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

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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/m², 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 ($15 \times 7 \text{ cm}^2$) 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 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^2 . 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 0.38m²/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/m². 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

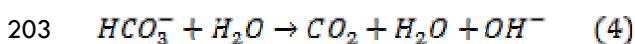
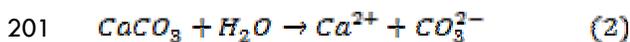
184 **Fig. 2. Effect of contact time on Cr percentage removal of the tannery wastewater during**
 185 **the EC and EC/ES coupling processes (eggshell dose = 20g/L, current density = 200A/**
 186 **m²).**
 187

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)₃ present in the solution greatly depend upon the pH and
 193 concentration of Al³⁺ 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 CaCO₃) to
 199 which the dissolution induces a formation of OH⁻ increasing tannery wastewater pH according
 200 to:

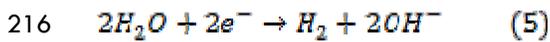


204 Otherwise, with the K_s value of Cr(OH)₃ as 10⁻³¹, the pH value for the precipitation limit of
 205 chromium hydroxide at the initial chrome III concentration 3.21g/L is calculated as 4.08. This

206 value is higher than the initial value of pH of EC/ES coupling process indicating that the
207 precipitation as Cr(OH)₃ 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⁻) that are continuously
215 generated from water reduction at the cathode as given by equation (5).



217 But Al³⁺ 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 CaCO₃ 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/m² 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/m², 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/m² respectively. This can be attributed to the increase
244 in the amount of Al (OH)₃ 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/m² 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/m²).**

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⁻¹) is the amount of chromium adsorbed per unit mass of the adsorbent at
290 equilibrium, q_t (mg g⁻¹) is the amount of a chromium absorbed per unit mass of the adsorbent
291 at current time t (min), and k_1 (min⁻¹) 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⁻¹ min⁻¹).

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⁻¹ and they are presented in Fig.7. The characteristic
342 peaks of the eggshells powder are 1395.25 cm⁻¹, 870.70 cm⁻¹ and 515.87 cm⁻¹ (fig7,a). They
343 were attributed to the vibration of C-O bond of carbonate (CO₃) 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 CO₃ 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⁻¹
348 which corresponds to O-H stretching vibrations of the physisorbed water [35]. The less
349 intense band at 1602 cm⁻¹ will be attributed to the deformation vibration of the water
350 molecules. At the low-intensity band, the peaks at 1115.5 cm⁻¹ and 606.34 cm⁻¹ correspond
351 probably to the M-OH and O-H stretching modes [36]. Where M is a metal (Cr³⁺ or Al³⁺).
352 From these spectra, it seems that hydroxyl groups are the main functional groups involved in
353 Cr³⁺ 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 Cr³⁺ and precipitated in the form of new metal molecules (co-
356 precipitation). (ii) Cr³⁺ was removed by adsorption and through ion exchange process on the
357 surface of Eggshell (iii) Cr³⁺ precipitated as Cr (OH)₃ 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/m² 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

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377

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382

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