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Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 2: Kinetic parameters

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ABSTRACT

The application of several monosolute equilibrium models has previously shown that Bromacil adsorption on SA-UF (Norit) powdered activated carbon (PAC) is probably effective on two types of sites. High reactivity sites were found to be 10–20 less present in a carbon surface than lower reactivity sites, according to the q_m values calculated by isotherm models. The aims of this work were trying, primarily, to identify the kinetic-determinant stage of the sorption of Bromacil at a wide range of initial pesticide concentrations (~5 to ~500 μg L^{-1} at pH 7.8), and secondly, to specify the rate constants and other useful design parameters for the application in water treatment. It was therefore not possible to specify *a priori* whether the diffusion or surface reaction is the key step. It shows that many of the tested models which describe the stage of distribution or the surface reaction are correctly applied. However, the diffusivity values (D and D_0) were found to be constant only constants for some specific experimental concentrations. The HSDM model of surface diffusion in pores was also applied but the values of the diffusion coefficient of surface (D_s) were widely scattered and reduce significantly with the initial concentration or the equilibrium concentration in Bromacil. The model of surface reaction of pseudo-second order fitted particularly well and led to constant values which are independent of the equilibrium concentration, except for the low concentrations where the constants become significantly more important. This last observation confirms perfectly the hypothesis based on two types of sites as concluded by the equilibrium data (part 1).

1. Introduction

Sorption at the interface liquid/solid, with a localized reaction in the pores (of adsorbents, ion exchangers, catalysts, etc.), is generally described by three major steps [1] in perfectly mixed system:

- the diffusion through the film surrounding the solid adsorbent particles, called also “external diffusion”;
- the diffusion in the pores of the adsorbent or “intra-particle diffusion”;
- the reaction of adsorption (and desorption) itself or “surface reaction”.

One (or more) of these steps can be kinetically decisive. The surface reaction is usually a quick step; some authors [2,3] consider that only the intra-particle diffusion govern the sorption kinetics. Desorption, when it occurs significantly (K_L low, $n_{\text{Freundlich}} > 1$), presents the same steps in reverse order.

Several equations are used for external diffusion [4,5]. This step is not often decisive, especially when the experimental system is well agitated.

According to the initial work of Weber and Morris [6], the kinetic expression of intra-particle diffusion is often presented by a linear variation of the concentration of adsorbate with the square root of the contact time, whose slope is equivalent to the rate constant [7–12]. Other models of intra-particle diffusion have been developed and used. Their development was based on the ancient works of Boyd et al. [13] and Vermeulen [14] or more recent works of Mathews and Weber [15] for the theory of “Homogeneous Solid Phase Diffusion Model”. These approaches can determine several types of diffusivity coefficients.

Regarding the step of “surface reaction”, the classic expressions of pseudo-first-order (so-called “Largergren”) [16] and pseudo-second-order kinetic models are often tested [9,17–22]. When the desorption step is also taken into account, a kinetic expression so-called “Langmuir” [22] or “Adams–Bohart–Thomas” [8] is sometimes used.

Some other general expressions can be found in the literature, such as “Bangham” [9,23] or “Statistic Rate Theory”

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Nomenclature

a/V or S_s	specific area of the solid / liquid interface
A_0, A_1, A_2, ...	parameters that describe the mathematical solution (from HSDM model)
C_e	Bromacil concentration at equilibrium (mg L^{-1}, μg L^{-1})
C_0	initial Bromacil concentration (mg L^{-1}, μg L^{-1})
C_t	solute concentration at each time t in the aqueous phase (mg L^{-1})
C^*	$C^* = (C_t - C_e)/(C_0 - C_e)$ (from HSDM model)
D	diffusivity (from Vermeulen) (m^2 s^{-1})
D_s	surface-diffusion coefficient (from HSDM model) (m^2 s^{-1})
D_0	diffusivity (from Rudzinski and Plazinski) (m^2 s^{-1})
DOC	dissolved organic carbon (mg L^{-1})
F_t	reaction advancement
k_{ads}	rate constant of adsorption (L mg−1 min^{-1})
k_{des}	rate constant of desorption (min^{-1})
k_f	transfert external coefficient (from Furusawa and Smith) (m min^{-1})
K_L	Langmuir- or Tóth-isotherm constant
k_V	diffusion constant of intra-particular (from Vermeulen) (min^{-1})
k_W	diffusion constant of intra-particular (from Weber et Morris) (m L^{-1} min$^{-0.5}$)
k_{1app}	rate constant of pseudo-first order (min^{-1})
k_{2app}	rate constant of pseudo-second order (L mg^{-1} min^{-1})
m	PAC mass (g)
$m_s = m/V$	PAC concentration (g L^{-1})
n	Tóth-isotherm constant
PAC	powdered activated carbon
q_e	PAC-surface-complex concentration at equilibrium (mg g^{-1})
q_m	Langmuir-maximum adsorption capacity (mg g^{-1})
q_t	PAC-surface-complexe concentration at time t (mg g^{-1})
R_a	radius of adsorbent (supposed spherical) (m)
S_s	specific area of adsorbent (or a/V) (m^{-1})
V	solution volume (L)

Greek letter

θ	surface coverage (q_e/q_m)

[23–27] which describes the rate of the reaction adsorption/desorption.

Most of the studies on the adsorption kinetics of a chemical compound in aqueous solution are generally conducted for narrow ranges of initial chemical compound and adsorbent concentrations, even sometimes on the basis of a single initial concentration and/or adsorbent.

In our study the application of several monosolute equilibrium isotherm models generally revealed [28] that the adsorption of an adsorbate (Bromacil) probably occurs on two types of activated carbon site (PAC Norit SA-UF). At very low adsorbate concentration (<10 μg L^{-1} in our case), these are high reactivity free sites (or pores) which react ($K_L \sim 10^3$ L mg^{-1}). When the initial adsorbate concentration is higher, a large proportion of this concentration mostly adsorbs on lower reactivity free sites ($K_L \sim 10$ L mg^{-1}). This second part of the study was carried out to confirm this hypothesis by applying kinetic models to assess our experimental results.

Our present work was carried out to investigate the apparent adsorption rate of Bromacil on a commercial powdered activated carbon (PAC Norit SA-UF) with very different initial Bromacil concentrations (~5 to ~400 μg L$^{-1)}$ and PAC concentrations ranging from 0.1 to 5 mg L^{-1}.

The results were interpreted in order to try to establish the key sorption step (or steps), and also to determine the values of the rate constants and other kinetic parameters by assessing their dependence on the equilibrium or initial concentration. Ten kinetic models were tested from more than 20 experiments with different initial concentrations. These data provided by this study should contribute to a better knowledge on the adsorption kinetics of a micropollutant on a PAC widely used in drinking water treatment.

2. Materials and methods

2.1. Kinetic experiments

The protocol for the equilibrium isotherm experiment [28] was also used for the kinetic experiments with two different reactors depending on the concentration ranges studied:

- an agitated and thermostated reactor with a maximum 15-L volume, for high and medium Bromacil concentrations;
- an agitated and nonthermostated reactor with a 250-L volume for very low Bromacil concentrations.

The Bromacil mother solution was prepared in ultrapure water (DOC ≤ 0.1 mg C L^{-1}). The solutions to adsorb were prepared by dilution with ultrapure water for the 15-L reactor, or reverse osmosis water (DOC = 0.1–0.12 mg L^{-1}) for the 250-L reactor. These solutions were buffered with sodium phosphate salts (NaH_2PO_4, H_2O and Na_2HPO_4), at a final ionic strength of 1.75×10^{-3} M. The pH of the final solution to study was adjusted to 7.8 ± 0.03. For plotting the adsorption kinetics, a PAC mass was introduced in the buffered Bromacil solution.

2.2. Powdered activated carbon and chemicals

Norit SA-UF powdered activated carbon was used in this study. This PAC was chosen because of its high mesopore and secondary micropore content and since it is commonly used in drinking water treatment, especially combined with ultrafiltration. The pore structure properties (PSPs) were extracted from literature (Table 1). The PSPs parameters were determined by the N_2 adsorption isotherm technique [32].

2.3. Analytical procedure

The sampling and analyses were carried out using the same protocols as in the equilibrium parameter study [28]. Before each analysis, a standard range was prepared to determine, as precisely as possible, the initial and equilibrium Bromacil concentrations using HPLC coupled with a UV detector, directly or after a preconcentration, depending on the Bromacil concentrations [28].

3. Results and discussion

3.1. General

More than 20 experiments were carried out with initial Bromacil concentrations (C_0) ranging from 5 to 400 μg L^{-1}. For each experiment, a PAC mass was chosen so that Bromacil adsorption would not exceed ~90% of the initial concentration. Table 2 presents these experiments, which are numbered 1–23 in decreasing order of equilibrium concentration (C_e). The results were processed in the form q_t *vs* C_t, where