Enhanced removal of 8-quinoline carboxylic acid in an activated carbon cloth by electroad sorption in aqueous solution

S. López-Bernabeu, R. Ruiz-Rosas, C. Quijada, F. Montilla, E. Morallón

aDepartamento de Química Física e Instituto Universitario de Materiales, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

bDepartamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

cDepartamento de Ingeniería Textil y Papelera. Universitat Politècnica de València. Pza Ferràndiz y Carbonell, E-03801 Alcoy (Alicante), Spain
Abstract

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

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

Corresponding author:

morallon@ua.es

Tel.: +34-965909590
Fax: +34-965909820
1. Introduction

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

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

Among various water purification and recycling technologies, adsorption is a fast, inexpensive and universal method (Ali and Gupta, 2006). It is one of the well-known methods used in removal of such hazardous compounds from polluted waters. In adsorption technology, one of the current challenges is the search for efficient and low cost high-surface area solid adsorbents. Modified clay adsorbents (Mekhloufi et al., 2013; Sánchez-Martin et al., 2006) and activated carbons (Ania and Béguin, 2007; Becker, 1980; Foo and Hameed, 2010; Hameed et al., 2009) have been studied for the purification of pesticide-polluted water.
Activated carbon is one of the oldest and the most widely used adsorbent material for this purpose due to its high efficiency, cost effectiveness and wide availability from a large number of natural or synthetic precursor materials (Le Cloirec and Faur-Brasquet, 2008; Moreno-Castilla, 2008; Newcombe, 2008). Activated carbon has been used in powder, granular (Eckenfelder, 1990; P. Lankford, 1990), and membrane forms (Baudu et al., 1991). These forms have been the primary adsorbent material for many adsorption studies of organic pollutants in water solution (Ania et al., 2002).

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

Moreover, activated carbon cloth has been successfully used for adsorption and electrodessorption processes of various inorganic and organic compounds (Cloirec and Faur, 2006; Mattson and Mark, 1971; Moreno-Castilla, 2004; Rodríguez-Reinoso, 1997). Adsorption and electrodessorption of related sulfur-containing anions onto carbon cloth was reported by Ayranci and Conway (Ayranci and Conway, 2001). Sulfide and thiocyanate anions were found to be adsorbed to greater extents than others. A reduction of 68 % in SCN\(^{-}\) concentration was achieved at open circuit with 0.5 g activated carbon cloth from 20 mL \(5 \cdot 10^{-4}\) M solution. This degree of removal was increased up to 95 % upon polarization of carbon cloth. Adsorbability of such impurity ions was related to their hydration properties in water.
In the same sense, the adsorption and electrosorption/desorption of pyridine (Py) (Niu and Conway, 2002a) was studied for the purification of industrial waste-waters. These authors studied this process using a high-area carbon cloth (C-cloth) electrodes as quasi-3-dimensional interfaces by in situ UV-Vis spectrophotometry and scanning kinetic techniques.

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

The adsorption of several herbicides on an activated carbon material has been previously studied by other authors (Ania and Béguin, 2007; Foo and Hameed, 2010). According to them, the chemical structure of the different pesticides plays an important role in the context of adsorption, as the presence of an aromatic ring in the structure assists dispersion interactions between electrons of the ring and the shell electrons of graphenic surface on carbon. Moreover, the adsorption of phenoxy-acid herbicides on activated carbon is influenced by the properties of the adsorbent (surface area, porosity and surface chemistry), the adsorbate (acidic herbicides, the presence of aromatic rings, molecular size, solubility and nature of substituent groups) as well as the characteristics of the solution (pH, ionic strength, etc.) (Hameed et al., 2009; Ignatowicz, 2009; Qiu et al., 2009).
On the other hand, the electroadsorption process is a subject that also has attracted great research interest. In general, electrosorption is defined as a current or polarization potential-induced adsorption phenomenon on the surface of the charged electrodes (Han et al., 2006). Specifically, when an external electrostatic field is imposed to the surface of the electrodes immersed in an aqueous electrolyte solution, charged ions are forced to move towards the oppositely charged electrodes, allowing the occurrence of charge separation across the interface (Li et al., 2008), resulting in the formation of strong electrical double layers near the high conductivity and high surface area surfaces (Oren, 2008). The effect of electric field on the adsorption process was studied by Ban et al. (Ban et al., 1998) who discussed the basis of electroadsorption on activated carbon as a treatment for removing pollutants from industrial effluents. Kitous et al. (Kitous et al., 2009) used a combination treatment for the removal of pesticide metribuzin (4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5-one) which consisted of adsorption on a granular activated carbon column followed by application of a potential. The results showed that the adsorption capacity was increased by over 100% compared to the absence of potential. Moreover, this process was used also for inorganic compounds like metal cations with the aim of reducing the contamination of wastewater (Afkhami et al., 2009). Farmer et al. (Farmer et al., 1997) studied the electroadsorption process of hexavalent chromium ion on a support based on carbon aerogel. The electroadsorption and electroadsorption process of dissolved arsenic in the presence of heavy metals (Cr, Ni and Fe) on a granular activated carbon has been studied by
Calo et al. (Calo et al., 2012). One of the conclusions was that the application of an anodic potential increased considerably the adsorption of As.

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

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

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

2. Experimental

2.1. Carbon materials and chemical reagents

The commercial activated carbon used in this work was an activated carbon cloth provided by Carbongen (Spain), which is referred to as HST07. The
samples were washed several times with distilled water until constant pH, and dried in an oven at very mild conditions (80 °C for 3 h) before each experiment. The herbicide 8-Quinolinecarboxylic acid which presents a reagent grade of 98% and the sodium sulfate were obtained from Sigma Aldrich. All solutions were prepared using distilled water.

The textural properties of the ACC (activated carbon cloth) (Table 1) was analyzed by physical adsorption of gases (N\textsubscript{2} at 77 K and CO\textsubscript{2} at 273 K) using an automatic adsorption system (Autosorb-6 Quantachrome Corporation) after samples out-gassing at 523 K under vacuum for 4 h. Nitrogen adsorption at 77 K was used for determining the total volume of pores (V\textsubscript{t}, determined at relative pressure of 0.99), the micropore volume (V\textsubscript{DR}(N\textsubscript{2}), pore size smaller than 2 nm), which is obtained from the Dubinin-Radushkevich (DR) equation (the range of relative pressures used for the DR analysis was: 0.005 < P/P\textsubscript{0} < 0.17), and the apparent specific surface area from the BET equation (S\textsubscript{BET}, applied at 0.05 < P/P\textsubscript{0} < 0.17). The CO\textsubscript{2} adsorption isotherm at 273 K was used to assess the narrowest micropores (V\textsubscript{DR}(CO\textsubscript{2}), pore size smaller than around 0.7 nm) also by application of the Dubinin-Radushkevich equation for relative pressures below 0.025 (Cazorla-Amorós et al., 1998, 1996; Rodríguez-Reinoso and Linares-Solano, 1989). As expected, ACC presents a well-developed pore structure, showing an apparent surface area of ca. 600 m\textsuperscript{2}/g. This surface area is provided by the presence of a pore system with a narrow pore size distribution that is centered in the micropore size region, as pointed out by the similar value of V\textsubscript{t} and V\textsubscript{DR}(N\textsubscript{2}). Since the micropore value determined by N\textsubscript{2} uptake (that
fills the wider micropores) seems to be higher than that determined using 
CO₂ adsorption (which fills the most restricted narrow micropores) the 
mean microporosity size is expected to be higher than 0.7 nm (Cazorla-
Amorós et al., 1998). The slit geometry of the micropores of activated 
carbons along with a mean micropore size in the range of 1 nm is especially 
well-fitted for obtaining a large adsorption uptake of 8-quinoline (ca. 0.9 nm in 
length and planar geometry), ensuring the availability of most of the surface 
area of ACC for the adsorption of 8-quinoline. Moreover, the distribution of 
porosity in activated carbon fibers is usually exposed to the surface of the 
fiber, perpendicular to the fiber axis and shows a low tortuosity (i.e. straight 
slit-like pores that runs in parallel from the external surface towards the 
center of the fiber). In consequence, the diffusion of molecules on ACCs is 
enhanced when compared to a GAC of similar properties, speeding up the 
adsorption rate of aromatic compounds and other adsorbates (Ayranci and 
Hoda, 2005; Brasquet and Le Cloirec, 1997).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) ( \text{m}^2 \text{g}^{-1} )</th>
<th>( V_{\text{DR}}(N_2) ) ( \text{cm}^3 \text{g}^{-1} )</th>
<th>( V_{\text{DR}}(CO_2) ) ( \text{cm}^3 \text{g}^{-1} )</th>
<th>( V_t ) ( \text{cm}^3 \text{g}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HST07</td>
<td>596</td>
<td>0.24</td>
<td>0.15</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 1: Textural parameters obtained from the \( N_2 \) and \( CO_2 \) isotherms using the BET Theory and Dubinin-
Radushkevich Theory.
2.2. Adsorption and electroadsorption procedures

2.2.1. Filter press adsorption and electroadsorption

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

A concentration of 8-QCA of 50 mg/L in 0.5 M Na₂SO₄ was used. A cell potential of 3 V was applied for 24 hours. The temperature was controlled during the experiment at 298 K. At specific time intervals, aliquots of 1 ml were withdrawn in order to monitor the 8-QCA concentration during the experiment, which was done using UV-Vis Spectroscopy (JASCO V-670 Spectrophotometer).

The amount of adsorbed herbicide was calculated by the difference between the initial concentration and the concentration after a given time, with their corresponding volumes, according to the following equation:
\[ q_t = \frac{C_0 V_0 - C_t V_t}{W} \]  

(1)

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

**2.2.2. Batch adsorption**

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

**2.2.3. Kinetic analysis**

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

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

(2)

Where \( q_e \) stands for the total uptake when the adsorption equilibrium is reached, \( D_e \) is the effective diffusivity of 8-QCA in the carbon fiber (m²/s) and \( d_f \) is the mean diameter of the carbon fiber (m), which was estimated to be around \( 10^{-4} \) m using scanning emission microscopy. The initial form of the model was simplified by Reichenberg (Reichenberg, 1953), obtaining the expression that follows:

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

(3)

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

(4)

\[ B = \frac{\pi^2}{4 d_f^2} \cdot D_e \]  

(5)

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

The absence of external mass transfer control in the activated carbon cloth have also been checked through the study of the Reynolds (Re), Sherwood (Sh) and Smichdt (Sc) numbers. For a liquid flowing across a bundle of
fibers, the fiber diameter can be used as the characteristic length (Coulson and Richardson, 1978):

\[ Sh = \frac{k_f d_f}{D_m} \]  \hspace{1cm} (6)

\[ Re = \frac{u d_f}{v} \]  \hspace{1cm} (7)

\[ Sc = \frac{v}{D_m} \]  \hspace{1cm} (8)

Where \( k_f \) stands for the external mass transfer coefficient \((\text{m/s})\), \( D_m \) is the molecular diffusivity of 8-QCA in 0.5M Na\(_2\)SO\(_4\) at room temperature (which have been evaluated as \(4.51 \cdot 10^{-10}\) m\(^2\)/s using the approximation proposed by Treybal (E.Treybal, 1981), \( u \) the lineal velocity of the liquid through the void space of the activated carbon cloth \((0.020\ \text{m/s in our experimental system})\), and \( v \) is the kinematic viscosity of the solution \((1.19 \cdot 10^{-6}\ \text{m}^2/\text{s})\). Similarly, the Sh number can be related to Re and Sc ones through the next expression (Yawalkar et al., 2002):

\[ Sh = \left(2 + 0.6 \cdot Re^{1/2} \cdot Sc^{1/3}\right) \]  \hspace{1cm} (9)

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

\[ Bi = \frac{k_f d_f}{D_m} = Sh \frac{D_m}{D_e} \]  \hspace{1cm} (10)
Given the maximum obtained value for $D_e$ is two order of magnitude lower than $D_m$ (as later discussed), the lack of external mass transfer control is ensured in our adsorption system.

### 3. Results and discussion

#### 3.1. Adsorption of 8-QCA

Fig. 1 shows the amount of adsorbed herbicide on the ACC with the increasing time, in both batch and electrochemical cell experiments at open circuit. It can be observed that working on batch adsorption has little effect on the adsorption capacity of the ACC and on the kinetics of the process, pointing out that both systems must be working under the same regime of mass transfer control. In neither case it was possible to achieve the complete removal of the 8-QCA, but a 52 % and 55 % for batch and filter-press conditions, respectively.

![Figure 1: Adsorption of 8-QCA onto ACC (HST07) in batch (filled triangles) and in filter-press at open circuit (open circles). 50 mg/L 8-QCA + 0.5M Na₂SO₄ solution.]
3.2. Effect of applied voltage

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

Figure 2: Amount of $8\cdot QCA$ adsorbed vs time in consecutive steps of 72 hours long, using HST07 ACC: 1) Adsorption at open circuit (filled triangles); 2) Cathodic electroadsorption at 3 V (empty triangles); 3) Adsorption/desorption at open circuit (filled squares). 50 mg/L $8\cdot QCA + 0.5\text{M Na}_2\text{SO}_4$ solution.

Results clearly reveal that open circuit adsorption is only capable of removing about 55 % of the total amount of $8\cdot QCA$ in solution (Fig. 2, filled triangles). Once an electric field is imposed by applying a difference of potential between the electrodes of 3 V, the adsorption rate is rapidly
increased and the surface of the polarized cloth is then able to adsorb the remaining \textit{S-QCA}, achieving nearly complete removal of the dissolved herbicide (Fig. 2, open triangles). Furthermore, the third stage demonstrates that switching off the applied voltage (i.e., returning to open circuit conditions) does not involve desorption of the pollutant (Fig. 2, filled squares), which suggests that the electrochemically-assisted removal of \textit{S-QCA} in the presence of an ACC is an irreversible process. Because of the use of low dc voltages, we can conclude that electroadsorption is an energy saving and potentially cost-effective purification technology for assisting the removal of dilute emerging pollutants, like herbicides, in wastewater by means of porous solid adsorbents. In the following sections the electroadsorption process will be studied in more detail.

### 3.3. Electroadsoption of \textit{S-QCA}

The imposition of an electrostatic field is known to promote an enhancement of the adsorption capacity of the porous surface and the possibility of speeding up the adsorption rate. The electroadsoption performance not only depends on the magnitude of the interfacial potential applied to the adsorbent, but also on its sign, i.e., on the electrode polarity. Cathodic and anodic electroadsoption experiments of \textit{S-QCA} on ACC were conducted by either pressing the cloth material against the stainless steel mesh cathode or the Ti/Pt expanded mesh anode. In both cases the applied cell voltage was 3 V. The results of the adsorbed herbicide with electrolysis time were plotted in Figure 3 and compared to open-circuit adsorption in the same
filter-press cell. Table 2 compares the removal efficiency attained after 2 hours and after 24 h for each treatment. As can be discerned, both cathodic and anodic electroadsorption processes enhance the adsorption kinetic rate of the herbicide in comparison with open circuit conditions. However, cathodic electroadsorption shows a far better overall performance than the anodic one in maximum removal capacity (which reaches 88 % of the total amount of dissolved $8\cdot QCA$ in about 120 min). Furthermore, it was observed that, unlike the cathodic process, during the anodic process the $8\cdot QCA$ removal proceed in two different regimes; (i) a fast elimination of the pollutant from the solution during the first hour of the treatment, (ii) followed by a much lower remediation rate for the rest of the experiment.

![Graph](image.png)

Figure 3: Amount of $8\cdot QCA$ adsorbed vs time in: cathodic electroadsorption (filled black circles) at 3V, anodic electroadsorption (filled reds circles) at 3 V and open–circuit adsorption in filter-press (empty circles) using HST07 ACC. 50 mg/L $8\cdot QCA$ + 0.5M Na$_2$SO$_4$ solution.
A possible explanation from differences in behavior between cathodic and anodic electroadsoption experiments comes from the oxidation of 8-QCA over the Ti-Pt Anode. ACCs are known for combining enhanced electrical conductivity with a large surface area (in this case, 0.8g provides a surface of more than 450 m$^2$). Since the area of Ti-Pt anode (2.3·10$^{-3}$ cm$^2$ effective area) and stainless steel cathode (3.2·10$^{-3}$ m$^2$ effective area) are much lower than the ACC one, when ACC is attached to either the cathodic or the anodic electrode, most of the active area of the given electrode will be provided by the carbon fiber cloth.

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

Contrariwise, attaching the ACC to the anode greatly hinders the activity of the Ti/Pt, since it will be providing only a small fraction of the active area of the electrode. Taking into account the measured pK$_a$s of the 8-QCA molecule (2.36 and 6.76) (Garribba et al., 2003) it follows that the pollutant molecule
is in its zwitterionic form (deprotonated carboxylate group and protonated quinoline nitrogen) at the electrolyte pH (5.4). Thus, adsorption at the initial stages over the positively polarized activated carbon cloth will proceed at faster rate during the formation of the electric double layer than in normal adsorption because electrostatic attraction between the positively polarized surface of the ACC and the negatively charge carboxylic group of the pesticide; unfortunately, the large amount of solvated SO$_4^{2-}$ anions in the media will also compete with the adsorption of the pesticide in this case, rendering a uptake lower than that reached in the equilibrium for normal adsorption (Han et al., 2006). Beyond that point, a higher uptake can only be attained through oxidation of 8-QCA by the Pt/Ti mesh, that also proceeds at much slower rate than in cathodic configuration.

This explanation is also supported by the higher current (which is directly related to the kinetics rate of the reactions that may occur over the electrodes) registered by the cell when ACC is attached to the cathode. Current intensity starts at 93 mA and then increases to be held around 180 mA from the first half hour until the end of the experiment. In anodic configuration, the current moves from 67 mA in the initial stage of the oxidation down to 25-30mA from two hours up to the end of the experiment.
Table 2: Removal efficiency of 8-QCA by different processes (2 hours long) using HST07 (ACC).

<table>
<thead>
<tr>
<th>Process</th>
<th>% 8-QCA removed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 2h</td>
</tr>
<tr>
<td>Bath adsorption</td>
<td>44</td>
</tr>
<tr>
<td>Open-circuit adsorption filter-press</td>
<td>45</td>
</tr>
<tr>
<td>Cathodic electroadsorption</td>
<td>87</td>
</tr>
<tr>
<td>Anodic electroadsorption</td>
<td>65</td>
</tr>
</tbody>
</table>

In order to check the above suggestion, an electrooxidation experiment of the herbicide 8-QCA was performed in a filter-press cell in the absence of the carbon material. Fig. 4 shows the UV-Vis spectra of the initial solution (red line) and after 24 h of electrolysis (black line) performed in the absence of ACC at the same cell potential of 3V. For the sake of comparison the UV-Vis spectrum recorded after 24 h of anodic electroadsorption is also depicted in the graph (blue line). The spectrum of dissolved 8-QCA shows a couple of sharp bands with maximum absorptions at 206 and 234 nm, which correspond to the \( \pi \pi^* \) electronic transitions of the condensed biaromatic system. Another smaller broad band appears in the range 270-350 nm with a maximum at 315 nm. This spectral profile has been earlier reported for protonated quinoline dissolved in aqueous media (Niu and Conway, 2002b).

Since the pesticide is in its zwitterionic form, the expected molecular structure is fully coherent with the recorded electron absorption spectrum. After 24 h of electrolysis in the absence of ACC inside the filter-press cell, two more absorption bands at 275 nm and 370 nm appeared. The first one
corresponds to the formation of quinone species. This assignment is also supported by the yellow coloration of the solution which gets darker as the experiment progresses. The band at higher wavelength is still of unknown nature, yet it lies in a region where hydroxi-quinolines show strong absorption bands (Tegge, 1968). Then, the 8-QCA compound is oxidized at the anode producing the formation of quinone-like species in solution. These oxidized species could be readily adsorbed on the activated carbon cloth in the electroadsorption experiments. Note that the spectrum recorded after 24 h in the presence of ACC attached to the anode seems to only reveal the characteristic spectral features of 8-QCA at very high dilution. Nevertheless, when the spectra of 8-QCA initial solution and electrotreated solution after 24h are normalized using their respective absorbance values at λ=316 nm and subtracted, an absorbance contribution in the UV region (200-300 nm) arises, that could be related to the presence of low amounts of aromatic species coming from the oxidation of 8-QCA in the solution after 24h of anodic electroadsorption treatment. This finding confirms that 8-QCA can be oxidized even when the electrochemical treatment is conducted with the ACC attached to the Ti/Pt anode.
Figure 4: UV-Visible spectra at different times of electrolysis of 8-QCA at 3 V experiment without ACC at time 0 (red line) and after 24 hours (black line). After 24 hours of anodic electrodosorption experiment at 3 V in presence of ACC (blue line) and difference spectrum of anodic electrodosorption (dot) obtained from the subtraction of red and blue spectra that has been normalized using the absorbance values at λ=316nm).

Interestingly, in the cathodic electrodosorption experiment the electrolyte moved from transparent to yellowish colour during the second hour of the treatment. Then, the solution turned again to transparent colour until no colour was seen in the third hour of the treatment. This seems to support that in the cathodic electrodosorption treatment, enhanced adsorption of 8-QCA is accompanied by its oxidation on the anode surface. The appearance of yellowish colour suggests that the oxidized products are formed over the Ti/Pt anode at a kinetic rate faster than their adsorption rate of the ACC on the cathode. As the experiment goes on, either these oxidized products are finally adsorbed on the ACC or they are oxidized again to form new oxidized products that are more prone to be adsorbed on the ACC.
In clear contrast, the solution remained transparent during the whole anodic experiment, which is pointing out that the oxidation kinetic rate of 8-QCA is lower than the adsorption rate of 8-QCA or its oxidized products over the ACC surface. Thus, the additional removal rate provided by the adsorption of 8-QCA oxidation compounds is much lower for the anodic experiment. These results seem to be in agreement with the differences in the adsorption behavior observed in Fig. 3.

### 3.4. Kinetic study

Figure 5 shows the Boyd plots for the cathodic, anodic electroadsortion and normal adsorption in the filter-press cell. They have been obtained applying equations 3 to 5 to the results of the kinetic experiments shown in Figure 3. It can be seen that the adsorption process in absence of applied potential presents a linear relationship between F(t) and t, and the absence of external mass transfer control is pointed out by the negligible value of the Y-intercept of the regression line. Similarly, the cathodic plot shows a large degree of linearity and intercept with the Y-axis value that is close to zero; nevertheless, a close inspection of the short times region reveals that in the first minutes of the treatment, adsorption was proceeding similarly to adsorption in absence of applied potential. This small induction time could be related to the time needed by the electrodes to reach a quasi-steady state. The most important result to note is the great increase in the slope of the Boyd plot, which speaks of the enhanced internal mass transfer rate on this experiments. The diffusivity coefficient value shows a 6-fold increase when
adsorption proceeds with ACC attached at the cathode and a cell voltage of 3V, rising from $1.1 \times 10^{-14}$ to $7.3 \times 10^{-14}$ m²/s. This enhancement is expectable in terms of the enhanced mobility of 8-QCA proceeding through the formation of quinolines, that could diffuse faster in the porosity of the adsorbent thanks to their smaller molecular size, rendering a faster adsorption rate than that of the original pollutant. On the other hand, the electrodosorption treatment where ACC was attached to the anode seems to produce a huge increase in the initial adsorption rate, followed by a lag period where the adsorption process seems to be finished. Thus, if only the short times (<10 minutes) are considered for estimation of the diffusion coefficient, a value of $2.25 \times 10^{-13}$ m²/s is found. Although the goodness of the fit is rather low and could not be considered as a representative value, the higher apparent diffusion coefficient will likely be reflecting the enhanced molecule mobility due to the action of the electric field, i.e. the electrostatic interaction between carbon surface and the pesticide molecules that takes place in adsorption sites that are only available when the carbon surface is positively polarized and that are readily accessible to the 8-QCA molecule.
Figure 5: Boyd plots and linear fits (if applicable) for cathodic (orange circles), anodic electroadsorption (blue circles) at 3 V process and vs open –circuit adsorption in filter-press (grey circles) using HST07 ACC. 50 mg/L 8- QCA + 0.5M NaSO₄ solution.

4. Conclusions

An activated carbon cloth has been used for enhanced removal of 8-QCA herbicide in dilute aqueous solution by electroadsorption in neutral electrolyte. Batch system adsorption experiments conducted with the HST07 activated carbon cloth and 50 ppm of 8-QCA revealed removal efficiencies of 52 % and 55 %, respectively. However, when an external 3 V dc voltage is applied (electroadsorption process) in a filter-press set-up, the removal of 8-QCA is strongly enhanced, especially when the ACC is located in close contact to the cathode (96 % removal). This enhancement has been proven to be irreversible, since the removed compounds remains adsorbed and did not elute to the solution even after switching off the applied potential.
The electrochemical treatment of the 8-QCA herbicide in the same filter-press device and in absence of activated carbon material leads to the oxidation of the pollutant with subsequent formation of quinones and other unidentified compounds that remain in solution and which are hardly oxidized in the conditions used in the experiment. These compounds seems to be readily removable by adsorption over ACC, although the oxidation rate of 8-QCA by the anode is affected by the emplacement of ACC. In anodic electroadsorption experiments (ACC acting as anode), the oxidation of 8-QCA seems to be slow, though enhanced adsorption rate of the pollutant thanks to the intervention of electrostatic forces is observed in the first minutes of the adsorption experiment. In cathodic configuration, enhanced uptake and rate of 8-QCA comes along with its faster oxidation rate and enhanced uptake of the oxidation products of the herbicide.

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

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6. References


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