Pollutant Removal from Wastewater at Different Stages of the Tanning Process by Electrocoagulation

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The removal of chemical oxygen demand (COD), total organic carbon (TOC), turbidity, and chromium content from tannery wastewater at different stages of the process was experimentally investigated using electrocoagulation (EC) with iron and aluminium electrodes. In the EC of the beamhouse wastewater (S1), the effects of initial pH and current density were analyzed and electrical energy consumption was determined. The COD and TOC in the solution were effectively removed, with an initial pH 7.0, using either metallic electrode. With a current density of 28 mA/cm² for an electrolysis procedure of 60 minutes, the removal efficiency of COD and TOC was 72% and 57% with aluminium electrodes and 69% and 60% with iron electrodes, respectively. The minimum energy consumption for the highest COD and TOC removal was 0.37 and 0.69 kWh/m³ when employing iron or aluminium electrodes, respectively. At the optimal conditions, removal efficiencies close to 100% for turbidity and chromium content for wastewaters S1-beamhouse, S2-tanning, S3-retanning, and S4-a mixture 1:1:1 (v/v/v) were achieved. Results show that a pseudosecond-order rate equation provides a good correlation for the removal rate of the parameters. Finally, the results indicate that for tannery wastewater, the EC process does not depend noticeably on the electrode material, but that the stage of the tanning process of wastewater sample has the principal effect on treatment efficiency.

1. Introduction

The city of Leon Guanajuato is the first most important tannery industrial area of Mexico having almost 800 companies that provide jobs, economic resources, and a better quality of life to citizens of the city [1]. It must be noted that these industrial activities use significant quantities of water and produce an average of 35 liters of wastewater per kg of treated hide [2, 3]. Generally, this tannery effluent does not meet the environmental regulations for discharge directly into the receiving water [4].

The tanning process is designed to transform skins in leather, a stable and nonputrescible product. There are four major groups of subprocesses or stages required to make finished leather: beamhouse operations, tanyard processes, retanning, and finishing. For each end product, the tanning process changes and the kind and amount of waste produces may vary over a wide range. Acids, tannins, alkalis, solvents, sulfides, dyes, chromium salts, auxiliaries, and many other compounds which are used in the transformation of raw or semipickled skins into commercial products are not completely fixed by skins and remain in the effluent. During retanning procedures, synthetic tannins, oils, and resins are added to form softer leather at varying doses. One of the refractory groups of chemicals in tannery effluents derives mainly from tannins. Synthetic tannins are characterized by complex chemical structures because they are composed of an extended set of chemicals such as phenol-, naphthalene-,
formaldehyde-, and melamine-based tannins and acrylic resins. Among synthetic tannins, the ones based on sulfonated naphthalenes and their formaldehyde condensates play a primary role, for volumes and quantity used in the leather tanning industry. The oils cover the greater COD sates play a primary role, for volumes and quantity used in sulfonated naphthalenes and their formaldehyde condensates. Among synthetic tannins, the ones based on formaldehyde-, and melamine-based tannins and acrylic resins. The conventional treatments of industrial effluent, including the biological technologies, have reported difficulties including poor biosolid separation, voluminous biological sludge, and low removal efficiencies due to the high concentrations of pollutants with low biodegradability [5, 6]. These problems, taken together, represent a serious and actual technological and environmental challenge with their use [7–9]. Currently, the aqueous streams of each stage of the tanning process are mixed together in balancing tanks and pretreated before biological treatment. However, the mixture of many of the compounds used in the process can be subsequently released into the environment because they remain in the wastewater even after conventional treatment [10].

Among the different wastewater treatments technologies available, the electrochemical processes constitute, without a doubt, the most important emergent approaches to resolve these water contamination problems [11–15]. There are several explanations, among these, include the fact that the active reagents can be generating in situ at the surface of the electrodes when applying a constant current [16]. Electrocoagulation (EC) is an electrochemical treatment technology, where the cation coagulants of iron or aluminium are generated by applying a direct current to the electrodes. During the process, metal hydroxides are produced that can act as coagulant/flocculant for the separation of charges pollutants from the wastewater. In this sense, the high amount of chromium and organic matter present in the tannery wastewater are removed from the water [4, 17, 18]. The EC efficiency depends on the interaction of different variables including (i) physicochemical characteristics of water (pH, conductivity, total solid, etc.); (ii) applied current density; (iii) material, distance, and configuration of the electrodes; and (iv) hydrodynamic parameters [16, 19, 20]. Understanding their interactions could help to design optimal treatment units in a range of predetermined operating conditions.

Examination of the available literature suggests that the treatment mechanism by electrocoagulation depends on the nature of the waste and the design of the EC device in use. It also appears that the treatment efficiency has to be based on the TOC, COD, turbidity, and concentration of toxic species (e.g., chrome) in the effluent to be treated [16, 20]. Wide ranges of parameters have been studied, and optimal operating conditions are proposed, typically, for a single type of wastewater source, without analyzing the different characteristics of the effluents by stage at the tannery process. The efficiency of the electrocoagulation technique for treatment of wastewaters generated at different stages of the tanning process was investigated. Analyses of the effects of initial pH, current density, and cathode materials were used to determine the optimal conditions for pollutants removal and the electrical energy consumption. Special attention was paid to the variations of COD and TOC levels, turbidity and chromium content with the amount of electrogenerated adsorbent, and the origin of wastewater. The adsorption kinetics of the electrocoagulants were analyzed using a pseudosecond-order kinetic model.

2. Materials and Methods

2.1. Tannery Wastewater. Leather processing involves a number of stages or unit operations including the beamhouse operations, tanning, retanning, and finishing. The beamhouse operation includes successively soaking, unhairing and liming, and bating and deliming. Furthermore, chromium tanning treatment involves degreasing and pickling. Finally, the other operations are conducted to produce finished leather with attention to its final use.

Wastewater utilized in this study was supplied by a leather plant located in CIATEC, Leon, Guanajuato, Mexico. It was collected in closed containers, by unit operation, and called beamhouse (S1), tanning (S2), retanning (S3), and a mixture 1:1:1 (v/v/v) of the three unit operations (S4). All the samples were preservation in accordance with Mexican standard NMX-AA-003-1980. The samples were collected in glass containers and transported in an ice bath until refrigeration at 4°C by no more than three days. Table 1 presents the main chemical and physical characteristics of these wastewater samples before treatment.

2.2. Experimental Setup. The experimental setup used for the electrocoagulation studies employed a typical electrochemical reactor with two parallel electrodes facing each other with a gap between the anode and cathode plates and supported horizontally by a nonconducting material to avoid any short circuits. The active electrode surface area was 72 cm² (6 cm × 12 cm) of iron (Fe) or aluminium (Al). In all cases, the two electrodes were of the same material and the distance between the anode and cathode plates was set at 3.0 cm. The electrodes were operated in a monopolar mode and connected to a B&K Precision 1621A DC power source to supply constant cell current of 2 A. The volume of wastewater was 1.0 L, and to achieve good mass transfer, a 600 rpm magnetic stirring agitator (Corning PC-420D) was used.

2.3. Chemicals and Analytical Measurements. All physicochemical parameter measurements were made for each pre- and posttreated sample. Sodium hydroxide (karal brand) was employed to adjust the pH of the initial solution, when it was required. The pH was measured by using a digital pH meter (Extech instruments, Model 407227). COD is an indicator of the degree of effluent pollution degree by regulatory agencies to gauge overall treatment plant effectiveness. Sample COD was determined by the opened reflux method established in Mexican standard NMX-AA-030/1-SCFI-2012. Wastewater remediation was monitored using TOC decay and measured by a Shimadzu TOC-L analyzer. Before analysis, samples withdrawn from the solutions treated by EC were filtered with Whatman 0.45 µm PTFE
filters. A digital conductivity meter (Hach, P1.4) was used to measure sample ionic conductivity. Turbidity (Nephelometric Turbidity Unit, NTU) was determined with a Hach, 2100P turbidity meter. Concentrations of Cr, Al, and Fe were determined by atomic absorption (Thermo Scientific, AAS iCE 3000), after dilution and acidification of the solution samples using nitric and hydrochloric acid in a volume proportion of 3:2 to totally dissolve the metal species. In most cases, the liquid fractions had to be filtered using conventional 0.45 μm filters to remove any suspended solids, prior to injection into the atomic absorption apparatus.

The removal efficiency was calculated with Equation (1), in which \( C_0 \) and \( C_t \) are the initial concentration and concentration at time \( t \), respectively, for the studied parameter (COD, TOC, turbidity, or chromium):

\[
\text{Removal efficiency} (\%) = \frac{C_0 - C_t}{C_0} \times 100. \tag{1}
\]

### 3. Results and Discussion

The composition of tannery wastewater is strongly dependent on the level of process optimization in the factory. Several publications have shown the efficiency of the treatment of tannery wastewater; however, most of the papers have focused their interest on the variables that affect the electrocoagulation process studying a single type of sample without an analysis of the wastewater’s origin. In this work, the optimal operational and economic conditions for the electrocoagulation process (initial pH, current density, and the energy consumption per volume) were developed using wastewater sample S1. These conditions were then applied to the remaining wastewater sources (S2–S4). The experiments were focused on dependence of the treatment efficiency to the electrode material and the wastewater sources.

#### 3.1. Effect of Initial pH

It has been established that pH is an important parameter influencing the performance of the EC process [20]. The effect of initial pH on the efficiency of COD and TOC removal is presented in Figure 1(a). High COD and TOC removal rates are a function of solution pH, and it has been reported that the optimal pH in an EC process is 7.0 [20]. To determine pH for maximal removal efficiency, testing was conducted at the pH of the solution (3.73) and a pH 7.0 modified with NaOH. The maximum removal attained was 72% of COD with aluminium electrodes and 60% of TOC with iron electrodes. During treatment testing, pH increased as a function of electrolysis time (Figure 1(b)) and its change is linked to the efficiency [4]. The pH increased for all studied samples as a consequence of continuous hydroxide ions (OH⁻) formation, from water reduction, at the cathode, equation (2) by Vik et al. [21]:

\[
2H_2O + 2e^{-} \rightarrow H_2 + 2OH^- \tag{2}
\]

According to the Pourbaix diagram, at pH 7.0, iron and aluminium are in the precipitated form, Fe(OH)₃ and Al(OH)₃, respectively. The decrease of removal efficiency at more acidic pH was attributed to an amphoteric behavior of Al(OH)₃ which leads to soluble Al³⁺ cations. It is well-known that these soluble species are not useful for water treatment. When the initial pH was kept in neutral, all the Al produced at the anode formed polymeric species and precipitated as Al(OH)₃, leading to more removal efficiency.

In general, the best removal efficiency for both electrodes materials was obtained at pH 7.0; hence, all subsequent tests were performed at pH 7.0.

#### 3.2. Effect of Current Density

The supply of current to the EC process determines the amount of Fe²⁺ or Al³⁺ ions released from the electrodes. The value of current density establishes the coagulant production rate and adjusts the rate, size of bubble production, and finally the growth of flocs. This parameter varied in the range 28–444 mA/cm² during testing.

Figure 2 shows the effect of current density on COD and TOC removal using both types of electrodes: iron (Figure 2(a)) and aluminium (Figure 2(b)). A decrease in current density from 444 to 28 mA/cm² showed an improved COD and TOC removal efficiency from 57% to 69% and 48% to 60%, respectively, for the Fe electrodes after 60 min of treatment (Figure 2(a)). Likewise, with the Al electrode, COD and TOC removal are improved from 59% to 72% and 38% to 57%, respectively, when the current density reduces from 111 to 28 mA/cm². However, with these electrodes increased, current density from 111 to 444 mA/cm² improved removal efficiency for COD (to 90%) but reduced TOC removal (to 42%). The literature has reported that too high values of current density would result in a significant decrease in current and, hence, treatment efficiency. Additionally, reports suggest that for the electrocoagulation system to operate for long periods of time without maintenance, their current density should be 20–25 mA/cm² unless there are measures taken for a periodical cleaning of electrodes surfaces [15]. With this in mind, it was decided to employ a current density of 28 mA/cm² in all subsequent experiments.

#### 3.3. Electrical Energy Consumption

The energy consumption per unit volume (ECv) is a very important economical
parameter in the EC process. This parameter was calculated using the following equation [22]:

$$\text{EC}_v (\text{kWh/m}^3) = \frac{E_{\text{cell}} I_{m} V_s}{V_s}$$

(3)

where $E_{\text{cell}}$ is the cell potential difference (V), $I$ is the applied current (A), $t_{m}$ is the total electrolysis time (h), and $V_s$ is the solution volume ($\text{m}^3$). The cost for each process was estimated from the $\text{EC}_v$ value assuming an average retail price of electricity for the industrial sector of US$ of 0.13 per kWh (Comisión Federal de Electricidad, CFE).

In Figure 3, current density is plotted against power consumed. Inspection of Figure 3(a) reveals that the minimum energy consumption for the highest COD and TOC removal was 0.37 kWh/m$^3$ at 28 mA/cm$^2$ current density after 60 min of electrolysis time with Fe electrodes. The calculated cost was 0.0481 (USD$ m$^{-3})$. The effect of the current density on the energy consumption and the removal efficiency of COD and TOC with Al
electrodes are shown in Figure 3(b). The minimum energy consumption for the highest TOC removal was 0.69 kWh/m³ at 28 mA/cm² current density after 60 min of electrolysis time. The calculated cost was 0.0897 (US$D m³). However, for the highest COD removal levels, the maximum energy consumption is required (0.9 kWh/m³) at a current density of 444 mA/cm² after 60 min of electrolytic time. The calculated cost was 0.117 (US$ m³). As shown in Figure 3, the EC, of water treated was higher, also represents the best removal of COD with Al electrodes. However, as the process is more expensive, the authors suggest the performance of a cost-benefit analysis before scaling up. Reports in the literature generally state that energy consumption increases with an increase in COD and TOC removal efficiency. Nevertheless, our results show the opposite with exception of the data at 444 mA/cm² using Al electrodes. This could be due to that the abatement of the last portions from waste removal is often more energy consuming as has been noted in the majority of pollution abatement systems. Additionally, EC is a very complex process with various mechanisms operating synergistically to cleaning water, meaning that results greatly depend on the treated water composition. The removal of COD, in comparison with TOC, was very effective, but required higher energy input for both types of electrodes.

### 3.4. Effect of Electrode Material

Results of wastewater sample treatments at different stages of the tanning process using an EC system at 28 mA/cm² over 60 minutes while employing Fe (Figure 4(a)) and Al (Figure 4(b)) electrodes, in a monopolar system, were analyzed. As shown from Figure 4, there were minimal differences between Fe and Al electrodes for the removal efficiency of COD under the same condition. The main difference is seen with the sample S2, where removal percentage is higher by almost 10% with Fe electrodes. For both electrodes, the sample S2 was the one that displayed the highest removal percentage for COD, probably because it was the one containing the lowest initial COD (3072.16 mg/L). The removal percentage of the products present in the different samples (S2, S3, and S4) during the EC process was monitored for TOC removal efficiency with electrolysis time. These results are shown in Figure 5(a) and 5(b) for Fe and Al electrodes, respectively. TOC of the three wastewater samples was found to decrease regularly as the electrolysis time increased. However, the removal of the organic pollutants could not be totally achieved by the treatment. The EC process seems to be at its maximum removal efficiency (75%) for S2 sample with Fe electrodes. The lowest TOC removal efficiency (10%) was with Al electrodes for sample S4. A general inspection of Figures 4 and 5 suggests that COD and TOC removal levels in the EC process does not noticeably depend on the electrode material, but more on the stage of the tanning process of the wastewater sample. This observation was also reported by Zongo et al. [23] during the EC of textile wastewaters with Al or Fe electrodes.

The removal of the COD, TOC, turbidity, and chrome pollutants from each sample source are including and compared in Figures 6(a) and 6(b) for Fe and Al electrodes, respectively. Regardless of the different initial concentrations, the removal of turbidity and total chromium for all wastewater samples with both electrodes was almost 100% after 60 min of electrolysis time. However, different results were observed for the removal efficiency of COD and TOC, due to the various mechanisms that could occur in the
If iron or aluminium electrodes are used, the electrogenerated ions will undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. By mixing the solution, hydroxide species are produced which cause the removal of pollutants by adsorption and coprecipitation. The removal efficiency of these pollutants depends directly on the concentration of hydroxyl and metal ions produced on the electrodes. The amount of adsorbent (metallic ions) has been determined from Faraday’s law (equation (4)):

\[ E_c = \frac{ItM}{ZF} \]

where \( I \) is the current in A, \( t \) is the time (s), \( M \) is the molecular weight, \( Z \) is the number of electrons involved, and \( F \) is the Faraday constant (96485.3 C/mol).

**Figure 4:** Removal efficiency of COD for an EC process with (a) Fe electrode and (b) Al electrode. Conditions: pH 7.0; S2 (tanning), S3 (retanning), and S4 (mixture) wastewater; electrolysis time = 60 min.

**Figure 5:** Removal efficiency of TOC for an EC process with (a) Fe electrode and (b) Al electrode. Conditions: pH 7.0; S2 (tanning), S3 (retanning), and S4 (mixture) wastewater; electrolysis time = 60 min.
Figure 7 presents the behavior of the wastewater sample source on the removal efficiency of COD and TOC, during the EC process with different levels of metallic ions. As expected, the amount of COD and TOC adsorption increased with the increase in adsorbent concentration, indicating that adsorption depends upon the availability of binding sites for the pollutants. Figures 7(a)–7(c) display the behavior for removal of COD and TOC between electrodes. Here, one sees that for the same metallic pairs, Fe or Al produces similar pollutant removal and that for all the sample sources, a greater COD removal efficiency is found. However, when focusing on sample type (S2, S3, and S4), some differences are observed. In Figure 7(a), displaying experimental experience for sample S2, removal of approximately 5% more COD and TOC is observed by iron adsorbent than aluminium adsorbent. Likely as the amount of adsorbent generated increases, the efficiency of the pollutant removal potential increases considerably with the wastewater source material. In Figure 7(b), for sample S3, one observes that the aluminium adsorbent provided the same removal efficiency, for both COD and TOC, as obtained with the iron adsorbent. Finally, in Figure 7(c), when considering sample S4, similar results as for S3 were seen for COD removal; however, 10% more TOC is removed with the increased generation of the iron adsorbent. All these results again suggest that the most important consideration in a successful tannery wastewater treatment program is the composition and source of the effluent.

Figure 7: Removal of COD and TOC for an EC process with different amounts of iron or aluminium adsorbent. Conditions: pH 7.0; S2 (a), S3 (b), and S4 (c) wastewater; electrolysis time = 60 min.
complicated relationships between the parameters of the electrocoagulation process in real industrial tannery wastewater. In this paper, we propose a pseudo-second-order equation in order to find a better fit than the first-order equation. The adsorption kinetic data of removal parameters (COD and TOC) have been analyzed. Due to the results, it was expected to find that absorption kinetics and equilibrium followed a pseudo-second-order equation:

$$\frac{t}{C} = \frac{1}{k'_c C_c} + \frac{1}{C_c} \times t,$$

where $C$ represents the residual solution concentration at a time $t$ in the solution, $C_c$ is the concentration coefficient, $k'_c$ is the reaction rate coefficient, and $t$ is the time. The linear graph of $t/C$ as a function of the time presents a slope of $1/C_c$ and $(1/k'_c) \times C_c^2$ as the intercept. Tables 2 and 3 show the kinetic coefficients obtained for the Fe and Al electrodes, respectively. A better fit of the pseudo-second-order kinetic model was observed for the removal of TOC with iron electrodes, representing chemical adsorption through the formation of chemical bonds between adsorbent and adsorbate on a monolayer in the surface [24, 25] than in the other cases.

4. Conclusions

This investigation has demonstrated that EC with Fe or Al electrodes is an effective method to clarify tannery wastewater at different stages of the process. EC provided considerable reduction in the COD, TOC, turbidity, and chromium content. The effect of various EC operational parameters employed throughout the test cycles for the various wastewater streams was developed on the beamhouse wastewater (S1) sample. Fe and Al electrodes were most effective in removing COD and TOC with an initial pH 7.0. Our results showed that the highest COD removal efficiency (90%) was provided by aluminium electrodes at 444 mA/cm$^2$. However, this condition required a much higher energy input, and the electrode wear was worst. The team, therefore, selected the current density of 28 mA/cm$^2$ removing 72% (COD) and 57% (TOC) with iron electrodes and 69% (COD) and 60% (TOC) with aluminium electrodes. This current density required minimum energy consumption for optimal COD and TOC removal during testing. At this current density, total energy consumption was 0.37 and 0.69 kWh/m$^3$, at a calculated cost of 0.0481 and 0.0897 (US$ m$^{-3}) using Fe and Al electrodes, respectively. At optimal conditions, the removal of turbidity and total chromium for all wastewater samples (S1, S2, S3, and S4) with either electrode material was almost 100% after 60 min of electrolysis time. A maximum observed removal efficiency of TOC (75%) was during testing on the S2 sample using Fe electrodes and the lowest (10%) when using Al electrodes on the sample S4. Considering adsorbent quantity, tests suggest that the removal of contaminant by adsorption depends upon the availability of binding sites for the pollutants, suggesting a pseudo-second-order kinetic model, which exhibited good correlation with the experimental results. Finally, the team’s test results demonstrated that the EC process does not depend significantly on the electrode material, when performed at optimal operating conditions, but rather successful decontamination showed a significant correlation to the origin of the wastewater samples.

Data Availability

The Excel and Origin data used to support the findings of this study are currently under embargo while the research findings are commercialized. Requests for data, 12 months after publication of this article, will be considered by the corresponding author.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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