



**HAL**  
open science

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

Saliha Elabbas, Nawel Adjeroud, Laila Mandi, Fatima Berrekhis, Marie-Noëlle Pons, Jean Pierre Leclerc, Naaila Ouazzani

### ► To cite this version:

Saliha Elabbas, Nawel Adjeroud, Laila Mandi, Fatima Berrekhis, Marie-Noëlle Pons, et al.. Eggshell adsorption process coupled with electrocoagulation for improvement of chromium removal from tanning wastewater. *International Journal of Environmental Analytical Chemistry*, 2020, pp.1-13. 10.1080/03067319.2020.1761963 . hal-02897411

**HAL Id: hal-02897411**

**<https://hal.univ-lorraine.fr/hal-02897411>**

Submitted on 18 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

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

3  
4           \*Saliha Elabbas <sup>a,b</sup>, Nawel Adjeroud<sup>c</sup>, Laila Mandi <sup>a,b</sup>, Fatima Berrekhis <sup>d</sup>, Marie Noelle  
5                   Pons <sup>e</sup>, Jean Pierre Leclerc <sup>e</sup>, Naaila Ouazzani <sup>a,b</sup>,

6  
7           <sup>a</sup>Laboratoire Eau, Biodiversité et Changement climatique, Faculté de Sciences Semlalia, BP2390,  
8                   Université Cadi Ayyad, Marrakech, Morocco.

9           <sup>b</sup>Centre National d'Etude et de Recherche sur l'Eau et l'Énergie (CNEREE), BP511, Université Cadi  
10                   Ayyad, Marrakech, Morocco.

11           <sup>c</sup>Laboratoire de Biomathématiques, Biophysique, Biochimie, et Scientométrie, Faculté des Sciences de  
12                   la Nature et de la Vie, Université de Bejaia, 06000 Bejaia, Algérie.

13  
14           <sup>d</sup>Equipe de Physico-chimie des Matériaux, École Normale Supérieure, Université Cadi Ayyad,  
15                   BP2400, 40000 Marrakech, Morocco.

16           <sup>e</sup>Laboratoire Réactions et Génie des Procédés, (UMR CNRS 7274), Université de Lorraine, 1 rue  
17                   Grandville, 54001 Nancy cedex, France.

18           **\*Corresponding author**

19  
20           **E-mail: salihaelabbas@gmail.com**

21  
22           Abstract:

23           The present work deals with the removal of trivalent chromium from chrome tanning effluent  
24           in a batch stirred electrocoagulation cell with aluminum alloy coupled with biosorption using  
25           Eggshell (ES). Effects of operating time, current density and adsorbent dose have been  
26           investigated. Compared to a simple electrocoagulation (EC), the concentration of chromium  
27           using a coupled or combined EC/ES process has been successfully reduced to  
28           environmentally acceptable levels even with a concentrated tanning effluent (3.21 g/L). The  
29           maximum uptake of chromium ions was obtained at lower current densities of 200 A/m<sup>2</sup>, at  
30           operating time of 110 min and with the eggshell dose of 12 g/L. The energy consumption  
31           during the coupled electrocoagulation/adsorption process was also reduced comparatively to  
32           the simple electrocoagulation. A pseudo-second order chemical sorption model satisfactorily  
33           described kinetic data. The water treated by this technique, respects the strengths Moroccan  
34           standards and the method was found to be highly efficient and relatively fast compared to  
35           existing conventional techniques.

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

### 38 *1. Introduction*

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

42 Chromium tanning process is one of the most common methods for processing hides.  
43 However, these tanning processes pose a threat to the environment because they carry variety  
44 of organic compounds and are very loaded with chromium reflected by high values of  
45 chemical oxygen demand (COD) and chromium III discharged into receptor media [2]. The  
46 chemical oxidation of Cr (III) to Cr (VI) as a consequence of natural bio-transformations in  
47 the environment is a source of possible mutagenic and carcinogenic hazards [3, 4]. Driven by  
48 this concern, several methods have been tested to remove Cr and other pollutants from a  
49 tannery wastewater. **Meunier et al [5]** have reported chromium removal of more than 99%  
50 with an initial concentration of 100 mg/L by using either electrocoagulation or chemical  
51 precipitation. **Keerthi et al [6]** have tested a hybrid membrane bioreactor with a COD  
52 removal of 72.69% from wastewater with an initial COD concentration at 1600 mg/L.  
53 Through the use of a cation exchange resin **Sahu et al [7]** reported to remove 96% of Cr (III)  
54 from from a 500 ppm Cr waste tannery solution (pH=2,7). **Song et al [8]** have obtained a  
55 COD removal of 30–37% with an initial concentration of 3300 mg/L from a tannery  
56 wastewater by coagulation process. Using infiltration percolation, **Tiglyene et al [9]** have  
57 reported that a total chromium undergoes an overall removal of 98% with an initial  
58 concentration of 1230.5mg/L. Finally, phytoremediation has been investigated too for  
59 treatment of such waste, as done by **Mandi et al [10]**. **El-Khateeb et al [11]** have reported  
60 The chromium concentration was reduced at 99.99 % from tannery waste water using  
61 electrocoagulation process assisted by chemical oxidation with an initial concentration of  
62 3,844 mg/L but this concentration appears very small compared to the initial concentration  
63 treated in this work. Among these methods, the electrocoagulation process provides a simple,  
64 reliable, and cost-effective method for the treatment of tannery wastewater concentrated of  
65 chromium without the need for additional chemicals, and thus, without the production of  
66 secondary pollution [12]. The main advantage of electrocoagulation is its ability to treat  
67 simultaneously a wide range of type of pollutants as such organic matter, heavy metals, dyes,  
68 minerals and several others types of effluents [13, 14, 15].

69 In addition, Adsorption has also been used for treatment of tannery effluents [16, 17].  
70 **Fabbricino et al [2]** have reported 90% of Cr (III) removal from an initial concentration of  
71 6100 mg/L using adsorption in an environment friendly cycle with recovery of the metal.  
72 **Fahim et al [18]** reported adsorption of nearly 99% of the chromium from tannery  
73 wastewater with initial concentration 5500 mg/L using activated carbon obtainable from sugar  
74 processing industries. Using activated carbon prepared from date palm waste **Nayl et al [19]**  
75 have reported that COD removal percentage of 95.4 and 92.8% for BOD was obtained with  
76 carbon dosage of 0.1 g/100 mL of solution. Using Wollastonite Ceramic/CuO Nano-  
77 Composite. **Ammar et al [20]** have reported cadmium ions removal reached 98.88% with  
78 initial concentration of 25 mg/L. The aim of the present study was to investigate the treatment  
79 of highly polluted traditional tannery wastewater by eggshell with initial concentration 3.21g/  
80 Cr (III).

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

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

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

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

110

## 111 **2. Experimental**

112

### 113 **2.1. Effluent samples**

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

118

119 **Table 1 resumes the characteristics of the tested raw wastewater.**

120 **SD Standard Deviation**

121

### 122 **2.2. Experimental set-up**

123 The electrocoagulation treatment was carried out in a closed system under solution recycle  
124 functioning as a batch system. The electrocoagulation cell, consisting of two identical  
125 polymethylmethacrylate (Perspex) halves was 20 cm long, 10 cm wide and 5 cm thick. Alloy  
126 aluminium plates (15×7 cm<sup>2</sup>) acting as facing electrodes, were imbedded in the polymeric  
127 halves, as described by **Elabbas et al. [17]**. The active electrode surface was  
128 first mechanically polished under water with abrasive paper, rinsed with distilled water and  
129 dried prior to its immersion in the wastewater. The obtained surface area of the electrodes were  
130 connected to a DC power supply (AFX 2930 SB) providing current densities in the range of  
131 200-400 A/m<sup>2</sup>. The current was kept constant during each run. The schematic diagram of the  
132 complete electrocoagulation system is shown in Figure 1.

133

134 **Fig.1. Experimental set-up.**

135

136

137 **2.3. Preparation of the adsorbent**

138

139 The adsorbent eggshell used in this study was coming from local cafeterias waste. The  
140 collected eggshell is just washed with distilled water to remove the adhered particles then it  
141 was dried at the ambient atmosphere for several days. The dried slices were ground, sieved  
142 and stored in a dessicator for further use. The size of the seeds of the eggshell used is between  
143 1mm and 2mm [1].

144 **2.4. Batch Electrocoagulation /Adsorption coupling process**

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

156

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

158 
$$R(\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

159

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

162 **3. Results and discussion**

163

164 **3.1. Characterization of eggshell**

165

166 The results of the BET method showed that the average specific surface area of the eggshell is  
167 0.38m<sup>2</sup>/g. In addition, the average particle size and the median pore diameter of eggshell are  
168 158.64 nm and 144.5 nm respectively [1].

169

170 **3.2. Effect of electrolysis time on treatment**

171

172 As seen in Fig.2, the effects of electrolysis time on chromium removal were investigated in  
 173 the range of 5-360 min at a current density of 200A/m<sup>2</sup>. As indicated, the chromium removal  
 174 efficiency increased with an increase in electrolysis time. Almost 99% of chromium removal  
 175 was achieved after 240 min by the electrocoagulation process; this behavior could be  
 176 explained by the much higher amounts of aluminum oxides generated over time.  
 177 The addition of the natural material of the eggshell in the electrocoagulation cell resulted in a  
 178 faster removal. 99% of the chromium was removed at 110 min. The highest enhancement of  
 179 chromium removal by adding the eggshell can be attributed to the fact that the system took  
 180 benefit from both reactions simultaneously, electrocoagulation and adsorption processes. Our  
 181 previous experiments on Cr adsorption onto eggshell showed Cr removal efficiency reaching  
 182 nearly 99% but after 840 min contact time [1].

183

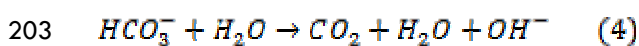
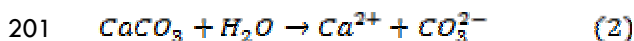
184 **Fig. 2. Effect of contact time on Cr percentage removal of the tannery wastewater during**  
 185 **the EC and EC/ES coupling processes (eggshell dose = 20g/L, current density = 200A/**  
 186 **m<sup>2</sup>).**  
 187

188

### 189 3.3. *pH evolution during treatment*

190 The pH of the solution has an important role in the performance of the electrocoagulation and  
 191 the sorption processes and its change during the treatment affects the treatment efficiency [27,  
 192 28] The different forms of Al (OH)<sub>3</sub> present in the solution greatly depend upon the pH and  
 193 concentration of Al<sup>3+</sup> ions in the media [29].

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



204 Otherwise, with the K<sub>s</sub> value of Cr(OH)<sub>3</sub> as 10<sup>-31</sup>, the pH value for the precipitation limit of  
 205 chromium hydroxide at the initial chrome III concentration 3.21g/L is calculated as 4.08. This

206 value is higher than the initial value of pH of EC/ES coupling process indicating that the  
207 precipitation as Cr(OH)<sub>3</sub> would take place.

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

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



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

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

225

226 **Fig.3. pH evolution of the tannery wastewater during the EC and EC/ES coupling**  
227 **processes (operating time = 120min, current density = 200A/m<sup>2</sup> and eggshell dose =**  
228 **20g/L)**  
229

230

### 231 3.4. *Effect of current density*

232

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

236 In this study, three values of current density, 200, 300 and 400 A/m<sup>2</sup>, were chosen to be  
237 applied during simple EC (Electrocoagulation) and EC/ES (Electrocoagulation and  
238 adsorption) coupling processes to evaluate their effect on chromium removal.



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

241 In the simple electrocoagulation (Fig.4a), the chromium removal efficiency increased with an  
242 increase in current density, with yields of 87%, 95.4% and 99.7% achieved after 240 min at  
243 current densities of 200, 300, and 400 A/m<sup>2</sup> respectively. This can be attributed to the increase  
244 in the amount of Al (OH)<sub>3</sub> being generated in situ whose flocs behave as an adsorbent for  
245 chromium ions. Besides the precipitation of the metal hydroxides at the cathode, this high  
246 removal efficiency is attributed to the coprecipitation of Cr (III) with aluminum hydroxides  
247 due to pH increase [17].

248

249 With respect to the simple EC results, the addition of 20 g/L of eggshell as optimum dose [1]  
250 in the electrocoagulation cell resulted in faster chromium removal (Fig.4b).The highest  
251 enhancement of chromium was only obtained for 80 min. An increase in current density from  
252 200 to 400 A/m<sup>2</sup> yields to an improved efficiency of chromium removal from 97 to more than  
253 99 %.

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

257

258 **Fig.4. Effect of current density on percentage of chromium removal of the tannery**  
259 **wastewater by both processes: EC (a) and EC/ES coupling process (b). (eggshell dose =**  
260 **20g/L).**

261

### 262 3.5. *Effect of eggshell dose*

263

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

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

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

275

276 **Fig. 5. Effect of adsorbent concentration on Cr removal of the tannery wastewater**  
277 **(operating time = 120min, current density = 200A/m<sup>2</sup>).**

278

279

280

### 281 **3.6. Determination of equation rate constant**

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

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

286

$$287 \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

288

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

$$293 \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

294

295 Where  $K_2$  is the rate constant of the pseudo-second-order equation (g mg<sup>-1</sup> min<sup>-1</sup>).

296

297 The experimental kinetic data were adjusted according to the indicated models and the  
298 coefficients of correlation as well as the rate constants of both models are given in Table 2.

299 The values of coefficient of determination  $R^2$  for the pseudo second order is relatively high  
300 (>0.99). This fact indicates that the second-order equation model provided the best correlation  
301 with experimental results and the sorption of chromium follows the pseudo-second-order  
302 kinetic model.

303 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  
304 dose of eggshell increases from 0 to 12 g/L but above this dose the rate constant remains  
305 stable.

306

### 307 **3.7 Energy consumption**

308

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

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

$$314 \quad EEC \left( \frac{kWh}{kg} \right) = \frac{UIt}{(C_0 - C_t)V} \quad (8)$$

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

318  
319 Fig.6 shows the energy consumption per kg of Cr(III) removed from the chrome tanning  
320 wastewater treated by the simple electrocoagulation and the EC/ES coupling process versus  
321 electrolysis time. The eggshell addition leads to a reduction of the electrical energy  
322 consumption compared to simple EC process.

323 In the case of the EC, the plot indicated a rapid initial reduction of the energy consumption.  
324 This highest energy consumption will be related to the solution pH value in the initial stage of  
325 the process in contrast to EC/ES process, the addition of eggshell elevated the wastewater pH  
326 value consequently the energy consumption is lower. After 2 h of the wastewater treatment,  
327 the chromium removal efficiency and the electrical energy consumption values were 99.96%,  
328 1.09 kWh/kg and 62.4%, 1.67 kWh/kg for EC/ES and EC processes, respectively. The  
329 coupling process is more suitable from economical point of view since the required time is  
330 lower and the chromium removal efficiency is higher than those of the simple EC process.

331 The decrease of the specific energy consumption is related to the efficiency of the coupling  
332 process on chromium removal efficiency; the greater the chromium removal efficiency, the  
333 lower the specific electrical energy consumption per kg of the removed Cr.

334 **Fig.6. Specific energy consumption after treatment by simple EC and EC/ES coupling**  
335 **process of tanning wastewater.**  
336

### 337 3.8. FT-IR studies of sludge

338

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

358

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

361

### 362 3. *Conclusion*

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

366 The addition of Eggshell, as an adsorbent to the electrocoagulation reactor resulted in a  
367 remarkable increase in the removal rate of chromium. In comparison to conventional  
368 techniques, the coupling process achieves faster removal of chromium at lower current  
369 densities, operating time and energy consumption. The optimal conditions were found to be:  
370 adsorbent dose of 12 g/L, current density of 200 A/m<sup>2</sup> and 110 min of contact time. The  
371 kinetic followed a pseudo-second order model, as shown from the values of the correlation  
372 coefficient. It was shown that the EC/ES coupling technique for chromium removal is much  
373 cheaper than the conventional EC technique due to remarkable reductions in energy  
374 consumption and adsorbent dose.

375

376 **Acknowledgements**

377

378 The authors would like to acknowledge the France-Morocco cooperation for the financial  
379 support of this work in the frame work of the “Water and Environment Competency Pole”  
380 project (Project MESRSFC/SCAC (Recherche) 2012) (2012-2014). In addition, the authors  
381 greatly thank the manager for the leather industry Mr. Slaissi Abd Aljalil for his help.

382

383 **References :**

384

385

386 [1] Elabbas, S., Ouazzani, N., Mandi, L., Berrekhis, F., Perdicakis, M., Pontvianne, S., Pons,  
387 M.N., Lapicque, F., Leclerc, J.P. Treatment of highly concentrated tannery waste water using  
388 electrocoagulation: Influence of the quality of aluminium used for the electrode. J.  
389 Hazard.Mater. 319, 69-77. 2016. <https://doi.org/10.1016/j.jhazmat.2015.12.067>

390

391 [2] Fabbicino, M., Naviglio, B., Tortora, G., d’Antonio, L. An environmental friendly cycle  
392 for Cr(III) removal and recovery from tannery wastewater. J. Environ. Manage. 117, 1-6. 2013.  
393 <https://doi.org/10.1016/j.jenvman.2012.12.012>

394

395 [3] Apte, A.D., Tare, V., Bose, P. Extent of oxidation of Cr(III) to Cr(VI) under various  
396 conditions pertaining to natural environment. J. Hazard. Mater. 128, 164-174. 2006.  
397 <https://doi.org/10.1016/j.jhazmat.2005.07.057>

398

399 [4] Dai, R., Liu, J., Yu, C., Sun, R., Lan, Y., Maob, J.-D. A comparative study of oxidation of  
400 Cr(III) in aqueous ions, complex ions and insoluble compounds by manganese-bearing  
401 mineral (birnessite). Chemosphere . 76, 536-541. 2009.  
402 <https://doi.org/10.1016/j.chemosphere.2009.03.0079>

403

404 [5] Meunier, N., Drogui, P., Montane, C., Hausler, R., Mercier, G., Blais, J.-F. Comparison  
405 between electrocoagulation and chemical precipitation for metals removal from acidic soil  
406 leachate. J. Hazard. Mater. B 137, 581–590. 2006.  
407 <https://doi.org/10.1016/j.jhazmat.2006.02.050>

408

409 [6] Keerthi, S., Mahalakshmi, M., Balasubramanian, N. Development of hybrid membrane  
410 bioreactor for tannery effluent treatment. J. Desalination. 309, 231–236. 2013.  
411 <https://doi.org/10.1016/j.desal.2012.10.014>

412

413 [7] Sahu, S.K., Meshram, P., Pandey, B.D., Kumar, V., Mankhand, T.R. Removal of  
414 chromium(III) by cation exchange resin, Indion 790 for tannery wastetreatment,  
415 Hydrometallurgy. 99, 170–174. 2009. <https://doi.org/10.1016/j.hydromet.2009.08.002>

416

417 [8] Song, Z., Williams, C.J., Edyvean, R.G.J. Treatment of tannery wastewater by chemical  
418 coagulation. J. Desalination. 164 (3), 249–259. 2004. [https://doi.org/10.1016/S0011-9164\(04\)00193-6](https://doi.org/10.1016/S0011-9164(04)00193-6)

419

420 [9] Tiglyene, S., Jaouad, A., Mandi, L. Treatment of tannery wastewater by infiltration  
421 percolation: chromium removal and speciation on soil. J. Environ. Technol. 29, 613–624. 2008.  
422 <https://doi.org/10.1080/09593330801983888>

423

424

- 425 [10] Mandi, L., Tiglyene, S., Jaouad, A. Depuration of tannery effluent by phytoremediation  
426 and infiltration percolation under arid climate, in: M. ElMoeujabber, L. Mandi, G. Trisorio-  
427 Liuzzi, I. Martin, A. Rabi, R. Rodriguez (Eds.), Technological Perspectives for rational Use of  
428 Water Resources un theMediterranean Region, 009, Bari CIHEAM, 2009, pp. 199–205.  
429 <http://om.ciheam.org/om/pdf/a88/00801195>.  
430
- 431 [11] El-Khateeb, M.A., Nashyb, El-Shahat H.A., Abdel Ghanyc, N.A., Awadd, Ahmed M.  
432 Environmental impact elimination of chrome tanning effluent using electrocoagulation  
433 process assisted by chemical oxidation. Desalin Water Treat. 147-152.  
434 <https://doi.org/10.5004/dwt.2017.20250>  
435
- 436 [12] Pereira de Carvalho, H., Huang, J., Zhao, M., Liu, G., Dong, L., Liu, X. Improvement of  
437 Methylene Blue removal by electrocoagulation/banana peel adsorption coupling in a batch  
438 system. J. Alexandria. Engin., 54, 777-786. 2015.  
439 <https://doi.org/10.1016/j.aej.2015.04.003>  
440
- 441
- 442 [13] Zodi, S., Merzouk, B., Potier, O., Lopicque, F., Leclerc, J.-P. Direct red 81 dye removal  
443 by a continuous flow electrocoagulation/flotation reactor. J. Sep. Purif. Technol. 108 , 215–  
444 222. 2013. <https://doi.org/10.1016/j.seppur.2013.01.052>  
445
- 446 [14] Oncel, M.S., Muhcu, A., Demirbas, E., Kobya, M. A comparative study of chemical  
447 precipitation and electrocoagulation for treatment of coal acid drainage wastewater, J.  
448 Environ. Chem. Eng. 1, 989–995. 2013. <https://doi.org/10.1016/j.jece.2013.08.008>  
449
- 450 [15] Attour, M. Touati, M., Tlili, M., Ben Amor, M., Lopicque, F., Leclerc, J.-P. Influence of  
451 operating parameters on phosphate removal from water by electrocoagulation using aluminum  
452 electrodes. J. Sep. Purif. Technol. 123, 124–129. 2014.  
453 <https://doi.org/10.1016/j.seppur.2013.12.030>  
454
- 455 [16] Oumani, A., Mandi, L., Berrekhis, F., Ouazzani.N. Removal of Cr<sup>3+</sup> from tanning  
456 effluents by aadsorption onto phosphate mine waste : Key parameters and mechanisms. J.  
457 Hazard. Mater . IN PRESS. 2019. <https://doi.org/10.1016/j.jhazmat.2019.05.111>  
458
- 459 [17] Elabbas, S., Mandi, L., Berrekhis., Pons, M.N., Leclerc, J.P., Ouazzani, N. Removal of  
460 Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous  
461 materials: Eggshell and powdered marble. J. Environ. Manag, 166,589-595.2016.  
462 <https://doi.org/10.1016/j.jenvman.2015.11.012>  
463
- 464 [18] Fahim, N.F., Barsoum, B.N., Eid, A.E., Khalil, M.S. Removal of chromium(III) from  
465 tannery wastewater using activated carbon from sugar industrial waste, J. Hazard. Mater.  
466 B136, 303–309. 2006. <https://doi.org/10.1016/j.jhazmat.2005.12.014>  
467
- 468 [19] Nayl. A.A., Elkhashab, R.A., EL Malah.T., Yakout. S.M., El-Khateeb, M. A.,  
469 Mohamed Ali. M. S., Ali, H.M. Adsorption studies on the removal of COD and BOD from  
470 treated sewage using activated carbon prepared from date palm waste. Environmental Science  
471 and Pollution Research. 24(28):222, 84-93. 2017. <https://doi.org/10.1007/s11356-017-9878-4>  
472  
473  
474

- 475 [20] Ammar. N., Fahmy, A., Sayed Kanawy, I., Esmat, M.A.H., El-Khateeb, M.  
476 Wollastonite ceramic/CuO nano-Composite For cadmium ions removal from waste water. J.  
477 Egyptian of Chemistry. 60(5), 817-23. 2017.  
478 <https://doi.org/10.21608/EJCHEM.2017.1289.1076>  
479  
480  
481  
482 [21] Kebir, M., Trari, M., Maachi, R., Nasrallah, N., Bellal, B., Amrane, A. Relevance of a  
483 hybrid process coupling adsorption and visible light photocatalysis involving a new hetero-  
484 system CuCO<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> for the removal of hexavalent chromium. J. Environ. Engin. Process.  
485 3,548–559. 2015. <https://doi.org/10.1016/j.jece.2014.12.024>  
486  
487 [22] Durante, C., Cuscov, M., Isse, A.A., Sandona, G., Gennaro, A. Advanced oxidation  
488 processes coupled with electrocoagulation for the exhaustive abatement of Cr-EDTA. J. Water  
489 Res. 45 (5), 2122-2130. 2011. <https://doi.org/10.1016/j.watres.2010.12.022>.  
490  
491 [23] Vivek Narayanan, N., Ganesan, M. Use of adsorption using granular activated carbon  
492 (GAC) for the enhancement of removal of chromium from synthetic wastewater by  
493 electrocoagulation. J. Hazard. Mater. 161, 575–580.2009.  
494 <https://doi.org/10.1016/j.jhazmat.2008.03.113>.  
495  
496 [24] Secula, M.S., Cagnon, B., De Oliveira, T.F., Chedeville, O., Fauduet, H. Removal of  
497 acid dye from aqueous solutions by electrocoagulation/GAC adsorption coupling: kinetics and  
498 electrical operating costs. J. Taiwan Inst. Chem. Eng. 43 (5),767-775. 2012.  
499 <https://doi.org/10.1016/j.jtice.2012.03.003>  
500  
501 [25] Ouaissaa, Y.A., Chabania, M., Amrane, A., Bensmaili, A., Integration of electro  
502 coagulation and adsorption for the treatment of tannery wastewater – The case of an Algerian  
503 factory, Rouiba, Procedia.Engi. 33 98-101. 2012.  
504 <https://doi.org/10.1016/j.proeng.2012.01.1181>  
505  
506 [26] Li, L, L., Feng, X. –Q., Han, R.-P., Zang, S. –Q., Yang, G., Cr(VI) removal by the  
507 electrochemical ion –exchange process, Environ. Technol. 35.2272-2279. 2012.  
508 <http://dx.doi.org/10.4067/S0717-97072019000404597>  
509  
510 [27] Canizares, P., Jiménez, C., Martínez, F., Rodrigo, M.A., Sáez, C. The pH as a key  
511 parameter in the choice between coagulation and electrocoagulation for the treatment of  
512 wastewaters, J. Hazard. Mater. 163,158–164.2009.  
513 <https://doi.org/10.1016/j.jhazmat.2008.06.073>  
514  
515  
516 [28] Chojnacka, K., Biosorption of Cr(III) ions by eggshells. J. Hazard. Mater. B121, 167-  
517 173. 2005. <https://doi.org/10.1016/j.jhazmat.2005.02.004>  
518  
519 [29] Jiang, J., Graham, N., Andre, C., Kelsall, G.H., Brandon, N. Laboratory study of  
520 electrocoagulation–flotation for water treatment, Water Res. 36, 4064–4078.2002.  
521 [https://doi.org/10.1016/s0043-1354\(02\)00118-5](https://doi.org/10.1016/s0043-1354(02)00118-5)  
522  
523 [30] Zachara, J.M., Cowan, C.E., Resch, C.T. Sorption of divalent metals on calcite.  
524 Geochim. Cosmochim. Acta. 55, 1549–1562 .1991. [https://doi.org/10.1016/0016-7037\(91\)90127-Q](https://doi.org/10.1016/0016-7037(91)90127-Q)  
525

- 526 [31] Sui, Y., Wu, D., Zhang, D., Zheng, X., Hu, Z., Kong, H. Factors affecting the sorption of  
527 trivalent chromium by zeolite synthesized from coal fly ash. *J. Colloid Interface Sci.* 322, 13–  
528 21. 2008. <https://doi.org/10.1016/j.jcis.2008.02.048>  
529
- 530 [32] Ho, Y.S., McKay, G. Pseudo-second order model for sorption processes. *Process*  
531 *Biochem.* 34, 451-465.1999. [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5)  
532
- 533 [33] Bayramoglu, M., Kobya, M., Can, O.T., Sozbir, M. Operating cost analysis of  
534 electrocoagulation of textile dye wastewater, *Sep. Purif. Technol.* 37,117-125. 2004.  
535 <https://doi.org/10.1016/j.seppur.2003.09.002>  
536
- 537 [34] Ghanbari, F., Moradi, M., Eslami, A., Emamjomeh, M.M. Electrocoagulation/Flotation  
538 of Textile Wastewater with Simultaneous Application of Aluminum and Iron as Anode,  
539 *Environ. Processes.* 1, 447-457. 2014. <https://doi.org/10.1007/s40710-014-0029-3>  
540
- 541 [35] Chattelet, L., Bottero, J.Y., Yvon, J., Bouchelaghem, A. Competition between  
542 monovalent and divalent anions for calcined and uncalcined hydrotalcite: anion exchange and  
543 adsorption sites. *Colloids and Surfaces SURFACES A: Physicochemical and Engineering*  
544 *Aspects.* 111,167-175. 1996. [https://doi.org/10.1016/0927-7757\(96\)03542-X](https://doi.org/10.1016/0927-7757(96)03542-X)  
545
- 546 [36] Zhouri, E., El hajbi, A. preparation and characterization of a new lamellar double  
547 hydroxide [CdCrCl]. *Ann. Chim. Sci. Mat* ,24, 57-62.1999. [https://doi.org/10.1016/S0151-](https://doi.org/10.1016/S0151-9107(99)80035-X)  
548 [9107\(99\)80035-X](https://doi.org/10.1016/S0151-9107(99)80035-X)