Treatment of Tannery Effluent Using Combined Electrocoagulation and Adsorbent of Powdered Marble

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Received: 22 Sep, 2022 | Accepted: 26 Oct, 2022 | Published: 10 Nov, 2022

Abstract

This paper discusses the ability to remove chromium and COD from a real chrome tanning wastewater by use of Electrocoagulation (EC) coupled with adsorption using Powdered Marble (PM) added to a batch stirred EC cell with a pair of duralumin electrodes. The effects of current density, adsorbent dose and contact time were studied.

In comparison to the conventional EC process, the coupling of electrocoagulation and adsorption using powdered marble showed that the addition of an appropriate powdered marble improved the removal of Cr(III) and COD using lower current densities and a short contact time. Nearly 99% of Cr(III) and COD were removed from tanning effluent with an initial chromium concentration of 3.21 g/L and COD of 3.75 g/L. the results obtained showed better performance using combined electrocoagulation and adsorbent of powdered marble compared to the simple EC.

Keywords: Powdered marble; Chromium; Chemical oxygen demand; Electrocoagulation; Adsorption; Energy consumption

Introduction

In Morocco, due to the poor distribution of natural water and poorly managed human activities, many regions are suffering from a constant increase in drinking water needs. This water deficit is now accentuated with the development of the industrial sector, which not only consumes huge quantities of water, but also contributes to the pollution and degradation of surface and groundwater quality [1].

The Tanning industry plays an important role in the global economy, particularly in Morocco tannery industries use a lot of chemicals and produce huge volumes of wastewater and solid waste [2] consequently, tanning industries have been known as a pollution source in Morocco, in fact, they always reject into the environment a large amount of wastewaters, which is loaded with toxic pollutants.

The waste generated rises significant environmental problems due to various contaminants especially a Chemical Oxygen Demand (COD) and a chromium concentration greater than 3 g/L [1,3,4]. Due to its composition, it requires treatment before being released into the environment [5,6].

Chromium mineral is needed for humans in modest quantities but must receive from our meals [7]. It is improves human body weight by extra decomposing fat from the body. Chromium regulates blood sugar, improves cognitive function, and breaks down fats and carbohydrates, all of which are crucial for overall health; but over consumption of chromium may result in very harmful to human health and the environment in general [8,9].

There are various processes for the treatment of effluent tannery, such as chemical precipitation [10], which is the most treatment to remove chromium and organic contaminants. But it has the disadvantage of producing sludge with high trivalent chromium and organic matter content.

There are also many other efficient process for chromium removal, such as ion exchange, nanomaterial adsorption, biosorption, electrocoagulation, biological and membrane treatment [8,11-13], phytoremediation [14], infiltration and percolation [15] and membrane filtration [16]. Nevertheless, cost-effectiveness and technical complications are two important facts limiting their generalized use, especially for ion exchange processes and membrane treatment.

Priebe GPS, et al. applied anaerobic digestion to remove chromium-containing wastewater from a leather factory. Despite high levels of biogas production, increasing chromium content in the fermentation substrates decreased methane efficiency [6].

Among the different techniques mentioned before, electrocoagulation removes suspended solids, toxic metals, emulsified oils, microorganisms and various contaminants from tannery wastewater [17]. This technique has successfully used an iron anode
in electrocoagulation to remove chromium ions from effluent tannery. The electrocoagulation provides a simple, reliable, and cost-effective technique for treating chromium-concentrated in effluent tannery without additional chemicals, and thus without producing sludge [18].

The electrocoagulation is an electrochemical process, leads to dissolution of the anode metal with simultaneous formation of ions hydroxyl and hydrogen gas at the cathode. The metal hydroxides, which destabilize and aggregate suspended particles, precipitated by adsorbing dissolved contaminants. Hydroxides react with suspended solids as well as with certain dissolved compounds and allow their coagulation, then the flocculation of the particles agglomeration [7]. After treatment, the effluent is decanted in order to separate the clear liquid [19-21].

Electrocoagulation has been used in several of the above mentioned results and it has been successfully applied to treat numerous varieties of wastewater, either industrial or urban origin choice of EC materials is very essential electrode materials, generally, are aluminum. They are cheap, readily available, and have been proven effective [3].

Another effective technique is adsorption, which is a surface phenomenon, it rests on intermediate attractions between the solute and the adsorbent. The adsorption process continues until an equilibrium is obtained, to which corresponds an equilibrium concentration of the solute [22]. Adsorption is advantageous due to its low operating costs, simplicity of design and its ability to remove toxic compounds [23].

Similarly, adsorption using low costs adsorbents has proved been shown to be a very effective method for removing chromium from effluent tannery [3]. Indeed, Guimarães T, et al. have reported adsorption capacity 148.03 g/l of chromium on powdered marble with an initial concentration of 2000 mg/L of Cr(III) [24]. El Maguana Y, et al. have showed that the yield was 58.52 % and the adsorption of methylene blue was 49.01 mg/L [25].

This work aims to investigate the ability to use two effective techniques for the treatment of tannery effluent, namely the adsorption process using a low-cost natural sorbent, combined with electrocoagulation (EC), so that powdered marble is used directly in the electrocoagulation reactor. In this experiment, real tannery wastewater is studied with initial chromium concentration of 3.21 g/L. The optimal operating conditions were determined: the effect of treatment time, adsorbent dose and current density on the removal efficiency was explored; also the energy consumption is discussed.

Materials and Methods
Effluent sample

The samples used in this work were obtained from a chromium-tanning tank in a small semi traditional tannery in Marrakech city, having a capacity of treatment of about 500 skin /day. pH (1.25 w/v soil water) and Electrical conductivity (1.5 w/v soil water suspensions) and were detected using a multiparameter probe type LF 92 WTW. Available P (P(OH)) are determined by the Olsen method [26], and Total Kjeldahl Nitrogen (NTK) was determined using the Kjeldahl method [27]. Major and trace element analyses were conducted by X-ray fluorescence spectrometry (Olympus, UK) and Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA-6300), respectively. Heavy metal concentrations were determined after total digestion of a 0.50 g of a dry sample of mine tailings, at 500°C. The sample was digested in 7 mL Nitric Acid (HNO₃) (65% w/w), 2 mL Hydrofluoric Acid (HF) (40% w/w), and 1 mL Perchloric Acid (HClO₄) (60% w/w) in a Teflon beaker. The sample solutions were filtered with a 0.45 mm cellulose nitrate filter and the volume adjusted to 10 mL with 0.1 M HNO₃. The chromium calibration curve was prepared using standard solutions from Prolabo (France). COD was measured by the dichromate method and subsequent measurement of the optical density using a HACH 2400 spectrophotometer (Loveland, Colorado) [1].

The removal efficiency (Re %) of each pollutant (COD and chromium) was calculated using the following equation:

\[ \text{Re} \% = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \]

where \( C_i \) and \( C_f \) represent the initial and the final concentrations respectively.

Powdered marble sample

The powdered marble was collected from a large private marble processing unit. Before mixing, the powdered marble were air-dried at 70°C for 48 hours and sieved to 2 mm. The morphology of powdered marble samples was captured by a Scanning Electron Microscopy (SEM, Philips-XL30). The median pore diameter, the specific surface area, and the surface weighted mean were measured by porosimeter, nitrogen adsorption using the Brunauer-Emmett-Teller (BET) method (Micromeritics/Gemini-2372), and laser granulometry model Mastersizer 2000 Ver. 5.60, respectively. The pHpzc (pH of the Point of Zero Charge) was determined by the procedure described by Rivera-Utrill [28]. Fourier Transform Infrared Spectroscopy (FTIR) using Bruker Vertex 70 spectrometer was conducted to identify the functional groups and molecular composition of powdered marble surfaces.

Experimental set-up

The electrochemical runs were carried out in a discontinuous treatment reactor (Figure 1) by recirculation of 2 L water volume through a flow system composed of a reservoir tank, a peristaltic pump, and an electrochemical cell. The peristaltic pump (Masterflex L/S, USA) allows fluid recirculation and provide a flow of up to 2000 mL/min. The electrocoagulation cell, provided with aluminum electrodes, consisted of two identical polymethyl methacrylate halves (20 cm × 10 cm × 5 cm) in which aluminum electrode plates (15 cm × 7 cm × 1.2 cm) are imbedded. The distance between both electrodes is constant and equal to 1 cm for all experiments. After each run, sulfuric acid solution of 2% (v/v) is poured on the surface of the electrodes. Their surfaces are manually polished with abrasive paper and rinsed with distilled water before each run. The effective area for electrolysis of each electrode is 105 cm². The electrodes were related to a laboratory DC power supply (EA-PS 3065-10 B, UK) that provides current range between 0 and 10 A, the used current was held constant all along the experimental runs. The reservoir tank was connected to a water-filled cylinder used to quantify released hydrogen principally from the cathode during the runs. This cylinder was filled with tap water using a vacuum pump (Vacuubrand MZ2N, Germany) prior to each run. A gentle mechanical agitation (150 rpm) was set inside the reservoir tank with an agitator control (EUROSTAR 60 control, IKA, France). The schematic diagram of the complete electrocoagulation system is shown in figure 1.

Results and Discussion

Physico-chemical characteristics of raw wastewater

The composition of the tannery wastewater are determined using Standard Methods and are presented in table 1.

The effluent was characterized by very high chromium content near 3.21 g/L and about 3.75 g/L of COD. The composition of tannery wastewater presented in Table 1.
wastewater is strongly depending on the level of optimization of the factory. If the modern industry releases less polluted wastewater, the majority of semi-traditional industries used very concentrated solutions of chromium to guaranty the quality of the treatment. Genawi NM, et al. obtained similar chromium, and chromium parameters of untreated tannery wastewater, and chromium represented the main inorganic hazard element [29].

Characterization of powdered marble

The characterization results revealed that alkalinity, fineness, and purity are the most relevant characteristics found in the powdered marble used as an adsorbent (Table 2). The primary mineral composition was Calcite, and subordinate minerals (less than 5) in addition to quartz, dolomite, and diopside. The pH values measured of four samples were ranged from 8.80 to 9.1, while the average value ranged from 8.91 to 0.01. The electroconductivity varied from 128 to 1.30 ms/m and the percentage of calcium carbonate was 98.00% to1.07%. The chemical composition shows the abundance of calcite and the presence of the following impurities: Si, Fe, Mg, Al and K (Table 2). Moreover, the use of powdered marble exhibited low concentrations of Cu and Zn. The pHpzc of the powdered marble was previously studied by Elabbas S, et al. to be nearly 11. Since this pHpzc value was higher than 7, this would indicate that the powdered marble was loaded under the experimental conditions. The composition of powdered marble presents finely distributed particles with an average particle size of 6.61 mm, a high specific surface area of 3.32 m²/g and a median pore diameter of 162.2 nm [1]. The mentioned characteristics of marble powder show that it can be considered as a suitable alternative to lower soil acidity.

Current density effect

The Cell current is a decisive parameter in the electrochemical process. The current density amount precise the rate of coagulant production, and regulates the rate and the size of bubble production, and therefore affects floc growth [1]. In the present study, the current density values applied were 200, 300 and 400 A/m². These current densities were maintained during different periods varying from 5 min to 240 min and from 5 min to 360 min for EC and EC/PM pairings, figure 2 showed current density effect on Cr(III) reduction as a function of time by both processes: EC (Figure 2a) and EC/PM combination (Figure 2b).

In the simple electrocoagulation (Figure 2a), the efficiency of chromium removal was increased with a higher level of density, with efficiencies of 87%, 95.4%, and 99.7% were reached after 240 min at 200, 300, and 400 A/m² current densities, respectively. Hamadan and El-Naas reported that the chromium removal from groundwater increased with an increase in the current density and achieved 100% removal at a CD of 7.9 mA/cm² [30].

The addition of a 12 g weight of powdered marble to the electrocoagulation cell resulted in faster chromium removal compared to the simple EC technique. Maximum chromium removal is noticed at 200, 300, and 400 A/m² current densities, respectively. Hamadan and El-Naas reported that the chromium removal from groundwater increased with an increase in the current density and achieved 100% removal at a CD of 7.9 mA/cm² [30].

At acidic pH, Cr ions are eliminated by both precipitation and co-precipitation. These two mechanisms are not sufficient for effective chromium removal. Thus, adsorption improves the efficiency of the treatment especially in the case of an effluent with high chromium content (3.21 g/L).

Table 1: Main characteristic of raw wastewater tested.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (at 25°C)</td>
<td>3.81</td>
<td>0.10</td>
</tr>
<tr>
<td>EC (mS/cm) (at 25°C)</td>
<td>60.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Cl (g/L)</td>
<td>11.6</td>
<td>0.5</td>
</tr>
<tr>
<td>COD (g/L)</td>
<td>3.75</td>
<td>0.10</td>
</tr>
<tr>
<td>SO₄²⁻ (g/L)</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td>NH₄⁺ (mg/L)</td>
<td>33.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Total P (mg/L)</td>
<td>7.0</td>
<td>0.2</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>2.1</td>
<td>0.1</td>
</tr>
<tr>
<td>HCO₃⁻ (g CaCO₃/L)</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr(III) (g/L)</td>
<td>3.21</td>
<td>0.05</td>
</tr>
</tbody>
</table>

SD: Standard Deviation.

Table 2: Chemical composition and trace elements of powdered marble used as adsorbent.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO% Wt</td>
<td>92.11</td>
<td>2.33</td>
</tr>
<tr>
<td>MgO% Wt</td>
<td>3.79</td>
<td>2.06</td>
</tr>
<tr>
<td>Al₂O₃ Wt</td>
<td>0.62</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe₂O₃ Wt</td>
<td>0.46</td>
<td>0.06</td>
</tr>
<tr>
<td>MnO% Wt</td>
<td>0.32</td>
<td>0.02</td>
</tr>
<tr>
<td>K₂O % Wt</td>
<td>0.25</td>
<td>0.09</td>
</tr>
<tr>
<td>Na₂O% Wt</td>
<td>0.17</td>
<td>1.06</td>
</tr>
<tr>
<td>SiO₂ % Wt</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>Total Zn (mg/kg)</td>
<td>20</td>
<td>1.20</td>
</tr>
<tr>
<td>Total Cu (mg/kg)</td>
<td>16</td>
<td>0.80</td>
</tr>
</tbody>
</table>


Figure 1: Experimental set-up [14].
enhanced with increasing current density, with efficiencies of 91%, 95% and 96% were attained after only 210 min at current densities of 200, 300 and 400 A/m² respectively.

Indeed, the main reactions for electrocoagulation method using aluminum electrode are as [31]:

Anode: \( \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \) (1)

Cathode: \( 3\text{H}_2\text{O} + 3e^- \rightarrow 3/2\text{H}_2 + 3\text{OH}^- \) (2)

The two ions \( \text{Al}^{3+} \) and \( \text{OH}^- \) react with each other to form \( \text{Al(OH)}_3 \).

\( \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \)

Therefore, rapid adsorption of soluble organic compounds and trapping of colloidal particles are promoted by formation of hydroxides metal with a large surface area. The combination of electrocoagulation process with powder marble having a specific surface area of 3.32 m².g⁻¹, and median pore diameter of 162.2 nm [1] accelerates COD elimination.

**Effect of powdered marble concentration**

Figure 4 shows a comparison of chromium removal efficiency evolution for both processes simple EC and coupled EC/ES at different concentrations of powdered marble varying from 6 to 12 g/L. In compared to the simple EC technique, the additional 6 g/L ES to the electrocoagulation cell increased chromium removal from 50% to 60%. This percentage was further enhanced with an increase in the adsorbent dose to 99% chromium removal after a time of 100 min. At a dose of powdered marble greater than 10 g/L there was no significant improvement in chromium removal rate.

Figure 4b shows the effect of marble powder dose against time on COD removal. An increase in the marble powder dose from 0 to 12 g/L improves the COD removal efficiency from 70 to 99% for the duralumin electrode within 180 min of treatment.

**pH evolution during treatment:**

The pH variation value has a significant role on the performances of the two processes; electrocoagulation and sorption. Also the change of the pH during the processing is related to the effectiveness [32,33]. Many chemical composition of Al(OH)₃ present in the solution are strongly depending on the pH and Al³⁺ ion concentration in the medium [34].

The figure 5 reveals the pH variation of the tannery wastewater during the EC and EC/PM processes. The initial pH of the electrocoagulation process was 3.81, which correlates with the original pH of the tanning wastewater; however the original pH of the EC/PM processes was 4.61. The marble powder waste consists mainly of calcite (CaCO₃). As the dissociation of this calcite (as a poorly soluble salt mineral) induces OH generation, the pH of the suspension increases [3].
Figure 4: Effect of adsorbent concentration on the percentage of removal (operating time=120min, current density=200A/m²).

Figure 5: pH value variation over the processes of EC and EC/PM.

Furthermore, the removal of ions may be also hindered at lower pH due to the solubility of PM, which consists mainly of CaCO₃ and MgCO₃. It was evident that the removal of Cu(II) and Cr(III) ions is pH-dependent. At lower pH values, the protonation of functional groups on the surface of the MW is favored leading to lower metal uptake [24].

In both cases, the pH increases continuously and stabilizes after 90 min. During EC, the final pH is 5.5, whereas during EC/PM coupling, the pH increase was observed up to 7.

Impact of electrolysis time during the treatment

Regarding the adsorption, the figure 6a analyses the evolution of chromium removal efficiency in accordance to the time; an increase in chromium removal percentage is noticed with the enhancement of contact time, achieving almost 99% of removal rate at 30 min for powdered marble; this is corresponding to 261 g of chromium removed per kg of adsorbents respectively [1].

Moreover, as shown in figure 6b. The impact of electrolysis time on the chromium removal was investigated in the range 5-360 min at a density of 200 A/m². As the results indicate, the chromium removal efficiency is boosted with electrolysis time augmentation. Practically 99% of chromium removal content was attained after 360 min of electrocoagulation, the reason behind this behavior can be the generated amount of aluminum oxides being much higher over time.

Adding natural powdered marble to the electrocoagulation cell contributed a faster chromium removal. 100% of the chromium content was removed after 100 minutes. The greater improvement in chromium removal after adding the bio-adsorbent is due to that the system underwent both reactions simultaneously, electrocoagulation and also the adsorption process. Durmaz and Çiner have reported Maximum COD and TSS removal achieved are 49% and 42%, respectively with aluminum electrocoagulation at 60 min electrolysis time [35].

Similar results are reported by Elabbas S, et al. using electrocoagulation and eggshell. The maximum uptake of chromium ions was obtained at lower current densities of 200 A/m², operating time of 110 min and with the eggshell dose of 12 g/L.

Energy consumption

In this study, we deal with a specific case of highly concentrated effluents, therefore the energy consumption was calculated in terms of kWh per kg of chromium eliminated to analyze the positive effect
possible. It is estimated using the following equation 4:

\[
C_{t} = \frac{C_{0} \cdot t}{U} + \frac{I \cdot t}{V}
\]

where:
- \(U\) is the cell voltage measured during the electrolysis (V),
- \(I\) the applied electrical current (A),
- \(t\) the current time of treatment (min),
- \(V\) the reactor volume (L),
- \(C_{0}\) and \(C_{t}\) are the initial chromium concentration and the concentration at time \(t\) (in mg/L).

Figure 7 investigated the energy consumption corresponding to Cr(III) content removed from chrome tanning wastewater treated with simple electrocoagulation and EC/PM coupling. For both treatments, the energy consumption increases with higher percentage of chromium removed [36].

The addition of powdered marble reduces the electrical energy consumption by 50 to 70% compared to EC and improves the treatment rate to reduce the metal ion concentration below the legally acceptable levels.

The optimization of the EC process and energy consumption was accomplished by lowering the current density and treatment time values. Many researchers have tried to reduce energy consumption in EC process by its combination with electro-Fenton processes [37], the transition from direct current to alternating current [38], and by coupling the process with advanced ozone oxidation system [39].

Conclusion

The funding has demonstrated that the removal of chromium(III) from chrome tanning with aluminum electrodes by electrocoagulation and adsorption using powdered marble is a practicable and low energy consuming process.

The inclusion of powdered marble as an adsorbent in the electrocoagulation reactor has led to a significant enhancement in chromium removal efficiency with increase of pH and conductivity. This might explain the improved removal efficiency and the lower electric consumption. For pH lower than 4, Al\(^{3+}\) is the predominant species, but does not present coagulant properties. From 4 to 9, different species of ions with coagulant proprieties are formed, usually improving the overall efficiency within this range. However, this highly depends on the heavy metal to be removed and the optimal precipitation pH range. Therefore, metal species solubility is important for determining the optimum pH for precipitation and coagulation. On the other hand, higher conductivity usually improves the process’s efficiency due to higher coagulation species formation by diminishing the solution resistance and lowering the required electric tension to operate for the same intensity. In comparison with conventional techniques, the coupling process provided faster chromium removal at lower current densities, operating time, and power consumption. Optimal conditions were determined to be an adsorbent dosing rate of 12 g/L, a current density of 200 A/m\(^2\) and a contact time of 100 minutes.

It has been shown that the EC/PM coupling technique for chromium removal is significantly more economical than the conventional EC.
technique due to the noticeable reduction in energy consumption and adsorbent dose.

The main advantage of electrocoagulation and adsorption coupling method is its ability to treat simultaneously a wide range of type of pollutants including organic matter, heavy metals but their drawbacks are that they cause acidification of the treated water and the production of large quantities of sludge. We have chosen to work with the wastewater samples from a chromium tanning tank in order to regenerate the chrome(III) and allowing it to be reused.

Acknowledgements

This work has been conducted in the frame of the “project of the Pole of Competence on Water and Environment” supported by French-Morocco cooperation (Project MESRSFC/SCAC (Recherche) 2012) (2012-2014).

References


