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Efficiency of three powdered activated carbons for the adsorption of atrazine and diuron—use of some models

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ABSTRACT: The removal of atrazine and diuron, two widely used pesticides, was studied on three Powdered Activated Carbons (PAC) (kinetics and isotherms), and different adsorption models were tested: direct (saturation), Langmuir Freundlich, Adams–Bohart, Elovich, Kiselev and Fowler–Guggenheim. The results indicated that the PAC F400 from Chemviron was the best for adsorption of the two pesticides, according to its microporous structure. The Langmuir model seemed to be the best for calculating the maximal adsorption capacities and equilibrium constants. However, use of the other models showed that the adsorption was exothermic, and also realised the value of the equilibrium constant.

INTRODUCTION

Atrazine (or triazine) and diuron are widely found herbicides in natural waters, and atrazine has sometimes been considered a pollution indicator[1,2]. Traditional clarifying treatments are not sufficient for their removal, so other physical processes have been suggested in order to produce drinking quality water, such as ozone oxidation [3], hydrogen peroxide–ozone degradation [4] or ultra and nanofiltration [5]. Adsorption, on powdered activated carbon (PAC) during the clarifying step, or on granular activated carbon (GAC) during biological filtration [6], remains the most widely used and the most efficient method [7]. The modelling of this adsorption by the Langmuir method was widely used both for a single solute and for competitive multiple adsorption [8].

The aim of this study was to compare the behaviour of three types of PAC in their removal of atrazine and diuron. The types of powdered carbon were selected according to their method of preparation and their origin, and thus the mineral cations on their surface. Using various different mathematical models, the adsorption capacity of each PAC was determined. It has previously been shown that released cations could have a large influence upon the adsorption of organic species [9].

MATERIALS AND METHODS

Reagents

The atrazine and diuron selected for these studies were obtained from Chem Service, Interchim, France and were of analytical grade. Their solubility in water was 35 and 42 mg/L, and maximum UV absorbancies were 222 and 211 nm for atrazine and diuron, respectively. Atrazine, a basic compound (pK = 1.68), always remains in its molecular form in water. The solutions (pH = 5.5 $\pm$ 0.2) were prepared in distilled water: for atrazine (22 mg/L), the solution had to be shaken for 1 week before dissolving, but diuron dissolved much faster (40 mg/L). After filtration through a 0.3 μm membrane, solutions were kept at 4 °C, in darkness. The pH of all the solutions was 5.5 $\pm$ 0.2.

Standards (of atrazine and diuron) were used to determine the initial concentration C_0 of the working solutions which were obtained by dilution.

Cations were prepared from RP-Normapur commercial products of Prolabo, and were used in solution in water.

Instrumentation

Herbicides were analysed by UV absorption with a Shimadzu UV 160A spectrophotometer (passing strip 1 nm), fitted with 1 or 5 cm quartz tanks.

Some of the analysis of herbicides were carried out with an HPLC apparatus: an L6000 Hitachi pump fitted with a RP 18 column (Lichrosorb, 7 μm, 25 cm) and a AS 2000A Hitachi detector. The mobile phase was water/methanol (20:80) and the injected volume 20 μL.

Cation analyses were carried out by ionic chromatograhy: a Dionex DX 100 apparatus was used, a water standard solution was of 30mS sensitivity: 0.2 p.p.m. of Na^+ (NaCl), 0.2 p.p.m. of K^+ (KCl), 1.25 p.p.m. of Mg^{2+} ($MgCl_2$) and 1.25 p.p.m. of Ca^{2+} ($CaCl_2$).

Powdered activated carbons (PAC)

The selected powdered carbons were: F400 (Chemviron), Acticarbone 25K (Ceca) and Picazine (Pica). The material was directly produced in a powdered form with grains smaller than 50 μm. The raw carbon samples were then washed:

- a 20 mg sample of F400 or Acticarbone 25K was shaken for

24 h in 2 L of 1 M HCl so that the carboxylate groups were transformed into carboxylic acids [10]. After filtration through 0.3 μm nitrocellulose filters, the PAC was washed with distilled water until all the chloride ions were removed and pH was fixed at 5.5 $\pm$ 0.2.

- a 20 mg sample of Picazine was shaken with 2 L of NaOH (15×10^{-3} M) for 24 h and then filtered through a 0.3 μm nitrocellulose filter. PAC was washed with distilled water until the pH was fixed to 5.5 $\pm$ 0.2.

The products were then dried at 100 °C and stored.

In order to determine the quantity of ions released by the PAC, 100 mg of the raw carbons were shaken with 200 mL of distilled water for 72 h, and the filtrate was then analysed.

Total acidity was measured according to the method of Boehm *et al*. [11].

The main characteristics of PAC are given in Table 1.

Adsorption studies

Batch experiments were performed at 20 $\pm$ 2 °C with 125 mL bottles filled with 100 mL of the herbicide solutions (C_0 = 50 μM for atrazine and 100 μM for diuron) and a constant mass of PAC, 4 mg (m = 40 mg/L) for kinetics and 1–10 mg (10 < m < 100 mg/L) for isotherms. The bottles were closed and placed in a horizontal shaker (90 r.p.m.).

At a fixed time for the kinetic tests, the suspensions were filtered through a 0.3 μm cellulose filter and the solution was subsequently analysed to determine the herbicide residual concentration C_r; the adsorbed concentration is $C_{ad} = C_0 - C_r$.

For isotherm studies, the same treatment was carried out after the equilibration time (according to kinetic experiment results).

RESULTS AND DISCUSSION

Kinetics

The adsorption of atrazine did not change irrespective of whether or not the PAC was washed. The equilibrium time chosen for isotherm study was 3 h.

However, the nature of the PAC was important, and the adsorption was best with the F400 from Chemviron. However, a small difference was apparent for the Ceca PAC, perhaps due to the macroporous structure of this carbon (Fig. 1).

For the adsorption of diuron a small difference appears for the PAC from PICA (Fig. 2), perhaps due to a repulsion of the PO_4^{3-} groups on the surface of the raw PAC.

Generally, adsorption was a function of the specific area of the PAC and of its iodine number.

The use of the Adams & Bohart model [12] for different kinetics results, failing the desorption at the beginning of the phenomena, led to the kinetic constant of the adsorption k_a (Table 2) and to a first maximal adsorption capacity qm for the different PAC (Table 3).

$$\delta q/\delta t = k_a.C_r\,(qm - q),$$

where $q = C_{ad}/m$

For atrazine, different values of k_a indicated a great difference between the Chemviron F400 PAC and the Ceca PAC, on which the adsorption is slower. For the diuron, in contrast, the kinetic constants are nearly the same whatever the nature of the PAC. The volumes of the two molecules ($2–3 \times 10^{-22}$ cm^3) calculated by the methods of Abraham & Gowan [13] confirm that they could adsorb on microporous surfaces, and that this is more difficult for the macroporous PAC from Ceca.

Table 1 Some characteristics of selected raw powdered activated carbons

	F400	PICAzine	CECA
Origin*	bituminous coal	wood	pine wood
Activation*	high temperature	chemical	vapour
	under O_2	500 °C	900–1000 °C
Specific area* (m^2/g)	1490	1235	915
Iodine number* (mg/g)	1050	923	750–780
Porous structure*	micro	micro	macro
Total acidity of surface functions (mEq/g)	0.23	1.64	0.29
Main released ions (g/100 g PAC)			
Ca^{2+}	0.18	0.20	0.30
Mg^{2+}	0.02	0.03	0.09
Na^{+}	0.01	0.03	0.02
K^{+}	0.01	0.06	0.40
PO_4^{-3}	0.01	19.75	0.15

* Manufacturer's data.

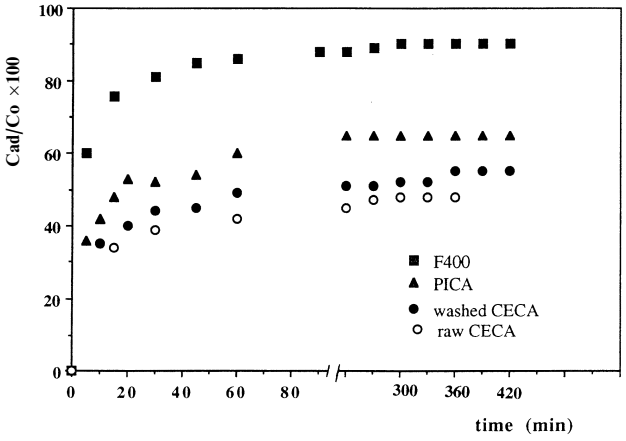

Fig. 1 Adsorption kinetics of atrazine (50 μM) on different types of PAC (40 mg/L); pH = 5.5 ± 0.2; temperature = 20 ± 2 °C.

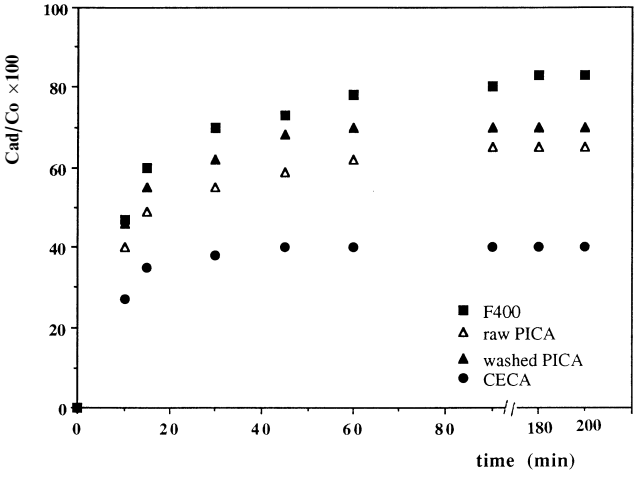

Fig. 2 Adsorption kinetics of diuron (100 μM) on different types of PAC (40 mg/L); pH = 5.5 ± 0.2; temperature = 20 ± 2 °C.

Isotherms

Different models were used to exploit experiments, generally plotting $q = C_{ad}/m$ as a function of Cr. The main result of the isotherm tests was a value of qm the theoretical maximal capacity of the PAC for the organics.

The first method was by direct representation (saturation).

Langmuir's model [14] is a model which is widely used to describe physical adsorption on to activated carbon, even though it is principally designed for a simple molecule layer adsorption without interaction. Its linear form is [15]:

$$1/q = 1/(qm.K) \times 1/C_r + 1/qm$$

where K is the thermodynamic equilibrium constant of adsorption. The Freundlich model [16] is more general and can be employed for different materials:

$$\log q = \log K_f + 1/n \,.\, \log C_r$$

where K_f and n are Freundlich constants

The Elovich model [17] is also a kinetic model which leads to the maximal capacity qm and to the equilibrium constant K:

$$\mathrm{Ln}\, q/C_r = \mathrm{Ln}\, K.\, qm - q \,.\, 1/qm$$

The results of isotherms for different washed PAC and for the two pesticides are given in Table 3. It appears (i) that capacities are nearly identical whatever the PAC, with direct and Langmuir isotherms, the Langmuir model seems to describe this adsorption correctly, and (ii) that the PAC F400 from Chemviron is a good adsorbant for the two pesticides.

The differences between the maximal adsorption capacity obtained from the models are also smaller for the F400 PAC, and the adsorption capacities were comparable for atrazine and diuron. The macroporous Ceca carbon was the PAC which gave the smaller adsorption for atrazine.

It should be noted that the qm varied according to the specific area of the PAC (Figs 3 and 4), with smaller differences for diuron. The equilibrium constants calculated from the Langmuir model are shown in Table 4; they can be compared with those of other models.

An attempt to explain these results based on other models was made as follows:

The Elovich model:

$$\mathrm{Ln}\, q/qm = \mathrm{Ln}\, K.qm - q\,(1/qm)$$

The maximal adsorption capacity seems to be undervalued (Table 3) and the values of K, the equilibrium constant, are then increased.

The Kisselev model [18]:

$$[1/(1-\theta).C_r] = (K/\theta) + K.K_n$$

and the Fowler & Guggenheim model:

$$\mathrm{Ln}\,[C_r.(1-\theta)/\theta] = -\,\mathrm{Ln}\, K + (2\, W.\theta/R.T)$$

Table 2 Kinetic constants for adsorption of atrazine and diuron on PAC according to the Adams & Bohart model, pH = 5.5 ± 0.2, temperature = 20 ± 2 °C. k_a (L/min/mmol ± 0.2)

	raw F400	washed F400	raw PICA	washed PICA	raw CECA	washed CECA
atrazine	19.4	–	11.9	–	3.2	2.3
diuron	2.0	1.2	1.6	1.6	1.8	1.6

Table 3 Theorical maximal adsorption for washed carbons according to differents models for isotherms, qm ± 0.1 (mmol/g)

	F400	PICA	CECA
atrazine			
direct	1.1	1.0	0.7
Langmuir	1.2	1.1	0.7
Freunlich	1.2	0.5	0.5
Adams & Bohart	1.1	0.8	0.6
			0.4*
Elovich	1.1	0.5	0.1
diuron			
direct	1.2	1.2	1.2
Langmuir	1.4	1.4	1.2
Freunlich	0.8	1.1	1.2
Adams & Bohart	1.2	0.6	1.0
	2.5*	1.5*	0.6*
Elovich	0.5	0.4	0.9.

* Value for raw carbon.

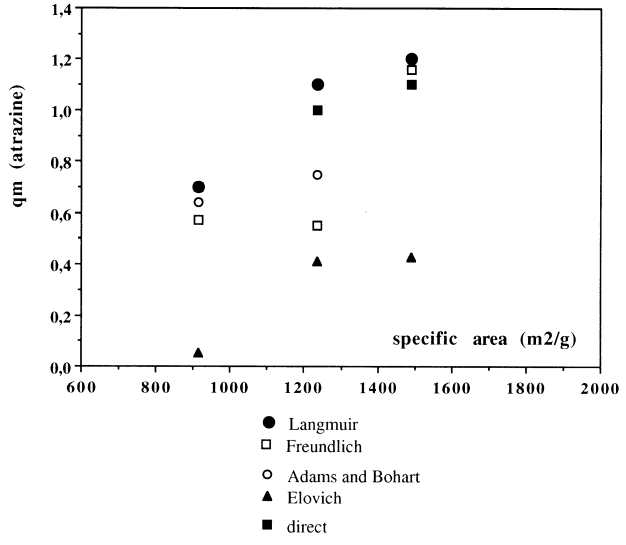

Fig. 3 Maximal capacities values according to specific area of different PACs for atrazine.

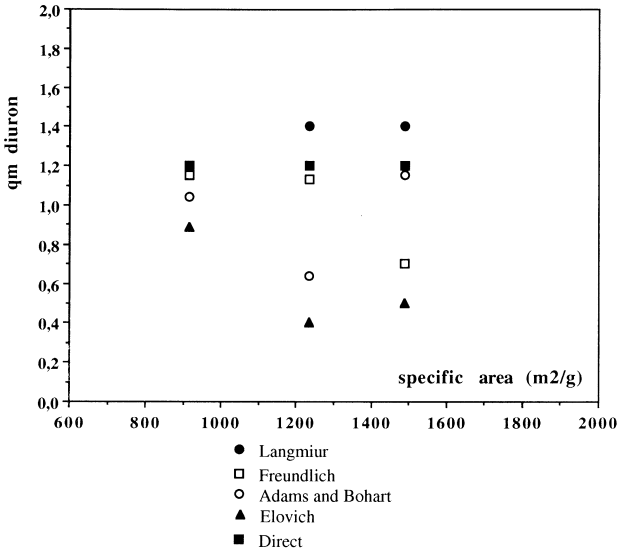

Fig. 4 Maximal capacities values according to specific area of different PACs for diuron.

(with $\theta = q/qm$), led to constant equilibrium values which were close to those of the Langmuir model (Table 4), but the heat of reaction W does not seem to be significant.

The heat of adsorption value (ΔQ) calculated by the Temkin equation seems to be better (Table 5), and shows that adsorption is an exothermic phenomena:

$$\theta = (R.T/\Delta Q)\ \mathrm{Ln}\ K_0 + (R.T/\Delta Q)\mathrm{Ln}\ C_r\ (K_0.e^{-\Delta Q/R.T})$$

The addition to the reaction of a cation (Ca^{2+}, Cu^{2+}, Ba^{2+}, Mg^{2+}) at a concentration of 10–100 μM, did not give significant differences for the adsorption values; only a small decrease for diuron with the PAC from Chemviron and Pica (about 6%), possibly due to the formation of an unidentified complex. This result indicates that the washing of PAC liberates some sites for adsorption which were not fromed as a result of the release of cations.

CONCLUSIONS

Our experiments the adsorption of atrazine and diuron on to different PACs (from Chemviron, Pica and Ceca) have demon-

Table 4 Thermodynamic equilibrium constant for atrazine and diuron adsorption on washed PAC according different model, $K \pm 0.1$ (L/mol)

	F400	PICA	CECA
atrazine			
Langmuir	19.2×10^5	2.4×10^5	8.6×10^5
Fowler–Guggenheim	25.4×10^5	2.2×10^5	14.6×10^5
Kiselev	41.0×10^5	2.7×10^5	11.0×10^5
diuron			
Langmuir	3.3×10^5	4.0×10^5	2.8×10^5
Fowler–Guggenheim	24.4×10^5	7.2×10^5	2.8×10^5
Kiselev	19.0×10^5	5.5×10^5	3.1×10^5

Table 5 Main parameters according to Freundlich & Temkin models

	F400	PICA	CECA
atrazine			
Freundlich K_f ($\pm$ 0.1) (mmol/g)	1.2	0.6	0.6
n ($\pm$ 0.2)	4.0	3.8	10.5
Temkim ΔQ ($\pm$ 0.5) (kJ/mol)	16.3	13.2	30.7
diuron			
Freundlich K_f ($\pm$ 0.1) (mmol/g)	0.7	1.1	1.2
n ($\pm$ 0.2)	4.2	9.6	3.3
Temkim ΔQ ($\pm$ 0.5) (kJ/mol)	9.9	17.5	10.9

strated that the microporous PAC F400 from Chemviron and the Picazine from Pica were the best PACs for the adsorption of the two herbicides. The Acticarbone from Ceca was not as efficient.

The use of different mathematical models led to a calculation of the maximal adsorption capacity of PAC and to the value of equilibrium constant. The Langmuir model seems to be better than the others, but the results from these other models were also interesting and showed that the adsorption was an exothermic phenomena, the equilibrium constant of which could be calculated.

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