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Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 1. Equilibrium parameters

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ABSTRACT

This study was carried out to investigate the adsorption equilibrium and kinetics of a pesticide of the uracil group on powdered activated carbon (PAC). The experiments were conducted at a wide range of initial pesticide concentrations (~5 μg L^{-1} to ~500 μg L^{-1} at pH 7.8), corresponding to equilibrium concentrations of less than 0.1 μg L^{-1} for the weakest, which is compatible with the tolerance limits of drinking water. Such a very broad range of initial solute concentrations resulting powdered activated carbon (PAC) concentrations (0.1–5 mg L^{-1}) is the main particularity of our study. The application of several monosolute equilibrium models (two, three or more parameters) has generally shown that Bromacil adsorption is probably effective on two types of sites. High reactivity sites ($K_L \sim 10^3$ L mg^{-1}) which are 10–20 less present in a carbon surface than lower reactivity sites ($K_L \sim 10$ L mg^{-1}), according to the q_m values calculated by two- or three-parameter models. The maximum capacity of the studied powdered activated carbon (PAC), corresponding to monolayer adsorption, compared to the Bromacil molecule surface, would be between 170 mg g^{-1} and 190 mg g^{-1}. This theoretical value is very close to the experimental q_m values obtained when using linearized forms of Langmuir, Tóth and Fritz–Schluender models.

1. Introduction

When treating surface water to obtain drinking water, filtration on granular activated carbon (GAC) is a process that is used worldwide, especially at the end of treatment, after clarification of water (coagulation, flocculation, decantation, sand filtration) and ozonation, before final disinfection by chlorine (or derivatives). Over the last two decades, GAC filtration has been frequently replaced, at the same waterworks level, by adsorption on powdered activated carbon (PAC) coupled with liquid–solid separation (lamellar decantation, microfiltration or ultrafiltration). The PAC doses used, in this case, are a few mg/L. Crystal® and Carboflux® are the best known processes in France running on this principle. Regardless of how the activated carbon is implemented, the main objective of this drinking water treatment phase is to eliminate organic micropollutants (such as pesticides) in order to achieve very low residual concentrations. European regulations specify a maximum concentration of 0.1 μg L^{-1} for each pesticide (and related products) in water intended for human consumption [1]. Most academic studies on the adsorption of chemical compounds in aqueous solution on PAC are generally carried out with initial chemical compound concentrations of a few mg/L or more. In these studies, the range of initial chemical compound concentrations is often fairly reduced. Moreover, these compounds are generally simple aromatic compounds (i.e. phenols) or even dyes. These potential pollutants and their concentration are usually selected on the basis of analytical considerations. However, it is hard or even impossible to apply the published results in industrial conditions, particularly with respect to pesticides at concentrations of a few μg L^{-1}. Moreover, concerning activated carbon, the chosen experimental variable is generally the adsorbent mass, seldom the initial solute concentration. As for pesticides, many academic and applied research studies have obviously been published on the adsorption of atrazine at very low concentrations especially in natural water [2,3] or in the presence of natural organic matter [4–6].

This study was carried out to assess the adsorption equilibrium and kinetics of a pesticide of the uracil group on powdered activated carbon at a wide range of initial pesticide concentrations corresponding to minimum equilibrium concentration values of less than 0.1 μg L^{-1}, which is compatible with drinking water tolerance limits.

This publication presents the results of the most academic part of some experiments on PAC adsorption of a pesticide in buffered pure water, and their interpretation according to known models. The determined equilibrium constants (part 1) and kinetic con-

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Nomenclature

$B_T = q_m RT/\Delta Q$	constant in Temkin isotherm
C_e	Bromacil concentration at equilibrium ($\mathrm{mg\,L^{-1}}$, $\mathrm{\mu g\,L^{-1}}$)
C_s	solute solubility ($\mathrm{mg\,L^{-1}}$)
C_0	initial Bromacil concentration ($\mathrm{mg\,L^{-1}}$, $\mathrm{\mu g\,L^{-1}}$)
$K_d = q_e/C_e$	distribution coefficient ($\mathrm{L\,g^{-1}}$)
K_E	Elovich equilibrium constant ($\mathrm{L\,mg^{-1}}$)
K_F	Freundlich constant indicative of the relative adsorption capacity of the adsorbent ($\mathrm{mg^{(1-n)}\,L^{n}\,g^{-1}}$)
K_L	Langmuir equilibrium constant ($\mathrm{L\,mg^{-1}}$)
K_T	Temkin equilibrium constant ($\mathrm{L\,mg^{-1}}$)
m	PAC mass (g)
$m_s = m/V$	PAC concentration ($\mathrm{g\,L^{-1}}$)
n	Freundlich constant indicative of the intensity of the adsorption
PAC	powdered activated carbon
q_0	solute concentration initially present on PAC ($\mathrm{mg\,g^{-1}}$)
q_e	PAC surface complex concentration at equilibrium ($\mathrm{mg\,g^{-1}}$)
q_m	maximum adsorption capacity from Langmuir ($\mathrm{mg\,g^{-1}}$)
$q_{m\mathrm{DR}}$	maximum adsorption capacity in the micropores from Dubinin-Radushkevich ($\mathrm{mg\,g^{-1}}$)
T	absolute temperature (K)
TOC	total organic carbon
V	solution volume (L)
ΔQ	variation of adsorption energy ($\mathrm{J\,mol^{-1}}$)

Greek letters

β	constant of adsorption energy $E = 1/(\beta)^{0.5}$
ε	potentiel of Polanyi $= RT\ln(C_s/C_e)$
θ	surface coverage (q_e/q_m)

stants (part 2) should ultimately be useful for studies on adsorption in real water (containing natural organic material as co-adsorbate), and for defining the essential needs to better design industrial installations.

The pesticide studied was Bromacil. This herbicide is used to control perennial grasses, brush, and weeds on non-agricultural land. It is also used for selective weeding in citrus and pineapple crop fields [7]. Bromacil is not photodegradable on the soil surface, stable to photolysis in water, except under alkaline conditions, stable to hydrolysis in water between pH 5 and 9 [8] and soluble in water, so it may be readily leached into the soil and thus contaminate groundwater [9]. It has been found in groundwater in Florida, at 300 $\mathrm{\mu g\,L^{-1}}$ [10], and more recently in natural waters of Martinique at concentrations of up to 2 $\mathrm{\mu g\,L^{-1}}$ in the presence of other pesticides, such as chlordecon, hexachlorocyclohexane beta (HCH-β) and aldicarb derivatives [11].

2. Materials and methods

2.1. Equilibrium experiments

A similar protocol was used for all equilibrium isotherm experiments, but with three different reactors according to the studied concentration ranges:

- experiments in two perfectly agitated and thermostated reactors with a maximum volume of 5 L or 15 L, respectively for the high and medium Bromacil concentrations,
- experiments in an agitated and nonthermostated 250 L reactor, for very low Bromacil concentrations.

2.1.1. Isotherm for high and medium Bromacil concentrations

The Bromacil mother solution was prepared in ultrapure water ($18\ \mathrm{M\Omega\,cm^{-1}}$, TOC $\leq 0.1\ \mathrm{mg\,C\,L^{-1}}$) at a concentration below the solubility limit reported in the literature. No organic solvent was used to increase the Bromacil solubility. The daughter solutions were prepared by dilution with the same water, buffered with sodium phosphate salts (NaH_2PO_4, H_2O and Na_2HPO_4), to achieve a final ionic strength of 1.75×10^{-3} M. The final pH of the studied solution was adjusted to 7.8 ± 0.03. For plotting the adsorption isotherms, different PAC masses (0.25–5 $\mathrm{mg\,L^{-1}}$) were added to the buffered Bromacil daughter solution. The solutions were agitated with a magnetic stirrer (5 L reactor) or a recirculation pump (15 L reactor) at a constant temperature of $20 \pm 1\ ^\circ$C, in the dark, for a contact time of 24 h. Samples were collected and then filtered on fibreglass membranes (Whatman GF/C 1.2 μm filter or Minisart GF/F 0.7 μm syringe) to measure the Bromacil concentrations.

2.1.2. Isotherm for low Bromacil concentrations

Bromacil solutions were prepared under the same conditions as above. However, the volume of purified water needed (250 L) led us to use reverse osmosis water ($3–10\ \mathrm{M\Omega\,cm^{-1}}$, TOC = 0.1–0.12 $\mathrm{mg\,L^{-1}}$) instead of ultrapure water. For adsorption isotherms, different PAC masses (0.1–1 $\mathrm{mg\,L^{-1}}$) were added into a 250 L volume reactor containing the Bromacil solutions (initial concentration 4–6 $\mathrm{\mu g\,L^{-1}}$, pH 7.8, $I = 1.75 \times 10^{-3}$), for a contact time of 7 days. The solutions were agitated with a blade linked to an electric motor, with a stirring speed of about 400 rpm. Agitation was started an hour before injecting the PAC so as to properly mix the solution. For each sample, 10 times a litre of solution was drawn off and reintroduced into the reactor before sampling the solution for membrane filtration and analysis. Minisart GF/F 0.7 μm fibreglass filters were used.

Table 1
Bibliographic data on the PAC used in this study.

	PAC “SA-UF” from France [12,13]	PAC “SA-UF” from France [5]	PAC “SA-UF” from Netherland [5]
BET surface area	$1112\ \mathrm{m^2\,g^{-1}}$	$1085\ \mathrm{m^2\,g^{-1}}$	$1112\ \mathrm{m^2\,g^{-1}}$
Ashes	8.17%	–	–
Humidity	2%	–	–
Apparent density	$0.16\ \mathrm{g\,cm^{-3}}$	–	–
Average geometric diameter	6 μm	–	–
Volume of primary micropores (<8 Å)	$0.343\ \mathrm{cm^3\,g^{-1}}$	$0.226\ \mathrm{cm^3\,g^{-1}}$	$0.214\ \mathrm{cm^3\,g^{-1}}$
Volume of secondary micropores (>8 Å)	$0.194\ \mathrm{cm^3\,g^{-1}}$	–	–
Volume of mesopores (20–500 Å)	$0.357\ \mathrm{cm^3\,g^{-1}}$	$0.885\ \mathrm{cm^3\,g^{-1}}$	$0.844\ \mathrm{cm^3\,g^{-1}}$
Surface area of micropores	$733\ \mathrm{m^2\,g^{-1}}$	$662\ \mathrm{m^2\,g^{-1}}$	$615\ \mathrm{m^2\,g^{-1}}$
Surface area of mesopores	$379\ \mathrm{m^2\,g^{-1}}$	$423\ \mathrm{m^2\,g^{-1}}$	$421\ \mathrm{m^2\,g^{-1}}$