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Mechanism of adsorption and electrosorption of bentazone on activated carbon cloth in aqueous solutions

*Conchi O. Ania, François Béguin**

CRMD, CNRS-University, 1B rue de la Férollerie, 45071 Orléans, France

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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. A pH increase from acidic to basic reduces the uptake, with capacities going from 127 down to 80 mg/g at pH 2 and 7, respectively. Increasing the oxygen content of the carbon cloth causes a decrease in the bentazone 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 nature of the adsorbent. Anodic polarization of the carbon cloth noticeably enhances the adsorption of bentazone, to an extent depending on the current applied to the carbon electrode. The electrosorption is promoted by a local pH decrease provoked by anodic decomposition of water in the pores of the carbon cloth.

1. 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 led to an increase in their level in wastewater rom industrial and human activities. Moreover, pesticides are considered by the EU as priority pollutants (Directive 2000/60/EC, 2000) 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. Pesticides are commonly present in low concentrations, and seldom exceed water-quality standards. However, high concentrations can appear in surface water during runoff in agricultural areas soon after pesticide application to the farm field, and in water from urban basins as a consequence of urban development and abusive household uses.

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, which make the whole process not affordable from an economical point of view. Reverse osmosis, ion-exchange resins and adsorption on activated carbons are among the most utilized (Karanfil, 2006; Pintar, 2005; Hinkebein and Price, 2005). Their major drawbacks are a poor economic feasibility, a limited applicability and effectiveness, and a short lifetime due to low regeneration capacities.

*Corresponding author. Tel.: +33 238255375.
E-mail address: beguin@cnrs-orleans.fr (F. Béguin).
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On the other hand, electrosorptive techniques employing high surface area electrodes of nano-textured materials (such as activated carbons) have been developed as a potential technology for removing toxic pollutants from aqueous solutions (Oren and Soffer, 1983; Alfarra et al., 2002; Niu and Conway, 2002a–c; Niu and Conway, 2003; Matlosz and Newman, 1986; Ying et al., 2002; Afkhami and Conway, 2002; Ayranci and Conway, 2001; Han et al., 2006a, b). The working principle of electrosorption is based on imposing an external electric field in order to 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; Alfarra et al., 2002; Matlosz and Newman, 1986; Ying et al., 2002; Afkhami and Conway, 2002) and a few organic molecules, i.e., phenol and aniline (Niu and Conway, 2002a–c; Niu and Conway, 2003; Ayranci and Conway, 2001; Han et al., 2006a, b). Although the results have shown good efficiency of ions removal, and that polarization of the carbon surface in a suitable electrolyte could, to some extent, improve the adsorption of some organic pollutants, scarce works report the application of this technique to the removal of pesticides or more complicated polycyclic aromatic compounds (Niu and Conway, 2002a–c; Niu and Conway, 2003; Ban et al., 1998). In this regard, the adsorption of pesticides constitutes an interesting field of research due to their increasing use in both industrial and domestic applications. Particularly, the use of bentazone, a post-emergence herbicide, has become very popular for the control of broad-leaved weeds and crops since 2003 after the ban of atrazine in the EU. In association, the herbicides alachlor and bentazone can be substituted for atrazine to provide the same spectrum of action on weds in cereal grain crops (mainly maize and rice), resulting in new environmental risks (Dousset et al., 2004). Moreover, this herbicide has a relatively high mobility in water. So far, bentazone adsorption has been reported on carbon materials, although neither the use of electrochemical techniques, nor the effects of the adsorbent properties on the overall adsorption capacity have been yet explored (Ayranci and Hoda, 2004).

The main objective of this research is to explore the application of electrosorptive techniques for the removal of bentazone, using activated carbon cloth as electrode. The efficiency of the electrosorption process was carefully investigated. Special attention was paid to the many factors (heterogeneity of the carbon surface, solution pH, current) that affect the complex process of adsorption and electrosorption from diluted solutions.

2. Materials and methods

2.1. 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 °C during one week. Then, it was dried at 80 °C 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 °C 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. For clarity, the molecular structure of bentazone is shown in Fig. 1.

2.2. Equilibrium adsorption isotherms in open-circuit (OC)

Adsorption of bentazone from aqueous solutions was measured at room temperature in a stirred batch system. Kinetic studies revealed that the adsorption equilibrium was established after 3 days. Details of the procedure followed for the measurement of the adsorption isotherms are described elsewhere (Ania et al., 2004). Briefly, different amounts of carbons (from 5 to 100 mg) were weighed and added to flasks containing 0.05 L of a bentazone solution of concentration 20 mg L^{-1}, and shaken for 72 h. Equilibrium concentrations of the solutions were measured using a UV spectrometer (Uvikon Xs, Bio-TEk Instruments) at the corresponding maximum absorption wavelength depending on the solution pH. The equilibrium data were fitted to the so-called Langmuir–Freundlich (LF) single solute isotherm (Derylo–-Marczewska et al., 1984), which has the equation:

$$\vartheta_t = \frac{q_e}{q_0} = \frac{(KC)^n}{1+(KC)^n},$$

where q_e is the adsorbed amount of solute per unit gram of adsorbent, q_0 is its maximum adsorption per unit mass of the adsorbent, K is the Langmuir-type constant defined by the van't Hoff equation, and the exponential term n represents the heterogeneity parameter. The effect of solution pH on adsorption in OC was investigated using HCl/KCl 0.1 M (pH 2) and phosphate (pH 7) buffers.

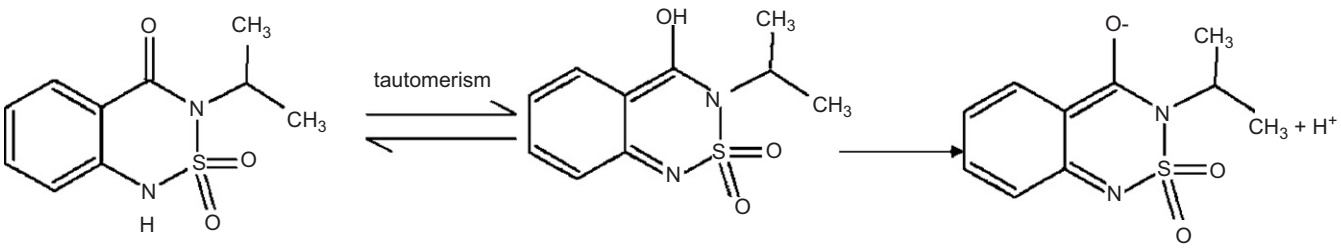

Fig. 1 – Molecular structure of bentazone, keto-enol tautomerism (Peter et al., 1999) and dissociation equilibrium.