Environmental Research 237 (2023) 117095

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Treatment of salt from hides curing stage by electrocoagulation for use in the pickling stage of the tanning industry

Luana Sarinho [a,b,d], Pedro Carvalho [b], Diana Patoilo [d], João Peres Ribeiro [a,d], José Baião da Cruz [c], Joaquim Gaião [c], Catarina Marques [a,d], Maria Isabel Nunes [a,d,*]

[a] CESAM – Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193, Aveiro, Portugal
[b] CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
[c] CTIC – Centro Tecnológico das Indústrias do Couro, Apartado 158, São Pedro, 2384-909, Alcanena, Portugal
[d] DAO – Department of Environment and Planning, University of Aveiro, 3810-193, Aveiro, Portugal

ARTICLE INFO

Keywords:
Contaminated salt
Electrocoagulation
Pickling
Tanning
TOC
Valorisation

ABSTRACT

The raw materials for the tanning industry, namely hides and skins, are preserved (curing stage) and carried with common salt, i.e., sodium chloride (NaCl). Proceeding to conversion into leather, pickling is a key stage of the tannery process, which entails high demand of water and salt. In this work, the salt-derived brine (SdB) generated from the curing of hides was treated by iron-driven electrocoagulation (EC), aiming at its later application in the pickling stage of the tanning industry, promoting a transition to zero waste emission policy. Focusing on reducing the brine's total organic carbon (TOC), central composite rotational design and response surface methodology were adopted to study the effect of electrolysis time (6.2–14.2 min) and current density (74–431 $A{\cdot}m^{-2}$) on the treatment of the SdB (≅ 7.5 % wt. NaCl). The quality of the treated brines was then assessed in pickling trials and compared with virgin brine. 68–83 % removal of TOC from the SdB were achieved under electrolysis time ranging 6.2–14.2 min and current density ranging 126–252 $A{\cdot}m^{-2}$. Under these operating ranges the quality of the wet-blue leathers was guaranteed. Lowest power consumption (0.44 $kWh{\cdot}m^{-3}$) was achieved under electrolysis time of 6 min and current density of 126 $A{\cdot}m^{-2}$, yielding 68 % removal of TOC. Moreover, the shrinkage temperature of the hides was improved with treated brine (103.5 °C–110.5 °C) compared to virgin brine (103.0 °C). The present study provides strong evidence that contaminated salt from the curing stage can be valorised within the tanning industry through electrocoagulation treatment and then used in another production stage, instead of being landfilled.

1. Introduction

The raw materials for the tanning industry, namely hides and skins, need to be treated with several chemicals across different stages of production, to obtain the leather (Nur-A-Tomal et al., 2022). Generally, each 1000 kg of raw bovine hides will yield approximately 250 kg of leather, generating also 15–50 m^3 of wastewater and 450–730 kg of solid waste (Black et al., 2013; Hu et al., 2011). The preservation (curing stage) of 1000 kg of raw hides requires 300–400 kg of common salt, i.e., sodium chloride - NaCl (Hu et al., 2011), to prevent the degradation during the timeframe between leaving the slaughterhouse and entering the tannery (Black et al., 2013) - approximately 13–17 % salt is fixed into the hide (Uddin et al., 2022). In this matter, and although alternatives are available, the salting continues to be preferred over other methods due to lower cost of the common salt and easy accessibility (Nur-A-Tomal et al., 2021). One of the output streams of the curing stage is precisely the salt, which at that point is contaminated with animals' manure, hair, blood, etc., leading this material to be usually landfilled (Black et al., 2013). Current legislation regarding landfilling of wastes with high organic content presents increasing restrictions (Black et al., 2013). Moreover, high levels of salinity affect landfill biogas production, inhibiting not only biogas generation, but also the degradation of organic compounds (Ogata et al., 2016). In this framework, a solution to valorise contaminated salt is needed, to complement the already existing works on the search for more eco-friendly methods to cure raw hides (Al-Jabari et al., 2021; Kanagaraj et al., 2015; Nur-A-Tomal et al., 2021; Selvi et al., 2022; Tamil Selvi et al., 2020).

Pickling is another key stage of the tannery processes, in which the

* Corresponding author. Dep. de Ambiente e Ordenamento, Universidade de Aveiro. Campus Universitário de Santiago, 3810-193, Aveiro, Portugal.
E-mail address: isanunes@ua.pt (M.I. Nunes).

https://doi.org/10.1016/j.envres.2023.117095
Received 2 March 2023; Received in revised form 4 September 2023; Accepted 5 September 2023
Available online 6 September 2023

hides are immersed in an acid brine solution thereby sterilising and improving the penetration of the subsequent tanning material (Black et al., 2013; Li et al., 2009). This stage entails high demand of water and salt, which is used to avoid acidic hide swelling (Li et al., 2009; Martinho et al., 2015). The pickling wastewaters, i.e., contaminated brines, have high salt content (≅ 7.5–8 % wt. NaCl), and therefore have high electrical conductivity (Martinho et al., 2015; Sundarapandiyan et al., 2010). The Best Available Techniques document for the Tanning of Hides and Skins (Black et al., 2013) suggests the reuse of contaminated brine (prepared with salt from curing) in the pickling stage, after treatment by membrane filtration, however the high initial investment cost strongly hinders the application of this technique (Martinho et al., 2015; Zhao et al., 2019). Hence, it has become imperative and challenging to find a cleaner, cost-effective, and sustainable solution to deal with the contaminated salt from curing stage, in order to allow its further use in the pickling stage. Electrocoagulation (EC) has been pointed out as a promising process (simple and economic) to treat saline wastewaters (Abbasi et al., 2022; Akansha et al., 2020; Tegladza et al., 2021), with the electrical conductivity of the solution under treatment playing an important role (Darvishmotevalli et al., 2019; Yavuz and Ögütveren, 2018). EC relies on electric current to remove contaminants without requiring the addition of chemicals (Nampoothiri et al., 2016). Recognized advantages of this process include the use of simple equipment, low operating cost (depending on electrodes used), and reduced formation of sludge compared with chemical coagulation (Ahmed et al., 2012; Syaichurrozi et al., 2020). In EC the coagulant is generated *in situ* by electrolytic oxidation of a suitable anode material, which is most often aluminium (Al) or iron (Fe), releasing Al^{3+} ($4.0 < pH < 6.5$) or Fe^{2+} ($6.0 < pH < 8.0$), respectively (Kara et al., 2013; Weiss et al., 2021). These ions are hydrolysed in the bulk solution to form various monomeric and polymeric species, which transform into insoluble (oxy) hydroxides. Such compounds will neutralize the electrostatic charges on the surface of suspended solids and coagulate with the organic pollutants in water, allowing for easy separation from the liquid phase (Tegladza et al., 2021). In the process, water is also electrolysed, producing small bubbles of oxygen at the anode and hydrogen gas (H_2) at the cathode. The hydrogen bubbles adsorb the flocs, through natural buoyancy, promoting their flotation to the surface where they can be more easily concentrated, collected, and removed (Naje et al., 2016). A complex set of reactions occurs during the EC process, including chemical oxidation and reduction, adsorption, decomposition, precipitation and flotation (Syaichurrozi et al., 2020). The key reactions driving EC using Fe electrodes are well described by Eqs. (1)–(4) (Abbasi et al., 2022; Isik et al., 2020). Later, the Fe^{2+}/Fe^{3+} ions released from the anode react with hydroxide ions (OH^-) to form insoluble coagulants of $Fe(OH)_z$ (where z is the number of electron transfer: 2 or 3) (Syaichurrozi et al., 2020).

In anode:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$Fe \rightarrow Fe^{3+} + 3e^- \quad (2)$$

In cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (4)$$

The goal of this work was to treat contaminated salt from the curing of hides for subsequent use of its brine in the pickling stage of the tanning industry (Fig. 1). To that end, contaminated salt was dissolved in water and the resulting salt-derived brine (SdB) was treated by electrocoagulation, with iron electrodes. To the best of the authors' knowledge, it is the first time that salt from curing is treated by EC aiming to be reused within the producer industry, under circular economy thinking, and promoting a transition to zero waste emission policy. Response surface methodology (RSM) was applied to determine the effect of electrolysis time, t (min) and current density, J ($A{\cdot}m^{-2}$) on the removal of total organic carbon (TOC) from the SdB. The quality of the treated brines (tB) was then assessed in pickling and tanning trials, in parallel with virgin brine, to guarantee enough quality in the brine for pickling application. Envisioning a future scale-up of the proposed solution, power consumption was also estimated, as it strongly influences the economic viability of the treatment solution.

2. Materials and methods

2.1. Curing salt-derived brine sample

A composite sample of real contaminated salt from hides' curing stage was prepared from samples provided by a Portuguese tannery industry collected in two months. The salt samples were firstly sieved (< 4 mm) to remove coarse contaminant particles (manure, hair, blood, etc.), and then dissolved in tap water. The resulting contaminated curing salt-derived brine was labelled as SdB, which had approx. 7.5 % wt. salt (as received), the usual salt concentration used in pickling stage (Black et al., 2013). SdB was characterized by standard methods (see Section 2.5). Three repetitions were performed in the SdB sample characterization. Table 1 presents the mean values of each quality parameter and respective standard deviations of the SdB.

The pH of the SdB was slightly alkaline and suitable for the EC

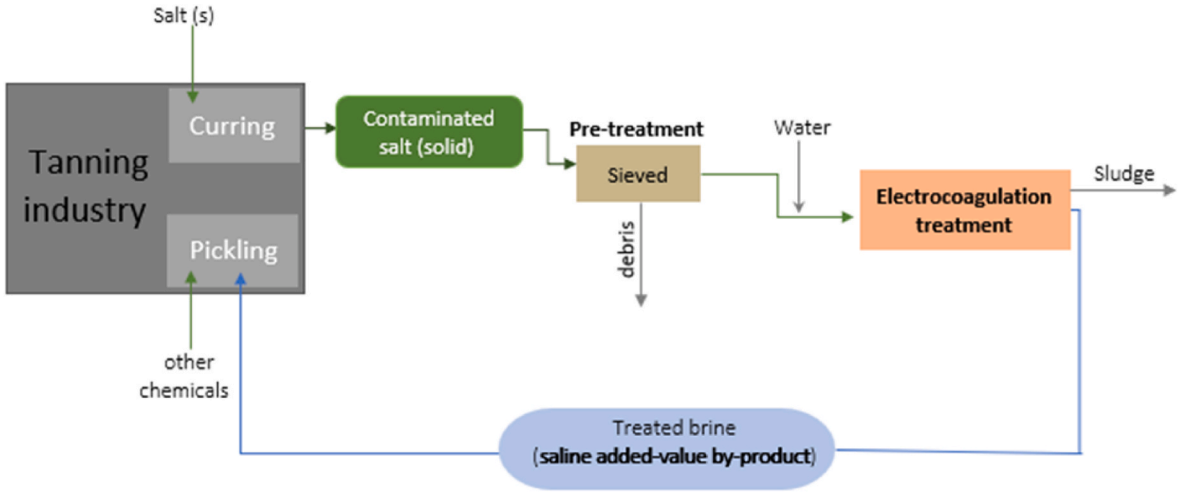

Fig. 1. General approached proposed to treat SdB by EC under circular economy thinking.

Table 1
Quality parameters of the curing SdB used in this work.

Parameter	Mean ± s
Total Organic Carbon, TOC [mg·L^{-1}]	137.7 ± 2.5
Total Suspended Solids [mg·L^{-1}]	1073.3 ± 52.2
Volatile Suspended Solids [mg·L^{-1}]	397.3 ± 6.1
Total Dissolved Solids [g·L^{-1}]	70.2 ± 1.1
pH	7.8 ± 0.4
Conductivity [mS·cm^{-1}]	74 ± 3.1

process, requiring no prior adjustment (Kara et al., 2013; Weiss et al., 2021).

The total dissolved solids content was slightly less than 7.5% which was not an unexpected result, since the brine was prepared with salt as received (after being sieved), i.e., it was not pure salt, but hydrated and with contaminants that can be water soluble or not. Concerning the suspended solids, around 37 % were (volatile) organic matter.

2.2. Experimental setup and procedure

EC assays were performed in a batch reactor with a working capacity of 1 L, equipped with two iron plate electrodes, as shown in Fig. 2. The iron electrodes (79.2 cm^2 of total contact area) were placed 10 cm apart and connected to a D.C. power supply (MLINK, RYI). All assays started at room temperature (*c.a.* 20 °C) at pH = 7.8 ± 0.4, which was the original SdB pH. To avoid electrode passivation and promote equal wear out, the electrode polarity was reversed in each experiment. After the predefined electrolysis time, the power supply was turned off and the treated brine was transferred to a graduated cylinder for 1 h of settling. At that time, supernatant liquid, which accounted for 80–95 % (v/v) of the raw SdB volume (i.e., 5–20 % (v/v) of sludge), was collected and analysed in terms of TOC, according to Method 5310B (Greenberg et al., 1999). Additional aliquots, from each experimental condition, were collected and proceeded for wet-blue leather pickling trials. These trials were performed with bovine skin flaps, from the neck area, already delimed and purged. A control pickling assay was also conducted with a virgin brine, i.e., a brine prepared with virgin salt. All pickling trials were conducted at lab-scale to evaluate the most relevant properties of the leather (ISO 5433-Leather — Bovine Wet Blue — Specification, 2013), namely thickness, shrinkage temperature, grease content, free fatty acids (FFA) content, and hexavalent chromium content (Cr_2O_3).

An estimate of power consumption, of the lab-scale EC process, was determined by multiplying the current intensity, voltage and electrolysis time for each assay.

2.3. Experimental design

Several parameters can influence the efficiency of the electrocoagulation process, such as electrode material, current density, electrolysis time, electrodes distance, pH, conductivity, temperature and initial organic content. This work aimed to carry out a treatment with minimal (or no) addition of chemical and physical agents. Thus, the initial values of pH, conductivity, temperatures, TOC content were the natural of the raw SdB. Concerning the electrode material, as stated before, it was chosen iron foreseeing in the future the use of scrap materials (cheaper and efficient (Brillas and Martínez-Huitle, 2015; Gondudey et al., 2020)). The distance between the two electrodes was defined based on preliminary experiments. Finally, two independent operating variables were studied: current density and electrolysis time. Response surface methodology was applied to assess the influence of these variables on the removal of TOC (dependent variable) from the SdB. This allowed the mapping of the region under study and the selection of the best operating conditions. CCRD was used to plan the experiments. Table 2 presents the predefined experimental ranges for each independent variable, with "±1″, "0″ and "± 1.42″ representing, respectively, the factorial points, the central point and the axial points of the design (Rodrigues and Iemma, 2014). The selection of electrolysis time range was based on preliminary experiments which showed that treatment times above 15 min did not improve TOC removal for this contaminated brine. The current density range was selected considering, on the one hand the power supply limitation (i.e., a current density below 70 A·m^{-2} was not feasible), and on the other hand a current density above 500 A·m^{-2} is not recommended due to high power and electrodes consumption. A total of 12 experiments were carried out, including 4 repetitions at the central point. To prevent systemic errors, the assays were performed randomly.

Table 2
Experimental range of the studied independent variables used in the CCRD.

Independent variable	−1.42	−1	0	+1	+1.42
Current density [A·m^{-2}]	74	126	252	379	431
Electrolysis time [min]	6.2	7.0	10.0	13.0	14.2

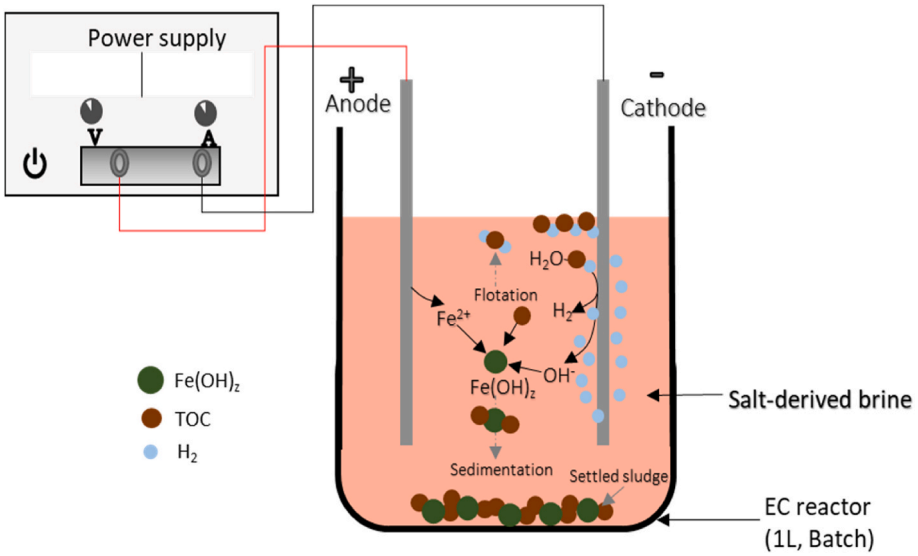

Fig. 2. Schematic diagram of the electrocoagulation reactor and the reactions occurring on each electrode.

2.4. Statistical data treatment

A second order polynomial model with interactions was used to fit the experimental results, according to Eq. (5).

$$Z = k + ax_1 + bx_1^2 + cx_2 + dx_2^2 + ex_1x_2 \quad (5)$$

where Z is the fitted response (removal of TOC), $k, a, b, (\ldots)$ to e are the regression coefficients, x_1 and x_2 represent the current density and electrolysis time, respectively. The adequacy of the model was verified by an analysis of variance (ANOVA). The quality of the regression model was expressed by the coefficient of determination R^2, R^2_{adj}, and by the Lack of Fit. The residuals plots analysis was performed to validate the model assumptions (normality and randomness of residuals) (Ribeiro et al., 2020; Vargas et al., 2021). All statistical analyses were performed with StatSoft Statistica® v. 8.0 software. A 95 % confidence level was adopted.

2.5. Analytical methods

TOC concentration was determined according to the standard method 5310 B (Greenberg et al., 1999) with a Sievers InnovOx TOC analyser. Standard methods 2540 C, 2540 D and 2540 E (Greenberg et al., 1999) were adopted in the determination of total dissolved solids, total suspended solids, and volatile suspended solids, respectively. pH and electrical conductivity were measured with a Consort Instrument® multi-parameter meter. Finally, the assessment of the properties of the leather after the pickling stage was carried out according to the methods stated in ISO 5433 (ISO 5433-Leather — Bovine Wet Blue — Specification, 2013).

3. Results and discussion

3.1. Treatment of salt-derived brine by electrocoagulation

The second order model fitted to the experimental results is described by Eq. (6).

$$Z = 42.61 + 0.094x_1 - 3.0 \times 10^{-4}x_1^2 + 3.480x_2 - 0.245x_2^2 + 0.009x_1x_2 \quad (6)$$

The ANOVA of the regression (Table 3) shows that the model provided a good fit ($R^2 \cong 0.954$; $R^2_{adj} \cong 0.915$), which highlights the quality of the fit (see also Fig. 3 (d)) and non-statistically significant Lack of Fit (p-value > 0.05). Thus, as R^2 is higher than 0.8, the model had a good fit to the experimental data (Darvishmotevalli et al., 2019) and can be used to analyse the EC treatment of SdB.

The assumptions of the regression model were validated by the analysis of the residual plots, as shown in Fig. 3.

The straight line along the data (Fig. 3 (a)) indicates that the residuals follow a normal distribution. Fig. 3 (b) validates the randomness of the residuals, equal number of points above and below the central horizontal line and no data points stands out from the basic random pattern of the other residuals. No outliers were identified in Fig. 3 (c), since all values lied within the range ± 3.0 standard deviations around the mean. Furthermore, good correlations between predicted and observed values (Fig. 3 (d)) confirm the adequacy of the model to predict the TOC removal for any given operating condition within the experimental range tested in this work (see Table 2).

Table 3
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	160.8	1	160.8	44.06	0.007
x_1^2	133.1	1	133.1	36.47	0.009
x_2	36.08	1	36.08	9.888	0.051
x_2^2	26.38	1	26.38	7.229	0.074
x_1x_2	41.63	1	41.63	11.41	0.043
Lack of fit	7.318	3	2.439	0.668	0.626
Pure error	10.95	3	3.649		
Total	395.7	11			
	$R^2 \cong 0.954$	$R^2_{adj} \cong 0.915$			

The ANOVA results for the coefficients of the variables revealed that both linear and quadratic terms of the current density (x_1 and x_1^2) had statistically significant effects on the removal of TOC (p-value <0.05), as shown in Table 4.

Moreover, the interaction term also played a statistically significant role in the removal of TOC. In other words, the effect of current density on TOC removal depends on the value of the electrolysis time and the effect of the latter on TOC removal also depends on current density value. Abbasi et al. (2022) employed an EC process with iron rod electrodes to remove colour from a wastewater generated in an liquorice industry. The colour removal was accelerated with increasing current density and electrolysis time, since more coagulation ions were released from the sacrificial anode, and H_2 generation was faster. The authors recognized that electrolysis time and current density were the key control parameters to achieve optimum operating condition of the EC process. Similar results were observed by Chen et al. (2021) when studying the application of EC to remove chemical oxygen demand (COD) from a swine wastewater. These authors reported an increase on COD removal with the increase of current density and electrolysis time, using iron electrodes and initial pH of 6.3. Even using wastewaters from different sources, these works showcase the positive effect of current density and electrolysis time during the process, which highlight the attractiveness of the EC process.

The response surface presented in Fig. 4 depicts the effect of current density and electrolysis time on the removal of TOC from the SdB. Overall, the removal of TOC in the tested experimental ranges varied between 65 and 83 %.

The highest removal of TOC was registered for the highest electrolysis time and current density tested. When current density increased from 74 $A{\cdot}m^{-2}$ to 379 $A{\cdot}m^{-2}$ and the electrolysis time raised from 10 min to 13 min, the removal of TOC increased from 65 % to 83 %. Since the electrocoagulation system is electrolytically operated, the current density determines the rate of coagulant (anode) and gas bubbles (cathode) generated (Kim et al., 2020). At higher current density, the amount of metal (in this work, iron) oxidized in the anode increases, resulting in a higher formation of (oxy)hydroxide flocs (Syaichurrozi et al., 2020), which in turn leads to higher coagulation of contaminants. Furthermore, bubbles density increases and their sizes decrease with increasing current density and electrolysis time, which also promotes faster removal of pollutants (Abbasi et al., 2022). Isik et al. (2020) observed the same trend when treating a pistachio processing wastewater by EC. These authors studied the effect of current density and reaction time on COD removal (initial value: 25,315 ± 87 $mg{\cdot}L^{-1}$). Iron electrodes were used for each experiment (25 ± 1 °C and pH = 5.79 ± 0.01) and placed with an inter-electrode distance of 2 cm. The authors observed that the COD removal was positively affected (5–40 %) by increasing current density from 25 to 300 $A{\cdot}m^{-2}$ and electrolysis time from 30 to 240 min. Contrary results were obtained by Oden and Sari-Erkan (2018), who studied the effects of current density (16–48 $A{\cdot}m^{-2}$) and electrolysis time (10–30 min) on the removal of COD from metal plating wastewater by EC using iron electrodes. These authors reported antagonistic effect between the two studied parameters, and only current density had significant effect on COD removal.

In the present work, for an electrolysis time until 9 min, an increase in current density - for values up the middle of the tested range - favoured the removal of TOC (Fig. 4). However, when the current density increased beyond these values, a decrease in TOC removal was observed. In turn, for electrolysis times greater than 9 min, an increase in current density always had a positive effect on TOC removal.

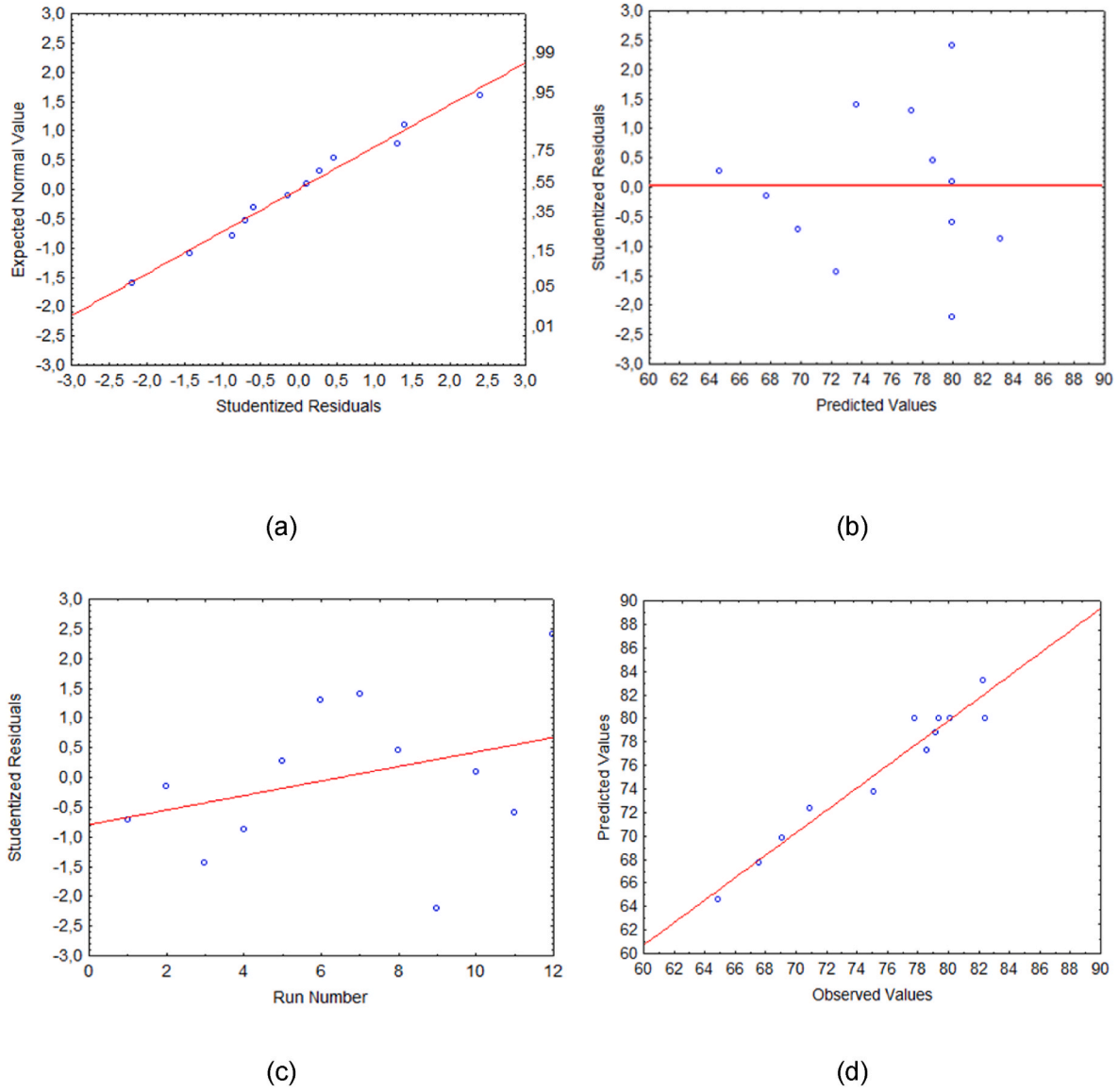

Fig. 3. Analysis of the suitability of the quadratic model (Eq. (7)) used to describe the removal of TOC from the SdB by EC: (a) normal (%) probability vs studentized residuals; (b) studentized residuals vs predicted response; (c) outlier t plot; (d) predicted vs observed values.

Table 4
Regression coefficients of the fitted model and respective significance.

Model variables	Estimate coefficient	Std. error	*p* - value
Intercept	42.61	11.79	0.036
x_1	0.094	0.035	0.075
x_1^2	0.003	0.000	0.009
x_2	3.480	1.963	0.174
x_2^2	−0.245	0.091	0.074
x_1x_2	0.009	0.003	0.043

Similar results were registered by Arslan et al. (2023) in the treatment of turnip juice wastewater by electrocoagulation with iron electrodes. For 30 min of electrolysis time, increasing current density from 50 $A{\cdot}m^{-2}$ to 100 $A{\cdot}m^{-2}$ did not cause a significant change in COD removal. On the other hand, treating tannery wastewater by EC, Azarian et al. (2018) observed no significant change in treatment efficiency due to an increase in electrolysis time from 10 to 25 min, using the same current density (170 $A{\cdot}m^{-2}$).

The trends observed in Fig. 4 may be explained by three main reasons (An et al., 2023; Arslan et al., 2023; Galvão et al., 2020; Syaichurrozi et al., 2020): (i) at very high current density, considerable energy is wasted heating the wastewater, which results in decreased EC efficiency; (ii) the upward flux of the excessive generated hydrogen gas on the cathode (Eq. (3) - (4)) and the excess suspended flocs in the reactor can result in the re–dispersion of iron hydroxide flocs, as well as the lower flocculation efficiency and higher turbidity; and (iii) final pH affects the amount of (oxy)hydroxide flocs formed: reduction of H_2O (cathode) results in the formation of OH^- ion and H_2 gas (Eq. (3) - (4)), however, the OH^- is not completely consumed in the formation of $Fe(OH)_z$ and the excessive presence of those anions increases the solution pH during the EC process.

Concerning evidences of the effect of the excessive hydrogen has on the flocculation process, Syaichurrozi et al. (2020) applied an EC process (with iron electrodes) in order to study the kinetics of pollutant removal in a vinasse wastewater, and concluded that the use of very high current and lower electrolysis time can lead to an excessive formation of hydrogen bubbles and the coagulants formed could easily be strapped to the surface of solution before they adsorbed and entrapped the pollutants.

In the present work, neither final temperature nor H_2 gas released

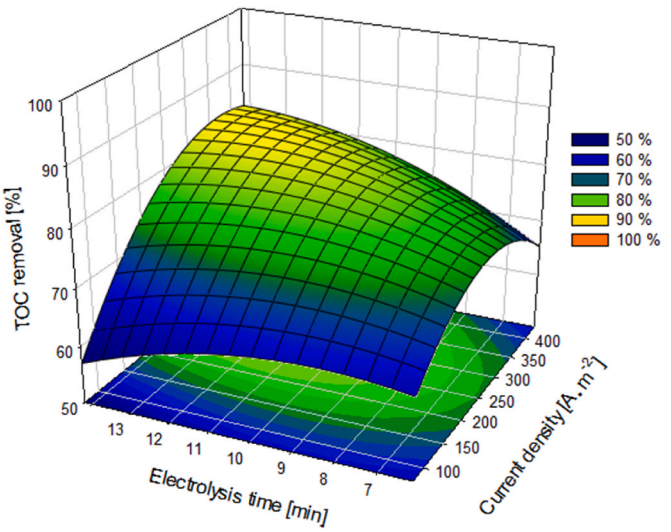

Fig. 4. Influence of current density and electrolysis time on the removal of TOC from the SdB by electrocoagulation.

during the EC process were not measured, but final pH was measured, and it was registered an increase 4–20 % after EC treatment in all assays (data not shown). The tB, corresponding to the maximum TOC removal efficiency (83%) observed in this work had a final pH of 9.58. Other authors also observed the same pH trend during the EC treatment of wastewaters. Arslan et al. (2023) reported a more noticeable increase in pH when the current density and electrolysis time were higher. Can et al. (2014) studied the effect of some operating parameters on the arsenic removal by EC using iron electrodes, and concluded that the pH rise during EC affected arsenic solubility and hence its removal; starting at pH = 7, by the end of treatment (30 min at current density of 5.4 $A{\cdot}m^{-2}$) the pH reached 10.74. The same pH evolution was observed with aluminium electrodes in the treatment of landfill leachate in the work conducted by Galvão et al. (2020). They observed an increase in pH from 7.0 to 9.7 after 90 min of EC process (current density = 161.08 $A{\cdot}m^{-2}$). Given that the solubility of the formed (oxy)hydroxide flocs depends on the pH (Can et al., 2014), it is important to understand more about the reactions that take place in the reactor. Garcia-Segura et al. (2017) reviewed the fundamentals of EC process with Fe and Al electrodes, stating that the formation of insoluble $Fe(OH)_2$ favours flocculation, with that species remaining in equilibrium with Fe^{2+} under pH up to 9.5, and with monomeric species $Fe(OH)^+$ (pH 9.5 up to 11.4) and $Fe(OH)_3^-$ (pH 11.8 to 14.0). Although the Fe^{3+} species favours even more the coagulation-flocculation process, $Fe(OH)_3$ is the only species present in solution under pH ranging 6.2–9.6 (Garcia-Segura et al., 2017). For pH higher that 9.6, $Fe(OH)_4$ is also present in solution, which is not the most desirable scenario, given its poor coagulative performance (Barrera-Díaz et al., 2003). Beyond a more pronounced increase in pH when the current density and electrolysis time is higher, also more sludge can also be produced due to the high dissolution rate of the iron anode electrode (Garcia-Segura et al., 2017).

Somehow, the promising results obtained in this work, with iron electrodes, were not a surprise. Some works (e.g., Kim et al. (2020), Chen et al. (2021), Igwegbe et al. (2021) and Kara et al. (2013)) have already evaluated the performance of Al and Fe electrodes in the EC process, the latter being the one with better performance, partly due to the amount of flocculants produced to remove the pollutants. Moreover, Akansha et al. (2020) observed that, to achieve similar removal of COD from dairy industry wastewater, higher current was required with Al electrodes than with Fe ones; which indirectly lead to a higher operating cost. Nevertheless, all cited works above deal with wastewaters with low salt concentrations, in comparison to the matrix (SdB) used in current work. Thus, this study is pointing out a promising brine treatment process and alternative to the membrane filtration.

3.2. Application of the treated brines in hide's pickling

The results obtained in the quality tests of chrome-tanned leathers using treated brine in pickling stage are presented in Table 5.

Regarding the quality parameters for the wet-blue leathers, regardless of the EC operating condition, higher leather shrinkage temperature was observed with the replacement of virgin brines by tB, which is a promising result. Despite the thicknesses of the leathers pickled with tB were always lower than that of the ones pickled with virgin brine (3.91 mm), that did not affect the final quality of the leather. On the other hand, the quality of the leather obtained from experiments tB_5 and tB_6 can be compromising in future applications, given the chromium oxide content (below 3.5). The condition of maximum removal of TOC (assay tB_4) yielded a wet-blue leather with excess FFA content (above the limit of 0.1 % (ISO 5433-Leather — Bovine Wet Blue — Specification, 2013)), which also occurred in condition tB_3.

Considering the values of the quality parameters for the wet-blue leathers after pickling and tanning stages with EC treated brine, as well as the results from RSM, the following EC conditions are recommended to treat the curing salt-derived brines: electrolysis time between 6.2 and 14.2 min, and current density between 126 $A{\cdot}m^{-2}$ and 252 $A{\cdot}m^{-2}$, corresponding to 68–83 % removal of TOC. In this range, enough quality of the leathers could be guaranteed using tB. Therefore, any final decision about the optimal operating conditions of the EC treatment must ultimately rely on a second factor: economic performance, namely power consumption.

3.3. Estimates of power consumption in EC treatment

Envisioning a future pilot-scale of the proposed treatment, power consumption evaluation can help in the final decision on operating conditions. Fig. 5 depicts the effect of current density and electrolysis time on power consumption for removal of TOC $\geq$ 68 %, corresponding to the minimum value where the quality of the leathers was not compromised (in this study).

The highest levels of power consumption were estimated for the highest values of current density, which is easily explained by the linear dependence of power consumption from current density. For instance, increasing the current density from 126 $A{\cdot}m^{-2}$ to 431 $A{\cdot}m^{-2}$, for the same electrolysis time (7 min), the power consumption is 8 times higher, but the removal of TOC did not increase. Azarian et al. (2018) observed the same trend when treating a tannery wastewater by EC process. The power consumption for an electrolysis time of 10 min was 4.9 $kWh{\cdot}m^{-3}$, increasing to 9.0 $kWh{\cdot}m^{-3}$ for 25 min of electrolysis. In the present work, the increase in power consumption was not associated with any significant change in the efficiency of the treatment, contrarily to what was reported by Can et al. (2014). These authors observed an increase in arsenic removal from wastewater (88.9–99.7 %) when the current density was increased from 1.8 $A{\cdot}m^{-2}$ to 10.70 $A{\cdot}m^{-2}$, with corresponding increase in power consumption (from 0.06 to 1.23 $kWh{\cdot}m^{-3}$).

In this work, the minimum power consumption to achieve 68 % removal of TOC would be 0.44 $kWh{\cdot}m^{-3}$, with a current density of 126 $A{\cdot}m^{-2}$ and 6 min electrolysis time. On the other hand, if maximum (83 %) removal of TOC would be targeted, the lowest possible power consumption would be 5.42 $kWh{\cdot}m^{-3}$, corresponding to a current density = 379 $A{\cdot}m^{-2}$ and electrolysis time of 12 min. Considering the objective of this work, from an economic point of view, since the minimum requirement is a TOC removal $\geq$ 68%, the optimal operating condition would be the one with lower power consumption.

4. Conclusions

A contaminated salt-derived brine produced in the curing of hides from the tanning industry was successfully treated by EC process,

Table 5
Effect of the application of tB as a replacement for virgin brines on the quality of wet-blue leathers.

EC operating condition				Wet-blue leathers quality parameters				
Assay reference	J [A·m-2]	t [min]	TOC[a] [mg·L-1]	Thickness [mm]	Shrinkage temperature [°C]	Grease [%]	FFA [%]	Cr_2O_3 [%]
Virgin brine				3.91	103.0	0.5	<0.10	4.1
tB_1	126	7.0	42.5	2.82	103.5	0.9	0.10	4.0
tB_2	126	13.0	44.7	3.35	106.0	1.2	0.10	4.7
tB_3	379	7.0	40.0	3.58	109.0	3.5	0.30	4.0
tB_4	379	13.0	24.4	3.02	109.0	3.4	0.30	4.0
tB_5	74	10.0	48.3	2.90	110.5	1.5	0.10	3.2
tB_6	431	10.0	29.5	3.23	109.5	2.9	0.10	3.4
tB_7	252	6.2	34.3	3.45	109.0	1.9	<0.10	4.6
tB_8	252	14.2	28.6	3.47	110.0	2.9	0.10	5.3
tB_9	252	10.0	30.6	3.61	110.0	1.9	0.10	4.0
tB_{10}	252	10.0	27.4	3.48	109.0	1.1	0.10	3.7

[a] after EC treatment.

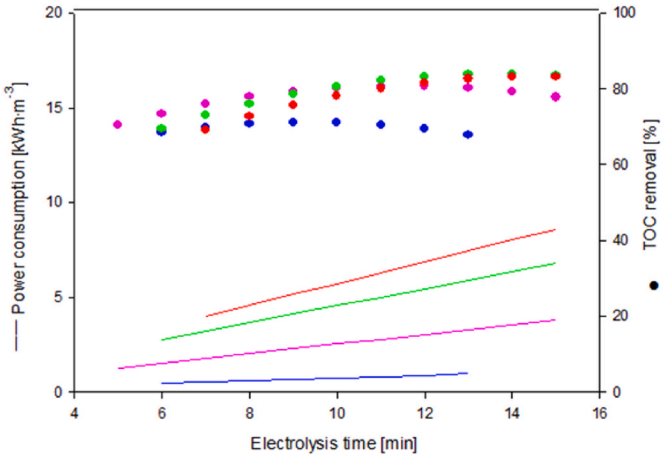

Fig. 5. Power consumption (solid lines) and TOC removal (solid symbols) for different experimental conditions.

achieving 68–83 % removal of TOC. The treated brines were successfully used in a wet-blue leather pickling trials with bovine hides. The leathers had characteristics equal to or superior to those registered with virgin brine, which would entail significant reduction of water footprint and economic savings at an industrial scale. Thus, to not compromise the wet-blue leathers, the EC operating conditions to treat the SdB are suggested: electrolysis time ranging 6.2–14.2 min, and current density ranging 126–252 $A{\cdot}m^{-2}$. From the economical point of view, to achieve a TOC removal of at least 68% with the minimum needed power consumption (0.44 $kWh{\cdot}m^{-3}$), a current density of 126 $A{\cdot}m^{-2}$ and 6 min of electrolysis time are suggested. Although some sludges are produced during the EC treatment, the amount of solid waste that will be landfilled will drastically decrease in tanneries' industries, compared to the current situation. This research work opens a new path for the valorisation of contaminated salt contributing to improve the sustainability and circularity of the tanneries' industrial process by exploring solutions to reduce the consumption of raw materials (salt and water) and the emissions (solid waste) into the environment.

Credit author statement

Luana Sarinho: Conceptualization; Formal analysis; Investigation; Methodology; Writing – original draft; Writing – review & editing. Pedro Carvalho: Project administration; Writing – original draft; Writing – review & editing; Supervision. Diana Patoilo: Investigation; Methodology. João Peres Ribeiro: Investigation; Writing – original draft. José Baião da Cruz: Investigation; Methodology. Joaquim Gaião: Project administration; Writing – original draft: Investigation; Writing – original draft. Maria Isabel Nunes: Conceptualization; Methodology; Writing – original draft; Writing – review & editing; Supervision

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.

Data availability

Data will be made available on request.

Acknowledgements

This work is financed by Portugal (2020) through European Regional Development Fund (ERDF) in the frame of CENTRO2020 in the scope of the project SimBioSalt, CENTRO-01-0247-FEDER-069712. The work was developed within the scope of the project CICECO – Aveiro Institute of Materials, UIDB/50011/2020 + UIDP/50011/2020 + LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC) and CESAM (UIDP/50017/2020 + UIDB/50017/2020 + LA/P/0094/2020), financed by national funds through the FCT/MCTES. J.P. Ribeiro and C. Marques acknowledges FCT for their PhD Grant (SFRH/BD/141133/2018) and (BD/08959/2021), respectively.

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 (2) https://doi.org/10.1016/j.jece.2021.106686.

Ahmed, M.T., Chaabane, T., Maachi, R., Darchen, A., 2012. Efficiency of a pretreatment by electrocoagulation with aluminum electrodes in a nanofiltration treatment of polluted water. Procedia Eng. 33 (December), 465–474. https://doi.org/10.1016/j.proeng.2012.01.1226.

Akansha, J., Nidheesh, P.V., Gopinath, A., Anupama, K.V., Suresh Kumar, M., 2020. Treatment of dairy industry wastewater by combined aerated electrocoagulation and phytoremediation process. Chemosphere 253. https://doi.org/10.1016/j.chemosphere.2020.126652.

Al-Jabari, M., Sawalha, H., Pugazhendhi, A., Rene, E.R., 2021. Cleaner production and resource recovery opportunities in leather tanneries: technological applications and perspectives. Bioresour. Technol. Rep. 16 https://doi.org/10.1016/j.biteb.2021.100815.

An, B.H., Xu, D.M., Geng, R., Cheng, Y., Qian, R.B., Tang, X.C., Fan, Z.Q., Chen, H. Bin, 2023. The pretreatment effects of various target pollutant in real coal gasification gray water by coupling pulse electrocoagulation with chemical precipitation methods. Chemosphere 311 (P1). https://doi.org/10.1016/j.chemosphere.2022.136898.

Arslan, H., Gun, M., Akarsu, C., Bilici, Z., Dizge, N., 2023. Treatment of turnip juice wastewater by electrocoagulation/electroflotation and electrooxidation with aluminum , iron , boron - doped diamond , and graphite electrodes. Int. J. Environ. Sci. Technol. 20 (1), 53–62. https://doi.org/10.1007/s13762-022-03994-3.

Azarian, G., Miri, M., Nematollahi, D., 2018. Combined electrocoagulation/electrooxidation process for the COD removal and recovery of tannery industry

wastewater. Environ. Prog. Sustain. Energy 37 (2), 637–644. https://doi.org/10.1002/ep.12711.
Barrera-Díaz, C., Ureña-Nuñez, F., Campos, E., Palomar-Pardavé, M., Romero-Romo, M., 2003. A combined electrochemical-irradiation treatment of highly colored and polluted industrial wastewater. Radiat. Phys. Chem. 67 (5), 657–663. https://doi.org/10.1016/S0969-806X(02)00497-8.
Black, M., Canova, M., Rydin, S., Maria Scalet, B., Roudier, S., Delgado Sancho, L., 2013. Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins. https://doi.org/10.2788/13548.
Brillas, E., Martínez-Huitle, C.A., 2015. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. Appl. Catal. B Environ. 166–167, 603–643. https://doi.org/10.1016/j.apcatb.2014.11.016.
Can, B.Z., Boncukcuoglu, R., Yilmaz, A.E., Fil, B.A., 2014. Effect of some operational parameters on the Arsenic removal by electrocoagulation using iron electrodes. J. Environ. Health Sci. Eng. 12 (1), 1–10. https://doi.org/10.1186/2052-336X-12-95.
Chen, R., Wu, L., Zhong, H., Liu, C., Qiao, W., Wei, H., 2021. Evaluation of electrocoagulation process for high-strength swine wastewater pretreatment. Separ. Purif. Technol. 272 (February) https://doi.org/10.1016/j.seppur.2021.118900.
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.
Galvão, N., Beber, J., Souza, D., Magno, C., Vidal, D.S., 2020. Landfill leachate treatment by electrocoagulation : effects of current density and electrolysis time. J. Environ. Chem. Eng. 8 (5) https://doi.org/10.1016/j.jece.2020.104368.
Garcia-Segura, S., Eiband, M.M.S.G., de Melo, J.V., Martínez-Huitle, C.A., 2017. Electrocoagulation and advanced electrocoagulation processes: a general review about the fundamentals, emerging applications and its association with other technologies. J. Electroanal. Chem. 801, 267–299. https://doi.org/10.1016/j.jelechem.2017.07.047. July.
Gondudey, S., Chaudhari, P.K., Dharmadhikari, S., Thakur, R.S., 2020. Treatment of sugar industry effluent using an electrocoagulation process: process optimization using the response surface methodology. J. Serb. Chem. Soc. 85 (10), 1357–1369. https://doi.org/10.2298/JSC200319037G.
Greenberg, A., Clesceri, L., Eaton, A. (Eds.), 1999. Standard Methods for the Examination of Water and Wastewater, twentieth ed. American Public Health Association, American Water Works Association, Water Environment Federation, Baltimore.
Hu, J., Xiao, Z., Zhou, R., Deng, W., Wang, M., Ma, S., 2011. Ecological utilization of leather tannery waste with circular economy model. J. Clean. Prod. 19 (2–3), 221–228. https://doi.org/10.1016/j.jclepro.2010.09.018.
Igwegbe, C.A., Onukwuli, O.D., Ighalo, J.O., Umembamalu, C.J., 2021. Electrocoagulation-flocculation of aquaculture effluent using hybrid iron and aluminium electrodes: a comparative study. Chem. Eng. J. Adv. 6 https://doi.org/10.1016/j.ceja.2021.100107.
Isik, Z., Arikan, E.B., Ozay, Y., Bouras, H.D., Dizge, N., 2020. Electrocoagulation and electrooxidation pre-treatment effect on fungal treatment of pistachio processing wastewater. Chemosphere 244. https://doi.org/10.1016/j.chemosphere.2019.125383.
ISO 5433-Leather, 2013. Bovine wet blue, pp. 1–10. Specification 2013.
Kanagaraj, J., Senthilvelan, T., Panda, R.C., Kavitha, S., 2015. Eco-friendly waste management strategies for greener environment towards sustainable development in leather industry: a comprehensive review. J. Clean. Prod. 89, 1–17. https://doi.org/10.1016/j.jclepro.2014.11.013.
Kara, S., Gürbulak, E., Eyvaz, M., Yüksel, E., 2013. Treatment of winery wastewater by electrocoagulation process. Desalination Water Treat. 51 (28–30), 5421–5429. https://doi.org/10.1080/19443994.2013.770223.
Kim, M.K., Kim, T., Kim, T.K., Joo, S.W., Zoh, K.D., 2020. Degradation mechanism of perfluorooctanoic acid (PFOA) during electrocoagulation using Fe electrode. Separ. Purif. Technol. 247 https://doi.org/10.1016/j.seppur.2020.116911.
Li, K., Chen, H., Wang, Y., Shan, Z., Yang, J., Brutto, P., 2009. A salt-free pickling regime for hides and skins using oxazolidine. J. Clean. Prod. 17 (17), 1603–1606. https://doi.org/10.1016/j.jclepro.2009.06.004.
Martinho, A., Crispim, F., Gaião, J., Silva, N., 2015. Boas práticas para o setor de curtumes. https://austra.pt/documentos/documentacao/manual_boas_praticas_curtumes.pdf.
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 (3), 263–292. https://doi.org/10.1515/revce-2016-0019.
Nampoothiri, H., Maninal, Soloman, 2016. Control of electrocoagulation batch reactor for oil removal from automobile garage wastewater. Procedia Technol. 24, 603–610. https://doi.org/10.1016/j.protcy.2016.05.136.
Nur-A-Tomal, Hashem, A., Zahin, E., Pulok, L., Das, R., Mim, S., 2021. Goatskin preservation with plant oil: significant chloride reduction in tannery wastewater. Environ. Sci. Pollut. Control Ser. 28 (10), 12889–12897. https://doi.org/10.1007/s11356-020-11311-z.
Nur-A-Tomal, S., Biswal, S., Pahlevani, F., Sahajwalla, V., 2022. Recycling tannery solid wastes as an alternative carbon resource for ironmaking. J. Mater. Cycles Waste Manag. 24 (5), 2030–2040. https://doi.org/10.1007/s10163-022-01465-y.
Oden, M.K., Sari-Erkan, H., 2018. Treatment of metal plating wastewater using iron electrode by electrocoagulation process: optimization and process performance. Process Saf. Environ. Protect. 119, 207–217. https://doi.org/10.1016/j.psep.2018.08.001.
Ogata, Y., Ishigaki, T., Nakagawa, M., Yamada, M., 2016. Effect of increasing salinity on biogas production in waste landfills with leachate recirculation: a lab-scale model study. Biotechnol. Rep. 10, 111–116. https://doi.org/10.1016/j.btre.2016.04.004.
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 (4) https://doi.org/10.1016/j.jece.2020.104032.
Rodrigues, M.I., Iemma, A.F., 2014. In: Press, C. (Ed.), Experimental Design and Process Optimization. CRC Press. https://doi.org/10.1201/b17848.
Selvi, A.T., Khambhaty, Y., Sugapriya, S., Jayakumar, G.C., 2022. Vegetable wastes as a bio-additive for low-salt preservation of raw goat skin: an attempt to reduce salinity in leather manufacture. Environ. Sci. Pollut. Control Ser. 29 (21), 31374–31383. https://doi.org/10.1007/s11356-021-18001-4.
Sundarapandiyan, S., Chandrasekar, R., Ramanaiah, B., Krishnan, S., Saravanan, P., 2010. Electrochemical oxidation and reuse of tannery saline wastewater. J. Hazard Mater. 180 (1–3), 197–203. https://doi.org/10.1016/j.jhazmat.2010.04.013.
Syaichurrozi, I., Sarto, S., Sediawan, W.B., Hidayat, M., 2020. Mechanistic models of electrocoagulation kinetics of pollutant removal in vinasse waste_ Effect of voltage. J. Water Proc. Eng. 36 https://doi.org/10.1016/j.jwpe.2020.101312.
Tamil Selvi, A., Brindha, V., Vedaraman, N., Kanagaraj, J., Sundar, V.J., Khambhaty, Y., Saravanan, P., 2020. Eco-friendly curing of hides/skins using phyto based Citrus limon leaves paste. J. Clean. Prod. 247 https://doi.org/10.1016/j.jclepro.2019.119117.
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. Protect. 146, 169–189. https://doi.org/10.1016/j.psep.2020.08.048.
Uddin, M.M., Hasan, M.J., Mahmud, Y., Uddin, N., Rahman, K.T., Nishad, I.J.A., Shamsuddin, S.M., 2022. A cleaner goatskin preservation with leaf paste and powder; an approach for salinity remediation in tannery wastewater. Clean. Eng. Technol. 6 https://doi.org/10.1016/j.clet.2021.100357.
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.
Weiss, S.F., Christensen, M.L., Jørgensen, M.K., 2021. Mechanisms behind pH changes during electrocoagulation. AIChE J. 67, 1–13. https://doi.org/10.1002/aic.17384.
Yavuz, Y., Ögütveren, Ü.B., 2018. Treatment of industrial estate wastewater by the application of electrocoagulation process using iron electrodes. J. Environ. Manag. 207, 151–158. https://doi.org/10.1016/j.jenvman.2017.11.034.
Zhao, D., Lee, L.Y., Ong, S.L., Chowdhury, P., Siah, K.B., Ng, H.Y., 2019. Electrodialysis reversal for industrial reverse osmosis brine treatment. Separ. Purif. Technol. 213, 339–347. https://doi.org/10.1016/j.seppur.2018.12.056.