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Adsorption and thermal desorption of the herbicide fluroxypyr on activated carbon fibers and cloth at different pH values

L.M. Pastrana-Martínez [a], M.V. López-Ramón [a], C. Moreno-Castilla [b],*

[a] Departamento de Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain
[b] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

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ABSTRACT

Adsorption of fluroxypyr was studied at pH values between 2 and 10 and at temperatures of 298 and 313 K. Adsorption capacity decreased when the solution pH increased. This was explained by changes in fluroxypyr solubility and in dispersive and electrostatic adsorbent–adsorbate interactions with the increase in pH. The highest adsorption was found at pH 2, when the solubility was the lowest and only dispersive interactions operated. An increase in temperature produced a decrease in adsorption capacity. Thermal desorption of fluroxypyr up to 1073 K left a residue on the carbon surface, which increased with higher adsorption pH. Differential thermogravimetry (DTG) profiles showed two desorption peaks at pH values of 2 and 4 and only one peak at pH values of 7 and 10. The appearance of one or two peaks may be related to the type of adsorbate–adsorbent interactions established during adsorption. The predominance of electrostatic interactions favours the strongly bound or chemisorbed fluroxypyr. One important conclusion is that the highest amounts of fluroxypyr are adsorbed and thermally desorbed when there are only non-electrostatic interactions between fluroxypyr molecules and carbon surface. Activation desorption energy and pre-exponential factor were obtained from the shift in temperature of desorption peaks with higher heating rate.

1. Introduction

Herbicides are among the most widespread micropollutants and can be found in many surface and groundwaters due to their extensive use in agriculture. They can be hazardous to the environment and to humans, and their removal from water is very frequently required. Thus, the European maximum threshold limit for herbicides in drinking water [1] is 0.1 μg/L, although higher concentrations have sometimes been detected.

The herbicide fluroxypyr is registered for utilization in cereals, olive trees, and fallow croplands, where it is widely used to control broadleaf weeds. Its chemical formula is 4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid and it belongs to the pyridine family. It is usually commercialized as an ester (Starane) that is rapidly degraded to fluroxypyr acid. The Environmental Protection Agency (USA) classifies it with category II toxicity and as an unlikely carcinogenic, although toxicity assays in rats have demonstrated nephrotoxicity and impaired renal function [2].

Organic micropollutants can be removed from water either by adsorption on a porous solid or by mineralization *via* heterogeneous catalysis. Thus, Aramendía et al. [3] studied the photocatalytic degradation of fluroxypyr in aqueous solution using TiO_2 as photocatalyst. However, no studies could be found on the adsorption of fluroxypyr on porous solids.

Because of their porous texture, surface area, and surface chemistry, powdered and granular activated carbons are commonly used in water treatments to remove organic micropollutants [4]. However, activated carbon fibers and cloths are increasingly proposed as better adsorbents than granular activated carbons because they generally show much higher adsorption kinetics and adsorption capacity. Adsorption from diluted aqueous solutions on carbons depends on the characteristics of the carbon surface, the characteristics of the adsorbate, the solution chemistry, and the temperature [5].

The solution pH, one of the factors controlling the solution chemistry, is very important when the adsorbate is a weak electrolyte. Both dissociation of the adsorbate and surface charge of the adsorbent depend on the solution pH, which therefore controls adsorbate–adsorbent interactions during the adsorption process. The solution pH can also control the desorption step after exhaustion of the adsorption capacity of the adsorbent. Thermal desorption of pollutants from exhausted or spent activated carbons is of major interest because it allows regeneration of the adsorbent for its reutilization in another adsorption cycle.

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* Corresponding author. Fax: +34 958248526.
E-mail address: cmoreno@ugr.es (C. Moreno-Castilla).

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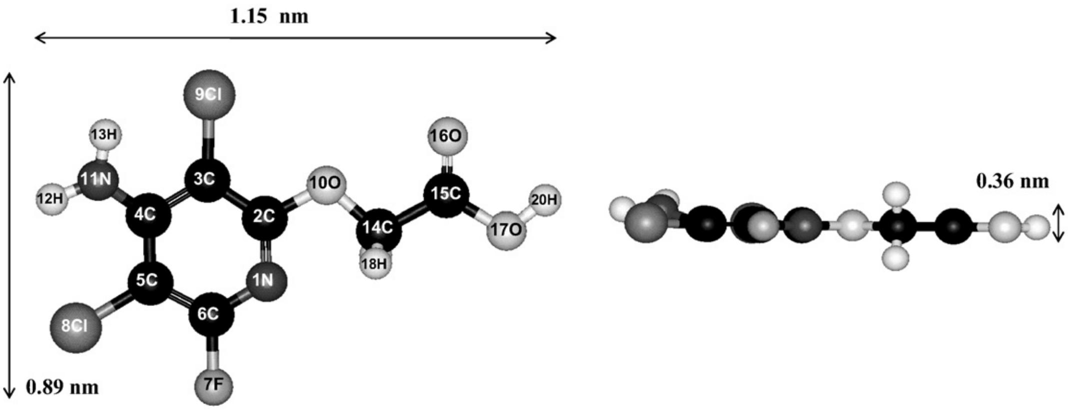

Fig. 1. Molecular dimensions of fluroxypyr.

The present study investigated the effect of solution pH on the adsorption of fluroxypyr from diluted aqueous solutions on activated carbon fibers and cloth and on the thermal desorption of fluroxypyr up to 1073 K.

2. Materials and methods

Two commercial activated carbons were used in this study: an activated carbon fiber (ACF) with diameter of 9 μm and length of 3 mm and an activated carbon cloth (ACC) with thickness of 0.45 mm, both supplied by Kynol Europe. The as-received ACC was cut in circles of 6 mm of diameter for the experiments.

Carbon adsorbents were characterized by N_2 adsorption at 77 K [6], obtaining the surface area, S_{BET}, by application of the BET equation. The Dubinin–Radushkevich and Stoeckli equations [7] were also applied to obtain the micropore volume, W_0, and mean micropore width, L_0. The mesopore volume of samples was obtained from the difference between the amount of N_2 adsorbed at a relative pressure of 0.95 and the W_0.

The oxygen content of activated carbons was obtained by using an elemental analyzer (Fisons Carlo Erba 1108). Ash content was determined by burning a portion of activated carbon in a furnace at 1083 K and weighing the remaining mass. The pH at the point of zero charge (pH_{PZC}) was determined from potentiometric titration as described in detail elsewhere [6,8].

The herbicide was supplied by Sigma–Aldrich with a purity of 99%. The molecular structure of fluroxypyr is depicted in Fig. 1. Its molecular dimensions were obtained from data collected by X-ray diffraction. To determine all possible conformers of the molecule, a scan was carried out at the DFT/B3LYP level of theory with the Pople's basis 6-31 + G* [9]. Only the dihedral angles C14-O10-C2-C3 and O16-C15-C14-O10 (see Fig. 1) varied in the scan, and remaining molecular parameters were unchanged. Using Gaussian 03, Revision C.02 calculation [10], two conformers were obtained, the more stable of which had C14-O10-C2-C3 and O16-C15-C14-O10 close to 180° and 0°, respectively. At the same level of theory, this structure was again optimized at the isolated molecule approximation, giving a dipolar moment of 1.26 Debyes.

In order to simulate solvent effects on the molecular structure, a polarizable continuum model calculation within integral equation formalism [9] was carried out at the same level of theory. A value of 1.74 Debyes was obtained for the dipolar moment. The "effective fluroxypyr molecular area" was obtained from a volume calculation implemented in Gaussian 03.

The herbicide was also characterized by potentiometric titration to determine its speciation diagram as a function of the pH, which yields information on the distribution of the different forms (neutral, anionic, or cationic) in aqueous medium at different pH values [11].

Adsorption isotherms of fluroxypyr from aqueous solutions were obtained by using 0.05 g of carbon and 500 mL of herbicide solutions at concentrations ranging from 5 to 90 mg/L. Adsorption was carried out at 298 and 313 K using unbuffered and buffered (at pH of 2, 7 and 10) fluroxypyr solutions. A pH of 2 was obtained with a buffer composed of phosphoric acid and monobasic potassium phosphate; pH 7 with monobasic potassium phosphate and dibasic sodium phosphate; and pH 10 with boric acid, potassium chloride, and sodium hydroxide. The pH of the unbuffered fluroxypyr solution was taken as 4 (although it slightly changed with the herbicide concentration). Thermostated suspensions were mechanically shaken at 300 rpm during one or two days for ACF or ACC, respectively, although equilibrium was reached in several hours. Equilibrium concentrations were spectrophotometrically determined at 212 nm using a CECIL double-beam spectrophotometer model CE7200. Lamber–Beer's law was determined for each pH used.

ACC was selected to study the thermal desorption of fluroxypyr after its adsorption at different pH values because it was easily handled than ACF. For this purpose, 0.05 g of ACC was soaked in 500 mL of fluroxypyr solution containing 90 mg/L of the herbicide and the corresponding buffer. After equilibrium was reached, the amount adsorbed was determined by UV-spectrophotometry. After adsorption, the sample was dried in an oven at 383 K for 24 h and the cool sample was then carefully weighed, calculating the percentage weight loss at 383 K, W_{383}.

After thermal desorption of the oven-dried spent ACC, DTG profiles were obtained using a Mettler-Toledo thermobalance model TGA-STDA 851. Sample was heated to 1073 K in dry nitrogen ($80\ cm^3/min$) at heating rates of 10–40 K/min following a method described elsewhere [12,13]. The DTG of the oven-dried spent ACC at each pH was corrected with a blank obtained after soaking ACC for two days in a solution containing only the buffer. The percentage of weight loss after heating at 1073 K, W_{1073}, was obtained from these experiments. All weight loss calculations were made with respect to the amount of adsorbed fluroxypyr obtained from UV-spectrophotometry.

3. Results and discussion

The molecular structure and dimensions of fluroxypyr are depicted in Fig. 1, its speciation diagram is shown in Fig. 2, and some of its physical characteristics are compiled in Table 1. According to the molecular dimensions of fluroxypyr, it can gain access to the microporosity of the adsorbents. Fluroxypyr has a relatively high dipolar moment, and its solubility in water at 298 and 313 K markedly increases when the solution pH rises from 2 to 10. This is due to an increase in the dissociation of the fluroxypyr molecules in the same direction. Thus, the speciation diagram