Pollutant removal from tannery effluent by electrocoagulation

Fernando R. Espinoza-Quiñones*, Marilda M.T. Fornari, Aparecido N. Módenes, Soraya M. Palácio, Fernando G. da Silva Jr., Nayara Szymanski, Alexander D. Kroumov, Daniela E.G. Trigueros

West Parana State University, Department of Chemical Engineering - Post Graduate Program, rua da Faculdade. 645, Jd. La Salle, 85903-000, Toledo, PR, Brazil

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ABSTRACT

An electrocoagulation laboratory scale system was studied for the removal of organic and inorganic pollutants from a wastewater of leather finishing industrial process. In order to obtain optimal values of the system state variables, a fractional factorial 2^3 experimental design was applied. The electrocoagulation process response was evaluated on the basis of chemical oxygen demand (COD), turbidity, total suspended solid, total volatile solid, and elements concentration values. The interactions between initial pH and electrolysis time, as well as between initial pH and current density were significant only for the total chromium removal. The reactor working conditions close to natural effluent pH and electrolysis time in the range of 30–45 min were enough to achieve the cost-effective reduction of COD, turbidity and chromium concentrations. The electrocoagulation method has shown similar pollutant removal efficiencies when compared with the conventional one and can be used successfully for industrial applications. Based on its low operational cost, the electrocoagulation method could be recommended instead of the conventional one.

1. Introduction

In the last decade, a lot of studies for wastewater treatment have been reported based on the alternative electrocoagulation (EC) technique, which ensures good quality effluent before its disposal into aquatic environment. The electroflotation (EF) process could cause a floatation of coagulated pollutants to the surface of a water body because of the simultaneous formation of tiny gas bubbles generated from electrolysis of aqueous solutions [1]. Due to their inherent simplicity of design and operation, together with the growing need for small-scale cost-effective water treatment systems, the EC and EF technologies have received a renewed interest for industrial applications. Another advantage of the EC and EF technologies is their feature of simultaneous precipitation and separation of the pollutant substances by hydrogen bubbles emanated from cathode [2]. Nowadays, there is no dominant reactor design in use, because of the lack of any quantitative evaluation of major interactions taking place inside the EC reactor [3]. Despite of this, a lot of studies have proved the viability of the EC technology and its development because of their removal ability. A wide range of organic and inorganic pollutants from the agro-food industries [4], olive oil production [5], metal working processes [6–8], wastewaters [9], synthetic metal solution [10–12], textile industry [13,14],

synthetic solution [15], leather industry [16], and leachate [17] have been purified by applying this technique. The most preferable electrode materials in electrochemical coagulation are Al or Fe [18], creating a unique chemical/physical environment, which allows destabilization of the pollutant matter and its subsequent coagulation and flotation, thus avoiding addition of another coagulant agent.

All the mechanisms associated with the EC process need further clarification and understanding [19]. According to the current theory of EC, by means of generated coagulants *in situ* via dissolving of metal anode, formation of ions by water electrolysis at the cathode, and consequently their movement throughout the polluted medium by electric field where chemical reactions occurred, the pollutants are transformed into amorphous precipitates or absorbed forms on hydroxides such as $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)_4^-$ and $FeO(OH)$ at the anode. Further, flocculated particles are floated out from the liquid phase through the released cathode hydrogen gas [1,18].

The purpose of this study was to investigate and to test the best iron electrode, based on EC reactor operating parameters (ROPs) for by-product pollutant removal from a leather finishing industrial process. To estimate the reactor efficiency the following criteria were used: chemical oxygen demand (COD), turbidity, total suspension, volatile and fixed solids, and chemical element concentration values. A statistical design was applied in order to obtain optimal reactor performance for the pollutant removal from a characteristic tannery industrial effluent (TIE). The emphasis was on a total chromium removal from the wastewater before its disposal into any

Nomenclature

A_e	effective superficial area (cm^2)
b	linear coefficients in Eq. (3)
C	"C" element concentration ($mg L^{-1}$)
d	internal electrode distance (cm)
E	electric field strength in Eq. (9) ($V m^{-1}$)
FWHM	full width at half maximum
HP-Ge	hyper-pure germanium
i	current density ($mA cm^{-2}$)
I	fluorescence intensity in Eq. (2) (cps)
k_1	Brownian coagulation rate constant in Eq. (10) ($L mg^{-1} s^{-1}$)
k_2	rate constant in Eq. (10) (s^{-1})
$K\alpha$	X-ray line
N	number of variables in Eq. (3)
q	reactor operating variable in Eq. (3)
q_0	constant in Eq. (3)
R	response function
S_r	relative-to-gallium sensitivity in Eqs. (1) and (2)
t	electrolysis time (min)
v_e	electrophoretic velocity in Eq. (9) ($cm s^{-1}$)
V	applied voltage (V)
V_{eff}	total volume of treated effluent (m^3)
w	weight (interaction) coefficient
x	geometric parameter of electrode size (cm)
Z	atomic number in Eqs. (1) and (2)

Greek letters

ε	dielectric constant
ζ	zeta potential
η	dynamic viscosity

aquatic environment, and to model chromium removal kinetics in basic environment.

2. Materials and methods

2.1. Samples

A large amount of samples used in this study was obtained from an equalization tank of a non-treated TIE, which in fact was a wastewater of leather finishing processing factory located in Toledo, Paraná (Brazil). Samples of TIE were collected and stored in several 5 L polyethylene containers, and kept at 4 °C until their use. The wastewater was sampled twice during this study (collections 1 and 2) and the initial characteristics varied with time. For comparison purpose, clarified effluents obtained by a conventional physical–chemical process-based treatment were also collected from the same factory and stored. Before the EC treatments, all tannery effluent samples were preserved according to the standard methodologies recommended by the American Public Health Association [20]. Small portions of TIE and clarified effluent samples were stored for characterization.

2.2. EC reactor

A laboratory-scale EC reactor with 20.5 cm diameter and 30 cm height was built from polyethylene material and used in the present study. A valve was installed at the bottom of the reactor in order to withdraw the precipitated material through a sludge chamber. Pair of iron plates (7 cm width, 14 cm height, and 0.15 cm thickness) was used as electrodes. In the upper part of the EC reactor, two iron electrode plates were firmly assembled in an upright position and

arranged parallel to each other with a gap between the anode and cathode plates, using a non-conducting horizontal adjustable support to avoid any short-circuits. The active electrode surface area was 80.5 cm^2 (7 cm × 11.5 cm). Both electrodes were positioned in the EC reactor containing TIE with 5 L working volume. The minimal and maximal distances between the anode and cathode plates were set up at 4.0 and 11.0 cm, respectively. The electrodes were operated in mono-polar mode and connected to terminals of direct current power supply (Instrutemp DC Power Supply, FA 1030), which provided stabilized currents and voltages, ranging from 0 to 10 A, and from 0 to 30 V, respectively, and containing internal digital ammeter and voltmeter.

2.3. Chemicals

The used chemicals were of analytical-reagent grade. In order to obtain the sensibility curves for synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) spectrometer, several mixtures of multi-elemental standards (from a set of mono-element standards ($1.0 g L^{-1}$ for AAS) were used at different concentrations.

2.4. Batch experiments

Before each EC experiment, the pH adjustments of TIE were done with NaOH (6 M) and H_2SO_4 (3 M) and the electrodes were washed thoroughly with water to remove surface grease and any solid residues. In a typical run, performed at room temperature, 5 L representative TIE sample was placed into the EC reactor. Due to the high TIE conductivity, it was not necessary to add any chemical to increase the current. During the experiment, the direction of the current was reversed every 30 min to limit the formation of passivated layers [1]. For the applied 6–15 V voltage ranges to the reactor electrodes, high current densities have been established ($43–68 mA cm^{-2}$) and thus high bubble densities could be reached, allowing both coagulation and flotation processes to take place in the polluted media [3]. At the end of each run, the floated and precipitated materials were withdrawn and the clarified effluent sample was pipetted out from the reactor, and then allowed to settle for a few hours in polyethylene flask. Finally, the clarified supernatant liquid was collected and preserved according to the standard methods [20], and stored for characterization.

2.5. Analytical measurements

All physicochemical parameter measurements were made applying the standard methods [20] for each non- and treated sample. The COD is an indicator of the effluent pollution degree and is used by regulatory agencies to gage overall treatment plant [19]. The COD was determined by the open reflux/titrimetric method. The pH was measured by using a digital pH meter (Model Hach). A digital conductivity meter (WTW, model LF 191) was used for measurements of the samples ionic conductivity. Turbidity (Nephelometric Turbidity Unit, NTU) was determined with a turbidity-meter Tecnal, model TB1000. After a separation from the liquid phase by drying up to 105 °C, the total suspended solids (TSSs) were measured. Afterwards, the dried TSS was ignited at 550 °C and the weight loss was reported as total volatile solid (TVS), while the residual weight was determined as total fixed solids (TFS). Hence, the organic matter removal efficiency from a polluted effluent could be estimated through the TVS removal.

The SR-TXRF measurements were performed using a polychromatic X-ray beam from the D09-XRF beam line at Brazilian Light Synchrotron Laboratory (LNLS) with 20 keV maximum energy. For SR-TXRF analysis, a 2 mL aliquot of each filtered sample was taken and a 20 μL standard solution ($1.0 g Ga L^{-1}$) was added as an internal standard. Afterwards, an aliquot of 5 μL was deposited on

a pre-cleaned acrylic disk (Ø30 mm and 3 mm thick) and dried at room temperature. The same procedure was repeated for the multi-elemental standards at five different concentrations. All the disk-samples were prepared in triplicates, except for the standard ones, which were in quintuplicate. Each reflector disk-sample was positioned for the total reflection condition, and the acquisition time was set up at 100 s. For X-ray detection, a HP-Ge detector with 160 eV FWHM@Mn-Kα line was used. All X-ray spectra were analyzed using the AXIL program [21], which permits to identify and extract the background subtracted peak areas of each X-ray line characterizing the elements in the sample. An exponential-type function was fitted in good agreement with the relative-to-gallium sensitivity experimental data for light elements (see Eq. (1)). The elements concentrations in liquid samples were determined by Eq. (2).

$$S_r(Z) = \exp(-22.811 + 1.438 \times Z - 0.0227 \times Z^2) \qquad (1)$$

$$C(Z) = \frac{I_Z}{I_{Ga}} \times \frac{C_{Ga}}{S_r(Z)} \qquad (2)$$

where Z is the atomic number ranging from 14 to 40, I represents the fluorescent intensity of the element, C (mg L^{-1}) represents the concentration of the element in the liquid phase and C_{Ga} stands for the internal standard concentration (10 mg Ga L^{-1}).

2.6. Factorial design

Nowadays, a statistical approach of experimental design is almost inevitable because the pollutant removal efficiency of EC processes depends on many operational parameters. A factorial design, which combines a two-level full or fractional factorial 2^{N-1} design and one point at the center of each experimental region, was applied for four parameters: initial pH (5–9), current density (43–68 mA cm^{-2}), electrolysis time (10–30 min) and internal electrode distance (4–11 cm).

In an analytical EC process, where ROP could influence an experimental response, the observed response is a certain function of the parameter levels and could be optimized by applying the Lagrange criteria [22]. Based on 11 preliminary EC experiments, response functions (R) were built in 3D graphs. The experimental data were also fitted by using a second order model (see Eq. (3)) for COD, turbidity, final pH, TSS, TVS, TFS, Cr, Ca, Zn and Fe (non-treated TIE from collection 1) thus showing their dependencies from the ROP values.

$$R = q_0 + \sum_{i=1}^{N} b_i q_i + \sum_{i=1}^{N} \sum_{j \neq 1}^{N} w_{ij} q_i q_j \qquad (3)$$

where R is the experimental response, q is the set of ROP values, q_0 is the constant, b is the set of coefficients of the linear terms, w is the set of weight coefficient representing the interactions between the ROP values, and N is the number of ROP.

Table 1
Physicochemical characteristics and elements concentrations of TIE.

Parameter	Collection 1		Collection 2	
	Non-treated	Clarified	Non-treated	Clarified
pH	7.6	8.5	7.8	6.8
Conductivity (mS cm^{-1})	14.2	12.1	21.1	15.4
Turbidity (NTU)	1,016	60	917	44
COD (mg L^{-1})	17,618	7,949	12,225	5,717
TSS (mg L^{-1})	20,498	16,206	42,460	15,760
TFS (mg L^{-1})	12,817	13,212	19,164	12,061
TVS (mg L^{-1})	7,681	2,994	23,296	3,699
Cr (mg L^{-1})	44	0.4	50	1.0
Ca (mg L^{-1})	372	368	858	364
K (mg L^{-1})	50	42	85	43
Zn (mg L^{-1})	0.4	0.1	0.5	0.7
Fe (mg L^{-1})	3.9	0.7	4.4	0.8

3. Results and discussion

3.1. Factorial design-based EC tests

The typical characteristics of TIE and clarified effluent samples are presented in Table 1. After performing the preliminary EC tests, the experimental response of characteristic parameters of TIE were calculated and their coefficients of linear terms and interactions were also extracted and summarized in Table 2. The significance of the ROP effects and their possible combined actions were checked out by applying a variance analysis, with a 95% confidence level ($p < 0.05$), using the Statistica® software, version 8.0.

The variance analysis results have shown that the initial pH value influenced significantly the final pH, TFS, Cr, and Na removal values, where a positive effect was observed only for final pH value. It is a well-known fact that EC processes are strongly pH dependent, because iron ions are difficult to aggregate under acidic conditions, while complexes such as iron hydroxides can be formed at alkaline pH, and at high initial pH conditions they are expected to shift the final pH towards alkaline region due to the generations of hydroxyl radicals. The chemical reactions taking place at the anode are given as follows [1].

For iron anode:

$$Fe - 2e \rightarrow Fe^{2+}, \qquad (4)$$

at alkaline conditions

$$Fe^{2+} + 3OH^- \rightarrow Fe(OH)_2, \qquad (5)$$

at acidic conditions

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-. \qquad (6)$$

In addition, there is an oxygen evolution reaction

$$2H_2O - 4e \rightarrow O_2 + 4H^+. \qquad (7)$$

The reaction at the cathode is

$$2H_2O + 2e \rightarrow H_2 + 2OH^-. \qquad (8)$$

Table 2
Linear and quadratic coefficients associated with the reactor EC system parameters, which were extracted from the correlation models for each pollution indicator parameter of non-treated TIE (collection 1, with initial pH 7.6), within a 95% confidence level ($p < 0.05$).

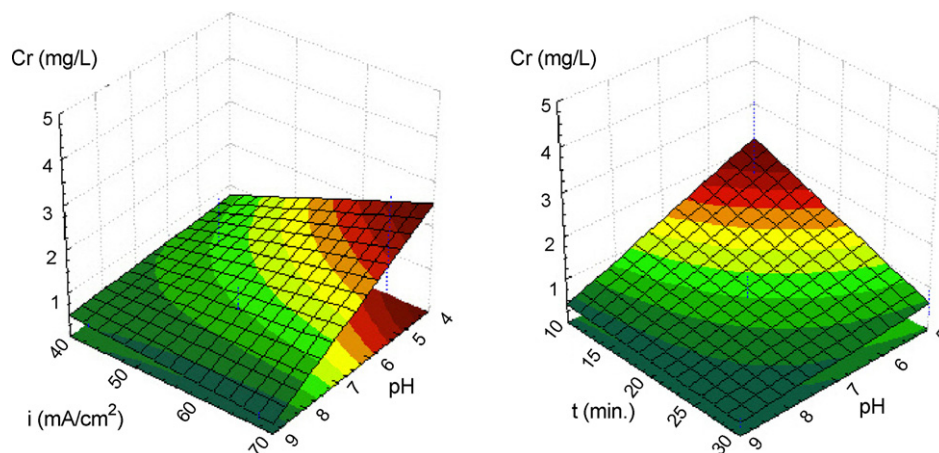| Parameter	q_0	Linear coefficient (b)				Interaction coefficient (w)	
		Initial pH	t	d	i	Initial pH and t	Initial pH and i
Final pH	8.10	0.40	0.20	0.09	0.13		
TFS	10,241	−1089					
TVS	2,628				−769		
Cr	0.94	−0.50	−0.44			0.34	0.36
Ca	169	−102	−48				
Voltage	13.9			4.45	2.83		

Fig. 1. Experimental response surface results obtained by applying a 2^3 factorial design for Cr concentration removal during EC experiments, by using the non-treated TIE from collection 1 (initial pH 7.6) and showing the geometrical nature of the surface according to the sign and magnitudes of the statistically significant interaction coefficients between current density, electrolysis time and initial pH (see Table 2) within the minimum and maximum analyzed levels.

The negative effects were observed for TFS, Cr, and Na values, indicating their higher removal when pH value is close to the alkaline region. In particular, removal of Cr ions can be significantly affected by pH, because the solubility of metal hydroxide species strongly depends on the chemistry of the polluted medium [11], suggesting an improvement of metal removal when pH is in the alkaline region.

Moreover, the current density changes have significantly influenced the final pH, TVS and applied voltage values, resulting in higher removal fraction only for TVS when the current density is increasing. It is because the organic matter is easily destabilized and forms flocks. In addition, the electrolysis time has influenced the final pH, Cr and Ca concentrations, resulting in a higher removal of Cr and Ca values. Both initial pH and electrolysis time have shown a negative effect on the Cr removal. The Cr removal efficiency could be improved at high initial pH and long electrolysis time. When initial pH, current density and electrolysis time have simultaneously reached their higher levels, Cr concentration was found at a minimum value. The final pH value was also increased when any ROP values were independently increasing.

The combined action of initial pH and current density, as well as of initial pH and electrolysis time, has significantly influenced only the total chromium removal (see response surfaces shown in Fig. 1). A preliminary evaluation of the response surfaces can be done by using the signs and magnitudes of the quadratic coefficients in Eq. (3), which values are shown in Table 2. Because the interaction coefficients are positive, the response surface can pass through a minimum. Within the minimum and maximum levels of current density, the Cr concentration values at the end of EC process have the same order of high level of initial pH, with a broad minimum region of Cr response. Analyzing the experimental response surfaces, we observed that there are small differences between the pollutant removal values for a wide final pH range (7.5–9.0). It was verified that for the given experimental conditions, a significant correlation between the COD and the ROP values did not exist.

3.2. Effect of initial pH

Based on the factorial design results, different EC experiments were performed, where the reactor performance was as follows: 4.0 cm internal electrode distance, 68 mA cm^{-2} current density, and 30 min electrolysis time. For this experimental set up, the 6.5–9.0 initial pH interval-based EC experiments have shown a high efficiency on the effluent transparency with almost the same 99%
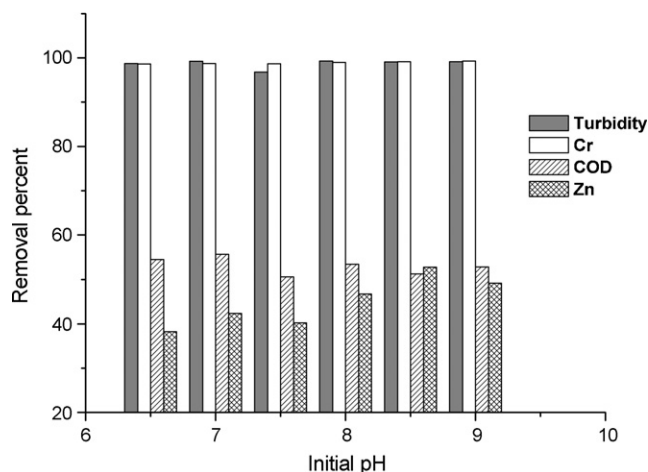

Fig. 2. Reduction factors (turbidity, Cr, COD, K and Zn, %) as a function of initial pH for an EC system by using the non-treated TIE from collection 2 (initial pH 7.8) and working with iron electrodes.

turbidity reduction for all studied initial pH (see Fig. 2). As summarized in Table 3, the results for the TSS, TFS, and TVS suggested that the EC method has achieved a high efficiency of the organic matter removal, associated with the amount of TVS which is close to the 80% reduction for a wide range of effluent pH values. Approximately 50% reduction of TSS amount was obtained for the 7.5–9.0 initial effluent pH interval, while at pH 6.5 and 7.5 the reduction

Table 3
Reduction values (%) of physicochemical parameter and elementary concentration for non-treated TIE (from collection 2, with initial pH 7.8), by using iron electrodes and operating pH range of the reactor 6.5–9.0, 68 mA cm^{-2} current density, and 4.0 internal-electrode distance.

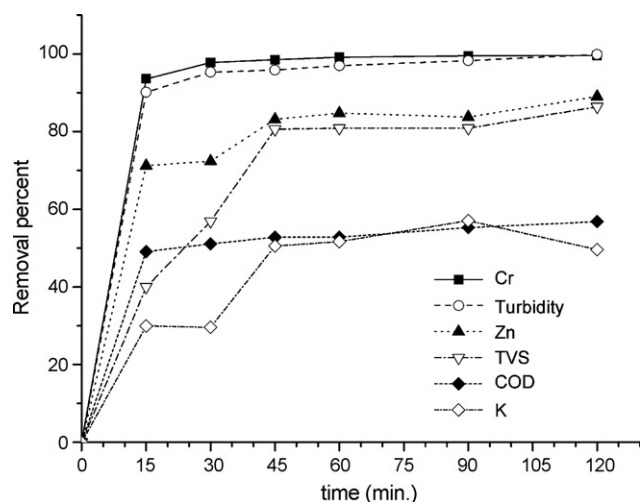| Parameter	Reduction values (%)					
Initial pH	6.5	7.0	7.5	8.0	8.5	9.0
Final pH	7.7	7.9	7.9	8.0	8.7	9.3
Turbidity	98.7	99.2	96.8	99.2	99.1	99.1
COD	54.6	55.7	50.6	53.5	51.3	52.9
TSS	69.9	52.1	27.9	52.6	50.1	51.2
TFS	47.7	18.6	19.0	17.7	15.6	10.8
TVS	88.3	79.6	35.2	81.4	78.4	84.4
Cr	98.6	98.7	98.7	99.0	99.1	99.2
Ca	67.7	65.4	80.2	69.2	80.2	82.3
K	38.8	42.4	40.0	47.1	52.9	49.4
Zn	78.0	84.0	88.0	84.0	84.0	88.0

Fig. 3. Reduction factors profiles (Cr, turbidity, Zn, TVS, COD and K, %) as a function of electrolysis time for an EC system by using the non-treated TIE from collection 2 (initial pH 7.8), iron electrodes with 4.0 cm internal electrode distance, and 68 mA cm^{-2} current density.
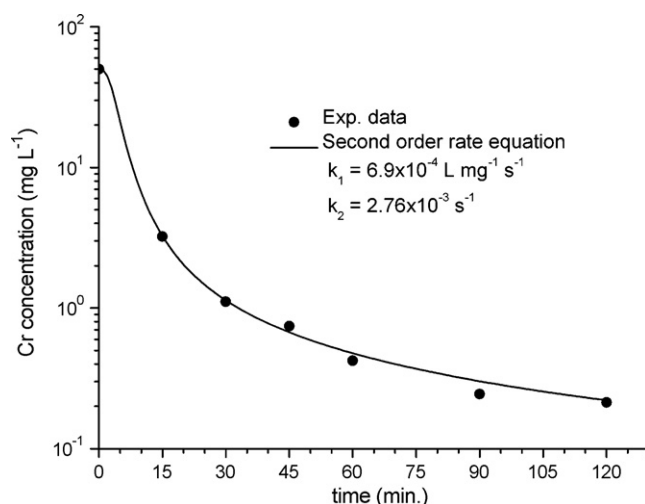

Fig. 4. Residual chromium concentration profiles in TIE (from collection 2) by using iron electrodes with at 4.0 cm internal electrode distance, and 68 mA cm^{-2} current density.

was about 70% and 30%, respectively (Table 3). In the case of TFS, the reduction were approximately 10% and 50% for 9.0 and 6.5 pH values, respectively, while for other ones 20% reduction was observed (Table 3). For calcium concentration, a removal between 60% and 80% was achieved for a pH effluent interval 7.0–9.0. Other removal percent tendencies for COD, chromium, potassium and zinc as a function of pH are illustrated in Fig. 2. As can be seen in Fig. 2, 99% reduction for chromium and 50% for COD were achieved for all EC treatments. Nevertheless, the increase of the initial effluent pH has not significantly contributed for the pollutant removal efficiency. Hence, a narrow pH interval near to natural non-treated effluent (7.8) pH could be used.

3.3. Effect of operational time

Taking into account the pollutant removal tendencies together with the change of the initial pH values, different EC experiments were performed by using electrolysis time as a control parameter for the following conditions: 7.5 initial pH, 4.0 cm internal electrode distance, and 68 mA cm^{-2} current density values. As can be seen in Fig. 3, the electrolysis time interval of 30–45 min was enough to achieve the satisfactory reduction factors for low electrical power costs. The following reduction intervals were obtained: 90–99% for turbidity; 30–60% for TSS; 40–80% for calcium concentrations. The reductions of Cr, K, Zn, COD and TVS as a function of electrolysis time are shown in Fig. 3 as well.

3.4. Chromium removal kinetics

During the EC process, the adsorbed chromium ions in a colloidal medium were present as charged colloidal particles, which were under the electrophoresis effect and the influence of an external electric field. Colloids with high zeta potential or electrical-kinetic potential (negative or positive) are electrically stabilized, while colloids with low zeta potentials tend to coagulate. Assuming a low zeta potential, the velocity of the particles with respect to a medium at rest follows Henry's formula for non-conducting particles and it is described by [23]

$$v_e = \frac{2}{3}\frac{\varepsilon\zeta}{\eta}f(\kappa a)E \tag{9}$$

where E is the electric field strength, ζ is the zeta potential, ε stands for the dielectric constant of the fluid phase, η is the dynamic vis-

cosity of the fluid, and $f(\kappa a)$ varies smoothly from 1.0, for low κa value, to 1.5 as κa approaches infinity.

Assuming that the electrophoretic velocity of these particles is time independent, the particulate concentration in the colloidal medium is reduced in time according to a simple exponential form, with a rate constant proportional to the particle velocity [24]. Moreover, considering a Brownian coagulation between particles, the loss of particles due to coagulation is expressed as a second order relation [24] represented by

$$\frac{dC}{dt} = -k_1 C^2 [1 - \exp(-k_2 t)]^2 \tag{10}$$

where C is the time-dependent concentration of particulate, k_1 is the Brownian coagulation rate constant, $k_2 = v_e/x$ is the rate constant, v_e is the electrophoretic velocity, $x = V/A_e$ is the geometric parameter of the electrode size, V is the suspension volume, and A_e is the effective superficial area of the electrode.

The parameter identification procedure was based on the particle swarm optimization (PSO) global optimizer [25] coded in Maple® software. The evaluated constant values were as follows: $k_1 = 6.9 \times 10^{-4}$ L mg^{-1} s^{-1} and $k_2 = 2.76 \times 10^{-3}$ s^{-1} for the PSO objective function of 0.011 and residual χ^2 equal to 0.0022. The residual chromium concentration in the fluid phase is achieved for a suspension volume of 5×10^3 cm^3 and the colloidal particle velocity of 0.17 cm s^{-1}. In Fig. 4 both the experimental and model profiles of the chromium removal are shown, where a perfect match was observed up to 2 h of process.

The Cr removal dynamics (see Fig. 4) can be explained as follows. At the beginning of the process, the Cr particles are neutralized and under the effect of electric field migrate to the anode, where their electrical charge is neutralized by ferrous ions. After 15 min, a sharp drop in Cr concentration (about 93%) can be observed because of the particle coagulation in the bulk. After 60 min of electrolysis process time, most of the chromium particles were neutralized. Thus, the concentration was below 0.5 mg L^{-1} which was under the threshold concentration for chromium release into aquatic environment, according to the Brazilian environmental legislation norms.

3.5. Pollutant removal comparison

The pollutant removal efficiency for both EC process- and conventional-based tannery effluent treatments were compared and shown in Fig. 5. The conventional process was based on the use of a coagulant and coagulant agents followed by decantation. The
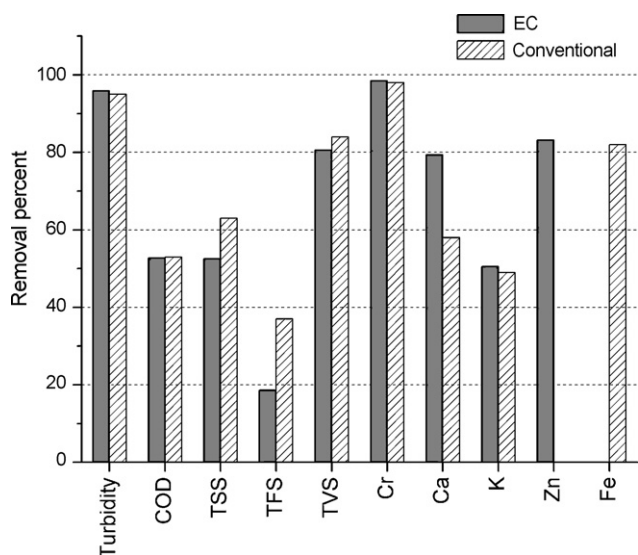
Fig. 5. Removal factors for physicochemical parameters and elements when applied to the EC processes (treated TIE from collection 2) and conventional ones (clarified effluent from the real wastewater plant) close to the natural effluent pH. The EC treatment operational conditions were as follows: 45 min electrolysis time, 4.0 cm internal electrode distance, 68 mA cm^{-2} current density.

EC treatment system was operated for 45 min of electrolysis time, 4.0 cm internal electrode distance, 68 mA cm^{-2} current density and a natural effluent pH. As can be seen in Fig. 5, after both treatments almost the same 96% and 98% reduction were obtained for turbidity and chromium concentration values, respectively, while a reduction greater than 80% was obtained for the volatile total solids. However, the calcium removal using the EC treatment was about 80%, which showed 15% better performance than the conventional one. The zinc concentration removal (80%) was also achieved in EC treatment, but no response for the conventional one. Both treatments have allowed a 50% COD reduction values. For TSS and TFS, the conventional treatment was slightly better than the EC one, but the removal factors were less than 65% for both methods.

3.6. Operational cost analysis

Nowadays, the operational cost of any effluent treatment method is included in the optimization procedure and is an important criterion for evaluation of the method's applicability at industrial scale. The EC reactor operational costs as US$ m^{-3} of the treated tannery effluent can be calculated by considering two parameters: the amount of energy consumption and the amount of electrode material used.

The electrical operational cost (EOC) is mainly composed of the electrical energy consumed as kWh/m^3 of the treated tannery effluent and the electrical energy price (EEP) as US$/kWh. The EOC can be estimated by applying Eq. (11). In addition, the material cost (MC) is included as a part of the operational cost. The formation of MC takes into account the maximum possible mass of iron theoretically dissolved by the anode (derived from the Faraday's law [18]) per m^3 of treated tannery effluent and the electrode material price (EMP) as US$/kg of iron. The MC parameter can be estimated by using Eq. (12).

$$\text{EOC} = \frac{V \times i \times A_e \times t}{V_{eff}} \times \text{EEP} \qquad (11)$$

where EOC is the electrical operating cost (US$ m^{-3}), V is the applied voltage (V), i is the current density (A cm^{-2}), A_e is the effective superficial area (cm^2), t is the operational time (h), V_{eff} stands for the total volume of treated effluent (m^3), and EEP is the electrical energy price (US$/kWh).

$$\text{MC} = \frac{i \times A_e \times t \times M}{n \times F} \times \frac{\text{EMP}}{V_{eff}} \qquad (12)$$

where MC is the material cost (US$ m^{-3}), EMP is the electrode material price (US$ g^{-1}), M is the relative molar mass of the concerned electrode (g mol^{-1}), n is the number of electrons in oxidation/reduction reaction, F is the Faraday's constant (96,500 C mol^{-1}), and V_{eff} is the total volume of treated effluent (m^3).

Working at 68 mA cm^{-2} and varying the electrolysis time from 0 to 60 min, the EC reactor operational costs have linearly increased from 0.0 to 1.64 US$ m^{-3}, based on the following EEP and EMP values: US$ 0.14/kWh for Brazilian industrial use and US$ 2.94/kg of iron, respectively. In comparison with the operational cost (only reactants) of conventional method (US$ 3.50 m^{-3} in Brazilian tannery factory), the EC method is evidently cheaper than the conventional one. The conventional method gave Cr residual concentration of 1.0 mg L^{-1} which does not meet environmental regulations norms. In order to achieve 0.5 mg L^{-1} maximum limit on Cr concentration recommended by the Brazilian environmental norms, it was necessary to include additional purification step. Applying EC reactor and after 60 min of operation, Cr concentration values were below this limit and operational cost was below US$ 1.7 m^{-3} of the treated tannery effluent.

4. Conclusions

The preliminary EC results based on the factorial design have shown small increases in the pollutant removal for high initial pH values, which may be explained by the high conductivity values of natural effluent. Hence, the EC system was operated close to the natural effluent pH, where satisfactorily results were achieved. By increasing the electrolysis time, high removal factors have been reached on turbidity, chromium and calcium concentrations. In the special case of chromium, its coagulation rate can be described by a second order rate equation. Based on the simulation results, it was possible experimentally to obtain a concentration reduction for the tested ROP. The final Cr concentration values after 60 min of operation were below the recommended limit by the Brazilian environmental norm. Low electrolysis times were enough to obtain high removal factors for the most pollutant concentrations. The combined EC method has shown a great potential for the pollutant removal from tannery effluent, due to the similar high removal efficiencies of metals and organic compounds when compared with the conventional one. Due to the lower EC operational cost this method can be successfully used for industrial applications of effluent treatments containing metals and organic pollutants.

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