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Enhanced chromium removal from tannery wastewater through electrocoagulation with iron electrodes: Leveraging the Box-Behnken design for optimization

Edwar Aguilar-Ascón^{a,*}, Liliana Marrufo-Saldaña^b, Walter Neyra-Ascón^c

^a Universidad de Lima, Instituto de Investigación Científica, Grupo de Investigación en Tecnologías Exponenciales, Estudios Generales, Av. Javier Prado 4600, Surco, Lima, Perú

^b Centro de Innovación Productiva y Transferencia Tecnológica del Cuero, Calzado e Industrias Conexas Producción, (CITEccal Lima) - ITP, Av. Caquetá 1300, Rímac, Lima, Perú

^c Universidad de Lima, Instituto de Investigación Científica, Av. Javier Prado 4600, Surco, Lima, Perú

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ABSTRACT

This study is focused on reducing total chromium level in tannery wastewater through the electrocoagulation process, in order to comply with the maximum permissible limits (MPL) and to determine the effects from its main operating factors. For this purpose, a batch electrocoagulation reactor was manufactured using iron electrodes. Next, the response surface methodology was applied in the experimental design using a Box–Behnken design (BBD) with three factors: current intensity, treatment time, and *pH* level. In addition, the total chromium removal percentage was taken as a response variable. The corresponding statistical analysis revealed that the treatment time, current intensity, and *pH* level variables were significant at a confidence level of P - value < 0.05. Obtained in this study for a 99% total chromium removal were: current intensity (*I*) = 2.9*A*, time (*t*) = 18.1 *min*, and *pH* = 5.6. Our results indicated that the electrocoagulation process effectively removes total chromium from tannery effluents up to MPL values.

1. Introduction

One of the most critical concerns reported by the tanning industry is wastewater management since approximately $45 - 50 m^3$ of effluents are produced per ton of tanned leather [1]. These wastewater effluents are characterized by high levels of pollutants, such as the biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (SST), sulfides, and chromium.

The tanning process that produces high pollution load can be divided into three stages: the beamhouse stage, the tanning stage, and the finishing stage. In the beamhouse stage, the leather is prepared for crosslinking the tanning agent. In this stage, the salt used for preserving the skin is removed, any remnants of hair and meat are removed, and the leather is divided to meet the desired thickness, thereby producing a high organic load and chlorides in the effluents. In the tanning stage, the decalcifying agents and the remains from proteins other than collagen are removed, and the skin is brought to an acidic *pH* level so that basic chromium sulfate can be cross-linked to collagen, the main tanning agent used in Peru as well as the most prominent pollutant in these effluents. Subsequently, the

* Corresponding author.

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E-mail addresses: eaguilaa@ulima.edu.pe (E. Aguilar-Ascón), lmarrufo@itp.gob.pe (L. Marrufo-Saldaña), wneyraa@gmail.com (W. Neyra-Ascón).

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leather is retanned, dyed, and oiled to improve its physicomechanical properties. The last stage is finishing; the leather is given its final appearance using resins, waxes, polymers, and lacquers, which are based on organic and aqueous solvents, thus generating emissions mainly into the atmosphere (Fig. 1). Several research studies have already focused on finding chromium removal alternatives. This pollutant comes from using basic chromium sulfate as a tanning agent. In the environment, the most stable forms of chromium are in oxidation state (III) and (IV) Hiller et al., 2020 [2]. Chromium (III) is characterized by its oxidation capacity under certain environmental conditions, which in turn determines its ecotoxicity; even though in small concentrations, it is part of the metabolic processes of plants, animals, and humans. Nevertheless, chromium (III) in high concentrations and in its IV oxidation state is dangerous because it is able to penetrate cell membranes via diffusion through ion channels. Studies have shown that a concentration > 10 mg/L Cr(III) in culture medium and concentrations of > 50 mg/Kg Cr(VI) in soil limit the germination of seeds of plant species [3]. Likewise, it has been determined that Damage to DNA, in human being, may be caused by Cr (VI) at 0.2 mg/mL and Cr (III) at 0.1 mg/mL [4].

The negative environmental impact of tanning has been widely studied and evidenced and therefore this industry is considered one of the most polluting [5–8]. The pollutant load of their effluents is characterized by high levels of DOC, BOD, sulfides, TSS, chromium, ammonia nitrogen among others [5,9]. In Peru, Supreme Decree No. 010-2023-minam updated the maximum permissible limits for tannery effluents; however, compliance with these limits is a challenge because most companies, mainly SMEs, do not have efficient treatment systems. In regions of Peru, such as Arequipa and Trujillo, tanneries are located around a body of water and there is a general request for the development of common treatment plants, while in the Lima region, tanneries are atomized and need to move from sedimentation ponds to technological solutions that minimize the pollutant load. Sewage sludge can be managed by disposal in controlled landfills, but it is possible to recover chromium and use the remaining organic matter as a source for biogas production or as material for composting [10].

The electrocoagulation process consists of applying an electrical current to two electrodes. Herein, one electrode acts as a sacrificial anode and the other as a cathode [11,12]. This produces metal ions that allow the formation of coagulants on site by electrochemical dissolution at the sacrificial anode without adding chemicals Lu et al., 2021 [13]. The cathode releases hydrogen gas by reducing H_2O and the oxygen generated at the anode leads to a flotation process that causes suspended particles in the wastewater to rise to the water surface [13,14]. The most commonly used electrode materials are iron (F_e) and aluminum [15]. The mechanisms below describe the formation of iron hydroxides. Equations (1)–(4) show the mechanisms describing the formation of iron hydroxides.



Fig. 1. Tanning process in the tannery industry [3].

• On the anodic electrode surface:

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

• At the vicinity of the electrode:

At alkaline conditions

Table 1

Articles related to this study.

Item	Artículo	Tipo de agua	Material de electrodos	Concentración inicial de cromo $Cr_i(mg/L)$	Eficiencia de eliminación de cromo (%)	Costo (US\$ /m ³)	Consumo de energía (<i>kWh</i> / <i>m</i> ³)	Referencia
1	Optimized Total Chromium Removal from Tannery Wastewater using Electrocoagulation and Iron Electrodes: Application of the Box Rehnken Design (BBD)	Tannery wastewater	Fe-Fe	121.35	99.9	0.223	0.58	Aguilar (2021)
2	Treatment of raw tannery wastewater by electrocoagulation technique: optimization of effective parameters using Taguchi method	Tannery wastewater	Fe–Fe	570	99.7	0.70	Can be calculated	Deghles, A., & Kurt, U. (2015)
3	Influence of experimental parameters in the treatment of tannery wastewater by electrocoagulation	Tannery wastewater	Fe–Fe	75 y 32	99	2.01	see	Aboulhassan, M. A. et al., (2018)
4	The investigation of chemical coagulation and electrocoagulation processes for tannery wastewater treatment using response surface methodology	Tannery wastewater	Fe–Fe	400 ± 20	98.2	4.84	see	Sari, (2018)
5	Organic and inorganic matter removal from tannery wastewater using the	Tannery wastewater	Al-Al	2000–2300	98	0.8817	2.37	Bing, (2022)
6	Treatment of highly concentrated tannery wastewater using electrocoagulation: Influence of the quality of aluminium used for the electrode	Tannery wastewater (tanning process)	Al–Al	7000	98.1 (dilución 1:6)	More than 20	More than 20	Elabbas S. et al., (2016)
7	Reduction of turbidity and chromium content of tannery wastewater by electrocoagulation process.		Al–Al	236.62	93	More than 20	41.36	Mounir Z, (2018)
8	Chromium removal from industrial effluent by electrocoagulation: Operating cost and kinetic analysis	Tannery wastewater	Fe–Fe	82.7	99.64	0.0277 to 0.207	0.333 to 2.499	Patel, S., & Parikh, S. (2021)
9	Electrocoagulation of chromium in tannery wastewater by a composite anode modified with titanium: parametric and kinetic study	Tannery wastewater	(Fe + Ti)– C	10.0	99.16	-	-	Guiju Li, (2019)
10	Enhanced treatment of tannery wastewater using the electrocoagulation process combined with UVC/VUV photoreactor: Parametric and mechanistic evaluation.	Tannery wastewater	Al-Al	30.11	39.79	-	_	Moradi, M., & Moussavi, G. (2018)
11	Environmental impact elimination of chrome tanning effluent using electrocoagulation process assisted by chemical oxidation	Tannery wastewater	Acero	3844 ± 1200	99.99	_	-	El-Khateeb, (2017)

(2)

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_{2}$$

At acidic conditions

 $Fe^{2+} + (1/4)O_2 + (5/2)H_2O \to Fe(OH)_3(s) + 2H^+$ (3)

• On the cathodic electrode surface:

$$2H_2O + 2e \to H_2 + 2OH^- \tag{4}$$

Therefore, chromium removal is crucial in effluent treatment systems, wherein different techniques have already been studied, such as adsorption, coagulation-flocculation, osmosis, and electrocoagulation. Electrocoagulation has some advantages over other technologies, such as low sludge production [16], no use of chemicals, lower treatment costs, low energy requirements and can be powered by solar energy. On the other hand, it has disadvantages such as the passivation of electrodes and the need for maintenance [17]. Several research studies have already focused on the reduction of chromium in tannery effluents. In one of these studies, El-Taweel et al., 2015 [18] efficiently removed 90% of chromium (IV) using iron electrodes. In addition, Mella et al., 2015 [19] was able to remove 90.27% of chromium using iron electrodes at 2.5 V and after 100 *min* of treatment. Elabbas et al., 2016 [20] removed 99% of chromium (III) from tannery wastewater using aluminum electrodes. Furthermore, Khan et al., 2019 [21] showed that 100% of Cr (VI) was effectively removed using iron electrodes at a *pH* of 3.0 by applying a current of 1.48 *A* for 21.47 *min*. In contrast, Genawi NM et al., 2020 [22] reported ~ 100% chromium removal by using iron electrodes at a current density of 13 *mA/cm²*, *pH* of 7, and concentration the chromium of 750 *ppm*. Table 1 below shows some additional studies with this work.

Therefore, the objective of this research work was to treat real tannery wastewater with electrocoagulation using iron electrodes in order to reduce the levels of chromium concentration and to determine its efficiency, cost and data that will contribute to its scaling up. It is important to point out that this particular wastewater has different characteristics from those generated in other countries due to the incipient technology used in the processes of the tannery industry in Peru, hence the importance of having real data to find a solution to the environmental problem caused by this industry.

2. Materials and methods

2.1. Raw tannery wastewater

The raw tannery wastewater used in our experiment was supplied by *Centro de Innovación Tecnológica del Cuero y Calzado e Industrias Conexas* (CITEccal is the Spanish acronym) from their pilot tanning effluent treatment plant. The wastewater sample was taken at the outlet of the tanning plant settling tank in order to remove the larger particles. This water presents very similar characteristics to that produced by the tanning industry, as indicated in Table 2. In addition to high concentrations of organic matter and chromium, this water also exhibits high conductivity values, which demands higher electrical current.

2.2. Electrocoagulation reactor

For these purposes, a batch reactor with the following dimensions was used: length: 30 *cm* ; width: 20 *cm*; and height: 25 *cm*. In total, we used eight iron electrodes that worked as anodes and cathodes: each of them was 10 *cm* wide and 10 *cm* long, with a total area of 100 *cm*². The electrodes were completely submerged in the wastewater. In the reactor the height of the water was 20 *cm* leaving 5 *cm* free space for the accumulation of sludge. Due to the high conductivity values, we used a serial configuration of the electrodes with a spacing of 2 *cm* to reduce electric current demands within. Power was supplied from a 0 - 24 V power source, with current range of 0 - 10 A (See Fig. 2).

2.3. Experimental procedure

Table 2

The experiments were done under three different conditions of pH (8.5,7, and 5.5), current intensity (1,2, and 3 A), and treatment time (7,14, and 21 min). To measure pH, conductivity and temperature, an Oakton *PCS* 35 multiparameter was used. In addition, the following method was used to quantify total chromium (response variable): *EPA* 200.8 : 1994 *Rev* 5.4. Determination of Trace Ele-

Physicochemical effluent analysis.						
Parameter	Value	LMP				
Chromium (mg/L)	121.35 ± 14.56	<0.5				
pH	8.5 ± 0.017	6.0–9.0				
Conductivity $(\mu S / cm)$	10560 ± 1584	No report				
Turbidity (NTU)	1330 ± 384.4	No report				
COD (mg/L)	5016.9 ± 401.35	<50				
Chloride (mg/L)	3505.3 ± 525.3	No report				



Fig. 2. Diagram of the electrocoagulation reactor with serial electrodes; (1) electrocoagulation cell, (2) power source, (3) iron electrodes (cathode and anode), (4) sampler, (5) wastewater, (6) DC ammeter.

ments in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry. To determine the percentage of total chromium removal, Equation (5) was used.

For total chromium:

$$Y_n = \Re R = \left(\frac{Cr_i - Cr_f}{Cr_i}\right) \times 100$$
(5)

where:

%R : Percentage of total chromium removal.

Cri : Concentration of total initial chromium.

Cr_f : Concentration of total final chromium.

2.4. Box-Behnken experimental design

The response surface method (RSM) is a methodology used for developing optimization models and processes [23]. As depicted in Equation (6) below, RSM represents independent parameters quantitatively.

$$y = f(x_1, x_2, x_3, \dots, x_n) \pm \varepsilon$$
(6)

where y is the dependent variable (response parameter), f is the response function, e is the experimental error, and $x_1, x_2, x_3, ..., x_n$ are the independent parameters.

The relationship between the independent and dependent variables is illustrated in Equation (7) below using a quadratic model.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3$$
(7)

where β_0 is the intercept; β_1 , β_2 and β_3 are the linear coefficients; β_{11} , β_{22} and β_{33} are the quadratic coefficients; and β_{12} , β_{13} and β_{23} are the interaction coefficients.

A Box–Behnken experimental design was used to find the main effect on total chromium removal from the operational factors, and to determine the operational factor values that reach maximum chromium removal efficiency. To perform our statistical analysis, we used the Design Expert 11.1 software, which reported an analysis of variance (ANOVA) table at a 95% confidence level, and the quality of fit of the polynomial model was expressed by the coefficient of determination: R^2 and R_{adj} . The experimental design had three factors, three levels, and thirteen experiments with two central points. The factors considered as independent variables were electric current intensity (x_1) , treatment time (x_2) , and $pH(x_3)$. As a response variable, we used the percentage of total chromium removal (y_1) (shown in Table 3).

Factor	Variables	Levels			
		-1	0	+1	
<i>x</i> ₁	Current Intensity (A)	1	2	3	
<i>x</i> ₂	Time (<i>min</i>)	7	14	21	
<i>x</i> ₃	pH	5.5	7	8.5	

3. Results and discussion

3.1. Results from the Box-Behnken design

The results from total chromium removal expressed as the variable and response by the electrocoagulation were proposed according to the design matrix in Table 4. The Box–Behnken design included 13 experiment sets and 2 core experiments. The statistical analysis was performed using Design Expert 11.1 software. Using multiple regression analysis, the chromium removal percentage response variable (y_1) was correlated with three design factors (x_1, x_2, x_3) using the second order polynomial (Eq. (7)). Table 5 below presents the quadratic regression model for total chromium removal $(y_1, \%)$, in terms of coded factors.

The adequacy of the total chromium removal model using iron electrodes was also verified based on the regression coefficient R^2 , the adjusted R^2 value, the predicted R^2 value, the *F* value, and the *P* – values (see Table 5).

In addition, an ANOVA yielded a 95% confidence level, comparing the variation sources against Fisher's distribution (F - test) to validate the viability of the regression model. The regression coefficient (R^2) is an important parameter for validating model adequacy and this value must be at least 0.80 for the model to be a good fit [24]. In this study, the R^2 value for total chromium removal with iron electrodes is $R^2 = 0.9796$, which demonstrates a good model adequacy. The adjusted R^2 and predicted R^2 values were 0.94 and 0.56, respectively, as shown in Table 6. The predicted R^2 values are the values predicted by the design, which measures the variation of the data predicted by the model. The results reveal that the time, current intensity, and *pH* variables were significant based on the response variable (y) at a confidence level of P - value < 0.05.

Fig. 3 denotes both the experimental and predicted values from our model. Here, both the observed and obtained values are very close to linearity, thereby indicating that both values are accurate and reliable.

3.2. Effect of current intensity

Current intensity is the most important parameter in the electrocoagulation process as it controls both coagulant dosing rates and reaction rates within the medium [25]. As current intensity increases, the amount of anodic iron dissolution also increases, which leads to better coagulation. However, very high current intensity values applied for a long time may decrease efficiency due to oxygen production and the passivation of the electrodes [26]. For the treatments, current intensities of 1, 2, *and* 3 *A* were used. As shown in Fig. 4a y 4b, the percentage of total chromium removal increases as current intensity increases. The foregoing happens because current intensity produces anodic dissolution of iron and generates hydroxocationic complexes or iron hydroxide, which, due to surface complexation and electrostatic attraction [25,27], agglomerate particles and remove pollutants [28]. This is reflected in the results from applying 2 *and* 3 *A*, with which 94% efficiency is achieved after 14 *min* of treatment. This result is lower than the values reported by Genawi, who achieved an efficiency close to 100% using iron electrodes and applying current densities of 13 mA/cm.² [20]. El-Taweel also reported obtaining maximum efficiency using iron electrodes at 1 *A* for 15 *min*. These results were justified because these experiments used synthetic water [17]. Furthermore, Deghles obtained a higher 99% efficiency at a current density of 30 mA/cm.² and a treatment time of 25 *min* [28].

3.3. Effect of pH level

Several studies have demonstrated that pH modifies surface particle charges and affects the speciation of iron species, thus significantly influencing the electrocoagulation process mechanism [24,26]. Metal hydroxide precipitations are controlled by pH level

Table 4Box–Behnke design for chromium removal.

Exp. No		Factors		Chromium Removal (%)	(%)
	Current intensity (A)	Treatment Time (min)	pH	Actual value	Predicted value
	<i>x</i> ₁	<i>x</i> ₂	$\overline{x_3}$	<i>y</i> ₁ <i>a</i>	y_1p
1	2	21	5.5	92	96
2	2	21	8.5	27	33
3	2	7	8.5	18	14
4	1	14	8.5	17	14
5	1	7	7	26	33
6	2	14	7	27	27
7	1	21	7	38	35
8	3	21	7	71	64
9	3	14	5.5	94	97
10	2	14	7	26	27
11	1	14	5.5	85	84
12	3	7	7	31	34
13	3	14	8.5	31	32
14	2	7	5.5	91	85
15	2	14	7	28	27

Table 5

Statistical parame	eters obtained	using RSM for	r chromium	removal	(%).
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Response	R ² (%)	$\frac{Adj - R^2}{(\%)}$	р 	Quadratic Response Model based on Least Squares
Chromium Removal (%) (Chromium removal,%	0.9796); y _a (Curre	0.9428 ent intensity,1	0.0011 A); x_1 (<i>Time</i>	$ \begin{array}{l} y_{\alpha}=762.22222-40.70833x_{1}-6.44048x_{2}-167.52778x_{3}+1.0000x_{1}x_{2}+0.833333x_{1}x_{3}+0.190476x_{2}x_{3}+7.12500x_{1}^{2}+0.150510x_{2}^{2}+10.05556x_{3}^{2}\\ e,min); \ x_{2} \ (pH); \ x_{3} \end{array} $

ANOVA table.

Source	Sum of Squares	DF	MS	F Value	P-Value		
Model	12309.65	9	1367.74	26.64	0.0011		
x_1 : Current Intensity (A)	465.13	1	465.13	9.06	0.0298		
x_2 : Time (<i>min</i>)	480.50	1	480.50	9.36	0.0281		
$x_3: pH$ Level	9045.13	1	9045.13	176.15	< 0.0001		
$x_1 x_2$	196.00	1	196.00	3.82	0.1082		
$x_1 x_3$	6.25	1	6.25	0.1217	0.7414		
$x_2 x_3$	16.00	1	16.00	0.3116	0.6008		
x_{1}^{2}	187.44	1	187.44	3.65	0.1143		
x_{2}^{2}	200.83	1	200.83	3.91	0.1049		
x ₃ ²	1890.06	1	1890.06	36.81	0.0018		
Residual	256.75	5	50.35				
Lack of fit	254.75	3	84.92	84.92	0.0117		
Pure Error	2.00	2	1.0000				
Total Cor.	12566.40	14					
$R^2 = 97.96$ %, Adj $R^2 = 94.28$ %							



Fig. 3. Regression plot illustrating the correlation between experimental data and predicted values obtained using the response surface methodology, describing percentage removal of chromium.

variations, which remove pollutants and agglomerate coagulants when acting as coagulants [27]. The F_e^{3+} generated will undergo immediate reactions producing several monomeric or polymeric metal complexes, such as $F_e(OH)_3$, $F_e(OH)_4^-$, $F_e(H_2O)_3(OH)_3$, $F_e(H_2O)_6^{3+}$, $F_e(H_2O)_5(OH)_2^+$, $F_e(H_2O)_4(OH)_2^+$, $F_e(H_2O)_8(OH)_2^{4+}$, and $Fe_2(H_2O)_6(OH)_4^{2+}$ [29]. These compounds remain in the medium as an aqueous suspension, which can remove pollutants from wastewater by coagulation within a *pH* range of 2 – 6 [27,29]. To determine the effects of *pH* on total chromium removal, we used *pH* valsues between 5.5 *and* 8.5 in this study. In Fig. 4b y 4c, shows that the best efficiencies were obtained at pH = 5.5, where a maximum chromium removal value of 94% was achieved with a current









(caption on next page)

Fig. 4. Three-dimensional and contour response surface charts for biochemical oxygen demand removal percentages a) current intensity and treatment time; b) current intensity and *pH* level; and c) treatment time and *pH* level.

intensity of 3 amperes and a time of 14 minutes. This result is consistent with the values reported by Shahriari, who obtained the highest chromium removal efficiency at an optimum pH of 6, who reported that the hydroxide produced formed a gelatinous sediment of iron hydroxide and then a cosediment of iron and chromium was formed [30]. Chromium (+3) at acidic pH, lower than 3, remains in its ionic form, as OH- radicals increase, they form complexes with chromium, reaching higher pH, this causes the precipitation of chromium hydroxide (Covarrubias, C. et al. ,2005; Basaldella, E, 2007). In addition, Golder reported that the optimum pH for chromium removal in monopolar and bipolar configurations was 6 and 5.5, respectively [31]. Furthermore, Genawi indicated that, when using iron electrodes, the maximum chromium removal efficiency occurred at pH values close to 7 [21]. In contrast, Deghles reported a 99% chromium removal efficiency at pH levels of 7 – 8 when using iron electrodes [28]. However, during the experiments, a disadvantage of using iron electrodes was observed; the treated water turned black due to the reaction of F_e^{2+} , F_e^{3+} , and H_2S , HS^- , S_2^- , which generated a black F_eS precipitate [32].

3.4. Effect of treatment time

Treatment times have a direct effect on electrocoagulation process efficiencies [33]. This parameter influences the production rate of coagulant, OH^- , and H_2 , as well as affects the cost-effectiveness of the process [33,34]. Hence, we varied the treatment time in the range of 7 – 21 *min*.

As shown in Table 3 and Fig. 4a y 4c, the results from this parameter confirm that the total chromium removal efficiency increases over the course of treatment time. It is observed that at a treatment time of 7 min, the lowest efficiency values are obtained, ranging from 17% to 31%. On the other hand, at 7 and 14 minutes of treatment at a *pH* of 5.5, 90% efficiency is exceeded. This is very similar to the values reported by El-Taweel, where the processes reach their maximum chromium removal efficiency after 14 *min* [17]. However, these values are not consistent with Deghles, whose processes achieved their best efficiency at 25 *min* of treatment [23]. Furthermore, De la Luz-Pedro reports treatment times > 60 *min* for the removal of chromium [35]. Hence, we must determine our optimal treatment time because very long treatment times lead to high electrode and energy consumption [36].

3.5. Optimization of total chromium removal via electrocoagulation

The Box–Behnken response surface methodology was used for numerical optimization to determine the optimal parameters to maximize total chromium removal efficiency (*y*). The effects of the process variables are shown in Fig. 4a,b,c, which represent the three-dimensional and contour (two-dimensional) response surface plots, which use the mathematical models developed in Equation (7), wherein chromium removal percentage variations may be observed, according to the variation of their current intensity (x_1), treatment time (x_2), and *pH* level (x_3), factors. The optimization model predicted the following parameters for optimal conditions: current intensity 2.9 *A*, *pH* = 5.6, and treatment time 18.1 *min*. Under these conditions, 99.9% total chromium removal efficiency was achieved.

3.6. Operation costs

The operation costs for laboratory scale units are estimated considering energy costs and the quantity of materials and chemicals consumed. Herein, the operation costs were calculated as follows:

$$C_{opT} = C_{op1} + C_{op2} \tag{8}$$

where, C_{opT} represents total operation costs, C_{op1} the electrode consumption operation costs, and C_{op2} the energy consumption operation costs. Rewriting Equation (8) explicitly:

$$C_{opT} = \rho_{electrodes} x \, \omega_{electrodes} + \rho_{energy} x \, \beta_{energy} \tag{9}$$

where, $\rho_{electrodes}$ represents the price of the electrode material, and $\omega_{electrodes}$ the consumed electrode material weight, which could be estimated as follows:

$$\omega_{electrodes} = \eta_c \, x \, \omega_c + \eta_a \, x \, \omega_a \tag{10}$$

where, $\omega_{electrodes}$ represents the total electrode weight, η_c the number of cathodes, η_a the number of anodes, ω_c the cathode weight (g), and ω_a the anode weight (g).

While ρ_{energy} represents the price per energy unit, and β_{energy} (*kWh*/*m*³) is the energy consumed. The latter is calculated as follows:

$$C_e = \frac{U \, x \, I \, x \, t}{V \, x \, 1000} \tag{11}$$

where, C_e represents the energy consumption (kWh /m³), U is the potential (V), I is the current (A), t is the treatment time ((h), and V is

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the water volume (m^3) , respectively.

The operating cost for the electrocoagulation process treatment has been estimated based on the unit prices of the Peruvian market in January 2023 (the cost of energy is 0.194 US\$/kWh, and the cost of 1 Kg of aluminum is of US\$ = 2.486). The consumed amounts of both energy and electrode material have been calculated as per Equations (8,9,10 and 11), respectively. The operational cost from Equation (9) for the electrocoagulation process treatment is about 0.223US\$/m³.

4. Conclusions

This study shows that electrocoagulation with iron electrodes is effective in reducing total chromium from raw tannery wastewater. According to the experimental design results, current intensity, treatment time, and *pH* levels are crucial for total chromium removal. The high $R^2 = 0.9796$ and adj $R^2 = 0.9428$ values confirm a good fit of the model used for total chromium removal. To achieve 99% efficiency in the removal of total chromium, a current intensity (I) = 2.9 A, time (t) = 18.1 min and pH = 5.6 should be used. Based on these results, we infer that changing the *pH* level of the effluent helps in obtaining the highest possible efficiency using iron electrodes. It is also important to note that iron electrodes cause treated tannery water to turn black, which originates from the reactions between iron ions and sulfide compounds. The data obtained in this study allow us to have relevant information for future designs of pilot or larger scale plants and thus define an optimal treatment ril to solve the environmental problem generated by the effluents of the tannery industry. In addition, it is proven that electrocoagulation is efficient for chromium removal; however, due to the characteristics of the effluent, it is recommended to add other technologies such as advanced oxidation and filtration to comply with the environmental standard.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Edwar Aguilar-Ascón: Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. Liliana Marrufo-Saldaña: Writing – review & editing, Methodology, Formal analysis. Walter Neyra-Ascón: Writing – review & editing, Visualization, Software.

Declaration of competing interest

First of all, I would like to greet you and hereby state that all the authors who have participated in the preparation of this article have no conflict of interest and agree with the regulations of the journal.

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References

- Kanagaraj J., Senthivelan T., Panda R.C., Kavitha S., Eco-friendly waste management Strategies for greener environment towards sustainable development in leather industry: a comprehensive review, J. Clean. Prod. (2014),89,1-17,https://doi.org/10.1016/j.jclepro.2014.11.013.
- [2] M.M. Hiller, R.W. Leggett, A biokinetic model for trivalent or hexavalent chromium in adult humans, J. Radiol. Prot. (2020) 19–39, https://doi.org/10.1088/ 1361-6498/ab4286.
- [3] D. Srivastava, M. Tiwari, P. Dutta, P. Singh, K. Chawda, M. Kumari, D. Chakrabarty, Chromium Stress in plants: Toxicity, Tolerance and Phytoremediation, Sustainability 13 (9) (2021) 4629, https://doi.org/10.3390/su13094629.
- [4] M.K. Murthy, P. Khandayataray, S. Padhiary, D. Samal, A review on chromium health hazards and Molecular mechanism of chromium bioremediation, Rev. Environ. Health 38 (3) (2022) 461–478, https://doi.org/10.1515/reveh-2021-0139. PMID: 35537040.
- [5] P. Thanikaivelan, J.R. Rao, B.U. Nair, T. Ramasami, Recent Trends in leather Making: processes, problems, and pathways, Crit. Rev. Environ. Sci. Technol. 35 (1) (2005) 37–79, https://doi.org/10.1080/10643380590521436.
- [6] G. Lofrano, S. Meriç, G.E. Zengin, D. Orhon, Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review, Sci. Total Environ. 461–462 (2013) 65–281, https://doi.org/10.1016/j.scitotenv.2013.05.0.
- [7] A. Hira, H. Pacini, K. Attafuah-Wadee, M. Sikander, R. Oruko, A. Dinan, Mitigating tannery pollution in Sub-Saharan Africa and South Asia, J. Develop. Soc. 38 (3) (2022) 360–383, https://doi.org/10.1177/0169796X221104856.
- [8] F. Chiampo, S. Shanthakumar, R. Rajamanickam, G. Ganapathy, Tannery: environmental impacts and sustainable technologies, Mater. Today: Proc. (2023), https://doi.org/10.1016/j.matpr.2023.02.025.
- [9] S. Venkatasubramanian, Towards environmental protection and process safety in leather processing a comprehensive analysis and review, Process Saf. Environ. Protect. 163 (2022) 703–726, https://doi.org/10.1016/j.psep.2022.05.062.
- [10] M.A. Moktadir, J. Ren, J. Zhou, A systematic review on tannery sludge to energy route: current practices, impacts, strategies, and future directions, Sci. Total Environ. 901 (2023) 166244, https://doi.org/10.1016/j.scitotenv.2023.166244.
- [11] M. Amarine, B. Lekhlif, M. Sinan, A. El Rharras, J. Echaabi, Treatment of nitrate- rich groundwater using electrocoagulation with aluminum anodes, Groundwater for Sustainable Development 11 (2020) 100371.

- [12] J.N. Hakizimana, N. Najid, B. Gourich, C. Vial, Y. Stiriba, J. Naja, Hybrid electrocoagulation/electroflotation/electrodisinfection process as a pretreatment for seawater desalination, Chem. Eng. Sci. 170 (2017) 530–541.
- [13] J.B. Lu, W. Zhang, X.T. Zhang, G.F. Si, P. Zhang, B.X. Li, R.X. Su, X. Gao, Efficient removal of Tetracycline-Cu complexes from water electrocoagulation technology, J. Clean. Prod. 289 (2021) 125729.
- [14] T. Ouslimane, S. Aoudj, M. Amara, et al., Removal of copper and fluoride from mixed Cu-CMP and Fluoride-bearing wastewaters by electrocoagulation, Int. J. Environ. Res. 11 (2017) 677–684, https://doi.org/10.1007/s41742-017-0058-7.
- [15] M. Elazzouzi, K. Haboubi, M.S. Elyoubi, Electrocoagulation flocculation as a lowcost process for pollutants removal from urban wastewater, Chem. Eng. Res. Des. 117017 (2017) 614–626, https://doi.org/10.1016/j.cherd.2016.11.011.
- [16] E. Aguilar, Elimination of Chemical Oxygen Demand from Domestic Residual Water by Electrocoagulation with Aluminum and Iron Electrodes, 2018.
- [17]] A.K. Shahedi, F. Darban, A. Taghipour, A. Jamshidi-Zanjani, Review on industrial wastewater treatment via electrocoagulation processes, Curr. Opin. Electrochem. 22 (2020) 154–169, https://doi.org/10.1016/j.coelec.2020.05.009. ISSN 2451-9103.
- [18] E.M. El-Taweel, I. Nassef, D. Elkheriany, Sayed, Removal of Cr(VI) ions from waste water by electrocoagulation using iron electrode, Egypt, J. Petrol. 24 (2015) 183–192, https://doi.org/10.1016/j.ejpe.2015.05.011.
- [19] B. Mella, A.C. Glanert, M. Gutterres, Removal of chromium from tanning wastewater and its reuse, Process Saf. Environ. Protect. 95 (2015) 195–201.
- [20] N. Elabbas, L. Ouazzani, F. Mandi, M. Berrekhis, S. Perdicakis, M.N. Pontvianne, F. Pons, J.P. Lapicque, Treatment of highly concentrated tannerywastewater using electrocoagulation: influence of the quality of aluminiumused for the electrode, J. Hazard Mater. 319 (2016) 69–77, https://doi.org/10.1016/j. jhazmat.2015.12.067.
- [21] S.U. Khan, D.T. Islam, I.H. Farooqi, S. Ayub, F. Basheer, Hexavalent chromium removal in an electrocoagulation column reactor: process optimization using CCD, adsorption kinetics and pH modulated sludge formation, Process Saf. Environ. Protect. 122 (2019) 118–130, https://doi.org/10.1016/j.psep.2018.11.024.
- [22] N.M. Genawi, M.H. Ibrahim, M.H. El-Naas, A.E. Alshaik, Chromium removal from tannery wastewater by electrocoagulation: optimization and sludge characterization, Water 12 (5) (2020) 1374, https://doi.org/10.3390/w12051374.
- [23] K. Ravikumar, B. Deebika, K. Balu, Decolourization of aqueous dye solutions by a novel adsorbent: application of statistical designs and surface plots for the optimization and regression analysis, J. Hazard Mater. 22 (2005) 75–83.
- [24] K.K. Garg, B. Prasad, Development of Box Behnken design for treatment of terephthalic acid wastewater by electrocoagulation process: optimization of process and analysis of sludge, J. Environ. Chem. Eng. 4 (2016) 178–190.
- [25] M. Nasrullah, A.W. Zularisam, S. Krishnan, M. Sakinah, L. Singh, Y.W. Fen, High performance electrocoagulation process in treating palm oil mill effluent using high current intensity application, Chin. J. Chem. Eng. 27 (2019) 208–217, https://doi.org/10.1016/j.cjche.2018.07.021.
- [26] M. Piña, A. Martín, C. Gonzáles, F. Prieto, A. Guevara, J. García, Revisión de variables de diseño y condiciones de operación en la electrocoagulación, Rev. Mex. Ing. Quim. 10 (2) (2011) 257–271. Recuperado de, http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S1665-27382011000200010.
- [27] P. Drogui, M. Asselin, S.K. Brar, H. Benmoussa, J.F. Blais, Electrochemical removal of pollutants from agro-industry wastewaters, Purif. Technol. 61 (2008 Sep) 301–310, https://doi.org/10.1016/j.seppur.2008.10.013.
- [28] T. Karichappan, S. Venkatachalam, P.M. Jeganathan, Optimization of electrocoagulation process to treat grey wastewater in batch mode using response surface methodology, J Environ Health Sci Engineer 12 (2014) 29, https://doi.org/10.1186/2052-336X-12-29.
- [28]a A. Deghles, U. Kurt, Treatment of raw tannery wastewater by electrocoagulation technique: optimization of effective parameters using Taguchi method, Desalination Water Treat. 57 (2016) 14798–14809, https://doi.org/10.1080/19443994.2015.1074622.
- [29] M.G. Arroyo, V. Pérez-Herranz, M.T. Montañés, J. García-Antón, J.L. Guiñón, Effect of pH and chloride concentration on the removal of hexavalent chromium in a batch electrocoagulation reactor, J. Hazard Mater. 169 (1–3) (2009) 1127–1133, https://doi.org/10.1016/j.jhazmat.2009.04.089.
- [30] T. Shahriari, G.N. Bidhendi, N. Mehrdadi, et al., Removal of chromium (III) from wastewater by electrocoagulation method, KSCE J. Civ. Eng. 18 (2014) 949–955, https://doi.org/10.1007/s12205-014-0642-8.
- [31] A. Golder, A. Samanta, S. Ray, Removal of trivalent chromium by electrocoagulation, Separ. Purif. Technol. 53 (1) (2007) 33–41, https://doi.org/10.1016/j. seppur.2006.06.010.
- [32] J. Feng, Y. Sun, Z. Zheng, J. Zhang, S. Li, Y. Tian, Treatment of tannery wastewater by electrocoagulation, J. Environ. Sci. 19 (2007) 1409–1415, https://doi. org/10.1016/S1001-0742(07)60230-7.
- [33] F.E. Titchou, H. Zazou, H. Afanga, J. El Gaayda, R.A. Akbour, M. Hamdani, Removal of persistent organic pollutants (POPs) from water and wastewater by adsorption and electrocoagulation process, Groundwater for Sustainable Development (2021), https://doi.org/10.1016/j.gsd.2021.100575.
- [34] W. Jiang, Y. Chen, Y. Liu, Performance investigation of an electrocoagulation reactor with electrodes' polarity crossly oriented in emulsified oil separation, Energy Fuel. 33 (2019) 9014–9022, https://doi.org/10.1021/acs.energyfuels.9b02133JournalPre-proof.
- [35] A. De la Luz-Pedro, E.F. Martínez Prior, M.H. López-Araiza, S. Jaime-Ferrer, A. Estrada-Monje, J.A. Banuelos, Pollutant Removal from Wastewater at Different Stages of the Tanning Process by Electrocoagulation.
- [36] O.T. Can, M. Kobya, E. Demirbas, M. Bayramoglu, Treatment of the textile wastewater by combined electrocoagulation, Chemosphere 62 (2006), https://doi. org/10.1016/j.chemosphere.2005.05.022, 181e187.