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Research article

Optimization of electro-Fenton process applied to the treatment of codfish brines in a context of industrial symbiosis

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ABSTRACT

The ancient method of preserving fish by salting is still widely practiced but generates two challenging waste streams: contaminated salt (solid) and brine (liquid). Conventional treatment methods are ineffective in reducing the organic content of brine due to its high salt content (≅ 25–30 % wt. NaCl). Although advanced oxidation processes are extensively used for treating certain wastewaters, their application to real saline effluents near saturation, such as food industry brines, remains underexplored. This study optimized the electro-Fenton (EF) process for treating real contaminated brines from the codfish industry, aiming to reuse the treated brines in the pickling stage of the tannery industry, thereby diverting waste streams from environment disposal. A central composite experimental design and response surface methodology were used to evaluate the effects of three EF process operating variables: (i) current density (76–429 A m^{-2}), (ii) electrolysis time (1.0–10.0 min), and (iii) hydrogen peroxide concentration ([H_2O_2], 50–201 mM), using iron electrodes. The primary goal was to maximize total organic carbon (TOC) removal from codfish brine. Additionally, the specific roles of reactive oxygen and chlorine species responsible for TOC removal (such as $HO^{\bullet}$, $Cl^{\bullet}$, ClO, $O_2^{\bullet-}/HO_2^{\bullet}$ and $HClO/OCl^{-}$) were investigated using scavengers. The results revealed that $O_2^{\bullet-}$, $HO_2^{\bullet}$ were the main active species. The optimal EF operating conditions were determined to be a current density of 275 A m^{-2}, electrolysis time of 5.2 min, and [H_2O_2] of 91 mM, resulting in a 70 % removal of TOC. The treated brines, diluted to ≅ 7.5–8.0 % wt. NaCl, were tested in hide pickling trials to assess their impact on the quality of the wet-blue leathers. Results showed that the treated brines did not affect leather quality; instead, they enhanced shrinkage temperature from 103 °C to 112 °C. This increase of shrinkage temperature broadens the potential applications of the leather, making it suitable for a wider range of markets and products. Furthermore, the chromium oxide content fixed in the leather increased from 4.1 % to 5.3 %, reducing chromium in the industrial wastewater generated at the end of the process. This valorisation of codfish brines presents a promising opportunity for industrial symbiosis between the codfish and the tannery industries.

1. Introduction

Saline wastewater, *aka* brine (i.e., an aqueous solution saturated with NaCl), is produced by several sectors, including desalination plants (Panagopoulos, 2022), oil and gas (An et al., 2017), coal (Zhong et al., 2021), textile (Ramos et al., 2021), fish processing (Giwa et al., 2017), leather (Maharaja et al., 2021), among others. The management of brines in these sectors has become a major environmental concern. Proper disposal is critical, as large quantities of brine discharged into the environment can adversely affect wastewater treatment plants and lead to the wastage of resources(Mavukkandy et al., 2019; Partal et al., 2022). Industries like codfish processing, often located near coastlines, tend to discharge brine directly into the sea, which could cause long-term negative effects on marine ecosystems (Partal et al., 2022). The increasing number of inland industries, coupled with water scarcity, has led to an increase in desalination plants. Although these plants

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produce clean water, the disposal of their brine byproduct remains a significant environmental burden (Mavukkandy et al., 2019; Panagopoulos, 2022). Therefore, there is a pressing need for innovative approaches to reduce brine discharge into the environment and to mitigate its ecological impact when such discharge is unavoidable.

Recent efforts have focused on the potential for water and salt recovery, aiming to reduce dependency on natural resources by adopting a circular economy approach (Chen et al., 2021; Giwa et al., 2017; Mavukkandy et al., 2019). However, treating brines for reuse in other industrial processes, particularly within the scope of industrial symbiosis to achieve zero liquid discharge, remains unexplored. Conventional treatment processes are often ineffective at reducing the organic content of saturated brines, such as those produced by the codfish industry, where high salt concentrations may hinder or suppress microbial activity in both aerobic and anaerobic biological processes (Kokabian et al., 2013; Maharaja et al., 2021). On the other hand, treated codfish brines hold potential to be reused in other industrial applications, such as the pickling stage in tanneries. This process requires significant quantities of water and salt (≅ 7.5–8 % wt. NaCl) to prevent acidic hide swelling (Bes-Piá et al., 2008; Sarinho et al., 2023).

In recent years, electrochemical technologies, including electrocoagulation (EC) and electrooxidation (EO), based on Advanced Oxidation Processes (AOPs), have gained attention for wastewater treatment. These technologies have demonstrated effectiveness in: (i) removing several pollutants from industrial wastewaters, including contaminated brines, (ii) offering cost advantages over alternative technologies, and (iii) providing potentially greater efficiency (Alam et al., 2022; GilPavas et al., 2017; Kuleyin et al., 2021; Nidheesh and Gandhimathi, 2012; Suman et al., 2021). In the EC process, aluminium or iron electrodes are commonly used as anodes to generate coagulant agents *in situ* through electrolytic oxidation, promoting pollutant removal (GilPavas et al., 2017). The ions released (Al^{3+} or Fe^{2+}) are hydrolysed in the bulk solution (Eq. (2)), forming various monomeric and polymeric species that ultimately transform into insoluble (oxy) hydroxide (Tegladza et al., 2021). The dissolution of metal from anode can be estimated using the Faraday's law (Eq. (1)).

$$W_{th} = \frac{I \times t \times M_w}{Z \times F} \tag{1}$$

Where W_{th} is the theorical mass of metal dissolved (g), I is the applied current intensity (A), t is the electrolysis time (s), M_w is the molecular weight of the metal, Z is the number of electrons involved in the redox reactions, and F is the Faraday's constant (96,500 C mol^{-1}).

Additionally, water is electrolysed, generating oxygen at the anode and hydrogen gas at the cathode (Eqs. (3)–(4)), which enhances the removal of organic material through flotation (Naje et al., 2016). The EO process focuses on the electrogeneration of hydroxyl radicals ($HO^{\bullet}$), powerful and non-selective oxidant with a potential of +2.80 V, which attack pollutant molecules present in the wastewater (GilPavas et al., 2017; Cuerda-Correa et al., 2020). EO process can occur in two main ways: (i) direct oxidation, where pollutants adsorbed onto the anode surface decompose through electron transfer, without requiring an oxidizing agent; and/or (ii) indirect oxidation, where pollutants decompose via oxidation reactions with *in situ* or externally added oxidants, such as hypochlorite, chlorine and hydrogen peroxide (H_2O_2, E^o = + 1.76 V) (Guo et al., 2022; Kuleyin et al., 2021; Cuerda-Correa et al., 2020). A key advantage of the direct EO process is that it does not require the external addition of reagents for hydroxyl radical's production. However, the process can become costly due to the need for inert anode electrodes, such as boron-doped diamond (BDD), titanium (Ti), graphite, or platinum (Pt) (Nidheesh et al., 2018; Sun et al., 2021). The combination of EC and indirect EO processes (e.g., electro-Fenton) has proven highly effective in treating industrial wastewaters due to the generation of strongly oxidizing species through electric current (Afanga et al., 2020; Barrera-Díaz et al., 2014; García-Espinoza et al., 2023; GilPavas et al., 2019). Generally, the electrochemically-assisted Fenton process, which uses iron as catalyst, can follow four different approaches depending on the addition or formation mechanism of the Fenton reagent (Abbasi et al., 2022; Doumbi et al., 2022; Nidheesh et al., 2018; Ramos et al., 2021; Ribeiro et al., 2020; Ribeiro and Nunes, 2021): (i) Fe^{2+} is externally added and H_2O_2 is indirectly generated through oxidation reactions with inert electrodes; (ii) both Fe^{2+} and H_2O_2 are externally added to produce $HO^{\bullet}$ in the electrolytic cell, with Fe^{2+} being regenerated at the cathode; (iii) Fe^{2+} and H_2O_2 are electrogenerated using a sacrificial anode and an inert cathode; and (iv) H_2O_2 is externally added, and Fe^{2+} provided from sacrificial iron anodes, Eq. (2).

In anode:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2}$$

In cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

In the latter approach, the Fe^{2+} ions released from the anode react with H_2O_2, generating three main oxidants (Eqs. (5)–(8)): $HO^{\bullet}$, hydroperoxyl radical ($HO_2^{\bullet}$, E^o = +1.44 V) and superoxide anion ($O_2^{\bullet-}$, E^o = +0.93 V) (Andrés et al., 2023; Cuerda-Correa et al., 2020). These species actively degrade the organic matter in solution.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\cdot} \tag{5}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \tag{6}$$

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \tag{7}$$

$$O_2^{\cdot-} + H^+ \leftrightarrow HO_2^{\cdot} \tag{8}$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \tag{9}$$

Some of the limitations of the Fenton process include the rapid oxidation of iron into less reactive species and the generation of large amounts of sludge (Ribeiro and Nunes, 2021). Although both Fe^{2+} and Fe^{3+} can generate $HO^{\bullet}$, the reaction in Eq. (6) is significantly slower than that in Eq. (5), leading to excess iron hydroxides and subsequent sludge formation. To overcome these drawbacks, the electro-Fenton process has been proposed as an alternative (De Carluccio et al., 2024; Yáñez-Ángeles et al., 2025). The EF process is typically conducted under acidic conditions (pH ≅ 3) to promote the formation of highly reactive, non-selective intermediate species that initiate the oxidation of organic compounds (Afanga et al., 2020; Nidheesh and Gandhimathi, 2012; Ribeiro et al., 2020). Its overall performance and stability are influenced by wastewater composition, operating conditions, and reactor design (Guo et al., 2022; Peng et al., 2025). Additionally, increasing solution conductivity enhances EF efficiency, making it particularly suitable for treating saline wastewater (Alam et al., 2022; Pasciucco et al., 2025; Peng et al., 2025). In the presence of high NaCl concentrations, chloride ions (Cl^-) can react with H_2O_2 and $HO^{\bullet}$ to form reactive chlorine species, such as $Cl^{\bullet}$, $Cl_2^{\bullet-}$, $ClO^{\bullet}$, Cl_2, and HClO (Lai et al., 2021). Several studies have demonstrated the effectiveness of the EF process in treating saline wastewater. For instance, Darvishmotevalli et al. (2019) successfully removed 91.78 % of COD from a synthetic saline wastewater (≅ 3 % wt. NaCl) using EF. Similarly, Chai et al. (2021) highlighted the EF process's potential as an emerging technology for treating high-salinity (1 % wt. NaCl) organic wastewater. On the other hand, elevated Cl^- concentrations in wastewater can significantly impair the efficiency of organic matter removal by AOPs (Chen et al., 2022; Li et al., 2024; Yang et al., 2023). Yang et al. (2023) observed that increasing Cl^- concentrations from 0.5 to 2 M reduced total organic carbon (TOC) removal in the UV/H_2O_2 process, with TOC removal of 23.56 % and 13.82 %, respectively, compared to 12.31 % in the absence of Cl^-. These findings suggest that scavenging effects by Cl^- become particularly more pronounced at higher Cl^- concentrations, reducing the removal of organic matter. While the performance of AOPs for treating saline wastewater has been widely discussed (Huang et al., 2024; Ye et al., 2024), their application to real streams remains limited (Carneiro et al., 2024), particularly for highly saline solutions near saturation (≅ 30.0 % wt. NaCl at 25 °C), where the reactive medium is still not well understood. Moreover, to the best of the authors' knowledge, no reported studies have incorporated saline solutions from the food industry, treat them, and subsequently reuse them in another industrial sector. Addressing this research gap, the present study evaluated efficiency of the EF process in the reducing organic content in real codfish industry brine for its potential reuse in the tanning industry. The specific objectives were to: (i) optimize the EF process for treating contaminated codfish brine (CcB); (ii) identify the predominant reactive oxygen species (ROS) involved in organic matter oxidation; and (iii) assess the applicability of the treated brines (tB) for hide pickling.

The innovation of the present work lies in its novel approach for treating and valorising saline waste from the codfish industry within the framework of industrial symbiosis. By contributing to the development of a zero-liquid discharge system, this study plays a crucial role in enhancing the sustainability and circularity of the codfish industry. Instead of disposing these materials into the environment, they are reintegrated into the economic cycle, thereby reducing environmental impact and creating new opportunities for industrial applications. Furthermore, this research highlights the urgent need to scale these technologies to an industrial level, thereby promoting sustainable practices across different industries processes.

2. Materials and methods

To achieve the study's objectives, CcB was treated at lab scale by EF process, employing iron electrodes and externally added hydrogen peroxide as the oxidant. The effects of electrolysis time (t, min), current density (J, $A \cdot m^{-2}$), and H_2O_2 concentration ($[H_2O_2]$) on removal of TOC from CcB were evaluated. After treatment, each brine from the different experimental condition was diluted (≅ 7.5–8.0 % wt. NaCl) and subjected to laboratory hide pickling trials to assess its effect on the quality of the wet-blue leathers.

Additionally, the contribution of ROS, including HO•, Cl•, ClO•, $HClO/OCl^-$ and O_2•−/HO_2•, to TOC removal was investigated using scavengers.

2.1. Chemicals

Hydrogen peroxide (H_2O_2, 30 % wt./v), sulfuric acid (H_2SO_4, 96 %), sodium nitrite ($NaNO_2$, ≥97 %) and sodium sulphite (Na_2SO_3, 98 %) were purchased from Fisher Chemical. Tert-butyl alcohol (TBA – $C_4H_{10}O$, ≥99 %), chloroform ($CHCl_3$, 99 %) and ammonium sulphate ($(NH_4^+)_2SO_4$, ≥99 %) were obtained from VWR Chemicals. All chemicals were used as received, without further purification, and all solutions were prepared using distilled water.

2.2. Contaminated codfish brines

A real contaminated and NaCl-saturated brine from a Portuguese codfish industry was treated by EF process. Two grab samples were collected at different time periods, and their physical-chemical composition characterized using standard methods (see Section 2.6). The mean values of each parameter (based on three repetitions) and the corresponding standard deviations (s) are shown in Table 1.

Most of the suspended solids in the brine samples were inorganic (≅ 89 % wt.). As shown in Table 1, the high conductivity and TDS values indicate a significant concentration of dissolved salts, corresponding to approximately 28 % wt. NaCl. The pH was slightly acidic and therefore required adjustment to 2 − 3 before EF treatment. Regarding TOC content, the recorded values in both samples were of the same order of magnitude as those reported by Souli et al. (2023) for fish canning wastewater.

Table 1
Physico-chemical characterization of the contaminated codfish brines used in this study.

Parameter	Sample 1 (S_1)	Sample 2 (S_2)
	Mean ± s	Mean ± s
Total Organic Carbon, TOC [$mg\ L^{-1}$]	4280.2 ± 13.4	5852.2 ± 57.5
Absorbable Organic Halides, AOX [$mg\ L^{-1}$]	–	15.4 ± 1.2
Total Suspended Solids [$mg\ L^{-1}$]	9651.0 ± 204.9	8171.9 ± 131.5
Volatile Suspended Solids [$mg\ L^{-1}$]	989.4 ± 8.3	767.5 ± 36.4
Total Dissolved Solids, TDS [$g\ L^{-1}$]	279.1 ± 14.4	284.3 ± 7.8
pH	6.1 ± 0.3	6.4 ± 0.3
Conductivity [$mS\ cm^{-1}$]	322.5 ± 0.3	304.8 ± 0.1

S_1- sample used in the assays tB_1 to tB_{17}; S_2- sample used in the assays tB_{18} and R_{s1} to R_{s5}.

2.3. Brine treatment and application

The schematic representation of the experimental procedure for the treatment assays of CcB is shown in Fig. 1. The batch reactor used in this study had a working volume of 1 L and was equipped with two iron plates electrodes, with a total contact area of 79.2 cm^2, placed 10 cm apart. These electrodes were connected to a DC power supply (MLINK, RYI). The iron released from the sacrificial anode served a dual purpose in the EF process, acting both a catalyst (see Eq. (2)) and a coagulant, facilitating electrocoagulation. Before treatment, the pH of CcB was adjusted to 2.4 using sulfuric acid (H_2SO_4, 36 N), the same acid used in hide pickling stage. The oxidant (H_2O_2) was then added in a single step under agitation using an open straight two-bladed polymer impeller. The DC power supply was switched on with pre-set current intensity and voltage values, and electrolysis time was recorded. After the pre-established electrolysis time had elapsed, the power supply was switched off, and the brine was transferred to a graduated cylinder for a 1 h settling period to allow suspended particles to settle. Supernatant samples were collected, immediately quenched with a 1.5 M of sodium sulphite aqueous solution, preserved (with pH adjustment using H_2SO_4 if needed), and stored at temperature below 4 °C for subsequent TOC quantification and hide pickling tests. All EF assays were performed at room temperature (*c.a.* 20 °C) without addition of supporting electrolytes, relying on the raw conductivity of the CcB. To prevent electrode passivation and ensure even wear, the electrode polarity was reversed before each assay.

The hide pickling assays were performed using bovine skin flaps from the neck area, which had been previously delimed and purged. A reference pickling assay was also conducted using virgin brine prepared with virgin salt as a control. These trials were carried out at lab-scale to evaluate various leather properties/contents, namely thickness, shrinkage temperature, grease content, free fatty acids (FFA) content, and hexavalent chromium content.

2.4. Statistical data treatment of EF process

The central composite rotatable design (CCRD) and the response surface methodology (RSM) were used to evaluate the effect of three operating variables (i.e., independent variables or factors) on TOC removal (i.e., dependent variable or response), namely: current density, electrolysis time and H_2O_2 concentration. This approach allows for the investigation of both individual effects and the interaction effects between these variables. For further details on this methodology and examples of its application, see, for instance, Ribeiro et al. (2020), Rodrigues and Iemma. (2014) and Vargas et al. (2021).

Table 2 presents the predefined ranges for the experimental design, where "-1", "0", "+1" and ± "1.68" represent the minimum, central, maximum, and axial points, respectively. These ranges were determined

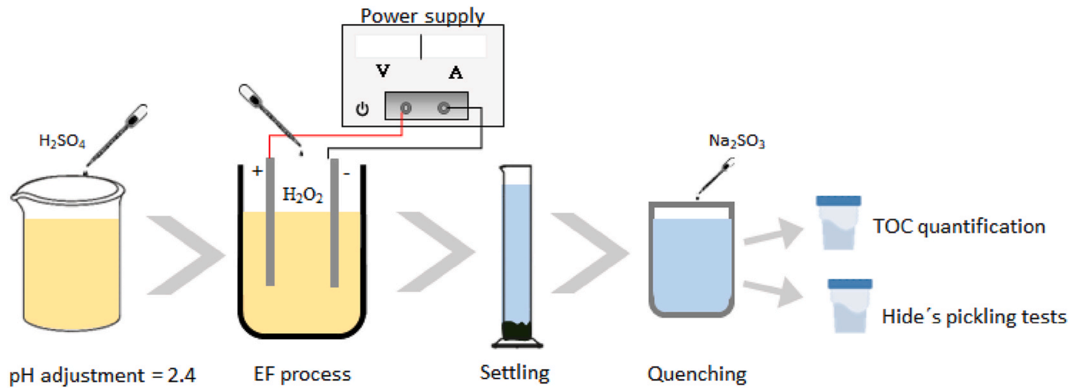

Fig. 1. Schematic diagram of brine treatment by the EF process.

Table 2
Experimental range of the studied independent variables used in the CCRD experiments for optimization of TOC removal efficiency by electro-Fenton process.

Independent variable	−1.68	−1	0	+1	+1.68
Current density, J [A m^{-2}]	76	151	252	353	429
Electrolysis time, t [min]	1.0	3.6	6.0	8.4	10.0
[H_2O_2] [mM]	50	80	125	170	201

based on preliminary screening experiments (data not shown) and a literature review. A total of 17 assays were performed, including 3 repetitions at the central point, to assess statistical inferences and process repeatability. The assays were carried out in random order to minimize systematic errors, with the central point repetitions scheduled at the beginning, middle, and end of the trial sequence.

The regression model fitted to the experimental data was a second order polynomial function, as described in Eq. (10).

$$Y = k + ax_1 + bx_1^2 + cx_2 + dx_2^2 + ex_3 + fx_3^2 + gx_1x_2 + hx_1x_3 + jx_2x_3 \quad (10)$$

where Y represents the fitted response (TOC removal), $k, a, b, \ldots, j$ are the regression coefficients. The terms x_1, x_2 and x_3 represent the independent variables: current density, electrolysis time and [H_2O_2], respectively. The last three terms of Eq. (10) correspond to the interactions between the operating variables. An analysis of variance (ANOVA) of the regression was performed to evaluate the model's adequacy. The determination coefficients (R^2 and $R^2_{adjusted}$) and the Lack of Fit test were used as metrics to assess the model's goodness-of-fit. Standardized residuals plots were analysed to validate the model's underlying assumptions. Once the best-fitting regression model was identified and validated, the optimal operating conditions were determined using RSM. To further validate the model, three experimental runs were performed under the predicted optimal conditions, allowing for comparison between the model-predicted and experimental results. The composite sample of the three treated brines (tB_{18}) was also used for hide's pickling trials. A 95 % confidence level was adopted for statistical analyses. Statistical analysis was performed using StatSoft Statistica® v. 8.0 software.

2.5. Reactive oxygen species

After determining the optimal EF experimental conditions, an additional set of EF experiments was conducted to evaluate the contribution of different ROS on TOC removal (Table 3). Scavenging reagents were added to the brine after pH adjustment and prior to the addition of the H_2O_2, following the procedure described in Section 2.3. Each experiment was performed in triplicate.

Table 3
Scavenging reagents and their respective ratios to the oxidant used in the electro-Fenton process.

Assay reference	Scavenging reagents	ROS scavenged	Scavenging reagent:H_2O_2 (mol:mol)	References
Rs_1	TBA	$HO^•$, $Cl^•$, $ClO^•$	1:1	Lal and Garg (2017)
Rs_2	$NaNO_2$	$HO^•$	1:1	Ren et al. (2022)
Rs_3	$CHCl_3$	$O_2^{•-}/HO_2^•$	2:1	Lal and Garg (2017)
Rs_4	$(NH_4^+)_2SO_4$	$HClO/OCl^-$	3:1	Ren et al. (2022)
Rs_5	$(NH_4^+)_2SO_4$ and TBA	$HClO/$ $OCl^-HO^•$, $Cl^•$, $ClO^•$	3:1 and 1:1	Lal and Garg (2017) Ren et al. (2022)

Table 4
ANOVA results of the response surface quadratic model with interactions.

Variable	Sum of squares	Degrees of freedom	Mean square	F – value	p - value
x_1	312.8	1	312.8	202.6	0.005
x_1^2	2.724	1	2.724	1.765	0.315
x_2	894.5	1	894.5	579.6	0.002
x_2^2	316.5	1	316.5	205.1	0.005
x_3	3.931	1	3.931	2.547	0.252
x_3^2	4.734	1	4.734	3.068	0.222
x_1x_2	396.2	1	396.2	255.7	0.004
x_1x_2	20.80	1	20.80	13.48	0.067
x_2x_3	39.16	1	39.16	25.37	0.037
Lack of fit	142.7	5	28.53	18.48	0.052
Pure error	3.087	2	1.543		
Total	2031.5	16			
	$R^2 \cong 0.929$	$R^2_{adj} \cong 0.836$			

2.6. Analytical methods

TOC concentration was quantified according to standard method 5310 B (American Public Health Association APHA et al., 1999) using a Sievers InnovOx lab TOC analyser. Solids quantification was performed following standard methods 2540 C (Total Dissolved Solids), 2540 D (Total Suspended Solids), and 2540 E (Volatile Suspended Solids) (American Public Health Association APHA et al., 1999). pH and electrical conductivity were measured with a Consort Instrument® multi-parameter meter. The properties of the leather after the pickling tests were assessed using procedures outlined in ISO 5433 (2013). AOX was quantified by coulometric titration, following EN 16166:2012, ISO

9562:2004, and EPA Method 1650C, using a Thermo TOC 1200 AOX/-Total Carbon Analyser.

3. Results

3.1. Optimization of electro-Fenton process

Table 5 presents the TOC concentrations of the treated brines (assay tB1 to tB17) under each experimental condition tested. TOC removals were calculated using these values and the initial TOC concentration of brine sample S_1 (shown in Table 1). The best-fitting model for TOC removal is given in Eq. (11), with an $R^2 \cong 0.93$ and $R^2_{adjusted} \cong 0.84$, indicating that 93 % of the variability in the data was explained by the model. Additionally, Figure. S1 (d) confirms the model's adequacy, as the predicted values closely align with the observed ones along a 45° diagonal line. According to Darvishmotevalli et al. (2019), an R^2 above 0.80 is typically considered acceptable for good agreement between predicted and experimental values. Moreover, the model's Lack of Fit was statistically non-significant (p-value = 0.052), suggesting that the regression model adequately predicts the effects of the three independent variables studied on the response variable.

$$Y = 64.91 + 9.417x_1 + 0.9351x_1^2 - 15.83x_2 - 8.726x_2^2 - 1.073x_3 + 1.328x_3^2 + 14.07x_1x_2 + 3.225x_1x_3 - 4.425x_2x_3 \quad (11)$$

The assumptions of the regression model were validated by the analysis of residuals plots (Fig. S1) and no outlier was identified.

Each term in the model was tested for significance and the results are presented in Table 4.

The results presented in Table 4 indicate that both the linear and quadratic terms of the electrolysis time (x_2 and x_2^2) had statistically significant effects on TOC removal (p-value <0.05), as well as the linear term of current density (x_1). Two significant interaction terms were identified: one between current intensity and electrolysis time (positive sign) and another between electrolysis time and $[H_2O_2]$ (negative sign). The positive interaction refers to synergistic effects; in other words, when electrolysis time is higher, the effect of $[H_2O_2]$ on TOC removal increases and vice versa. The order of significance of the three factors influencing TOC removal is electrolysis time > current density > $[H_2O_2]$.

Similar findings were reported by Karabacakoğlu and Karaduman (2024), who investigated the effects of voltage, $[H_2O_2]$, pH, electrode spacing, and electrolysis time on the removal of reactive yellow 145 azo dye using EF process (anode: iron; cathode: carbon fibre). They found that $[H_2O_2]$ was the only variable that did not significantly affect removal efficiency, with the order of impact being voltage > electrode spacing > electrolysis time > pH > $[H_2O_2]$. The authors also identified a relationship between $[H_2O_2]$ and removal efficiency. While it might have seemed intuitive that increasing the $[H_2O_2]$ would enhance the generation of $HO^{\bullet}$ radicals, this relationship was not linear. The authors highlighted that increasing the $[H_2O_2]$ can promote secondary reactions, such as those described in Eq. (6), which generate $HO_2^{\bullet}$ radicals with a lower oxidation potential compared to $HO^{\bullet}$ radicals. Furthermore, when both H_2O_2 and Fe^{2+} ions are present in excess, additional reactions, like those detailed in Eq. (7) and Eq. (9), may occur, further inhibiting removal efficiency. Meng et al. (2022) also explored the EF process to treat cooking wastewater using an iron cathode and titanium anode. They found that voltage and electrode spacing were the most significant variables affecting COD removal, likely because current density decreases as the electrode spacing increases. Conversely, Ghjair et al. (2023) reported that for COD removal from hospital wastewater using iron and stainless-steel electrodes, the linear terms of $[H_2O_2]$, current density, and electrolysis time were statistically significant ($[H_2O_2]$ > current density > electrolysis time), but the interaction effects were not. Guvenc et al. (2017), investigating the EF process for removing COD, phenol, and Ca^{2+} from paper mill wastewater, ranked the significance of variables as pH > current density > $[H_2O_2]$ > electrolysis time. The differences in results across studies may stem from variations in wastewater sources and electrode materials, underscoring the importance of customizing EF optimization to the specific effluent and its post-treatment use.

The response surface plots showing the TOC removal registered in this work are depicted in Fig. 2. TOC removals achieved after brine treatment by EF ranged from 35 to 70 %.

For a given $[H_2O_2]$ within the tested ranges, TOC removal can be achieved by either using a lower current density with a shorter electrolysis time or, alternatively, a higher current density with a longer electrolysis time (Fig. 2 (a)). From an economic perspective, the latter approach is preferable, as reducing electrolysis time could help lower costs while maximizing treatment efficiency. When electrolysis times exceed 6 min and current density falls below 300 A m^{-2}, TOC removal remained low (20–40 %), suggesting that H_2O_2 rapidly oxidized organic

Table 5
Effect of electro-Fenton treated brines on the quality parameters of chrome tanned leathers.

Assay	EF experimental condition					Wet-blue' leathers quality parameters				
	J [A m^{-2}]	t [min]	$[H_2O_2]$ [mM]	[Fe][a] [mM]	TOC[b] [mg L^{-1}]	Thickness [mm]	Shrinkage T [°C]	Grease [%]	FFA [%]	Cr_2O_3 [%]
Virgin brine						3.91	103.0	0.5	<0.10	4.1
tB_1	76	6.0	125	1.12	1617	3.92	109.0	1.2	<0.10	4.1
tB_2	429	6.0	125	6.34	1317	3.63	108.5	1.1	<0.10	4.8
tB_3	252	1.0	125	0.62	1517	4.23	109.5	1.0	<0.10	4.4
tB_4	252	10.0	125	6.22	2770	3.31	110.5	1.1	0.20	5.1
tB_5	252	6.0	50	3.73	1513	3.67	110.5	1.3	0.10	4.5
tB_6	252	6.0	201	3.73	1373	3.36	109.5	0.9	0.10	4.8
tB_7	151	3.6	80	1.34	1327	3.29	109.5	1.0	0.10	5.0
tB_8	353	3.6	80	3.13	1427	3.36	107.5	0.7	<0.10	4.8
tB_9	151	8.4	80	3.13	2227	3.36	109.5	1.1	<0.10	4.5
tB_{10}	151	3.6	170	1.34	1347	3.45	108.5	1.2	<0.10	5.4
tB_{11}	353	8.4	80	7.31	1253	3.80	110.5	1.4	<0.10	4.6
tB_{12}	353	3.6	170	3.13	1300	3.96	108.5	0.1	<0.10	4.2
tB_{13}	151	8.4	170	3.13	2757	3.63	112.0	1.7	0.20	4.4
tB_{14}	353	8.4	170	7.31	1373	3.32	108.5	1.3	0.10	5.1
tB_{15}	252	6.0	125	3.73	1547	3.37	107.0	1.2	0.10	5.2
tB_{16}	252	6.0	125	3.73	1457	3.72	102.5	0.9	0.10	4.1
tB_{17}	252	6.0	125	3.73	1453	3.79	104.0	1.6	<0.10	4.3
tB_{18}	278	5.2	91	3.07	1767	3.92	109.5	0.7	<0.10	4.8

[a] predicted by Eq. (1).
[b] after EF treatment.

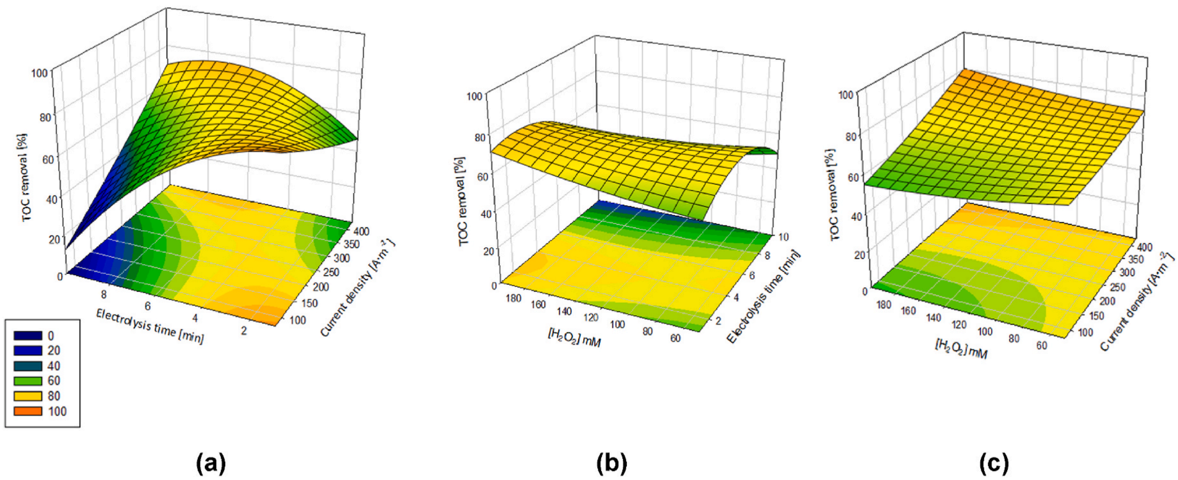

Fig. 2. Response surface plots of TOC removal as a function of: (a) electrolysis time and current density for $[H_2O_2] = 125$ mM, (b) electrolysis time and $[H_2O_2]$ for current density $= 252$ A m^{-2}, (c) $[H_2O_2]$ and current density for electrolysis time $= 3.6$ min. The gradient colour legend, which represents TOC removal [%], is common to all three plots.

pollutants in the CcB within a short time frame.

Nidheesh and Gandhimathi (2012) noted in their review that EF efficiency decreases at higher current density. Similarly, Pasciucco et al. (2025) investigated the optimal operating conditions for treating secondary tannery effluents at neutral pH using EF process. Among the variables studied - current density, $[H_2O_2]$, and electrolysis time -current density was identified as the most significant variable influencing COD removal. The authors observed that increasing current density accelerates the electrochemical reactions by promoting Fe^{2+} ion release. However, employing high current densities may lead to several undesirable effects, such as corrosion of the anode surface and increased iron sludge production. Furthermore, increased current results in excess of iron and H_2 gas in solution, causing competitive reactions between hydroxyl radicals and excess ferrous ions, as described in Eqs. (6)–(9) (Doumbi et al., 2022).

Fig. 2 (b) shows that for an electrolysis time of 6 min, increasing $[H_2O_2]$ leads to a slow decrease in TOC removal. This decline in efficiency for longer electrolysis times can be attributed to three potential factors (Doumbi et al., 2022; Yavuz et al., 2014): (i) insufficient Fe^{2+} to catalyse the generation of $HO^{\bullet}$ from H_2O_2; (ii) formation of hydrogen gas at the cathode, which may inhibit $HO^{\bullet}$ production; and (iii) the formation of more persistent low molecular weight compounds that are harder to degrade. To evaluate the first factor, the iron released from the anode was estimated using Eq. (1) for all experimental conditions, with the corresponding the values presented in Table 5. A comparison between tB_{13} and tB_{14}, both with the same treatment time (8.4 min) and $[H_2O_2]$ (170 mM) but different iron concentrations, highlights the impact of Fe^{2+} availability. tB_{14}, with an iron concentration estimate of 7.31 mM, achieved 68 % TOC removal, whereas tB_{13}, with only 3.13 mM of iron, achieved 36 %.

Within the tested ranges, a combination of lower current density and lower $[H_2O_2]$ provided better TOC removal for a given electrolysis time (Fig. 2 (c)). James and Garg (2024) reported similar findings in their study on the EF process (with H_2O_2 externally added and Fe from sacrificial anodes) for removing high concentrations of sulphides and phenols from synthetic sulphidic spent caustic wastewater. Phenol removal increased from 65 % to 85.5 % as $[H_2O_2]$ rose from 260 mM to 790 mM, but further increases in $[H_2O_2]$ showed only marginal improvements ($\cong$ 90 % at $[H_2O_2] = 1000$ mM), with an electrolysis time of 2 h. They also observed that increasing current density from 10 to 20 A m^{-2} reduced phenol removal from 98 % to 95 %, under the same electrolysis time. Similarly, Doumbi et al. (2022) observed low degradation of organic matter for current intensities up to 0.3 A when applying EF process to treat tannery wastewater using graphite electrodes (with iron externally added). Likewise, Yu et al. (2023) reported the same trend when applying EF for the removal of pesticides from wastewater, with iron added externally and titanium plate with ruthenium-iridium coating serving as the anode. They recommended using a low current density ($\leq$200 A m^{-2}) and an electrolysis time within 1 h. When applying a direct EO process (with BDD electrodes) for removing pharmaceutical compounds from real urban wastewater, Jiménez-Bambague et al. (2023) found that high current values can accelerate the production of H_2O_2 and Fe^{2+}, contributing to TOC removal up to a maximum point, beyond which removal efficiency declines. These studies consistently highlight the importance of optimizing current density and $[H_2O_2]$ to balance reactive species generation and minimize side reactions that could hinder pollutant degradation. In line with these findings, the model from Eq. (11) predicts the following optimal operating conditions: current density of 275 A m^{-2}, electrolysis time of 5.2 min and $[H_2O_2]$ of 91 mM, resulting in a predicted TOC removal of $\cong$ 70 %. The three experimental runs carried out under these optimal conditions achieved a TOC removal of 69.8 % $\pm$ 0.6 %, thereby validating the model. In addition, the power consumption under these optimal conditions was 0.61 kWh m^{-3} of treated brine, which falls within the range reported in previous studies on electrochemical processes applied to real wastewater (Rodríguez-Peña et al., 2024; Sarinho et al., 2023).

3.2. Contribution of reactive oxygen species to TOC removal

To identify the predominant ROS involved in the oxidation of organic matter during the EF process, experiments were performed using radical scavengers. The results from these experiments were compared with the treatment of codfish brine under optimal operating conditions, without scavengers (tB18), as presented in Fig. 3.

Adding scavengers, such as TBA and $(NH_4^+)_2SO_4$, to the reaction medium decreased TOC removal from 70 % (tB_{18}) to 48–49 % (Rs_1 and Rs_4, respectively). Notably, $CHCl_3$ exhibited the strongest inhibitory effect ($Rs_3 = 28$ %), indicating that $O_2^{\bullet-}/HO_2^{\bullet}$ radicals, rather than $HO^{\bullet}$, played a central role in the EF process when applied to the wastewater matrix of this study. This is consistent with the findings of Lai et al. (2023), who investigated polycyclic aromatic hydrocarbons (PAHs) removal in a Fenton/Cl^- system using simulated sludge solid phase. In that study, p-benzoquinone, which targets $O_2^{\bullet-}/HO_2^{\bullet}$, notably inhibited PAHs removal, and an increased Cl^- content ($\geq$1000 mg L^{-1}) corresponded to an increased contribution of $O_2^{\bullet-}/HO_2^{\bullet}$ radicals in the process. Chen et al. (2022) also observed that in a FeSiB/H_2O_2 system with specific Cl^- concentrations, TBA did not exhibit the strongest inhibitory

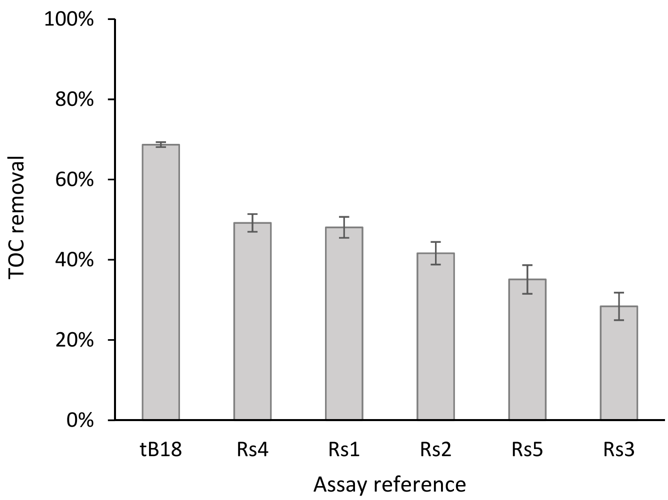

Fig. 3. Effect of radical scavengers on TOC removal during electro-Fenton process compared to treated brine (tB18) in the absence of scavengers.

effect. Using scavengers like methanol for $HO^•$ and $SO_4^{•-}$), TBA (for $HO^•$), and furfuryl alcohol (for $^1O_2$) at 10 mM, they found that the removal of azo dye OII decreased, after 60 min, from 83.43 % to 67.39 %, 70.45 % and 32.93 % with methanol, TBA and furfuryl alcohol, respectively.

Given the high salt content in codfish brine, Cl^- ions could react with H_2O_2 and $HO^•$ to form ROS that promote the process's efficiency, which may explain the lower TOC removal observed in Rs_3 (see Eq. (6)). Yang et al. (2023) investigated Cl^- effects on TOC removal in an UV/H_2O_2 system, reporting that TOC removal increased with Cl^- concentration from 0 M to 2 M. They suggested that $HO^•$ not only attacks pollutants but also interacts with H_2O_2 or HO_2^-, generating $HO_2^•$. Other studies also report enhanced organic compound removal when AOPs are applied to wastewater containing Cl^-. For instance, Khatri et al. (2018) observed maximum TOC removal from synthetic wastewater by EF when NaCl was used as a supporting electrolyte, compared to Na_2SO_4 and KCl. Rahmani et al. (2015) similarly found that COD removal efficiency increased from 47 % to 72 % with NaCl, attributed to indirect double oxidation (by $HO^•$ and active Cl^-). However, Titchou et al. (2022) reported varied TOC removal efficiencies when applying EF process to textile wastewater containing dye pollutants using a BDD/carbon felt cell with different supporting electrolyte. Specifically, with 100 mM NaCl, TOC removal reached 68 %, whereas with 50 mM Na_2SO_4, the TOC removal improved to 90 %. Chen et al. (2022) highlighted a critical issue with high salinity wastewaters: the formation of chlorinated organic byproducts, especially absorbable organic halides (AOX). Their study found that AOX concentration increased by approximately 91 % in the presence of 30 g L^{-1} NaCl during AOP. These findings are similar to those of the present study, where AOX concentrations in codfish brine increased by approximately 48 % after treatment under optimal conditions (tB_{18}). While AOX formation is a concern in AOPs applications due to potential toxicity (Xu et al., 2020), in this study, the treated brine was not intended for discharge but for reuse in the pickling stage of leather tanning. The next section discusses the application of this treated brine in hide pickling, where the presence of AOX did not compromise the quality of the hides.

3.3. *Application of the treated brines in hide's pickling*

After EF treatment, the brines remained saturated with salt (≅ 27 % wt. NaCl) and, as reported by Sarinho et al. (2023), required dilution to ≅ 7.5–8 % wt. NaCl for laboratory hide pickling trials. Table 5 presents the results of quality tests, based on ISO 5433 (2013) conducted on chrome-tanned leathers using EF-treated brine in pickling stage. The application of EF-treated brine yielded promising results compared to virgin brine. Notably, wet-blue leathers treated with EF-processed brine exhibited higher shrinkage temperatures, indicating improved thermal stability. Shrinkage temperature increased from 103 °C (virgin brine) to 113 °C (tB13). Similar findings were reported by Sarinho et al. (2023), where a salt-derived brine, generated from the curing of hides and treated by electrocoagulation, also enhanced the shrinkage temperature of the hides (103.5 °C–110.5 °C). Furthermore, the chromium oxide content consistently exceeded 3.5 %, meeting the ISO 5433 (2013) specification ($Cr_2O_3 > 3.5$ %).

Regarding FFA, all tested conditions - except for assays tB4 and tB13 - produced treated brines that maintained the required quality parameters for wet-blue leathers. Specifically, shrinkage temperature remained above 100 °C, Cr_2O_3 content exceeded 3.5 %, and FFA stayed within the acceptable limit of ≤0.10 % (ISO 5433, 2013). However, brines from tB_4 and tB_{13} exhibited excessive FFA levels, which may compromise leather quality in future applications.

Overall, the results indicate that TOC removal above 35 % is sufficient to ensure satisfactory leather quality, as long as FFA remains below the required threshold. These findings reinforce the viability of EF-treated brine for reuse in the pickling stage while maintaining compliance with ISO 5433 (2013) standards.

4. Challenges and future perspectives

The EF process, like the traditional Fenton process, has already been implemented at an industrial scale; however, its widespread adoption remains limited due to several challenges. Despite its proven effectiveness, key barriers such as energy consumption, efficiency, and operating costs still hinder broader application. Ribeiro et al. (2024) reported that, in the Fenton process, the continuous loss of iron ions and the formation of solid sludge require additional management strategies. Another critical limitation is the high cost of chemical reagents, particularly the hydrogen peroxide, which significantly impacts process economics. Additionally, Feijoo et al. (2023) highlighted that the acid conditions required for the Fenton-based processes, including EF, further increase operating costs. In the case of EF, these costs are compounded by electrode maintenance and energy consumption (Rodríguez-Peña et al., 2024). In this study, the EF process demonstrated advantages that could help mitigate some of these challenges. When applied to saline wastewaters, which naturally have high conductivity, EF can operate at lower current densities, reducing overall energy consumption. Regarding the electrode materials, using scrap iron electrodes presents a cost-effective alternative by lowering reagents expenses while also facilitating easier replacement. Although H_2O_2 remains a key oxidant in Fenton-based processes (Ribeiro et al., 2024), identifying alternative oxidants could further reduce costs and potentially lessen the overall environmental impact. Therefore, future research should explore alternative oxidants, assess EF performance in real, complex wastewater matrices, and conduct Life Cycle Assessment studies to enhance the economic and environmental viability of EF technologies.

5. Conclusions

The electro-Fenton process was investigated for treating saturated brines from the codfish industry focusing on maximizing the organic matter removal. Among the three operating variables studied, current density and electrolysis time had the most significant impact on TOC removal. The optimal conditions - current density of 275 A m^{-2}, electrolysis time of 5.2 min and [H_2O_2] of 91 mM - achieved a TOC removal of 70 %. Most treated brines did not compromise wet-blue leather quality, demonstrating their potential for reuse in the pickling stage of the tanning industry. Additionally, an increase in shrinkage temperature was observed in almost all experimental conditions tested, suggesting that leather processed with the treated brines could meet more demanding quality requirements for broader applications.

Additionally, the specific roles of reactive oxygen and chlorine species responsible for TOC removal was tested, and the addition of chloroform as a scavenger underscored the role of superoxide radicals over hydroxyl radicals in TOC removal. This insight enhances understanding of the reactive species' contributions in the electro-Fenton process applied to high-salinity wastewater. The synergistic effects between chlorine and $HO^{\bullet}$ remain unclear, and further investigation is recommended to clarify the underlying mechanisms. During the electro-Fenton process, iron dissolution could increase operating costs, using scrap iron as sacrificial electrodes presents a cost-effective alternative. Future research should focus on scaling up the process, assessing economic viability, and optimizing *in situ* H_2O_2 generation or alternative oxidants to improve efficiency. Overall, this study demonstrates the potential of treated brines for reuse in the tanning industry, promoting industrial symbiosis and contributing to a circular economy and enhancing resource efficiency.

CRediT authorship contribution statement

Luana Sarinho: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Pedro Carvalho:** Writing – review & editing, Supervision, Funding acquisition. **Diana Patoilo:** Investigation. **João Peres Ribeiro:** Writing – review & editing, Formal analysis. **Joaquim Manuel Gaião:** Writing – review & editing, Investigation. **José Baião da Cruz:** Investigation. **Catarina Marques:** Data curation. **Maria Isabel Nunes:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2025.125205.

Data availability

Data will be made available on request.
Results (Original data) (Google drive)

References

Abbasi, S., Zinatizadeh, A.A., Mirghorayshi, M., Zinadini, S., McKay, T., 2022. Electrocoagulation technique for continuous industrial licorice processing wastewater treatment in a single reactor employing Fe-rod electrodes: process modeling and optimization and operating cost analysis. J. Environ. Chem. Eng. 10, 1–11. https://doi.org/10.1016/j.jece.2021.106686.

Afanga, H., Zazou, H., Titchou, F.E., Rakhila, Y., Akbour, R.A., Elmchaouri, A., Ghanbaja, J., Hamdani, M., 2020. Integrated electrochemical processes for textile industry wastewater treatment: system performances and sludge settling characteristics. Sustain. Environ. Res. 2, 1–11. https://doi.org/10.1186/s42834-019-0043-2.

Alam, R., Khan, S.U., Usman, M., Asif, M., Farooqi, I.H., 2022. A critical review on treatment of saline wastewater with emphasis on electrochemical based approaches. Process Saf. Environ. Prot. 158, 625–643. https://doi.org/10.1016/j.psep.2021.11.054.

American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), 1999. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association, Washington, D.C.

An, C., Huang, G., Yao, Y., Zhao, S., 2017. Emerging usage of electrocoagulation technology for oil removal from wastewater: a review. Sci. Total Environ. 579, 537–556. https://doi.org/10.1016/j.scitotenv.2016.11.062.

Andrés, C.M.C., Pérez de la Lastra, J.M., Andrés Juan, C., Plou, F.J., Pérez-Lebeña, E., 2023. Superoxide anion chemistry—its role at the core of the innate immunity. Int. J. Mol. Sci. 24, 1–41. https://doi.org/10.3390/ijms24031841.

Barrera-Díaz, C., Frontana-Uribe, B., Bilyeu, B., 2014. Removal of organic pollutants in industrial wastewater with an integrated system of copper electrocoagulation and electrogenerated H2O2. Chemosphere 105, 160–164. https://doi.org/10.1016/j.chemosphere.2014.01.026.

Bes-Piá, A., Cuartas-Uribe, B., Mendoza-Roca, J.A., Galiana-Aleixandre, M.V., Iborra-Clar, M.I., Alcaina-Miranda, M.I., 2008. Pickling wastewater reclamation by means of nanofiltration. Desalination 221, 225–233. https://doi.org/10.1016/j.desal.2007.01.079.

Carneiro, M.A., de Kroon, E., Vital, B., Pereira, S.P., Agostinho, L.L.F., 2024. Electrochemical process of chlorination and energy generation as viable alternatives for SWRO brine valorization. Desalination 586, 1–18. https://doi.org/10.1016/j.desal.2024.117875.

Chai, Y., Qin, P., Wu, Z., Bai, M., Li, W., Pan, J., Cao, R., Chen, A., Jin, D., Peng, C., 2021. A coupled system of flow-through electro-Fenton and electrosorption processes for the efficient treatment of high-salinity organic wastewater. Sep. Purif. Technol. 267, 1–13. https://doi.org/10.1016/j.seppur.2021.118683.

Chen, Q., Burhan, M., Wakil, M., Ybyraiymkul, D., Hassan, F., Li, Y., Choon, K., 2021. A zero liquid discharge system integrating multi-effect distillation and evaporative crystallization for desalination brine treatment. Desalination 502, 1–12. https://doi.org/10.1016/j.desal.2020.114928.

Chen, S., Li, M., Ji, Q., Feng, T., Lan, S., Yao, K.F., 2022. Effect of the chloride ion on advanced oxidation processes catalyzed by Fe-based metallic glass for wastewater treatment. J. Mater. Sci. Technol. 117, 49–58. https://doi.org/10.1016/j.jmst.2021.11.044.

Cuerda-Correa, E.M., Alexandre-Franco, M.F., Fernández-González, C., 2020. Advanced oxidation processes for the removal of antibiotics from water. An overview. Water 12, 1–51. https://doi.org/10.3390/w12010102.

Darvishmotevalli, M., Zarei, A., Moradnia, M., Noorisepehr, M., Mohammadi, H., 2019. Optimization of saline wastewater treatment using electrochemical oxidation process: prediction by RSM method. MethodsX 6, 1101–1113. https://doi.org/10.1016/j.mex.2019.03.015.

De Carluccio, M., Barboza, P., Attarian, P., Ahangarnokolaei, M.A., Rizzo, L., 2024. Olive mill wastewater co-treatment: effect of (electro)Fenton processes and dilution ratio on moving bed biofilm reactor performance. J. Clean. Prod. 447, 1–9. https://doi.org/10.1016/j.jclepro.2024.141526.

Doumbi, R.T., Bertrand Noumi, G., Ngobtchok, B., Domga, 2022. Tannery wastewater treatment by electro-Fenton and electro-persulfate processes using graphite from used batteries as free-cost electrode materials. Case Stud. Chem. Environ. Eng. 5, 1–9. https://doi.org/10.1016/j.cscee.2022.100190.

Feijoo, S., Yu, X., Kamali, M., Appels, L., Dewil, R., 2023. Generation of oxidative radicals by advanced oxidation processes (AOPs) in wastewater treatment: a mechanistic, environmental and economic review. Rev. Environ. Sci. Biotechnol. 22, 205–248. https://doi.org/10.1007/s11157-023-09645-4.

García-Espinoza, J.D., Treviño-Reséndez, J., Robles, I., Acosta-Santoyo, G., Godínez, L. A., 2023. A review of electro - Fenton and ultrasound processes: towards a novel integrated technology for wastewater treatment. Environ. Sci. Pollut. Control Ser. 32, 1–23. https://doi.org/10.1007/s11356-023-29877-9.

Ghjair, A.Y., Abbar, A.H., 2023. Applications of advanced oxidation processes (Electro-Fenton and sono-electro-Fenton) for COD removal from hospital wastewater: optimization using response surface methodology. Process Saf. Environ. Prot. 169, 481–492. https://doi.org/10.1016/j.psep.2022.11.039.

GilPavas, E., Arbeláez-Castaño, P., Medina, J., Acosta, D.A., 2017. Combined electrocoagulation and electro-oxidation of industrial textile wastewater treatment in a continuous multi-stage reactor. Water Sci. Technol. 76, 2515–2525. https://doi.org/10.2166/wst.2017.415.

GilPavas, E., Dobrosz-Gómez, I., Gómez-García, M.-Á., 2019. Optimization and toxicity assessment of a combined electrocoagulation, H_2O_2/Fe^{2+}/UV and activated carbon adsorption for textile wastewater treatment. Sci. Total Environ. 651, 551–560. https://doi.org/10.1016/j.scitotenv.2018.09.125.

Giwa, A., Dufour, V., Marzooqi, F., Al, Kaabi M. Al, Hasan, S.W., 2017. Brine management methods: recent innovations and current status. Desalienación 407, 1–23. https://doi.org/10.1016/j.desal.2016.12.008.

Guo, Z., Zhang, Y., Jia, H., Guo, J., Ming, X., Wang, J., 2022. Electrochemical methods for landfill leachate treatment: a review on electrocoagulation and electrooxidation. Sci. Total Environ. 806, 1–19. https://doi.org/10.1016/j.scitotenv.2021.150529.

Guvenc, S.Y., Erkan, H.S., Varank, G., Bilgili, M.S., Engin, G.O., 2017. Optimization of paper mill industry wastewater treatment by electrocoagulation and electro-Fenton processes using response surface methodology. Water Sci. Technol. 76, 2015–2031. https://doi.org/10.2166/wst.2017.327.

Huang, Y., Li, X., Feng, K., 2024. Effect of chloride ions on the reactive species change pathway and removal performance in the MW/Co^{2+}/PMS process. J. Environ. Chem. Eng. 12, 1–9. https://doi.org/10.1016/j.jece.2024.114537.

ISO, 2013. Leather — Bovine Wet Blue — Specification, ISO 5433. International Organization for Standardization, Geneva, Switzerland.

James, M.S., Garg, A., 2024. Performance of electro-Fenton process for the treatment of synthetic sulphidic spent caustic waste stream generated from petroleum refineries. Chemosphere 346, 1–10. https://doi.org/10.1016/j.chemosphere.2023.140572.

Jiménez-Bambague, E.M., Madera-Parra, C.A., Rangel-Delgado, M.F., Quintero-Martinez, I., Miranda-Mosquera, D., Aristizabal-Apolinar, J.S., Machuca-Martínez, F., 2023. Photo-Fenton and Electro-Fenton performance for the removal of pharmaceutical compounds in real urban wastewater. Electrochim. Acta 442, 1–11. https://doi.org/10.1016/j.electacta.2023.141905.

Karabacakoğlu, B., Karaduman, S., 2024. Reactive yellow 145 removal by electro-Fenton with Fe–carbon fiber electrode pair: optimization of process variables based on response surface methodology. Chem. Pap. 78, 1671–1685. https://doi.org/10.1007/s11696-023-03194-4.

Khatri, I., Singh, S., Garg, A., 2018. Performance of electro-Fenton process for phenol removal using Iron electrodes and activated carbon. J. Environ. Chem. Eng. 6, 7368–7376. https://doi.org/10.1016/j.jece.2018.08.022.

Kokabian, B., Bonakdarpour, B., Fazel, S., 2013. The effect of salt on the performance and characteristics of a combined anaerobic-aerobic biological process for the treatment of synthetic wastewaters containing Reactive Black 5. Chem. Eng. J. 221, 363–372. https://doi.org/10.1016/j.cej.2013.01.101.

Kuleyin, A., Gök, A., Akbal, F., 2021. Treatment of textile industry wastewater by electro-Fenton process using graphite electrodes in batch and continuous mode. J. Environ. Chem. Eng. 9, 1–9. https://doi.org/10.1016/j.jece.2020.104782.

Lai, X., Ning, X., Li, Y., Huang, N., Zhang, Y., Yang, C., 2023. Formation of organic chloride in the treatment of textile dyeing sludge by Fenton system. J. Environ. Sci. (China) 125, 376–387. https://doi.org/10.1016/j.jes.2021.11.024.

Lai, X., Ning, X., Zhang, Y., Li, Y., Li, R., Chen, J., Wu, S., 2021. Treatment of simulated textile sludge using the Fenton/Cl − system: the roles of chlorine radicals and superoxide anions on PAHs removal. Environ. Res. 197, 1–11. https://doi.org/10.1016/j.envres.2021.110997.

Lal, K., Garg, A., 2017. Utilization of dissolved iron as catalyst during Fenton-like oxidation of pretreated pulping effluent. Process Saf. Environ. Prot. 111, 766–774. https://doi.org/10.1016/j.psep.2017.09.005.

Li, C., Xu, X., Liu, M., He, S., Qian, Y., Li, Z., 2024. Treatment of high-salinity organic wastewater by advanced oxidation processes: research progress and prospect. J. Water Proc. Eng. 60, 1–12. https://doi.org/10.1016/j.jwpe.2024.105272.

Maharaja, P., Sivashankaran, S., Nagabalaji, V., Srinivasan, S.V., Swarnalatha, S., Karthikeyan, S., Sekaran, G., 2021. Simultaneous brine recovery and water depollution in highly saline leather industry wastewater using a united halophiles supported nano porous carbon catalyst. J. Clean. Prod. 326, 1–11. https://doi.org/10.1016/j.jclepro.2021.129419.

Mavukkandy, M.O., Chabib, C.M., Mustafa, I., Al Ghaferi, A., AlMarzooqi, F., 2019. Brine management in desalination industry: from waste to resources generation. Desalination 472, 1–18. https://doi.org/10.1016/j.desal.2019.114187.

Meng, G., Jiang, N., Wang, Y., Zhang, H., Tang, Y., Lv, Y., Bai, J., 2022. Treatment of coking wastewater in a heterogeneous electro-Fenton system: optimization of treatment parameters, characterization, and removal mechanism. J. Water Proc. Eng. 45, 1–11. https://doi.org/10.1016/j.jwpe.2021.102482.

Naje, A.S., Chelliapan, S., Zakaria, Z., Ajeel, M.A., Alaba, P.A., 2016. A review of electrocoagulation technology for the treatment of textile wastewater. Rev. Chem. Eng. 33, 263–292. https://doi.org/10.1515/revce-2016-0019.

Nidheesh, P.V., Gandhimathi, R., 2012. Trends in electro-Fenton process for water and wastewater treatment: an overview. DES 299, 1–15. https://doi.org/10.1016/j.desal.2012.05.011.

Nidheesh, P.V., Zhou, M., Oturan, M.A., 2018. An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. Chemosphere 197, 210–227. https://doi.org/10.1016/j.chemosphere.2017.12.195.

Panagopoulos, A., 2022. Brine management (saline water & wastewater effluents): sustainable utilization and resource recovery strategy through Minimal and Zero Liquid Discharge (MLD & ZLD) desalination systems. Chem. Eng. Process. Process Intensif. 176, 1–12. https://doi.org/10.1016/j.cep.2022.108944.

Partal, R., Basturk, I., Murat Hocaoglu, S., Baban, A., Yilmaz, E., 2022. Recovery of water and reusable salt solution from reverse osmosis brine in textile industry: a case study. Water Resour. Ind. 27, 1–11. https://doi.org/10.1016/j.wri.2022.100174.

Pasciucco, E., Pasciucco, F., Panico, A., Iannelli, R., Pecorini, I., 2025. Optimization of a Fenton-based process as a tertiary treatment of tannery wastewater through response surface methodology. J. Water Proc. Eng. 69, 1–12. https://doi.org/10.1016/j.jwpe.2024.106588.

Peng, Q., Yu, J., Pang, Y., Deng, L., Tang, J., Wang, J., Wu, N., Tang, L., 2025. Prospects of advanced oxidation processes for high-salinity coking wastewater treatment: a strategy to support sustainable management. Resour. Conserv. Recycl. 212, 1–12. https://doi.org/10.1016/j.resconrec.2024.107880.

Rahmani, A.R., Nematollahi, D., Azarian, G., Godini, K., Berizi, Z., 2015. Activated sludge treatment by electro-Fenton process: parameter optimization and degradation mechanism. Kor. J. Chem. Eng. 32, 1570–1577. https://doi.org/10.1007/s11814-014-0362-2.

Ramos, M.D.N., Santana, C.S., Velloso, C.C.V., da Silva, A.H.M., Magalhães, F., Aguiar, A., 2021. A review on the treatment of textile industry effluents through Fenton processes. Process Saf. Environ. Prot. 155, 366–386. https://doi.org/10.1016/j.psep.2021.09.029.

Ren, Y.Y., Liu, C., Luo, Y.Y., Mehmood, T., Zheng, Y.L., 2022. Disposal of MIEX desorbent at high salinity by ZVI/H_2O_2Fenton-like system: optimization, performance and mechanisms. J. Environ. Chem. Eng. 10, 1–10. https://doi.org/10.1016/j.jece.2022.108647.

Ribeiro, J.P., Marques, C.C., Portugal, I., Nunes, M.I., 2020. Fenton processes for AOX removal from a kraft pulp bleaching industrial wastewater: optimisation of operating conditions and cost assessment. J. Environ. Chem. Eng. 8, 1–10. https://doi.org/10.1016/j.jece.2020.104032.

Ribeiro, J.P., Nunes, M.I., 2021. Recent trends and developments in Fenton processes for industrial wastewater treatment – a critical review. Environ. Res. 197, 1–17. https://doi.org/10.1016/j.envres.2021.110957.

Ribeiro, P., Sarinho, L., Nunes, M.I., 2024. Application of life cycle assessment to Fenton processes in wastewater treatment – a review. J. Water Proc. Eng. 57, 1–10. https://doi.org/10.1016/j.jwpe.2023.104692.

Rodrigues, M.I., Iemma, A.F., 2014. Experimental Design and Process Optimization. CRC Press, pp. 1–336. https://doi.org/10.1201/b17848.

Rodríguez-Peña, M., Natividad, R., Barrera-Díaz, C.E., Balderas Hernández, P., Alanis Ramírez, C.I., Roa-Morales, G., 2024. Current perspective of advanced electrochemical oxidation processes in wastewater treatment and life cycle analysis. Int. J. Electrochem. Sci. 19, 1–8. https://doi.org/10.1016/j.ijoes.2024.100589.

Sarinho, L., Carvalho, P., Patoilo, D., Ribeiro, J.P., Baião da Cruz, J., Gaião, J., Marques, C., Nunes, M.I., 2023. Treatment of salt from hides curing stage by electrocoagulation for use in the pickling stage of the tanning industry. Environ. Res. 237, 1–8. https://doi.org/10.1016/j.envres.2023.117095.

Souli, I., Afonso, C., Lopes, A., Pacheco, M.J., Ciríaco, L., Labiadh, L., Ammar, S., Fernandes, A., 2023. Treatment of fish canning wastewater by electrochemical oxidation process. J. Water Proc. Eng. 56, 1–7. https://doi.org/10.1016/j.jwpe.2023.104423.

Suman, H., Sangal, V.K., Vashishtha, M., 2021. Treatment of tannery industry effluent by electrochemical methods: a review. Mater. Today Proc. 47, 1438–1444. https://doi.org/10.1016/j.matpr.2021.03.300.

Sun, J., Liu, L., Yang, F., 2021. Electro-enhanced chlorine-mediated ammonium nitrogen removal triggered by an optimized catalytic anode for sustainable saline wastewater treatment. Sci. Total Environ. 776, 1–10. https://doi.org/10.1016/j.scitotenv.2021.146035.

Tegladza, I.D., Xu, Q., Xu, K., Lv, G., Lu, J., 2021. Electrocoagulation processes: a general review about role of electro-generated flocs in pollutant removal. Process Saf. Environ. Prot. 146, 169–189. https://doi.org/10.1016/j.psep.2020.08.048.

Titchou, F.E., Zazou, H., Afanga, H., Jamila, E.G., Ait Akbour, R., Hamdani, M., Oturan, M.A., 2022. Comparative study of the removal of direct red 23 by anodic oxidation, electro-Fenton, photo-anodic oxidation and photoelectro-Fenton in chloride and sulfate media. Environ. Res. 204, 1–9. https://doi.org/10.1016/j.envres.2021.112353.

Vargas, E., Ospina, L., Neves, M.C., Tarelho, L.A.C., Nunes, M.I., 2021. Optimization of FAME production from blends of waste cooking oil and refined palm oil using biomass fly ash as a catalyst. Renew. Energy 163, 1637–1647. https://doi.org/10.1016/j.renene.2020.10.030.

Xu, R., Xie, Y., Tian, J., Chen, L., 2020. Adsorbable organic halogens in contaminated water environment: a review of sources and removal technologies. J. Clean. Prod. 283, 1–17. https://doi.org/10.1016/j.jclepro.2020.124645.

Yáñez-Ángeles, M.J., González-Nava, V.J., Castro-Fernández, J.A., García-Estrada, R., Espejel-Ayala, F., Reyes-Vidal, Y., Rivera-Iturbe, F.F., Cárdenas, J., Bustos, E., 2025. Textile-washing wastewater treatment using ozonolysis, electro-coagulation, and electro-oxidation. Electrochim. Acta 512, 1–11. https://doi.org/10.1016/j.electacta.2024.145473.

Yang, B., Luo, Q., Li, Q., Jia, R., Liu, Y., Huang, X., Zhou, M., Li, L., 2023. Dye mineralization under UV/H_2O_2 promoted by chloride ion at high concentration and the generation of chlorinated byproducts. Sci. Total Environ. 857, 1–11. https://doi.org/10.1016/j.scitotenv.2022.159453.

Yavuz, Y., Shahbazi, R., Koparal, A.S., Öğütveren, Ü.B., 2014. Treatment of Basic Red 29 dye solution using iron-aluminum electrode pairs by electrocoagulation and electro-Fenton methods. Environ. Sci. Pollut. Control Ser. 21, 8603–8609. https://doi.org/10.1007/s11356-014-2789-8.

Ye, M., Luo, Z., Jin, W., Wang, X., Zhang, T., Liu, X., 2024. Degradation of organic pollutants by the Cl−/PMS process. Environ. Sci. Pollut. Control Ser. 31, 42921–42930. https://doi.org/10.1007/s11356-024-34005-2.

Yu, W., Lai, F., He, J., He, K., Wang, R., Li, D., Chen, Q., 2023. Catalytic performances and leaching behavior of typical natural iron minerals as electro-Fenton catalysts for mineralization of imidacloprid. J. Ind. Eng. Chem. 118, 132–146. https://doi.org/10.1016/j.jiec.2022.10.052.

Zhong, L., Jiang, X., Zhang, R., Shao, J., Chi, L., Wang, Y., Jia, J., Ying, D., 2021. Green utilization of the concentrated brine from two-stage membranes in coal chemical industry using selectrodialysis with bipolar membrane. Sep. Purif. Technol. 256, 1–10. https://doi.org/10.1016/j.seppur.2020.117816.