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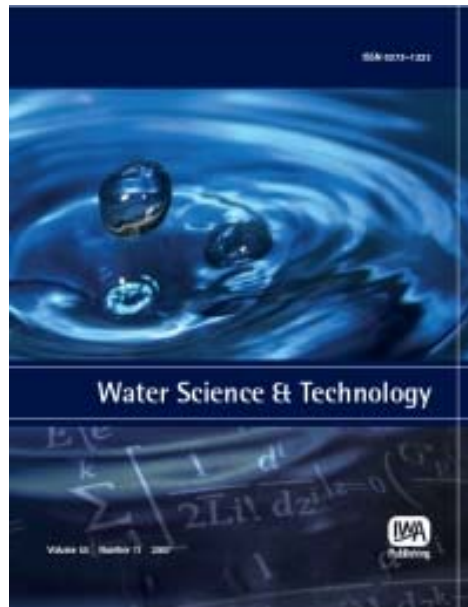


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## The removal of the trivalent chromium from the leather tannery wastewater: the optimisation of the electro-coagulation process parameters

E. GilPavas, I. Dobrosz-Gómez and M. Á. Gómez-García

### ABSTRACT

The capacity of the electro-coagulation (EC) process for the treatment of the wastewater containing  $\text{Cr}^{3+}$ , resulting from a leather tannery industry placed in Medellín (Colombia), was evaluated. In order to assess the effect of some parameters, such as: the electrode type (Al and/or Fe), the distance between electrodes, the current density, the stirring velocity, and the initial  $\text{Cr}^{3+}$  concentration on its efficiency of removal ( $\%R\text{Cr}^{3+}$ ), a multifactorial experimental design was used. The  $\%R\text{Cr}^{3+}$  was defined as the response variable for the statistical analysis. In order to optimise the operational values for the chosen parameters, the response surface method (RSM) was applied. Additionally, the Biological Oxygen Demand ( $\text{BOD}_5$ ), the Chemical Oxygen Demand (COD), and the Total Organic Carbon (TOC) were monitored during the EC process. The electrodes made of aluminium appeared to be the most effective in the chromium removal from the wastewater under study. At pH equal to 4.52 and at  $28^\circ\text{C}$ , the optimal conditions of  $\text{Cr}^{3+}$  removal using the EC process were found, as follows: the initial  $\text{Cr}^{3+}$  concentration =  $3,596 \text{ mg/L}$ , the electrode gap =  $0.5 \text{ cm}$ , the stirring velocity =  $382.3 \text{ rpm}$ , and the current density =  $57.87 \text{ mA/cm}^2$ . At those conditions, it was possible to reach 99.76% of  $\text{Cr}^{3+}$  removal, and 64% and 61% of mineralisation (TOC) and COD removal, respectively. A kinetic analysis was performed in order to verify the response capacity of the EC process at optimised parameter values.

**Key words** | chromium removal, electro-coagulation, statistical optimisation, tannery wastewater

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### INTRODUCTION

The industry of the leather tannery is considered as one of the most pollutant in the world. During the tanning process different kinds of hazardous and low biodegradable chemicals, such as: acids, dyes, surfactants, natural or synthetic tanning agents, etc..., are used to convert animal skin into an unchangeable product. In 2005 (Buljan 2005) the total global quantity of skins was nearly  $8 \times 10^6 \text{ t}$  as wet salted weight a year and tanning workshops worldwide used  $4 \times 10^6 \text{ t}$  of chemicals, producing over  $3 \times 10^8 \text{ t}$  of wastewater and about  $8 \times 10^6 \text{ t}$  of solid waste and dewatered sludge. In this sense, the leather tannery wastewater represents a severe environmental problem.

Chromium is the most employed substance during the leather tanning since it presents the most appropriate ratio: product quality characteristics/cost. Approximately, 8 wt.% of chromium salt is added to the tanning solution. However, c.a. 10–15% of the used chromium leaves the process with the wastewater. Moreover, the obtained wastewater presents a huge salinity, reaching conductivities around 10,000–12,000 S/cm, resulting from the salty baths used during the leather preparation and the tanning. In the environment, chromium exists in trivalent ( $\text{Cr}^{3+}$ ) and hexavalent ( $\text{Cr}^{6+}$ ) forms. The  $\text{Cr}^{6+}$  is highly toxic and carcinogenic while in its trivalent state, in trace amounts, it is an essential

nutrient for plants and animal metabolism. On the other hand,  $\text{Cr}^{3+}$  has also shown its potential toxicity mainly in aqueous media (Zaroual *et al.* 2009).

For those reasons, there is a strong interest to develop methods for the efficient chromium removal, among them: precipitation (Song *et al.* 2004), adsorption (Mor *et al.* 2007), microemulsion (Dantas Neto *et al.* 2004), membrane separation (Ortega *et al.* 2005), biological process (Srivastava & Thakur 2006), etc... However, it should be noted that most of these methods present some technical and economical limitations. Recently, the electro-coagulation process (EC) has been successfully applied to treat an important variety of industrial wastewater, including one containing chromium. The EC process provides several advantages, among them: the lack of the necessity to include additional chemical additives, the simply constructed and easy to operate equipment, low investment and operative costs, and finally very low sludge generation.

Electrocoagulation globally results in  $\text{OH}^-$  formation, as a consequence of the increase in pH during the operation. The EC process uses continuous current in order to form flocs of metal hydroxides by the electro-coagulation of soluble anodes. At the same time, gaseous  $\text{H}_2$  is formed on the cathode, which helps the flotation of particles to the solution surface. Finally, the colloidal materials are agglomerated and next eliminated by flotation or decantation. This implies the presence of three main physico-chemical processes: the superficial reaction on the electrode surface; the formation of coagulants by electrolytic oxidation; and the adsorption of colloidal particles in the coagulant and their removal by sedimentation or flotation. The right selection of the electrode's material is one of the key parameters for the EC process. The most widely used electrode materials in the EC process are aluminium (Al) and iron (Fe), considering as advantages their price and availability. The electrical current causes the dissolution of those metals into wastewater as  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}$ , respectively. Subsequently, at the appropriate pH, the  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Cr}^{3+}$  ions form complexes with  $\text{OH}^-$  species. Ionic metal hydroxides are soluble, whereas the solubility of neutral  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$  is very low and they can be considered as solids. The details of the removal mechanism of  $\text{Cr}^{3+}$  have already been presented elsewhere (Zongo *et al.* 2009).

The optimisation of the EC process implies the establishment of the operational conditions for the  $\text{Cr}^{3+}$  removal from the wastewater. Considering the numerous quantities of variables and interactions involved in such a process, its analysis requires a lot of effort and is time-consuming. The experimental design technique is an efficient method to

establish the relative importance between many variables and their interactions (Montgomery 2005). Among the analytical methods the response surface method (RSM) was chosen and implemented (GilPavas & Gómez-García 2009).

This study presents the application of the EC process for the treatment of the wastewater containing  $\text{Cr}^{3+}$ , resulting from the local leather tannery industry, placed at the metropolitan area of Medellin (Colombia). The factory, whose aqueous residuals are analysed in this study, releases 23  $\text{m}^3/\text{day}$  of a wastewater characterised by a high concentration of organic matter. For the EC process, both Fe and Al anodes were tested as "sacrificed" anode. The effect of the initial  $\text{Cr}^{3+}$  concentration, the type of electrode material (Al and/or Fe), the distance between electrodes, the current density, and the stirring velocity on the efficiency of  $\text{Cr}^{3+}$  removal was studied. Additionally, the Biological Oxygen Demand ( $\text{BOD}_5$ ), the Chemical Oxygen Demand (COD), and the Total Organic Carbon (TOC) were monitored during the EC process. The efficiency of  $\text{Cr}^{3+}$  removal was defined as the response variable for the statistical analysis. The RSM was used in order to define the optimal operational values of chosen parameters.

## MATERIALS AND METHODS

### Wastewater samples

The industrial leather tanning process under study is operated in a batch mode. Depending on the characteristics of the processed leather, the chromium charge used for the process and consequently the chromium residual content in the wastewater stream can vary from one batch to another. The wastewater samples were taken twice per day, during ten days, directly from the leather tannery industry. Before analysis, they were stored and transported following the standard procedures (Standard Methods 2005).

### Analytical methods

After the EC process, and before the analysis, the samples were filtered in order to remove the electro-coagulated material. The standard methods were used for the quantitative analysis of the chromium content, the COD, the  $\text{BOD}_5$ , and the TOC (Standard Methods 2005). The remaining  $\text{Cr}^{3+}$  was determined by the colorimetric method (3500 B-Cr). The COD analyses were performed following the closed reflux method, with colorimetric measurements (method 5220D).

The TOC was evaluated with a Shimadzu analyser (model TOC-5000A), method 5310D, and the BOD<sub>5</sub> measurements were performed following the respirometric method 5210D (Standard Methods 2005). The Fe and Al concentrations were monitored following the 3500A-Fe and 3500 B-Al methods, respectively.

The Cr<sup>3+</sup> removal efficiency (%RCr<sup>3+</sup>) was calculated using the following expression:

$$\%RCr^{3+} = \frac{(C_{Cr^{3+},0} - C_{Cr^{3+}})}{C_{Cr^{3+},0}} \times 100 \quad (1)$$

where  $C_{Cr^{3+},0}$  and  $C_{Cr^{3+}}$  correspond to the initial and final Cr<sup>3+</sup> concentrations, respectively.

### Electro-coagulation cell

A plexiglass 0.3 L batch jacketed cell (with dimensions 10 cm × 6 cm × 5 cm) was used for the wastewater treatment experiments. It contains two vertical plate electrodes, made of iron (Fe) and/or aluminium (Al), each having an area of 27 cm<sup>2</sup> (with dimensions: 9 cm width, 3 cm height, and 0.1 cm thickness). For the kinetic studies, another plexiglass 1.024 L batch jacketed cell was used, with the electrodes having an area of 90 cm<sup>2</sup> (with dimensions: 15 cm width, 6 cm height, and 0.1 cm thickness). In both cases, electrodes were connected in a monopolar arrangement. The reaction mixture was stirred mechanically. The voltage was regulated with a BK-Precision (0-30 V, 0-5 A) source. The temperature of the experiment (28°C) was controlled using a Poly-science712 thermostat, connected directly to the jacket. Before each run, the electrodes were washed with acetone in order to remove any trace of surface grease. Additionally, the electrode surfaces were cleaned by dipping them for 5 min in an aqueous solution of HCl (35%) and of hexamethylenetetramine (2.80%). A schema of the electro-oxidation cell is presented in Figure 1.

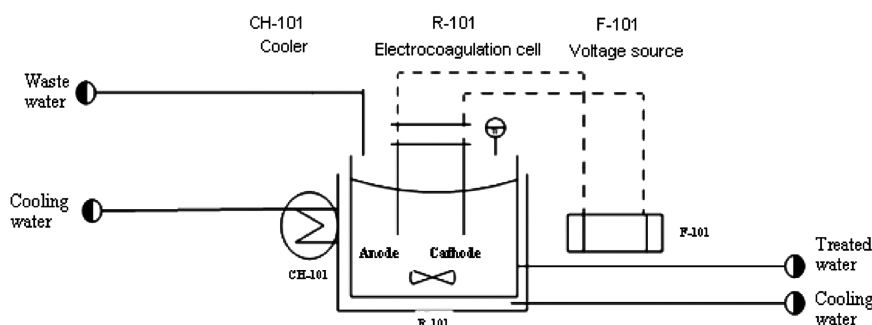


Figure 1 | The representation of the electro-coagulation cell.

### Preliminary analysis of wastewater samples

Figure 2 presents the variations of Cr<sup>3+</sup> and COD concentrations for the analysed wastewater samples during the complete sampling period (ten days).

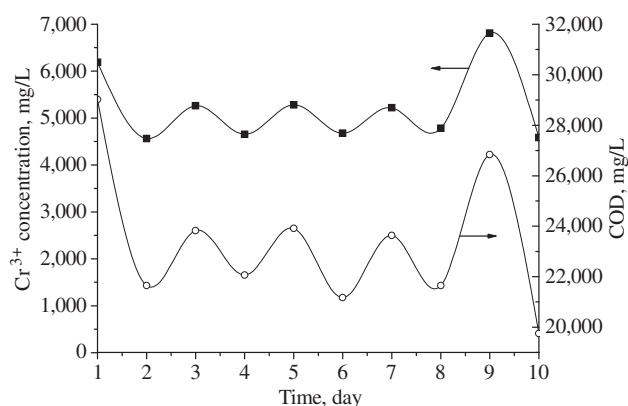
The significant changes in the Cr<sup>3+</sup> and COD concentrations were detected during the analysed sampling period (ten days). In order to obtain their representative average values for the further study, the statistical analysis using Statgraphics 5.1 was made (not shown here). The maximum variation detected in Cr<sup>3+</sup> and COD concentrations was 49.3 and 47%, respectively. The representative wastewater pH was 4.5. The average values of the main characteristics of the wastewater stream are presented in Table 1.

One can see that the wastewater contains mainly organic compounds, used in large quantities during the tannery process (Table 1). The low BOD<sub>5</sub>/COD value indicates that the analysed effluent is highly toxic, eliminating the possibility of its biological treatment (Marco *et al.* 1997). Compared to the Colombian wastewater regulations, all parameters significantly exceed the standards (Table 1).

### Experimental design and statistical analysis

The RSM was implemented to establish the optimal operational conditions of the EC process for a maximum Cr<sup>3+</sup> removal. A multifactorial experimental design was defined in order to evaluate the influence of several parameters including: the type and the separation (gap) between electrodes, the stirring velocity, the Cr<sup>3+</sup> concentration, and the current density. Based on the characteristics of the wastewater (Table 1) and its previous statistical analysis, three different levels (values) were chosen for each parameter. Table 2 presents the variable levels and their codifications.

Two different groups of experiments were planned. In a first group of experiments (group A in Table 2), the effects of the gap between electrodes and the stirring velocity were



**Figure 2** | The evolution of  $\text{Cr}^{3+}$  and COD concentrations in the wastewater during the complete sampling period (ten days).

analysed and finally optimised. Next, according to the optimised values, a second group of experiments were performed (group B in Table 2). It includes as variables the type of electrode (Al–Al, Fe–Fe, and Al (anode) – Fe (cathode)), the initial  $\text{Cr}^{3+}$  concentration, and the current density.

All variables were coded according to equation (2):

$$X_i = \frac{(x_i - x_{pc})}{\Delta x_i} \quad (2)$$

where  $X_i$  is the code level,  $x_i$  is the uncoded value,  $x_{pc}$  corresponds to uncoded value at the central point, and  $\Delta x_i$  is the change value between levels (Montgomery 2005).

The experiments were programmed using Statgraphics 5.1. Thus, nine and 15 tests with replica, for the A and B group of experiments, respectively, were randomly made in order to avoid any systematic error (Montgomery 2005). In all cases, 60 min electrolysis was employed. The statistical analysis was based on the analysis of variance (ANOVA), Pareto diagram, Box–Benkhen response surface plot, and the variation coefficients. For the response surface method, the

**Table 1** | The characterisation of the wastewater stream resulting from the tannery industry under analysis

Parameter	Units	Average value	Colombian regulation standards (Act 1594)
Conductivity	mS/cm	12	
Chromium content	mg/L	5,200	1
COD	mg/L	23,350	2,000
BOD <sub>5</sub>	mg/L	1,475	1,000
BOD <sub>5</sub> /COD		0.06	
TOC	mg/L	7,500	
Colour		Intense green	
Salinity	‰	7.2	
Viscosity	cP	1.0	
Density	g/cm <sup>3</sup>	0.9	

experimental results were adjusted to a second order multi-variable polynomial, as presented in equation (3):

$$Y_i = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} X_{ij} \quad (3)$$

where  $Y_i$  is the response variable: the percentage of chromium removal ( $\%RCr^{+3}$ );  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  are the regression coefficients which correspond to the intersect, lineal, quadratic, and interactions, respectively; and  $X_i$  and  $X_j$  are the independent variables. The quality of this model and its prediction capacity are related to the variation coefficient,  $R^2$ .

For the kinetic studies only optimised variable values were used. The electrolysis time was 60 min. The samples were taken for the analysis every 10 min.

**Table 2** | The chosen variable levels from the experimental design

Group of experiment	Variable	X Code		
		–1 Level 1	0 Level 2	1 Level 3
(A)	Electrode gap (cm)	0.5	1.5	2.5
	Stirring velocity (rpm)	370	560	720
(B)	Current density (mA/cm <sup>2</sup> )	37.04	74.08	111.11
	Initial $\text{Cr}^{3+}$ concentration (mg/L)	3,280.3	4,456.8	5,456.7
	Electrode type	Al–Al	Fe–Fe	Al–Fe

**Table 3** | The experimental data of  $\text{Cr}^{3+}$  removal efficiency, according to the experimental design, as a function of the electrode gap and the stirring velocity

Run	Electrode gap (cm)	Stirring velocity (rpm)	% $\text{RCr}^{3+}$	
			Block 1	Block 2 Replica
1	0.5	720	38.16	44.44
2	0.5	370	79.87	79.47
3	2.5	560	36.23	43.24
4	1.5	720	29.79	32.37
5	2.5	720	31.08	34.78
6	2.5	370	32.37	40.82
7	1.5	560	60.06	61.35
8	0.5	560	59.90	57.73
9	1.5	370	36.23	35.99

## RESULTS AND DISCUSSION

### The effect of the electrode gap and the stirring velocity on the EC process

The experiments were performed with the wastewater as received from the industry, keeping the parameter values presented in Table 1. It is well known that pH is a very important parameter for the EC process, since the formation of ionic species strongly depends on it. The original wastewater pH (4.52) was preserved, since it corre-

sponds to optimal pH values, as suggested for the EC processes (Zaroual *et al.* 2009). Similarly, the initial conductivity of the wastewater (12.05 mS/cm) corresponds to the suggested values,  $> 1,000$  S/cm (Zaroual *et al.* 2009). Preliminary tests (not shown here) demonstrated good compatibility to the data reported in the above references.

For the first group of experiments (group A in Table 2) the current density was fixed at  $60 \text{ mA/cm}^2$  using Al (anode) and Fe (cathode) as electrodes. The results of  $\text{Cr}^{3+}$  removal efficiency during 60 min electrolysis, as a function of the electrode gap and the stirring velocity, are presented in Table 3.

The highest  $\text{Cr}^{3+}$  removal efficiency was 79.87%, for the electrode gap and the stirring velocity of 0.5 cm and 370 rpm, respectively (Table 3). The chromium is expected to be removed (precipitated) as  $\text{Cr}(\text{OH})_3$ . The *F* and *P* values for all the linear and interaction effects of the parameters are given in Table 4.

As it could be seen (Table 4), the *P* value for the linear and interaction effects of the two factors, the stirring velocity and the electrode gap, are lower than 0.05, except for the BB interaction ( $P = 0.2283$ ). It means that those factors and interactions are highly significant for the % $\text{RCr}^{3+}$  at a confidence level of 95.0%.

In order to define the optimal values of the two analysed parameters, the electrode gap and the stirring velocity, the regression equation was used. Figure 3 presents its graphical representation.

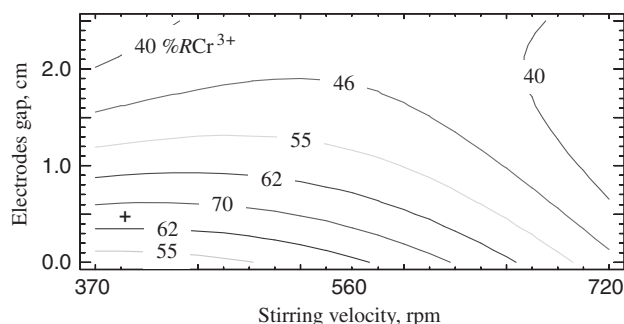
One can see that the most favourable conditions for  $\text{Cr}^{3+}$  removal can be achieved applying the electrode gap of 0.5 cm and the stirring velocity of 382.5 rpm. These values were kept for the second group of experiments (group B in Table 2).

**Table 4** | The ANOVA for  $\text{Cr}^{3+}$  removal efficiency, as a function of the stirring velocity and the electrodes gap

Factor	Square sum	Freedom degrees	Mean Square	F-ratio	P-value
A: Stirring velocity (or St)	738,371	1	738,371	9.78	0.0096
B: Electrodes gap	1,657.93	1	1,657.93	21.96	0.0007
AA	411.08	1	411.08	5.45	0.0396
AB	602.22	1	602.22	7.98	0.0165
BB	122.88	1	122.88	1.63	0.2283
Total error	830.39	11	75.49		
Total	4,401.87	17			

$R^2 = 81.13\%$





**Figure 3** | The response surface plot of  $\text{Cr}^{3+}$  removal efficiency: reaction time = 60 min; temperature = 28°C; the current density = 60 mA/cm<sup>2</sup>; electrodes: Al (anode) and Fe (cathode).

### The effect of the current density, the initial $\text{Cr}^{3+}$ concentration, and the electrode type on the EC process

The second group of experiments (group B in Table 2) was performed considering the previously optimised parameters: the electrode gap = 0.5 mm and the stirring velocity = 382.5 rpm, as well as at the pH = 4.52 and the temperature 28°C. Since the original industrial wastewater samples presented

different  $\text{Cr}^{3+}$  content, it was not necessary to modify their concentrations. Table 5 shows the experimental results of  $\text{Cr}^{3+}$  removal efficiency, after 60 min electrolysis, as a function of the current density, the initial  $\text{Cr}^{3+}$  concentration, and the electrode type.

It is possible to see that the highest  $\text{Cr}^{3+}$  removal efficiency was 99.99%, for the current density of 74.08 mA/cm<sup>2</sup> and the initial  $\text{Cr}^{3+}$  concentration of 3,280.3 mg/L, using Al as anode material. Moreover, the application of aluminium electrodes allows obtaining very clear and stable effluent, whereas in the case of iron electrodes the effluent turned from green to turbid yellow (probably as a result of the presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the medium). Thus, Al electrodes were chosen for the further studies.

The ANOVA results for the chromium removal efficiency, as a function of the current density, the chromium concentration and the electrode type, are presented in Table 6.

For the statistical analysis, it was defined a 95% confidence level. It means that there is not a considerable effect of the electrode type on the  $\text{Cr}^{3+}$  removal efficiency (Table 6), as also presented elsewhere (Daneshvar 2004). Figure 4 shows

**Table 5** | The experimental data for  $\text{Cr}^{3+}$  removal efficiency, as a function of the current density, the initial  $\text{Cr}^{3+}$  concentration (level), and the electrode type

Run	Current density (mA/cm <sup>2</sup> )	Initial $\text{Cr}^{3+}$ concentration (mg/L)	Electrode type (anode-cathode)	% $\text{RCr}^{3+}$	
				Block1	Block 2 Replica
1	111.11	4,456.8	Al–Al	92.22	91.21
2	74.08	5,456.7	Al–Fe	78.26	73.43
3	74.08	4,456.8	Fe–Fe	87.20	88.36
4	37.04	4,456.8	Al–Al	98.14	97.08
5	74.08	3,280.3	Al–Al	98.85	99.99
6	111.11	5,456.7	Fe–Fe	50.24	48.90
7	74.08	3,280.3	Al–Fe	94.78	93.78
8	74.08	4,456.8	Fe–Fe	87.98	88.50
9	37.04	3,280.3	Fe–Fe	95.97	96.02
10	37.04	5,456.7	Fe–Fe	56.33	61.35
11	111.11	3,280.3	Fe–Fe	90.61	91.12
12	37.04	4,456.8	Al–Fe	95.27	96.13
13	111.11	4,456.8	Al–Fe	91.94	92.37
14	74.08	5,456.7	Al–Al	77.68	75.65
15	74.08	4,456.8	Fe–Fe	88.31	87.85



**Table 6** | The ANOVA for the  $\text{Cr}^{3+}$  removal efficiency, as a function of the current density, the initial  $\text{Cr}^{3+}$  concentration and the electrode type

Factor	Squares sum	Freedom degrees	Mean square	F-ratio	P-value
A: CD	142.103	1	142.103	6.93	0.0164
B: Ci ( $\text{Cr}^{3+}$ )	3,578.34	1	3,578.34	174.67	0.0000
C: Electrode	13.8087	1	13.8087	0.67	0.4218
AA	77.3982	1	77.3982	3.78	0.0669
AB	8.57601	1	8.57601	0.42	0.5254
AC	2.75655	1	2.75655	0.13	0.7178
BB	890.039	1	890.039	43.44	0.0000
BC	9.32688	1	9.32688	0.46	0.5080
CC	666.207	1	666.207	32.52	0.0000
Blocks	0.1389	1	0.1389	0.01	0.9352
Total error	389.245	19	20.4866		
Total	6,004.28	29			

$R^2 = 93.405\%$

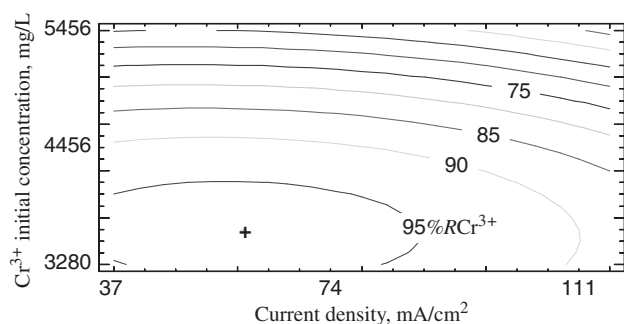
the interaction effect of the current density and the initial  $\text{Cr}^{3+}$  concentration, using Al as electrode material.

It is possible to infer that the optimal values for  $\text{Cr}^{3+}$  removal, for the second group of parameters, are: the initial  $\text{Cr}^{3+}$  concentration = 3,596 mg/L and the current density = 57.87 mA/cm<sup>2</sup> (Figure 4).

Thus, it is possible to summarise that the percentage of  $\text{Cr}^{3+}$  removal efficiency is:

Inversely proportional to:

- The distance between electrodes: A short gap between electrodes allows overpassing the medium resistance, regenerating the current for the exchange between electrons from electrodes and ions or molecules from the

**Figure 4** | The response surface plot of the  $\text{Cr}^{3+}$  removal efficiency: reaction time = 60 min; temperature = 28°C; electrodes: Al; the electrode gap = 0.5 mm; the stirring velocity = 382.5 rpm.

solution. However, very short distance between electrodes can potentially lead to the circuit damage by short circuit (Golder *et al.* 2007).

- The stirring velocity: Low stirring velocities favour the coagulation process (Golder *et al.* 2007). Moreover, an appropriate stirring velocity avoids the formation of ions-saturated zones around the electrodes, improving the mass transfer efficiency, reducing the possible passivation of the electrodes and distributing in the correct way bubbles of the produced hydrogen and oxygen. It leads to the decrease in the energy consumption. Additionally, the increase in the stirring velocity speeds up the flow of ions towards the electrodes which results in the formation of higher amount of products. Table 3 shows the effect of the stirring velocity on the  $\text{Cr}^{3+}$  removal efficiency. The removal of 79.87%  $\text{Cr}^{3+}$  occurs applying the stirring velocity of 370 rpm. The decrease in the chromium removal at higher velocities can be related to the formation and detachment of salt deposits, which disturb the recovery process floating around the electrodes. A stirring velocity of 382.5 rpm was selected as the optimal one.

Proportional to:

- The current density: This parameter combines the effect of cell current and the effective surface area of electrodes. The dissociation of different soluble species from

the electrodes increases the pH of the solution and favours the chemical precipitation of Fe/Al hydroxides (Murugananthan *et al.* 2004). In our case, an increase in pH of 79.5% was detected.

- ii. The initial  $\text{Cr}^{3+}$  concentration: At low initial  $\text{Cr}^{3+}$  concentration, the removal rate is very low. On the other hand, at high initial  $\text{Cr}^{3+}$  concentration, its removal efficiency decreases very fast due to the electrode saturation, as a result of the formation of an oxide layer on the electrode surface. Thus, an intermediate  $\text{Cr}^{3+}$  concentration is expected to be the most favourable.

The comparison of the observed and predicted values obtained using a quadratic regression model is presented in Figure 5.

The data are adjusted to a straight line with a correlation factor  $R^2$  equal to 0.93405. The quadratic regression model allows obtaining the Equation (4), which presents the percentage of  $\text{Cr}^{3+}$  removal efficiency as a function of the current density (CD), the distance between electrodes (Gap), and the initial  $\text{Cr}^{3+}$  concentration ( $C_i$ ).

$$\begin{aligned} \%RCr^{3+} = & 109.41 + 0.293 \times CD + 28.87 \times C_i - 42.26 \\ & \times Gap - 0.0024 \times CD^2 - 0.028 \times CD \times C_i \\ & + 0.016 \times CD \times Gap - 10.98 \times C_i^2 + 1.08C_i \\ & \times Gap + 9.5 \times Gap^2 \end{aligned} \quad (4)$$

A series of experiments was performed at optimised conditions, in order to analyse the biodegradability and the removal kinetics of  $\text{Cr}^{3+}$ , COD, and TOC.

### The $\text{Cr}^{3+}$ removal kinetics

In order to verify the response capacity of the EC process, three different initial concentrations of  $\text{Cr}^{3+}$  were chosen for this part of the study: 3,280, 4,456.8, and 5,456.7 mg/L. The results are presented in Figure 6.

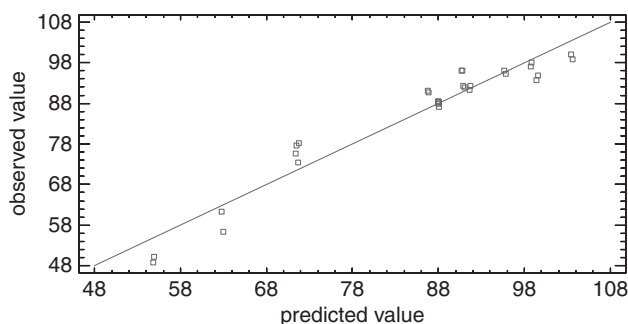


Figure 5 | The comparison of observed and predicted values for the  $\%RCr^{3+}$ .

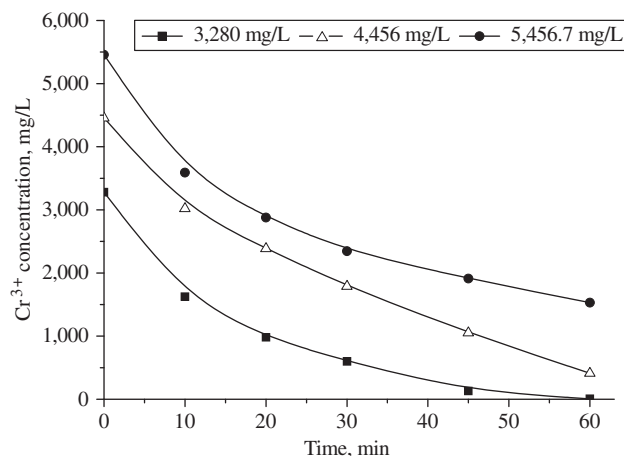


Figure 6 | The  $\text{Cr}^{3+}$  removal kinetics by the electro-coagulation process.

During the EC process, the removal of  $\text{Cr}^{3+}$  occurs mainly during the first 10 min of the reaction (ca. 50%). During the experiment, chromium was precipitated or co-precipitated (with other metals) as hydroxides and separated from solution by sedimentation or filtration. Based on the kinetic analysis (not shown here), the linear correlation between  $\text{Cr}^{3+}$  concentration and time was found. This is a typical behaviour representing the power law rate kinetics. As expected, the higher initial concentration of  $\text{Cr}^{3+}$ , the higher reaction time for its removal is needed. In fact, for the most diluted sample (the initial concentration of  $\text{Cr}^{3+} = 3,280.3$  mg/L) the kinetic constant was equal to  $0.0839 \text{ min}^{-1}$  (first order kinetics), whereas for the most concentrated solution (the initial concentration of  $\text{Cr}^{3+} = 5,456.7$  mg/L) the data fix to a second order kinetic power law model with constant rate equals to  $8 \times 10^{-6} \text{ L (mg.min)}^{-1}$ .

### The COD and the TOC removal kinetics

Figures 7 and 8 present the kinetics results of the COD and the TOC removal, respectively, obtained by the EC process for their different initial concentrations. In the case of the most diluted samples, one can see that, after 60 min of the EC process, the COD and the TOC are removed to ca. 60% and 51%, respectively. The removal rate is significantly higher during the first 30 min of the reaction. From the kinetic analysis (not shown here) the linear correlation between both COD and TOC concentrations and time was found, representing a first order rate law model. Both COD and TOC removal rates highly depend on their initial concentrations. In fact, for COD data, for the most diluted sample (10,544 mg/L) the kinetic constant equals  $0.0167 \text{ min}^{-1}$ , whereas for the

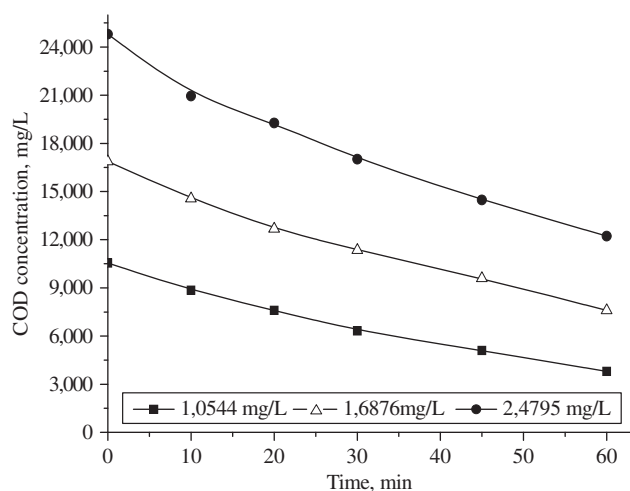


Figure 7 | The COD removal kinetics for the electro-coagulation process.

most concentrated solution (24,795 mg/L) it is equal to  $0.012 \text{ min}^{-1}$ .

### Biodegradability analysis

Table 7 summarises the evolution of the COD and the BOD<sub>5</sub> concentrations, after 60 min of reaction, for the three different initial conditions.

The biodegradability of the samples highly depends on the COD and the BOD<sub>5</sub> initial concentrations (Table 7). After 60 min of reaction, the increase in biodegradability reaches 77% and 39%, for the most and the less concentrated samples, respectively. Nevertheless, at those conditions, the wastewater still remains toxic for microorganisms since the BOD<sub>5</sub>/COD ratio is lower than 0.40, which corresponds to the biodegradability limit (Marco *et al.* 1997). However, it is important to stress that both the wastewater after the EC

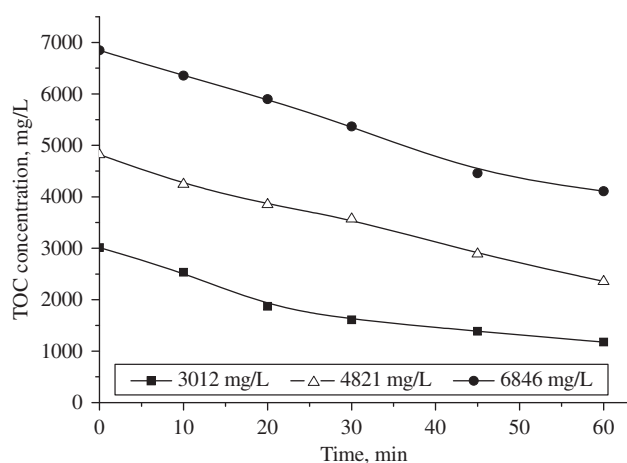


Figure 8 | The TOC removal kinetics for the electro-coagulation process.

Table 7 | The variation of biodegradability as a function of three different COD and BOD<sub>5</sub> initial concentrations

Time (min)	COD (mg/L)	BOD <sub>5</sub> (mg/L)	BOD <sub>5</sub> /COD
0	10,544	831.5	0.079
60	4,217.72	590.4	0.14
0	16,876	1,185.67	0.070
60	7,600	795.56	0.1047
0	24,795	1,586.91	0.064
60	12,231.42	1,093.7	0.089

process and the recovered chromium ( $\text{Cr}(\text{OH})_3$ ) can be returned and used again in the tanning process. In fact, this is already in practice in the factory under study, but using a chemical precipitation method.

### CONCLUSIONS

For the studied conditions, it was demonstrated that the electro-coagulation process is a very useful tool for the treatment of the wastewater resulting from the leather tannery industry placed in Medellin (Colombia). Basing on the statistical analysis, the optimal conditions of  $\text{Cr}^{3+}$  removal using the EC process were found, as follows: the current density =  $57.87 \text{ mA/cm}^2$ , the electrode material: Al, the electrode gap = 0.5 cm, and the initial  $\text{Cr}^{3+}$  concentration = 3,596 mg/L. The electrolysis process performed at those conditions, during 60 min, guarantees that the percentage of  $\text{Cr}^{3+}$  removal reaches the value of 99.76%. Moreover, the COD and the TOC removals achieve 64% and 61%, respectively. It represents an important increase in the biodegradability of the analysed wastewater. Based on the results of the kinetics studies, it is possible to foresee that, during the reaction time lower than 2 h, the concentration of chromium residual decreases below 1 mg/L (maximum limit for Colombian regulations). The scale-up of the EC process of this study is now in progress.

### ACKNOWLEDGEMENTS

The authors thank the Dirección de Investigación de la Universidad EAFIT, Medellin – Colombia for financial support of this research. The staff of the Laboratorio de Ingeniería de Procesos are also recognised for their participation.

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