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Eggshell adsorption process coupled with electrocoagulation for improvement of chromium removal from tanning wastewater

*Saliha Elabbas ^{a,b}, Nawel Adjeroūd^c, Laila Mandi ^{a,b}, Fatima Berrekhis ^d, Marie Noelle Pons ^e, Jean Pierre Leclerc ^e, Naaila Ouazzani ^{a,b},

^aLaboratoire Eau, Biodiversité et Changement climatique, Faculté de Sciences Semlalia, BP2390, Université Cadi Ayyad, Marrakech, Morocco.

^bCentre National d'Etude et de Recherche sur l'Eau et l'Énergie (CNEREE), BP511, Université Cadi Ayyad, Marrakech, Morocco.

^cLaboratoire de Biomathématiques, Biophysique, Biochimie, et Scientométrie, Faculté des Sciences de la Nature et de la Vie, Université de Bejaia, 06000 Bejaia, Algérie.

^dEquipe de Physico-chimie des Matériaux, École Normale Supérieure, Université Cadi Ayyad, BP2400, 40000 Marrakech, Morocco.

^eLaboratoire Réactions et Génie des Procédés, (UMR CNRS 7274), Université de Lorraine, 1 rue Grandville, 54001 Nancy cedex, France.

***Corresponding author**

E-mail: salihaelabbas@gmail.com

Abstract:

The present work deals with the removal of trivalent chromium from chrome tanning effluent in a batch stirred electrocoagulation cell with aluminum alloy coupled with biosorption using Eggshell (ES). Effects of operating time, current density and adsorbent dose have been investigated. Compared to a simple electrocoagulation (EC), the concentration of chromium using a coupled or combined EC/ES process has been successfully reduced to environmentally acceptable levels even with a concentrated tanning effluent (3.21 g/L). The maximum uptake of chromium ions was obtained at lower current densities of 200 A/m², at operating time of 110 min and with the eggshell dose of 12 g/L. The energy consumption during the coupled electrocoagulation/adsorption process was also reduced comparatively to the simple electrocoagulation. A pseudo-second order chemical sorption model satisfactorily described kinetic data. The water treated by this technique, respects the strengths Moroccan standards and the method was found to be highly efficient and relatively fast compared to existing conventional techniques.

Keywords: chromium tanning, coupled electrocoagulation/adsorption, aluminum alloy, eggshell, energy consumption.

1. Introduction

The manufactures of leather have been an important activity since antiquity; it is a transformation process of animal hides into leather involving various chemical and mechanical operations to clean the skin of meat, fat and hair [1].

Chromium tanning process is one of the most common methods for processing hides. However, these tanning processes pose a threat to the environment because they carry variety of organic compounds and are very loaded with chromium reflected by high values of chemical oxygen demand (COD) and chromium III discharged into receptor media [2]. The chemical oxidation of Cr (III) to Cr (VI) as a consequence of natural bio-transformations in the environment is a source of possible mutagenic and carcinogenic hazards [3, 4]. Driven by this concern, several methods have been tested to remove Cr and other pollutants from a tannery wastewater. **Meunier et al** [5] have reported chromium removal of more than 99% with an initial concentration of 100 mg/L by using either electrocoagulation or chemical precipitation. **Keerthi et al** [6] have tested a hybrid membrane bioreactor with a COD removal of 72.69% from wastewater with an initial COD concentration at 1600 mg/L. Through the use of a cation exchange resin **Sahu et al** [7] reported to remove 96% of Cr (III) from from a 500 ppm Cr waste tannery solution (pH=2,7). **Song et al** [8] have obtained a COD removal of 30–37% with an initial concentration of 3300 mg/L from a tannery wastewater by coagulation process. Using infiltration percolation, **Tiglyene et al** [9] have reported that a total chromium undergoes an overall removal of 98% with an initial concentration of 1230.5mg/L. Finally, phytoremediation has been investigated too for treatment of such waste, as done by **Mandi et al** [10]. **El-Khateeb et al** [11] have reported The chromium concentration was reduced at 99.99 % from tannery waste water using electrocoagulation process assisted by chemical oxidation with an initial concentration of 3,844 mg/L but this concentration appears very small compared to the initial concentration treated in this work. Among these methods, the electrocoagulation process provides a simple, reliable, and cost-effective method for the treatment of tannery wastewater concentrated of chromium without the need for additional chemicals, and thus, without the production of secondary pollution [12]. The main advantage of electrocoagulation is its ability to treat simultaneously a wide range of type of pollutants as such organic matter, heavy metals, dyes, minerals and several others types of effluents [13, 14, 15].

In addition, Adsorption has also been used for treatment of tannery effluents [16, 17]. **Fabbricino et al [2]** have reported 90% of Cr (III) removal from an initial concentration of 6100 mg/L using adsorption in an environment friendly cycle with recovery of the metal. **Fahim et al [18]** reported adsorption of nearly 99% of the chromium from tannery wastewater with initial concentration 5500 mg/L using activated carbon obtainable from sugar processing industries. Using activated carbon prepared from date palm waste **Nayl et al [19]** have reported that COD removal percentage of 95.4 and 92.8% for BOD was obtained with carbon dosage of 0.1 g/100 mL of solution. Using Wollastonite Ceramic/CuO Nano-Composite. **Ammar et al [20]** have reported cadmium ions removal reached 98.88% with initial concentration of 25 mg/L. The aim of the present study was to investigate the treatment of highly polluted traditional tannery wastewater by eggshell with initial concentration 3.21g/Cr (III).

Moreover, in the pursuit of improving the efficiency of Cr treatment, several combination processes have been studied in order to optimize the treatment efficiency, the energy consumption and the electrolysis time. **Kebir et al [21]** have reported the best chromium (VI) removal when using visible light photocatalysis coupled with the adsorption on an agricultural farm plant (Sauge). For 150 mg/L, as initial amount chromium of this tannery wastewater, the removal yield increased from 45% (only by or using biosorption) to 82.6% at lower time by the coupling process. **Durante et al [22]** have studied advanced oxidation processes coupled with electrocoagulation for the exhaustive abatement of Cr-EDTA. The results reported that electrocoagulation with ozonization pretreatment would be a suitable means of decontamination of Cr from synthetic effluents. **Pereira de Carvalho et al [12]** have studied banana peel adsorption coupled with electrocoagulation for methylene blue removal; they showed that the efficiency removal was achieved to approximately 99%. Based on the high removal efficiency, short contact time and low energy consumption, **Vivek Narayanan and Ganesan [23]** have tested the coupling electrocoagulation and adsorption on granular activated carbon for chromium removal with efficiencies as high as 97%. A similar success was obtained for the same combination when treating acid dye from aqueous solutions [24].

In our knowledge, excepting some studies done by **Ouaissaa et al [25]** where they have tested the electrocoagulation combined with activated carbon adsorption, there is no other works investigating the coupling electrocoagulation and adsorption for removing Cr from tanning effluents.

Furthermore, there is no published work dealing with combination between aluminum alloy electrocoagulation and adsorption using naturals and low cost materials.

In the present paper, it was proposed to apply a low-cost natural sorbent (Eggshell) in aluminum electrocoagulation reactor for chromium removal from tannery wastewater and comparing the combined processes with simple electrocoagulation. The effects of the current density, treatment time and adsorbent dose on the removal efficiency were explored and the energy consumption was also discussed. In addition, the pseudo-first order and pseudo-second order kinetics models were tested on both simple EC and EC/ES coupling processes.

2. Experimental

2.1. Effluent samples

The samples used in this work were obtained from a chromium-tanning tank in a semi traditional tannery in the Marrakech city having a capacity of treatment of about 500 hides /day. Generally, the main inorganic contaminant of tannery wastewater is chromium with a concentration range of 0.5-7 g/L [16, 17, and 26].

Table 1 resumes the characteristics of the tested raw wastewater.

SD Standard Deviation

2.2. Experimental set-up

The electrocoagulation treatment was carried out in a closed system under solution recycle functioning as a batch system. The electrocoagulation cell, consisting of two identical polymethylmethacrylate (Perspex) halves was 20 cm long, 10 cm wide and 5 cm thick. Alloy aluminium plates ($15 \times 7 \text{ cm}^2$) acting as facing electrodes, were imbedded in the polymeric halves, as described by **Elabbas et al. [17]**. The active electrode surface was first mechanically polished under water with abrasive paper, rinsed with distilled water and dried prior to immersion in the wastewater. The obtained surface area of the electrodes was 106 cm^2 . The gap between anode and cathode was maintained at 2 cm. The electrodes were connected to a DC power supply (AFX 2930 SB) providing current densities in the range of 200-400 A/m^2 . The current was kept constant during each run. The schematic diagram of the complete electrocoagulation system is shown in Figure 1.

Fig.1. Experimental set-up.

2.3. Preparation of the adsorbent

The adsorbent eggshell used in this study was coming from local cafeterias waste. The collected eggshell is just washed with distilled water to remove the adhered particles then it was dried at the ambient atmosphere for several days. The dried slices were ground, sieved and stored in a dessicator for further use. The size of the seeds of the eggshell used is between 1mm and 2mm [1].

2.4. Batch Electrocoagulation /Adsorption coupling process

The coupling experiment was investigated as follows: tested amounts of eggshell were mixed with 2L of tannery effluent in the electrocoagulation cell. All experiments were conducted at ambient temperature and stirred at 200 rpm. The solution was continuously circulated in the flow circuit by means of a peristaltic pump at 50 ml /min. Aliquots were sampled from the reservoir, at regular time intervals (every 10 minutes) and then filtered (0.45 µm pore size) prior to analysis by atomic absorption spectrophotometer (AAS; Thermo scientific iCE 3300, Germany). The chromium calibration curve was prepared using standard solutions from Prolabo (France). pH was continuously measured with a multi-parameter instrument (Consort C931, Turnhout, Belgium). The Fourier transform infrared spectroscopy (FTIR), (JASCO FT IR-4600) was used to evaluate bonding patterns of compounds present in Eggshell (ES), in sludge after Electrocoagulation and Electrocoagulation/ adsorption coupling processes.

The chromium removal percentage (R %) was calculated by the following formula:

$$R(\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

Where C_0 is the initial concentration of metal (mg/L) and C_f is the equilibrium metal concentration (mg/L).

3. Results and discussion

3.1. Characterization of eggshell

The results of the BET method showed that the average specific surface area of the eggshell is 0.38m²/g. In addition, the average particle size and the median pore diameter of eggshell are 158.64 nm and 144.5 nm respectively [1].

3.2. Effect of electrolysis time on treatment

As seen in Fig.2, the effects of electrolysis time on chromium removal were investigated in the range of 5-360 min at a current density of 200A/m². As indicated, the chromium removal efficiency increased with an increase in electrolysis time. Almost 99% of chromium removal was achieved after 240 min by the electrocoagulation process; this behavior could be explained by the much higher amounts of aluminum oxides generated over time.

The addition of the natural material of the eggshell in the electrocoagulation cell resulted in a faster removal. 99% of the chromium was removed at 110 min. The highest enhancement of chromium removal by adding the eggshell can be attributed to the fact that the system took benefit from both reactions simultaneously, electrocoagulation and adsorption processes. Our previous experiments on Cr adsorption onto eggshell showed Cr removal efficiency reaching nearly 99% but after 840 min contact time [1].

Fig. 2. Effect of contact time on Cr percentage removal of the tannery wastewater during the EC and EC/ES coupling processes (eggshell dose = 20g/L, current density = 200A/m²).

3.3. pH evolution during treatment

The pH of the solution has an important role in the performance of the electrocoagulation and the sorption processes and its change during the treatment affects the treatment efficiency [27, 28] The different forms of Al (OH)₃ present in the solution greatly depend upon the pH and concentration of Al³⁺ ions in the media [29].

Fig.3 shows the pH variation of the tannery wastewater during the EC and EC/ES coupling process, with an eggshell dose of 20 g/L at current density 200A/. The initial pH in the case of EC was 3.81 corresponding to initial pH of tannery wastewater but the initial pH of EC/ES coupling process was observed to be 4.61. This difference of initial pH in EC/ES coupling process can be seen as a result of addition of eggshell waste (mainly composed of CaCO₃) to which the dissolution induces a formation of OH⁻ increasing tannery wastewater pH according to:

Otherwise, with the K_s value of Cr(OH)₃ as 10⁻³¹, the pH value for the precipitation limit of chromium hydroxide at the initial chrome III concentration 3.21g/L is calculated as 4.08. This

value is higher than the initial value of pH of EC/ES coupling process indicating that the precipitation as $\text{Cr}(\text{OH})_3$ would take place.

So, the removal of Cr(III) might occur through more than one type of mechanism: adsorption and heterogeneous precipitation in the form of hydroxides, carbonates and hydroxycarbonates composites [30]. As consequence, the initial pH after the addition of the eggshell improves the Cr removal efficiency in comparison to the simple EC.

During the treatment, in both cases, the pH increased continuously until 110 min where it stabilized to a final value of 5.5 for EC and 6.5 for coupled EC/ES process. However, the pH increase is mainly attributed to the production of hydroxide ions (OH^-) that are continuously generated from water reduction at the cathode as given by equation (5).

But Al^{3+} products at the anode oxidation were dissolved and their hydrolysis products slow down the rise of pH. Secula et al [24] attributed this difference to the fact that the simply EC process is only slightly affected by low acidic pH values especially during the initial stage of the process. The addition of eggshell mainly consisted of CaCO_3 can act as an excellent acid-neutralizing agents (Eq. 2, 3 and 4) and elevate the pH value to enhance the ion exchange and adsorption and to cause surface precipitation of chromium hydroxide [31].

As consequence, the combination of both processes reduces treatment time and improve the efficiency of chromium abatement.

Fig.3. pH evolution of the tannery wastewater during the EC and EC/ES coupling processes (operating time = 120min, current density = 200A/m² and eggshell dose = 20g/L)

3.4. Effect of current density

Cell current is an important parameter in the electrochemical processes. The amount of current density determines the coagulant production rate, and adjusts the rate and size of the produced bubbles, and hence affects the growth of flocs [17].

In this study, three values of current density, 200, 300 and 400 A/m², were chosen to be applied during simple EC (Electrocoagulation) and EC/ES (Electrocoagulation and adsorption) coupling processes to evaluate their effect on chromium removal.

Fig.4 shows the effect of current density on Cr (III) removal versus time by both processes: EC (Fig. 4a) and EC/ES coupling process (Fig. 4b).

In the simple electrocoagulation (Fig.4a), the chromium removal efficiency increased with an increase in current density, with yields of 87%, 95.4% and 99.7% achieved after 240 min at current densities of 200, 300, and 400 A/m² respectively. This can be attributed to the increase in the amount of Al (OH)₃ being generated in situ whose flocs behave as an adsorbent for chromium ions. Besides the precipitation of the metal hydroxides at the cathode, this high removal efficiency is attributed to the coprecipitation of Cr (III) with aluminum hydroxides due to pH increase [17].

With respect to the simple EC results, the addition of 20 g/L of eggshell as optimum dose [1] in the electrocoagulation cell resulted in faster chromium removal (Fig.4b).The highest enhancement of chromium was only obtained for 80 min. An increase in current density from 200 to 400 A/m² yields to an improved efficiency of chromium removal from 97 to more than 99 %.

The rapid chromium removal can be attributed to the synergetic effect of both reactions; the EC effect and the adsorption process. According to these results, the lower current density was chosen as the optimum density in order to avoid high energy consumption.

Fig.4. Effect of current density on percentage of chromium removal of the tannery wastewater by both processes: EC (a) and EC/ES coupling process (b). (eggshell dose = 20g/L).

3.5. Effect of eggshell dose

Fig.5 compares the evolution of chromium removal efficiency for simple EC and EC/ES coupling process at different eggshell doses ranging between 10 and 20 g/L during 120 min.

Compared to the simple EC technique, the addition of a dose of 10 g/L of ES in the electrocoagulation cell resulted in a slight increase of chromium removal. The low increase may be attributed to the insufficient eggshell amount added face to the chromium present in the solution. However the addition of a dose of 12 g/L of ES has increased the chromium removal at more than 99% instead of 63% observed in the case of the simple EC after the electrolysis time of 110 min. The results could be attributed to the increase of more available adsorption surface area and sites [27]. Further increase of Eggshell dose beyond 12 g/L leads to a steady

(or stable) removal efficiency, because almost all the ions had been bound to the eggshell or to the aluminum flocs and to the establishment of equilibrium between the ions.

Fig. 5. Effect of adsorbent concentration on Cr removal of the tannery wastewater (operating time = 120min, current density = 200A/m²).

3.6. Determination of equation rate constant

In order to investigate the kinetics models of Cr(III) ions removal by the conventional electrocoagulation and the coupling processes, the linear pseudo-first order and pseudo-second order models were tested to fit the experimental data.

The pseudo first-order model can be expressed as equation 6:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

Where q_e (mg g⁻¹) is the amount of chromium adsorbed per unit mass of the adsorbent at equilibrium, q_t (mg g⁻¹) is the amount of a chromium absorbed per unit mass of the adsorbent at current time t (min), and k_1 (min⁻¹) is the equilibrium rate constant of the pseudo-first-order model. The pseudo-second-order rate is given by equation 7 as [32] :

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where K_2 is the rate constant of the pseudo-second-order equation (g mg⁻¹ min⁻¹).

The experimental kinetic data were adjusted according to the indicated models and the coefficients of correlation as well as the rate constants of both models are given in Table 2. The values of coefficient of determination R^2 for the pseudo second order is relatively high (>0.99). This fact indicates that the second-order equation model provided the best correlation with experimental results and the sorption of chromium follows the pseudo-second-order kinetic model.

As shown clearly in table 2, the rate constant (k_2) increases from $6.8 \cdot 10^{-6}$ to $3.13 \cdot 10^{-5}$ when the dose of eggshell increases from 0 to 12 g/L but above this dose the rate constant remains stable.

3.7 Energy consumption

The electrical energy consumption is a significant parameter to the application of the process, mostly because it is related to the operating cost [33, 34].

The energy consumption was calculated in terms of kWh per kg of removed chromium to analyze the possible positive effect in this specific case of very concentrated effluents. It is estimated using equation 8):

$$EEC \left(\frac{kWh}{kg} \right) = \frac{UIt}{(C_0 - C_t)V} \quad (8)$$

Where U is the cell voltage measured during the electrolysis (V), I the applied electrical current (A), t the current time of treatment (h), and V the reactor volume (L), C_0 (g/L) and C_t (g/L) are the initial chromium concentration and the concentration at time t respectively

Fig.6 shows the energy consumption per kg of Cr(III) removed from the chrome tanning wastewater treated by the simple electrocoagulation and the EC/ES coupling process versus electrolysis time. The eggshell addition leads to a reduction of the electrical energy consumption compared to simple EC process.

In the case of the EC, the plot indicated a rapid initial reduction of the energy consumption. This highest energy consumption will be related to the solution pH value in the initial stage of the process in contrast to EC/ES process, the addition of eggshell elevated the wastewater pH value consequently the energy consumption is lower. After 2 h of the wastewater treatment, the chromium removal efficiency and the electrical energy consumption values were 99.96%, 1.09 kWh/kg and 62.4%, 1.67 kWh/kg for EC/ES and EC processes, respectively. The coupling process is more suitable from economical point of view since the required time is lower and the chromium removal efficiency is higher than those of the simple EC process. The decrease of the specific energy consumption is related to the efficiency of the coupling process on chromium removal efficiency; the greater the chromium removal efficiency, the lower the specific electrical energy consumption per kg of the removed Cr.

Fig.6. Specific energy consumption after treatment by simple EC and EC/ES coupling process of tanning wastewater.

3.8. FT-IR studies of sludge

In order to determine the functional groups responsible of Cr(III) adsorption, the infrared spectra of the samples eggshell powder, EC process and EC/ES coupling process sludge were recorded in the range 400 – 4000 cm⁻¹ and they are presented in Fig.7. The characteristic peaks of the eggshells powder are 1395.25 cm⁻¹, 870.70 cm⁻¹ and 515.87 cm⁻¹ (fig7,a). They were attributed to the vibration of C-O bond of carbonate (CO₃) groups. However, the spectra of EC (fig7,b) and EC/ES (fig7,c) processes sludge showed that a chemical change occurred and the CO₃ ions disappeared from the They exhibit a number of absorption peaks, indicating the complex nature of the studied material. The two spectra are similar but in the case of EC process the spectrum exhibits a lower intensity. A board peak was observed at 3382.53 cm⁻¹ which corresponds to O-H stretching vibrations of the physisorbed water [35]. The less intense band at 1602 cm⁻¹ will be attributed to the deformation vibration of the water molecules. At the low-intensity band, the peaks at 1115.5 cm⁻¹ and 606.34 cm⁻¹ correspond probably to the M-OH and O-H stretching modes [36]. Where M is a metal (Cr³⁺ or Al³⁺). From these spectra, it seems that hydroxyl groups are the main functional groups involved in Cr³⁺ bonding. The ability of eggshell to take up Cr(III) suggests the following probable mechanisms : (i) the Eggshell dissolves to release aqueous species (carbonate, calcium, etc.) which probably combined with Cr³⁺ and precipitated in the form of new metal molecules (co-precipitation). (ii) Cr³⁺ was removed by adsorption and through ion exchange process on the surface of Eggshell (iii) Cr³⁺ precipitated as Cr (OH)₃ form.

Fig.7. FT-TR spectra of eggshell powder (a), EC waste (b) and EC/ES coupling process waste (c).

3. Conclusion

From our present study, it was found that the removal of chromium (III) from the chrome tanning using aluminum electrodes by the electrocoagulation/adsorption coupling process using eggshell was feasible and presented low cost process.

The addition of Eggshell, as an adsorbent to the electocoagulation reactor resulted in a remarkable increase in the removal rate of chromium. In comparison to conventional techniques, the coupling process achieves faster removal of chromium at lower current densities, operating time and energy consumption. The optimal conditions were found to be: adsorbent dose of 12 g/L, current density of 200 A/m² and 110 min of contact time. The kinetic followed a pseudo-second order model, as shown from the values of the correlation coefficient. It was shown that the EC/ES coupling technique for chromium removal is much cheaper than the conventional EC technique due to remarkable reductions in energy consumption and adsorbent dose.

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