



ELECTROCOAGULATION TREATMENT OF TANNERY WASTEWATER

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ABSTRACT: The presence of chromium and organic compounds in the effluents tannery is an important issue in industry. The aim of this study is to propose a new technical process to removing trivalent chromium and organic compounds from tannery wastewater as a possible alternative to the conventional chemical methods. Electrocoagulation technique with aluminium sacrificial anode was used to treat this type of wastewater. The effect of current density and the loading charge were studied in an attempt to achieve a higher removal capacity. Results obtained show that the charge loading was the only variable that affected the treatment efficiency significantly. The analysis of the residual chromium by atomic absorption spectrophotometer and the measuring of the COD of the treated effluents show that electrocoagulation technique is found to be quite effective and is highly competitive as an alternative chemical method for treating tannery wastewater.

Key Words: Electrocoagulation, Chromium, Tannery wastewater, Chemical oxygen demand.

RESUME: La présence de chrome et des produits organiques dans les effluents des tanneries est un problème majeur dans l'industrie. Le but de cette étude est de proposer une nouvelle technique d'élimination de chrome trivalent et des composés organiques des eaux usées des tanneries comme étant un alternatif des méthodes chimiques connues. La technique d'électrocoagulation qui utilise une anode soluble d'aluminium est utilisée pour traiter ce type d'eaux usées. L'influence de la densité de courant et de la quantité de charge est étudiée afin d'atteindre une capacité d'élimination élevée. Les résultats obtenus montrent que seulement la quantité de charge affecte l'efficacité du traitement. Les analyses du chrome résiduel par absorption atomique et la mesure de la DCO des rejets traités montrent que l'électrocoagulation est une technique efficace et peut remplacer les méthodes chimiques classiques utilisées pour traiter les eaux usées des tanneries.

Mot clés : Electrocoagulation, Chrome, Eaux usées des tanneries, Demande chimique en oxygène.

1. INTRODUCTION:

Liquid wastes discharged by the industrial activities is often contaminated by a variety of solutes which are classified as pollutants and have negative effects on the water environment. For example, the manufacturing processes for leather tanning require considerable quantities of wastewater which contains trivalent chromium Cr (III) and many organic compounds which have² been known to cause several health problems to animals and human beings. The undesirable effects of the chromium ions on all the elements of ecosystem lead to the adsorption of coercive norms concerning their rates in wastewaters [1]. On the other hand, the national and international

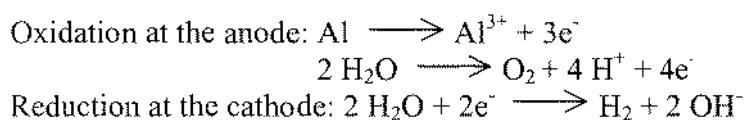


regulations tend to become more strict and constraining, so that most of the countries are now concerned with environment [2].

Various techniques have been employed for the treatment of heavy metals and especially the chromium in the tanning baths, like ions exchange on some resins [3], the electrochemical treatment [4, 5] and precipitation [6, 7]. The precipitation is most widely applied among these techniques and is considered to be the most economical. However, this technique produce a large amount of precipitate sludge that requires further treatment. The ion-exchange can effectively reduce chromium ions, but their use was limited due to a number of disadvantages such as material and operational high cost in addition to the limited pH range for the ion-exchange resin.

The purpose of this research was the develop an alternative method for the elimination of chromium ions and organic pollutants from the tannery wastewaters. We report here the use of the electrocoagulation technique for the treatment of this industrial effluents. The electrocoagulation is a simple and efficient method where the flocculating agent is generated by electro-oxidation of a soluble anode, generally made of iron or aluminium. In this process, the treatment is done without the addition of any chemical coagulant or flocculant thus reducing the amount of sludge which must be disposed [8].

The electrocoagulation process consists in generating, in the aqueous solution, some metallic ions by using of soluble anodes (iron or aluminium). The major reactions likely to take place with aluminium are described as follows:



During electrolysis the aluminium ions formed by the oxidation of aluminium anode react with hydroxyl ions to form $\text{Al}(\text{OH})_3$. The aluminium hydroxide flocks act as adsorbents for pollutants (metal ions, organic molecules....) and so eliminate them from the solution. The gas bubbles of oxygen and hydrogen which are created respectively at the anode and the cathode induce flotation of the flocks. The mechanism of pollutants removal by electrocoagulation at a sacrificial aluminium anode is quite complex. Indeed, it is generally believed that there is a combination of the processes of electrocoagulation and electroflotation. However, this does not exclude the occurrence of a direct electrochemical oxidation or reduction of the pollutant at the electrodes [8]. In this process, the treatment is done without the addition of any chemical substances.

The electrocoagulation technique has been successfully used to treat oil wastes, where removal efficiencies as high as 99 % were achieved [9-11]. A similar success was obtained in treating dye-containing solution [12-15], restaurant wastewater [16], potable [17] and urban wastewater [18].

In this work, the efficiency of electrocoagulation in removing chromium from wastewaters of tannery unit and the reduce of its chemical oxygen demand (COD) was reported. The effect of the current density and the loading charge were studied to optimise the operational conditions.

2. EXPERIMENTAL STUDIES:

The electrocoagulation treatment was carried out using wastewater sample, collected from a tannery unit. The characteristics of wastewater were: $\text{pH} = 3.5$; $\text{COD} = 2400 \text{ mg.L}^{-1}$ and $[\text{Cr}^{3+}] = 1140 \text{ mg.L}^{-1}$. The electrodes used in this study consisted of aluminium plates (100 x 50 x 0.5 mm) of 99% purity, purchased from Prolabo society. A 200 ml samples of a wastewater collected from a tannery unit were electrochemically treated in an electrocoagulation glass cell (thermostatted jacket) fitted with three parallel aluminium electrodes spaced by 5 mm and dipped in the wastewater.

The electric power source was a Radiometer potentiostat/galvanostat of the type DEA 332 interfaced to an IBM personal computer used in galvanostatic mode to supply a constant current. The electrodes were connected in such manner that the central electrode functioned as sacrificial anode, while the two others as cathodes. The current intensity values were less than 1.25 A.

To follow the progress of the treatment, samples were periodically taken from the reactor, filtrated to eliminate the flocs formed during the electrolysis, and residual concentrations of chromium ions (Cr^{3+}) ions were determined by atomic absorption spectrophotometry (Perkin Elmer, model 3100, USA).

Chemical oxygen demand (COD) was measured using COD reactor and direct reading spectrophotometer (DR/2000, HACH, USA).

3. RESULTS AND DISCUSSION:

The wastewater samples of tannery unit were electrochemically treated in the electrocoagulation glass cell at fixed operating conditions. The working parameters of the electrolysis were controlled for each kinetic experiment, so that several series of kinetic experiments could be performed for various given values of the current density: 10, 15, 20 and 25 $\text{mA}\cdot\text{cm}^{-2}$ in order to optimise the operational conditions.

In this section, we present the kinetic elimination of chromium ions at fixed current density ($J = 10 \text{ mA}\cdot\text{cm}^{-2}$). Figure 1 shows that the concentration decreased with increasing treatment time. For example, after 50 minutes of treatment, 62% of the initial concentration was eliminated. This result shows that the electrocoagulation technique can be successfully used to separate the chromium from residual water of tanneries.

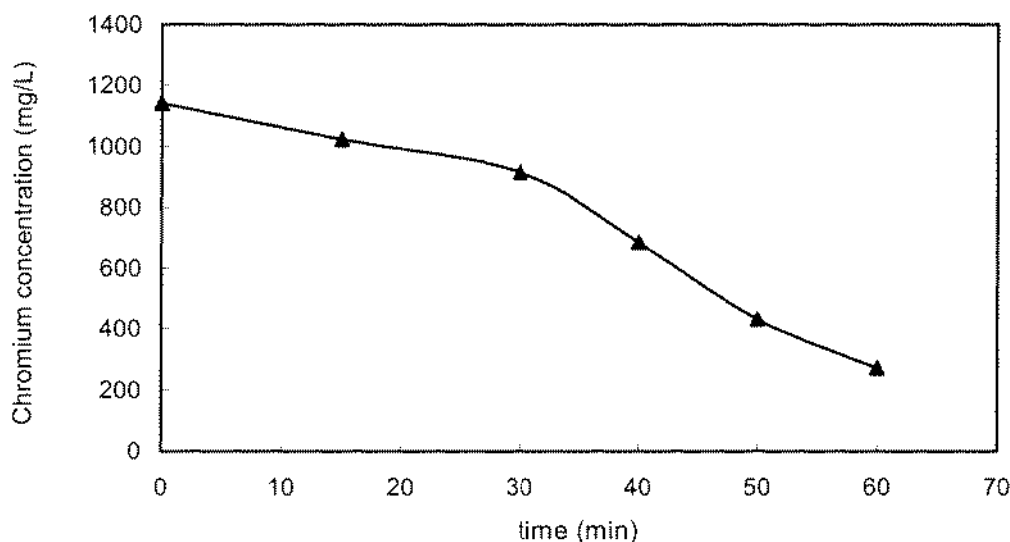


Figure 1: Effect of the treatment time on the residual concentration of chromium ions removal. Original concentration of Cr^{3+} 1140 $\text{mg}\cdot\text{L}^{-1}$, $J = 10 \text{ mA}\cdot\text{cm}^{-2}$, anode surface $S = 50 \text{ cm}^2$.

3. 1. Effect of current density and charge loading:

Many studies have reported that current density can influence the treatment efficiency of the electrochemical process [18]. The efficiency of separation process was higher when the gas bubbles



are as small as possible [19]. On the other hand, it has been established that the bubbles size decreases with increasing current density. This conclusion was made based on the experimental conditions where the charge loading was also changed. Therefore, it remains unclear whether the treatment efficiency was affected by current density or by charge loading.

In the present study, the current density effect was investigated at the same charge loading by varying the applied current. The result presented in Fig. 2 show that the current density had no significant effect on the chromium removal in the large range from 10 to 25 mA.cm⁻² at a fixed charge loading of 1500 C. This indicates that it is not the current density but the charge loading that really affects the treatment efficiency.

Table 1: Effect of current density on chromium ions removal. Original concentration of Cr³⁺ 1140 mg.L⁻¹, charge loading Q = 1500 C, anode surface S = 50 cm².

J (mA.cm ⁻²)	10	15	20	25
Removal efficiency (%)	62	64	59	61

The mechanisms of electrocoagulation for wastewater treatment are very complex. It is generally believed that there are three other possible mechanisms involved besides electrocoagulation; i. e., electroflotation, electrochemical oxidation and adsorption [16]. Nevertheless, all the mechanisms highly depend on charge loading.

In this section we study the effect of the charge loading on the effective removal capacity of chromium. It appears from the results shown in figure 3 that the residual concentration of chromium after an electrocoagulation treatment decreased with charge loading. After a charge loading beyond 2200 C, the chromium removal efficiency was about 90 %. Beyond this optimum charge loading, the residual concentration of Cr³⁺ reaches a plateau and remains approximately constant. It is clear that the increase of charge loading beyond this value, have no effect on removal efficiency.

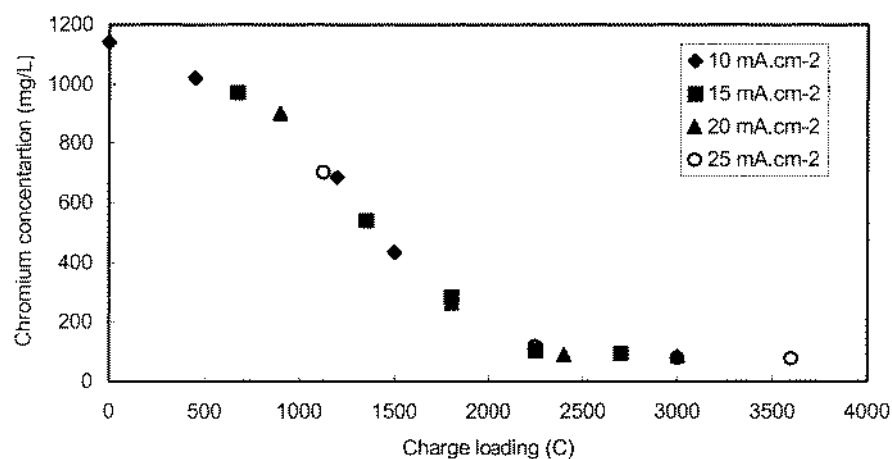


Figure 2: Effect of charge loading on chromium ions removal. Original concentration of Cr³⁺ 1140 mg.L⁻¹, anode surface S = 50 cm².

In conclusion, the separation of chromium ions from tannery wastewater by electrocoagulation technique depends only on the charge loading.

3. 2. Chemical oxygen demand (COD) reduction:

The electrocoagulation technique seems to be an ideal choice for removal the chromium in the tannery wastewater. In this section, we focus our research to study also the elimination of organic compound by the measurements of the COD reduction of wastewater treated electrochemically at pH=3.5. Fig. 4 illustrates the effect of charge loading in the COD reduction. The initial COD value (2400 mg.L^{-1}) decreased to less than 360 mg.L^{-1} with a charge loading $Q=2400 \text{ C}$ corresponding to a removal efficiency about 85%. Beyond that charge loading, the chemical oxygen demand of the treated wastewater remains approximately constant because the flocks surface was saturated by the organic compounds. The electrocoagulation treatment of tannery wastewater evidence the effective removal of both chromium ions and dissolved organic compounds present in the tannery wastewater.

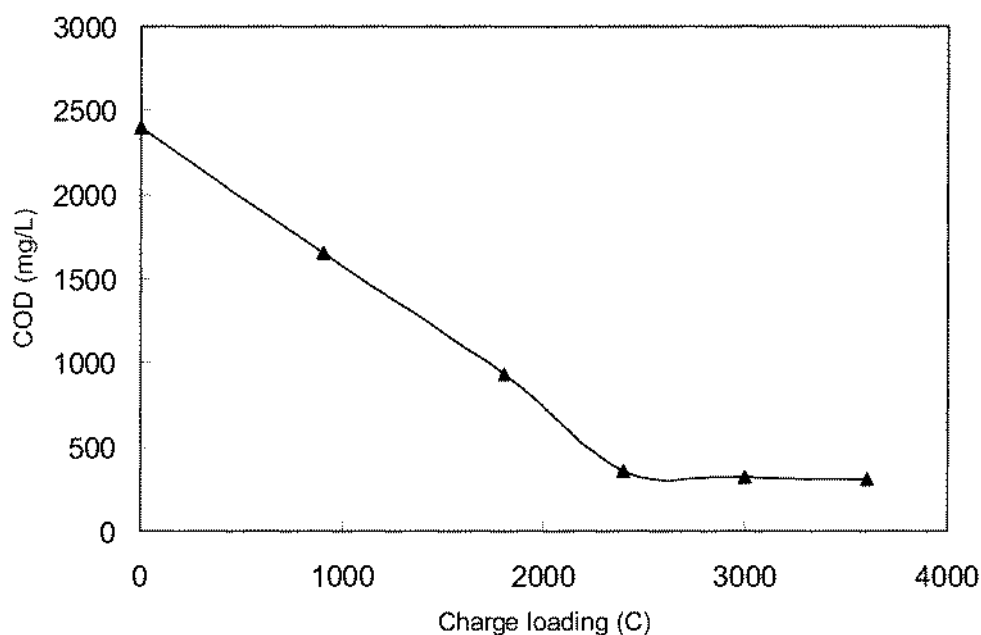


Figure 4: Effect of charge loading on COD removal. $J = 10 \text{ mA.cm}^{-2}$, anode surface $S = 50 \text{ cm}^2$.

4. CONCLUSION

The electrocoagulation is a feasible process for treating the tannery wastewater, characterized by high chromium concentration. Aluminium electrodes are used in this application. In this study, the influence of the current density and charge loading was studied. The results show that the current density has not effect on the pollutant removal efficiency and the charge loading is the most important operational variable. The results obtained after the electrocoagulation treatment at a fixed working conditions showed that this technique could be used as a possible alternative to conventional coagulation technique already used in the tannery unit.

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