REVERSIBLE ELECTROSORPTION OF BENTAZONE ON ACTIVATED CARBON CLOTH

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Abstract

An electrochemical technique has been applied to enhance the removal of a common herbicide (bentazone) from aqueous solutions using an activated carbon cloth as electrode. In open-circuit (OC) conditions, a pH increase reduces the uptake and rate of bentazone adsorption. Also, increasing the oxygen content (i.e., acidic nature) of the carbon cloth causes a decrease in the loading capacity at all pH values. This indicates that adsorption is governed by both dispersive and electrostatic interactions, the extent of which is controlled by the solution pH and the surface functionalization of the adsorbent. Anodic polarization of the carbon cloth noticeably enhances the adsorption of bentazone, the extent depending on the applied current. The electrosorption is promoted via π-π dispersive interactions with the aromatic ring approaching to the carbon surface, although attractive electrostatic interactions between the anionic form of bentazone and the positively charged carbon surface might also occur. Bentazone is desorbed by reversing the polarization to the cathodic side. Hence, the electrochemical technique allows to perfectly control the level of water pollution by pesticides and to regenerate the activated carbon.

Introduction

Lately, there has been an increasing trend in the total volume of sales of agricultural pesticides, being herbicides one of the biggest groups used in the European Union (EU). Their repetitive utilization to maintain health crops has lead to an increase of their level in wastewater from industrial and human activities. Moreover, pesticides are considered by the EU as priority pollutants (Directive 2000/60/EC) as they are highly noxious, long-term persistent and highly mobile throughout the environment, and most of them also present carcinogenic properties. Therefore, the issue of their removal has become a field of growing interest.

Intensive interest has arisen in recent years on the development of procedures for the purification of wastewater. Among the conventional methods, biological treatment is by far the most widely applied and a cost effective one. Unfortunately this alternative cannot deal with the non-biodegradable organic compounds (aromatics, polycylic aromatic hydrocarbons, pesticides) present in wastewater, which in addition are very often inhibitors of the biological processes. These compounds have to be eliminated by high cost and irreversible methods, whose major drawbacks are a poor economic feasibility, a limited applicability and effectiveness, and a short lifetime due to low regeneration capacities.

On the other hand, electrosorptive techniques employing high surface area electrodes of nano-textured materials have been developed as a potential technology for removing toxic pollutants from aqueous solutions. The working principle of electrosorption is based on imposing an external electric field in order to

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force charged species such as ions to move toward oppositely charged electrodes. Until now, extensive research has been carried out on the electrosorption of toxic inorganic ions (Oren and Soffer, 1983) and a few organic molecules -i.e., phenol and aniline- (Niu and Conway, 2002a-b; Niu and Conway, 2003; Ayranci and Conway, 2001; Han et al., 2006). In contrast, scarce works report the application of this technique to the removal of pesticides or more complicated polycyclic aromatic compounds (Niu and Conway, 2002a-b; Niu and Conway, 2003), which constitutes an interesting field of research due to their increasing use in both industrial and domestic applications.

The main objective of this research is to explore the application of electrosorptive techniques for the removal of bentazone (a post-emergence herbicide widely used in agricultural and household applications) using activated carbon cloth as electrode. The efficiency of the electrosorption process was carefully investigated. Special attention was paid to the various factors (heterogeneity of the carbon surface, solution pH, current) that affect the complex process of adsorption and electrosorption from diluted solutions.

Materials and methods

Materials

A commercial activated carbon cloth -*AX*-, obtained from physical activation of rayon and supplied by ACTITEX (France) was chosen for this study. Before usage, *AX* was washed with distilled water at 60 ºC during one week. Then, it was dried at 80 ºC overnight and stored in a dessicator until use. In order to modify the surface chemistry, the carbon cloth was oxidized with ammonium persulfate in water solution as described elsewhere (Ania et al, 2004). After oxidation, the sample was washed and dried at 110 ºC overnight; it will be labeled as AXO. Bentazone [3-Isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one-2, 2-dioxide]- with the highest purity specification was obtained from Aldrich.

Kinetics of adsorption / electrosorption

Kinetics of adsorption/electrosorption were determined in 20 mL of bentazone aqueous solution (initial concentration 20 ppmw) with a fixed adsorbent mass (11 ± 0.5 mg). However, due to the low electrical conductivity of the pesticide solutions, 0.01 mol L^{-1} Na_2SO_4 (having a pH around 5-6) was used as inert supporting electrolyte for the electrosorption experiments. The carbon cloth was cut up in desired dimensions, weighed accurately, and attached to a gold disk used as current collector, this acting as working electrode. A platinum grid served as an auxiliary electrode and Hg/Hg_2SO_4 as reference electrode. Small samples of the solution (2 mL) were taken out at predetermined time intervals to measure the pH evolution and the concentration of the pollutant during sorption, using UV spectrophotometry (Uvikon Xs, Bio-TEk Instruments). The extracted samples were re-introduced in the cell in order to avoid changes in the total volume of solution. This procedure enabled to investigate kinetics of adsorption under both open-circuit (OC) and polarization at different current values of + 1, + 2 and + 5 mA (i.e., galvanostatic mode). The adsorption rate constants were determined from the first-order adsorption kinetics equation.

Textural and chemical characterization of the carbon cloths

Nanotexture of the carbon cloths was characterized by N_2 adsorption at -196 ºC (Autosorb-1, Quantachrome). Before the experiments, the samples were outgassed under vacuum at 120 °C overnight. The isotherms were used to calculate the specific surface area, S_{BET}, total pore volume, V_T, and pore size distribution using the density functional theory (DFT). Additionally, the distribution of pores smaller than 0.7 nm (narrow micropores) was assessed from CO_2 adsorption isotherms at 0 ºC with DR formulism. The materials were further characterized by elemental analysis and the determination of the point of zero charge (pH_{PZC}) by mass-titration as described elsewhere (Noh and Schwarz, 1989).

Results And Discussion

Characterization of the carbon cloths

Nanotextural data of the *AX* and *AXO* cloths are presented in Table 1. The *AX* carbon cloth presents a large surface area and porosity, as evaluated by gas adsorption data. A further analysis of the PSD combining the information of N_2 and CO_2 adsorption isotherms shows that the pore volume determined by CO_2 is larger than the corresponding volume of micropores "seen" by N_2, indicating that the microporosity of the carbon cloth is mainly composed of pores narrower than 0.7 nm. Moreover, the volume of mesopores accounts for less than 10 % of the overall porosity.

Table 1. Textural and Chemical Characteristics of the Studied Cloths

Sample	S_{BET} [$m^2 g^{-1}$]	V_{TOTAL} [$cm^3 g^{-1}$]	$V_{micropores}$ [$cm^3 g^{-1}$][a]	$V_{mesopores}$ [$cm^3 g^{-1}$][a]	V_{CO2} [$cm^3 g^{-1}$][b]	O (% wt.)	pH_{PZC}
AX	926	0.440	0.329	0.086	0.353	8.27	5.7
AXO	960	0.482	0.331	0.127	0.345	19.17	2.5

[a] evaluated from the DFT method applied to the N_2 adsorption isotherms at 77K

[b] evaluated from the DR method applied to the CO_2 adsorption isotherms at 273 K

The oxidized sample *AXO* shows minor changes in the pore volumes, as compared to the initial counterpart. This affects mainly the pores of larger size (mesopores), as evidenced by the pore size distribution (PSD) evaluated by the DFT method. An exhaustive analysis of the PSD combining the information of N_2 and CO_2 adsorption isotherms also corroborates this fact, as the narrow microporosity evaluated from the CO_2 data remains almost constant in both cloths. It can be inferred from these results that the carbon cloth modification turns out in almost negligible alterations in microporosity, and a slight increase in mesopore volume. It can be seen that oxidation produces a three-fold increase of oxygen amount in the *AXO* sample. As expected, the oxidized sample becomes more acidic ($pH_{PZC} = 2.5$) confirming that the majority of the functionalities created are of an acidic nature.

Adsorption of bentazone at open-circuit (OC)

The rate of bentazone adsorption on both carbons was compared at different pH values by measuring the variation of concentration as a function of time, using solutions of equal volume and initial concentration and carbon-cloth pieces of equal mass. In all cases, the experimental data were fitted by a pseudo-first-order kinetics, with correlation coefficients higher than 0.98 (Table 2). This result is in good agreement with those reported by Ayranci et al. on a carbon adsorbent with more developed porosity (Ayranci and Hoda, 2004).

Table 2. Adsorption/electrosorption Parameters of First-Order Adsorption Kinetics for Bentazone at Different pH Values (pH ~5.5 for 0.01 mol.L^{-1} Na$_2$SO$_4$) using Open-Circuit (A) and Anodic Polarization (B).

A)		q_e [mg g^{-1}]	K_{ads} x 10^3 [min^{-1}]	r^2	B)		q_e [mg g^{-1}]	K_{ads} x 10^3 [min^{-1}]	r^2
pH 2	AX	27.7	37.64	0.995	OC	AXO	16.5	12.37	0.998
	AXO	22.8	18.30	0.993	**ANODIC POLARIZATION**				
Na$_2$SO$_4$ 0.01M	AX	27.4	22.54	0.994					
	AXO	16.5	12.37	0.998	+ 1 mA	AXO	17.2	13.37	0.991
pH 7	AX	26.3	20.64	0.995	+ 2 mA	AXO	17.7	19.99	0.988
	AXO	3.4	9.54	0.999	+ 5 mA	AXO	19.3	24.30	0.990

Figure 1 shows different adsorption behaviors, being the adsorption rate much faster for the non oxidized carbon cloth -*AX*-, and also in acidic medium, the later being more significant in the *AXO* sample. Since the analysis of the textural properties of *AXO* revealed very small changes in the porous network, this behavior is certainly linked to the functionalities created on the carbon surface. The enhanced uptake under acidic pH conditions (Figure 1), suggests that bentazone is preferentially adsorbed in a molecular form. Due to the complex structure of bentazone, several adsorptive forces may occur simultaneously.

The decrease of adsorption rate observed after oxidation is most probably due to the alteration of the π electronic density on the carbon surface as a result of its functionalization. It is well-known that the oxygenated functionalities are mainly located at the edges of the basal planes and the entrance of the pores in activated carbons (Donnet, 1982). Taking this into account, functionalization of the carbon cloth withdraws π-electrons from the graphene layers, and then the contribution of dispersive interactions to adsorption is lessened. Competitive adsorption of water molecules must also be considered, since the carbon cloth becomes more hydrophilic upon oxidation. The oxygen groups are ideal sites for water adsorption, favoring the creation of water clusters at the entrance of the pores. Those hydration clusters might effectively reduce and/or hinder the accessibility and affinity of a polyaromatic molecule as bentazone to the inner porous texture (Franz et al., 2000). This would also explain the slower adsorption rate of *AXO* vs the *AX* sample. Hence, the surface is more densely populated by bentazone molecules for carbon materials with the smallest oxygen content and the largest regions of high π-electron density.
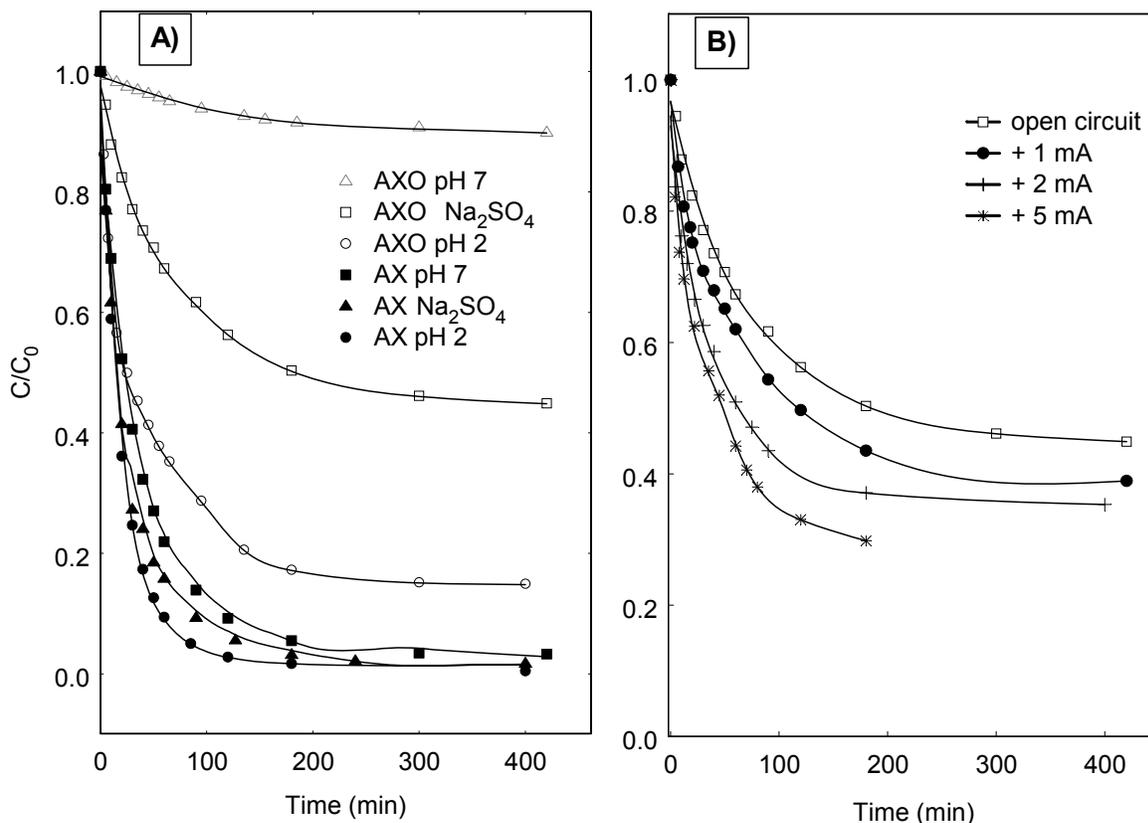
Figure 1. (A) Concentration Decay Curves of Bentazone in open-circuit conditions on the Carbon Cloths AX (Solid Symbols) and AXO (Empty Symbols) at Different pH Values.

(B) Concentration Decay Curves of Bentazone on the AXO Cloth under Open-Circuit (OC) and Anodic Galvanostatic Polarization, in a Non-Buffered Solution (0.01 mol L^{-1} Na_2SO_4 as Supporting Electrolyte). Symbols Represent Experimental Data and Solid Lines the Fitting to the Kinetics Model.

The increase of capacity and rate of adsorption at acidic pH in both carbons is reasonably linked with two factors: the ionization of the adsorbate and the charges on the carbon surface. With a pK_a of 3.3, bentazone exists predominantly in anionic form under pH conditions near neutrality (more than 99 mol % at pH = 6-7), and the neutral molecule is the main structure in solution at pH = 2. The decrease of the amount adsorbed at higher pH suggests a weaker interaction of the carbon surface with deprotonated (anionic) bentazone than with its neutral form. Consequently bentazone is preferentially adsorbed in a molecular form. Similar results on the pH-dependence of bentazone adsorption on soils and clays have been reported (Boivin et al., 2004).

Conversely, pH changes may also affect the adsorptive process through functional groups dissociation on the adsorbent surface; the carbon surface may be either positively or negatively charged depending on the nature of the carbon cloth. At a given pH, the carbon surface and the adsorbate species may coexist in a

complex system, in which the same or opposite charges maybe present, resulting in some widely different adsorption schemes. At acidic pH, all acidic groups on the carbon cloth are protonated and bentazone is mainly non-dissociated, thus repulsive the electrostatic interactions are minimized and the adsorption is enhanced through dispersive interactions. This effect is more remarkable in the *AXO* sample. At higher pH, the adsorption is drastically reduced since negative charges along the edges of the graphitic layers repel the bentazone anions, thereby reducing access of ions to the graphene surface.

Adsorption of bentazone under polarization

To ensure that bentazone is not oxidized or reduced during the electrosorption process, the electrochemical stability of the pesticide was investigated. Cyclic voltammograms of the aqueous 0.01 mol L^{-1} Na$_2$SO$_4$ solution, with and without the targeted pollutant, were recorded at a scan rate of 20 mVs^{-1} in the potential range between - 0.85 and + 1.25 V vs Hg/Hg$_2$SO$_4$. No differences were found in the cyclic voltammograms when the herbicide is present in the solution; this was confirmed by monitoring the UV absorption spectra, which indicated that bentazone is stable in this potential range.

Anodic polarization (positive) was applied to the carbon cloth at constant current (i.e., galvanostatic conditions) in the un-buffered solution, which resulted in an enhancement of the adsorption rate, as it can be seen in Figure 1. Increasing the anodic current from + 1 mA to + 5 mA substantially improved the adsorption rate, as it can also be seen from the parameters of first-order kinetics (Table 2). In fact, positive polarization causes a rise of electrode potential (the latter being more important with increasing the applied current) up to a value that enables the electrolyte decomposition at the working electrode according to:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
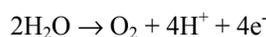
The generation of protons in the pores of the working electrode gives rise to a local pH decrease, which we believe should be responsible for the improved adsorption rate, given that the ionization of bentazone and the charge of the carbon surface functionalities are being altered. Both the anionic forms of surface functionalities and bentazone (predominant in un-buffered solution, as stated above) are protonated to their neutral form, thus enhancing the adsorption rate, which confirms the trend observed in OC.

It should also be mentioned that, due to oxygen evolution, a slight functionalization of the carbon cloth might occur. Oxidation can also cause a collapse of the porous texture of the carbon cloth, particularly if it is carried out under sever conditions (Harry et al., 2007). In this study, the mild experimental conditions of the electrochemical treatment (current up to +5 mA during 3 hours) prevented a large deterioration of the porous texture of the AX carbon cloth, with only a 12 % decrease in the micropore volume evaluated by CO$_2$ adsorption (after anodic oxidation in the absence of the adsorbate, to eliminate any effect due to adsorption). Based on the mechanism proposed for adsorption under OC conditions, modification of surface functionality could have a negative effect on bentazone uptake. Since it is not the case, one has to conclude that oxygen evolution produces either acidic groups in small amount or surface groups which dissociation is not pH dependent.

Therefore it is reasonable to presume that bentazone is electrosorbed via π-π dispersive interactions with the aromatic ring approaching to the carbon surface. Attractive electrostatic interactions between the anionic form of bentazone (if still remaining in the solution) and the positively charged carbon surface (induced by the anodic polarization) might also occur to some extent. A similar mechanism and orientation has been proposed for electrochemical enhanced adsorption of aniline on activated carbon fibers (Han et al., 2006), with electrosorption taking place through the aromatic ring approaching the charged carbon surface. Hence, in non buffered Na_2SO_4, it might be concluded that the pesticide shifted to its neutral form due to local pH decrease in the pores of the carbon electrode, becoming adsorbed on the carbon cloth to a larger rate, as evidenced by the kinetics and equilibrium adsorption isotherms in OC.

It is interesting to point out that the passage of charge in the non-buffered solution gave rise to a slight pH increase (up to one unit increase). This is linked to the faradaic production of OH^- ions at the counter electrode during polarization. Although the OH^- ions created should be neutralized by the H^+ liberated at the working electrode, in this case the pH balance does not apply because the anodic process includes the non-faradaic charging (electrical double layer) of the high surface area carbon cloth. This behavior has also been reported for the electrosorption of azine-type pollutants (Niu and Conway, 2002a). Although the increase is small, this might appreciably affect the efficiency of the electroadsorptive removal of the pollutant. In other words, the generation of protons at the working electrode seems to be critical for the enhancement of electrosorption.

In order to explore the reversibility of the electrochemical process, the carbon cloth saturated with the herbicide in OC conditions was subjected to cathodic polarization at galvanostatic conditions (i.e., - 5 mA). The current passing through the carbon electrode resulted in a decrease of the cell potential down to -1.7 V *vs* Hg/Hg_2SO_4. UV absorption spectra of the pesticide solution were continuously recorded upon galvanostatic cathodic polarization and no structural alterations were detected, confirming the electrochemical stability of bentazone under cathodic polarization. During electrolysis, the amount of bentazone in solution increased with time, indicating that it is being reversibly desorbed from the activated carbon. These results point out that bentazone molecules are weakly adsorbed (no strong or irreversible interactions occur between the adsorbate and the carbon) on the carbon cloth and that the adsorbate does not undergo decomposition and/or polymerization. This observation is in good agreement with the mechanism of bentazone adsorption proposed in earlier works (Ania and Béguin, 2007).

To summarize, it can be inferred that the adsorption rate of this herbicide is mainly controlled by the solution pH and it can be improved by anodic polarization on carbon-based electrodes. Moreover, reversal of polarization (i.e., cathodic) results in the desorption of bentazone.

Conclusions

The adsorption/ desorption of a common herbicide in aqueous solution by an activated carbon cloth was investigated by means of electrochemical techniques. The adsorption process depends on two important

factors: the solution pH and the degree of functionalization of the carbon surface. Oxidation of carbon diminishes both the loading capacity and the adsorption rate of bentazone, while acidic solution pH seems to favor the uptake.

Applying an anodic polarization to the carbon cloth enhances the adsorption rate of bentazone. Moreover, this kind of experiment enables to better understand the adsorption process, and to clarify the role of pH in the overall process. Local pH changes occurring in the pores of the working carbon electrode during polarization seem to be critical for the enhancement of bentazone removal. Due to the high electrode potentials reached, protons are generated in the working electrode during polarization and the rate of adsorption is thereby enhanced. These results corroborate those obtained at open circuit conditions and enable to propose a mechanism of adsorption/electrosorption of bentazone on carbons through a main contribution of π-π dispersive interactions.

Under cathodic polarization of a pre-exhausted carbon cloth, the retained pesticide is reversibly desorbed. Neither textural nor chemical changes are produced in the carbon cloth upon polarization in the absence of the adsorbate. Consequently, the electrochemical desorption of the herbicide is attributed to the charges (and/or pH change) created on the carbon electrode.

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