO_3H$) for improved solubility, while alginate sulfation increases negative charge density, useful for heparin-mimicking applications [170, 171].

In a study, Dong et al. [165] sulfonated microcrystalline cellulose with an SO_3–pyridine complex. The obtained material revealed fast metal adsorption kinetics and preferentially captured $Fe^{3+} > Pb^{2+} > Cu^{2+}$ mainly by its $—SO_3^-$ groups. Similarly, Hamza et al. [172] reacted cellulose with sulfamic acid and produced aerogel spheres with dense $—SO_3H$ groups, which showed high adsorption potential for Pb^{2+} and also methylene blue. Sulfonation of other biopolymers for metal recovery applications was also studied. For example, glutaraldehyde-cross-linked chitosan was converted into sulfo-chitosan with an in situ $NaNO_2/NaHSO_4$ sulfating reagent. The Li^+ uptake of the sulfonated chitosan jumped from 34 to 138 mg g^{-1}, and the sorbent retained >90% efficiency through eighteen acid regeneration cycles when recovering Li from spent battery leachate.

Phosphorylation, though less common than other methods like sulfonation, enhances metal-binding capacity, bioactivity, and ionic interactions, making it particularly useful in biomedical applications, metal recovery, and flame-retardant materials [173, 174]. Phosphorylation was applied to cellulose, chitosan, keratin, and silk, often to improve their chelation properties and affinity for metal ions. However, its broader application is limited due to the complexity of the reaction and the lower availability of phosphorylating agents compared to sulfonation. An example of effective phosphorylation is the study by Zhao et al. [175], where they synthesized a phosphorylated chitosan–lignin composite using phosphorus pentoxide in methanesulfonic acid. The introduced phosphate groups enhanced material's affinity for Pb^{2+} and Cu^{2+}, achieving maximum adsorption capacities of 207.9 mg g^{-1} and 100.0 mg g^{-1}, respectively.

Thiolation reactions are essential for introducing sulfur-containing groups, which have a high affinity for precious metals such as Pd, Pt, and Au [176]. This reaction is typically achieved using thiolating agents (like thioglycolic acid, isothiocyanates) or by reducing disulfide bonds to generate free thiol (—SH) groups (Reaction 9) [177, 178]. The resulting materials exhibit exceptional selectivity and stability, minimizing metal leaching during recovery processes, and making thiolated biopolymers particularly suited for precious metal recovery from acidic leachates due to strong metal–sulfur interactions [176].

$$\begin{aligned} &\mathrm{R\,(-OH, - COOH, - NH_2 etc.)} \\ &\quad + \mathrm{thiolationagentn} \rightarrow \mathrm{R - S - H + byproducts} \end{aligned} \tag{9}$$

Chitosan is the main focus of thiolation, thanks to its reactive amine and hydroxyl groups and the clear benefits these modifications provide for chitosan's applications (Figure 7A). Thiolation of chitosan is often done by coupling cysteine or 3-mercaptopropionic acid to chitosan's amine [179] to exploit the unique chemistry of thiols, which can form disulfide bonds. Thiolated chitosan can also undergo self-cross-linking (disulfide formation) to form gels in situ, useful for controlled release [180]. Moreover, thiol groups can chelate certain metals and act as antioxidants, opening other applications [181]. Yong et al. [182] immersed chitosan beads in ethanol/CS_2 for extended thiolation yields, $—CS_2^-$ motifs and —S—S— cross-links, boosting Cd^{2+} uptake (q_{max} ~243 mg g^{-1}) and giving acid-stable beads suitable for flow reactors. Song et al. [183] thiolated chitosan with L-cysteine, quaternized it, and anchored Fe_3O_4 nanoparticles (NPs) to create a magnetic thiolated/quaternized-chitosan composite with efficient adsorption potential at pH 7 for Pb^{2+} and also As^{5+}, As^{3+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, and Zn^{2+}. Few other biopolymers have seen as much focus on thiolation. Xu et al. [184], for example, directly thiolated cellulose in a DBU/DMSO/CO_2 medium with methyl 3-mercaptopropionate, introducing thiol and disulfide groups, resulting in cellulose ester that anchored Au^{3+} (up to 415 mg g^{-1}) selectively over competing metal ions like Ni^{2+}, Pt^{3+}, and Pd^{2+} with reusability potential for five cycles.

Although numerous functionalization strategies were reported, their performance differs substantially depending on the dominant metal–ligand interaction mechanism and the chemical environment. Electrostatically driven modifications, such as sulfonation and phosphorylation, enhance uptake of hard divalent and trivalent cations under mildly acidic to neutral conditions, yet they rarely provide true selectivity in multi-metal systems, as binding is primarily charge driven. Grafting and amidation increase ligand density and structural stability, particularly for cellulose and chitosan backbones, but their effectiveness is often limited by restricted accessibility of functional sites due to steric hindrance or excessive cross-linking. As a result, reported high adsorption capacities do not always translate to improved performance under dynamic or competitive conditions. In contrast, thiolation provides superior affinity toward soft and noble metals through strong inner-sphere metal–sulfur coordination, maintaining effectiveness even in acidic chloride media where metals exist as stable chloro-complexes. However, susceptibility of thiol groups to oxidation may compromise long-term stability. Achieving true discrimination among chemically similar ions, especially in complex hydrometallurgical leachates, requires the deliberate incorporation of metal-specific coordination environments. The next section will explore how these ligands can be integrated into biopolymer matrices to improve selectivity and binding affinity for targeted metal ions.

3.4 | Metal-Specific Ligand Incorporation

High selectivity in metal-ion binding rests on the strategic choice and incorporation of ligands into biopolymer matrices (Table 4). Ligand-based approaches mainly rely on inner-sphere coordination governed by hard–soft acid–base (HSAB) principles, ligand geometry, and donor atom identity, enabling discrimination between chemically similar metal ions. Such ligands are typically introduced through the chemical functionalization strategies outlined in section 3.3.

Among various methods, one widely adopted tactic involves using polyaminocarboxylate ligands, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA), which are highly effective for divalent and trivalent metal-ion chelation. Sultana et al. [202] demonstrated that incorporating EDTA into cellulose enables it to serve as a cross-linking agent while providing selective, robust chelation of divalent heavy metal ions (Figure 8). Similarly, DTPA, with additional carboxylate groups, excels at binding trivalent ions like Nd^{3+} and Eu^{3+} [203]. These ligands can be covalently linked to biopolymers via esterification or amidation, enabling tailored metal selectivity (Figure 8). These studies employed spectroscopic techniques, such as FTIR and solid-state ^{13}C NMR, to confirm the successful grafting of polyaminocarboxylate functionalities onto

TABLE 4 | Metal classes, HSAB-based donor preferences, and representative intrinsically selective ligands used in biopolymer-based metal separation.

Metal class/Representatives	HSAB/donor preference	Representative selective ligands	Refs.
Precious metals (e.g., Pd^{2+}, Pt^{2+}, Au^{3+})	Soft acid–soft base coordination Redox-assisted binding	Thiols, disulfides, thioamides, mercaptobenzimidazole, phosphines, porphyrins	[51, 185–188]
REEs (e.g., Nd^{3+}, Dy^{3+}, Eu^{3+})	Hard acid coordination Size and geometry discrimination	Lanmodulin, diglycolamide ligands, macrocyclic polyaminocarboxylates	[189–192]
Toxic heavy metals (e.g., Pb^{2+}, Cd^{2+}, Hg^{2+})	Soft/borderline metal affinity Biomimetic sequestration	Metallothioneins, phytochelatins, cysteine-rich peptides, thiol-rich ligands	[193–196]
Transition/base metals (e.g., Cu^{2+}, Ni^{2+}, Co^{2+})	Geometry-controlled coordination Borderline HSAB behavior	Salen-type ligands, cyclams, terpyridines	[197–199]
Alkali metals (e.g., K^+, Na^+, Ca^{2+})	Size-fit host–guest recognition	Crown ethers (e.g., 18-crown-6), calixarenes	[200, 201]

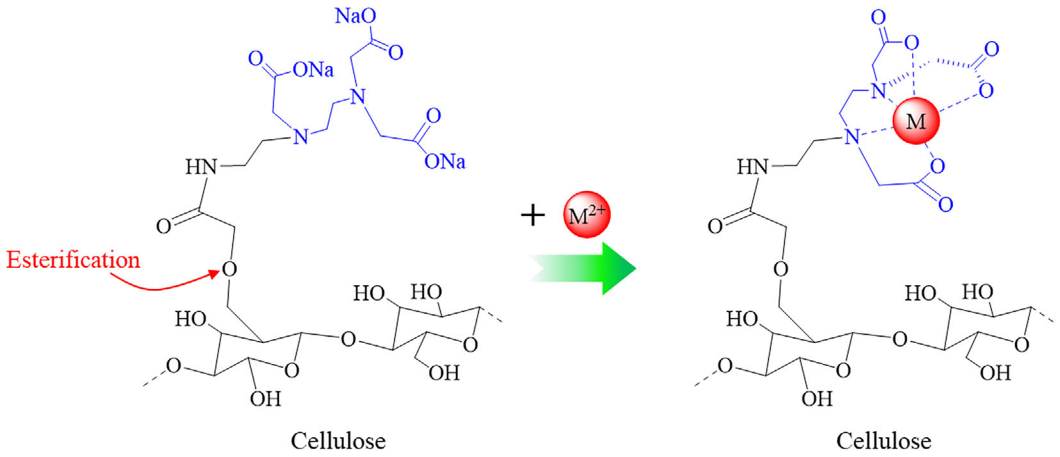


FIGURE 8 | Incorporation of Na-EDTA ligand onto cellulose structure for chelation of divalent metal ions, adapted from Hu et al. [204].

cellulose backbones [204]. In addition, shifts in FTIR vibrational bands associated with carboxylate and amide groups after metal adsorption indicate coordination through oxygen- and nitrogen-donor sites of the immobilized ligands [203, 204]. Such spectral changes, together with the strong pH dependence of metal uptake, are consistent with the formation of multidentate metal–ligand complexes, where amino-carboxylate groups coordinate metal ions through inner-sphere chelation analogous to EDTA-type complexes [204]. Combined with adsorption studies such as pH-dependent experiments and isotherm analysis, these observations support a chelation mechanism consistent with EDTA-like amino-carboxylate groups.

Moreover, peptides are enriched in amino acids that confer strong binding properties. Notably, histidine-rich peptides, boasting imidazole side chains, can be covalently attached to polysaccharides like cellulose or chitosan [205]. The imidazole rings of histidine serve as the primary binding sites, coordinating with transition metals through lone-pair donation from nitrogen atoms, forming stable metal–ligand complexes [205–207]. Additionally, the amino ($-NH_2$) groups of histidine may also participate in metal binding, particularly under conditions where these groups are protonated or deprotonated, creating bidentate or tridentate coordination environments. These coordination mechanisms make histidine-functionalized biopolymers effective metal adsorbents. In industrial wastewater treatment, for instance, histidine-modified chitosan beads have demonstrated the ability to reduce heavy metal concentrations to parts-per-billion levels, revealing their efficacy in metal removal [205, 208].

Different classes of proteins selectively bind metal ions, playing key roles in biological processes. Phytochelatins, small cysteine-rich peptides, chelate and sequester toxic metals in plants, especially at higher levels in hyperaccumulators [209]. Previous studies have shown that synthetic phytochelatin–cellulose constructs enable efficient and reusable Cd^{2+} removal in column systems [193], while more recent phytochelatin–inspired copolymers grafted onto silica or cellulose achieve ultrahigh Cd^{2+} affinity and drinking–water–level removal in flow systems [194]. Metallothioneins (MTs), another key protein class, use cysteine-rich domains to form stable metal–thiolate clusters, a critical pathway for metal homeostasis and detoxification in living cells [210]. MTs bind metals through cysteine thiolate clusters, while histidine and acidic residues in bacterial MTs enable binding to harder ions such as U^{6+} [195, 211]. In these studies [195, 211], the coordination environment and U–MT interactions were investigated using spectroscopic techniques including NMR, XPS, UV–visible spectroscopy, and mass spectrometry. These analyses indicate that uranium binding involves a heterogeneous donor environment within the protein, with contributions from cysteine, histidine, and acidic residues. In contrast to the classical thiolate cluster formation observed for softer metal ions, U(VI) binding is largely associated with coordination to O-donor groups such as carboxylate side chains, consistent with the hard Lewis acid character of the uranyl ion (UO_2^{2+}). This suggests that MTs accommodate uranium through a mixed donor coordination environment rather than the canonical metal–thiolate cluster typical of Cd^{2+} or Zn^{2+} binding. MTs affinity for soft and borderline cations follows Cd > Pb > Cu > Hg > Zn ≈ Ag >> Ni > Co, with negligible binding to Mn, Mg, Al, Tl, Cr, V, and Fe [212, 213]. Immobilization on biopolymers enhances MT stability, selectivity, and reusability; for example, a crab MT fused to a cellulose-binding module removed >99% Cd^{2+} with high capacity, rapid kinetics, and at least six reuse cycles, while favoring Cd^{2+} over other divalent metals [214]. Similar cellulose-anchored MT constructs have also been reported for Pb^{2+} and Zn^{2+} [196]. Another notable protein in this context is Lanmodulin (LanM), a highly stable lanthanide-binding protein from bacteria with lanthanide-dependent metabolism. LanM undergoes large conformational rearrangements upon rare earth element (REE) binding and displays picomolar affinity, with strong preference to light REEs (La^{3+}–Sm^{3+}) over heavier ones [189, 190]. Covalent grafting of LanM onto polysaccharides such as agarose via thiol–maleimide coupling yields robust, reusable supports [189]. In a study, Dong et al. [215] immobilized LanM on agarose to create an all-aqueous, solvent-free REE recovery platform that binds at low pH, separates Nd/Dy and Y/Nd to high purity, partitions light REEs from heavy REEs. The binding mechanism and selectivity of REEs toward LanM-based materials have been elucidated through complementary spectroscopic, structural, and thermodynamic studies. Circular dichroism and fluorescence measurements revealed REE-dependent conformational responses, whereas SEC–MALS, SAXS, and isothermal titration calorimetry showed that Hans-LanM undergoes metal-sensitive monomer–dimer equilibria, with light REEs promoting markedly stronger dimerization than heavier REEs. X-ray crystallography further demonstrated that picometre-scale differences in ionic radius alter the coordination environment and second-sphere hydrogen-bonding network at the metal-binding sites, thereby propagating into distinct quaternary structures and enhanced REE selectivity [190, 215].

Another potent strategy leverages thiol-based ligands, renowned for their strong affinity toward metals that exhibit a preference for soft donor atoms. According to the HSAB principle, soft acids such as Au^{3+}/Au^{+}, Pd^{2+}, Pt^{2+}, Cd^{2+}, and Hg^{2+} preferentially bind to soft bases like thiols (—SH) or disulfides (—S—S—). This enhanced performance with thiol groups arises from the formation of highly stable metal–thiolate or metal–disulfide complexes, which effectively immobilize the metal ions within the biopolymer matrix [216]. Moreover, soft-acid Pd^{2+}/Pt^{2+} bind disulfides via two competing pathways: (i) intact S,S' coordination that yields mono- or binuclear complexes and (ii) redox-driven cleavage to thiolate (± sulfinate) species. Ligand steric, pH, and oxidizing power shift the balance between preservation and rupture of the S—S bond (Figure 9) [51, 217]. Because S—S stretching occurs in the low-frequency IR region, conventional FTIR provides limited information on disulfide coordination. Therefore, the coordination pathways and the fate of the S—S bond in these systems have been elucidated using techniques such as Raman spectroscopy, NMR, UV–visible spectroscopy, and X-ray photoelectron spectroscopy (XPS), together with DFT calculations that evaluate the stability and energetics of the different metal–sulfur coordination modes [51, 216, 217].

Keratin, a cysteine-rich biopolymer, contains abundant disulfide bonds that contribute to its notable mechanical stability and insolubility. These structural features make keratin a promising natural candidate for the highly selective adsorption of soft metal ions, such as Cd^{2+} [218] and Pd^{2+} [219], without the need for additional chemical modification. Moreover, by covalent functionalization of biopolymers with sulfur-containing functionalities into biopolymers such as cellulose, keratin, or chitosan, the resulting materials exhibit enhanced selectivity and binding strength toward soft metal ions. For instance, thiol-functionalized cellulose has shown exceptional sequestration of Hg^{2+} from polluted water over other metals such as Co, Cu, Zn, and Pb [220]. In another study, chitosan was functionalized with 2-mercaptobenzimidazole, introducing soft sulfur and nitrogen donor sites that enabled strong Pd^{2+} coordination, resulting in a highly selective and efficient adsorbent for Pd recovery [185].

Incorporating amine ($—NH_2$) containing chemicals into a biopolymer enhances its ability to selectively separate metal ions based on charge interactions. Under acidic, chloride-rich conditions, protonation of amino groups ($—NH_2 \rightarrow —NH_3^{+}$) facilitates the selective adsorption of negatively charged metal complexes, such as $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$, whereas increasing the pH causes these groups to lose their positive charge and become neutral ($—NH_2$), thereby reducing their affinity for anionic species while promoting the adsorption of positively charged metal ions (Figure 10) [221, 222]. This pH-dependent selectivity is beneficial for the efficient separation and recovery of metals from specific matrices. Figure 10, adapted from studies by Kettum et al. [223] and Mosai and Tutu [224], represents the adsorption of $[PtCl_6]^{2-}$ and Cu^{2+} by protonated and neutral amine groups, respectively. The role of amine groups in metal binding is typically assessed through pH-dependent adsorption behavior together with spectroscopic characterization, particularly FTIR and XPS, which are commonly employed to identify changes in nitrogen functionalities associated with metal coordination [222, 224].

Moreover, crown ethers stand out as a versatile class of ligands for selective metal binding. Crown ethers present specific binding ability, metal complex stability, and high extraction efficiency, which are influenced by various factors, such as the diameter of the cavity and the type of donor atom in the crown ether, as well as the size and charge of the metal ion, the choice of diluents, and the nature of the counter ion [225]. These macrocyclic compounds contain a ring of repeating oxygen donor sites that exhibit a pronounced preference for alkali metal ions, such as Na^{+}, K^{+}, or Li^{+}, based on a size-fit principle [226]. Moreover, crown ethers with sulfur atoms preferentially bind to soft acid metal ions like Hg^{2+} or Pd^{2+} [226]. For instance, Ciopec et al. [227] grafted dibenzo-30-Crown-10 ether on the surface of chitosan and observed a high selectivity and adsorption capacity toward

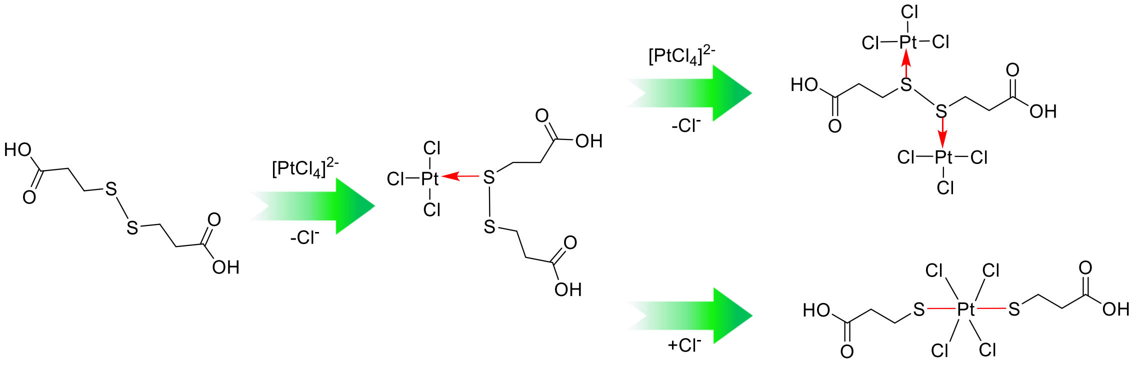


FIGURE 9 | Suggested Pt^{2+} interaction with disulfides from dithiodipropionic acid, adapted from Petrov [51].

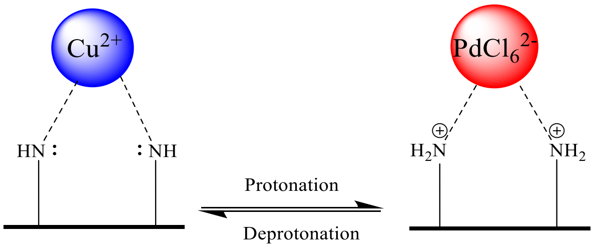


FIGURE 10 | Protonation-state switching of amine sites under basic (left, adapted from Kettum et al. [223]) and acidic (right, from Mosai and Tutu [224]) conditions and its consequent influence on binding with Cu^{2+} and $[PdCl_6]^{2-}$.

Ru^{3+} (Figure 11). Moreover, 18-crown-6 with a cavity size well-matched to the ionic radius of K^+, was stabilized on chitosan and resulted in high selectivity in complex mixtures (Figure 11) [200]. As another example, immobilized and stabilized crown ethers on cellulose have been shown to be selective for the separation and retention of Gd [228].

Likewise, other macrocycles such as porphyrins, cyclens, and calixarenes, which can form precise coordination environments for specific metals, can be integrated into biopolymers, creating effective and selective materials for capturing and separating various metal ions. Hong et al. [229] demonstrated that alkyl-linked porphyrin porous polymers exhibit high selectivity for precious metals, achieving up to 95.6% Au recovery from e-waste leachates, attributed to their well-defined microporosity and strong chelation capabilities. Their multiple donor atoms (e.g., nitrogen and oxygen) can be arranged in specific geometries that favor the binding of particular metals [230].

Taking cues from nature, siderophore-inspired ligands further expand the toolkit for selective metal capture. Hydroxamate or catecholate groups, when introduced onto biopolymers such as alginate or chitosan, chelate Fe^{3+} with exceptionally high affinity, mirroring the function of bacterial siderophores [231]. This biomimetic strategy has been successfully applied to eliminate trace levels of iron in challenging conditions, such as acidic mine drainage, demonstrating how natural chelators can be harnessed to enhance the performance of engineered materials. In a related study, Rahman et al. [232] modified cellulose by grafting methyl acrylate via ceric ammonium nitrate-initiated polymerization, which was then reacted with hydroxylamine to form poly(hydroxamic acid), providing strong chelation sites for efficient heavy metal adsorption.

The effectiveness of metal-specific ligand incorporation cannot be evaluated solely on intrinsic metal–ligand affinity, but must be considered within the coupled chemical environment defined by the biopolymer support, the target metal speciation, and the surrounding matrix. While strong chelators such as polyaminocarboxylates provide high binding constants across a broad range of metal ions, their limited selectivity can become a liability in multi-metallic systems, where competitive binding may suppress discrimination between chemically similar ions. Conversely, soft donor ligands, including thiols and disulfides, outperform oxygen- and nitrogen-based ligands for noble and toxic soft metals. However, their performance is strongly dependent on redox conditions, chloride activity, and ligand stability, which can shift metal speciation or induce ligand degradation. Macrocyclic and protein-based ligands offer superior selectivity through geometric and preorganized coordination environments, yet their effectiveness is often constrained by steric accessibility, immobilization efficiency, and compatibility with the chemical functionality of the biopolymer matrix. Importantly, the native chemistry of the biopolymer itself may compete with or modulate ligand binding, particularly at high ligand loadings or under conditions where protonation, swelling, or matrix–metal interactions dominate. Consequently, ligand selection should be guided not only by HSAB considerations, but by an integrated assessment of metal speciation, competing ions, support chemistry, and process constraints, as ligand-based strategies outperform simpler functionalization routes only when these factors are deliberately aligned.

3.5 | Performance Implications of Chemical Modification

Diverse chemical modification routes, from straightforward derivatization to graft copolymerization, have markedly improved the ability of biopolymers to capture specific metal ions. While increased ligand density often enhances adsorption capacity in single-component systems, true selectivity must be evaluated under competitive multi-metal conditions using selectivity coefficients or separation factors. Table 5 compiles illustrative examples for alginate, cellulose, chitosan, lignin, pectin, and keratin, linking each modification type to its

TABLE 5 | Examples of chemically modified biopolymers, modification types, target metal ions, and the responsible functional groups.

Biopolymer	Modification type	Introduced functional groups/changes	Target metal ions	Effect on adsorption capacity
Alginate	Urea modification (covalent attachment)	Amine groups	Cd^{2+}, Zn^{2+} [234], Hg^{2+} [235], Cr^{6+} [236]	New N-donor sites introduced alongside alginate's O-donors, improving multi-metal adsorption efficiency
	Polyethylenimine (PEI) incorporation (cross-linked composite hydrogel)	Polyamine chains (rich in $-NH_2$ groups)	Cu^{2+}, Pb^{2+} [234], Au^{3+} [237]	The presence of both N and O donor atoms greatly enhances metal binding potential.
	Fe^{3+}, Mg^{2+} ion cross-linking	Metal-loaded porous structure	Cd^{2+}, Pb^{2+} [238], As^{5+} [239]	Hybrid anion-exchanger with remarkably high performance for toxic metal separation.
Cellulose	Grafting with glycidyl methacrylate + polyethyleneimine	Surface-grafted epoxy polymer subsequently aminated with branched polyethyleneimine	Cu^{2+} [240]	Introduced many chelating amine sites
	Oxidation + Schiff-base with L-lysine	Dialdehyde cellulose reacted with L-lysine, adding imine linkages and amine functionality	Hg^{2+} [241]	Generated multiple new binding sites ($-NH$ and $-COO^-$)
	Succinic anhydride modification (carboxylation of nanocellulose)	Added abundant carboxylate groups ($-COO^-$ Na^+) on cellulose nanocrystal surface	Pb^{2+}, Cd^{2+} [242]	Greatly enhanced cation exchange capacity
	Inorganic NPs composite (Cellulose/c)	Loaded cellulose with ZrO_2 NPs (high surface area, polar surface)	Ni^{2+} [243]	ZrO_2 provided additional binding sites mainly as surface hydroxyls
	Maleic anhydride graft (carboxylic derivative)	Introduced polycarboxylic acid groups on cellulose	Hg^{2+} [244]	Carboxyl-rich cellulose with better metal adsorption affinity
Chitosan	Cross-linking with glutaraldehyde (chemical cross-linker)	Formed imine bridges between chitosan chains	Cu^{2+} [245]	Yields acid-stable, insoluble chitosan at low pH
	Graft polymerization with polyacrylonitrile	Grafted linear $-(CH2-CH(CN))-$ chains (nitrile $-C{\equiv}N$ groups) onto chitosan backbone	Cr^{6+} and Cu^{2+} [246]	Significantly enhanced metal adsorption capacity. Nitrile groups can be post-hydrolyzed to amide/carboxylate, aiding metal binding.

(Continues)

TABLE 5 | (Continued)

Biopolymer	Modification type	Introduced functional groups/changes	Target metal ions	Effect on adsorption capacity
Thiourea functionalization (two-step: O-carboxymethylation + Schiff base with thiourea)	Introduced thiourea moieties (—NH—C(=S)—NH_2) on chitosan matrix	Hg^{2+} [247]	Thiourea-modified chitosan showed high affinity for Hg^{2+} due to soft S donor.	
Lignin	Graft copolymerization (lignosulfonate with acrylamide and maleic anhydride)	Introduced amide (—$CONH_2$) and additional carboxyl (—COOH) groups onto sulfonated lignin backbone	Heavy metals [248]	Multiple new S, N, O functional sites created; enhanced polyvalent binding capacity for heavy metal ions
	Amination (functionalized with polyamine)	Added pendant amine groups (—NH_2) to lignin (e.g., via ethylenediamine or polyethylenimine)	Cd^{2+}, Cr^{6+}, As^{5+}, Ni^{2+} [249]	Amino-functional lignin with improved capacity for various metal ions
	Xanthation (CS^2 treatment of alkali lignin)	Introduced trithiocarbonate (—CSS^-) groups analogous to xanthate on lignin	Pb^{2+}, Cu^{2+} [250]	Greatly enhanced "soft" metal binding, confirming —CSS^- groups as effective chelating sites for heavy metals.
	Phenolation using pyrogallol, followed by reaction with tetraethylenepentamine to form polycatecholamine	Phenolic hydroxyl (—OH) from pyrogallol; amine groups (—NH_2, —NH—) from TEPA	Cr^{6+} [251]	Enhanced adsorption (up to 602 mg g^{-1} at pH 2), Cr^{6+} was also partially reduced to Cr^{3+} by phenol groups
Pectin	Ethylenediamine amidation + composite gelation	Amine-functionalized pectin (—NH_2 blended with alginate; embedded Fe_3O_4 NPs	Pb^{2+} [252]	The EDA-modified pectin/alginate matrix has improved chelation (due to added —NH_2)
Keratin	Grafting with 4-nitroaniline, followed by reduction to aromatic amine, and Schiff base formation using benzaldehyde derivatives	Aromatic imine groups (—C=N—), plus electron-donating groups (—OH, —OCH_3, —NH_2) depending on benzaldehyde used	Pb^{2+}, Cu^{2+} [253]	Schiff base modification improved chelation and affinity via enhanced electron density around imine nitrogen
	Functionalization with graphene oxide	Enhanced surface area and oxygen-containing functional groups from graphene oxide	Pb^{2+}, Cd^{2+} [254]	increased active sites and synergistic effects between keratin and graphene oxide

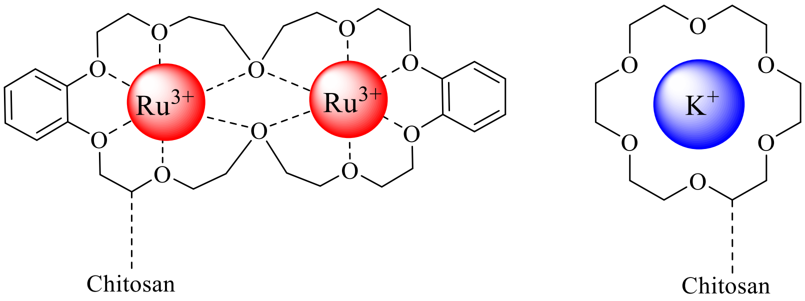


FIGURE 11 | Recovery of Ru and K using dibenzo-30-Crown-10 (left, adapted from Ciopec et al. [227]) and 18-crown-6 (right, from Gromov et al. [200]) doped chitosan.

preferred metal targets and the functional groups responsible for the observed gains.

In practice, adsorption behavior in modified biopolymers can be interpreted through three main uptake regimes linking structure to performance. Inner-sphere coordination or chelation, provided by donor atoms such as N, O, or S introduced through functionalization, typically governs metal selectivity by forming direct coordination bonds with compatible ions, often rationalized through HSAB considerations. Outer-sphere electrostatic interactions or anion exchange dominate when surface groups are protonated, where adsorption is driven by charge attraction and therefore strongly depends on pH and background ionic composition. Finally, transport- and accessibility-limited uptake occurs when pore structure, cross-link density, or semi-crystallinity restricts diffusion to internal binding sites, resulting in lower effective capacity or slower kinetics despite high theoretical ligand density. Together, these regimes illustrate how coordination chemistry, surface charge, and structural accessibility collectively determine adsorption performance.

Research has progressed from simply multiplying reactive sites to deliberately tailoring surface chemistry for particular coordination motifs. Guided largely by HSAB considerations [233], current work favors N-, S-, and O-containing groups capable of discriminating between competing ions. However, the dominant interaction pathway is also strongly influenced by the protonation state of the material. For instance, in N-donor biopolymers such as chitosan, the protonation state of amine groups determines whether the material behaves primarily as a chelating ligand or as an anion exchanger. In addition, hydrometallurgical chloride media shift many target metals into stable anionic chloro-complexes (e.g., $PdCl_4^{2-}$), altering the basis of selectivity and favoring adsorption on positively charged surfaces through electrostatic attraction or on donor groups capable of competing with chloride via inner-sphere coordination. Even so, perfect selectivity in multicomponent or extreme-pH environments remains elusive. Cross-linking and hybridization help improve mechanical and chemical resilience, although sometimes at the expense of adsorption kinetics or processability.

While chemical functionalization enables high selectivity and tunable coordination environments, it often introduces additional economic and environmental burdens associated with ligand synthesis, coupling reagents, solvent use, and post-treatment steps. These costs must be weighed against performance gains, particularly when simpler strategies based on native functional groups or minimally modified biopolymers already achieve sufficient selectivity under process-relevant conditions.

In practice, the effectiveness of introduced functional groups depends on key surface chemistry descriptors. The surface charge state, commonly expressed by the point of zero charge (PZC), governs electrostatic interactions, with adsorption of cationic species generally favored above PZC and anionic species favored below it. Moreover, effective adsorption depends on site accessibility rather than total ligand density, and can be strongly influenced by ionic competition in complex solutions, where background ions such as chloride may suppress charge-driven uptake.

Recent studies integrate chemical functionalization with hierarchical design, such as embedding functionalized NPs in polymer matrices or forming stimuli-responsive hydrogels, to combine high binding affinity with facile regeneration and process compatibility. These advances underline a key insight: adsorption efficiency is governed not only by chemistry but also by architecture. The accessibility of active sites, diffusion pathways, and bulk durability are all determined by the material's physical structure. Accordingly, the field is moving toward integrated strategies where chemical and structural engineering act in concert. The next sections, therefore, turn to physical and morphological treatments, like particle-size reduction, porosity control, film and fiber fabrication, that unlock the full potential of the chemically modified biopolymers described above.

4 | Physical and Structural Treatments

Beyond chemical functionalization, physical and structural strategies offer powerful tools to tune the metal-binding performance of bio-based materials. These methods typically modify surface chemistry, topography, and porosity, affecting parameters like functional group accessibility, diffusion rates, and adsorption kinetics. The main categories include surface functionalization (via plasma, ultraviolet/ozone, or irradiation), surface area enhancement, and film-based assembly techniques.

4.1 | Surface Functionalization by Physicochemical Treatments

4.1.1 | Physical Adsorption of Metal Extractants

Physical adsorption of extractants onto biopolymers enhances metal-binding performance through non-covalent interactions like van der Waals forces, hydrogen bonding, and electrostatic attractions, offering a simple and reversible alternative to chemical modification [255]. Biopolymers such as cellulose, chitosan, and lignin, with abundant hydroxyl, amine, or carboxyl groups, serve as ideal substrates, stabilizing extractants like chelating agents (e.g., crown ethers, phosphonates) or nanostructured materials (e.g., NPs, MOFs) [256]. Chitosan's amine groups, for example, have been shown to anchor imidazolium-based ILs via hydrogen bonding, enabling selective uptake of Cr^{6+}, with a remarkable uptake capacity of ~125 mg g^{-1} [257].

Nanostructured extractants further boost performance. MOFs adsorbed onto cellulose nanofibers selectively capture REEs [258], while iron oxide NPs on chitin enhance heavy metal removal and enable magnetic recovery [259]. Techniques like dip-coating or immersion facilitate extractant loading, though parameters like pH and contact time must be optimized to prevent leaching [256]. Applications include wastewater treatment and precious metal recovery [260], but challenges like extractant stability under harsh conditions (e.g., extreme pH) require strategies such as porous biopolymer designs or protective coatings. Despite its simplicity, physical adsorption of metal extractants onto biopolymer matrices is inherently less robust than covalent chemical modification, as weak non-covalent interactions can result in extractant leaching under the acidic, high-ionic-strength, or prolonged operating conditions typical of hydrometallurgical processes. In contrast, chemically grafted extractants offer greater stability and reusability but require more complex synthesis, making physical adsorption more suitable for mild or short-term applications.

4.1.2 | Plasma Treatment

Plasma treatment is a well-established technique for modifying the surface properties of polymers without affecting their bulk characteristics. In the context of biopolymers, low-temperature plasmas (e.g., radio-frequency or dielectric barrier discharge) can introduce an array of functional groups, such as hydroxyl, carboxyl, amino, or carbonyl groups by bombarding the surface with energetic ions, electrons, and radical species [261]. Depending on the gas atmosphere used (e.g., oxygen, nitrogen, argon, ammonia), plasma treatment can either oxidize, etch, or functionalize the surface, increasing surface energy and creating reactive sites that enhance metal-binding capacity [262]. As an example, plasma oxidation of chitin or cellulose fibers can improve hydrophilicity and introduce carboxyl and carbonyl groups, thereby increasing their affinity toward specific metal ions [263]. Similarly, plasma treatments using ammonia or nitrogen-containing gases can generate amino functionalities on the surface of lignocellulosic materials, keratin films, or chitosan membranes [264]. These newly formed amine groups not only enhance the adsorption of cationic and anionic metal ions/complexes but also provide additional sites for further chemical grafting if a higher selectivity or capacity is needed. Another advantage of plasma-based modifications is their environmental friendliness, as they typically require no toxic reagents and consume minimal solvents [265]. However, the treated biopolymers can undergo partial chain scission or degrade under prolonged plasma exposure, necessitating careful optimization of process parameters (e.g., exposure time, power, gas flow rate) [266]. When considering plasma treatment, factors such as the surface-limited nature of the modification, sensitivity to process parameters, and susceptibility to aging or environmental exposure should be carefully considered, as they can influence long-term stability, reproducibility, and scalability of adsorbents under realistic operating conditions.

These benefits of plasma modification have been effectively demonstrated in various studies focused on enhancing metal adsorption performance. Zong et al. [267] treated multi-walled carbon nanotubes with nitrogen plasma and grafted sodium carboxymethyl cellulose onto their surface, introducing carboxyl, hydroxyl, and amino groups. This modification increased Eu^{3+} adsorption capacity to about 53 mg g^{-1}, nearly ten times higher than that of untreated carbon nanotubes. In a more recent work, Dhanabal et al. [268] developed biodegradable films composed of zein and chitosan, then treated them with oxygen glow-discharge plasma. The treatment introduced hydroxyl groups and increased surface roughness and porosity, greatly enhancing Cu^{2+} maximum adsorption capacity to 195 mg.g^{-1}.

4.1.3 | UV and Ozone Treatment

Ultraviolet (UV) and ozone treatments are widely used to oxidize and modify polymeric surfaces. When biopolymers are exposed to UV radiation, particularly in the presence of atmospheric oxygen, photochemical reactions can break covalent bonds in the macromolecular chains and generate free radicals. These radicals subsequently react with oxygen or moisture, forming new functional groups such as carbonyls, hydroxyls, and carboxyls [269]. This photo-oxidation process increases surface polarity and can create additional adsorption sites for metal ions.

Ozonation can be performed either in tandem with UV radiation (e.g., UV/O_3 systems) or as a standalone process by bubbling ozone-rich gas through biopolymer solutions, suspensions, or onto solid films [270]. In both scenarios, ozone molecules readily cleave carbon–carbon double bonds (if present) and oxidize available sites, introducing aldehyde, ketone, and carboxyl moieties. In a study, ozone treatment of lignin was reported to increase its phenolic hydroxyl content, which can enhance the chelation of specific metals, including Fe^{3+}, Cu^{2+}, or REE [271]. However, similar to plasma treatments, excessive UV or ozone exposure can degrade the polymer backbone, reducing mechanical stability [270]. Therefore, these methods are typically applied as surface-specific treatments or for partial oxidation, carefully balancing the creation of new binding sites against structural deterioration.

4.1.4 | Electron Beam or Gamma Irradiation

High-energy irradiation techniques, such as electron beam (e-beam) and gamma (γ) irradiation, are effective for modifying biopolymer surfaces through radical-mediated processes. When exposed to ionizing radiation, the polymer matrix undergoes bond scission and free radical formation, which can trigger cross-linking, chain cleavage, or grafting reactions, depending on the biopolymer type and radiation parameters [272]. In metal recovery applications, controlled doses of radiation

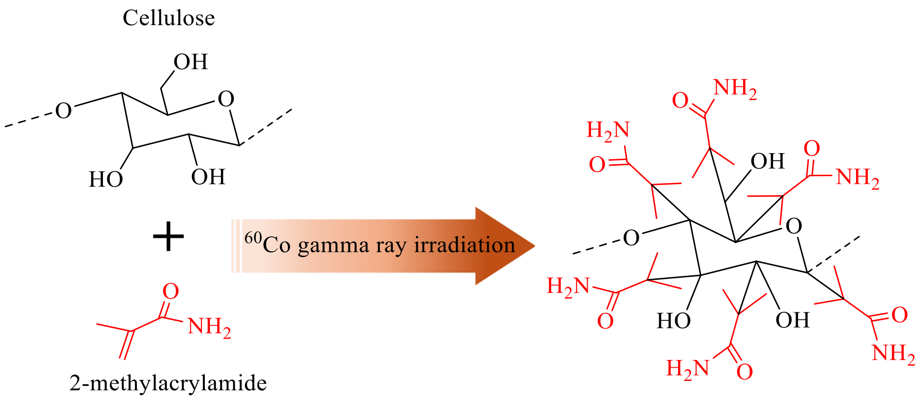


FIGURE 12 | Gamma irradiation grafting reaction between cellulose unit and 2-methylacrylamide, adapted from Zhang et al. [275].

are often used to graft or implant specific functional groups such as carboxyl, phosphate, or sulfonate onto the polymer backbone, enhancing metal adsorption [273]. When considering electron beam or gamma irradiation for biopolymer modification, high capital costs, safety requirements, and radiation-induced degradation must be weighed against scalability, durability, and cost-performance trade-offs.

For instance, gamma irradiation was effectively employed to induce free radicals on chitosan, enabling grafting copolymerization with acrylic acid to generate hydrogels rich in carboxylic groups, thereby enhancing heavy metal adsorption performance [274]. Moreover, as shown by Zhang et al. [275], gamma rays produce free radicals in high molecular weight cellulose, facilitating 2-methylacrylamide grafting (Figure 12). This process simultaneously enhances the solubility of high molecular weight cellulose in a NaOH/urea system and introduces amide functional groups, improving its adsorption capacity [275]. Similarly, e-beam irradiation has been employed to generate radicals on cellulose substrates, enabling the grafting of functional monomers like acrylic acid and glycidyl methacrylate [276].

4.1.5 | Considerations and Design Guidance

Physicochemical surface treatments offer reagent-free, fast routes to upgrade natural or pre-formed (Section 6) structures by enriching near-surface functionality. Their principal strengths are the ability to place active sites exactly where mass transfer is fastest and to decouple interfacial chemistry from bulk mechanics and porosity. Yet their limitations are evident: effects are largely confined to nanometric layers that can age, non-covalent phases may leach under harsh low-pH/high-salinity conditions, and modification can be spatially heterogeneous in thick or porous bodies. Thus, improvements seen in batch assays often diminish under process-relevant conditions with complex speciation and flow [277]. From a sustainability perspective, physicochemical and chemical modification routes should also be evaluated in terms of reagent intensity, energy input, and waste generation, as these factors can partially offset the inherent environmental advantages of biopolymer-based materials. Thorough validation under flow with real leachates, defined speciation, full mass balances, and durability, should therefore be considered integral to method development.

In practical applications, these treatments are most powerful when employed as priming steps or stabilizing frameworks rather than as standalone modifications. Plasma or UV activation can be used to introduce controlled populations of reactive groups, followed by graft-from coupling of selective ligands to secure durable binding motifs [278]. MOFs and NPs can be stabilized through biopolymer or ultrathin cross-linked interlayers [279], host–guest trapping [280], or core–shell encapsulation [281], reducing leaching and extending operational lifetimes. Across all approaches, systematic characterization of surface chemistry is essential, alongside careful mapping of dose-response or energy-response windows to prevent over-oxidation, chain scission, or backbone degradation. Just as importantly, surface chemistry must be matched to the speciation of the target matrix to maximize selectivity, stability, and long-term process compatibility.

4.2 | Surface Area Enhancement

4.2.1 | Particle Size Reduction and Surface Area Enhancement

Reducing a material to micro or nanoscale, such as producing nanocellulose, nanolignin, or nanochitin, greatly increases surface area and exposes more functional groups per unit mass. Techniques like milling, grinding, ultrasonication, and high-pressure homogenization can generate micro- or nanosized particles, enhancing the kinetics and capacity of metal binding [282–285]. High surface areas are especially beneficial in adsorption-based applications, where rapid and efficient metal uptake is essential. However, the size of the material should be carefully selected based on the application, as controlling fine nanosized materials can pose significant challenges in large-scale processes. Issues such as agglomeration, material loss during handling, and difficulties in separation and/or recovery of fine particles must be considered when scaling up. Balancing material size to optimize both reactivity and manageability is therefore crucial for practical implementation. One way to keep nano reactivity while solving operability is to anchor the NPs on a micro-core. For example, Chaturbedi et al. [286], lightly coated hetero-aggregates (≈1.8 mm alginate beads carrying a sparse shell of 250 nm chitosan NPs) and delivered about 154 mg g^{-1} of Cu^{2+}, an order-of-magnitude jump over the bare bead and even higher than free NPs when normalized to wet mass. Because the NP layer is thin, diffusion resistance stayed low, and crucially, $Cu^{2+}/MoO_4{}^{2-}$ selectivity increased (Cu/Mo q_{max} ratio ≈ 27), since both the negative alginate interior and the positive chitosan shell could cooperate in binding Cu^{2+}. The bead's millimeter size means it can be filtered, back-washed, or packed in a column without dust losses.

4.2.2 | Porosity Control and Template-Directed Synthesis

Controlling the internal porosity and pore structure of biopolymers can optimize metal-ion diffusion to binding sites. This can be achieved via templating methods, freeze-drying [287], supercritical drying [288], or using sacrificial templates (e.g., salts or colloidal particles) that can be leached out after the formation of the matrix [289]. Other methods include phase separation, where thermally or solvent-induced phase separation creates distinct porous structures, and electrospinning, which forms fibrous materials with controlled porosity and high surface area by adjusting parameters like solution viscosity and electric field strength [290, 291].

In a study, Boccia et al. [292] prepared a cellulose-nanofiber/chitosan aerogel reinforced with acid-activated montmorillonite by freezing the hydrogel from one side, letting the growing ice crystals template vertical, lamellar channels. After sublimation, the monolith exhibited an aligned macroporous network (porosity > 95%, average channel width ≈ 20–40 μm). The oriented pores cut diffusion paths dramatically: Cu^{2+}, Cd^{2+}, and Pb^{2+} were all taken up to equilibrium within minutes, and the maximum capacities reached 80–130 mg g^{-1} while remaining almost unchanged after five adsorption–desorption cycles. The authors credit the directional pores for the fast kinetics and the easy re-elution of metal ions because the solution can penetrate the whole scaffold without tortuous dead-ends. In another study, calcium alginate/chitosan composite beads were gelled in the presence of dispersed $CaCO_3$ powder [293]. During mild acid washing, the $CaCO_3$ dissolved, leaving behind interconnected macropores (average 5–50 μm) throughout the 3-mm bead. The resulting material showed a Langmuir capacity of 291 mg g^{-1} for Cu^{2+}, over threefold higher than non-porous alginate beads. The authors emphasized that the removable salt template simultaneously created a high internal surface area and left extra Ca^{2+} sites that favor ion-exchange with divalent metals [293].

4.2.3 | Layer-By-Layer Assembly and Thin-Film Fabrication

Layer-by-layer (LbL) assembly of biopolymers is a method in which alternating layers of oppositely charged or complementary functional biopolymers (e.g., chitosan, alginate, and cellulose derivatives) are sequentially deposited to create thin films or coatings with tunable thickness and surface properties [294, 295]. By carefully selecting and combining biopolymers that bear specific chemical groups (such as carboxyl, amine, or hydroxyl), one can introduce binding sites for metal ions directly into each layer [294]. This hierarchical approach not only preserves the native biopolymer functionality but also maximizes surface area and adsorption capacity [296]. Once assembled, the LbL films or coatings offer a high density of functional groups that can chelate or bind metal ions from solutions, making them particularly effective for water treatment applications or resource recovery where removal or capture of heavy metals is desired [296].

A representative example is provided by Kazemi et al. [297], who developed a polyethersulfone (PES) ultrafiltration membrane with enhanced photocatalytic activity (Figure 13). They first applied 3.5 bilayers of chitosan (positively charged) and sodium alginate (negatively charged) onto the PES surface through LbL assembly, thereby enriching the surface with amino ($-NH_2$) and carboxyl ($-COOH$) groups while maintaining membrane porosity. $Fe^0@WO_3$ NPs (zero-valent Fe NPs supported on or embedded within WO_3) were then anchored onto the outer chitosan layer to form the final photocatalytic membrane (Figure 13). When tested for Cr^{6+} removal under visible light, the modified membrane outperformed pristine PES, with rejection improving from less than 20% (pristine PES) to over 99% at 5 mg L^{-1} and 78% at 50 mg L^{-1}. This enhancement was attributed to the abundance of protonated amino groups in the chitosan layers, which electrostatically pre-concentrate chromate anions, and the thin-film architecture, which shortens diffusion paths while facilitating Cr^{6+} photoreduction to Cr^{3+} for more efficient capture.

4.2.4 | Practical Gains and Process Liabilities

Surface-area engineering enhances metal adsorption primarily by increasing the accessibility of binding sites and reducing diffusion limitations, which translates into higher apparent capacities and faster kinetics. However, these benefits come with inherent constraints. NPs tend to agglomerate, complicating recovery; aerogels and cryogels, while highly porous, may shed fines and lose structural integrity under hydraulic stress; and thin multilayered films are prone to swelling, interdiffusion, or delamination in harsh acidic environments. At larger scales, improvements in sorption kinetics may be counterbalanced by challenges such as higher pressure drop, fouling, or increased solvent and energy demands.

In addition to total surface area, adsorption performance is governed by the interfacial density and accessibility of functional groups available for metal binding. The effective concentration of active sites at the solid–solution interface is often significantly lower than the theoretical ligand density because a fraction of functional groups may reside within sterically hindered domains or regions that are poorly accessible to solvated metal complexes. Factors such as pore tortuosity, cross-link density, polymer chain packing, and swelling behavior can restrict mass transfer and reduce the fraction of sites participating in adsorption. Moreover, the relationship between pore size and the hydrated radius of metal species determines whether diffusion into internal domains is thermodynamically and kinetically feasible. Interfacial properties such as surface hydrophilicity and wettability further influence adsorption by controlling solvent penetration and the effective exposure of binding sites; materials exhibiting lower contact angles typically allow more efficient wetting and improved access to internal coordination domains. Consequently, the apparent adsorption capacity and kinetics are governed not

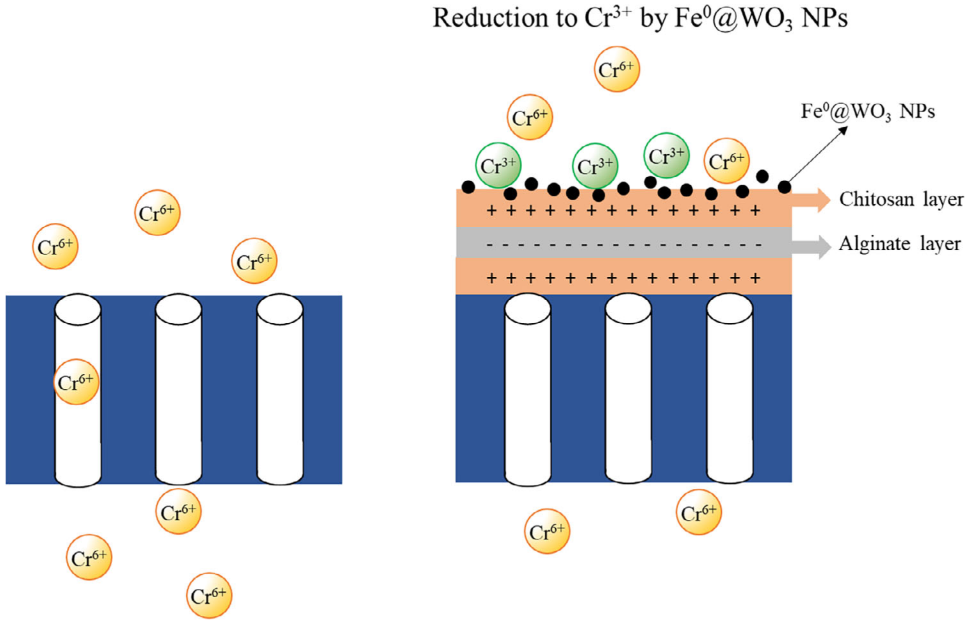


FIGURE 13 | Schematic representation of the multilayer polyethersulfone membrane modified with $Fe^0@WO_3$ NPs and chitosan–alginate bilayers, showing the visible-light-driven photocatalytic removal of Cr^{6+} from aqueous solution. Adapted with permission from Kazemi et al. [297]. Copyright 2025, Elsevier.

only by the chemical identity and nominal density of functional groups but also by the structural architecture that regulates site accessibility and mass transport under realistic solution conditions.

Robust designs mitigate these drawbacks by confining nanostructures within stable supports, while maintaining hierarchical porosity (as discussed in Section 4.1.5). Macropores provide convective pathways to resist clogging, whereas meso- and micropores preserve site density. Mechanical reinforcement can be introduced through modest cross-linking, fibrillar additives (e.g., nanocellulose whiskers), ultrathin inorganic layers, or the design of composites and hybrid materials (Section 5). Such strategies enhance wet modulus and resistance to deformation without blocking access to active sites. For thin coatings, strong interfacial bonding between layers is essential to prevent delamination under flow. At the same time, the deposition method should be scalable and uniform; approaches such as spray coating, spin coating, electrophoretic deposition, or roll-to-roll processing are advantageous because they maintain permeability while allowing controlled layering [298, 299]. These methods can also generate gradient architectures, where the distribution of functional groups across the film enhances pre-concentration, selective binding, or even in-film redox transformations [300].

For translation into real process environments, evaluation should extend beyond batch adsorption assays. Relevant parameters include permeability and pressure–flux behavior, breakthrough capacity, mass-transfer-zone length, mechanical stability under backwashing, chemical resistance to oxidants or chlorine, and multi-cycle durability. Equally important are techno-economic and life-cycle assessments, which should report regenerant consumption, adsorbent lifetime, and end-of-life options such as recycling or safe incineration.

Current research focuses predominantly on chitosan, alginate, and cellulose derivatives, while other renewable matrices such as lignin, hemicellulose, bacterial cellulose, pectin, keratin, and starch remain underexplored. Extending surface-area engineering strategies to these less-studied polymers, or different composites would broaden the available chemistries and may yield materials with improved stability or selectivity in chloride-rich and acidic environments. Low-cost feedstocks, such as lignosulfonates from paper mills or keratin from poultry waste, could further improve economic feasibility for large-scale deployment.

5 | Composite and Hybrid Materials

Beyond introducing metal-interacting groups or applying physical treatments, integrating biopolymers with natural or synthetic components broadens their applicability and enhances metal-binding performance. The combination of biopolymers with complementary substances, along with targeted chemical modifications and physical treatments, creates composites and hybrids with synergistic properties. These modifications enhance adsorption capacity, mechanical strength, chemical stability, and metal selectivity. These strategies are discussed in the following sections.

5.1 | Inorganic–Biopolymer Hybrids

By incorporating metal oxides, silicates, or clay minerals into biopolymer matrices, hybrids with synergistic properties can be formed. The inorganic phase often provides additional adsorption sites, improves mechanical strength, and enhances thermal or chemical stability [301, 302]. These materials can be incorporated through methods such as physical blending (such as physically modified chitosan with silicon dioxide) [303], in situ precipitation (such as chitosan/hydroxyapatite nanocomposites) [304], or sol–gel processing (such as hybrid sol–gel electrospun silica-cellulose base nanofibers) [305], depending on the compatibility of the biopolymer with the inorganic additive. For instance, NPs or nanosheets can be dispersed in a polymer solution before gelation or printing, ensuring homogeneous distribution within the matrix. Alternatively, the biopolymer may be cross-linked in the presence of inorganic particles, which become entrapped within the polymer network [306].

A classic example is chitosan–clay composites, which not only display enhanced adsorption capacities for heavy metals but also gain superior mechanical robustness compared to pristine chitosan [307]. In the realm of water remediation, alginate or chitosan functionalized with layered double hydroxides (LDHs) can serve as efficient, high-capacity adsorbents. By integrating magnetic NPs (e.g., Fe_3O_4) into the biopolymer matrix, the hybrids become magnetically recoverable, greatly simplifying separation processes [308].

When designing inorganic–biopolymer hybrids, additional functionalization steps described previously, such as surface modification or cross-linking the biopolymer chains, can further enhance mechanical and thermal properties, as well as control porosity and adsorption behavior.

5.2 | Biopolymer–Biopolymer Blends

Blending different biopolymers often yields a synergy that capitalizes on each component's unique functional groups and structural characteristics. For example, combining a S-rich protein like keratin with a carboxyl or amino-rich polysaccharide, such as cellulose or chitosan, respectively, can produce a composite that presents multiple classes of binding sites (e.g., thiols, carboxyls, hydroxyls, or amino) [309, 310], broadening the spectrum of metals that can be sequestered. Beyond increasing metal-binding diversity, such composites also benefit from the robust fibrous network of cellulose (or the gel-forming properties of alginate) and the functional flexibility of keratin, thereby enhancing both mechanical stability and adsorption capacity [310]. This approach is particularly valuable in wastewater treatment or similar approaches, where efficient separation of metals from diverse groups is required [311].

Similarly, chitosan or keratin blends with lignin illustrate how introducing amine groups (from chitosan or keratin) and phenolic hydroxyl groups (from lignin) can improve selectivity and binding efficiency toward specific metals [312]. The incorporation of these amine groups can also fine-tune the material's response to varying pH conditions, further optimizing metal uptake [313, 314]. In addition, carefully adjusting the relative proportions of each biopolymer can modulate properties such as solubility, swelling behavior, thermal, and structural stability [315, 316]. This tailoring strategy enables the development of versatile biopolymer blends that can be customized for diverse applications, ranging from wastewater remediation to catalysis, where enhanced adsorption, structural integrity, and chemical functionality are paramount.

5.3 | Nanoparticle and Molecular Functionalization for Enhanced Metal Adsorption

Functionalizing biopolymers with metallic NPs [317, 318], quantum dots (QDs) [319–322], or metal–organic frameworks (MOFs) [258, 323–325] can greatly enhance their metal adsorption capacity and specificity. The surface attachment of some of these functional agents, such as QDs, may also impart sensing capabilities, enabling the development of biosensors that not only capture a target metal but also signal its presence [319, 321]. Techniques such as physical adsorption [326], chemical grafting, in situ synthesis, blending, or cross-linking [327] are used to embed these materials within films, hydrogels, or fibers, improving metal adsorption and sensing performance.

Incorporating stimuli-responsive components, such as temperature-sensitive polymers, pH-responsive groups, or photoactive units, into biopolymers can create dynamic systems with tunable metal-binding behavior. For example, pH-responsive chitosan hydrogels have been developed to adsorb heavy metals such as copper and zinc at neutral pH and release them in acidic environments, enabling effective recovery cycles [328–330]. Additionally, photoactive MOFs have been employed to selectively bind metals under specific light wavelengths [331, 332].

5.4 | Practical Considerations

Composite and hybrid architectures offer clear advantages over pristine biopolymers. By combining complementary functional groups, they enhance the density and diversity of metal-binding sites and, when required, can be engineered to simultaneously capture a broad range of metal species. Selectivity can be tuned via the inorganic phase or by grafting tailored ligands. Nanostructured fillers and templated porosity shorten diffusion paths and expose more active surface, boosting adsorption kinetics; inorganics also stiffen gels, films, and fibers, while blends reduce brittleness, enabling robust beads, membranes, aerogels, and electrospun/printed fibers. In practice, embedding iron oxides alongside other functional nanophases (metallic NPs, QDs, MOFs), couples' separation and function in one body: magnetic domains enable rapid recovery; MOFs/QDs add selective coordination and sensing; redox- or photoactive units enable stimulus-responsive release.

These benefits carry trade-offs in realistic matrices. In low-pH, chloride-rich streams, hybrids with inorganic fillers may suffer dissolution, ion exchange, or redox reactions (LDHs and some oxides are especially vulnerable [333, 334]). Magnetic recovery can degrade over time via oxidation, aggregation, or surface corrosion; in columns, attrition raises fines and increases pressure drop [335]. Protective shells (silica/carbon) or conformal 2D coatings help suppress oxidation/leaching and stabilize interfaces.

Flow performance and sustainability also demand attention. Hierarchical pores (micro–meso–macro) balance high capacity with fast transport and low pressure drop; greener fabrication (e.g., closed-loop solvent recovery for sol–gel/templating) reduces environmental burden. Blends can suffer limited mis-

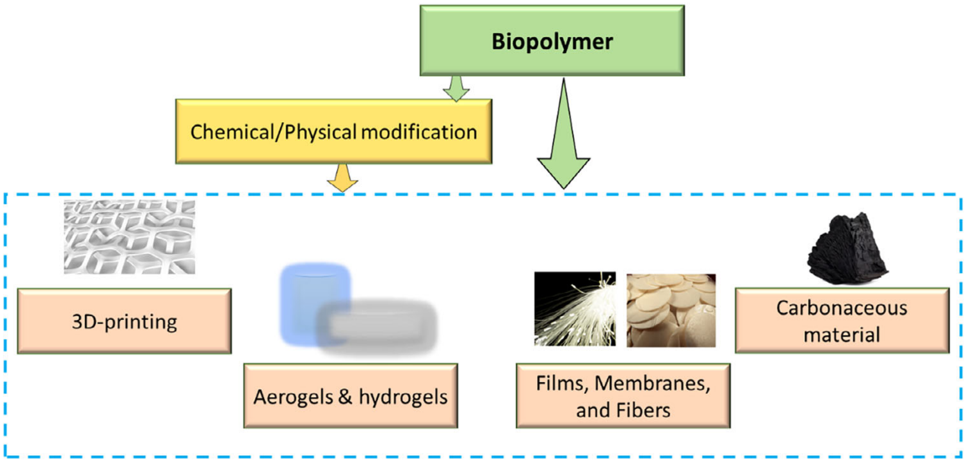


FIGURE 14 | Overview of the advanced architectures and design strategies outlined in Section 6.

cibility, phase segregation, and batch variability from natural feedstocks; strong cross-linkers may block sites or introduce extractables, and pH-responsive domains can swell and again increase pressure drop and fouling. Productive routes include mapping miscibility windows and network topology, using mild/orthogonal cross-linking that preserves accessibility, and designing sequence-defined or blocky architectures to control domain distribution and transport. Rigorous stability assessment (accelerated acid/oxidant aging, extended fixed-bed cycling with full mass balances) should accompany capacity and kinetics.

Finally, embedding metallic NPs, QDs, or MOFs, whether with iron oxides or instead of them, raises issues of phase stability, leaching, pore blockage, and safety. Physical attachment sheds under acid/high ionic strength; in situ growth or high loadings can occlude transport; photoactive systems may generate ROS that damage the matrix [336]. Reporting should normalize capacity to active-phase loading and accessible surface/crystallinity, quantify flux and low pressure, track leached mass per cycle, and demonstrate long-horizon cycling in relevant leachates with complete mass balances.

6 | Advanced Processing and Material Architectures

Having established the fundamental properties of biopolymers and their metal-binding functionalities and having explored strategies to enhance and tailor these properties in previous sections, the next logical step is to consider how these engineered materials can be further transformed into advanced architectures that broaden their practical utility. The conversion of biopolymers into formats such as activated carbons, thin films, membranes, fibers, aerogels, hydrogels, and the subsequent assembly of these components into hierarchical or hybrid structures can profoundly affect their metal-interaction performance. An overview of these advanced architectures is illustrated in Figure 14.

6.1 | Conversion into Carbonaceous Adsorbents and Activated Carbons

Biopolymers rich in carbon, such as cellulose, lignin, chitosan, or other biomasses, can be thermochemically transformed into carbonaceous adsorbents. Processes like pyrolysis, hydrothermal carbonization, and chemical activation yield materials with extensive internal surface areas, diverse pore structures, and abundant surface functional groups.

When lignocellulosic biomass, chitinous shells, or other similar biomaterials are subjected to pyrolysis at elevated temperatures (typically 400–800°C) in an inert atmosphere, stable carbon-rich solids known as biochars form [337]. Subsequent activation steps, often involving steam or chemical agents (e.g., KOH, H_3PO_4), not only create micropores and mesopores by etching the carbon matrix but also modify or introduce functional groups onto the surface [338]. The resulting activated carbons can exhibit surface areas exceeding 1000 $m^2\ g^{-1}$, dramatically increasing metal-binding sites exposure and enhancing adsorption kinetics [337, 339]. Chaisit et al. (2020) prepared activated carbon from cassava starch using KOH at ratios of 1:1, 1:3, and 1:5 (KOH:starch). The surface area increased from 14.8 to 1350 $m^2\ g^{-1}$ with higher KOH ratios, with SEM images showing the progressive porosity increase and surface roughness (Figure 15). KOH activated carbon has been widely shown as efficient material for heavy metal adsorption; for example, Douglas-fir biochar with large surface area (~1050 $m^2\ g^{-1}$) was shown Langmuir capacities of 140 mg g^{-1} for Pb^{2+}, 127 mg g^{-1} for Cr^{6+}, and 29 mg g^{-1} for Cd^{2+}, more than triple those of the non-activated char, thanks to abundant micropores and newly exposed oxygenated sites that favor inner-sphere complexation [340].

Such porous activated carbons derived from bio-based precursors can be further modified to tailor their metal selectivity. Techniques include grafting amino [342], carboxyl [343], thiol [344], or phosphonate groups [345] onto the carbon surface, enabling stronger and more efficient binding interactions with specific metal ions and improving both selectivity and adsorption

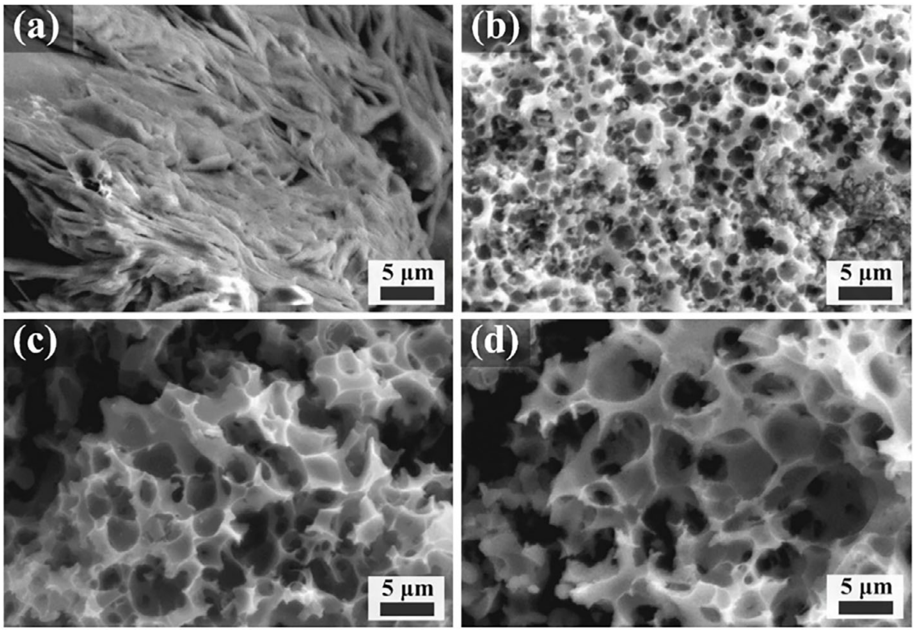


FIGURE 15 | SEM images of (A) non-activated carbon and activated carbons prepared with cassava starch:KOH ratios of (B) 1:1, (C) 1:3, and (D) 1:5. Reproduced from open access work of Chaisit et al. [341].

capacity. As an example, chitosan flakes carbonized at 600°C and activated with a K_2CO_3/urea blend yielded a nitrogen-doped carbon (≈16 wt% N, 1556 $m^2\ g^{-1}$, 0.69 $cm^3\ g^{-1}$) [346]. Its amine-rich surface removed > 95% of Cr^{6+} and Pb^{2+} within 30 min, clear evidence that nitrogen donor sites can drive fast and selective metal chelation [346].

6.2 | Fabrication of Films, Membranes, and Fibers

Transforming modified biopolymers into films or membranes adds a level of morphological control and processability. These two-dimensional architectures can act as selective barriers, support layers, or sensor substrates, depending on their thickness, porosity, and surface chemistry.

6.2.1 | Thin Films and Coatings

Casting solutions of biopolymers such as chitosan, alginate, lignin, pectin, or protein-based materials onto substrates, followed by drying, can produce thin films that retain metal-binding functionalities [347]. Cross-linking (e.g., with genipin or citric acid) can improve film strength, stability, and metal retention under diverse pH and ionic conditions [118, 119]. Not only can such films serve in metal adsorption [348, 349], but they can also serve as edible coatings that stabilize essential trace metals in food packaging, preserving nutritional quality and preventing oxidative degradation [350, 351]. In other scenarios, thin bio-based coatings on medical devices or sensors can capture targeted metal ions for diagnostic or therapeutic purposes [352]. For instance, Liu et al. [353] prepared a chitosan-based film blended with polyethylene glycol and cross-linked with genipin, forming a robust, water-insoluble coating rich in surface amine groups. This film exhibited high adsorption capacities for Pb^{2+} (~113 mg g^{-1}) and Ni^{2+} (~40 mg g^{-1}), maintained stability from pH 3 to 10, and retained about 80% of its initial capacity over five reuse cycles, revealing its durability and practical potential for treating metal-contaminated water [353].

6.2.2 | Membrane Technologies

Controlling parameters such as solution concentration, biopolymer molecular weight, and the specific conditions of phase inversion or electrospinning enables the fabrication of biopolymer membranes with precisely tuned pore sizes, surface chemistries, and charge densities [354]. By manipulating these factors, it is possible to tailor the membrane morphology, from symmetric to asymmetric structures, and optimize the distribution and density of functional groups [354]. Common biopolymers used for metal ion separation include cellulose acetate, chitosan, and protein–polysaccharide blends [354, 355]. Each material offers unique advantages: cellulose acetate exhibits robust mechanical properties and chemical stability; chitosan contains abundant amino groups that can bind or repel specific ions; and protein–polysaccharide systems can be engineered for a range of charge interactions [356]. Together, these materials afford membranes capable of selectively removing or concentrating particular metal ions from complex solutions.

The mechanism underlying metal ion separation in these biopolymer membranes often involves a combination of size exclusion, electrostatic interactions, and chelation [357]. Beyond conventional separation, advanced designs incorporate responsive or smart layers with immobilized metal-chelating ligands, enabling the membrane to open or close in response to stimuli such as pH changes or the presence of specific ions, thus providing better control over separation efficiency [358–360].

Beyond selectivity, membrane architecture strongly governs mass transport and overall performance. Thin, highly porous membranes with well-defined pore size distributions reduce diffusion resistance, enabling higher flux and faster adsorption–desorption kinetics, whereas thicker or poorly interconnected structures impede ion transport [194]. Hierarchical or asymmetric architectures, incorporating macro- and mesopores or porosity gradients, further minimize diffusion barriers and improve access to active sites, revealing the criticality of architectural design as chemical functionality.

6.2.3 | Electrospun Fibers

Electrospinning enables the production of nanofibers with diameters in the sub-micron range, dramatically increasing the surface area-to-volume ratio and thus enhancing metal-binding capacity and kinetics [348]. The versatility of this technique allows the use of diverse biopolymer feedstocks, including lignin, chitosan, alginate, collagen, and cellulose derivatives, each offering distinct binding sites (e.g., phenolic, amino, or hydroxyl groups) and customizable fiber morphologies [361]. As a result, electrospun mats exhibit high adsorption efficiencies even in dilute metal solutions, making them promising for environmental remediation and resource recovery [361].

Beyond adsorption, these nanofibrous mats can be chemically or physically modified to deliver beneficial ions in biomedical contexts. For instance, incorporating Ag or Zn ions into electrospun dressings can provide antimicrobial or tissue-regenerative properties, aiding wound healing and infection control [362]. The lightweight and flexible nature of electrospun membranes also facilitates their integration into portable devices and wearable sensors, expanding their utility from water purification systems to real-time monitoring of metal ion concentrations in various environments [363].

Electrospinning provides flexible strategies for incorporating polymeric fibers, enabling the design of systems with specific profiles and functionalities. These structural features not only enhance the accessibility of functional groups but also provide flexible platforms for further chemical modification. As illustrated in Figure 16, different electrospinning configurations, such as blend, emulsion, coaxial, or side-by-side spinning, enable the incorporation of active compounds directly into the fiber matrix or in defined domains, producing architectures that can influence stability, diffusion pathways, and interaction efficiency [364]. Such electrospun systems combine structural versatility with chemical tunability, making them promising candidates for advanced separation processes in hydrometallurgy and environmental remediation.

The performance of electrospun fiber assemblies is governed by their hierarchical pore structure and overall thickness. Their interconnected pore networks reduce external diffusion resistance and facilitate rapid mass transfer. Incorporation of hydrophilic or charged additives can further enhance accessibility of binding sites and improve wettability, thereby promoting higher solution permeability and reducing fouling. However, excessive thickness of the electrospun layer may introduce internal diffusion limitations. Therefore, precise control of fiber diameter, layer thickness, and porosity is essential to balance adsorption efficiency with effective mass transfer under operational conditions [361].

6.3 | Aerogels, Hydrogels, and Other Porous 3D Structures

Shaping biopolymers into three-dimensional porous structures offers additional pathways for controlling metal-ion interactions. These lightweight, high-porosity architectures provide a large surface area, enhancing accessibility to interior functional groups and improving interaction efficiency.

6.3.1 | Hydrogels and Ion-Responsive Gels

Hydrogels formed by cross-linking metal-binding biopolymers (e.g., alginate, pectin, chitosan) create soft, water-swollen networks with tunable chelating properties [12, 365]. These networks can be assembled through ionic or covalent cross-linking, enabling control over mechanical strength, porosity, and responsiveness to environmental factors [365]. For example, Zhang et al. [366] grafted deoxyribonucleic acid (DNA) onto cellulose backbones to create bio-based hydrogels, offering a sustainable solution for environmental remediation. Moreover, Lone et al. [367] developed a cost-effective, biodegradable gelatin–chitosan hydrogel cross-linked with glutaraldehyde, with tunable swelling/deswelling behavior for the efficient adsorption of Hg^{2+} through chelation by amine and hydroxyl groups. These hydrogels, leveraging charge-assisted hydrogen bonding, achieve high contaminant-capture capacity and mechanical strength, enabling efficient sequestration of heavy metal ions, with minimal interference from coexisting substances. By adjusting pH or ionic strength, the hydrogel can selectively release or capture metal ions, making it highly effective in metal recovery systems. Dynamic swelling and deswelling cycles allow for repeated adsorption and desorption of heavy metals, thus reducing operational costs and improving resource recovery [368]. Beyond industrial applications, the versatility of these hydrogels extends to agricultural systems. They can be designed to gradually supply essential micronutrients (like Fe or Zn) to plant roots, enhancing nutrient efficiency and crop productivity [369].

The three-dimensional network of hydrogels governs ion transport to internal binding sites. A balanced combination of nano- and micro-scale pores enables rapid diffusion of solvated ions while maintaining mechanical stability. Cross-linking density, extractant dosage, pore size distribution, and water content critically affect diffusion coefficients and swelling kinetics: highly cross-linked and/or functionalized gels exhibit smaller pores and slower diffusion, whereas more open networks enhance mass transport but may reduce structural integrity [368]. Hierarchical or asymmetric hydrogel membranes with engineered pore gradients can further improve ion transport by promoting directional or convective flow.

6.3.2 | Polymeric Gel Materials

Freeze-drying, supercritical drying, or templating methods applied to biopolymer gels produce aerogels or cryogels with

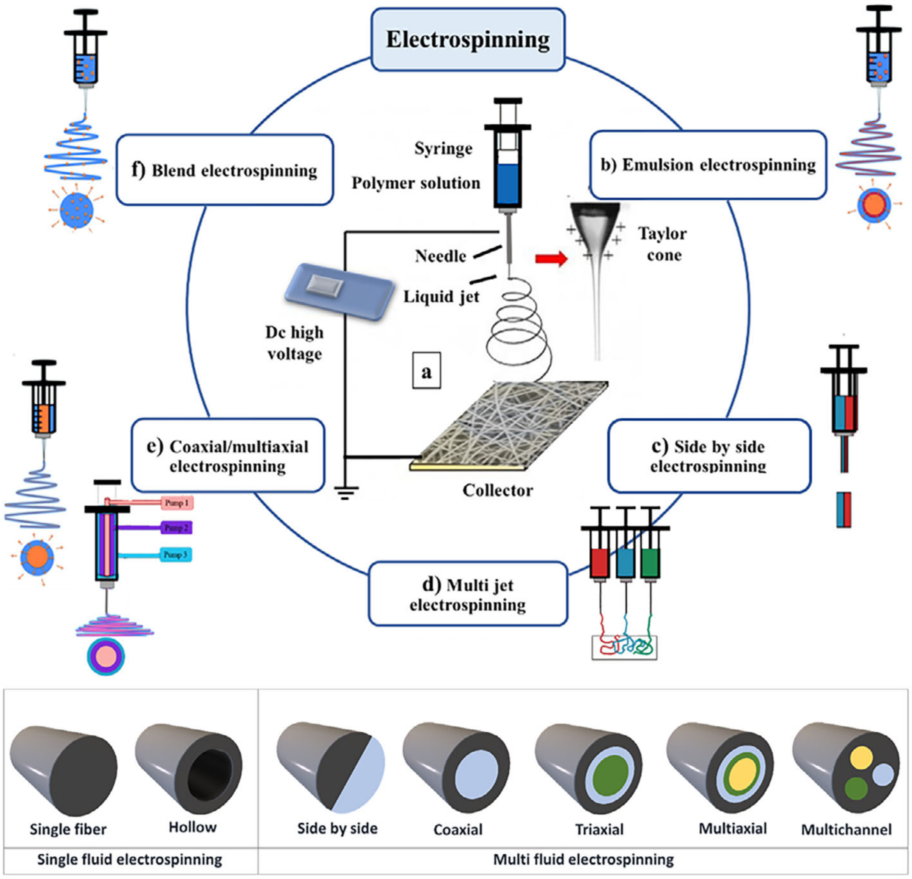


FIGURE 16 | Routes for incorporating active compounds into polymer carriers, and below, the cross-section of fibers generated using different electrospinning methods, reproduced from the open-access work of Zare et al. [364].

extensive pore networks and very low densities [370]. These 3D scaffolds can encapsulate metal ions, metal NPs, or metal-binding ligands, resulting in lightweight adsorbents, catalysts, or sensor components [370–372]. Different biopolymer-based aerogels, including lignin, cellulose, chitosan, alginate, or their hybrids [373–376], and cryogels based on chitosan, keratin, cellulose, or their hybrids [377–379], have been developed for environmental remediation purposes, indicating that their high potential in water purification applications, offering a low environmental impact solution for removing contaminants from water sources. Cheng et al. [380] developed a chemically cross-linked cellulose nanofiber-supported cryogel using γ-glycidoxypropyltrimethoxysilane and branched polyethylenimine. The resulting flexible 3D network, rich in amino groups, exhibited a high Cu^{2+} adsorption capacity (138 mg.g^{-1}) at pH 5 and maintained 75% of its capacity after four adsorption–desorption cycles, demonstrating good reusability and mechanical stability. In another study, Braga et al. [381] developed carboxymethyl cellulose–sugarcane bagasse cryogels for treating multi-metal waste solutions. The material exhibited strong selectivity toward Cu^{2+} over Ni^{2+} and other coexisting metals, achieving ~97% Cu^{2+} removal and a maximum adsorption capacity of ~44 mg g^{-1} in fixed-bed tests at pH 7, attributed to metal–OH chelation and metal–carboxylate interactions.

Mass transport in aerogels and cryogels is governed by their highly porous and often hierarchical networks. Interconnected or directionally aligned macropores reduce diffusion distances and enable rapid solution penetration, leading to fast adsorption kinetics and high utilization of internal sites. Hierarchical structures combining macro- and mesopores support convective flow and high flux, while microporous domains provide a large surface area for binding. In contrast, predominantly microporous materials may experience intraparticle diffusion limitations and slower adsorption rates.

6.3.3 | 3D-Printed Biopolymer Architectures

Advances in 3D printing enable the precise fabrication of biopolymer-based structures optimized for different applications, including metal ion adsorption. Methods such as fused deposition modeling (FDM), direct ink writing (DIW), stereolithography (SLA), and bioprinting were employed to construct scaffolds from keratin, chitosan, alginate, cellulose, and lignin derivatives [382–384]. By controlling viscosity, rheology, and cross-linking, these polymers can be formulated into printable inks or filaments while preserving their chelating functionalities [382].

Once printed, the resulting architectures exhibit hierarchical porosity, featuring macro-channels from layering and intrinsic micro- or mesopores that enhance metal ion diffusion and binding [385]. Postprocessing techniques such as freeze-drying, chemical cross-linking, or thermal treatments, further improve

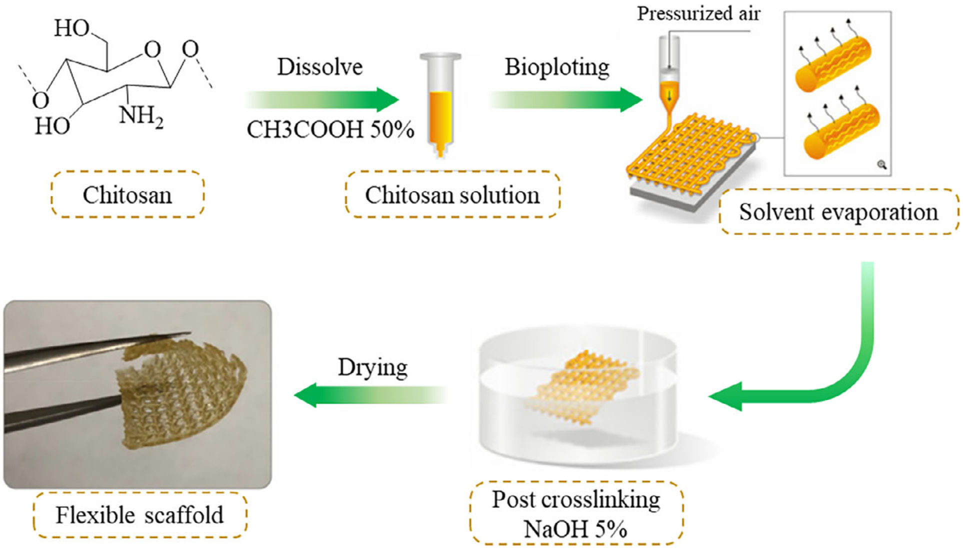


FIGURE 17 | Schematic illustration representing stages including solution preparation, fabrication of 3D-printed chitosan scaffolds (10% (w/v)) and solvent evaporation, adapted with permission from Sadeghianmaryan et al. [386]. Copyright 2025, Elsevier.

mechanical properties and adsorption performance. Sadeghianmaryan et al. [386] developed 3D-printed chitosan scaffolds using a straightforward extrusion method, followed by ambient drying to preserve structural integrity (Figure 17). After air drying, the 3D-printed material was cross-linked by immersing it in 5% NaOH, which deprotonated $-NH_3^+$ groups to $-NH_2$, promoting ionic interactions and hydrogen bonding, and enhancing structural stability.

Mass transport considerations are central to the design of 3D-printed biopolymer scaffolds for metal recovery. Additive manufacturing, particularly when combined with thermally induced phase separation, produces lattices with hierarchical porosity: macro-channels from the printed scaffold geometry enable convective flow and shorten diffusion paths, while micropores provide high surface area for adsorption. This structure ensures rapid solution permeation, uniform contact with active sites, and high removal efficiency. The approach yields stable mechanical integrity, easy recovery, and reusability over multiple cycles, making it highly effective for continuous-flow heavy metal removal from water [387].

Additionally, these 3D-printed biopolymer scaffolds can host metal NPs, enabling simultaneous adsorption and catalytic transformations. Incorporating NPs into the ink or through post-printing reduction steps boosts functionality, while complex lattice or honeycomb geometries maximize surface area and minimize material usage, ideal for continuous flow systems with efficient mass transfer and low pressure drop [36, 388]. Moreover, Gong et al. [389] developed "shrinking printing," where 3D-printed hydrogels made from anionic polymers such as hyaluronic acid methacrylate or alginate are immersed in a polycationic chitosan solution. The resulting charge complexation induces water expulsion, reducing linear dimensions by up to 60% while maintaining structural integrity and cytocompatibility [389]. This approach improves resolution without requiring complex hardware upgrades, making it suitable for creating high-precision scaffolds for metal ion adsorption.

3D-printed materials are relatively underutilized in metal adsorption studies; however, they recently gained more attention for their potential in metal recovery and removal applications. Notable examples include 3D-printed porous chitosan/ZIF-67 composites that selectively adsorbed Pb^{2+} from water with high efficiency through ion exchange and surface complexation mechanisms [390]. Another study fabricated reusable chitosan monoliths via SLA printing, achieving fast Cu^{2+} removal with a maximum capacity of 13.7 mg g^{-1} and up to 92% desorption using EDTA, demonstrating high reusability and structural stability [391]. Furthermore, Liakos et al. [392] developed heat-extruded PCL/alginate composite filaments for FDM printing, which were used to create biomimetic structures capable of adsorbing Cu^{2+} up to 90 mg g^{-1}, even under dynamic conditions such as flow-through application.

6.4 | Advantages and Disadvantages of Biopolymer-Based Structures

Biopolymer-based architectures, such as films, membranes, fibers, aerogels, hydrogels, and 3D-printed structures, enhance the metal-binding potential of biopolymers for environmental and resource recovery approaches, as detailed in sections 6.1 to 6.3 and summarized in Table 6. These advanced forms offer morphological control but face practical challenges.

Biopolymers, sourced from renewable and often low-cost waste materials like lignin, chitosan, and keratin, offer sustainable and biodegradable alternatives for advanced material architectures. Their inherent functional groups facilitate robust metal-binding interactions with minimal chemical modification, enhancing eco-friendliness. These materials can be transformed into versatile

TABLE 6 | Overview of biopolymer-based structures and representative examples of their conversion into functional materials applied in metal adsorption.

Subtype	Fabrication method	Enhanced properties	Biopolymer-based example
Carbonaceous adsorbents	Pyrolysis, activation (KOH/H_3PO_4)	Surface area	Cellulose [393], chitosan [393], lignin [394]
Thin films/coatings	Solvent Casting	Morphological control, stability, reusability	Calcium Alginate [395], chitosan [396]
Membranes	Phase inversion, electrospinning	Pore tuning, ion selectivity	Cellulose [355], keratin [397]
Electrospun fibers	Electrospinning (blend/coaxial)	Surface area, tunable fiber, rapid kinetics	Chitosan [398], gelatin [399], cellulose [400]
Hydrogels	Ionic/covalent cross-linking, graft polymerization	High surface area, swelling tunability, dynamic release	Cellulose [366], gelatin–chitosan [367], alginate [401]
Aerogels/cryogels	Freeze-drying, templating	High surface area, high porosity, low density	Alginate [373], cellulose [379], chitosan [378]
3D-printed structures	FDM, DIW, SLA	Hierarchical porosity, custom geometry	Chitosan [390], alginate [392]

forms, including membranes, fibers, hydrogels, aerogels, and 3D-printed scaffolds, to meet diverse application demands in metal remediation and recovery. Activated carbons derived from biopolymers achieve high surface areas (often >1000 m^2/g), rivaling synthetic resins in adsorption capacity. Hydrogels and aerogels provide exceptional porosity and tunable swelling, enabling dynamic metal capture and release for reusable systems. The structural and chemical flexibility of biopolymers allows precise performance optimization, while their reactive chemistries support easy functionalization to improve metal selectivity. Additionally, 3D printing enables intricate architectural control, maximizing surface accessibility and facilitating integration into advanced platforms like continuous-flow recovery systems or real-time sensors.

However, biopolymers often lack mechanical strength, limiting their use in high-stress settings and requiring reinforcement. They are prone to degradation under harsh conditions like extreme pH or microbial exposure, affecting durability. Advanced processing methods, such as electrospinning or 3D printing, can be costly or hard to scale. Natural variability causes inconsistent performance, and selectivity in complex mixtures is challenging due to competitive ion binding. High hydrophilicity may cause swelling or dissolution, demanding careful design. Furthermore, their performance can vary with solution conditions, and achieving consistent quality at an industrial scale remains a challenge. In contrast, synthetic adsorbents often offer superior robustness, predictable selectivity, and mature manufacturing pathways.

7 | Industrial Translation and Market Readiness

While biopolymer-based adsorbents have demonstrated promising performance at the laboratory scale, their transition into industrial practice requires evaluation beyond selectivity and adsorption capacity. Industrial translation demands reproducibility, durability under realistic operating conditions, scalable processing routes, and clear economic justification relative to established technologies.

7.1 | Technical and Performance Barriers to Industrial Deployment

Despite the promising laboratory performance of engineered biopolymer adsorbents, translation to industrial practice has been limited and faces several bottlenecks. Natural biopolymers can exhibit batch-to-batch variability in composition and molecular weight, leading to inconsistent adsorption capacities; their selectivity in complex effluents is often lower than that of synthetic ion-exchange resins and declines after a few regeneration cycles. The weaker mechanical strength of many biopolymer-derived architectures and their susceptibility to swelling or degradation under extreme pH, salinity, or microbial attack impede their use in continuous-flow systems and necessitate reinforcement or composite fabrication.

Scale-up also presents engineering challenges. Most studies remain at laboratory scale, and the absence of pilot-scale demonstrations means that process parameters (flow rates, packing density, and sorbent lifetime) are not well established. Adsorption processes often struggle to treat large volumes and to handle multi-metal mixtures; competing ions slow uptake and increase retention times. Immobilization strategies can enhance mechanical robustness and enable reuse, but current techniques (e.g., embedding cells on carriers or magnetic nanoparticles) can be costly and are not yet optimized for industrial throughputs. Furthermore, research predominantly uses synthetic or simplified wastewaters; evaluation with real industrial effluents is necessary to assess fouling, sorbent poisoning, and pre-treatment requirements.

In addition to these technical barriers, the field suffers from a lack of systematic quantitative benchmarking across materials. Adsorption capacities, selectivity factors, kinetics, and reusability are frequently reported under non-comparable experimental conditions, including different initial concentrations, pH ranges, ionic strengths, competing ions, and solid-to-liquid ratios. As summarized in Table 7, reported values often originate from synthetic single-metal systems, whereas performance in real

TABLE 7 | Comparison of pristine and modified biopolymers with commercial resins for Cu^{2+} adsorption based on adsorption capacity from aqueous solutions, selectivity, and cost. Costs are approximate bulk prices for raw adsorbent materials (USD per gram) and may vary with grade and supplier. Values are reported as q_{max} under the conditions specified in the cited studies. Selectivity should be interpreted in the context of competitive systems.

	Adsorbent material	Modification	q_{max} (Cu^{2+}) (mg g^{-1})	Cu^{2+} selectivity	Kinetics (min)	Reusability (cycles)	Solution type	Approx. cost (USD g^{-1})	Refs.
Native biopolymer	Cellulose	None (nanoscale fibers)	5.7 (batch)	$>Ni^{2+}$	60-120	—	Synthetic	~0.005	[404, 405]
	Chitosan	None (unmodified)	123 (batch)	—	30-60	—	Synthetic	~0.01	[406, 407]
	Wool keratin	None (unmodified)	11- 58.9 (continuous/batch)	$>Ni^{2+}>Co^{2+}$	60-480	—	Synthetic	~0.012	[408, 409, 397]
	Alginate	Ionically cross-linked (Ca^{2+})	44.6 (batch)	$>Zn^{2+}$	120	—	Synthetic	~0.01	[410, 411]
Modified biopolymer	Cellulose	$-COO^{-}$ functionalization	257.9 (batch)	$>Zn^{2+}$ $>Fe^{3+}>Cd^{2+}$	180	5	Synthetic	~0.0045	[412, 413]
	Chitosan	DETA & amino acids grafted	209.5 (batch)	—	60	6	Synthetic	Not reported	[414]
	Nanocellulose	Oxidized nanocellulose	184.2 (batch)	—	120	4	Synthetic	~0.012	[415]
	Chitosan	Citric acid-modified	312.5 (batch)	$>Fe^{3+}>Pb^{2+}$	420	3	Synthetic	~0.78	[416]
	Alginate–Pectin	Ionic surfactant SDS	823.2-1020 (continuous/batch)	$>Ni^{2+} > Zn^{2+}$	60	10	Synthetic/real effluent	~0.0015	[402]
	Alginate beads	Magnetic biochar encapsulated	234.1 (batch)	$>Cd^{2+}$	180	3	Synthetic	~0.0014–0.0039	[417]
Synthetic resin	Amberlyst 36	Sulfonated cation exchange resin	125.0 (continuous/batch)	$\approx Fe^{3+} \gg$ others	40	Reused (cycles NR)	Synthetic/real leachate	~0.328	[418, 419]
	Dowex G-26	Sulfonated cation exchange resin	41.6 (batch)	—	30	3	Synthetic	~0.047	[420, 421]
	Dowex M-4195	Bis(2-pyridylmethyl)amine group	40.0 (batch)	$>Ni^{2+}\approx Co^{2+}>Pb^{2+}$	1440	—	Synthetic	Not available	[422]
	Amberlite IR 120	Sulfonated cation exchange resin	7 -115 (continuous/batch)	$Zn^{2+}>Ni^{2+}>Cu^{2+}>Cd^{2+}$	14-30	5	Synthetic/real leachate	~0.079	[423–425]
	Amberlite IRC-748	Iminodiacetate chelating group	200 (batch)	$>Zn^{2+}>Fe^{3+}>Cd^{2+}$	60	5	Synthetic	~0.11	[403, 426]

effluents or leachates can differ substantially due to complex speciation and competitive adsorption. The absence of standardized performance indicators and harmonized testing protocols complicates direct comparisons between pristine and modified biopolymers, and between biopolymers and established commercial resins. Without standardized evaluation frameworks that incorporate column testing, multi-cycle stability, and realistic matrices, it remains difficult to identify genuinely application-ready materials. This comparability gap not only obscures true technological progress but also hinders techno-economic assessment, as process design and cost estimation depend critically on reliable, transferable performance metrics.

Beyond these engineering constraints, systematic quantitative benchmarking remains a critical need for application-driven development. Although numerous adsorption capacities, selectivity trends, kinetic data, and reusability cycles are reported in the literature, these metrics are often obtained under disparate experimental conditions, limiting direct comparability. To address this, Table 7 compiles representative pristine and modified biopolymers alongside commercial resins, explicitly indicating adsorption capacity, selectivity, kinetic ranges, reusability, and solution type. Where possible, values are distinguished between synthetic model solutions and real or leachate-based matrices, as performance can differ substantially due to complex speciation, competing ions, and fouling effects. Nevertheless, the lack of normalized testing protocols, such as standardized initial concentrations, ionic strengths, column conditions, and cycling criteria, continues to complicate cross-material evaluation. Without harmonized benchmarking frameworks and clearer reporting of operating conditions, it remains challenging to identify truly application-ready materials or to rationally compare emerging biopolymers with established ion-exchange resins. This interpretability gap ultimately constrains reliable process design and underscores the importance of integrating quantitative performance metrics with techno-economic considerations.

7.2 | Economic Viability

Economically, the application of biopolymers in metal recovery-related applications faces a dual-edged sword. In principle, a sorbent made from abundant biomass could cost orders of magnitude less than a specialty synthetic resin. Indeed, many biopolymers are essentially agricultural or industrial waste, available at a marginal price. This gives them a significant cost advantage if minimal processing is required. Yet the extensive processing required to match the performance of synthetic materials can erode this edge. However, in scenarios targeting high-value metals (e.g., platinum group metals or rare earths), the economics shift favorably, transforming biopolymers from mere waste treatment tools into profitable platforms for resource recovery. A direct comparison between biopolymer-based adsorbents and conventional synthetic resins reveals both their progress and remaining gaps. Table 7 compiles data on maximum Cu^{2+} adsorption capacity, selectivity, and cost per gram of several sorbents: pristine biopolymers, chemically modified biopolymers, and benchmark commercial resins. The trends indicate that pristine biopolymers, while having lower metal uptakes, are extremely cheap and environmentally benign, making them suitable for large-volume, low-cost applications, especially when interaction with a specific metal is not the target (e.g., heavy metal removal from wastewater or acid mine drainage). For instance, raw chitosan, keratin, or alginate material might only bind on the order of a few tens of milligrams of Cu^{2+} per gram in unaltered form, but it costs very little and requires no chemical treatment, a compelling trade-off for situations where ultra-high capacity is not critical. In contrast, modified biopolymers (those augmented with extra functional groups or composite structures) show markedly higher capacities and metal specificity, often rivaling or even exceeding commercial ion-exchange resins (Table 7). Additionally, modified biopolymers generally exhibit excellent performance-to-cost ratios. Even when their adsorption capacities rival or exceed those of synthetic resins, their ingredient costs remain low. As a concrete example, Sireesha and Sreedhar [402] developed a biochar–alginate–pectin composite bead with an impressive Cu^{2+} adsorption capacity of ∼937.4 mg g^{-1}. This is nearly an order of magnitude higher than many conventional biosorbents. It notably outperforms the standard iminodiacetate resin Amberlite IRC-748, which has a Cu uptake of ∼250–300 mg g^{-1} under similar conditions [403]. The composite's production cost was only ∼$1.51/kg (∼0.0015 USD/g), due to the use of low-cost agricultural biochar and polysaccharides. In contrast, commercial resins like Amberlite cost $110/kg and rely on petrochemical feedstocks [403]. Similarly, carboxymethyl cellulose/alginate beads, with Cu^{2+} capacities similar to Amberlite (∼286 mg g^{-1}), can be produced at a fraction of the cost [402], revealing their economic potential. That said, commercial resins still outperform in many respects. The compiled data indicate that commercial resins remain more selective for Cu^{2+} over competing ions, thanks to decades of optimization in ligand density, porosity, and cross-linking. They also exhibit superior durability across tens of use cycles, an aspect where many biopolymers are not extensively tested. Biopolymer performance is advancing rapidly, and with targeted modification strategies, these materials may approach or exceed synthetic resins in capacity and selectivity. While commercial resins currently hold a lead in fine-tuned performance, biopolymer adsorbents are closing the gap and offer compelling advantages in cost and environmental impact.

8 | Critical Perspective

Bio-based polymers, such as cellulose, chitin, lignin, keratin, collagen, and alginates, are promising platforms for metal capture because they pair abundant renewable feedstocks with metal-binding motifs (hydroxyl, carboxyl, amine, thiol, and phenolic). Their chemical structures can be systematically engineered through covalent modification, cross-linking, and control of form factors (e.g., beads, fibers, membranes, and monoliths) to tune adsorption selectivity, capacity, kinetics, and mechanical stability across applications ranging from wastewater polishing to the recovery of precious and rare-earth metals from complex leachates. Industrial performance of these materials is governed by a coupled structure–function–process relationship, where binding chemistry (donor atom type and ligand density), material architecture (porosity, cross-link density, and swelling behavior), and operating chemistry (pH, ionic strength, and metal speciation) collectively determine site accessibility, adsorption selectivity, and mass-transfer behavior under realistic process conditions. Despite these advantages, the transition from laboratory promise to industrial implementation remains constrained by six interconnected challenges:

i. Material consistency and specification control remain fundamental barriers to translation. Natural feedstocks exhibit intrinsic variability in molecular weight distribution, chemical composition, functional group density, crystallinity, ash content, and impurity profiles. This batch-to-batch variability propagates into adsorption performance and complicates reproducibility, particularly in regulated sectors where guaranteed specifications are mandatory. Translation will therefore require standardized preprocessing, clear physicochemical descriptors, and quality-control metrics that quantitatively link polymer structure and surface chemistry to adsorption performance. Without such specification-driven frameworks, low-cost biomass cannot reliably yield low-cost sorbents with reproducible behavior.

ii. Operational stability under realistic conditions presents an equally critical constraint. Many native or lightly modified biopolymers lose capacity in aggressive environments characterized by strong acidity, oxidants, or high ionic strength, where conventional petrochemical ion-exchange resins remain robust. These limitations often originate from intrinsic polymer chemistry. For instance, chitosan becomes soluble under acidic conditions due to protonation of amine groups, alginate gels may destabilize when chelating agents remove cross-linking ions, and cellulose can undergo acid-catalyzed hydrolysis of glycosidic bonds, progressively weakening the polymer structure. While ligand grafting, cross-linking, and templated porosity can enhance selectivity and chemical resistance, these modifications introduce synthetic complexity, potential leachable compounds, and added cost. Long-term chemical and mechanical stability under cyclic adsorption–desorption conditions, particularly in continuous-flow systems, remains insufficiently demonstrated. Stability assessment must therefore extend beyond equilibrium batch tests to include breakthrough behavior, competitive ion effects, swelling and attrition resistance, and multi-cycle durability under realistic speciation conditions.

iii. Process integration and regeneration performance ultimately determine industrial relevance. Adsorption efficiency alone does not define industrial viability. Sorbents must exhibit low pressure drop, limited swelling, resistance to attrition, and predictable mass-transfer behavior in packed or structured beds. Recent studies highlight the importance of evaluating materials under continuous-flow conditions. For example, functionalized biopolymer aerogel beads have been tested in fixed-bed columns with breakthrough curves described using the Thomas model and regenerated using citric acid eluents [427]. Similarly, alginate-based composite beads have been investigated for La(III) recovery in fixed-bed columns, demonstrating stable breakthrough performance and efficient desorption using 1 M HCl with high recovery yields [428]. Regeneration strategies must deliver concentrated eluates with minimal reagent consumption and limited capacity decay across cycles. In many reported systems, regeneration chemistry becomes the dominant operational cost or source of secondary waste. Designing sorbents and regeneration protocols as a coupled system is therefore essential. Future development of biopolymer-based adsorbents should prioritize modification strategies that balance selectivity gains with economic viability and environmental footprint, favoring low-toxicity reagents, solvent recycling, and scalable processing routes compatible with industrial deployment.

iv. Economic and environmental realism must accompany material innovation. Although biomass precursors are inexpensive, the total cost of ownership is governed by processing, shaping, activation, service life, regeneration efficiency, and end-of-life management. Energy-intensive fabrication routes such as electrospinning or supercritical drying, as well as harsh functionalization chemistries, can negate sustainability advantages. The business case is strengthened in high-value streams, particularly when materials maintain performance over multiple adsorption–desorption cycles with minimal capacity loss and low eluate volumes, yielding concentrated metal products. Early integration of techno-economic analysis (TEA) and life-cycle assessment (LCA) with process-level inventories is critical to prevent the field from optimizing performance metrics that are economically or environmentally irrelevant at scale. Indeed, techno-economic studies comparing chitosan-derived sorbents with commercial ion-exchange resins show that regeneration efficiency and sorbent lifetime often dominate the overall treatment cost [429], emphasizing the need to evaluate adsorption performance together with process economics.

v. Mechanistic understanding and standardized benchmarking represent additional structural weaknesses in the field. A further limitation of the field is the predominance of equilibrium capacity metrics and simplified model fits, often obtained in single-metal synthetic systems. In hydrometallurgical contexts, metal speciation, complexation equilibria, and competitive adsorption fundamentally govern selectivity and kinetics. Mechanism-driven design, supported by advanced characterization, speciation analysis, and structure–function correlations, should replace purely empirical screening approaches and be supported by direct evidence linking functional groups to metal binding. In parallel, the absence of harmonized testing protocols (pH control, ionic strength, competing ions, cycling criteria, and column testing standards) hinders rational benchmarking and obscures meaningful comparison with commercial ion-exchange resins. Beyond equilibrium capacity, studies should therefore report dynamic metrics such as breakthrough capacity, mass-transfer behavior, regeneration efficiency, and multi-cycle stability under realistic solution conditions [430].

vi. Positioning against mature technologies further defines the adoption landscape. Biopolymer-based sorbents are not entering an empty landscape; they compete with decades-optimized synthetic resins that offer proven durability, well-characterized regeneration chemistry, and established supply chains. Industrial adoption will therefore depend not on achieving marginally higher laboratory capacities, but on demonstrating reproducibility, durability, and process compatibility under conditions where conventional materials already perform reliably.

Regulatory acceptance and market adoption further depend on validated pilot-scale data, low extractables, long-term stability, and secure feedstock supply chains. Policy drivers supporting critical raw material recovery and low-carbon technologies create strong incentives, but industrial deployment will favor materials that combine reproducibility, durability, and straightforward processing over maximal laboratory capacities.

Progress will hinge on coordinated advances that connect molecular design to process performance:

i. discovery and integration of metal-specific ligands that remain active in acidic, basic, or saline media;
ii. scalable modification routes that minimize toxic reagents and leachable species;
iii. architectures that balance hierarchical porosity with mechanical integrity and low hydraulic resistance;
iv. durable regeneration using benign eluents that deliver high-purity concentrates and enable multiple reuse cycles; and
v. standardized testing protocols linking molecular design to column-scale performance, supported by integrated TEA and LCA at early development stages.

Through targeted research and process-aware engineering, biopolymer-based sorbents can become both efficient and economically competitive with commercial resins, positioning them to approach or rival the performance of established synthetic resins in capacity, selectivity, and reusability, while delivering verifiable sustainability gains.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analysed during the current study

References

1. H. Ding, S. Yuan, S. Lei, W. Wang, G. Wen, and Z. Dong, "Technology and Principle on Preferentially Selective Lithium Extraction for Spent Ternary Lithium Batteries: a Review," *Separation and Purification Technology* 355 (2025): 129691, https://doi.org/10.1016/j.seppur.2024.129691.

2. S. Gulliani, M. Volpe, A. Messineo, and R. Volpe, "Recovery of Metals and Valuable Chemicals from Waste Electric and Electronic Materials: A Critical Review of Existing Technologies," *RSC Sustain* 1, no. 5 (2023): 1085–1108, https://doi.org/10.1039/D3SU00034.

3. J. Yan, J. Wei, F. Zhang, et al., "Comprehensive Review on Recovery of Platinum Group Metals from Spent Automotive Catalysts by Metal Capture Technology: Present Progress and Outlook," *Journal of Environmental Chemical Engineering* 12, no. 5 (2024): 114017, https://doi.org/10.1016/j.jece.2024.114017.

4. N. A. A. Qasem, R. H. Mohammed, and D. U. Lawal, "Removal of Heavy Metal Ions from Wastewater: A Comprehensive and Critical Review," *Npj Clean Water* 4, no. 1 (2021): 36, https://doi.org/10.1038/s41545-021-00127-0.

5. S. R. Dhokpande, S. M. Deshmukh, A. Khandekar, and A. Sankhe, "A Review Outlook on Methods for Removal of Heavy Metal Ions from Wastewater," *Separation and Purification Technology* 350 (2024): 127868, https://doi.org/10.1016/j.seppur.2024.127868.

6. A. Sieber, S. Spiess, W. Y. Rassy, et al., "Fundamentals of Bio-Based Technologies for Selective Metal Recovery from Bio-Leachates and Liquid Waste Streams," *Frontiers in Bioengineering and Biotechnology* 12 (2025): 1528992, https://doi.org/10.3389/fbioe.2024.1528992.

7. P. R. Yaashikaa, J. Palanivelu, and R. V. Hemavathy, "Sustainable Approaches for Removing Toxic Heavy Metal from Contaminated Water: A Comprehensive Review of Bioremediation and Biosorption Techniques," *Chemosphere* 357 (2024): 141933, https://doi.org/10.1016/j.chemosphere.2024.141933.

8. J. R. Dodson, H. L. Parker, A. Muñoz García, et al., "Bio-Derived Materials as a Green Route for Precious & Critical Metal Recovery and Re-Use," *Green Chemistry* 17, no. 4 (2015): 1951–1965, https://doi.org/10.1039/C4GC02483D.

9. A. Nobahar, E. T. Fitas, M. C. Costa, and J. D. Carlier, "Acid Mine Drainage Bioremediation Using Bacteria Enriched from the Confluence Zone between Its Flow and Treated Sewage," *International Journal of Environmental Science and Technology* 22 (2024): 7487–7506, https://doi.org/10.1007/s13762-024-06160-z.

10. A. Nobahar, J. D. Carlier, and M. C. Costa, "Recovery of Catalytic Metals from Leaching Solutions of Spent Automotive Catalytic Converters Using Plant Extracts," *Clean Technologies and Environmental Policy* 25 (2023): 2707–2726, https://doi.org/10.1007/s10098-023-02523-1.

11. E. Khademian, E. Salehi, H. Sanaeepur, F. Galiano, and A. Figoli, "A Systematic Review on Carbohydrate Biopolymers for Adsorptive Remediation of Copper Ions from Aqueous Environments-Part A: Classification and Modification Strategies," *Science of The Total Environment* 738 (2020): 139829, https://doi.org/10.1016/j.scitotenv.2020.139829.

12. C. Zhao, G. Liu, Q. Tan, et al., "Polysaccharide-Based Biopolymer Hydrogels for Heavy Metal Detection and Adsorption," *Journal of Advanced Research* 44 (2023): 53–70, https://doi.org/10.1016/j.jare.2022.04.005.

13. B. G. Fouda-Mbanga, E. Prabakaran, and K. Pillay, "Carbohydrate Biopolymers, Lignin Based Adsorbents for Removal of Heavy Metals (Cd^{2+}, Pb^{2+}, Zn^{2+}) from Wastewater, Regeneration and Reuse for Spent Adsorbents Including Latent Fingerprint Detection: a Review," *Biotechnol Rep* 30 (2021): e00609, https://doi.org/10.1016/j.btre.2021.e00609.

14. X. Liang, S. Guo, X. Kuang, et al., "Recent Advancements and Perspectives on Processable Natural Biopolymers: Cellulose, Chitosan, Eggshell Membrane, and Silk Fibroin," *Science Bulletin* 69, no. 21 (2024): 3444–3466, https://doi.org/10.1016/j.scib.2024.08.023.

15. D. Park, Y.-S. Yun, and J. M. Park, "The Past, Present, and Future Trends of Biosorption," *Biotechnology and Bioprocess Engineering* 15, no. 1 (2010): 86–102, https://doi.org/10.1007/s12257-009-0199-4.

16. A. Nobahar, J. P. Lourenço, M. C. Costa, and J. D. Carlier, "Printed Circuit Boards Leaching Followed by Synthesis of Gold Nanoparticle Clusters Using Plant Extracts. Waste Biomass Valorization," 15, no. 4 (2024): 1999–2017, https://doi.org/10.1007/s12649-023-02272-8.

17. B. B. Kassie, T. M. Daget, and D. F. Tassew, "Synthesis, Functionalization, and Commercial Application of Cellulose-Based Nanomaterials," *International Journal of Biological Macromolecules* 278 (2024): 134990, https://doi.org/10.1016/j.ijbiomac.2024.134990.

18. O. F. Vilpoux and J. F. S. S. Junior, "Global Production and Use of Starch," in *Starchy Crops Morphology, Extraction, Properties and Applications* (Elsevier, 2023), pp. 43–66, https://doi.org/10.1016/B978-0-323-90058-4.00014-1.

19. ChemAnalyst. "Pectin Market Analysis: Industry Market Size, Plant Capacity, Production, Operating Efficiency, Demand & Supply Gap, End-User Industries, Sales Channel, Regional Demand, Company Share, Manufacturing Process, 2015-2034 [online]," *ChemAnalyst* (accessed 2026), https://www.chemanalyst.com/industry-report/pectin-market-3147.

20. S. Saji, A. Hebden, P. Goswami, and C. Du, "A Brief Review on the Development of Alginate Extraction Process and Its Sustainability," *Sustainability* 14, no. 9 (2022): 5181, https://doi.org/10.3390/su14095181.

21. Grand View Research, "Xanthan Gum Market 2024 - 2030 Size, Share & Trends Analysis Report By Application (Oil & Gas, Food & Beverage, Pharmaceutical, Cosmetics), By Region (North America, Europe, APAC, CSA, MEA), And Segment Forecasts," accessed July 2, 2025, https://www.grandviewresearch.com/industry-analysis/xanthan-gum-market.

22. J. Weng, A. Durand, and S. Desobry, "Chitosan-Based Particulate Carriers: Structure, Production and Corresponding Controlled Release," *Pharmaceutics* 15, no. 5 (2023): 1455, https://doi.org/10.3390/pharmaceutics15051455.

23. R. Shukla and M. Cheryan, "Zein: the Industrial Protein from Corn," *Industrial Crops and Products* 13, no. 3 (2001): 171–192, https://doi.org/10.1016/S0926-6690(00)00064-9.

24. O. Erenstein, M. Jaleta, K. Sonder, K. Mottaleb, and B. M. Prasanna, "Global Maize Production, Consumption and Trade: Trends and R&D Implications," *Food Secur* 14, no. 5 (2022): 1295–1319, https://doi.org/10.1007/s12571-022-01288-7.

25. B. Guo, L. Sun, S. Jiang, et al., "Soybean Genetic Resources Contributing to Sustainable Protein Production," *Theoretical and Applied Genetics* 135, no. 11 (2022): 4095–4121, https://doi.org/10.1007/s00122-022-04222-9.

26. S. Perța-Crișan, U. C. Ștefan, S. Gavrilaș, F. Oancea, and F.-D. Munteanu, "Closing the Loop with Keratin-Rich Fibrous Materials," *Polymers* 13, no. 11 (2021): 1896, https://doi.org/10.3390/polym13111896.

27. I. Group, "End Use (Food and Beverages, Pharmaceuticals, Cosmetics, Industrial, and Others), and Region 2025-2033," in *Casein Market Report by Product Type (Rennet Casein, Acid Casein)* (IMARC Group, 2024), https://www.imarcgroup.com/casein-market.

28. H. Y. Lim, S. Yusup, A. C. M. Loy, et al., "Review on Conversion of Lignin Waste into Value-Added Resources in Tropical Countries," *Waste Biomass Valorization* 12, no. 10 (2021): 5285–5302, https://doi.org/10.1007/s12649-020-01307-8.

29. M. Pagliaro, L. Albanese, A. Scurria, F. Zabini, F. Meneguzzo, and R. Ciriminna, "Tannin: a New Insight into a Key Product for the Bioeconomy in Forest Regions," *Biofuels, Bioproducts and Biorefining* 15, no. 4 (2021): 973–979, https://doi.org/10.1002/bbb.2217.

30. O. Jawhid, N. Seyedi, G. H. Zohuri, and N. Ramezanian, "Cellulose Schiff Base as a Bio-Based Polymer Ligand: Extraction, Modification and Metal Adsorption Study," *Journal of Polymers and the Environment* 29, no. 6 (2021): 1860–1868, https://doi.org/10.1007/s10924-020-02002-4.

31. G. Riyamol, J. Chengaiyan, S. S. Rana, F. Ahmad, S. Haque, and E. Capanoglu, "Recent Advances in the Extraction of Pectin from Various Sources and Industrial Applications," *ACS Omega* 8, no. 49 (2023): 46309–46324, https://doi.org/10.1021/acsomega.3c04010.

32. S. Saha, M. Zubair, M. A. Khosa, S. Song, and A. Ullah, "Keratin and Chitosan Biosorbents for Wastewater Treatment: a Review," *Journal of Polymers and the Environment* 27, no. 7 (2019): 1389–1403, https://doi.org/10.1007/s10924-019-01439-6.

33. S. Abdelkrim, A. Mokhtar, M. Hachemaoui, et al., "Divalent Cations@Carboxyl Groups Binding in the Alginate Complex: Density Functional Theory Approach," *Journal of Inorganic and Organometallic Polymers and Materials* (2024), https://doi.org/10.1007/s10904-024-03273-3.

34. L. Habasescu, M. Jureschi, B.-A. Petre, et al., "Histidine-Lacked Aβ(1–16) Peptides: PH-Dependent Conformational Changes in Metal Ion Binding," *International Journal of Peptide Research and Therapeutics* 26, no. 4 (2020): 2529–2546, https://doi.org/10.1007/s10989-020-10048-0.

35. M. S. Masri and M. Friedman, "Interactions of Keratins with Metal Ions: Uptake Profiles, Mode of Binding, and Effects on Properties of Wool," in *Protein-Metal Interactions*, (Ed: M. Friedman) (Springer New York, 1974), 551–587, https://doi.org/10.1007/978-1-4684-0943-7_24.

36. C. Fitz-Binder, T. Pham, and T. Bechtold, "A Second Life for Low-Grade Wool through Formation of All-Keratin Composites in Cystine Reducing Calcium Chloride–Water–Ethanol Solution," *Journal of Chemical Technology & Biotechnology* 94, no. 10 (2019): 3384–3392, https://doi.org/10.1002/jctb.6151.

37. N. R. Perron and J. L. Brumaghim, "A Review of the Antioxidant Mechanisms of Polyphenol Compounds Related to Iron Binding," *Cell Biochemistry and Biophysics* 53, no. 2 (2009): 75–100, https://doi.org/10.1007/s12013-009-9043-x.

38. R. Garcia-Valls and T. A. Hatton, "Metal Ion Complexation with Lignin Derivatives," *Chemical Engineering Journal* 94, no. 2 (2003): 99–105, https://doi.org/10.1016/S1385-8947(03)00007-X.

39. M. Huang, J. Guo, P. Zhou, et al., "Lignin-Coordination-Guided Fabrication of Well-Dispersed Metallic-Nitrogen-Carbon Catalysts to Enable Efficient Fenton-Like Chemistry," *Industrial Crops and Products* 222 (2024): 120060, https://doi.org/10.1016/j.indcrop.2024.120060.

40. A. R. F. Carreira, A. F. M. Nogueira, I. L. D. Rocha, et al., "Repurposing Kraft Black Liquor as Reductant for Enhanced Lithium-Ion Battery Leaching," *ChemSusChem* 17, no. 12 (2024): 202301801, https://doi.org/10.1002/cssc.202301801.

41. X. Guan, B. Zhang, Z. Wang, et al., "Natural Polyphenol Tannin-Immobilized Composites: Rational Design and Versatile Applications," *Journal of Materials Chemistry B* 11, no. 21 (2023): 4619–4660, https://doi.org/10.1039/D3TB00661A.

42. A. N. Ghanim, "Utilization of Date Pits Derived Bio-Adsorbent for Heavy Metals in Wastewater Treatment: Review," *Al-Qadisiyah J Eng Sci* 16, no. 1 (2023): 58–69, https://doi.org/10.30772/qjes.v16i1.910.

43. R. Wang, R. Liang, T. Dai, J. Chen, X. Shuai, and C. Liu, "Pectin-based Adsorbents for Heavy Metal Ions: a Review," *Trends in Food Science & Technology* 91 (2019): 319–329, https://doi.org/10.1016/j.tifs.2019.07.033.

44. S. Rashid, C. Shen, J. Yang, J. Liu, and J. Li, "Preparation and Properties of Chitosan–metal Complex: some Factors Influencing the Adsorption Capacity for Dyes in Aqueous Solution," *Journal of Environmental Sciences* 66 (2018): 301–309, https://doi.org/10.1016/j.jes.2017.04.033.

45. A. Caubet, V. Moreno, E. Molins, and C. Miravitlles, "Methionine and Histidine Pd(II) and Pt(II) Complexes: Crystal Structures and Spectroscopic Properties," *Journal of Inorganic Biochemistry* 48, no. 2 (1992): 135–152, https://doi.org/10.1016/0162-0134(92)80023-O.

46. N. M. Giles, A. B. Watts, G. I. Giles, F. H. Fry, J. A. Littlechild, and C. Jacob, "Metal and Redox Modulation of Cysteine Protein Function," *Chemistry & Biology* 10, no. 8 (2003): 677–693, https://doi.org/10.1016/S1074-5521(03)00174-1.

47. M. Nikoorazm, P. Moradi, N. Noori, and G. Azadi, "l-Arginine Complex of Copper on Modified Core–shell Magnetic Nanoparticles as Reusable and Organic–inorganic Hybrid Nanocatalyst for the Chemoselective Oxidation of Organosulfur Compounds," *Journal of the Iranian Chemical Society* 18, no. 2 (2021): 467–478, https://doi.org/10.1007/s13738-020-02040-8.

48. V. Chobot and F. Hadacek, “Iron and Its Complexation by Phenolic Cellular Metabolites,” *Plant Signaling & Behavior* 5, no. 1 (2010): 4–8, https://doi.org/10.4161/psb.5.1.10197.

49. L. McAfee, “Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry,” *Journal of Chemical Education* 77, no. 9 (2000): 1122, https://doi.org/10.1021/ed077p1122.1.

50. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, and R. S. C. Smart, “Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni,” *Applied Surface Science* 257, no. 7 (2011): 2717–2730, https://doi.org/10.1016/j.apsusc.2010.10.051.

51. A. I. Petrov, “Experimental and DFT Study of the Kinetics of the Interaction of Pt(II) and Pd(II) with Disulfides in Hydrochloric Acid Solutions,” *Inorganica Chimica Acta* 545 (2023): 121269, https://doi.org/10.1016/j.ica.2022.121269.

52. C. R. Chilakamarry, S. Mahmood, S. Saffe, et al., “Extraction and Application of Keratin from Natural Resources: a Review,” *3 Biotech* 11, no. 5 (2021): 220, https://doi.org/10.1007/s13205-021-02734-7.

53. K. Prasad and M. Sharma, “Green Solvents for the Dissolution and Processing of Biopolymers,” *Current Opinion in Green and Sustainable Chemistry* 18 (2019): 72–78, https://doi.org/10.1016/j.cogsc.2019.02.005.

54. M. A. R. Martins, F. H. B. Sosa, I. Kilpeläinen, and J. A. P. Coutinho, “Physico-Chemical Characterization of Aqueous Solutions of Superbase Ionic Liquids with Cellulose Dissolution Capability,” *Fluid Phase Equilibria* 556 (2022): 113414, https://doi.org/10.1016/j.fluid.2022.113414.

55. H. Wang, G. Gurau, and R. D. Rogers, “Ionic Liquid Processing of Cellulose,” *Chemical Society Reviews* 41, no. 4 (2012): 1519–1537, https://doi.org/10.1039/c2cs15311d.

56. I. Kilpeläinen, H. Xie, A. King, M. Granstrom, S. Heikkinen, and D. S. Argyropoulos, “Dissolution of Wood in Ionic Liquids,” *Journal of Agricultural and Food Chemistry* 55, no. 22 (2007): 9142–9148, https://doi.org/10.1021/jf071692e.

57. K.-J. Xu, B.-Q. Zhang, X. Qiao, and C.-Y. Liu, “Cellulose Solubility in Deep Eutectic Solvents: Inspecting Quantitative Hydrogen-Bonding Analysis,” *Chinese Journal of Polymer Science* 41, no. 1 (2023): 75–83, https://doi.org/10.1007/s10118-022-2801-6.

58. K. K. Puss, M. Loog, and S. Salmar, “Ultrasound Enhanced Solubilization of Forest Biorefinery Hydrolysis Lignin in Mild Alkaline Conditions,” *Ultrasonics Sonochemistry* 93 (2023): 106288, https://doi.org/10.1016/j.ultsonch.2022.106288.

59. F. H. B. Sosa, D. O. Abranches, A. M. D. C. Lopes, M. C. Da Costa, and J. A. P. Coutinho, “Role of Deep Eutectic Solvent Precursors as Hydrotropes: Unveiling Synergism/Antagonism for Enhanced Kraft Lignin Dissolution,” *ACS Sustainable Chemistry & Engineering* 12, no. 23 (2024): 8930–8940, https://doi.org/10.1021/acssuschemeng.4c02529.

60. D. Raikwar, K. Van Aelst, T. Vangeel, et al., “Elucidating the Effect of the Physicochemical Properties of Organosolv Lignins on Its Solubility and Reductive Catalytic Depolymerization,” *Chemical Engineering Journal* 461 (2023): 141999, https://doi.org/10.1016/j.cej.2023.141999.

61. C. Polesca, A. Al Ghatta, H. Passos, J. A. P. Coutinho, J. P. Hallett, and M. G. Freire, “Sustainable Keratin Recovery Process Using a Bio-Based Ionic Liquid Aqueous Solution and Its Techno-Economic Assessment,” *Green Chemistry* 25, no. 10 (2023): 3995–4003, https://doi.org/10.1039/D3GC00850A.

62. N. Zhang, Z. Wu, Z. Jiang, et al., “pH Mediated L-Cysteine Aqueous Solution for Wool Reduction and Urea-Free Keratin Extraction,” *Journal of Polymers and the Environment* 30, no. 7 (2022): 2714–2726, https://doi.org/10.1007/s10924-022-02383-8.

63. M. Dąbrowska, A. Sommer, I. Sinkiewicz, A. Taraszkiewicz, and H. Staroszczyk, “An Optimal Designed Experiment for the Alkaline Hydrolysis of Feather Keratin,” *Environmental Science and Pollution Research* 29, no. 16 (2022): 24145–24154, https://doi.org/10.1007/s11356-021-17649-2.

64. L. Alves, B. Medronho, F. E. Antunes, D. Topgaard, and B. Lindman, “Dissolution state of Cellulose in Aqueous Systems. 2. Acidic Solvents,” *Carbohydrate Polymers* 151 (2016): 707–715, https://doi.org/10.1016/j.carbpol.2016.06.015.

65. J. Cai and L. Zhang, “Rapid Dissolution of Cellulose in LiOH/Urea and NaOH/Urea Aqueous Solutions,” *Macromolecular Bioscience* 5, no. 6 (2005): 539–548, https://doi.org/10.1002/mabi.200400222.

66. R. P. Swatloski, S. K. Spear, J. D. Holbrey, and R. D. Rogers, “Dissolution of Cellose with Ionic Liquids,” *Journal of the American Chemical Society* 124, no. 18 (2002): 4974–4975, https://doi.org/10.1021/ja025790m.

67. I. Bodachivskyi, C. J. Page, U. Kuzhiumparambil, S. F. R. Hinkley, I. M. Sims, and D. B. G. Williams, “Dissolution of Cellulose: Are Ionic Liquids Innocent or Noninnocent Solvents?,” *ACS Sustainable Chemistry & Engineering* 8, no. 27 (2020): 10142–10150, https://doi.org/10.1021/acssuschemeng.0c02204.

68. N. Taheri, A. Abdolmaleki, and H. Fashandi, “Pyridinium-Based Ionic Liquid/Water Mixture Intended for Efficient Dissolution of Cellulose, Chitosan and Chitin: the Pivotal Contribution of Water,” *Carbohydrate Polymers* 195 (2018): 413–419, https://doi.org/10.1016/j.carbpol.2018.04.123.

69. P. Mäki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm, and J. P. Mikkola, “Dissolution of Lignocellulosic Materials and Its Constituents Using Ionic Liquids—A Review,” *Industrial Crops and Products* 32, no. 3 (2010): 175–201, https://doi.org/10.1016/j.indcrop.2010.04.005.

70. Y.-L. Chen, X. Zhang, T.-T. You, and F. Xu, “Deep Eutectic Solvents (DESs) for Cellulose Dissolution: a Mini-Review,” *Cellulose* 26, no. 1 (2019): 205–213, https://doi.org/10.1007/s10570-018-2130-7.

71. Z. Tong, J. Meng, S. Liu, et al., “Room Temperature Dissolving Cellulose with a Metal Salt Hydrate-Based Deep Eutectic Solvent,” *Carbohydrate Polymers* 272 (2021): 118473, https://doi.org/10.1016/j.carbpol.2021.118473.

72. M. Sawiak, B. Souto, L. Lawson, J. Lo, and P. Dolez, “Recovery of N-Methylmorpholine N-Oxide (NMMO) in Lyocell Fibre Manufacturing Process,” *Fibers* 13, no. 1 (2025): 3, https://doi.org/10.3390/fib13010003.

73. A. M. Striegel, “Advances in The Understanding of The Dissolution Mechanism of Cellulose In DMAc/LiCl,” *Journal of the Chilean Chemical Society* 48, no. 1 (2003), https://doi.org/10.4067/S0717-97072003000100013.

74. A. Isogai, “Emerging Nanocellulose Technologies: Recent Developments,” *Advanced Materials* 33, no. 28 (2021): 2000630, https://doi.org/10.1002/adma.202000630.

75. Y. J. Dias, A. Kolbasov, S. Sinha-Ray, B. Pourdeyhimi, and A. L. Yarin, “Theoretical and Experimental Study of Dissolution Mechanism of Cellulose,” *Journal of Molecular Liquids* 312 (2020): 113450, https://doi.org/10.1016/j.molliq.2020.113450.

76. D. Sikorski, K. Gzyra-Jagieła, and Z. Draczyński, “The Kinetics of Chitosan Degradation in Organic Acid Solutions,” *Mar Drugs* 19, no. 5 (2021): 236, https://doi.org/10.3390/md19050236.

77. W. Zhang and W. Xia, “Dissolution and Stability of Chitosan in a Sodium Hydroxide/Urea Aqueous Solution,” *Journal of Applied Polymer Science* 131, no. 3 (2014): app39819, https://doi.org/10.1002/app.39819.

78. L. Zhuang, F. Zhong, M. Qin, et al., “Theoretical and Experimental Studies of Ionic Liquid-Urea Mixtures on Chitosan Dissolution: Effect of Cationic Structure,” *Journal of Molecular Liquids* 317 (2020): 113918, https://doi.org/10.1016/j.molliq.2020.113918.

79. J. C. Roy, F. Salaün, S. Giraud, A. Ferri, G. Chen, and J. Guan, “Solubility of Chitin: Solvents, Solution Behaviors and Their Related Mechanisms,” in *Solubility of Polysaccharides*, ed. Z. Xu (InTech, 2017), https://doi.org/10.5772/intechopen.71385.

80. B. Ma, A. Qin, X. Li, and C. He, “High Tenacity Regenerated Chitosan Fibers Prepared by Using the Binary Ionic Liquid Solvent

(Gly·HCl)-[Bmim]Cl," *Carbohydrate Polymers* 97, no. 2 (2013): 300–305, https://doi.org/10.1016/j.carbpol.2013.04.080.

81. N. Özel and M. Elibol, "A Review on the Potential Uses of Deep Eutectic Solvents in Chitin and Chitosan Related Processes," *Carbohydrate Polymers* 262 (2021): 117942, https://doi.org/10.1016/j.carbpol.2021.117942.

82. D.-S. DA, I. Fraile-Gutiérrez, R. Gil-Gonzalo, N. Acosta, I. Aranaz, and A. R. Alcántara, "Strategies to Prepare Chitin and Chitosan-Based Bioactive Structures Aided by Deep Eutectic Solvents: a Review," *Catalysts* 14, no. 6 (2024): 371, https://doi.org/10.3390/catal14060371.

83. C. P. Jiménez-Gómez and J. A. Cecilia, "Chitosan: a Natural Biopolymer with a Wide and Varied Range of Applications," *Molecules (Basel, Switzerland)* 25, no. 17 (2025): 3981, https://doi.org/10.3390/molecules25173981.

84. A. V. Ilyina, V. E. Tikhonov, A. I. Albulov, and V. P. Varlamov, "Enzymic Preparation of Acid-Free-Water-Soluble Chitosan," *Process Biochemistry* 35, no. 6 (2000): 563–568, https://doi.org/10.1016/S0032-9592(99)00104-1.

85. A. Aluigi, M. Zoccola, C. Vineis, C. Tonin, F. Ferrero, and M. Canetti, "Study on the Structure and Properties of Wool Keratin Regenerated from Formic Acid," *International Journal of Biological Macromolecules* 41, no. 3 (2007): 266–273, https://doi.org/10.1016/j.ijbiomac.2007.03.002.

86. A. J. Poole, R. E. Lyons, and J. S. Church, "Dissolving Feather Keratin Using Sodium Sulfide for Bio-Polymer Applications," *Journal of Polymers and the Environment* 19, no. 4 (2011): 995–1004, https://doi.org/10.1007/s10924-011-0365-6.

87. Y. Ji, J. Chen, J. Lv, Z. Li, L. Xing, and S. Ding, "Extraction of Keratin with Ionic Liquids from Poultry Feather," *Separation and Purification Technology* 132 (2014): 577–583, https://doi.org/10.1016/j.seppur.2014.05.049.

88. J. Wang, H. Gao, C. Qin, et al., "Experimental and Theoretical Study on the Extraction of Keratin from human Hair Using Protic Ionic Liquids," *Journal of Molecular Liquids* 368 (2022): 120626, https://doi.org/10.1016/j.molliq.2022.120626.

89. C. Qin, H. Gao, X. Liu, et al., "The Dissolution of human Hair Using Ionic Liquids through COSMO-RS Predication and Experimental Verification," *Journal of Molecular Liquids* 349 (2022): 118094, https://doi.org/10.1016/j.molliq.2021.118094.

90. A. Idris, R. Vijayaraghavan, U. A. Rana, D. Fredericks, A. F. Patti, and D. R. MacFarlane, "Dissolution of Feather Keratin in Ionic Liquids," *Green Chemistry* 15, no. 2 (2013): 525, https://doi.org/10.1039/c2gc36556a.

91. E.-M. Nuutinen, P. Willberg-Keyriläinen, T. Virtanen, et al., "Green Process to Regenerate Keratin from Feathers with an Aqueous Deep Eutectic Solvent," *RSC Advances* 9, no. 34 (2019): 19720–19728, https://doi.org/10.1039/C9RA03305J.

92. S. Y. Wong, C. C. Lee, A. Ashrafzadeh, S. M. Junit, N. Abrahim, and O. H. Hashim, "A High-Yield Two-Hour Protocol for Extraction of Human Hair Shaft Proteins," *PLoS One* 11, no. 10 (2016): 0164993, https://doi.org/10.1371/journal.pone.0164993.

93. A. Shavandi, T. H. Silva, A. A. Bekhit, and A. E.-D. A. Bekhit, "Keratin: Dissolution, Extraction and Biomedical Application," *Biomaterials Science* 5, no. 9 (2017): 1699–1735, https://doi.org/10.1039/C7BM00411G.

94. S. Gaikwad and M. J. Kim, "Fish by-Product Collagen Extraction Using Different Methods and Their Application," *Mar Drugs* 22, no. 2 (2024): 60, https://doi.org/10.3390/md22020060.

95. J. H. Bowes and R. H. Kenten, "The Effect of Alkalis on Collagen," *Biochemical Journal* 43, no. 3 (1948): 365–372, https://doi.org/10.1042/bj0430365.

96. A. Ciurzyńska, M. Janowicz, M. Karwacka, M. Nowacka, and S. Galus, "Development and Characteristics of Protein Edible Film Derived from Pork Gelatin and Beef Broth," *Polymers* 16, no. 7 (2024): 1009, https://doi.org/10.3390/polym16071009.

97. A. Tarannum, A. Adams, B. Blümich, and N. N. Fathima, "Impact of Ionic Liquids on the Structure and Dynamics of Collagen," *The Journal of Physical Chemistry B* 122, no. 3 (2018): 1060–1065, https://doi.org/10.1021/acs.jpcb.7b09626.

98. Z. Meng, X. Zheng, K. Tang, J. Liu, Z. Ma, and Q. Zhao, "Dissolution and Regeneration of Collagen Fibers Using Ionic Liquid," *International Journal of Biological Macromolecules* 51, no. 4 (2012): 440–448, https://doi.org/10.1016/j.ijbiomac.2012.05.030.

99. M. Bisht, M. Martins, A. Dias, S. P. M. Ventura, and J. A. P. Coutinho, "Uncovering the Potential of Aqueous Solutions of Deep Eutectic Solvents on the Extraction and Purification of Collagen Type I from Atlantic Codfish (*Gadus morhua*)," *Green Chemistry* 23, no. 22 (2021): 8940–8948, https://doi.org/10.1039/D1GC01432C.

100. M. P. Batista, N. Fernández, F. B. Gaspar, M. D. R. Bronze, and A. R. C. Duarte, "Extraction of Biocompatible Collagen from Blue Shark Skins through the Conventional Extraction Process Intensification Using Natural Deep Eutectic Solvents," *Frontiers in Chemistry* 10 (2022): 937036, https://doi.org/10.3389/fchem.2022.937036.

101. J. A. Matthews, G. E. Wnek, D. G. Simpson, and G. L. Bowlin, "Electrospinning of Collagen Nanofibers," *Biomacromolecules* 3, no. 2 (2002): 232–238, https://doi.org/10.1021/bm015533u.

102. G. Shanmugam, S. M. M. Reddy, V. Natarajan, and B. Madhan, "2,2,2-Trifluoroethanol Disrupts the Triple Helical Structure and Self-Association of Type I Collagen," *International Journal of Biological Macromolecules* 54 (2013): 155–159, https://doi.org/10.1016/j.ijbiomac.2012.12.014.

103. J. Yang, C. Ding, L. Tang, et al., "Novel Modification of Collagen: Realizing Desired Water Solubility and Thermostability in a Conflict-Free Way," *ACS Omega* 5, no. 11 (2020): 5772–5780, https://doi.org/10.1021/acsomega.9b03846.

104. Z. Zhang, W. Liu, D. Li, and G. Li, "Physicochemical Properties of Succinylated Calfskin Pepsin-Solubilized Collagen," *Bioscience, Biotechnology, and Biochemistry* 71, no. 8 (2007): 2057–2060, https://doi.org/10.1271/bbb.70055.

105. N. Vallejos, G. González, E. Troncoso, and R. N. Zúñiga, "Acid and Enzyme-Aided Collagen Extraction from the Byssus of Chilean Mussels (Mytilus Chilensis): Effect of Process Parameters on Extraction Performance," *Food Biophysics* 9, no. 4 (2014): 322–331, https://doi.org/10.1007/s11483-014-9339-2.

106. E. Melro, A. Filipe, A. J. M. Valente, et al., "Levulinic Acid: a Novel Sustainable Solvent for Lignin Dissolution," *International Journal of Biological Macromolecules* 164 (2020): 3454–3461, https://doi.org/10.1016/j.ijbiomac.2020.08.128.

107. E. M. Zadeh, S. F. O'Keefe, and Y.-T. Kim, "Utilization of Lignin in Biopolymeric Packaging Films," *ACS Omega* 3, no. 7 (2018): 7388–7398, https://doi.org/10.1021/acsomega.7b01341.

108. B. Manna, S. Datta, and A. Ghosh, "Understanding the Dissolution of Softwood Lignin in Ionic Liquid and Water Mixed Solvents," *International Journal of Biological Macromolecules* 182 (2021): 402–412, https://doi.org/10.1016/j.ijbiomac.2021.04.006.

109. M. Mohan, B. A. Simmons, K. L. Sale, and S. Singh, "Multiscale Molecular Simulations for the Solvation of Lignin in Ionic Liquids," *scientific reports* 13, no. 1 (2023): 271, https://doi.org/10.1038/s41598-022-25372-2.

110. R. M. Dias, L. C. G. Petrin, F. H. B. Sosa, A. M. Da Costa Lopes, J. A. P. Coutinho, and M. C. Da Costa, "Investigation of Kraft Lignin Solubility in Protic Ionic Liquids and Their Aqueous Solutions," *Industrial & Engineering Chemistry Research* 59, no. 40 (2020): 18193–18202, https://doi.org/10.1021/acs.iecr.0c02605.

111. B. Xue, Y. Yang, R. Tang, D. Xue, Y. Sun, and X. Li, "Efficient Dissolution of Lignin in Novel Ternary Deep Eutectic Solvents and Its Application in Polyurethane," *International Journal of Biological Macromolecules* 164 (2020): 480–488, https://doi.org/10.1016/j.ijbiomac.2020.07.153.

112. Y. Zhang, H. Ren, B. Li, et al., "Mechanistic Insights into the Lignin Dissolution Behavior in Amino Acid Based Deep Eutectic Solvents,"

International Journal of Biological Macromolecules 242 (2023): 124829, https://doi.org/10.1016/j.ijbiomac.2023.124829.

113. H. Ge, J. Wei, B. Zhu, et al., "Microscopic Mechanism Investigation of Extraction of Lignin by Benzyltriethylammonium Chloride-Based Deep Eutectic Solvents," *Journal of Molecular Liquids* 413 (2024): 125996, https://doi.org/10.1016/j.molliq.2024.125996.

114. W. Wu, P. Zhu, L. Luo, et al., "p-p-Toluenesulfonic Acid Enhanced Neutral Deep Eutectic Solvent Pretreatment of Soybean Straw for Efficient Lignin Removal and Enzymatic Hydrolysis," *Bioresource Technology* 395 (2024): 130338, https://doi.org/10.1016/j.biortech.2024.130338.

115. D. S. Zijlstra, C. W. Lahive, C. A. Analbers, et al., "Mild Organosolv Lignin Extraction with Alcohols: the Importance of Benzylic Alkoxylation," *ACS Sustainable Chemistry & Engineering* 8, no. 13 (2020): 5119–5131, https://doi.org/10.1021/acssuschemeng.9b07222.

116. J. V. Vermaas, M. F. Crowley, and G. T. Beckham, "Molecular Lignin Solubility and Structure in Organic Solvents," *ACS Sustainable Chemistry & Engineering* 8, no. 48 (2020): 17839–17850, https://doi.org/10.1021/acssuschemeng.0c07156.

117. S.-Y. Park, J.-H. Choi, J.-H. Kim, et al., "Peracetic Acid-Induced Kraft Lignin Solubilization and Its Characterization for Selective Production of Macromolecular Biopolymers," *International Journal of Biological Macromolecules* 161 (2020): 1240–1246, https://doi.org/10.1016/j.ijbiomac.2020.06.041.

118. A. C. Alavarse, E. C. G. Frachini, R. L. Da Silva, V. H. Lima, A. Shavandi, and D. F. S. Petri, "Crosslinkers for Polysaccharides and Proteins: Synthesis Conditions, Mechanisms, and Crosslinking Efficiency, a Review," *International Journal of Biological Macromolecules* 202 (2022): 558–596, https://doi.org/10.1016/j.ijbiomac.2022.01.029.

119. B. Jayachandran, T. N. Parvin, M. M. Alam, K. Chanda, and B. Mm, "Insights on Chemical Crosslinking Strategies for Proteins," *Molecules (Basel, Switzerland)* 27, no. 23 (8124): 8124, https://doi.org/10.3390/molecules27238124.

120. L. H. H. Olde Damink, P. J. Dijkstra, M. J. A. Van Luyn, P. B. Van Wachem, P. Nieuwenhuis, and J. Feijen, "Glutaraldehyde as a Crosslinking Agent for Collagen-Based Biomaterials," *Journal of Materials Science: Materials in Medicine* 6, no. 8 (1995): 460–472, https://doi.org/10.1007/BF00123371.

121. C.-H. Yao, B.-S. Liu, C.-J. Chang, S.-H. Hsu, and Y.-S. Chen, "Preparation of Networks of Gelatin and Genipin as Degradable Biomaterials," *Materials Chemistry and Physics* 83, no. 2–3 (2004): 204–208, https://doi.org/10.1016/j.matchemphys.2003.08.027.

122. Z. Sun, J. Liu, X. Wang, et al., "Epoxy Chitosan-Crosslinked Acellular Bovine Pericardium with Improved Anti-Calcification and Biological Properties," *ACS Applied Bio Materials* 3, no. 4 (2020): 2275–2283, https://doi.org/10.1021/acsabm.0c00067.

123. V. S. Ghorpade, "Preparation of Hydrogels Based on Natural Polymers via Chemical Reaction and Cross-Linking," (2020): 91–118, https://doi.org/10.1016/B978-0-12-816421-1.00004-5.

124. P. Hartrianti, L. T. H. Nguyen, J. Johanes, et al., "Fabrication and Characterization of a Novel Crosslinked human Keratin-Alginate Sponge," *Journal of Tissue Engineering and Regenerative Medicine* 11, no. 9 (2017): 2590–2602, https://doi.org/10.1002/term.2159.

125. Y. Numata, S. Masaki, and K. Tajima, "Mechanical Properties of a Bacterial Cellulose/Polyethylene Glycol Gel with a Peripheral Region Crosslinked by Polyethylene Glycol Diacrylate," *Polymer Journal* 48, no. 3 (2016): 317–321, https://doi.org/10.1038/pj.2015.104.

126. P. Shankar, T. Gomathi, K. Vijayalakshmi, and P. N. Sudha, "Comparative Studies on the Removal of Heavy Metals Ions onto Cross Linked Chitosan-g-Acrylonitrile Copolymer," *International Journal of Biological Macromolecules* 67 (2014): 180–188, https://doi.org/10.1016/j.ijbiomac.2014.03.010.

127. R. F. Correa, G. Colucci, N. Halla, et al., "Development of Chitosan Microspheres through a Green Dual Crosslinking Strategy Based on Tripolyphosphate and Vanillin," *Molecules (Basel, Switzerland)* 26, no. 8 (2325): 2325, https://doi.org/10.3390/molecules26082325.

128. U. Filipkowska and T. Jóźwiak, "Application of Chemically-Cross-Linked Chitosan for the Removal of Reactive Black 5 and Reactive Yellow 84 Dyes from Aqueous Solutions," *Journal of Polymer Engineering* 33, no. 8 (2013): 735–747, https://doi.org/10.1515/polyeng-2013-0166.

129. A. Webster, M. D. Halling, and D. M. Grant, "Metal Complexation of Chitosan and Its Glutaraldehyde Cross-Linked Derivative," *Carbohydrate Research* 342, no. 9 (2007): 1189–1201, https://doi.org/10.1016/j.carres.2007.03.008.

130. R. Laus and V. T. De Fávere, "Competitive Adsorption of Cu(II) and Cd(II) Ions by Chitosan Crosslinked with Epichlorohydrin–triphosphate," *Bioresource Technology* 102, no. 19 (2011): 8769–8776, https://doi.org/10.1016/j.biortech.2011.07.057.

131. M. Zhao, J. Zhao, Z. Huang, S. Wang, and L. Zhang, "One Pot Preparation of Magnetic Chitosan-Cystamine Composites for Selective Recovery of Au(III) from the Aqueous Solution," *International Journal of Biological Macromolecules* 137 (2019): 721–731, https://doi.org/10.1016/j.ijbiomac.2019.07.022.

132. J. P. Glusker, "Structural Aspects of Metal Liganding to Functional Groups in Proteins," (1991): 1–76, https://doi.org/10.1016/S0065-3233(08)60534-3.

133. A. Nobahar, J. D. Carlier, M. G. Miguel, and M. C. Costa, "A Review of Plant Metabolites with Metal Interaction Capacity: A Green Approach for Industrial Applications," *Biometals* 34 (2021): 761–793, https://doi.org/10.1007/s10534-021-00315-y.

134. X. Yang, Y. Wan, Y. Zheng, et al., "Surface Functional Groups of Carbon-Based Adsorbents and Their Roles in the Removal of Heavy Metals from Aqueous Solutions: a Critical Review," *Chemical Engineering Journal* 366 (2019): 608–621, https://doi.org/10.1016/j.cej.2019.02.119.

135. T. Heinze and T. Liebert, "Unconventional Methods in Cellulose Functionalization," *Progress in Polymer Science* 26, no. 9 (2001): 1689–1762, https://doi.org/10.1016/S0079-6700(01)00022-3.

136. Z. Luo, Y. Wang, Y. Xu, J. Wang, and Y. Yu, "Modification and Crosslinking Strategies for Hyaluronic Acid-Based Hydrogel Biomaterials," *Smart Medicine* 2, no. 4 (2023): 20230029, https://doi.org/10.1002/SMMD.20230029.

137. P. Willberg-Keyriläinen and J. Ropponen, "Evaluation of Esterification Routes for Long Chain Cellulose Esters," *Heliyon* 5, no. 11 (2019): e02898, https://doi.org/10.1016/j.heliyon.2019.e02898.

138. F. Seidi, M. R. Saeb, Y. Huang, A. Akbari, and H. Xiao, "Thiomers of Chitosan and Cellulose: Effective Biosorbents for Detection, Removal and Recovery of Metal Ions from Aqueous Medium," *The Chemical Record* 21, no. 7 (2021): 1876–1896, https://doi.org/10.1002/tcr.202100068.

139. A. D. Gupta, S. Pandey, V. K. Jaiswal, V. Bhadauria, and H. Singh, "Simultaneous Oxidation and Esterification of Cellulose for Use in Treatment of Water Containing Cu(II) Ions," *Carbohydrate Polymers* 222 (2019): 114964, https://doi.org/10.1016/j.carbpol.2019.06.003.

140. Q. Li, L. Chai, Q. Wang, Z. Yang, H. Yan, and Y. Wang, "Fast Esterification of Spent Grain for Enhanced Heavy Metal Ions Adsorption," *Bioresource Technology* 101, no. 10 (2010): 3796–3799, https://doi.org/10.1016/j.biortech.2010.01.003.

141. A. Das, T. Ringu, S. Ghosh, and N. Pramanik, "A Comprehensive Review on Recent Advances in Preparation, Physicochemical Characterization, and Bioengineering Applications of Biopolymers," *Polymer Bulletin* 80, no. 7 (2023): 7247–7312, https://doi.org/10.1007/s00289-022-04443-4.

142. M. I. Loría-Bastarrachea, H. J. Carrillo-Escalante, and M. J. Aguilar-Vega, "Grafting of Poly(acrylic acid) onto Cellulosic Microfibers and Continuous Cellulose filaments and Characterization," *Journal of Applied Polymer Science* 83, no. 2 (2002): 386–393, https://doi.org/10.1002/app.10026.

143. N. Maity and A. Dawn, “Conducting Polymer Grafting: Recent and Key Developments,” *Polymers* 12, no. 3 (2020): 709, https://doi.org/10.3390/polym12030709.

144. P. Purohit, A. Bhatt, R. K. Mittal, M. H. Abdellattif, and T. A. Farghaly, “Polymer Grafting and Its Chemical Reactions,” *Frontiers in Bioengineering and Biotechnology* 10 (2023): 1044927, https://doi.org/10.3389/fbioe.2022.1044927.

145. M. Á. Vega-Hernández, G. S. Cano-Díaz, E. Vivaldo-Lima, et al., “A Review on the Synthesis, Characterization, and Modeling of Polymer Grafting,” *Processes* 9, no. 2 (2021): 375, https://doi.org/10.3390/pr9020375.

146. C. Feng and X. Huang, “Polymer Brushes: Efficient Synthesis and Applications,” *Accounts of Chemical Research* 51, no. 9 (2018): 2314–2323, https://doi.org/10.1021/acs.accounts.8b00307.

147. R. Kumar, S. RKr, and A. P. Singh, “Grafted Cellulose: a Bio-Based Polymer for Durable Applications,” *Polymer Bulletin* 75, no. 5 (2018): 2213–2242, https://doi.org/10.1007/s00289-017-2136-6.

148. T. Aziz, A. Farid, F. Haq, et al., “A Review on the Modification of Cellulose and Its Applications,” *Polymers* 14, no. 15 (2022): 3206, https://doi.org/10.3390/polym14153206.

149. D. Kumar, J. Pandey, V. Raj, and P. Kumar, “A Review on the Modification of Polysaccharide through Graft Copolymerization for Various Potential Applications,” *Open Medicinal Chemistry Journal* 11, no. 1 (2017): 109–126, https://doi.org/10.2174/1874104501711010109.

150. K. Piekarska, M. Sikora, M. Owczarek, J. Jóźwik-Pruska, and M. Wiśniewska-Wrona, “Chitin and Chitosan as Polymers of the Future—Obtaining, Modification, Life Cycle Assessment and Main Directions of Application,” *Polymers* 15, no. 4 (2023): 793, https://doi.org/10.3390/polym15040793.

151. X. Zhou, H. A. Essawy, M. F. Mohamed, H. S. Ibrahim, and N. S. Ammar, “Grafting Polymerization of Acrylic Acid onto Chitosan-Cellulose Hybrid and Application of the Graft as Highly Efficient Ligand for Elimination of Water Hardness: Adsorption Isotherms, Kinetic Modeling and Regeneration,” *Journal of Environmental Chemical Engineering* 6, no. 2 (2018): 2137–2147, https://doi.org/10.1016/j.jece.2018.03.022.

152. P. K. Panda, A. Verma, and S. K. Jain, “Etherified Polysaccharides in Biomedical Applications,” (2020): 35–50, https://doi.org/10.1016/B978-0-12-821344-5.00002-3.

153. S. Toumi, M. M. Yahoum, S. Lefnaoui, et al., “Development of New Alkylated Carrageenan Derivatives: Physicochemical, Rheological, and Emulsification Properties Assessment,” *Sustainability* 15, no. 8 (6473), https://doi.org/10.3390/su15086473.

154. S. Petroni, I. Tagliaro, C. Antonini, et al., “Chitosan-Based Biomaterials: Insights into Chemistry, Properties, Devices, and Their Biomedical Applications,” *Mar Drugs* 21, no. 3 (2023): 147, https://doi.org/10.3390/md21030147.

155. V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault, and B. Boutevin, “Biobased Amines: from Synthesis to Polymers; Present and Future,” *Chemical Reviews* 116, no. 22 (2016): 14181–14224, https://doi.org/10.1021/acs.chemrev.6b00486.

156. M. Lubberink, W. Finnigan, and S. L. Flitsch, “Biocatalytic Amide Bond Formation. Green Chem,” 25, no. 8 (2023): 2958–2970, https://doi.org/10.1039/D3GC00456B.

157. J. B. Lindén, M. Larsson, S. Kaur, et al., “Polyethyleneimine for Copper Absorption II: Kinetics, Selectivity and Efficiency from Seawater,” *RSC Advances* 5, no. 64 (2015): 51883–51890, https://doi.org/10.1039/C5RA08029K.

158. L. Nicolle, C. M. A. Journot, and G.-L. S. Chitosan, “Chitosan Functionalization: Covalent and Non-Covalent Interactions and Their Characterization,” *Polymers* 13, no. 23 (2021): 4118, https://doi.org/10.3390/polym13234118.

159. E. Lam and U. D. Hemraz, “Preparation and Surface Functionalization of Carboxylated Cellulose Nanocrystals,” *Nanomaterials* 11, no. 7 (2021): 1641, https://doi.org/10.3390/nano11071641.

160. J. Zhao, X. Zhang, X. He, M. Xiao, W. Zhang, and C. Lu, “A Super Biosorbent from Dendrimer Poly(amidoamine)-Grafted Cellulose Nanofibril Aerogels for Effective Removal of Cr(vi),” *Journal of Materials Chemistry A* 3, no. 28 (2015): 14703–14711, https://doi.org/10.1039/C5TA03089G.

161. R. Zhu, C. Zhang, L. Zhu, et al., ““Three-Dimensional Environment-Friendly” Amino Acid Functionalized Chitosan: Uranium Adsorption Performance and Mechanism Research,” *Carbohydrate Polymers* 343 (2024): 122464, https://doi.org/10.1016/j.carbpol.2024.122464.

162. G. S. Baldwin, M. F. Bailey, B. P. Shehan, I. Sims, and R. S. Norton, “Tyrosine Modification Enhances Metal-Ion Binding,” *Biochemical Journal* 416, no. 1 (2008): 77–84, https://doi.org/10.1042/BJ20081059.

163. A. M. A. Nada, N. A. El-Wakil, M. L. Hassan, and A. M. Adel, “Differential Adsorption of Heavy Metal Ions by Cotton Stalk Cation-Exchangers Containing Multiple Functional Groups,” *Journal of Applied Polymer Science* 101, no. 6 (2006): 4124–4132, https://doi.org/10.1002/app.23569.

164. T. Zhao, M. Yang, L. Ma, et al., “Structural Modification and Biological Activity of Polysaccharides,” *Molecules* 28, no. 14 (5416), https://doi.org/10.3390/molecules28145416.

165. C. Dong, F. Zhang, Z. Pang, and G. Yang, “Efficient and Selective Adsorption of Multi-metal Ions Using Sulfonated Cellulose as Adsorbent,” *Carbohydrate Polymers* 151 (2016): 230–236, https://doi.org/10.1016/j.carbpol.2016.05.066.

166. J. Sánchez, B. Butter, and B. L. Rivas, “Biopolymers Applied To Remove Metal Ions through Ultrafiltration. A Review,” *Journal of the Chilean Chemical Society* 65, no. 4 (2020): 5004–5010, https://doi.org/10.4067/S0717-97072020000405004.

167. Y. Qin, X. Lin, Y. Lu, et al., “Preparation of a Low Reducing Effect Sulfonated Alkali Lignin and Application as Dye Dispersant,” *Polymers* 10, no. 9 (2018): 982, https://doi.org/10.3390/polym10090982.

168. W. Li, Y. Xue, M. He, et al., “Facile Preparation and Characteristic Analysis of Sulfated Cellulose Nanofibril via the Pretreatment of Sulfamic Acid-Glycerol Based Deep Eutectic Solvents,” *Nanomaterials* 11, no. 11 (2021), https://doi.org/10.3390/nano11112778.

169. S. Abd-elnaeem, A. Hafez, K. El-Khatib, H. Mohamed, M. Fouad, and E. Abadir, “Parameters Affecting Synthesis of Sulfonated Chitosan Membrane for Poly Electrolyte Membrane in Fuel Cells,” *Egyptian Journal of Chemistry 65, no 5* (2024), https://doi.org/10.21608/ejchem.2023.230907.8651.

170. R. J. Kelly, G. D. Ellis, R. J. Macdonald, R. A. McPherson, P. G. Middlewood, and M. G. Nuthall, “Keratin and Soluble Derivatives Thereof for a Nutraceutical and to Reduce Oxidative Stress and to Reduce Inflammation and to Promote Skin Health,” *United States Patent and Trademark Office* (2006), https://patents.google.com/patent/US20070065506A1/en.

171. R. Mhanna, J. Becher, M. Schnabelrauch, R. L. Reis, and I. Pashkuleva, “Sulfated Alginate as a Mimic of Sulfated Glycosaminoglycans: Binding of Growth Factors and Effect on Stem Cell Behavior,” *Advanced Biosystems* 1, no. 7 (2017): 1700043, https://doi.org/10.1002/adbi.201700043.

172. M. F. Hamza, H. Mira, Y. Wei, S. M. Aboelenin, E. Guibal, and W. M. Salem, “Sulfonation of Chitosan for Enhanced Sorption of Li(I) from Acidic Solutions—Application to Metal Recovery from Waste Li-Ion Mobile Battery,” *Chemical Engineering Journal* 441 (2022): 135941, https://doi.org/10.1016/j.cej.2022.135941.

173. E.-H. Ablouh, Z. Kassab, F. Semlali Aouragh Hassani, M. El Achaby, and H. Sehaqui, “Phosphorylated Cellulose Paper as Highly Efficient Adsorbent for Cadmium Heavy Metal Ion Removal in Aqueous Solutions,” *RSC Advances* 12, no. 2 (2022): 1084–1094, https://doi.org/10.1039/D1RA08060A.

174. G. I. Edo, W. Ndudi, A. AliBM, et al., “Biopolymers: an Inclusive Review,” *Hybrid Advances* 9 (2025): 100418, https://doi.org/10.1016/j.hybadv.2025.100418.

175. X. Zhao, Y. Fang, L. Xue, et al., "Phosphorylated Chitosan-lignin Composites for Efficient Removal of Pb(II) and Cu(II) from Aqueous Environments and Sustainable Upcycling of Spent Adsorbents," *International Journal of Biological Macromolecules* 304 (2025): 140840, https://doi.org/10.1016/j.ijbiomac.2025.140840.

176. M. Hyder and B. Ochiai, "Synthesis of a Highly Selective Scavenger of Precious Metals from a Printed Circuit Board Based on Cellulose Filter Paper Functionalized with a Grafted Polymer Chain Bearing *N*-Methyl-2-Hydroxyethylcarbamothioate Moieties," *ACS Omega* 7, no. 12 (2022): 10355–10364, https://doi.org/10.1021/acsomega.1c06988.

177. C. Ding and A. S. Matharu, "Recent Developments on Biobased Curing Agents: A Review of Their Preparation and Use," *ACS Sustainable Chemistry & Engineering* 2, no. 10 (2014): 2217–2236, https://doi.org/10.1021/sc500478f.

178. C. Yin, F. Huo, J. Zhang, et al., "Thiol-addition Reactions and Their Applications in Thiol Recognition," *Chemical Society Reviews* 42, no. 14 (2013): 6032, https://doi.org/10.1039/c3cs60055f.

179. R. Wibel, D. E. Braun, L. Hämmerle, et al., "Vitro Investigation of Thiolated Chitosan Derivatives as Mucoadhesive Coating Materials for Solid Lipid Nanoparticles," *Biomacromolecules* 22, no. 9 (2021): 3980–3991, https://doi.org/10.1021/acs.biomac.1c00776.

180. C. E. Kast and A. Bernkop-Schnürch, "Thiolated Polymers — Thiomers: Development and in Vitro Evaluation of Chitosan–thioglycolic Acid Conjugates," *Biomaterials* 22, no. 17 (2001): 2345–2352, https://doi.org/10.1016/S0142-9612(00)00421-X.

181. C. Federer, M. Kurpiers, and A. Bernkop-Schnürch, "Thiolated Chitosans: a Multi-talented Class of Polymers for Various Applications," *Biomacromolecules* 22, no. 1 (2021): 24–56, https://doi.org/10.1021/acs.biomac.0c00663.

182. S. K. Yong, N. Bolan, E. Lombi, and W. Skinner, "Synthesis and Characterization of Thiolated Chitosan Beads for Removal of Cu(II) and Cd(II) from Wastewater," *Water, Air, & Soil Pollution* 224, no. 12 (1720), https://doi.org/10.1007/s11270-013-1720-0.

183. X. Song, L. Li, L. Zhou, and P. Chen, "Magnetic Thiolated/Quaternized-Chitosan Composites Design and Application for Various Heavy Metal Ions Removal, Including Cation and Anion," *Chemical Engineering Research and Design* 136 (2018): 581–592, https://doi.org/10.1016/j.cherd.2018.06.025.

184. T. Xu, Y. Guo, L. Zhang, et al., "Sulfur-containing Cellulose Esters for Selectively Anchoring Gold for Water Catalytic Decontamination," *International Journal of Biological Macromolecules* 280 (2024): 135882, https://doi.org/10.1016/j.ijbiomac.2024.135882.

185. S. Sharma, M. Barathi, and N. Rajesh, "Efficacy of a Heterocyclic Ligand Anchored Biopolymer Adsorbent for the Sequestration of Palladium," *Chemical Engineering Journal* 259 (2015): 457–466, https://doi.org/10.1016/j.cej.2014.08.002.

186. Y. Hong, D. Thirion, S. Subramanian, et al., "Precious Metal Recovery from Electronic Waste by a Porous Porphyrin Polymer," *Proceedings of the National Academy of Sciences of the United States of America* 117, no. 28 (2020): 16174–16180, https://doi.org/10.1073/pnas.2000606117.

187. S. Chen, Y. Yang, F. Zi, X. Hu, and X. Li, "Constructing Phosphine-containing Microspheres for Selective Recovery of Gold(I) Thiosulfate Complex by Adjusting the Interaction Site," *Separation and Purification Technology* 362 (2025): 131636, https://doi.org/10.1016/j.seppur.2025.131636.

188. A. Butewicz, K. C. Gavilan, A. V. Pestov, Y. Yatluk, A. W. Trochimczuk, and E. Guibal, "Palladium and Platinum Sorption on a Thiocarbamoyl-Derivative of Chitosan," *Journal of Applied Polymer Science* 116, no. 6 (2010): 3318–3330, https://doi.org/10.1002/app.31877.

189. L. J. Daumann, "A Natural Lanthanide-Binding Protein Facilitates Separation and Recovery of Rare Earth Elements," *ACS Central Science* 7, no. 11 (2021): 1780–1782, https://doi.org/10.1021/acscentsci.1c01247.

190. J. A. Mattocks, J. J. Jung, C.-Y. Lin, et al., "Enhanced Rare-earth Separation with a Metal-sensitive Lanmodulin Dimer," *Nature* 618, no. 7963 (2023): 87–93, https://doi.org/10.1038/s41586-023-05945-5.

191. R. Bardovskyi, C. Ronco, and R. Benhida, "Synthesis, Characterization and Uptake Studies of Diglycolamic Acid and Diglycolamide Analogs Adsorbents for Extraction of Rare Earth Elements," *Minerals Engineering* 204 (2023): 108313, https://doi.org/10.1016/j.mineng.2023.108313.

192. P. Thakur, J. L. Conca, and G. R. Choppin, "Complexation Studies of Cm(III), Am(III), and Eu(III) with Linear and Cyclic Carboxylates and Polyaminocarboxylates," *Journal of Coordination Chemistry* 64, no. 18 (2011): 3214–3236, https://doi.org/10.1080/00958972.2011.616927.

193. Z. Xu, W. Bae, A. Mulchandani, R. K. Mehra, and W. Chen, "Heavy Metal Removal by Novel CBD-EC20 Sorbents Immobilized on Cellulose," *Biomacromolecules* 3, no. 3 (2002): 462–465, https://doi.org/10.1021/bm015631f.

194. M. Nakahata, A. Sumiya, Y. Ikemoto, et al., "Hyperconfined Bio-inspired Polymers in Integrative Flow-Through Systems for Highly Selective Removal of Heavy Metal Ions," *Nature Communications* 15, no. 1 (2024): 5824, https://doi.org/10.1038/s41467-024-49869-8.

195. T. V. Divya, B. Dutta, K. Bhattacharyya, K. C. Barick, and C. Acharya, "Bio–Nano Interactions of Recombinant Cyanobacterial Metallothionein with Magnetic Nanoparticles for the Removal of Cadmium and Uranium," *ACS Omega* 10, no. 25 (2025): 26743–26755, https://doi.org/10.1021/acsomega.5c01248.

196. W. Mwandira, K. Nakashima, Y. Togo, T. Sato, and S. Kawasaki, "Cellulose-metallothionein Biosorbent for Removal of Pb(II) and Zn(II) from Polluted Water," *Chemosphere* 246 (2020): 125733, https://doi.org/10.1016/j.chemosphere.2019.125733.

197. D. Hussein and H. H. Mihsen, *Synthesis and Characterization of Organosilicon Ligands and Used it in Removal of Some Divalent Metal Ions from their Aqueous Solutions*, (Master's thesis, Republic of Iraq Ministry of Higher Education and Scientific Research University of Kerbala College of Science, 2012).

198. W. Yang, S. Shirazian, R. Soltani, and M. H. Zare, "Bio-originated Mesosilicate SBA-15: Synthesis, Characterization, and Application for Heavy Metal Removal," *Npj Clean Water* 7, no. 1 (2024): 49, https://doi.org/10.1038/s41545-024-00340-7.

199. J. Husson, "Functional Materials from Biomass-Derived Terpyridines: State of the Art and Few Possible Perspectives," *International Journal of Molecular Sciences* 25, no. 16 (2024): 9126, https://doi.org/10.3390/ijms25169126.

200. V. F. Gromov, M. I. Ikim, G. N. Gerasimov, and L. I. Trakhtenberg, "Crown Ethers: Selective Sorbents of Radioactive and Heavy Metals," *Russian Journal of Physical Chemistry B* 15, no. 1 (2021): 140–152, https://doi.org/10.1134/S1990793121010036.

201. J.-J. Bian, S.-J. Tang, J. Miao, et al., "Synthesis of Supramolecular Polymers with Calix[4]Arene and β-cyclodextrin and Their Application in Heavy Metal Ion Absorption," *RSC Advances* 14, no. 48 (2024): 35697–35703, https://doi.org/10.1039/D4RA05559D.

202. S. Sultana, M. Mukta, R. MdH, et al., "EDTA-treated Fibrillated Cellulose Bio-Adsorbents From Okra Plant Biomass and Their Performance on Toxic Divalent Metal Ions Attenuation from Aqueous Solution," *Biomass Conversion and Biorefinery* 15 (2024): 15853–15866, https://doi.org/10.1007/s13399-024-06259-w.

203. J. Roosen and K. Binnemans, "Adsorption and Chromatographic Separation of Rare Earths with EDTA- and DTPA-functionalized Chitosan Biopolymers," *Journal of Materials Chemistry A* 2, no. 5 (2014): 1530–1540, https://doi.org/10.1039/C3TA14622G.

204. T. Hu, X. Hu, C. Tang, and D. Liu, "Adsorbent Grafted on Cellulose by in Situ Synthesis of EDTA-Like Groups and Its Properties of Metal Ion Adsorption from Aqueous Solution," *Cellulose* 29, no. 2 (2022): 941–952, https://doi.org/10.1007/s10570-021-04324-5.

205. Y. Chen, X. Wang, D. Hao, Y. Ding, and H. Fan, "Chelating Cellulose Functionalized with Four Amino Acids: A Comparative Study on the

Enhanced Adsorptive Removal of Cadmium and Lead Ions," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 650 (2022): 129599, https://doi.org/10.1016/j.colsurfa.2022.129599.

206. P. Deschamps, P. P. Kulkarni, M. Gautam-Basak, and B. Sarkar, "The Saga of Copper(II)–l-Histidine," *Coordination Chemistry Reviews* 249, no. 9–10 (2005): 895–909, https://doi.org/10.1016/j.ccr.2004.09.013.

207. M. T. Maia, D. N. Sena, G. B. Calais, F. M. T. Luna, M. M. Beppu, and R. S. Vieira, "Effects of Histidine Modification of Chitosan Microparticles on Metal Ion Adsorption," *Reactive and Functional Polymers* 154 (2020): 104694, https://doi.org/10.1016/j.reactfunctpolym.2020.104694.

208. H. Ishii, M. Minegishi, B. Lavitpichayawong, and T. Mitani, "Synthesis of Chitosan-amino Acid Conjugates and Their Use in Heavy Metal Uptake," *International Journal of Biological Macromolecules* 17, no. 1 (1995): 21–23, https://doi.org/10.1016/0141-8130(95)93513-W.

209. I. V. Seregin and A. D. Kozhevnikova, "Phytochelatins: Sulfur-Containing Metal(loid)-Chelating Ligands in Plants," *International Journal of Molecular Sciences* 24, no. 3 (2023): 2430, https://doi.org/10.3390/ijms24032430.

210. M. G. Vijver, C. A. M. Van Gestel, R. P. Lanno, N. M. Van Straalen, and W. Peijnenburg, "Internal Metal Sequestration and Its Ecotoxicological Relevance: a Review," *Environmental Science & Technology* 38, no. 18 (2004): 4705–4712, https://doi.org/10.1021/es040354g.

211. C. A. Blindauer and O. I. Leszczyszyn, "Metallothioneins: Unparalleled Diversity in Structures and Functions for Metal Ion Homeostasis and More," *Natural Product Reports* 27, no. 5 (2010): 720, https://doi.org/10.1039/b906685n.

212. I. Miyazaki and M. Asanuma, "Multifunctional Metallothioneins as a Target for Neuroprotection in Parkinson's Disease," *Antioxidants* 12, no. 4 (2023): 894, https://doi.org/10.3390/antiox12040894.

213. M. P. Waalkes, M. J. Harvey, and C. D. Klaassen, "Relative in Vitro Affinity of Hepatic Metallothionein for Metals," *Toxicology Letters* 20, no. 1 (1984): 33–39, https://doi.org/10.1016/0378-4274(84)90179-6.

214. X. Li, Y. Wang, M. J. C. Crabbe, L. Wang, W. Ma, and Z. Ren, "Genetically Modified Metallothionein/Cellulose Composite Material as an Efficient and Environmentally Friendly Biosorbent for Cd^{2+} Removal," *International Journal of Biological Macromolecules* 218 (2022): 543–555, https://doi.org/10.1016/j.ijbiomac.2022.07.144.

215. Z. Dong, J. A. Mattocks, G. J.-P. Deblonde, et al., "Bridging Hydrometallurgy and Biochemistry: a Protein-Based Process for Recovery and Separation of Rare Earth Elements," *ACS Central Science* 7, no. 11 (2021): 1798–1808, https://doi.org/10.1021/acscentsci.1c00724.

216. N. Yoshinari, N. Kuwamura, T. Kojima, and T. Konno, "Development of Coordination Chemistry with Thiol-containing Amino Acids," *Coordination Chemistry Reviews* 474 (2023): 214857, https://doi.org/10.1016/j.ccr.2022.214857.

217. A. I. Petrov, "Interaction of Disulfides with Metal Ions and Spectroscopic Identification of the Products," *Coordination Chemistry Reviews* 505 (2024): 215678, https://doi.org/10.1016/j.ccr.2024.215678.

218. F. Dhaouadi, L. Sellaoui, M. Badawi, et al., "Statistical Physics Interpretation of the Adsorption Mechanism of Pb^{2+}, Cd^{2+} and Ni^{2+} on Chicken Feathers," *Journal of Molecular Liquids* 319 (2020): 114168, https://doi.org/10.1016/j.molliq.2020.114168.

219. A. Nobahar, F. N. Braga, F. H. B. Sosa, N. Schaeffer, J. A. P. Coutinho, and H. Passos, "Waste–to–waste Valorization: Sustainable Palladium Recovery from Real Spent Catalytic Converter Leachates Using Chicken Feathers," *Waste Management* 212 (2026): 115349, https://doi.org/10.1016/j.wasman.2026.115349.

220. V. Algieri, A. Tursi, P. Costanzo, et al., "Thiol-functionalized Cellulose for Mercury Polluted Water Remediation: Synthesis and Study of the Adsorption Properties," *Chemosphere* 355 (2024): 141891, https://doi.org/10.1016/j.chemosphere.2024.141891.

221. S. Bekele, K. Singh, E. Helton, et al., "Molecular Dynamics Investigation into pH Dependent Metal Binding of the Intrinsically Disordered Worm Jaw Protein, Nvjp-1," *The Journal of Physical Chemistry B* 126, no. 35 (2022): 6614–6623, https://doi.org/10.1021/acs.jpcb.2c02807.

222. E. Guibal, M. Ruiz, T. Vincent, A. Sastre, and R. Navarro-Mendoza, "Platinum and Palladium Sorption on Chitosan Derivatives," *Separation Science and Technology* 36, no. 5–6 (2001): 1017–1040, https://doi.org/10.1081/SS-100103634.

223. W. Kettum, C. Samart, N. Chanlek, P. Pakawanit, P. Reubroycharoen, and G. Guan, "Enhanced Adsorptive Composite Foams for Copper (II) Removal Utilising Bio-renewable Polyisoprene-functionalised Carbon Derived from Coconut Shell Waste," *Scientific Reports* 11, no. 1 (2021): 1459, https://doi.org/10.1038/s41598-020-80789-x.

224. A. K. Mosai and H. Tutu, "Recovery of Platinum (IV) from Aqueous Solutions Using 3-Aminopropyl(Diethoxy)Methylsilane Functionalized Bentonite," *Journal of Dispersion Science and Technology* 43, no. 7 (2022): 1016–1027, https://doi.org/10.1080/01932691.2020.1847659.

225. V. I. Lakshmanan and S. A. Vijayan, "Review on Application of Crown Ethers in Separation of Rare Earths and Precious Metals," in *Extraction*, ed. G. Azimi, A. Forstner, R. Kappes, and T. Bhambhani (Springer International Publishing, 2018), 1913–1930, https://doi.org/10.1007/978-3-319-95022-8_159.

226. J. S. Bradshaw and R. M. Izatt, "Crown Ethers: the Search for Selective Ion Ligating Agents," *Accounts of Chemical Research* 30, no. 8 (1997): 338–345, https://doi.org/10.1021/ar950211m.

227. M. Ciopec, O. Grad, A. Negrea, et al., "Highly Efficient Recovery of Ruthenium from Aqueous Solutions by Adsorption Using Dibenzo-30-Crown-10 Doped Chitosan," *Polymers* 14, no. 8 (2022): 1551, https://doi.org/10.3390/polym14081551.

228. O. S. Serbanescu, A. M. Pandele, M. Oprea, A. Semenescu, V. K. Thakur, and S. I. Voicu, "Crown Ether-Immobilized Cellulose Acetate Membranes for the Retention of Gd (III)," *Polymers* 13, no. 22 (2021): 3978, https://doi.org/10.3390/polym13223978.

229. Y. Hong, V. Rozyyev, and C. T. Yavuz, "Alkyl-Linked Porphyrin Porous Polymers for Gas Capture and Precious Metal Adsorption," *Small Science* 1, no. 6 (2021): 2000078, https://doi.org/10.1002/smsc.202000078.

230. J. Son, Y. Hong, G. Han, T. S. Nguyen, C. T. Yavuz, and J.-I. Han, "Gold Recovery Using Porphyrin-based Polymer from Electronic Wastes: Gold Desorption and Adsorbent Regeneration," *Science of The Total Environment* 704 (2020): 135405, https://doi.org/10.1016/j.scitotenv.2019.135405.

231. G. Alberti, C. Zanoni, L. R. Magnaghi, and R. Biesuz, "Deferoxamine-Based Materials and Sensors for Fe(III) Detection," *Chemosensors* 10, no. 11 (2022): 468, https://doi.org/10.3390/chemosensors10110468.

232. R. MdL, H. B. Mandal, S. M. Sarkar, et al., "Synthesis of Tapioca Cellulose-Based Poly(hydroxamic acid) Ligand for Heavy Metals Removal From Water," *Journal of Macromolecular Science Part A* 53, no. 8 (2016): 515–522, https://doi.org/10.1080/10601325.2016.1189285.

233. R. G. Pearson, "Hard and Soft Acids and Bases, HSAB, Part 1: Fundamental Principles," *Journal of Chemical Education* 45, no. 9 (1968): 581, https://doi.org/10.1021/ed045p581.

234. C. Bertagnolli, A. Grishin, T. Vincent, and E. Guibal, "Recovering Heavy Metal Ions from Complex Solutions Using Polyethylenimine Derivatives Encapsulated in Alginate Matrix," *Industrial & Engineering Chemistry Research* 55, no. 8 (2016): 2461–2470, https://doi.org/10.1021/acs.iecr.5b04683.

235. A. Benettayeb, A. Morsli, E. Guibal, and R. Kessas, "New Derivatives of Urea-Grafted Alginate for Improving the Sorption of Mercury Ions in Aqueous Solutions," *Materials Research Express* 8, no. 3 (2021): 035303, https://doi.org/10.1088/2053-1591/abeabc.

236. R. R. Navarro, M. Furukawa, and M. Matsumura, "Hybrid Properties of Alginate-PEI Adsorbent for Chromium (VI) Removal from Aqueous Solutions," *Separation Science and Technology* 41, no. 16 (2006): 3619–3637, https://doi.org/10.1080/01496390600956910.

237. J. K. Bediako, S. Lin, A. K. Sarkar, et al., “Benignly-fabricated Crosslinked Polyethylenimine/Calcium-alginate Fibers as High-performance Adsorbents for Effective Recovery of Gold,” *Journal of Cleaner Production* 252 (2020): 119389, https://doi.org/10.1016/j.jclepro.2019.119389.

238. I. Ali, C. Peng, D. Lin, et al., “Encapsulated Green Magnetic Nanoparticles for the Removal of Toxic Pb^{2+} and Cd^{2+} from Water: Development, Characterization and Application,” *Journal of Environmental Management* 234 (2019): 273–289, https://doi.org/10.1016/j.jenvman.2018.12.112.

239. K. Z. Elwakeel, M. M. Ahmed, A. Akhdhar, M. G. M. Sulaiman, and Z. A. Khan, “Recent Advances in Alginate-based Adsorbents for Heavy Metal Retention from Water: a Review,” *Desalination and Water Treatment* 272 (2022): 50–74, https://doi.org/10.5004/dwt.2022.28834.

240. Y. Tang, Q. Ma, Y. Luo, L. Zhai, Y. Che, and F. Meng, “Improved Synthesis of a Branched Poly(ethylene imine)-Modified Cellulose-Based Adsorbent for Removal and Recovery of Cu(II) from Aqueous Solution,” *Journal of Applied Polymer Science* 129, no. 4 (2013): 1799–1805, https://doi.org/10.1002/app.38878.

241. S. Kumari and G. S. Chauhan, “New Cellulose–Lysine Schiff-Base-Based Sensor–Adsorbent for Mercury Ions,” *ACS Applied Materials & Interfaces* 6, no. 8 (2014): 5908–5917, https://doi.org/10.1021/am500820n.

242. X. Yu, S. Tong, M. Ge, et al., “Adsorption of Heavy Metal Ions from Aqueous Solution by Carboxylated Cellulose Nanocrystals,” *Journal of Environmental Sciences* 25, no. 5 (2013): 933–943, https://doi.org/10.1016/S1001-0742(12)60145-4.

243. S. B. Khan, K. A. Alamry, H. M. Marwani, A. M. Asiri, and M. M. Rahman, “Synthesis and Environmental Applications of Cellulose/ZrO_2 Nanohybrid as a Selective Adsorbent for Nickel Ion,” *Composites Part B: Engineering* 50 (2013): 253–258, https://doi.org/10.1016/j.compositesb.2013.02.009.

244. Y. Zhou, S. Fu, L. Zhang, H. Zhan, and M. V. Levit, “Use of Carboxylated Cellulose Nanofibrils-filled Magnetic Chitosan Hydrogel Beads as Adsorbents for Pb(II),” *Carbohydrate Polymers* 101 (2014): 75–82, https://doi.org/10.1016/j.carbpol.2013.08.055.

245. A. Benettayeb, S. Ghosh, M. Usman, et al., “Some Well-Known Alginate and Chitosan Modifications Used in Adsorption: A Review,” *Water* 14, no. 9 (2022): 1353, https://doi.org/10.3390/w14091353.

246. A. Shanmugapriya, R. Ramya, S. Ramasubramaniam, and P. Sudha, “Studies on Removal of Cr(VI) and Cu(II) Ions Using Chitosangrafted-Polyacrylonitrile,” *Archives of Applied Science Research* 3, 3 (2011): 424–435.

247. L. Wang, R. Xing, S. Liu, et al., “Synthesis and Evaluation of a Thiourea-Modified Chitosan Derivative Applied for Adsorption of Hg(II) from Synthetic Wastewater,” *International Journal of Biological Macromolecules* 46, no. 5 (2010): 524–528, https://doi.org/10.1016/j.ijbiomac.2010.03.003.

248. Q. Yao, J. Xie, J. Liu, H. Kang, and Y. Liu, “Adsorption of Lead Ions Using a Modified Lignin Hydrogel,” *Journal of Polymer Research* 21, no. 6 (2014): 465, https://doi.org/10.1007/s10965-014-0465-9.

249. A. L. Popovic, J. D. Rusmirovic, Z. Velickovic, et al., “Novel Amino-functionalized Lignin Microspheres: High Performance Biosorbent with Enhanced Capacity for Heavy Metal Ion Removal,” *International Journal of Biological Macromolecules* 156 (2020): 1160–1173, https://doi.org/10.1016/j.ijbiomac.2019.11.152.

250. Q. Wang, C. Zheng, W. Cui, et al., “Adsorption of Pb^{2+} and Cu^{2+} Ions on the CS_2-modified Alkaline Lignin,” *Chemical Engineering Journal* 391 (2020): 123581, https://doi.org/10.1016/j.cej.2019.123581.

251. Z. Zhang, Q. Liu, T. Gao, C. Qiao, J. Yao, and C. Zhang, “Phenolation of Lignin for Polycatecholamines to Remove Cr (VI),” *Journal of Water Process Engineering* 50 (2022): 103334, https://doi.org/10.1016/j.jwpe.2022.103334.

252. R.-H. Liang, Y. Li, L. Huang, et al., “Pb^{2+} Adsorption by Ethylenediamine-Modified Pectins and Their Adsorption Mechanisms,” *Carbohydrate Polymers* 234 (2020): 115911, https://doi.org/10.1016/j.carbpol.2020.115911.

253. A. A. Almoukayed and R. Barhoum, “Chemical Modification of Keratin Using Schiff Bases to Prepare Cation Exchangers and Study Their Adsorption Activity,” *Heliyon* 9, no. 5 (2023): e15567, https://doi.org/10.1016/j.heliyon.2023.e15567.

254. M. Zubair, M. S. Roopesh, and A. Ullah, “Nano-modified Feather Keratin Derived Green and Sustainable Biosorbents for the Remediation of Heavy Metals from Synthetic Wastewater,” *Chemosphere* 308 (2022): 136339, https://doi.org/10.1016/j.chemosphere.2022.136339.

255. Y. Liang, Y. Tang, and W. Feng, “Non-covalent Interactions in Action: Advancing Eutectogels for Enhanced Stability and Performance,” *Polymer* 307 (2024): 127262, https://doi.org/10.1016/j.polymer.2024.127262.

256. C. C. Carrion, M. Nasrollahzadeh, M. Sajjadi, B. Jaleh, G. J. Soufi, and S. Iravani, “Lignin, Lipid, Protein, Hyaluronic Acid, Starch, Cellulose, Gum, Pectin, Alginate and Chitosan-based Nanomaterials for Cancer Nanotherapy: Challenges and Opportunities,” *International Journal of Biological Macromolecules* 178 (2021): 193–228, https://doi.org/10.1016/j.ijbiomac.2021.02.123.

257. Y. Sheth, S. Dharaskar, M. Khalid, and R. Walvekar, “Investigating Chromium Cr(VI) Removal Using Imidazolium Based Ionic Liquid-Chitosan Composite Adsorptive Film,” *Journal of Molecular Liquids* 347 (2022): 118317, https://doi.org/10.1016/j.molliq.2021.118317.

258. H. Yang, L. Zhu, Y. Zhou, et al., “Engineering Modulation of Cellulose-Induced Metal–Organic Frameworks Assembly Behavior for Advanced Adsorption and Separation,” *Chemical Engineering Journal* 498 (2024): 155333, https://doi.org/10.1016/j.cej.2024.155333.

259. R. Bhateria and R. Singh, “A Review on Nanotechnological Application of Magnetic Iron Oxides for Heavy Metal Removal,” *Journal of Water Process Engineering* 31 (2019): 100845, https://doi.org/10.1016/j.jwpe.2019.100845.

260. H. N. Abdelhamid and A. P. Mathew, “Cellulose–metal Organic Frameworks (CelloMOFs) Hybrid Materials and Their Multifaceted Applications: a Review,” *Coordination Chemistry Reviews* 451 (2022): 214263, https://doi.org/10.1016/j.ccr.2021.214263.

261. K. Bazaka, M. V. Jacob, R. J. Crawford, and E. P. Ivanova, “Plasma-assisted Surface Modification of Organic Biopolymers to Prevent Bacterial Attachment,” *Acta Biomaterialia* 7, no. 5 (2011): 2015–2028, https://doi.org/10.1016/j.actbio.2010.12.024.

262. T. Desmet, R. Morent, N. De Geyter, C. Leys, E. Schacht, and P. Dubruel, “Nonthermal Plasma Technology as a Versatile Strategy for Polymeric Biomaterials Surface Modification: a Review,” *Biomacromolecules* 10, no. 9 (2009): 2351–2378, https://doi.org/10.1021/bm900186s.

263. Y. Cao, H. Hua, P. Yang, et al., “Investigation into the Reaction Mechanism Underlying the Atmospheric Low-temperature Plasma-induced Oxidation of Cellulose,” *Carbohydrate Polymers* 233 (2020): 115632, https://doi.org/10.1016/j.carbpol.2019.115632.

264. M. Mikula, B. Trnovec, L. Černáková, S. Šutý, and V. Jančovičová, “Stabilization of Paper by Nitrogen Plasma Assisted Application of Chitosan at Atmospheric Pressure,” *Acta Chimica Slovaca* 2 (2009): 62–69.

265. M. Vajpayee, M. Singh, and L. Ledwani, “Non-thermal Plasma Surface Modification as an Environmentally Benign Way to Improve Sustainable Textile Polymers,” in *AIP Conference Proceedings* (AIP, 2025), 030002, https://doi.org/10.1063/5.0247542.

266. P. Bhatt, V. Kumar, V. Subramaniyan, et al., “Plasma Modification Techniques for Natural Polymer-Based Drug Delivery Systems,” *Pharmaceutics* 15, no. 8 (2023): 2066, https://doi.org/10.3390/pharmaceutics15082066.

267. P. Zong, D. Cao, Y. Cheng, et al., “Enhanced Performance for Eu(III) Ion Remediation Using Magnetic Multiwalled Carbon Nanotubes Functionalized with Carboxymethyl Cellulose Nanoparticles Synthesized by Plasma Technology,” *Inorganic Chemistry Frontiers* 5, no. 12 (2018): 3184–3196, https://doi.org/10.1039/C8QI00901E.

268. V. D. MH, S. Gurusamy, and P. Paramasivam, “Effective Incorporation of Surface Functional Groups through Direct Current Glow Discharge Plasma Treatment to Increase the Chelation of Metal Ions onto Zein/Chitosan Composite Films,” *International Journal of Biological Macromolecules* 309 (2025): 143186, https://doi.org/10.1016/j.ijbiomac.2025.143186.

269. S. K. Nemani, R. K. Annavarapu, B. Mohammadian, et al., “Surface Modification of Polymers: Methods and Applications,” *Advanced Materials Interfaces* 5, no. 24 (2018): 1801247, https://doi.org/10.1002/admi.201801247.

270. X. Li, S. Ji, E. He, et al., “UV/Ozone Induced Physicochemical Transformations of Polystyrene Nanoparticles and Their Aggregation Tendency and Kinetics with Natural Organic Matter in Aqueous Systems,” *Journal of Hazardous Materials* 433 (2022): 128790, https://doi.org/10.1016/j.jhazmat.2022.128790.

271. Y. Zhang, R. Yan, T.-D. Ngo, et al., “Ozone Oxidized Lignin-based Polyurethane with Improved Properties,” *European Polymer Journal* 117 (2019): 114–122, https://doi.org/10.1016/j.eurpolymj.2019.05.006.

272. A. T. Naikwadi, B. K. Sharma, K. D. Bhatt, and P. A. Mahanwar, “Gamma Radiation Processed Polymeric Materials for High Performance Applications: a Review,” *Frontiers in Chemistry* 10 (2022): 837111, https://doi.org/10.3389/fchem.2022.837111.

273. E. M. Kornacka, G. Przybytniak, L. Fuks, M. Walo, and K. Łyczko, “Functionalization of Polymer Surfaces by Radiation-induced Grafting for Separation of Heavy Metal Ions,” *Radiation Physics and Chemistry* 94 (2014): 115–118, https://doi.org/10.1016/j.radphyschem.2013.05.047.

274. B. Xu and J. Wang, “Radiation-induced Modification of Chitosan and Applications for Water and Wastewater Treatment,” *Journal of Cleaner Production* 467 (2024): 142924, https://doi.org/10.1016/j.jclepro.2024.142924.

275. S. Zhang, J. Gu, B. Fan, L. Li, and B. Li, “Synthesis of 2-Methylacrylamide/High-Molecular-Weight Cellulose Using Gamma Ray Irradiation and Preparation of Cryogels for Removing Anionic Dyes,” *Cellulose* 29, no. 10 (2022): 5511–5527, https://doi.org/10.1007/s10570-022-04615-5.

276. M. Barsbay and O. Güven, “Surface Modification of Cellulose via Conventional and Controlled Radiation-Induced Grafting,” *Radiation Physics and Chemistry* 160 (2019): 1–8, https://doi.org/10.1016/j.radphyschem.2019.03.002.

277. M. Mozetič, “Aging of Plasma-Activated Polyethylene and Hydrophobic Recovery of Polyethylene Polymers,” *Polymers* 15, no. 24 (2023): 4668, https://doi.org/10.3390/polym15244668.

278. M. Bertin, E. M. Leitao, S. Bickerton, and C. J. R. Verbeek, “A Review of Polymer Surface Modification by Cold Plasmas toward Bulk Functionalization,” *Plasma Processes and Polymers* 21, no. 5 (2024): 2300208, https://doi.org/10.1002/ppap.202300208.

279. Y. Xiao, W. Zhang, Y. Jiao, Y. Xu, and H. Lin, “Metal-phenolic Network as Precursor for Fabrication of Metal-organic Framework (MOF) Nanofiltration Membrane for Efficient Desalination,” *Journal of Membrane Science* 624 (2021): 119101, https://doi.org/10.1016/j.memsci.2021.119101.

280. S. Yang, V. V. Karve, A. Justin, et al., “Enhancing MOF Performance through the Introduction of Polymer Guests,” *Coordination Chemistry Reviews* 427 (2021): 213525, https://doi.org/10.1016/j.ccr.2020.213525.

281. T. Min, Y. Lei, C. Cheng, Y. Luo, Y. Zhang, and J. Yue, “Highly Efficient Anchoring of γ-cyclodextrin-MOFs on Chitosan/Cellulose Film by in Situ Growth to Enhance Encapsulation and Controlled Release of Carvacrol,” *Food Hydrocolloids* 150 (2024): 109633, https://doi.org/10.1016/j.foodhyd.2023.109633.

282. A. Duval and M. Lawoko, “A Review on Lignin-based Polymeric, Micro- and Nano-Structured Materials,” *Reactive and Functional Polymers* 85 (2014): 78–96, https://doi.org/10.1016/j.reactfunctpolym.2014.09.017.

283. R. Dubey, Y.-R. Toh, and A.-I. Yeh, “Enhancing Cellulose Functionalities by Size Reduction Using Media-Mill,” *Scientific Reports* 8, no. 1 (2018): 11343, https://doi.org/10.1038/s41598-018-29777-w.

284. M. Bansal, B. Ram, G. S. Chauhan, and A. Kaushik, “l-Cysteine Functionalized Bagasse Cellulose Nanofibers for Mercury(II) Ions Adsorption,” *International Journal of Biological Macromolecules* 112 (2018): 728–736, https://doi.org/10.1016/j.ijbiomac.2018.01.206.

285. A. Kumar, P. Kumar, S. Chopra, and A. Sindhu, “Application of Chitosan Nanoparticles in the Adsorption of Heavy Metals from Wastewater: A Concise Review,” *Asian Journal of Research in Chemistry* (2023): 389–393, https://doi.org/10.52711/0974-4150.2023.00063.

286. A. Chaturbedi, S. Patil, R. Ramachandran, and N. C. Shapley, “Adsorption of Positively and Negatively Charged Heavy Metal Ions from Wastewater by Heteroaggregates of Biopolymer Particles,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 602 (2020): 124789, https://doi.org/10.1016/j.colsurfa.2020.124789.

287. S. A. El-Kholy, “Environmentally Benign Freeze-dried Biopolymer-Based Cryogels for Textile Wastewater Treatments: A Review,” *International Journal of Biological Macromolecules* 276 (2024): 133931, https://doi.org/10.1016/j.ijbiomac.2024.133931.

288. J. A. Kenar, “Porous Structures from Bio-Based Polymers via Supercritical Drying,” in *Porous Lightweight Composites Reinforced With Fibrous Structures*, (Springer, 2017), 207–243, https://doi.org/10.1007/978-3-662-53804-3_9.

289. M. E. Lamm, K. Li, J. Qian, et al., “Recent Advances in Functional Materials through Cellulose Nanofiber Templating,” *Advanced Materials* 33, no. 12 (2021): 2005538, https://doi.org/10.1002/adma.202005538.

290. J. Ding, J. Zhang, J. Li, et al., “Electrospun Polymer Biomaterials,” *Progress in Polymer Science* 90 (2019): 1–34, https://doi.org/10.1016/j.progpolymsci.2019.01.002.

291. R. Zeinali, L. J. Del Valle, J. Torras, and J. Puiggalí, “Recent Progress on Biodegradable Tissue Engineering Scaffolds Prepared by Thermally-Induced Phase Separation (TIPS),” *International Journal of Molecular Sciences* 22, no. 7 (2021): 3504, https://doi.org/10.3390/ijms22073504.

292. A. C. Boccia, M. Neagu, and A. Pulvirenti, “Bio-Based Aerogels for the Removal of Heavy Metal Ions and Oils from Water: Novel Solutions for Environmental Remediation,” *Gels* 10, no. 1 (2023): 32, https://doi.org/10.3390/gels10010032.

293. X. Liu, W. Ren, W. Song, et al., “Novel EDTA-chitosan/Alginate Porous Composite Beads for the Removal of Pb(ii) and Methylene Blue from Aqueous Solutions,” *RSC Advances* 15, no. 17 (2025): 11343–13728, https://doi.org/10.1039/D5RA00940E.

294. R. Aston, M. Wimalaratne, A. Brock, G. Lawrie, and L. Grøndahl, “Interactions between Chitosan and Alginate Dialdehyde Biopolymers and Their Layer-by-Layer Assemblies,” *Biomacromolecules* 16, no. 6 (2015): 1807–1817, https://doi.org/10.1021/acs.biomac.5b00383.

295. Z. Zhang, J. Zeng, J. Groll, and M. Matsusaki, “Layer-by-layer Assembly Methods and Their Biomedical Applications,” *Biomaterials Science* 10, no. 15 (2022): 4077–4094, https://doi.org/10.1039/D2BM00497F.

296. S. Wijeratne, M. L. Bruening, and G. L. Baker, “Layer-by-Layer Assembly of Thick, Cu^{2+} -Chelating Films,” *Langmuir* 29, no. 41 (2013): 12720–12729, https://doi.org/10.1021/la402633x.

297. M. Kazemi, M. Jahanshahi, and M. Peyravi, “Chitosan-sodium Alginate Multilayer Membrane Developed by Fe0@WO3 Nanoparticles: Photocatalytic Removal of Hexavalent Chromium,” *Carbohydrate Polymers* 198 (2018): 164–174, https://doi.org/10.1016/j.carbpol.2018.06.069.

298. A. H. Mostafavi, A. K. Mishra, F. Gallucci, et al., “Advances in Surface Modification and Functionalization for Tailoring the Characteristics of Thin Films and Membranes via Chemical Vapor Deposition Techniques,” *Journal of Applied Polymer Science* 140, no. 15 (2023): 53720, https://doi.org/10.1002/app.53720.

299. J. Park, K. Shin, and C. Lee, “Roll-to-Roll Coating Technology and Its Applications: a Review,” *International Journal of Precision Engineering*

and Manufacturing 17, no. 4 (2016): 537–550, https://doi.org/10.1007/s12541-016-0067-z.

300. S. Özenler, A. A. Alkan, U. S. Gunay, O. Daglar, H. Durmaz, and U. H. Yildiz, "Thickness Gradient in Polymer Coating by Reactive Layer-by-Layer Assembly on Solid Substrate," *ACS Omega* 8, no. 40 (2023): 37413–37420, https://doi.org/10.1021/acsomega.3c05445.

301. A. C. S. Alcântara and M. Darder, "Building up Functional Bionanocomposites from the Assembly of Clays and Biopolymers," *Chemical Record* 18, no. 7–8 (2018): 696–712, https://doi.org/10.1002/tcr.201700076.

302. W. Wijesinghe, M. Mantilaka, K. A. A. Ruparathna, R. Rajapakshe, S. A. L. Sameera, and M. Thilakarathna, "Filler Matrix Interfaces of Inorganic/Biopolymer Composites and Their Applications," in *Interfaces in Particle and Fibre Reinforced Composites* (Elsevier, 2020), 95–112, https://doi.org/10.1016/B978-0-08-102665-6.00004-2.

303. M. El-Barghouthi, A. Eftaiha, I. Rashid, M. Al-Remawi, and A. Badwan, "A Novel Superdisintegrating Agent Made from Physically Modified Chitosan with Silicon Dioxide," *Drug Development and Industrial Pharmacy* 34, no. 4 (2008): 373–383, https://doi.org/10.1080/03639040701657792.

304. Z. Ansari, M. Kalantar, A. Soriente, et al., "In-Situ Synthesis and Characterization of Chitosan/Hydroxyapatite Nanocomposite Coatings to Improve the Bioactive Properties of Ti6Al4V Substrates," *Materials* 13, no. 17 (2020): 3772, https://doi.org/10.3390/ma13173772.

305. T. Pirzada, Z. Ashrafi, W. Xie, and S. A. Khan, "Cellulose Silica Hybrid Nanofiber Aerogels: from Sol–Gel Electrospun Nanofibers to Multifunctional Aerogels," *Advanced Functional Materials* 30, no. 5 (2020): 1907359, https://doi.org/10.1002/adfm.201907359.

306. Y. Fukui, N. Kabayama, and K. Fujimoto, "Fine-tuning in Mineral Cross-linking of Biopolymer Nanoparticle for Incorporation and Release of Cargo," *Colloids and Surfaces B: Biointerfaces* 136 (2015): 168–174, https://doi.org/10.1016/j.colsurfb.2015.09.011.

307. V. N. Tirtom, A. Dinçer, S. Becerik, T. Aydemir, and A. Çelik, "Comparative Adsorption of Ni(II) and Cd(II) Ions on Epichlorohydrin Crosslinked Chitosan–clay Composite Beads in Aqueous Solution," *Chemical Engineering Journal* 197 (2012): 379–386, https://doi.org/10.1016/j.cej.2012.05.059.

308. J. Sun, Y. Chen, H. Yu, L. Yan, B. Du, and Z. Pei, "Removal of Cu2+, Cd2+ and Pb2+ from Aqueous Solutions by Magnetic Alginate Microsphere Based on Fe_3O_4/MgAl-layered Double Hydroxide," *Journal of Colloid and Interface Science* 532 (2018): 474–484, https://doi.org/10.1016/j.jcis.2018.07.132.

309. C. D. Tran and T. M. Mututuvari, "Cellulose, Chitosan, and Keratin Composite Materials. Controlled Drug Release," *Langmuir* 31, no. 4 (2015): 1516–1526, https://doi.org/10.1021/la5034367.

310. C. D. Tran and T. M. Mututuvari, "Cellulose, Chitosan and Keratin Composite Materials: Facile and Recyclable Synthesis, Conformation and Properties," *ACS Sustainable Chemistry & Engineering* 4, no. 3 (2016): 1850–1861, https://doi.org/10.1021/acssuschemeng.6b00084.

311. N. U. Rehman, K. S. Ullah, M. Sajid, I. Ihsanullah, and A. Waheed, "Preparation of Sustainable Composite Materials from Bio-Based Domestic and Industrial Waste: Progress, Problems, and Prospects: A Review," *Advanced Sustainable Systems* 8, no. 8 (2024): 2300587, https://doi.org/10.1002/adsu.202300587.

312. V. Nair, A. Panigrahy, and R. Vinu, "Development of Novel chitosan–lignin Composites for Adsorption of Dyes and Metal Ions from Wastewater," *Chemical Engineering Journal* 254 (2014): 491–502, https://doi.org/10.1016/j.cej.2014.05.045.

313. I. Aranaz, A. R. Alcántara, and M. C. Civera, "Chitosan: an Overview of Its Properties and Applications," *Polymers* 13, no. 19 (2021): 3256, https://doi.org/10.3390/polym13193256.

314. M. Škerget, M. Čolnik, L. F. Zemljič, et al., "Efficient and Green Isolation of Keratin from Poultry Feathers by Subcritical Water," *Polymers* 15, no. 12 (2023): 2658, https://doi.org/10.3390/polym15122658.

315. J. R. Barone, "Lignocellulosic Fiber-Reinforced Keratin Polymer Composites," *Journal of Polymers and the Environment* 17, no. 2 (2009): 143–151, https://doi.org/10.1007/s10924-009-0131-1.

316. W. J. Grigsby, S. M. Scott, M. I. Plowman-Holmes, P. G. Middlewood, and K. Recabar, "Combination and Processing Keratin with Lignin as Biocomposite Materials for Additive Manufacturing Technology," *Acta Biomaterialia* 104 (2020): 95–103, https://doi.org/10.1016/j.actbio.2019.12.026.

317. A. Ali, A. Mannan, I. Hussain, I. Hussain, and M. Zia, "Effective Removal of Metal Ions from Aquous Solution by Silver and Zinc Nanoparticles Functionalized Cellulose: Isotherm, Kinetics and Statistical Supposition of Process," *Environmental Nanotechnology, Monitoring and Management* 9 (2018): 1–11, https://doi.org/10.1016/j.enmm.2017.11.003.

318. D. K. Verma, R. Malik, J. Meena, and R. Rameshwari, "Synthesis, Characterization and Applications of Chitosan Based Metallic Nanoparticles: A Review," *Journal of Appliend and Natural Science* 13, no. 2 (2021): 544–551, https://doi.org/10.31018/jans.v13i2.2635.

319. S. Deng, J. Long, X. Dai, G. Wang, and L. Zhou, "Simultaneous Detection and Adsorptive Removal of Cr(VI) Ions by Fluorescent Sulfur Quantum Dots Embedded in Chitosan Hydrogels," *ACS Applied Nano Materials* 6, no. 3 (2023): 1817–1827, https://doi.org/10.1021/acsanm.2c04768.

320. L. Jing, Q. Ding, X. Li, et al., "Bifunctional Collagen fiber/Carbon Quantum Dot Fluorescent Adsorbent for Efficient Adsorption and Detection of Pb^{2+}," *Science of The Total Environment* 871 (2023): 161989, https://doi.org/10.1016/j.scitotenv.2023.161989.

321. P. Tewatia, V. Kaushik, M. S. Jyoti, D. Pathania, S. Singhal, and A. Kaushik, "Highly Fluorescent Composite of Boron Nitride Quantum Dots Decorated on Cellulose Nanofibers for Detection and Removal of Hg(II) Ions from Waste Water," *International Journal of Biological Macromolecules* 234 (2023): 123728, https://doi.org/10.1016/j.ijbiomac.2023.123728.

322. X.-Y. You, W.-M. Yin, Y. Wang, et al., "Enrichment and Immobilization of Heavy Metal Ions from Wastewater by Nanocellulose/Carbon Dots-Derived Composite," *International Journal of Biological Macromolecules* 255 (2024): 128274, https://doi.org/10.1016/j.ijbiomac.2023.128274.

323. V. Hegde, U. T. Uthappa, M. Suneetha, T. Altalhi, S. Soo Han, and M. D. Kurkuri, "Functional Porous Ce-UiO-66 MOF@Keratin Composites for the Efficient Adsorption of Trypan Blue Dye from Wastewater: A Step towards Practical Implementations," *Chemical Engineering Journal* 461 (2023): 142103, https://doi.org/10.1016/j.cej.2023.142103.

324. J. Li, G. Lin, Z. Zhong, et al., "A Novel Magnetic Ti-MOF/Chitosan Composite for Efficient Adsorption of Pb(II) from Aqueous Solutions: Synthesis and Investigation," *International Journal of Biological Macromolecules* 258 (2024): 129170, https://doi.org/10.1016/j.ijbiomac.2023.129170.

325. N. Wang, X.-K. Ouyang, L.-Y. Yang, and A. M. Omer, "Fabrication of a Magnetic Cellulose Nanocrystal/Metal–Organic Framework Composite for Removal of Pb(II) from Water," *ACS Sustainable Chemistry & Engineering* 5, no. 11 (2017): 10447–10458, https://doi.org/10.1021/acssuschemeng.7b02472.

326. N. P. Raval, P. U. Shah, and N. K. Shah, "Nanoparticles Loaded Biopolymer as Effective Adsorbent for Adsorptive Removal of Malachite Green from Aqueous Solution," *Water Conservation Science and Engineering* 1, no. 1 (2016): 69–81, https://doi.org/10.1007/s41101-016-0004-0.

327. A. Kaur, D. Singh, and D. Sud, "A Review on Grafted, Crosslinked and Composites of Biopolymer Xanthan Gum for Phasing out Synthetic Dyes and Toxic Metal Ions from Aqueous Solutions," *Journal of Polymer Research* 27, no. 10 (2020): 297, https://doi.org/10.1007/s10965-020-02271-6.

328. M. Karmakar, H. Mondal, T. Ghosh, P. K. Chattopadhyay, D. K. Maiti, and N. R. Singha, "Chitosan-grafted Tetrapolymer Using Two Monomers: PH-responsive High-performance Removals of Cu(II), Cd(II), Pb(II), Dichromate, and Biphosphate and Analyses of Adsorbed Microstructures," *Environmental Research* 179 (2019): 108839, https://doi.org/10.1016/j.envres.2019.108839.

329. S. C. Moreno-Rivas, M. J. Ibarra-Gutiérrez, D. Fernández-Quiroz, A. Lucero-Acuña, A. J. Burgara-Estrella, and P. Zavala-Rivera, "pH-Responsive Alginate/Chitosan Gel Films: an Alternative for Removing Cadmium and Lead from Water," *Gels* 10, no. 10 (2024): 669, https://doi.org/10.3390/gels10100669.

330. H.-A. S. Tohamy, M. El-Sakhawy, and B. Strachota, "Temperature- and pH-Responsive Super-Absorbent Hydrogel Based on Grafted Cellulose and Capable of Heavy Metal Removal from Aqueous Solutions," *Gels* 9, no. 4 (2023): 296, https://doi.org/10.3390/gels9040296.

331. M. Ikram, F. Hu, G. Peng, et al., "Light-Activated Fuel-Free Janus Metal Organic Framework Colloidal Motors for the Removal of Heavy Metal Ions," *ACS Applied Materials & Interfaces* 13, no. 43 (2021): 51799–51806, https://doi.org/10.1021/acsami.1c16902.

332. C.-Y. Wang, L. Ma, C.-C. Wang, P. Wang, L. Gutierrez, and W. Zheng, "Light-response Adsorption and Desorption Behaviors of Metal–Organic Frameworks," *Environmental and Functional Materials* 1, no. 1 (2022): 49–66, https://doi.org/10.1016/j.efmat.2022.05.002.

333. A. Varone, R. Narducci, A. Palombi, S. Rasulzade, R. Montanari, and M. Richetta, "Recent Developments in Layered Double Hydroxides as Anticorrosion Coatings," *Materials* 18, no. 15 (2025): 3488, https://doi.org/10.3390/ma18153488.

334. R. Yue, R. Zhu, S. Wang, et al., "The Role of pH on Structure, Corrosion Behavior and Biocompatibility of MgFe Layered Double Hydroxide Coating on Mg–Nd–Zn–Zr Alloy," *Scientific Reports* 15, no. 1 (2025): 14842, https://doi.org/10.1038/s41598-025-98555-2.

335. T. B. Mbuyazi and P. A. Ajibade, "Magnetic Iron Oxides Nanocomposites: Synthetic Techniques and Environmental Applications for Wastewater Treatment," *Discover Nano* 19, no. 1 (2024): 158, https://doi.org/10.1186/s11671-024-04102-9.

336. S. Rojas, J. García-González, P. Salcedo-Abraira, et al., "Ti-based Robust MOFs in the Combined Photocatalytic Degradation of Emerging Organic Contaminants," *Scientific Reports* 12, no. 1 (2022): 14513, https://doi.org/10.1038/s41598-022-18590-1.

337. D. Hopkins and K. Hawboldt, "Biochar for the Removal of Metals from Solution: a Review of Lignocellulosic and Novel Marine Feedstocks," *Journal of Environmental Chemical Engineering* 8, no. 4 (2020): 103975, https://doi.org/10.1016/j.jece.2020.103975.

338. J. Xiang, B. X. Luo, J. M. Li, et al., "Development of KOH and H_3PO_4-modified Composite Biochar from Corn Straw and Activated Sludge for Removing Methylene Blue," *International Journal of Environmental Science and Technology* 20, no. 2 (2023): 1673–1688, https://doi.org/10.1007/s13762-022-04062-6.

339. J. K. Bediako, E. Kudoahor, C.-R. Lim, et al., "Exploring the Insights and Benefits of Biomass-derived Sulfuric Acid Activated Carbon for Selective Recovery of Gold from Simulated Waste Streams," *Waste Management* 177 (2024): 135–145, https://doi.org/10.1016/j.wasman.2024.02.002.

340. A. Herath, C. A. Layne, F. Perez, E. B. Hassan, C. U. Pittman, and T. E. Mlsna, "KOH-activated High Surface Area Douglas Fir Biochar for Adsorbing Aqueous Cr(VI), Pb(II) and Cd(II)," *Chemosphere* 269 (2021): 128409, https://doi.org/10.1016/j.chemosphere.2020.128409.

341. S. Chaisit, N. Chanlek, J. Khajonrit, T. Sichumsaeng, and S. Maensiri, "Preparation, Characterization, and Electrochemical Properties of KOH-activated Carbon from Cassava Root," *Materials Research Express* 7, no. 10 (2020): 105605, https://doi.org/10.1088/2053-1591/abbf84.

342. C. Shi, R.-G. Zeng, S.-C. Yuan, et al., "Preparing a Heavy-metal Adsorbent Based on Alginate-Like Extracellular Polymers from Conventional Activated Sludge via Polyethyleneimine Grafting," *Sustainable Chemistry and Pharmacy* 38 (2024): 101472, https://doi.org/10.1016/j.scp.2024.101472.

343. M. Gineys, R. Benoit, N. Cohaut, F. Bèc, and S. Delpeux-Ouldriane, "Grafting of Activated Carbon Cloths for Selective Adsorption," *Applied Surface Science* 370 (2016): 522–527, https://doi.org/10.1016/j.apsusc.2015.11.257.

344. Y. Chen, F. Zi, X. Hu, et al., "Grafting of Organic Sulfur-containing Functional Groups on Activated Carbon for Gold(I) Adsorption from Thiosulfate Solution," *Hydrometallurgy* 185 (2019): 102–110, https://doi.org/10.1016/j.hydromet.2019.02.007.

345. T. Chen, C. Yan, Y. Wang, et al., "Synthesis of Activated Carbon-based Amino Phosphonic Acid Chelating Resin and Its Adsorption Properties for Ce(III) Removal," *Environmental Technology* 36, no. 17 (2015): 2168–2176, https://doi.org/10.1080/09593330.2015.1023365.

346. F. H. Emamy, A. Bumajdad, and J. P. Lukaszewicz, "Adsorption of Hexavalent Chromium and Divalent Lead Ions on the Nitrogen-Enriched Chitosan-Based Activated Carbon," *Nanomaterials* 11, no. 8 (2021): 1907, https://doi.org/10.3390/nano11081907.

347. C. I. La Fuente Arias, M. T. K. Kubo, C. C. Tadini, and P. E. D. Augusto, "Bio-based Multilayer Films: a Review of the Principal Methods of Production and Challenges," *Critical Reviews in Food Science and Nutrition* 63, no. 14 (2023): 2260–2276, https://doi.org/10.1080/10408398.2021.1973955.

348. D. Gandavadi, S. Sundarrajan, and S. Ramakrishna, "Bio-Based Nanofibers Involved in Wastewater Treatment," *Macromolecular Materials and Engineering* 304, no. 11 (2019): 1900345, https://doi.org/10.1002/mame.201900345.

349. M. Li, Z. Liu, S. Wang, et al., "Fluorescence Detection and Removal of Copper from Water Using a Biobased and Biodegradable 2D Soft Material," *Chemical Communications* 54, no. 2 (2018): 184–187, https://doi.org/10.1039/C7CC08035B.

350. O. M. Atta, S. Manan, A. Shahzad, M. Ul-Islam, M. W. Ullah, and G. Yang, "Biobased Materials for Active Food Packaging: A Review," *Food Hydrocolloids* 125 (2022): 107419, https://doi.org/10.1016/j.foodhyd.2021.107419.

351. B. A. Martins, P. B. S. De Albuquerque, and M. P. De Souza, "Bio-based Films and Coatings: Sustainable Polysaccharide Packaging Alternatives for the Food Industry," *Journal of Polymers and the Environment* 30, no. 10 (2022): 4023–4039, https://doi.org/10.1007/s10924-022-02442-0.

352. A. J. Nathanael and T. H. Oh, "Biopolymer Coatings for Biomedical Applications," *Polymers* 12, no. 12 (2020): 3061, https://doi.org/10.3390/polym12123061.

353. Y. Liu, W. Chen, and H.-I. Kim, "Removal of Lead and Nickel Ions from Wastewater by Genipin Crosslinked Chitosan/Poly(ethylene glycol) Films," *Journal of Macromolecular Science, Part A* 49, no. 3 (2012): 242–250, https://doi.org/10.1080/10601325.2012.649202.

354. M. Morales-Jiménez, D. A. Palacio, M. Palencia, M. F. Meléndrez, and B. L. Rivas, "Bio-Based Polymeric Membranes: Development and Environmental Applications," *Membranes* 13, no. 7 (2023): 625, https://doi.org/10.3390/membranes13070625.

355. S. Acarer-Arat, İ. Pir, M. Tüfekci, S. Güneş-Durak, A. Akman, and N. Tüfekci, "Heavy Metal Rejection Performance and Mechanical Performance of Cellulose-Nanofibril-Reinforced Cellulose Acetate Membranes," *ACS Omega* 9, no. 41 (2024): 42159–42171, https://doi.org/10.1021/acsomega.4c03038.

356. F. Galiano, K. Briceño, T. Marino, A. Molino, K. V. Christensen, and A. Figoli, "Advances in Biopolymer-based Membrane Preparation and Applications," *Journal of Membrane Science* 564 (2018): 562–586, https://doi.org/10.1016/j.memsci.2018.07.059.

357. A. Naeem, B. Saeed, H. AlMohamadi, et al., "Sustainable and Green Membranes for Chemical Separations: a Review," *Separation and Purification Technology* 336 (2024): 126271, https://doi.org/10.1016/j.seppur.2024.126271.

358. H. Kolya and C.-W. Kang, "Next-Generation Water Treatment: Exploring the Potential of Biopolymer-Based Nanocomposites in Adsorption and Membrane Filtration," *Polymers* 15, no. 16 (2023): 3421, https://doi.org/10.3390/polym15163421.

359. A. K. Mallik, S. F. Kabir, F. Bin Abdur Rahman, M. N. Sakib, S. S. Efty, and M. M. Rahman, "Cu(II) Removal from Wastewater Using Chitosan-based Adsorbents: a Review," *Journal of Environmental Chemical Engineering* 10, no. 4 (2022): 108048, https://doi.org/10.1016/j.jece.2022.108048.

360. J. Ostrowska-Czubenko, M. Gierszewska, and M. Pieróg, "pH-responsive Hydrogel Membranes Based on Modified Chitosan: Water Transport and Kinetics of Swelling," *Journal of Polymer Research* 22, no. 8 (2015): 153, https://doi.org/10.1007/s10965-015-0786-3.

361. T. C. Mokhena, V. Jacobs, and A. S. Luyt, "A Review on Electrospun Bio-based Polymers for Water Treatment," *Express Polymer Letters* 9, no. 10 (2015): 839–880, https://doi.org/10.3144/expresspolymlett.2015.79.

362. Q. Saiding and W. Cui, "Functional Nanoparticles in Electrospun Fibers for Biomedical Applications," *Nano Select* 3, no. 6 (2022): 999–1011, https://doi.org/10.1002/nano.202100335.

363. K. Halicka and J. Cabaj, "Electrospun Nanofibers for Sensing and Biosensing Applications—A Review," *International Journal of Molecular Sciences* 22, no. 12 (2021): 6357, https://doi.org/10.3390/ijms22126357.

364. M. Zare, K. Dziemidowicz, G. R. Williams, and S. Ramakrishna, "Encapsulation of Pharmaceutical and Nutraceutical Active Ingredients Using Electrospinning Processes," *Nanomaterials* 11, no. 8 (2021): 1968, https://doi.org/10.3390/nano11081968.

365. G. A. Appuhamillage, D. R. Berry, C. E. Benjamin, et al., "A Biopolymer-Based 3D Printable Hydrogel for Toxic Metal Adsorption from Water," *Polymer International* 68, no. 5 (2019): 964–971, https://doi.org/10.1002/pi.5787.

366. J. Zhang, J. C. White, J. He, et al., "Sustainable Bioactive Hydrogels for Organic Contaminant Elimination in Wastewater," *Nature Communications* 16, no. 1 (2025): 2512, https://doi.org/10.1038/s41467-025-57720-x.

367. S. Lone, D. H. Yoon, H. Lee, and I. W. Cheong, "Gelatin–chitosan Hydrogel Particles for Efficient Removal of Hg(II) from Wastewater," *Environmental Science: Water Research & Technology* 5, no. 1 (2019): 83–90, https://doi.org/10.1039/C8EW00678D.

368. M. Chen, A. Long, W. Zhang, et al., "Recent Advances in Alginate-based Hydrogels for the Adsorption–Desorption of Heavy Metal Ions from Water: a Review," *Separation and Purification Technology* 353 (2025): 128265, https://doi.org/10.1016/j.seppur.2024.128265.

369. M. Salimi, B. Channab, A. El Idrissi, M. Zahouily, and E. Motamedi, "A Comprehensive Review on Starch: Structure, Modification, and Applications in Slow/Controlled-release Fertilizers in Agriculture," *Carbohydrate Polymers* 322 (2023): 121326, https://doi.org/10.1016/j.carbpol.2023.121326.

370. S. Zhao, W. J. Malfait, N. Guerrero-Alburquerque, M. M. Koebel, and G. Nyström, "Biopolymer Aerogels and Foams: Chemistry, Properties, and Applications," *Angewandte Chemie International Edition* 57, no. 26 (2018): 7580–7608, https://doi.org/10.1002/anie.201709014.

371. J. M. Bloor, R. D. Handy, S. A. Awan, and D. F. L. Jenkins, "Graphene Oxide Biopolymer Aerogels for the Removal of Lead from Drinking Water Using a Novel Nano-Enhanced Ion Exchange Cascade," *Ecotoxicology and Environmental Safety* 208 (2021): 111422, https://doi.org/10.1016/j.ecoenv.2020.111422.

372. H. I. Syeda, S. Muthukumaran, and K. Baskaran, "Investigation of Regeneratable Biopolymer-based Aerogels for Heavy Metal Decontamination from Water: Quantum Chemical Analysis and Experimental Investigation," *Separation and Purification Technology* 353 (2025): 128311, https://doi.org/10.1016/j.seppur.2024.128311.

373. W. Li, S. Yang, Y. Wang, C. Peng, Y. Li, and E. Tao, "Selective Adsorption of Cu(II) on Amino-Modified Alginate-based Aerogel: as a Catalyst for the Degradation of Organic Contaminant," *International Journal of Biological Macromolecules* 278 (2024): 134700, https://doi.org/10.1016/j.ijbiomac.2024.134700.

374. Y. Liu, C. Jin, Z. Yang, G. Wu, G. Liu, and Z. Kong, "Recent Advances in Lignin-Based Porous Materials for Pollutants Removal from Wastewater," *International Journal of Biological Macromolecules* 187 (2021): 880–891, https://doi.org/10.1016/j.ijbiomac.2021.07.152.

375. J. Paul, A. Qamar, S. S. Ahankari, S. Thomas, and A. Dufresne, "Chitosan-based Aerogels: A New Paradigm of Advanced Green Materials for Remediation of Contaminated Water," *Carbohydrate Polymers* 338 (2024): 122198, https://doi.org/10.1016/j.carbpol.2024.122198.

376. H. I. Syeda and P.-S. Yap, "A Review on Three-dimensional Cellulose-based Aerogels for the Removal of Heavy Metals from Water," *Science of The Total Environment* 807 (2022): 150606, https://doi.org/10.1016/j.scitotenv.2021.150606.

377. A. Baimenov, D. A. Berillo, S. G. Poulopoulos, and V. J. Inglezakis, "A Review of Cryogels Synthesis, Characterization and Applications on the Removal of Heavy Metals from Aqueous Solutions," *Advances in Colloid and Interface Science* 276 (2020): 102088, https://doi.org/10.1016/j.cis.2019.102088.

378. M. García-Castrillo, G. Barandika, and E. Lizundia, "Low Environmental Impact Magnetic Chitosan and Chitin Cryogels for PFAS Remediation," *Advanced Functional Materials* 34, no. 46 (2024): 2405298, https://doi.org/10.1002/adfm.202405298.

379. S.-S. Li, Y.-L. Song, H.-R. Yang, Q.-D. An, Z.-Y. Xiao, and S.-R. Zhai, "Carboxymethyl Cellulose-based Cryogels for Efficient Heavy Metal Capture: Aluminum-mediated Assembly Process and Sorption Mechanism," *International Journal of Biological Macromolecules* 164 (2020): 3275–3286, https://doi.org/10.1016/j.ijbiomac.2020.08.186.

380. H. Cheng, Y. Li, B. Wang, et al., "Chemical Crosslinking Reinforced Flexible Cellulose Nanofiber-supported Cryogel," *Cellulose* 25, no. 1 (2018): 573–582, https://doi.org/10.1007/s10570-017-1548-7.

381. V. H. A. Braga, D. P. Fuentes, P. V. Oliveira, and D. F. S. Petri, "Biopolymer Cryogels for Enhanced Adsorption of Valuable Metals from Multi-metal Waste after Flocculation and Precipitation," *Journal of Environmental Chemical Engineering* 12, no. 5 (2024): 113306, https://doi.org/10.1016/j.jece.2024.113306.

382. N. Li, D. Qiao, S. Zhao, Q. Lin, B. Zhang, and F. Xie, "3D Printing to Innovate Biopolymer Materials for Demanding Applications: A Review," *Materials Today Chemistry* 20 (2021), 100459, https://doi.org/10.1016/j.mtchem.2021.100459.

383. J. Liu, L. Sun, W. Xu, Q. Wang, S. Yu, and J. Sun, "Current Advances and Future Perspectives of 3D Printing Natural-derived Biopolymers," *Carbohydrate Polymers* 207 (2019): 297–316, https://doi.org/10.1016/j.carbpol.2018.11.077.

384. C. Polesca, R. Sobreiro-Almeida, H. Passos, et al., "Engineered from Waste: Ionic Liquid Processing of Keratin for 3D Printing Biomedical Scaffolds," *ACS Materials Letters* (2025): 3370–3379, https://doi.org/10.1021/acsmaterialslett.5c00629.

385. N. Fijoł, A. Aguilar-Sánchez, and A. P. Mathew, "3D-printable Biopolymer-based Materials for Water Treatment: A Review," *Chemical Engineering Journal* 430 (2022): 132964, https://doi.org/10.1016/j.cej.2021.132964.

386. A. Sadeghianmaryan, S. Naghieh, H. Alizadeh Sardroud, et al., "Extrusion-based Printing of Chitosan Scaffolds and Their in Vitro Characterization for Cartilage Tissue Engineering," *International Journal of Biological Macromolecules* 164 (2020): 3179–3192, https://doi.org/10.1016/j.ijbiomac.2020.08.180.

387. Y. Wang, Y. Wang, S. Qiu, et al., "3D-Printed Filters for Efficient Heavy Metal Removal from Water Using PLA@CS/HAP Composites," *Polymers* 15, no. 20 (2023): 4144, https://doi.org/10.3390/polym15204144.

388. I. R. Woodward, L. Attia, P. Patel, and C. A. Fromen, "Scalable 3D-Printed Lattices for Pressure Control in Fluid Applications," *AIChE Journal* 67, no. 12 (2021): 17452, https://doi.org/10.1002/aic.17452.

389. J. Gong, C. C. L. Schuurmans, A. M. V. Genderen, et al., "Complexation-Induced Resolution Enhancement of 3D-Printed Hydrogel Constructs," *Nature Communications* 11, no. 1 (2020): 1267, https://doi.org/10.1038/s41467-020-14997-4.

390. T. Wu, H. Karimi-Maleh, Y. Li, et al., "3D-Printed Porous Chitosan/Metal–Organic Framework Composites as Effective Adsorbents to Remove Heavy Metals from Wastewater," *Chemical Engineering Journal* 493 (2024): 152780, https://doi.org/10.1016/j.cej.2024.152780.

391. D. Zhang, J. Xiao, Q. Guo, and J. Yang, "3D-printed Highly Porous and Reusable Chitosan Monoliths for Cu(II) Removal," *Journal of Materials Science* 54, no. 8 (2019): 6728–6741, https://doi.org/10.1007/s10853-019-03332-y.

392. I. L. Liakos, A. Mondini, E. D. Dottore, C. Filippeschi, F. Pignatelli, and B. Mazzolai, "3D printed Composites from Heat Extruded Polycaprolactone/Sodium Alginate filaments and Their Heavy Metal Adsorption Properties," *Materials Chemistry Frontiers* 4, no. 8 (2020): 2472–2483, https://doi.org/10.1039/D0QM00159G.

393. Z. Liu, Y. Sun, X. Xu, J. Qu, and B. Qu, "Adsorption of Hg(II) in an Aqueous Solution by Activated Carbon Prepared from Rice Husk Using KOH Activation," *ACS Omega* 5, no. 45 (2020): 29231–29242, https://doi.org/10.1021/acsomega.0c03992.

394. J. Yu, X. Yang, L. Xiao, et al., "Lignin-Derived Biochar for High-Performance Electrochemical Adsorption of Cd(II) from Aqueous Solutions," *Journal of Water Process Engineering* 77 (2025): 108452, https://doi.org/10.1016/j.jwpe.2025.108452.

395. C. Mohammed, S. Mahabir, K. Mohammed, N. John, K.-Y. Lee, and K. Ward, "Calcium Alginate Thin Films Derived from *Sargassum natans* for the Selective Adsorption of Cd^{2+}, Cu^{2+}, and Pb^{2+} Ions," *Industrial & Engineering Chemistry Research* 58, no. 3 (2019): 1417–1425, https://doi.org/10.1021/acs.iecr.8b03691.

396. S. Samadi, F. Khalilian, and A. Tabatabaee, "Synthesis, Characterization and Application of Cu–TiO_2/Chitosan Nanocomposite Thin Film for the Removal of some Heavy Metals from Aquatic Media," *Journal of Nanostructure in Chemistry* 4, no. 1 (2014): 84, https://doi.org/10.1007/s40097-014-0084-3.

397. A. Aluigi, A. Corbellini, F. Rombaldoni, and G. Mazzuchetti, "Wool-Derived Keratin Nanofiber Membranes for Dynamic Adsorption of Heavy-Metal Ions from Aqueous Solutions," *Textile Research Journal* 83, no. 15 (2013): 1574–1586, https://doi.org/10.1177/0040517512467060.

398. T. Siddike Moin, M. Rani Sarkar, M. F. Mahmud Chowdhury, M. M. Rahman, and M. N. Khan, "Electrospun Poly(vinyl alcohol)/Chitosan Nanofibers Embedded with a CuO–GO Nanocomposite for pH-Sensitive Adsorption of Heavy Metal Ions and Organic Dyes," *ACS Omega* 10, no. 19 (2025): 19294–19313, https://doi.org/10.1021/acsomega.4c08836.

399. E. Moradi, Z. Mehrani, and H. Ebrahimzadeh, "Gelatin/Sodium Triphosphate Hydrogel Electrospun Nanofiber Mat as a Novel Nanosorbent for Microextraction in Packed Syringe of La^{3+} and Tb^{3+} Ions Prior to Their Determination by ICP-OES," *Reactive and Functional Polymers* 153 (2020): 104627, https://doi.org/10.1016/j.reactfunctpolym.2020.104627.

400. H. Y. Choi, J. H. Bae, Y. Hasegawa, et al., "Thiol-functionalized Cellulose Nanofiber Membranes for the Effective Adsorption of Heavy Metal Ions in Water," *Carbohydrate Polymers* 234 (2020): 115881, https://doi.org/10.1016/j.carbpol.2020.115881.

401. H. Hao, "Engineered LDH-Alginate Composite Hydrogel Columns for Selective Heavy Metal Removal," *Frontiers in Chemistry* 13 (2025): 1649831, https://doi.org/10.3389/fchem.2025.1649831.

402. S. Sireesha and I. Sreedhar, "Unleashing the Potential of Cajanus Cajun Biochar Polymer Composite for Cu (II) Removal: Mechanism, Modification, and Application," *Environmental Science and Pollution Research* 32 (2024): 24072–24091, https://doi.org/10.1007/s11356-024-33551-z.

403. M. V. Dinu and E. S. Dragan, "Heavy Metals Adsorption on some Iminodiacetate Chelating Resins as a Function of the Adsorption Parameters," *Reactive and Functional Polymers* 68, no. 9 (2008): 1346–1354, https://doi.org/10.1016/j.reactfunctpolym.2008.06.011.

404. A. S. A. Mathematical, "Simulation of Copper and Nickel Ions Separation Using Prepared Nanocellulose Material," *Membranes* 13, no. 4 (2023): 381, https://doi.org/10.3390/membranes13040381.

405. N. Rajendran, T. Runge, R. D. Bergman, P. Nepal, and C. Houtman, "Techno-Economic Analysis and Life Cycle Assessment of Cellulose Nanocrystals Production from Wood Pulp," *Bioresource Technology* 377 (2023): 128955, https://doi.org/10.1016/j.biortech.2023.128955.

406. K. Benazouz, N. Bouchelkia, H. Moussa, et al., "Efficient Removal of Cu(II) from Wastewater Using Chitosan Derived from Shrimp Shells: a Kinetic, Thermodynamic, Optimization, and Modelling Study," *Water* 17, no. 6 (2025): 851, https://doi.org/10.3390/w17060851.

407. Straits Research. "Chitosan Market—Global Industry Analysis, Size, Share, Growth, Trends, and Forecast 2024-2032," accessed July 2, 2025, https://straitsresearch.com/report/chitosan-market.

408. L. Li, Y. Zeng, B. Ge, S. Liu, and R. Liu, "Complexation Mechanism and Adsorption Modes of Cu (II) Ions by Wool Keratin Powder," *Physica Scripta* 99, no. 11 (2024): 115017, https://doi.org/10.1088/1402-4896/ad8287.

409. "Trading Economics Wool 2025," accessed July 2, 2025, Available from: https://tradingeconomics.com/commodity/wool.

410. E. H. Gürkan and B. İlyas, "Adsorption of Copper, and Zinc Onto Novel Ca-alginate-biochar Composite Prepared by Biochars Produced from Pyrolysis of Groundnut Husk," *International Journal of Phytoremediation* 24, no. 13 (2022): 1350–1363, https://doi.org/10.1080/15226514.2022.2025759.

411. Tridge. "Export Price of Sodium Alginate From China," accessed July 2, 2025, https://dir.tridge.com/prices/sodium-alginate/CN.

412. Z. Sun, Y. Yin, Y. An, et al., "A Novel Modified Carboxymethyl Cellulose Hydrogel Adsorbent for Efficient Removal of Poisonous Metals from Wastewater: Performance and Mechanism," *Journal of Environmental Chemical Engineering* 10, no. 4 (2022): 108179, https://doi.org/10.1016/j.jece.2022.108179.

413. IMARC Group. "Carboxymethyl Cellulose (CMC) Prices, News, Market Analysis, and Forecast 2023," accessed July 2, 2025, https://www.imarcgroup.com/carboxymethyl-cellulose-pricing-report.

414. A. A. Al-Ghamdi, A. A. Galhoum, A. Alshahrie, Y. A. Al-Turki, A. M. Al-Amri, and S. Wageh, "Superparamagnetic Multifunctionalized Chitosan Nanohybrids for Efficient Copper Adsorption: Comparative Performance, Stability, and Mechanism Insights," *Polymers* 15, no. 5 (2023): 1157, https://doi.org/10.3390/polym15051157.

415. X. Sun, Y. Yang, Q. He, J. Li, R. Li, and H. Chen, "Adsorption Properties and Cost of Dicarboxylic Nanocellulose on Copper Ions for Wastewater Treatment," *Journal of Renewable Materials* 10, no. 3 (2022): 751–766, https://doi.org/10.32604/jrm.2022.016933.

416. P. K. Patel, L. M. Pandey, and R. V. S. Uppaluri, "Adsorption Behavior and Techno-economic Analysis of Citric Acid-modified Chitosan for Heavy Metal Removal from Wastewater," *Chemical Engineering Science* 315 (2025): 121868, https://doi.org/10.1016/j.ces.2025.121868.

417. D. B. Salem, A. Ouakouak, F. Touahra, et al., "Easy Separable, Floatable, and Recyclable Magnetic-biochar/Alginate Bead as Super-adsorbent for Adsorbing Copper Ions in Water media," *Bioresource Technology* 383 (2023): 129225, https://doi.org/10.1016/j.biortech.2023.129225.

418. E. Kendüzler and A. R. Türker, "Optimization of a New Resin, Amberlyst 36, as a Solid-Phase Extractor and Determination of Copper(II) in Drinking Water and Tea Samples by Flame Atomic Absorption Spectrometry," *Journal of Separation Science* 28, no. 17 (2005): 2344–2349, https://doi.org/10.1002/jssc.200500212.

419. Sigma-Aldrich. "Amberlyst 36 Ion Exchange Resin," accessed July 2, 2025, https://www.sigmaaldrich.com/PT/en/product/aldrich/436712?srsltid=AfmBOorr2YCa6UXF__KVXmdgq5NAh0-6XZQwJBYqNvFcuLqix_Hkr27a.

420. S. Elfeghe, S. Anwar, L. James, and Y. Zhang, “Adsorption of Cu(II) Ions from Aqueous Solutions Using Ion Exchange Resins with Different Functional Groups,” *The Canadian Journal of Chemical Engineering* 101, no. 4 (2023): 2128–2138, https://doi.org/10.1002/cjce.24632.

421. Sigma-Aldrich. “Dowex G26 Ion Exchange Resin, Hydrogen Form,” accessed July 2, 2025, https://www.sigmaaldrich.com/PT/en/product/sial/573663?srsltid=AfmBOop1D8P43hfVIMys-9VJfkEO1db0-VTtwMJ2hOqnCr4HX77bN66C.

422. C. V. Diniz, F. M. Doyle, and V. S. T. Ciminelli, “Effect of Ph on the Adsorption of Selected Heavy Metal Ions from Concentrated Chloride Solutions by the Chelating Resin Dowex M-4195,” *Separation Science and Technology* 37, no. 14 (2002): 3169–3185, https://doi.org/10.1081/SS-120006155.

423. M. K. Jha, N. Van Nguyen, J. Lee, J. Jeong, and J.-M. Yoo, “Adsorption of Copper from the Sulphate Solution of Low Copper Contents Using the Cationic Resin Amberlite IR 120,” *Journal of Hazardous Materials* 164, no. 2–3 (2009): 948–953, https://doi.org/10.1016/j.jhazmat.2008.08.103.

424. Sigma-Aldrich. “AmberliteTM IR-120, H^+ Form Report No.: Product No. 115131,” accessed July 2, 2025, https://www.sigmaaldrich.com/PT/en/product/mm/115131.

425. S. Kolbadinejad and A. Ghaemi, “Optimization of Simultaneous Adsorption of Nickel, Copper, Cadmium and Zinc from Sulfuric Solutions Using Weakly Acidic Resins,” *Scientific Reports* 14, no. 1 (2024): 7506, https://doi.org/10.1038/s41598-024-58366-3.

426. Avantor, “Amberlite IRC-748 Ion Exchange Resin,” accessed July 2, 2025, https://www.avantorsciences.com/ni/en/product/18041403/amberlite-irc-748-ion-exchange-resin.

427. H. I. Syeda, S. Muthukumaran, and K. Baskaran, “Dynamic Adsorption of Heavy Metals on Functionalized and Regeneratable Biopolymeric Aerogels: Fixed-bed Column Reactor Modelling and Dual Functionality Elution Technique,” *Separation and Purification Technology* 363 (2025): 131861, https://doi.org/10.1016/j.seppur.2025.131861.

428. D. Fila and D. Kołodyńska, “Fixed-Bed Column Adsorption Studies: Comparison of Alginate-Based Adsorbents for La(III) Ions Recovery,” *Materials* 16, no. 3 (2023): 1058, https://doi.org/10.3390/ma16031058.

429. P. K. Patel, L. M. Pandey, and R. V. S. Uppaluri, “Conceptual Techno-economic Analysis of Chitosan Derivative Resin and Commercial Sorbents for Multi-heavy Metal Removal,” *Separation and Purification Technology* 362 (2025): 131732, https://doi.org/10.1016/j.seppur.2025.131732.

430. I. Anastopoulos, D. A. Giannakoudakis, Z. Frontistis, A. A. Zorpas, I. Pashalidis, and K. Triantafyllidis, “Biomass-derived Adsorbents: Universal Database Development for Their Synthesis and Remediation Efficiency as a Necessary Step to Move from Laboratory- to Pilot-scale Applications,” *Current Opinion in Green and Sustainable Chemistry* 47 (2024): 100902, https://doi.org/10.1016/j.cogsc.2024.100902.