

1 **Enhanced removal of 8-quinoline carboxylic acid in an activated**
2 **carbon cloth by electroadsorption in aqueous solution**

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11

12 ***Abstract***

13 The effect of the electrochemical treatment (potentiostatic treatment in a
14 filter-press electrochemical cell) on the adsorption capacity of an activated
15 carbon cloth (ACC) was analyzed in relation with the removal of 8-
16 quinolinecarboxylic acid (*8-QCA*) pollutant from water. The adsorption
17 capacity of an activated carbon-cloth is quantitatively improved in the
18 presence of an electric field (electroadsorption process) reaching values of
19 96% in comparison to 55% in absence of applied potential. In addition, the
20 cathodic treatment results in higher removal efficiencies than the anodic
21 treatment. The enhanced adsorption capacity has been proved to be
22 irreversible, since the removed compound remains adsorbed after switching
23 the applied potential. The kinetics of the adsorption processes is also
24 improved by the presence of an applied potential.

25 *Keywords:* Water treatment, adsorption, electroadsorption, electrochemical
26 treatment, activated carbon cloth.

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33 **1. Introduction**

34 The large growth of industry and everyday human activities has brought an
35 increase in the volume and complexity of waste (solid, liquid or gaseous)
36 released to the environment. These effluents result in the pollution of
37 natural and drinking waters or in decreasing the quality of their
38 characteristics: appearance, taste and smell. Thus, new and more stringent
39 regulations and emissions limits are imposed and industrial activities are
40 required to seek new methods and technologies capable of effective removal
41 of heavy metal and persistent organics pollution, by reusing and recycling
42 the wastewater (Segneanu et al., 2013).

43 Pesticides are a group of hazardous compounds that may pollute water due
44 to their extensive application in agriculture as rodenticides, insecticides,
45 larvacides, miticides (acaricides), etc. Although much benefit is obtained
46 from their uses, they have some undesirable side effects such as toxicity,
47 carcinogenicity and mutagenicity (Becker, 1980; Kouras et al., 1998).

48 Among various water purification and recycling technologies, adsorption is a
49 fast, inexpensive and universal method (Ali and Gupta, 2006). It is one of
50 the well-known methods used in removal of such hazardous compounds
51 from polluted waters. In adsorption technology, one of the current
52 challenges is the search for efficient and low cost high-surface area solid
53 adsorbents. Modified clay adsorbents (Mekhloufi et al., 2013; Sánchez-
54 Martín et al., 2006) and activated carbons (Ania and Béguin, 2007; Becker,
55 1980; Foo and Hameed, 2010; Hameed et al., 2009) have been studied for
56 the purification of pesticide-polluted water.

57 Activated carbon is one of the oldest and the most widely used adsorbent
58 material for this purpose due to its high efficiency, cost effectiveness and
59 wide availability from a large number of natural or synthetic precursor
60 materials (Le Cloirec and Faur-Brasquet, 2008; Moreno-Castilla, 2008;
61 Newcombe, 2008). Activated carbon has been used in powder, granular
62 (Eckenfelder, 1990; P .Lankford, 1990), and membrane forms (Baudu et al.,
63 1991). These forms have been the primary adsorbent material for many
64 adsorption studies of organic pollutants in water solution (Ania et al., 2002).

65 Activated carbon cloth or fiber has also received considerable attention as a
66 potential adsorbent for water treatment applications. These materials in the
67 form of felt or cloth have the advantages of having high specific surface
68 area, mechanical integrity, easy handling and minimal diffusion limitation
69 to adsorption (Conway et al., 2001).

70 Moreover, activated carbon cloth has been successfully used for adsorption
71 and electroadsorption processes of various inorganic and organic compounds
72 (Cloirec and Faur, 2006; Mattson and Mark, 1971; Moreno-Castilla, 2004;
73 Rodríguez-Reinoso, 1997). Adsorption and electroadsorption of related
74 sulfur-containing anions onto carbon cloth was reported by Ayranci and
75 Conway (Ayranci and Conway, 2001). Sulfide and thiocyanate anions were
76 found to be adsorbed to greater extents than others. A reduction of 68 % in
77 SCN^- concentration was achieved at open circuit with 0.5 g activated carbon
78 cloth from 20 mL $5 \cdot 10^{-4}$ M solution. This degree of removal was increased up
79 to 95 % upon polarization of carbon cloth. Adsorbability of such impurity
80 ions was related to their hydration properties in water.

81 In the same sense, the adsorption and electroadsorption/desorption of
82 pyridine (Py) ([Niu and Conway, 2002a](#)) was studied for the purification of
83 industrial waste-waters. These authors studied this process using a high-
84 area carbon cloth (C-cloth) electrodes as quasi-3-dimensional interfaces by
85 in situ UV-Vis spectrophotometry and scanning kinetic techniques..

86 Removal of acid dyes ([Hoda et al., 2006](#)) from aqueous solutions by
87 adsorption onto high area activated carbon cloth (ACC) was investigated.
88 Kinetics of adsorption was followed by in situ UV-spectroscopy and the data
89 were treated according to pseudo-first order, pseudo-second order and
90 intraparticle diffusion models.

91 The adsorption of several herbicides on an activated carbon material has
92 been previously studied by other authors ([Ania and Béguin, 2007](#); [Foo and](#)
93 [Hameed, 2010](#)). According to them, the chemical structure of the different
94 pesticides plays an important role in the context of adsorption, as the
95 presence of an aromatic ring in the structure assists dispersion interactions
96 between electrons of the ring and the shell electrons of graphenic surface on
97 carbon. Moreover, the adsorption of phenoxy-acid herbicides on activated
98 carbon is influenced by the properties of the adsorbent (surface area,
99 porosity and surface chemistry), the adsorbate (acidic herbicides, the
100 presence of aromatic rings, molecular size, solubility and nature of
101 substituent groups) as well as the characteristics of the solution (pH, ionic
102 strength, etc.) ([Hameed et al., 2009](#); [Ignatowicz, 2009](#); [Qiu et al., 2009](#)).

103 On the other hand, the electroadsorption process is a subject that also has
104 attracted great research interest. In general, electrosorption is defined as a
105 current or polarization potential-induced adsorption phenomenon on the
106 surface of the charged electrodes ([Han et al., 2006](#)). Specifically, when an
107 external electrostatic field is imposed to the surface of the electrodes
108 immersed in an aqueous electrolyte solution, charged ions are forced to
109 move towards the oppositely charged electrodes, allowing the occurrence of
110 charge separation across the interface ([Li et al., 2008](#)), resulting in the
111 formation of strong electrical double layers near the high conductivity and
112 high surface area surfaces ([Oren, 2008](#)). The effect of electric field on the
113 adsorption process was studied by Ban et al. (Ban et al., 1998) who
114 discussed the basis of electroadsorption on activated carbon as a treatment
115 for removing pollutants from industrial effluents. Kitous et al. (Kitous et al.,
116 2009) used a combination treatment for the removal of pesticide metribuzin
117 (4-amino-6-*tert*-butyl-3-methylthio-1,2,4-triazin-5-one) which consisted of
118 adsorption on a granular activated carbon column followed by application of
119 a potential. The results showed that the adsorption capacity was increased
120 by over 100 % compared to the absence of potential. Moreover, this process
121 was used also for inorganic compounds like metal cations with the aim of
122 reducing the contamination of wastewater ([Afkhami et al., 2009](#)). Farmer et
123 al. (Farmer et al., 1997) studied the electroadsorption process of hexavalent
124 chromium ion on a support based on carbon aerogel. The electrodesorption
125 and electroadsorption process of dissolved arsenic in the presence of heavy
126 metals (Cr, Ni and Fe) on a granular activated carbon has been studied by

127 Calo et al. (Calo et al., 2012). One of the conclusions was that the
128 application of an anodic potential increased considerably the adsorption of
129 As.

130 In addition, processes of adsorption/electrosorption of methylpyridinium.
131 pyrazine and 1-quinoline at high specific-area C-cloth interfaces were
132 monitored and kinetically analyzed by in situ spectrophotometry coupled
133 with 'scanning-kinetics' techniques (Niu and Conway, 2002b). A rapid and
134 complete removal of methylpyridinium, pyrazine and 1-quinoline by
135 electrosorption under various conditions, preferably by negative current
136 polarization was achieved.

137 As an analogy to the present investigation, it has also been demonstrated
138 that Na montmorillonite modified by the addition of the ammonium acetate
139 exhibits interesting adsorption properties for the removal of 8-QCA
140 herbicide (Mekhloufi et al., 2013).

141 Thus, in this work the comparison between adsorption and
142 electroadsorption of a solution of the herbicide 8-quinolinecarboxylic acid in
143 neutral pH, has been studied on an activated carbon cloth using a filter-
144 press electrochemical cell.

145 **2. Experimental**

146 **2.1. Carbon materials and chemical reagents**

147 The commercial activated carbon used in this work was an activated carbon
148 cloth provided by Carbongen (Spain), which is referred to as *HST07*. The

149 samples were washed several times with distilled water until constant pH,
150 and dried in an oven at very mild conditions (80 °C for 3 h) before each
151 experiment. The herbicide 8-Quinolincarboxylic acid which presents a
152 reagent grade of 98% and the sodium sulfate were obtained from Sigma
153 Aldrich. All solutions were prepared using distilled water.

154 The textural properties of the ACC (activated carbon cloth) (Table 1) was
155 analyzed by physical adsorption of gases (N₂ at 77 K and CO₂ at 273 K)
156 using an automatic adsorption system (Autosorb-6 Quantachrome
157 Corporation) after samples out-gassing at 523 K under vacuum for 4 h.
158 Nitrogen adsorption at 77 K was used for determining the total volume of
159 pores (V_t, determined at relative pressure of 0.99), the micropore volume
160 (V_{DR}(N₂), pore size smaller than 2 nm), which is obtained from the Dubinin-
161 Radushkevich (DR) equation (the range of relative pressures used for the
162 DR analysis was: 0.005 < P/P₀ < 0.17), and the apparent specific surface area
163 from the BET equation (S_{BET}, applied at 0.05 < P/P₀ < 0.17). The CO₂
164 adsorption isotherm at 273 K was used to assess the narrowest micropores
165 (V_{DR}(CO₂), pore size smaller than around 0.7 nm) also by application of the
166 Dubinin-Radushkevich equation for relative pressures below 0.025 (Cazorla-
167 Amorós et al., 1998, 1996; Rodríguez-Reinoso and Linares-Solano, 1989). As
168 expected, ACC presents a well-developed pore structure, showing an
169 apparent surface area of ca. 600 m²/g. This surface area is provided by the
170 presence of a pore system with a narrow pore size distribution that is
171 centered in the micropore size region, as pointed out by the similar value of
172 V_t and V_{DR} (N₂). Since the micropore value determined by N₂ uptake (that

173 fills the wider micropores) seems to be higher than that determined using
 174 CO₂ adsorption (which fills the most restricted narrow micropores) the
 175 mean microporosity size is expected to be higher than 0.7 nm (Cazorla-
 176 Amorós et al., 1998). The slit geometry of the micropores of activated
 177 carbons along with a mean micropore size in the range of 1 nm is especially
 178 well-fitted for obtaining a large adsorption uptake of 8-QCA (ca. 0.9 nm in
 179 length and planar geometry), ensuring the availability of most of the surface
 180 area of ACC for the adsorption of 8-QCA. Moreover, the distribution of
 181 porosity in activated carbon fibers is usually exposed to the surface of the
 182 fiber, perpendicular to the fiber axis and shows a low tortuosity (i.e. straight
 183 slit-like pores that runs in parallel from the external surface towards the
 184 center of the fiber). In consequence, the diffusion of molecules on ACCs is
 185 enhanced when compared to a GAC of similar properties, speeding up the
 186 adsorption rate of aromatic compounds and other adsorbates (Ayranci and
 187 Hoda, 2005; Brasquet and Le Cloirec, 1997).

188

189 Table 1 Textural parameters obtained from the N₂ and CO₂ isotherms using the BET Theory and Dubinin-
 190 Radushkevich Theory.

Sample	$S_{BET} / \text{m}^2 \cdot \text{g}^{-1}$	$V_{DR}(N_2) / \text{cm}^3 \cdot \text{g}^{-1}$	$V_{DR}(CO_2) / \text{cm}^3 \cdot \text{g}^{-1}$	$V_t / \text{cm}^3 \cdot \text{g}^{-1}$
<i>HST07</i>	596	0.24	0.15	0.26

191

192

193 **2.2. Adsorption and electroadsorption procedures**

194 **2.2.1. Filter press adsorption and electroadsorption**

195 The electroadsorption experiments were carried out in an undivided filter-
196 press electrochemical cell with rectangular geometry of the electrodes (4x5
197 cm), a hydraulic diameter of 4.44 cm and an electrode geometric area of 20
198 cm². A scheme detailing the distribution of the elements used in the
199 construction of the cell can be seen in a previous work (Tabti et al. 2014).
200 The anode electrode was a platinized titanium electrode and the cathode
201 electrode was a stainless steel mesh, with an electrode spacing of 5 mm. The
202 ACC (0.8 g) was tightly attached to the electrode (anode or cathode)
203 depending on the electrochemical treatment. The electrode assembly was
204 then placed inside the electrochemical cell, and the electrolytic solution (400
205 mL) was continuously recirculated by a centrifugal pump at 18 mL/s.

206 A concentration of *δ-QCA* of 50 mg/L in 0.5 M Na₂SO₄ was used. A cell
207 potential of 3 V was applied for 24 hours. The temperature was controlled
208 during the experiment at 298 K. At specific time intervals, aliquots of 1 ml
209 were withdrawn in order to monitor the *δ-QCA* concentration during the
210 experiment, which was done using UV-Vis Spectroscopy (JASCO V-670
211 Spectrophotometer).

212 The amount of adsorbed herbicide was calculated by the difference between
213 the initial concentration and the concentration after a given time, with their
214 corresponding volumes, according to the following equation:

$$q_t = \frac{C_0V_0 - C_tV_t}{W} \quad (1)$$

215

216 where q_t (in mg/g) is the amount of organic pollutant adsorbed at time t per
217 unit mass of ACC, C_0 is the initial concentration (in mg/L), V_0 is the initial
218 volume (in L), C_t is the concentration of the organic pollutant in solution at
219 time t , V_t is the remaining volume of electrolyte inside the cell (in L) at time
220 t , and W is the weight of activated carbon used (in g).

221 *2.2.2. Batch adsorption*

222 Batch adsorption experiments lasted also 24 hours. These experiments were
223 performed for the sake of comparison with the electroadsorption and
224 adsorption experiments in filter-press conditions. Then, 0.2 g of ACC
225 samples were equilibrated for 24 h with 100 mL of aqueous solutions of 8-
226 QCA with a concentration of 50 mg/L in sealed flasks. The flasks were
227 shaken at constant speed (150 rpm) in a thermostatically controlled bath at
228 298 K. The ACC uptake of 8-QCA was monitored in the same terms detailed
229 in 2.2.1.

230 *2.2.3. Kinetic analysis*

231 Adsorption kinetics were studied by fitting experimental data of organic
232 adsorption from aqueous solutions using the Boyd model (Boyd et al., 1947).
233 It allows to determine whether the main resistance to mass transfer is
234 internal, i.e. the diffusion rate of 8-QCA inside the pores of the adsorbent is
235 the slowest mass transfer rate, or external, i.e. mass transfer across the

236 layer of stationary liquid that surrounds the particle of the adsorbent is the
 237 slowest process.

$$238 \quad \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2}{4 \cdot d_f^2} D_e \cdot t\right) \quad (2)$$

239 Where q_e stands for the total uptake when the adsorption equilibrium is
 240 reached, D_e is the effective diffusivity of 8-QCA in the carbon fiber (m^2/s)
 241 and d_f is the mean diameter of the carbon fiber (m), which was estimated to
 242 be around 10^{-4} m using scanning emission microscopy. The initial form of
 243 the model was simplified by Reichenberg (Reichenberg, 1953), obtaining the
 244 expression that follows:

$$245 \quad B \cdot t = F(t) = \left(\sqrt{\pi} - \sqrt{\pi - \left(\pi^2 \cdot \frac{q_t}{q_e} / 3\right)}\right)^2 \quad \frac{q_t}{q_e} < 0.85 \quad (3)$$

$$246 \quad B \cdot t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \quad \frac{q_t}{q_e} > 0.85 \quad (4)$$

$$247 \quad B = \frac{\pi^2}{4 \cdot d_f^2} \cdot D_e \quad (5)$$

248 The t vs $\left(\sqrt{\pi} - \sqrt{\pi - \left(\pi^2 \cdot \frac{q_t}{q_e} / 3\right)}\right)^2$ plot can be used for both determining the
 249 control of internal mass transfer, what is achieved if the plot is linear and
 250 pass through the origin, and the value of D_e , which can be drawn from the
 251 slope of the plot.

252 The absence of external mass transfer control in the activated carbon cloth
 253 have also been checked through the study of the Reynolds (Re), Sherwood
 254 (Sh) and Smichdt (Sc) numbers. For a liquid flowing across a bundle of

255 fibers, the fiber diameter can be used as the characteristic length (Coulson
256 and Richardson, 1978):

$$257 \quad Sh = \frac{k_f \cdot d_f}{D_m} \quad (6)$$

$$258 \quad Re = \frac{u \cdot d_f}{\nu} \quad (7)$$

$$259 \quad Sc = \frac{\nu}{D_m} \quad (8)$$

260 Where k_f stands for the external mass transfer coefficient (m/s), D_m is the
261 molecular diffusivity of 8-QCA in 0.5M Na₂SO₄ at room temperature (which
262 have been evaluated as $4.51 \cdot 10^{-10}$ m²/s using the approximation proposed by
263 Treybal ([E.Treybal, 1981](#)), u the lineal velocity of the liquid through the void
264 space of the activated carbon cloth (0.020 m/s in our experimental system),
265 and ν is the kinematic viscosity of the solution ($1.19 \cdot 10^{-6}$ m²/s). Similarly,
266 the Sh number can be related to Re and Sc ones through the next expression
267 (Yawalkar et al., 2002):

$$268 \quad Sh = (2 + 0.6 \cdot Re^{1/2} \cdot Sc^{1/3}) \quad (9)$$

269 Showing a value of 25.9 for the operational conditions used in the filter-
270 press adsorption experiments reported in this work. The mass Biot number
271 relates the rates of internal to external mass transfer:

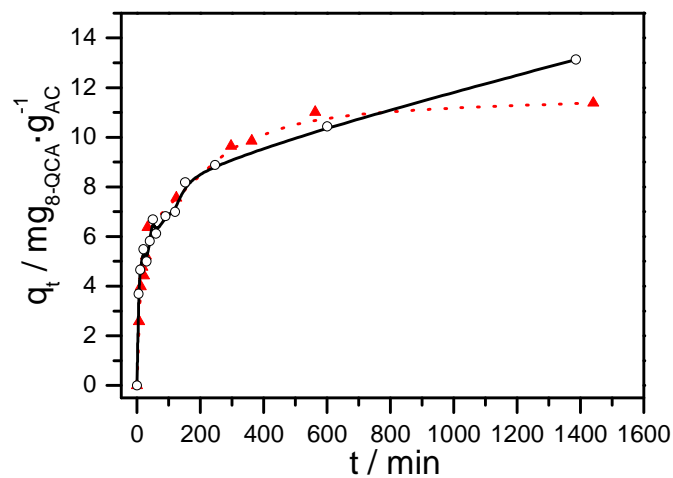
$$272 \quad Bi = \frac{k_f \cdot d_f}{D_m} = Sh \cdot \frac{D_m}{D_e} \quad (10)$$

273 Given the maximum obtained value for D_e is two order of magnitude lower
274 than D_m (as later discussed), the lack of external mass transfer control is
275 ensured in our adsorption system.

276 3. Results and discussion

277 3.1. Adsorption of δ -QCA

278 Fig. 1 shows the amount of adsorbed herbicide on the ACC with the
279 increasing time, in both batch and electrochemical cell experiments at open
280 circuit. It can be observed that working on batch adsorption has little effect
281 on the adsorption capacity of the ACC and on the kinetics of the process,
282 pointing out that both systems must be working under the same regime of
283 mass transfer control. In neither case it was possible to achieve the complete
284 removal of the δ -QCA, but a 52 % and 55 % for batch and filter-press
285 conditions, respectively.

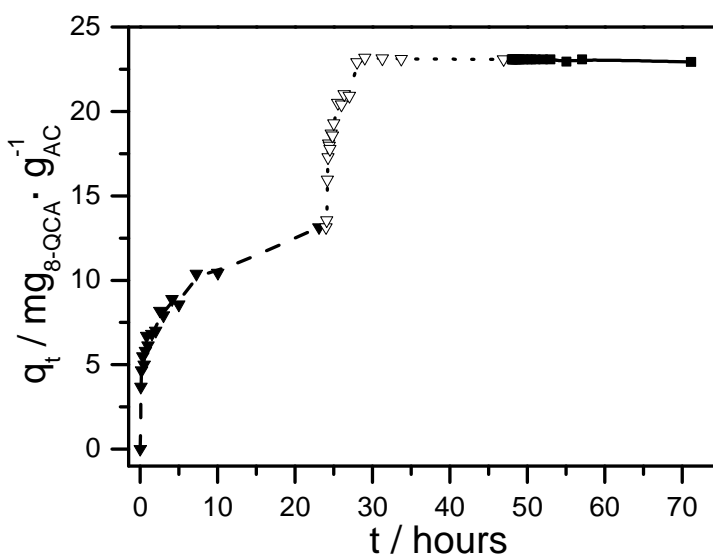


286

287 Figure 1: Adsorption of δ -QCA onto ACC (*HST07*) in batch (filled triangles) and in filter-press at open circuit (open
288 circles). 50 mg/L δ -QCA + 0.5M Na₂SO₄ solution.

289 3.2. Effect of applied voltage

290 Fig. 2 shows the enhancing effect of applying an external dc voltage on the
291 adsorption of *8-QCA* onto *HST07* ACC in a filter-press cell. This effect was
292 made evident in an adsorption-electroadsorption combined cycle of 72 hours
293 long, where the carbon cloth was kept in close contact with the cathode. The
294 cycle is divided in 3 stages of 24 hours each: 1) Adsorption process at open
295 circuit (filled triangles); 2) Electroadsorption process at 3 V (open triangles);
296 3) Adsorption/desorption process at open circuit (filled squares).



297

298 Figure 2: Amount of *8-QCA* adsorbed vs time in consecutive steps of 72 hours long, using *HST07* AC: 1) Adsorption
299 at open circuit (filled triangles); 2) Cathodic electroadsorption at 3 V (empty triangles); 3) Adsorption/desorption at
300 open circuit (filled squares). 50 mg/L *8-QCA* + 0.5M Na₂SO₄ solution.

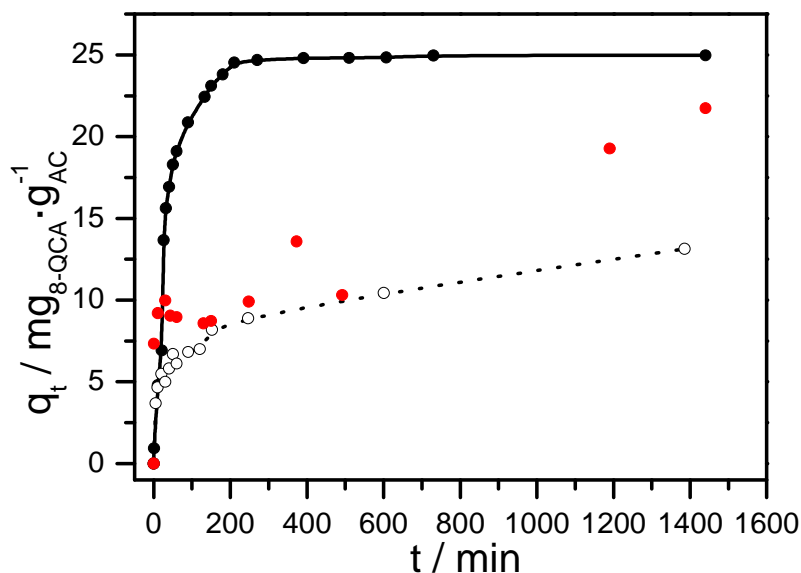
301 Results clearly reveal that open circuit adsorption is only capable of
302 removing about 55 % of the total amount of *8-QCA* in solution (Fig. 2, filled
303 triangles). Once an electric field is imposed by applying a difference of
304 potential between the electrodes of 3 V, the adsorption rate is rapidly

305 increased and the surface of the polarized cloth is then able to adsorb the
306 remaining *8-QCA*, achieving nearly complete removal of the dissolved
307 herbicide (Fig.2, open triangles). Furthermore, the third stage demonstrates
308 that switching off the applied voltage (i.e., returning to open circuit
309 conditions) does not involve desorption of the pollutant (Fig. 2, filled
310 squares), which suggests that the electrochemically-assisted removal of *8-*
311 *QCA* in the presence of an ACC is an irreversible process. Because of the use
312 of low dc voltages, we can conclude that electroadsorption is an energy
313 saving and potentially cost-effective purification technology for assisting the
314 removal of dilute emerging pollutants, like herbicides, in wastewater by
315 means of porous solid adsorbents. In the following sections the
316 electroadsorption process will be studied in more detail.

317 **3.3. ElectroadSORPTION OF *8-QCA***

318 The imposition of an electrostatic field is known to promote an enhancement
319 of the adsorption capacity of the porous surface and the possibility of
320 speeding up the adsorption rate. The electroadsorption performance not only
321 depends on the magnitude of the interfacial potential applied to the
322 adsorbent, but also on its sign, i.e., on the electrode polarity. Cathodic and
323 anodic electroadsorption experiments of *8-QCA* on ACC were conducted by
324 either pressing the cloth material against the stainless steel mesh cathode
325 or the Ti/Pt expanded mesh anode. In both cases the applied cell voltage was
326 3 V. The results of the adsorbed herbicide with electrolysis time were
327 plotted in Figure 3 and compared to open-circuit adsorption in the same

328 filter-press cell. Table 2 compares the removal efficiency attained after 2
 329 hours and after 24 h for each treatment. As can be discerned, both cathodic
 330 and anodic electroadsorption processes enhance the adsorption kinetic rate
 331 of the herbicide in comparison with open circuit conditions. However,
 332 cathodic electroadsorption shows a far better overall performance than the
 333 anodic one in maximum removal capacity (which reaches 88 % of the total
 334 amount of dissolved *8-QCA* in about 120 min). Furthermore, it was observed
 335 that, unlike the cathodic process, during the anodic process the *8-QCA*
 336 removal proceed in two different regimes; (i) a fast elimination of the
 337 pollutant from the solution during the first hour of the treatment, (ii)
 338 followed by a much lower remediation rate for the rest of the experiment.



339

340 Figure 3: Amount of 8-QCA adsorbed vs time in: cathodic electroadsorption (filled black circles) at 3V, anodic
 341 electroadsorption (filled reds circles) at 3 V and open-circuit adsorption in filter-press (empty circles) using *HST07*
 342 ACC. 50 mg/L *8-QCA* + 0.5M Na₂SO₄ solution.

343 A possible explanation from differences in behavior between cathodic and
344 anodic electroadsorption experiments comes from the oxidation of 8-QCA
345 over the Ti-Pt Anode. ACCs are known for combining enhanced electrical
346 conductivity with a large surface area (in this case, 0.8g provides a surface
347 of more than 450 m²). Since the area of Ti-Pt anode ($2.3 \cdot 10^{-3}$ cm² effective
348 area) and stainless steel cathode ($3.2 \cdot 10^{-3}$ m² effective area) are much lower
349 than the ACC one, when ACC is attached to either the cathodic or the
350 anodic electrode, most of the active area of the given electrode will be
351 provided by the carbon fiber cloth.

352 Consequently, when ACC is attached to the cathode, the much smaller area
353 of the Ti/Pt anode will be subjected to larger currents in order to reach the
354 imposed cell voltage of 3V. Since this electrode is strongly active for the
355 oxidation of aromatic compounds (as will be shown above), it will be able to
356 oxidize the pesticide in the solution. The obtained oxidized compounds (8-
357 hydroxyquinoline, quinoline and ring-opened oxidation products from
358 quinoline ([Thomsen, 1998](#)) are molecules of smaller size that are able to
359 adsorb at faster rate and in larger amounts than the original compound over
360 the surface of the negatively polarized ACC electrode. In fact, quinolines are
361 known to be more effectively removed by electroadsorption over activated
362 carbon cloths submitted to negative polarization ([Niu and Conway, 2002b](#)).

363 Contrariwise, attaching the ACC to the anode greatly hinders the activity of
364 the Ti/Pt, since it will be providing only a small fraction of the active area of
365 the electrode. Taking into account the measured pK_as of the 8-QCA molecule
366 (2.36 and 6.76) ([Garribba et al., 2003](#)) it follows that the pollutant molecule

367 is in its zwitterionic form (deprotonated carboxylate group and protonated
368 quinoline nitrogen) at the electrolyte pH (5.4). Thus, adsorption at the
369 initial stages over the positively polarized activated carbon cloth will
370 proceed at faster rate during the formation of the electric double layer than
371 in normal adsorption because electrostatic attraction between the positively
372 polarized surface of the ACC and the negatively charge carboxylic group of
373 the pesticide; unfortunately, the large amount of solvated SO_4^- anions in the
374 media will also compete with the adsorption of the pesticide in this case,
375 rendering a uptake lower than that reached in the equilibrium for normal
376 adsorption ([Han et al., 2006](#)). Beyond that point, a higher uptake can only
377 be attained through oxidation of 8-QCA by the Pt/Ti mesh, that also
378 proceeds at much slower rate than in cathodic configuration.

379 This explanation is also supported by the higher current (which is directly
380 related to the kinetics rate of the reactions that may occur over the
381 electrodes) registered by the cell when ACC is attached to the cathode.
382 Current intensity starts at 93 mA and then increases to be held around 180
383 mA from the first half hour until the end of the experiment. In anodic
384 configuration, the current moves from 67 mA in the initial stage of the
385 oxidation down to 25-30mA from two hours up to the end of the experiment.

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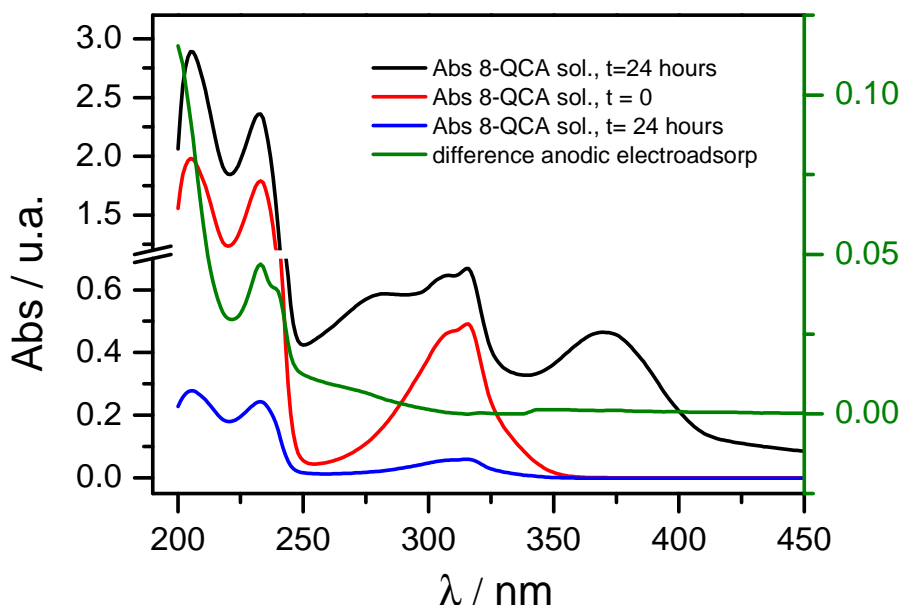
Table 2: Removal efficiency of 8-QCA by different processes (2 hours long) using HST07(ACC).

Process	% 8-QCA removed	
	At 2h	At 24h
Bath adsorption	44	52
Open-circuit adsorption filter-press	45	55
Cathodic electroadsorption	87	96
Anodic electroadsorption	65	84

389

390 In order to check the above suggestion, an electrooxidation experiment of
 391 the herbicide 8-QCA was performed in a filter-press cell in the absence of
 392 the carbon material. Fig. 4 shows the UV-Vis spectra of the initial solution
 393 (red line) and after 24 h of electrolysis (black line) performed in the absence
 394 of ACC at the same cell potential of 3V. For the sake of comparison the UV-
 395 vis spectrum recorded after 24 h of anodic electroadsorption is also depicted
 396 in the graph (blue line). The spectrum of dissolved 8-QCA shows a couple of
 397 sharp bands with maximum absorptions at 206 and 234 nm, which
 398 correspond to the $\pi\text{-}\pi^*$ electronic transitions of the condensed biaromatic
 399 system. Another smaller broad band appears in the range 270-350 nm with
 400 a maximum at 315 nm. This spectral profile has been earlier reported for
 401 protonated quinoline dissolved in aqueous media (Niu and Conway, 2002b).
 402 Since the pesticide is in its zwitterionic form, the expected molecular
 403 structure is fully coherent with the recorded electron absorption spectrum.
 404 After 24 h of electrolysis in the absence of ACC inside the filter-press cell,
 405 two more absorption bands at 275 nm and 370 nm appeared. The first one

406 corresponds to the formation of quinone species. This assignment is also
407 supported by the yellow coloration of the solution which gets darker as the
408 experiment progresses. The band at higher wavelength is still of unknown
409 nature, yet it lies in a region where hydroxi-quinolines show strong
410 absorption bands (Tegge, 1968). Then, the 8-QCA compound is oxidized at
411 the anode producing the formation of quinone-like species in solution. These
412 oxidized species could be readily adsorbed on the activated carbon cloth in
413 the electroadsorption experiments. Note that the spectrum recorded after 24
414 h in the presence of ACC attached to the anode seems to only reveal the
415 characteristic spectral features of 8-QCA at very high dilution.
416 Nevertheless, when the spectra of 8-QCA initial solution and electrotreated
417 solution after 24h are normalized using their respective absorbance values
418 at $\lambda=316$ nm and subtracted, an absorbance contribution in the UV region
419 (200-300 nm) arises, that could be related to the presence of low amounts of
420 aromatic species coming from the oxidation of 8-QCA in the solution after
421 24h of anodic electroadsorption treatment. This finding confirms that 8-QCA
422 can be oxidized even when the electrochemical treatment is conducted with
423 the ACC attached to the Ti/Pt anode.



424

425 Figure 4: UV-Visible spectra at different times of electrolysis of *8-QCA* at 3 V experiment without ACC at time 0
 426 (red line) and after 24 hours (black line). After 24 hours of anodic electroadsorption experiment at 3 V in presence
 427 of ACC (blue line) and difference spectrum of anodic electroadsorption (dot) obtained from the subtraction of red
 428 and blue spectra that has been normalized using the absorbance values at $\lambda=316\text{nm}$.

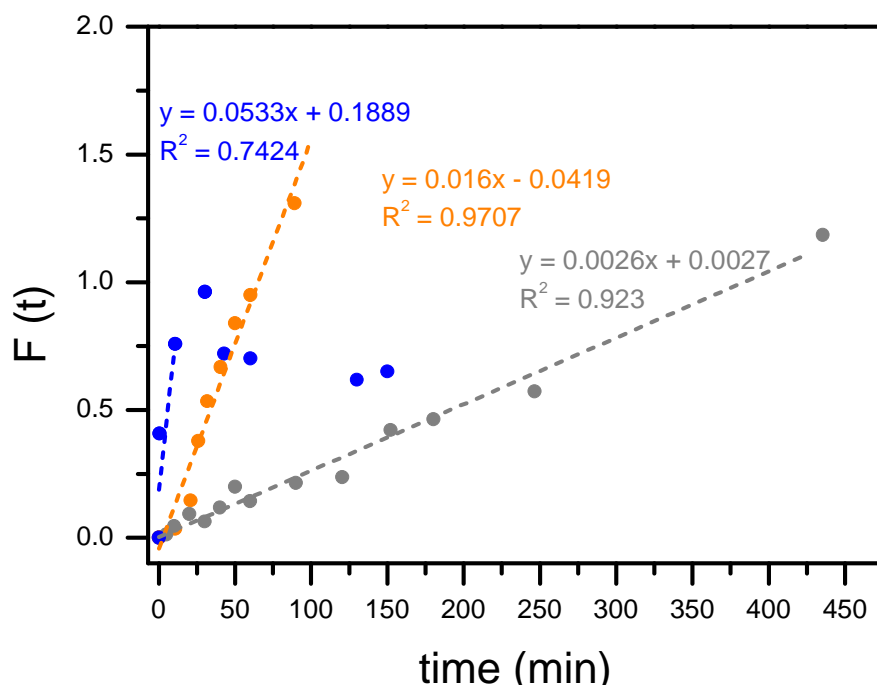
429 Interestingly, in the cathodic electroadsorption experiment the electrolyte
 430 moved from transparent to yellowish colour during the second hour of the
 431 treatment. Then, the solution turned again to transparent colour until no
 432 colour was seen in the third hour of the treatment. This seems to support
 433 that in the cathodic electroadsorption treatment, enhanced adsorption of 8-
 434 QCA is accompanied by its oxidation on the anode surface. The appearance
 435 of yellowish colour suggests that the oxidized products are formed over the
 436 Ti/Pt anode at a kinetic rate faster than their adsorption rate of the ACC on
 437 the cathode. As the experiment goes on, either these oxidized products are
 438 finally adsorbed on the ACC or they are oxidized again to form new oxidized
 439 products that are more prone to be adsorbed on the ACC.

440 In clear contrast, the solution remained transparent during the whole
441 anodic experiment, which is pointing out that the oxidation kinetic rate of 8-
442 QCA is lower than the adsorption rate of 8-QCA or its oxidized products
443 over the ACC surface. Thus, the additional removal rate provided by the
444 adsorption of 8-QCA oxidation compounds is much lower for the anodic
445 experiment. These results seem to be in agreement with the differences in
446 the adsorption behavior observed in Fig. 3.

447 **3.4. Kinetic study**

448 Figure 5 shows the Boyd plots for the cathodic, anodic electroadsorption and
449 normal adsorption in the filter-press cell. They have been obtained applying
450 equations 3 to 5 to the results of the kinetic experiments shown in Figure 3.
451 It can be seen that the adsorption process in absence of applied potential
452 presents a linear relationship between $F(t)$ and t , and the absence of
453 external mass transfer control is pointed out by the negligible value of the
454 Y-intercept of the regression line. Similarly, the cathodic plot shows a large
455 degree of linearity and intercept with the Y-axis value that is close to zero;
456 nevertheless, a close inspection of the short times region reveals that in the
457 first minutes of the treatment, adsorption was proceeding similarly to
458 adsorption in absence of applied potential. This small induction time could
459 be related to the time needed by the electrodes to reach a quasi-steady state.
460 The most important result to note is the great increase in the slope of the
461 Boyd plot, which speaks of the enhanced internal mass transfer rate on this
462 experiments. The diffusivity coefficient value shows a 6-fold increase when

463 adsorption proceeds with ACC attached at the cathode and a cell voltage of
464 3V, rising from $1.1 \cdot 10^{-14}$ to $7.3 \cdot 10^{-14}$ m²/s. This enhancement is expectable in
465 terms of the enhanced mobility of 8-QCA proceeding through the formation
466 of quinolines, that could diffuse faster in the porosity of the adsorbent
467 thanks to their smaller molecular size, rendering a faster adsorption rate
468 than that of the original pollutant. On the other hand, the electroadsorption
469 treatment where ACC was attached to the anode seems to produce a huge
470 increase in the initial adsorption rate, followed by a lag period where the
471 adsorption process seems to be finished. Thus, if only the short times (<10
472 minutes) are considered for estimation of the diffusion coefficient, a value of
473 $2.25 \cdot 10^{-13}$ m²/s is found. Although the goodness of the fit is rather low and
474 could not be considered as a representative value, the higher apparent
475 diffusion coefficient will likely be reflecting the enhanced molecule mobility
476 due to the action of the electric field, i.e. the electrostatic interaction
477 between carbon surface and the pesticide molecules that takes place in
478 adsorption sites that are only available when the carbon surface is positively
479 polarized and that are readily accessible to the 8-QCA molecule.



480
 481 Figure 5: Boyd plots and linear fits (if applicable) for cathodic (orange circles), anodic electroadsorption (blue
 482 circles) at 3 V process and vs open –circuit adsorption in filter-press (grey circles) using HST07 ACC. 50 mg/L 8-
 483 QCA + 0.5M Na₂SO₄ solution.

484 4. Conclusions

485 An activated carbon cloth has been used for enhanced removal of 8-QCA
 486 herbicide in dilute aqueous solution by electroadsorption in neutral
 487 electrolyte. Batch system adsorption experiments conducted with the HST07
 488 activated carbon cloth and 50 ppm of 8-QCA revealed removal efficiencies of
 489 52 % and 55 %, respectively. However, when an external 3 V dc voltage is
 490 applied (electroadsorption process) in a filter-press set-up, the removal of 8-
 491 QCA is strongly enhanced, especially when the ACC is located in close
 492 contact to the cathode (96 % removal). This enhancement has been proven to
 493 be irreversible, since the removed compounds remains adsorbed and did not
 494 elute to the solution even after switching off the applied potential.

495 The electrochemical treatment of the *8-QCA* herbicide in the same filter-
496 press device and in absence of activated carbon material leads to the
497 oxidation of the pollutant with subsequent formation of quinones and other
498 unidentified compounds that remain in solution and which are hardly
499 oxidized in the conditions used in the experiment. These compounds seems
500 to be readily removable by adsorption over ACC, although the oxidation rate
501 of 8-QCA by the anode is affected by the emplacement of ACC. In anodic
502 electroadsorption experiments (ACC acting as anode), the oxidation of 8-
503 QCA seems to be slow, though enhanced adsorption rate of the pollutant
504 thanks to the intervention of electrostatic forces is observed in the first
505 minutes of the adsorption experiment. In cathodic configuration, enhanced
506 uptake and rate of 8-QCA comes along with its faster oxidation rate and
507 enhanced uptake of the oxidation products of the herbicide.

508 The comparison of cathodic electroadsorption and batch adsorption kinetic
509 parameters suggests that the primary effect of the applied electric field is
510 the enhancement of the adsorption rate through an increased mobility of the
511 pollutant inside the pore network of the ACC. It is followed by an enhanced
512 adsorption capacity at equilibrium, which seems to be connected to both the
513 polarization of the ACC providing an improved interaction between 8-QCA
514 and the surface of the ACC, and the higher adsorption uptake showed by
515 ACC towards the quinolines-like and other oxidized products coming from
516 the oxidation of the pollutant on the anode. These results clearly points out
517 that electroadsorption using activated carbon cloths is a very promising and

518 cost-effective technology for the purification of surface and groundwater
519 contaminated from agricultural run-off.

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