

Kinetics of diuron and amitrole adsorption from aqueous solution on activated carbons

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Abstract

A study was conducted on the adsorption kinetics of diuron and amitrole from aqueous solutions on activated carbons of different particle sizes and on an activated carbon fiber. Different kinetic models were applied to the experimental results obtained. A pseudo-second-order rate equation fitted the adsorption kinetics data better than a pseudo-first-order rate equation. Amitrole showed faster adsorption kinetics compared with diuron because of the smaller size of the former herbicide, despite its lower driving force for adsorption. Both reaction rate constants increased when the particle size decreased. The activated carbon fiber and the activated carbon of smallest particle size (0.03 mm) showed similar adsorption kinetics. The intraparticle diffusion rate constant increased with higher initial concentration of herbicides in solution and with lower particle size of the adsorbent. This is because the rise in initial concentration increased the amount adsorbed at equilibrium, and the reduction in particle size increased the number of collisions between adsorbate and adsorbent particles. Demineralization of the activated carbon with particle size of 0.5 mm had practically no effect on the adsorption kinetics.

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1. Introduction

Contamination of surface and groundwater with herbicides may become an issue of major concern due to their intensive and widespread use in agricultural and urban areas [1]. Among the numerous agrochemicals in current use, diuron and amitrole are widely employed as pre- and post-emergence herbicides, respectively. Both are used to control broad-leaved weeds in different agricultural settings, e.g., fields for the cultivation of cotton, wheat, olive trees, and sugar cane, and even in urban areas. The two herbicides are also mixed together for some applications. Herbicide mixtures are frequently detected in streams, and the combined toxicity of these compounds in aquatic ecosystems may often be greater than that of any individual pesticide present [1].

Generally, the environmental fate of herbicides depends on the chemical transformations, degradation and transport. Transformation determines which herbicides are degraded in the environment, and how much of pesticides and their metabolites (degradation products) are present in the environment, where and for how long. Transport determines where and how herbicides move in the environment. Adsorption of herbicides from soil water to soil particles is one of the most important chemical processes that limits mobility in soils by reducing the amount of herbicides available to the percolating soil water [2].

Diuron is released to the environment during its use as a pre-emergence herbicide. Therefore, it is primarily released on soil although releases into water occur from runoff and possibly in wastewater. Diuron is a highly persistent and fairly immobile herbicide. When applied to soil it has a mean half-life of approximately 330 days and will not leach below 5–10 cm from the surface. The major product of the degradation compounds that were isolated was 3,4-dichloroaniline and this metabolite may be further metabolized to an azobenzene derivative [3].

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Amitrole has low soil persistence and high potential mobility in soils because it will not strongly adsorb to soil. Its half-life is 14 days. Degradation of amitrole in soil is usually fairly rapid but variable with soil type and temperature. Amitrole is stable to hydrolysis. Pesticides with similar properties have been found in ground water [4].

On the contrary, the water solubility of amitrole (280 g/L at 25 °C) is much higher than that of diuron (42 mg/L at 25 °C); therefore, amitrole can make a greater contribution to ground-water contamination via leaching.

Adsorption on activated carbons is known to be one of the best methods to remove this type of hazardous compounds from contaminated waters, and it has been widely used for water and wastewater treatments. The design of an adsorption process for water treatments requires knowledge of the adsorption kinetics and equilibrium data [5]. Adsorption equilibrium parameters were previously determined [6–9], in studies on the effects of carbon surface chemistry, adsorption temperature, solution pH and ionic strength on adsorption of diuron and amitrole from diluted aqueous solutions.

The objective of the present investigation was to determine the adsorption kinetics of diuron and amitrole on a series of activated carbons with different particle sizes and on an activated carbon fiber. Several kinetic models are available to describe porous solid adsorption processes. A lumped analysis of the adsorption kinetics was carried out in this study, which is generally adequate for practical applications [10–12]. Thus, three kinetic models were used. The first two described the adsorption process in the form of a rate constant, using pseudo-first-order and pseudo-second-order rate equations, both well-known models. The third model was the intraparticle diffusion model derived from Fick's law [5,10,11,13–17].

2. Materials and methods

Two carbon materials were used in this study, a granular activated carbon (GAC) and an activated carbon fiber (ACF), supplied by Waterlink Sutcliffe Carbons and Kynol Europe, respectively. The as-received GAC had a particle size of 1.5 mm and was then ground and sieved to a particle size of 0.5 or 0.03 mm. The GAC with 0.5 mm particle size was demineralized by treatment with a 5 M HCl solution followed by alternate treatments with concentrated HF and HCl solutions. The demineralized sample was then washed with distilled water until absence of halides in the wash. ACF was 9 µm in diameter and 3 mm in length.

The adsorbents were characterized by N₂ adsorption at –196 °C, obtaining the BET specific surface area and micropore volume (from DR equation). Adsorbents were also potentiometrically titrated, as described elsewhere, to determine the variation of surface charge as a function of solution pH [18], obtaining the pH at the point of zero charge (pH_{PZC}).

The herbicides diuron and amitrole were supplied by Sigma–Aldrich with a purity of 99%. The chemical formulas of diuron and amitrole are 3-(3,4-dichlorophenyl)-1,1-dimethylurea and 3-amino-1,2,4-triazole, respectively (see Fig. 1). Some characteristics of herbicides are listed in Table 1,

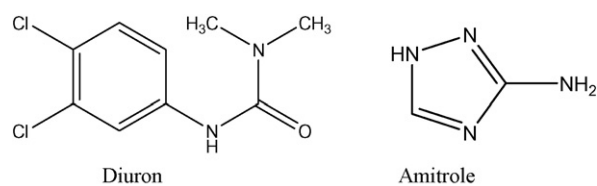


Fig. 1. Structure of the herbicides.

where K_{ow} is the octanol–water partition coefficient, a measure of hydrophobicity [19]. The molecular areas of these herbicides and the speciation diagrams as a function of solution pH were previously obtained [8].

Adsorption kinetics measurements were carried out at 25 °C following a previously used batch method [8,9] to determine adsorption isotherms of diuron and amitrole. Each data point was obtained by using 0.05 g of carbon and 500 mL of a solution containing 25 or 40 mg diuron/L, or 0.05 g of carbon and 100 mL of a solution containing 50 or 90 mg amitrole/L. These measurements were performed at least twice to know their reproducibility. Solutions were buffered at pH 7 with a monobasic potassium phosphate/dibasic sodium phosphate buffer and were 0.01 M in KCl. Suspensions were mechanically shaken at 300 rpm, and the concentration of solutions was periodically measured by spectrophotometry at wavelengths of 248 and 202 nm for diuron and amitrole, respectively, using a UV-Vis CECIL double beam spectrophotometer model CE7200. Shaking at 500 rpm gave similar results.

3. Results and discussion

Surface characteristics of GAC and ACF were previously published [18]. The GAC sample with a particle size of 1.5 mm had a BET specific surface area of 1191 m²/g, a micropore volume of 0.494 cm³/g and an ash content of 2.4%. These values showed practically no change when the particle size was reduced to 0.03 mm. Demineralized GAC sample with 0.5 mm particle size (GAC-D) had a BET surface area of 1144 m²/g, a micropore volume of 0.471 cm³/g and an ash content of 0.1%. Therefore, demineralization produced a very slight decrease in surface area and microporosity. ACF had a BET specific surface area of 1709 m²/g and a micropore volume of 0.734 cm³/g.

Potentiometric titrations of diuron and amitrole showed them to be neutral at pH 7 [8]. Values of pH_{PZC} were 7 for ACF and

Table 1
Characteristics of herbicides

Property	Diuron	Amitrole
Water solubility at 25 °C (g/L) [19,20]	0.042	280
log K_{ow} [19]	2.85	–0.97
pK _a ^a	3.7	4.3; 10.4
Dipolar moment (Debyes)	7.55	1.24
Length–width–height (nm)	1.29–0.77–0.74	0.75–0.62–0.37
Molecular area (nm ² /molecule)	0.75	0.39

^a Values obtained from potentiometric titrations [8].

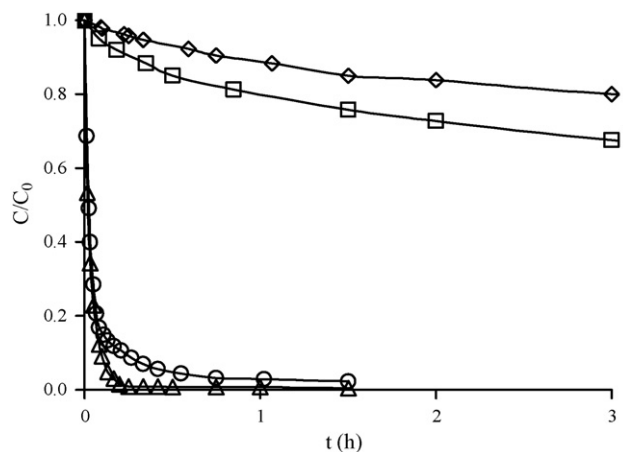


Fig. 2. Adsorption kinetics of diuron on GAC: $\phi = 1.5$ mm (\diamond), $\phi = 0.5$ mm (\square) and $\phi = 0.03$ mm (\circ) and on ACF (Δ). $C_0 = 40$ mg/L.

8.5 for GAC. Therefore, the adsorbate–adsorbent interactions under the experimental conditions used to determine adsorption kinetics (pH 7) were predominantly non-electrostatic. This is because the adsorbate and ACF were neutral and the surface charge of GAC was very slightly positive at pH 7 [18].

Figs. 2 and 3 depict the adsorption kinetics of diuron and amitrole, respectively, at one of the initial concentration used. The adsorption of organic compounds from a liquid onto a solid phase can be considered a reversible process with equilibrium established between the two phases. The kinetic models used in this study to describe the adsorption (reaction rates) were based on the assumption that adsorption of herbicides on activated carbons is a pseudo-first- or pseudo-second-order reversible process. These two well-known models have been applied to many adsorption processes [10–12,13,15–17]. Both models suppose that the difference between the solid phase concentration at time t , namely q , and the solid phase concentration at equilibrium, namely q_e , is the driving force for the adsorption. When the total rate of adsorption is proportional to this force, the kinetics obeys a pseudo-first-order model, but if it is proportional to the square of the driving force, the kinetics follows a pseudo-second-order model.

Table 2
Pseudo-first-order and pseudo-second-order rate constants, k_1 and k_2 , their correlation coefficients, R^2 , and uptake at equilibrium, q_e , experimental and calculated using both kinetic models for diuron adsorption on carbons

Carbon	ϕ (mm)	C_0 (mg/L)	Pseudo-first-order kinetic model			$q_e(\text{exp})$ (mg/g)	Pseudo-second-order kinetic model		
			k_1 (min^{-1})	R^2	$q_e(\text{cal})$ (mg/g)		$q_e(\text{cal})$ (mg/g)	k_2 (g/mg min)	R^2
GAC	1.5	25	$(4.7 \pm 0.2) \times 10^{-4}$	0.975	213.9	250.0	263.2	$(6.1 \pm 0.7) \times 10^{-6}$	0.997
		40	$(3.5 \pm 0.1) \times 10^{-4}$	0.984	271.1	319.0	322.6	$(5.1 \pm 0.7) \times 10^{-6}$	0.992
	0.5	25	$(8.8 \pm 0.4) \times 10^{-4}$	0.980	203.6	250.0	255.1	$(1.8 \pm 0.2) \times 10^{-5}$	0.999
		40	$(5.6 \pm 0.2) \times 10^{-4}$	0.975	233.6	327.0	334.1	$(9.4 \pm 1.1) \times 10^{-6}$	0.999
GAC-D	0.03	25	0.307 ± 0.022	0.960	177.3	250.0	253.2	$(4.9 \pm 0.6) \times 10^{-3}$	0.999
		40	0.274 ± 0.030	0.921	287.4	391.0	396.5	$(2.1 \pm 0.1) \times 10^{-3}$	0.999
ACF	0.009	25	$(8.7 \pm 0.5) \times 10^{-4}$	0.974	204.7	250.0	255.4	$(1.7 \pm 0.1) \times 10^{-5}$	0.999
		40	$(5.5 \pm 0.2) \times 10^{-4}$	0.985	253.2	340.0	344.8	$(1.0 \pm 0.1) \times 10^{-5}$	0.998
ACF	0.009	25	0.428 ± 0.006	0.998	224.0	250.0	253.3	$(5.5 \pm 0.7) \times 10^{-3}$	0.999
		40	0.361 ± 0.009	0.995	309.1	398.0	400.0	$(4.3 \pm 0.5) \times 10^{-3}$	0.999

Carbon mass = 0.05 g and solution volume = 500 mL.

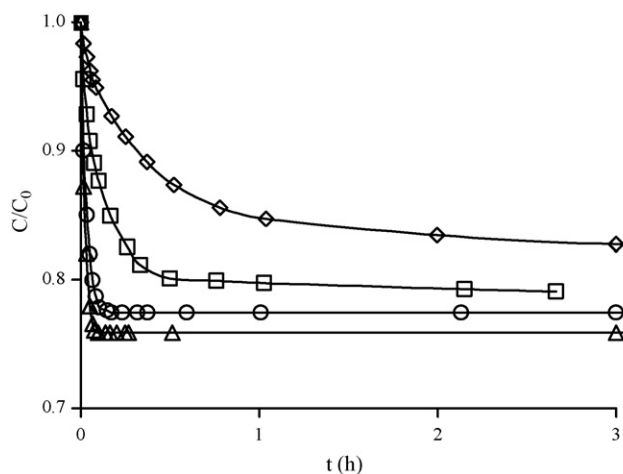


Fig. 3. Adsorption kinetics of amitrole on GAC: $\phi = 1.5$ mm (\diamond), $\phi = 0.5$ mm (\square) and $\phi = 0.03$ mm (\circ) and on ACF (Δ). $C_0 = 50$ mg/L.

The reaction order and rate constant can be determined from the adsorption experiment data by applying Eqs. (1) and (2).

$$\frac{dq}{dt} = k_1(q_e - q) \quad (1)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (2)$$

where k_1 , in min^{-1} , and k_2 , in g/mg min , are the pseudo-first-order and pseudo-second-order rate constants, respectively; q_e and q , in mg/g , as aforementioned are the adsorbate uptake at equilibrium and time t , respectively. After integration and applying boundary conditions, $t=0-t$ and $q=0-q_e$, the integrated forms of Eqs. (1) and (2) become, respectively:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

A straight line of the plot of $\ln(q_e - q)$ versus t in the first case or t/q versus t in the second case suggests the applicability of these kinetic models. Results obtained by applying the two models to the experimental data are given in Tables 2 and 3 for

Table 3

Pseudo-first-order and pseudo-second-order rate constants, k_1 and k_2 , their correlation coefficients, R^2 , and uptake at equilibrium, q_e , experimental and calculated using both kinetic models for amitrole adsorption on carbons

Carbon	ϕ (mm)	C_0 (mg/L)	Pseudo-first-order kinetic model			$q_e(\text{exp})$ (mg/g)	Pseudo-second-order kinetic model		
			k_1 (min^{-1})	R^2	$q_e(\text{cal})$ (mg/g)		$q_e(\text{cal})$ (mg/g)	k_2 (g/mg min)	R^2
GAC	1.5	50	0.024 ± 0.002	0.963	17.0	19.8	19.7	$(2.0 \pm 0.2) \times 10^{-3}$	0.999
		90	0.023 ± 0.001	0.991	25.2	27.4	27.5	$(1.4 \pm 0.1) \times 10^{-3}$	0.999
	0.5	50	0.105 ± 0.005	0.987	16.7	21.1	21.1	$(1.6 \pm 0.2) \times 10^{-2}$	0.999
		90	0.080 ± 0.007	0.940	22.0	27.9	27.9	$(4.0 \pm 0.5) \times 10^{-3}$	0.999
	0.03	50	0.629 ± 0.040	0.979	25.7	22.5	22.6	0.160 ± 0.020	0.999
		90	0.567 ± 0.030	0.983	27.1	28.5	28.6	0.127 ± 0.020	0.999
GAC-D	0.5	50	0.102 ± 0.006	0.954	15.1	19.8	19.8	$(1.4 \pm 0.1) \times 10^{-2}$	0.999
		90	0.073 ± 0.007	0.932	19.7	25.1	25.1	$(3.9 \pm 0.5) \times 10^{-3}$	0.999
ACF	0.009	50	0.885 ± 0.041	0.994	26.6	24.1	24.2	0.285 ± 0.034	0.999
		90	0.816 ± 0.038	0.989	32.8	30.2	30.2	0.189 ± 0.021	0.999

Carbon mass = 0.05 g and solution volume = 100 mL.

diuron and amitrole, respectively. These tables also show the correlation coefficients, R^2 , for both kinetics models. Results show that diuron and amitrole adsorption kinetics on all carbons used are better fitted by the pseudo-second-order equation. This is deduced from (i) the higher R^2 values obtained with this kinetic model and (ii) the similarity between the experimental adsorption capacity at equilibrium, q_e (exp), and that calculated from the pseudo-second-order kinetic model. Similar results were found for the adsorption kinetics of diuron onto an activated carbon cloth [21].

For a given carbon and initial concentration, both rate constant values showed a faster adsorption kinetics for amitrole than for diuron, despite the smaller driving force for adsorption of the former. This can also be observed in Figs. 2 and 3, which show that a much higher amount of diuron than amitrole was adsorbed at equilibrium but that this equilibrium was reached more quickly in the case of amitrole. On ACF, for instance, the equilibrium was reached at ~ 30 min for diuron versus ~ 5 min for amitrole. Amitrole has a faster adsorption kinetics because it has molecular dimensions smaller than diuron. The much higher amount of diuron adsorbed at equilibrium than that of amitrole was previously reported [8,9] and derives from the greater hydrophobicity of diuron and its higher dipolar moment than amitrole (Table 1). Therefore, hydrophobic and van der Waals interactions between the herbicides and the carbon surface are greater with diuron than with amitrole.

Regardless of the correlation coefficients, the rate constants k_1 and k_2 decreased with an increase in the initial herbicide concentration, which has also been reported with other adsorption systems [10,17,22]. However, for the same C_0 , the rate constants k_1 and k_2 markedly increased when the activated carbon particle size decreased from 1.5 to 0.03 mm. This is because, for a constant mass of adsorbent, an increase in the division of particles augments the external particle surface area exposed to the solution, thereby increasing the number of collisions between adsorbate and adsorbent and producing a higher rate of adsorption on smaller particles. Therefore, both the rate and extent of adsorption can be expected to increase with more finely divided and more porous solids [10,13]. Demineralization of GAC towards GAC-D had practically no effect on k_1 and k_2 val-

ues, likely because the initial amount of ash was low; therefore, its removal had a minimal impact on both the specific surface area and the microporosity of the adsorbent.

The k_1 and k_2 for diuron and amitrole on ACF were of the same order of magnitude as those on the GAC with a particle size of 0.03 mm. ACFs have attracted increasing attention in recent years as better adsorbents than granular activated carbons in gas phase applications, since they normally present much higher adsorption kinetics and adsorption capacity. This has been explained by the differences in porous network between the two types of adsorbents [23]. In ACF, micropores are directly accessible from the external surface of the fiber, whereas in GAC they are accessed via an interconnected network of meso and macropores. Hence, adsorptive molecules reach adsorption sites in ACF through the micropores, without the additional diffusion resistance of meso and macropores, which is usually the rate-controlling step in granular adsorbents.

It should also be taken into account that the diameter of commercial ACFs carbon fibers (0.006–0.017 mm) is, on average, around 100-fold smaller than the particle size of commercial GACs (0.6–4.0 mm) and slightly smaller than that of powder activated carbons (0.015–0.03 mm). These size differences can be expected to affect the adsorption kinetics in liquid phase, as shown by the present results. Thus, adsorption kinetics from liquid phase on activated carbon fibers should be faster than in granular activated carbons and more similar to that in powder activated carbons. This was demonstrated by the present results obtained with samples ACF and GAC with 0.03 mm particle size. In this case, therefore, the differences in adsorption kinetics between ACF and GAC appear more related to differences in their particle size than to differences in their porous network.

However, powder activated carbons are difficult to handle and cannot be used in fixed beds. These shortcomings are overcome by ACFs, which can be woven into carbon cloths and felts and are better adsorbents than GACs when used in this form.

The third kinetic model applied was the intraparticle diffusion model. This model assumes that the external mass transfer resistance in the aqueous phase is negligible, which is reasonable in well-shaken adsorption systems. The simplest model for diffusion in solid phase is the so-called homogeneous solid diffusion

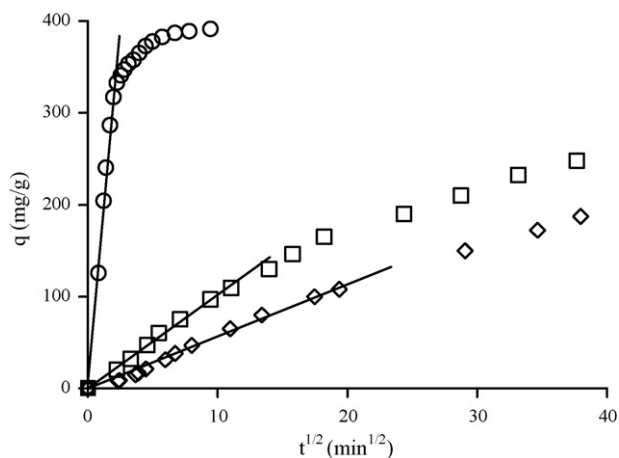


Fig. 4. Application of the intraparticle diffusion model to diuron adsorption on GAC: $\phi = 1.5$ mm (\diamond), $\phi = 0.5$ mm (\square) and $\phi = 0.03$ mm (\circ). $C_0 = 40$ mg/L.

model, which models mass transfer in the solid as diffusion in an amorphous and homogeneous sphere [5,10]. This intraparticle diffusion model is derived from Fick's second law, assuming that the particles are spherical and that the diffusivity, D_S , is constant in all points of the particles. It also assumes that the uptake of adsorbate by the adsorbent is small relative to the total quantity of adsorbate in the solution. The mathematical expression obtained for a short time period, i.e., for $q/q_e < 0.3$, is given by Eq. (5):

$$q = k_d t^{1/2} \quad (5)$$

where k_d , in $\text{mg/g min}^{1/2}$, is defined as the intraparticle diffusion rate constant [10,17,24], and related to the intraparticle diffusivity, D_S in cm^2/min , by Eq. (6)

$$k_d = \frac{6q_e}{r} \sqrt{\frac{D_S}{\pi}} \quad (6)$$

where q and q_e have the same meaning as before; r , in cm, is the spherical particle radius. A plot of q versus the square root of time would yield a straight line passing through the origin if the adsorption process obeyed the intraparticle diffusion model. Application of Eq. (5) to the adsorption kinetics of diuron and amitrole on GAC samples at the highest initial concentrations used are plotted in Figs. 4 and 5. There was a linear relationship for short t values, from which the intraparticle diffusion

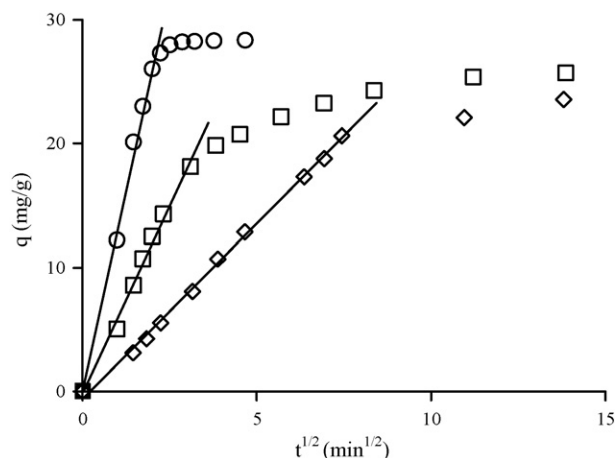


Fig. 5. Application of the intraparticle diffusion model to amitrole adsorption on GAC: $\phi = 1.5$ mm (\diamond), $\phi = 0.5$ mm (\square) and $\phi = 0.03$ mm (\circ). $C_0 = 90$ mg/L.

rate constant was calculated, obtaining the values compiled in Table 4.

Correlation coefficients were very high, demonstrating that the above model fits very well to the experimental data. The k_d for both diuron and amitrole increased with a higher initial concentration and a lower particle size of the adsorbent. This is because a rise in the value of C_0 increases q_e and, according to Eq. (6), k_d is directly related to q_e and inversely related to r . Moreover, for a constant adsorbent mass, smaller particles have more collisions with the adsorbate, increasing their adsorption rate in comparison with larger particles. Values of k_d were always lower for amitrole than for diuron, finally, demineralization had practically no effect on k_d values of diuron and amitrole.

4. Conclusions

Adsorption kinetics of diuron and amitrole on activated carbons with different particle sizes, and on an activated carbon fiber were better fitted by the pseudo-second-order rate equation than by the pseudo-first-order rate equation. Both reaction rate constants increased when the particle size decreased due to the increase in the number of collisions between adsorbate and adsorbent. Demineralization of the activated carbon had practically no effect on both rate constants, likely because the ash content was low.

Table 4
Intraparticle diffusion rate constant, k_d , for diuron and amitrole adsorption on GAC and GAC-D

Carbon	ϕ (mm)	Diuron			Amitrole		
		C_0 (mg/L)	k_d (mg/g min ^{1/2})	R^2	C_0 (mg/L)	k_d (mg/g min ^{1/2})	R^2
GAC	1.5	25	4.4 ± 0.1	0.990	50	2.3 ± 0.0	0.995
		40	5.6 ± 0.1	0.990	90	2.8 ± 0.0	0.995
	0.5	25	6.5 ± 0.1	0.998	50	4.8 ± 0.1	0.981
		40	10.1 ± 0.1	0.997	90	6.0 ± 0.1	0.992
	0.03	25	105.5 ± 2.6	0.980	50	10.0 ± 0.2	0.990
		40	158.5 ± 3.2	0.990	90	12.8 ± 0.2	0.992
GAC-D	0.5	25	6.7 ± 0.1	0.991	50	4.7 ± 0.1	0.993
		40	10.1 ± 0.2	0.994	90	5.9 ± 0.1	0.999

Adsorption kinetics of amitrole was faster than that of diuron, whereas the amount adsorbed at equilibrium was much lower with the former herbicide than with the latter. These results indicate that the time to reach the equilibrium was determined by the molecular size of the herbicides whereas the amount adsorbed at equilibrium was controlled by the hydrophobicity, solubility and dipolar moment of the herbicides.

The adsorption kinetics of the activated carbon fiber was similar to that of the activated carbon with smallest particle size (0.03 mm). According to this finding, differences in adsorption kinetics between activated carbon fibers and granular activated carbons appear more related to differences in their particle size than to differences in their porous network.

The intraparticle diffusion rate constant rose when the initial concentration of herbicides in solution increased and the particle size of the adsorbent decreased. This is because the rise in initial concentration increased the amount adsorbed at equilibrium and the decrease in particle size increased collisions between the adsorbate and adsorbent particles. Demineralization has practically no effect on adsorption kinetics, likely because the initial amount of ash is low and its removal has a minimal impact on the surface area and microporosity.

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