Adsorption of Pesticides onto Granular Activated Carbon: Determination of Surface Diffusivities Using Simple Batch Experiments

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Abstract. The Homogeneous Surface Diffusion Model (HSDM) has been successfully used to predict the adsorption kinetics for several chemicals inside batch adsorber vessels. In addition to the adsorption equilibrium, this model is based on external mass transfer and surface diffusion. This paper presents the determination of the surface diffusion coefficient (D_s) using a differential column batch reactor (DCBR). The adsorption kinetics for three pesticides onto granular activated carbon have been established experimentally. Their corresponding three diffusion coefficients were determined by fitting the computer simulations to the experimental concentration-time data. The results show that this original apparatus increases by an order of magnitude the range of reachable diffusion coefficient compared to perfectly mixed contactors. Moreover the computed D_s values are more accurate because of the better assessment of the external mass transfer coefficient (k_f) for fixed beds.

Keywords: liquid adsorption, differential column batch reactor, granular activated carbon, homogeneous surface diffusion model, pesticides, surface diffusivity

Introduction

Faced with an increasing contamination of natural waters by pesticides, adsorption onto activated carbon has become widely used in drinking water plants. The design of an adsorption treatment has to be based on the transient phenomenon which drives a given dissolved compound towards adsorption sites within the particles of powdered or granular activated carbon. The adsorption capacity, or adsorption equilibrium, is the attractive force. Two resistances hinder the progression of the compound: the crossing of the laminar boundary layer surrounding the particle (the external mass transfer) and the diffusion within the particle (the internal mass transfer). The latter can be a diffusion in the liquid phase contained in the pores or a diffusion of the molecules in the adsorbed state at the pore's surface. According to Komiyama and Smith (1974), the main diffusion mechanism is the surface diffusion. The used model combines external mass transfer and surface diffusion (the latter phenomenon is usually called HSDM for Homogeneous Surface Diffusion Model).

The characteristic parameter for the external mass transfer, the coefficient k_f, is likely to be estimated by semi-empirical equations. On the contrary, the surface diffusion coefficient D_s depends highly on the nature of the activated carbon, its structure, its preparation (raw material, calcination, activation), and on the nature and size of the adsorbed compound. Actually, only limited data is available and the large variability observed does not plead for a reliable correlation in the near future. The value of the surface diffusion coefficient has therefore to be obtained by fitting a HSDM model to some experimental data.

In order to obtain surface diffusivity values for some pesticides, kinetic experiments will be carried out with a differential column batch reactor (DCBR) rather than classical batch adsorber vessels. Described by Hand et al. (1983), this original apparatus, easy to set up, was chosen so that k_f effect could be minimised or, at

least, well defined. This results in more accurate D_s estimations. Once D_s is obtained for a given compound and a given activated carbon, it can be used in various adsorption treatments, like powdered activated carbon addition or granular activated carbon beds, where the same compound has to be adsorbed onto the same carbon.

Theory

Adsorption Theory

It is widely accepted that the process of adsorption can be represented by four consecutive steps (Noll et al., 1992). Figure 1 describes the progression of a molecule of adsorbate from the bulk towards the site of adsorption.

It is important to note that intraparticle mass transfer involves two different phenomena: porous diffusion (the adsorbate first diffuses in the liquid filling the pores and then is adsorbed) and surface diffusion (the adsorbate is first adsorbed then diffuses from one site to another).

The convective progression of step 1 appears to be very fast compared to the diffusion through the outer layer and within the particle. The concentrations of the liquid bulk will only be governed by the overall mass balance and the hydraulic behaviour of the vessel. An instantaneous reversible reaction is assumed for the

real adsorption step (step 4). The liquid phase concentration of adsorbate and the adsorbate load at the carbon's surface are locally related by an equilibrium law. Thus adsorption kinetic is governed by external mass transfer and internal diffusion i.e. by the coefficients k_f, D_p and D_s. In order to simplify simulations, models that take into account only two coefficients were developed. As noticed by Komiyama and Smith (1974), the contribution of D_s is 20 times as important as the D_p contribution. Later, in a review paper, Al Duri (1996) mentioned several other authors confirming this observation. Therefore a model based only on k_f and D_s will be used here.

The External Mass Transfer

The mass transfer through a diffusional boundary layer is represented by a linear driving force model, characterized by the coefficient k_f. This phenomenon occurs in numerous processes, not only adsorption but also catalysis for instance. It has been widely documented and, in various situations, empirical equations are now available. They give k_f as a function of the hydraulic behaviour in the vessel or in the surrounding of the particle, some physical properties of the solvent and the molecular diffusion of the solute (Noll et al., 1992; Ruthven, 1984). The k_f value is only affected by the particle size, but not by the nature or the porosity of the GAC.
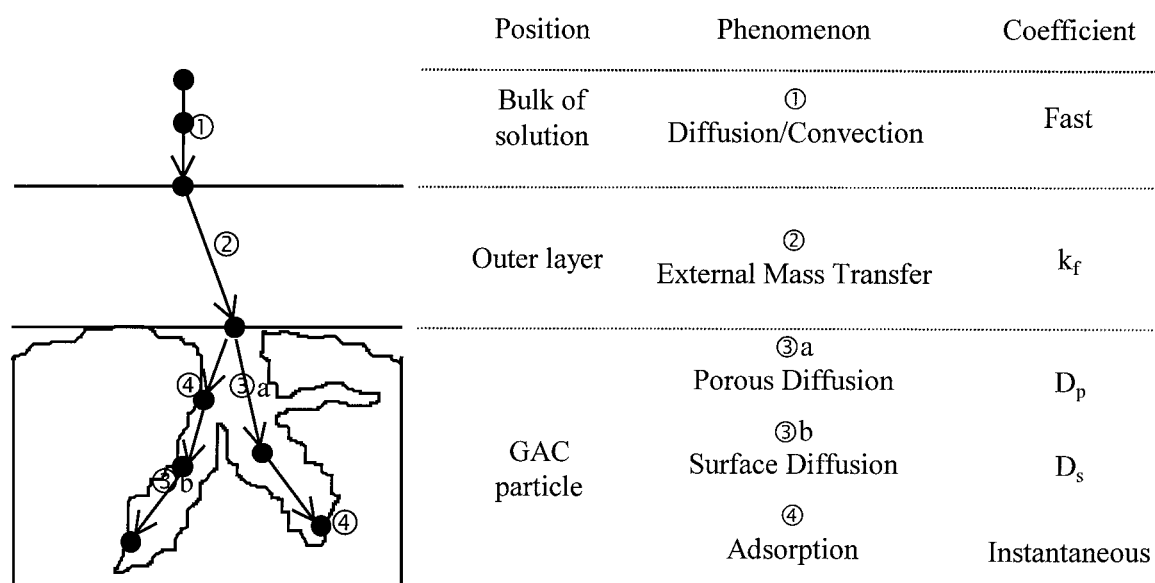
	Position	Phenomenon	Coefficient
	Bulk of solution	① Diffusion/Convection	Fast
	Outer layer	② External Mass Transfer	k_f
	GAC particle	③a Porous Diffusion	D_p
		③b Surface Diffusion	D_s
		④ Adsorption	Instantaneous

Figure 1.   The four steps of adsorption (adapted from Weber and Smith, 1987).

It should be noticed however that for non-ideally stirred vessels the k_f value will depend on issues like vessel shape, position, velocity, and type of stirrer, distance between stirrer and particle, and also particle size and density. As a result, one has usually to deal with a k_f distribution rather than a unique value.

Furthermore the molecular diffusion coefficient, D_{mol}, is needed for Sh and Sc numbers calculation. Several correlations, cited by Crittenden et al. (1987) and Noll et al. (1992), are likely to estimate D_{mol}.

Simplified Model of Adsorption: Homogeneous Surface Diffusion Model

Initiated by Rosen (1952), HSDM was first resumed by Weber and Chakravorti (1974). This model is also described as the Film-Solid Diffusion Model (Al Duri, 1996). The main hypothesis of HSDM is that porous diffusion is neglected, so that internal mass transfer is only due to surface diffusion. The HSDM assumptions are therefore the following:

1. the contactor's mass balance: according to our experiments, the mass balance of a discontinuous perfectly mixed vessel will be used.
2. internal mass transfer is only governed by surface diffusion.
3. external mass transfer is governed by a linear driving force.
4. at the solid/liquid interface, there is continuity between external mass transfer and internal diffusion.
5. at the solid/liquid interface, there is equilibrium between adsorbate concentration in the fluid and adsorbate load on the surface.
6. the particle of adsorbent is supposed to be spherical and homogeneous.

Some authors (Ruthven, 1984; Zhou and Martin, 1995) describe a relationship between final equilibrium surface loading and average surface diffusivity. However, the real influence is onto the local value of the surface diffusivity and is a result of the local surface load at any given time. Its mathematical expression and the leading parameters are very difficult to establish and to estimate, especially for complex surfaces like activated carbon. For this reason, surface diffusity will be assumed to be independent of the surface loading in HSDM. A dimensionless ratio can be defined, the Biot Number, which compares the initial external mass transfer for a nonloaded particle with an estima-tion of the initial surface diffusion for a particle without boundary layer (Noll et al., 1992; Roy et al., 1993). In other words, the largest possible external mass transfer rate is compared to the largest possible diffusion rate for a given situation. This dimensionless number has the following form:

$$\text{Biot} = \frac{k_f R_p C_0}{D_s \rho_a Q_0^*}$$

Traegner and Suidan (1989) noticed 3 typical cases:

– Biot $\gg$ 100, surface diffusion will always be the rate limiting mechanism, thus simulation results are very sensitive to D_s variations and insensitive to k_f variations. Clearly these conditions are not suitable for the determination of the external mass transfer coefficient by fitting the simulation to experimental data.
– Biot $\ll$ 1, external mass transfer always enforces its rate, thus simulation results are very sensitive to k_f variations and are insensitive to D_s variations. Clearly such experiments contain no information about the surface diffusion coefficient.
– Biot $\in [1; 100]$, both mechanisms are important, so model is sensitive to k_f and D_s. In this paper, the lower limit of the Biot number for the D_s determination will be established for a typical use in water treatment.

Equations of Homogeneous Surface Diffusion Model

The mathematical translation of the previous hypotheses is shown step by step in the following set of equations.

1. The overall mass balance for a discontinuous perfectly mixed vessel is:

$$\frac{dC_b}{dt} = -W \frac{dq_{avg}}{dt} \qquad (1\text{-}1)$$

where C_b is the liquid concentration of adsorbate in the bulk and W the GAC dosage (mass of carbon per liquid volume unit).

q_{avg} is the GAC average load and is calculated by the following equation:

$$q_{avg} = \frac{3}{R_p^3} \int_0^{R_p} q(r, t) r^2 \, dr \qquad (1\text{-}2)$$

with $q(r, t)$ the load profile along the radius at time t.

2. The internal mass transfer is in accordance with Fick's first law, so that:

$$\frac{\partial q(r, t)}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q(r, t)}{\partial r} \right) \qquad (2)$$

Boundary condition n°1:

$$\frac{\partial q(r, t)}{\partial r} = 0 \quad \text{at } r = 0, \forall t$$

This boundary condition expresses the spherical symmetry of the adsorbent particle (assumption n°6). As a consequence, no adsorbate molecule crosses the centre of the particle.

3 and 4. Continuity at the solid/liquid interface between external mass transfer and internal transport corresponds to the boundary condition n°2:

$$\rho_a D_s \frac{\partial q(r, t)}{\partial r} = k_f(C_b - C_s) \quad \text{at } r = R_p \qquad (3)$$

In Eq. (3), the left-hand term expresses the transfer due to surface diffusion whereas the right-hand term corresponds to the external mass transfer. The two transfer rates have to be equal at the adsorbent surface at any time.

5. Equilibrium at the solid/liquid interface is expressed by semi-empirical laws. Single solute adsorption can be described by usual models i.e. Freundlich and Langmuir equations (two fitted parameters) or Redlich-Peterson and Jossens-Myers equations (three fitted parameters) (Zhou, 1992).

Finally, the initial conditions specify that fresh GAC is added to a solution with an initial solute concentration C_0:

$$C_b(t) = C_0; C_s(t) = 0; q(r, t) = 0 \quad \text{at } t = 0, \forall r$$

A computer program developed in our laboratory solves the HSDM equations. An orthogonal collocation method is used to transform the partial differential equation into a set of ordinary differential equations (Villadsen and Stewart, 1967; Roy et al., 1993). A fourth order implicit integration method solves the algebraic-differential equation system and produces, as result, the time evolution of the bulk concentration and of the load profile along the grain radius. The current version of the code does not yet perform an automatic search for the Ds value based on some experimental data using a least square adjustment method. For the time being, this is done manually.

Experiments

Activated Carbon

We used a commercial granular activated carbon, widely used in water treatment plants: F400 provided by CHEMVIRON.

For its preparation, the GAC was first washed with ultra-pure water to remove fines, then plunged into ultra-pure water for 4 hours in order to eliminate possibly adsorbed organics. After being oven-dried at 105°C, the GAC is stored in a desiccator under vacuum conditions. For adsorption isotherms, the GAC was crushed. For DCBR studies, GAC is sieved into several particle size fractions and experiments were conducted with the main size fraction: diameter in the 1.00 to 1.25 mm range.

Pesticides

Experiments were conducted with three pesticides: atrazine, bromoxynil and diuron. They are pure and technical products.
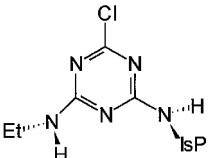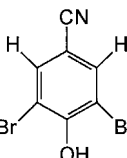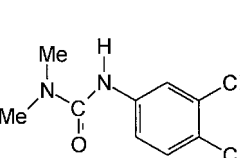
A 10 mg · L^{-1} stock-solution was prepared by dissolving each pesticide in ultra-pure water. This solution is stirred during 3 days in darkness to complete dissolution. Then dilute solutions were prepared from this mother-solution.

The choice of these pesticides was motivated by two reasons. First, they are not only widely used but they also appear more and more often at critical concentrations in raw water supplies. Secondly, they belong to different pesticide families, with potentially different behaviours towards the activated carbon. Table 1 shows their structure.

Adsorption Isotherms

Adsorption isotherm experiments were conducted with the usual bottle-point method. Varying and accurately determined amounts of crushed GAC were added to four out of five 2.5 L bottles containing 2 L of pesticide solution, the remaining bottle being used as reference. Bottles were sealed and magnetically stirred for 5 days

Table 1. Structure of the chosen pesticides.

	Atrazine	Bromoxynil	Diuron
Class	s-triazine	nitrile	substituted urea
Structure			

at 25°C. After 5 days, residual liquid concentrations were analyzed and adsorbate loads were derived from the mass balance. Adsorption isotherms are described by the Freundlich equation:

$$q_s = K C_s^{1/n}$$

For each pesticide, two series of experiments were performed at two different initial concentrations. Table 4 summarizes the initial concentrations of pesticide and the varying amounts of crushed GAC.

Differential Column Batch Reactor

Adsorption kinetic experiments were carried out with a differential column batch reactor. Hand et al. (1983) and Noll et al. (1992) described this apparatus. A pesticide solution is pumped from a stirred tank and flows through a small column that contains GAC. Then the solution is directed back to the tank. Figure 2 presents this apparatus.

Tank, column and flowmeter are made of glass. The total volume of pesticide solution contained in the tank is 5 L. The column, whose internal diameter is 8 mm,
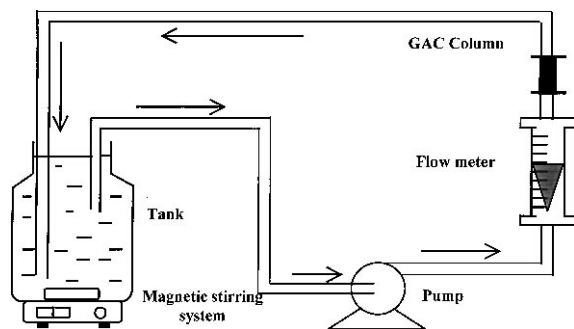

Figure 2. Principle of a Differential Batch Column Reactor.

is filled with 100 mg of GAC. The gear-pump is made of stainless steel and PTFE while tubing are made of polyamide. The choice of these materials was made in order to avoid any interference adsorption likely to alter our results. The pump provides a $100\,L \cdot h^{-1}$ flow, that is checked by the flowmeter. The whole unit is kept in darkness and at room temperature.

One advantage of DCBR apparatus is that, for high flowrates, it closely approaches the Discontinuous Perfectly Mixed Tank Reactor concept. As a consequence, we are allowed to use the overall mass balance [1-1] given above. It is mainly a means to gain some control over the turbulent flow pattern, which affects the external transfer, surrounding all the particles.

For classical adsorption kinetics, external mass transfer coefficient can be deduced from the first few minutes of adsorption (Walker and Weatherley, 1999; Ganguly and Goswamy, 1996). Nevertheless, some difficulties in k_f estimations may occur due to the choice of the first time interval used for k_f calculations or experimental uncertainties. In a DCBR, the GAC is set up like in a fixed bed, the external mass transfer coefficient can, therefore, be estimated using the more reliable k_f correlations for fixed beds. In addition, the influence of external mass transfer can be reduced by increasing the flowrate. Note that for k_f calculation, Hand et al. (1983) advocated the semi-empirical equation of Wakao and Funazkri (1978) for DCBRs. This correlation, developed for fixed-beds, takes the following form:

$$Sh = 2 + 1.1\,Re^{0.6}\,Sc^{1/3}$$

The experimental conditions are summarized in Table 2.

About 20 samples, each of them of 5 mL, are taken for analysis during a kinetic experiment. Thus, the total volume withdrawal represents about 2%, that is neglected and does not cause significant adsorbent enrichment.

Table 2.   DCBR conditions.

	Atrazine	Bromoxynil	Diuron
Flow ($L \cdot h^{-1}$)	100	100	100
Tank volume (L)	5	5	5
GAC density ($kg \cdot m^{-3}$)	750	750	750
Mean particle radius (mm)	0.5625	0.5625	0.5625
CAG mass (mg)	100.2	100.0	100.7
C_0 ($\mu g \cdot L^{-1}$)	481.1	715.6	471.1
Duration (days)	3	5	3

Table 3.   Analytical conditions.

	Atrazine	Bromoxynil	Diuron
Wavelength (nm)	220	288	245
Eluant composition (% v/v)	55/45	70/30	55/45
Eluant flow (ml/min^{-1})	0.8	0.7	0.8
Retention time (min)	13	2.7	12.5

Analysis

Pesticide concentrations are measured by High Performance Liquid Chromatography coupled with an UV diode array photodetector. Samples are filtered (MILLIPORE Millex HV25, 0.45 μm) before injection.

The WATERS HPLC line is composed by the following elements:

- pump controller 600.
- autosampler 717 (injection loop: 50 μL).
- guard column.
- C18 SYMMETRY® column (p.d. 5 μm; length 250 mm; i.d. 4.6 mm) for atrazine and diuron or CN NUCLEOSYL® column (p.d. 10 μm; length 250 mm; i.d. 4.6 mm) for bromoxynil
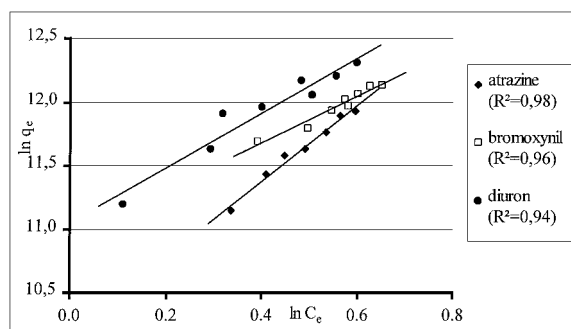

Figure 3.   Freundlich representation for the pesticides.

- photodiode array UV detector 996.
- software MILLENIUM®.

Analyses are performed with a water/acetonitrile eluant. Table 3 shows the analytical conditions.

Results and Discussion

Adsorption Equilibrium

The adsorption equilibrium of a pure compound does depend on the abundance of possible adsorption sites as well as site accessibility. Therefore geometrical considerations: pore size distribution and tortuosity, functionalities of activated carbon and adsorbate can affect the isotherm results. For the three studied pesticides, adsorption isotherm results and corresponding Freundlich modelisations are respectively shown in Fig. 3 and Table 4.

Diuron is more adsorbed than atrazine. This can be explained by the structure of the molecule. The diuron molecule appears to be more linear and flat than a molecule of atrazine because of an electron delocalization that stiffens the urea part and, consequently,

Table 4.   Equilibrium: conditions (initial concentration; crushed GAC amount) and results.

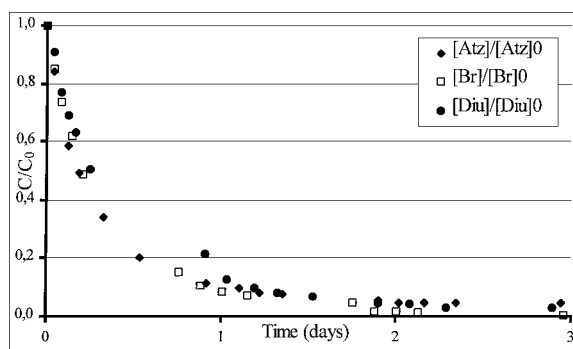|	Atrazine	Bromoxynil		Diuron
C_{01} ($\mu g \cdot L^{-1}$)	259.0	454.8		261.1
C_{02} ($\mu g \cdot L^{-1}$)	498.8	817.5		558.1
	Bottle 1	Bottle 2	Bottle 3	Bottle 4
Crushed GAC amount ($mg \cdot L^{-1}$)	0.7	1.5	2.3	3.1
	Atrazine/F400	Bromoxynil/F400		Diuron/F400
K [($\mu mol \cdot g^{-1}$) $\cdot$ ($\mu mol \cdot L^{-1}$)$^{-1/n}$]	607.2	573.0		875.2
n (dimensionless)	3.38	5.42		4.63

Figure 4. Adsorption of presticides onto DCBR.

keeps it in the plane of the phenyl group. On the other hand, the ethyl and isopropyl group of atrazine cannot be placed in the plane of the triazine because of steric hindrance. So that atrazine is less linear and more voluminous than diuron. For bromoxynil, the molecule is slightly larger than the diuron molecule, but has a greater functional variability than atrazine and hence a broader range of possible sites.

For the HSDM model, the equilibrium has to be determined at the particle surface. The Freundlich adsorption isotherm model was the best fit among the two parameters models. The three parameters models did not improve the least square criteria and were therefore disregarded.

These parameters are specific to a given compound—activated carbon couple.

Differential Column Batch Reactor Kinetics

The three experimental DCBR kinetics are presented Fig. 4 in reduced form: relative pesticide concentration versus time. The abbreviation Atz, Br and Diu are respectively used for atrazine, bromoxynil and diuron. [Atz] represents the atrazine liquid concentration and [Atz]0 the initial concentration.

Roughly speaking, atrazine and bromoxynil seem to have the same behaviour while the adsorption rate for diuron appears slower. Equilibrium is reached after two

to three days. Before any D_s determination, we need to evaluate the external mass transfer coefficient to be used in the model for each pesticide. Using the Wakao and Funazkri (1978) correlation, k_f values have been estimated for the three pesticides (see Table 5).

These values are, on average, one order of magnitude greater than k_f values observed for classical batch stirred reactors. For instance, for experiments carried out inside a batch adsorber vessel, Walker and Weatherley (1999) obtained 2.8×10^{-3} cm·s^{-1} for an acid dye, Ganguly and Goswamy (1996) got 2.5×10^{-3} cm·s^{-1} for acetic acid whereas Traegner and Suidan (1984) measured 6.6×10^{-3} cm·s^{-1} for PNP. The external mass transfer will significantly less limit the overall mass transfer rate in DCBRs than in usual batch vessels, even though we are fundamentally facing two identical reactors.

Discrimination Efficiency of the DCBR Model

As mentioned before, a minimal Biot number exists below which it will not the possible to determine any surface diffusion coefficient since the observed overall transfer rate will mainly be governed by the external transfer. The same happens to the simulations. In order to estimate that Biot number, we performed several kinetic calculations with various D_s values, in particular one with an exceptionally high D_s as an example of a kinetic limited only by the external transfer. The value of the corresponding D_s was chosen at 10^{-6} cm^2·s^{-1}. This last calculation will be used as reference against which the other kinetics will be compared. The comparison criteria is an average relative deviation, derived from a least square criteria, defined as follow:

$$S(\%) = 100 \cdot \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(2 \frac{C_{\text{ref}}(t_i) - C(t_i)}{C_{\text{ref}}(t_i) + C(t_i)} \right)^2} \quad (4)$$

Note that the farther D_s is from the D_s reference, the farther are the corresponding curves and, as a consequence, the greater is the comparison criteria S.

Table 5. Kinetics: D_s and k_f values.

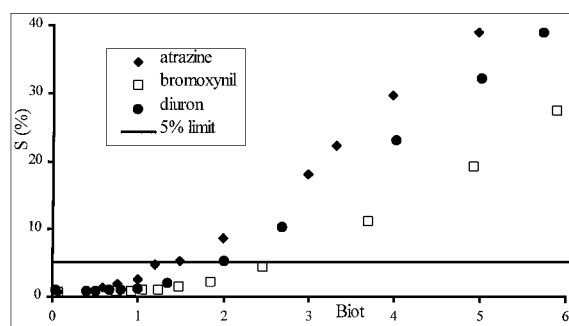|	Atrazine	Bromoxynil	Diuron
D_s (cm^2·s^{-1})	$5.0 \pm 0.8 \times 10^{-10}$	$4.0 \pm 0.7 \times 10^{-10}$	$6.5 \pm 2.6 \times 10^{-11}$
k_f (cm·s^{-1})	2.75×10^{-2}	2.60×10^{-2}	2.70×10^{-2}
Biot	12.0	18.9	61.9
Mean relative deviation	12.9	8.6	10.7

Figure 5. Relative mean deviation between a kinetic with surface diffusion and one without surface diffusion versus Biot number.

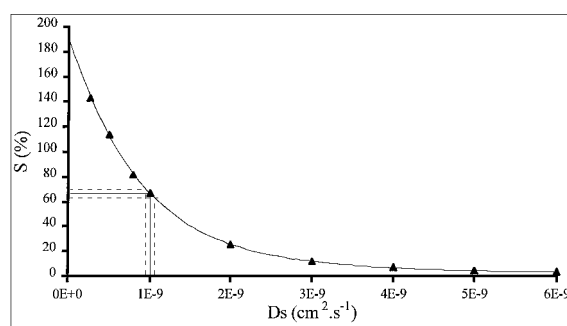*Figure 6.* Relative mean distance between a kinetic with surface diffusion and one without surface diffusion as a function of the D_s.

In Fig. 5, the evolution of the criteria S as a function of the Biot number is drawn for the three pesticides. The faculty to discriminate between two D_s values, when the experimental results are compared to the two simulations, will depend on the experimental measurement error for the concentrations. An average experimental error of 5% is arbitrarily assumed. Any two calculated kinetics, whose gap is within 5%, can not be statistically differentiated when compared to experimental results. As can be seen Fig. 5, below a certain Biot number, all the kinetics are within that 5% gap, thus defining a minimal differentiable Biot value. That critical value is not exactly the same for all the pesticides because adsorption equilibrium does also have an influence on mass transfer ($\text{Biot}_{\text{Atz}}^{\text{lim}} \approx 1.40$, $\text{Biot}_{\text{Br}}^{\text{lim}} \approx 2.60$, $\text{Biot}_{\text{Diu}}^{\text{lim}} \approx 1.95$). These values are in accordance with the segmentation proposed by Traegner and Suidan (1989) and presented in the theoritical part of this paper. If we reconsider the fact that k_f values for DCBRs are one order of magnitude greater than for usual stirred vessels, it follows that DCBRs allow for the determination of D_s values about one order of magnitude greater than stirred vessels.

Expressed in terms of D_s, this means also that a maximal obtainable D_s value can be defined for a given situation, i.e. k_f, R_p, C_0, q_0, ρ_a being constant. For our experimental conditions, maximal obtainable D_s values are in the range 3×10^{-9} to 6×10^{-9} cm$^2 \cdot$s^{-1}. Figure 6 shows, as an example, the comparison criteria as a function of D_s.

It can be noticed that the comparison criteria is more and more sensitive to D_s as it decreases. Furthermore, an estimation of an uncertainty range for D_s can be deduced using the curve of Fig. 6. Let's assume that the best fit for a kinetic was obtained for a $D_s = 1 \times 10^{-9}$ cm$^2 \cdot$s^{-1}. According to Fig. 6, this

corresponds to a 66.6% relative mean deviation compared to an "external transfer only" kinetic. If we also assume that we have to deal with an experimental error of 5%, meaning that the real kinetic might well be, on average, 5% above (slower) or below (faster) the measured one. The relative mean deviation of the real kinetic should be between 61.6% and 71.6%. Using again Fig. 6, we end up with a D_s uncertainty range from 0.93×10^{-9} to 1.07×10^{-9} cm$^2 \cdot$s^{-1}.

Estimation of the Surface Diffusion Coefficient

For the bromoxynil adsorption in a DCBR, an example of HSDM sensitivity towards D_s is given Fig. 7. Simulations are performed for increasing values of surface diffusivity.

To determine the D_s value for pesticides, computer simulations are achieved with different D_s. A manual minimisation is performed with a fitting criteria similar to [4] where the reference is given by the experimental data. When experimental data and simulation curve are in good agreement, the D_s value is accepted.
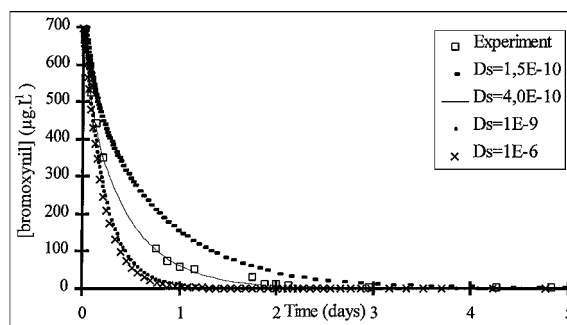

Figure 7. Simulation of bromoxynil adsorption for different D_s (cm$^2 \cdot$s^{-1}).

Table 6. D_s values for different organic compounds.

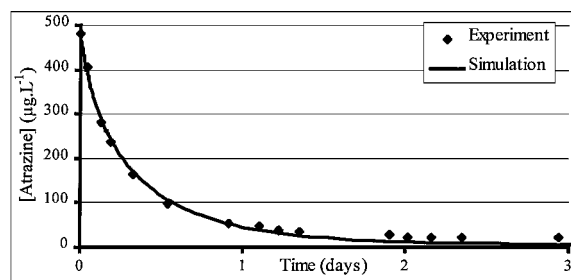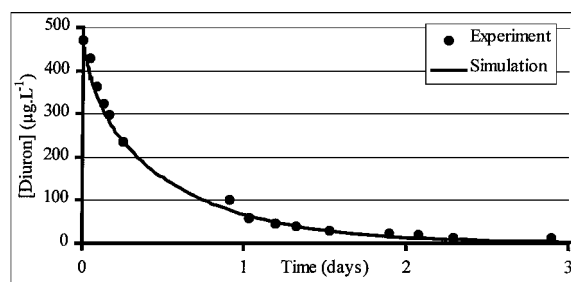| Reference	Compound	D_s (cm$^2 \cdot$ s^{-1})
Ganguly and Goswamy (1996)	Acetic acid	6.0–8.5×10^{-7}
Traegner and Suidan (1984)	*para*-nitrophenol	1.92×10^{-8}
Walker and Weatherley (1999)	Acid dye	1.5×10^{-9}
Mc Kay and Al Duri (1991)	Red dye; Yellow dye	1.3×10^{-10}; 8.5×10^{-11}

Figure 8. Simulation of atrazine adsorption.

Figure 9. Simulation of diuron adsorption.

The data, corresponding to the asymptotic limit of the kinetic has not been systematically accounted for in the criteria. They solely express the equilibrium finaly reached. Unfortunately, slight differences can sometimes be observed between the equilibrium predicted by the model, based on crushed GAC isotherms, and the true GAC equilibrium. These differences, being not related to any kinetic behaviour, are disregarded by restraining the criteria to the evolving part of the kinetic.

Figures 8 and 9 show DCBR kinetics and simulations for the two other pesticides, respectively atrazine and diuron.

For each pesticide, the D_s value, as well as its uncertainty range, is given Table 5 with the calculated k_f, the corresponding Biot number and the fitting criteria.

The identified Biot numbers are well above the discrimination limits discussed earlier. This implies that surface diffusion does have a overwhelming impact on the adsorption kinetic of the described experiments. The experimental data are therefore suitable for D_s determination.

Using a batch stirred reactor, Qi et al. (1994) studied adsorption of atrazine onto F400 powdered activated carbon. In deionized-distilled water, they obtained 1.32×10^{-12} cm$^2 \cdot$ s^{-1} for atrazine D_s, that is 100 times smaller than our computed value. This difference can be explained since the authors used a D_s-only model.

Table 6 gives values of D_s for several organic compounds. Studies mentioned in this table were carried out with GAC in classical batch stirred adsorbers.

These values cover a large range, because they deal with different families of organic compounds. For these molecules, the volume and the functionalities are disparate, which can explain this large range. It can also be noted that for huge molecule (like red and yellow dye) D_s is significantly smaller than for little molecules (acetic acid). The three studied pesticides have, roughly speaking, the same size, as a consequence the corresponding computed values of D_s are close.

The surface diffusivity for diuron is however significantly smaller than for atrazine and bromoxynil. On the other hand, the isotherm data showed that the GAC adsorption capacity for diuron is about 20% greater than for the two other pesticides. Thus, in a drinking water plant, even if the amount of diuron that could potentially be trapped by the activated carbon is more important than the amounts of atrazine and bromoxynil, it may not have enough contact time to be adsorbed. This clearly points out the need of rate studies for plant design and operation, in addition to equilibrium experiments. Of course, competition between several compounds (natural matter or contaminants) will also modify the adsorption (Gicquel et al., 1997) but this goes beyond the scope of this paper.

Conclusions

The differential column batch reactor associated with the Homogeneous Surface Diffusion Model appears to

be an efficient system for the determination of surface diffusion coefficients for granular activated carbon. Compared to stirred reactors, the range of obtainable D_s values has been increased by an order of magnitude. A better knowledge and control of the external transfer coefficient k_f, a narrower k_f distribution throughout the reactor, result in a greater precision of the estimated surface diffusivities. A rough confidence interval could also be proposed, based on the experimental error and the model sensitivity with respect to the diffusion coefficient.

Nomenclature

C	Liquid concentration ($\mu g \cdot L^{-1}$)
C_0	Initial liquid concentration ($\mu g \cdot L^{-1}$)
C_b	Liquid concentration in the bulk ($\mu g \cdot L^{-1}$)
C_s	Liquid concentration at liquid/solid interface ($\mu g \cdot L^{-1}$)
D_{mol}	Molecular diffusion coefficient ($cm^2 \cdot s^{-1}$)
D_p	Pore diffusion coefficient ($cm^2 \cdot s^{-1}$)
D_s	Surface diffusion coefficient ($cm^2 \cdot s^{-1}$)
K	Freundlich coefficient
k_f	External mass transfer coefficient ($cm \cdot s^{-1}$)
n	Freundlich coefficient
q	Absorbate load ($\mu g \cdot mg^{-1}$)
q_0	Initial absorbate load ($\mu g \cdot mg^{-1}$)
Q_0^*	Absorbate load in equilibrium with C_0 ($\mu g \cdot mg^{-1}$)
q_{avg}	Average absorbate load ($\mu g \cdot mg^{-1}$)
q_s	Absorbate load at liquid/solid interface ($\mu g \cdot mg^{-1}$)
r	Radial distance inside the particle of adsorbent (m)
R_p	Radius of adsorbent particle (m)
t	Time (s)
U_0	Superficial velocity ($m \cdot s^{-1}$)
W	GAC dosage ($mg \cdot L^{-1}$)
ρ	Liquid density ($g \cdot L^{-1}$)
ρ_a	Apparent adsorbent density ($g \cdot L^{-1}$)
μ	Liquid viscosity, Pl
Biot	Biot Number $= \frac{k_f R_p C_0}{D_s \rho_a Q_0^*}$
Sh	Sherwood Number $= \frac{2 R_p k_f}{D_{mol}}$
Sc	Schmidt Number $= \frac{\mu}{\rho D_{mol}}$
Re	Reynolds Number $= \frac{2 R_p \rho U_0}{\mu}$

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