



Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 3: Competition with natural organic matter

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ABSTRACT

This study (part 3) was carried out to investigate the effect of the natural organic matter (NOM) concentration on Bromacil (pesticide) adsorption on powdered activated carbon (PAC) in the same experimental conditions as in our previous studies (parts 1 and 2). Our previous findings showed that Bromacil adsorption in buffered pure water (pH 7.8) occurred at two types of site. In the presence of NOM (three kinds), we noted a significant reduction in Bromacil adsorption capacities due to the competitive effects exerted by NOM. Highly reactive sites (or pores) in PAC appeared to be blocked by NOM adsorption, as demonstrated by the application of a pseudo-single solute isotherm and of the simplified ideal adsorbed solution theory (IAST), regardless of the initial Bromacil and NOM concentrations. The competing effect of low-molecular weight NOM was found to be greater than the competing effect of high-molecular weight NOM. The pseudo-second order surface-reaction model fitted Bromacil adsorption particularly well, even in the presence of NOM. However, the adsorption–kinetic constant values were found to be independent of the aqueous equilibrium concentration of the target compound, contrary to that observed in pure water. The kinetic data thus confirmed that high reactivity PAC sites were blocked by NOM adsorption. A practical approach concluded this work.

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1. Introduction

Over the last two decades, granular activated carbon (GAC) filtration has frequently been replaced by adsorption on powdered activated carbon (PAC), because PAC can be applied only when needed in many drinking water treatment plants, and it is cheaper than GAC. Moreover, PAC can be combined with liquid–solid separation in specific reactor configurations (lamellar decantation or membrane filtration). PAC doses of just a few mg L^{-1} are used in this case. Crystal[®] and Carboflux[®] are the best known processes running on this principle in France. These hybrid systems make it possible to simultaneously remove dissolved and particulate contaminants and they allow for much longer carbon contact times than the standard reactor–hydraulic retention time. However, the main focus of such a treatment process is usually the removal of organic micropollutants (e.g. pesticides, pharmaceuticals, etc.) in order to achieve very low-residual concentrations. European reg-

ulations specify a maximum concentration of $0.1 \mu\text{g L}^{-1}$ for each pesticide (and related products) in drinking water.

Our recent previous studies [1,2] involved assessing the adsorption equilibrium and kinetics of a pesticide of the uracil group (Bromacil or 5-bromo-6-methyl-3-[1-methylpropyl]-2,4[1H, 3H]-pyrimidinedione; $\text{C}_9\text{H}_{13}\text{BrN}_2\text{O}_2$) on powdered activated carbon (Norit SA-UF), in a wide range of initial pesticide concentrations ($\sim 5 \mu\text{g L}^{-1}$ to $\sim 500 \mu\text{g L}^{-1}$), sometimes corresponding to minimum equilibrium concentration values of $<0.1 \mu\text{g L}^{-1}$ compatible with drinking water tolerance limits. The application of several mono-solute equilibrium models (with two, three or more parameters) generally showed that Bromacil adsorption in buffered pure water (pH 7.8) occurred at two types of site. At very low equilibrium adsorbate concentrations ($<10 \mu\text{g L}^{-1}$ in our case), it was high reactivity free sites or pores ($K_{(\text{Langmuir})} \sim 10^3 \text{L mg}^{-1}$, $q_{\text{m}(\text{Langmuir})} \sim 20 \text{mg g}^{-1}$) that reacted. When the equilibrium concentration was higher, a substantial proportion of this concentration was mostly adsorbed on lower reactivity free sites ($K_{(\text{Langmuir})} \sim 10 \text{L mg}^{-1}$, $q_{\text{m}(\text{Langmuir})} \sim 150 \text{mg g}^{-1}$). The magnitude of q_{m} corresponded to almost total coverage of the area occupied by activated carbon secondary micropores and mesopores.

These studies were carried out in buffered pure water at pH 7.8, without the presence of organic compounds other than

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Nomenclature

C_e	aqueous equilibrium solute concentration (mg L^{-1})
C_t	aqueous solute concentration at each time t (mg L^{-1})
C_0	aqueous initial solute concentration (mg L^{-1})
DOC	dissolved organic carbon (mg CL^{-1})
EBC	equivalent background compound
f	PAC fraction of sites (highly reactive or weakly reactive) available for Bromacil in OFW at pH 7.8
IAST	ideal adsorbed solution theory
$k_{\text{ads.}}$	adsorption rate constant, from Langmuir ($\text{L mg}^{-1} \text{min}^{-1}$)
$k_{\text{app.}}$	rate constant of pseudo-second order ($\text{g mg}^{-1} \text{min}^{-1}$)
K_F	adsorption capacity factor of Freundlich equation ($\text{mg}^{(1-n_F)} \text{L}^{n_F} \text{g}^{-1}$)
K_L	equilibrium constant of Langmuir equation (L mg^{-1})
K_T	equilibrium constant of Temkin equation (L mg^{-1})
m	PAC mass (g)
$m_s = m/V$	PAC concentration (g L^{-1})
n_F	isotherm exponent of Freundlich equation
NOM	natural organic matter
OFW	organic-free water
PAC	powdered activated carbon
q_e	solid-phase equilibrium solute concentration (mg g^{-1})
q_t	solid-phase solute concentration at each time t (mg g^{-1})
q_m	maximum adsorption capacity of Langmuir equation (mg g^{-1})
V	solution volume (L)
ΔQ	variation of adsorption energy of Temkin equation (kJ mol^{-1})

Bromacil. However, natural ground and surface waters contain natural organic matter (NOM), which is a complex mixture of several organic compounds, at concentrations ranging from some 0.1 to over 10 mg (in DOC) per litre. Competition between target trace compounds and NOM is common in activated carbon processes, especially for drinking water treatment. NOM has been shown to reduce the adsorption capacity of activated carbon for trace compounds typically present at concentrations in the microgram- or nanogram-per-litre levels. Some approaches to describe the competitive adsorption equilibrium in systems containing micropollutants and NOM have been described in the literature [3–6]. Most of them treat competing background organic matter as one hypothetical compound, the equivalent background compound (EBC) [4], and describe the adsorption characteristics of the bi-solute system by solving ideal adsorbed solution theory (IAST) equations [7,8].

Concerning the kinetics of Bromacil adsorption in buffered pure water (at pH 7.8), we showed [2] that many models are suitable, regardless of the considered step, e.g. intra-particle diffusion or surface reaction. It was therefore not possible to accurately determine *a priori* whether the diffusion or surface reaction was a key kinetic factor. The pseudo-second order surface-reaction model fitted particularly well, which seemed logical since its integration led to a solution similar to that obtained with integration of the Langmuir kinetic model. In this latter case, for equilibrium concentrations (C_e) over $\sim 10 \mu\text{g L}^{-1}$, the adsorption and desorption constants were relatively independent of C_e ($k_{\text{ads.}} = (0.31 \pm 0.16) \text{L mg}^{-1} \text{min}^{-1}$ and $k_{\text{des.}} = (2.8 \pm 1.4) \times 10^{-2} \text{min}^{-1}$). For $C_e \leq 10 \mu\text{g L}^{-1}$, the adsorption constants were significantly higher

($k_{\text{ads.}} = 2.73 \pm 0.95 \text{L mg}^{-1} \text{min}^{-1}$) and the desorption constants were significantly lower ($k_{\text{des.}} = (0.3 \pm 0.08) \times 10^{-2} \text{min}^{-1}$). This kinetic observation clearly confirmed the hypothesis based on two types on PAC for Bromacil adsorption in pure water.

NOM can also modify the adsorption kinetic rate of trace compounds. The competitive effect of NOM on the kinetic parameters of trace organic compounds is usually not described. Some authors [3–5,9] have identified direct site competition and pore blockage as the two primary mechanisms of competitive adsorption between trace compounds and NOM, with the effect depending on the molecular weight distribution of the NOM as well as the pore size distribution and configuration of activated carbon pores.

The present study was carried out to investigate the effect of the NOM concentration on Bromacil adsorption (equilibrium and kinetics) in the same experimental conditions as in our previous recent studies [1,2] on Bromacil adsorption in organic-free water at pH 7.8. Beyond the academic approach, this study was carried out to gain further insight into micropollutant adsorption on PAC carbon, i.e. a process which is being used to an increasing extent in drinking water treatment.

2. Materials and methods

2.1. Bromacil and NOM solutions

The Bromacil (Fluka-Riedel De Häens) stock solution was prepared in reverse osmosis water ($3\text{--}10 \text{M}\Omega \text{cm}^{-1}$, $\text{DOC} < 0.1 \text{mg L}^{-1}$) at a concentration below the solubility limit reported in the literature. No organic solvent was used to increase Bromacil solubility. The solution was verified as being very stable [1]. Dilutions from stock were prepared with the same water, buffered with sodium phosphate salts (NaH_2PO_4 , H_2O and Na_2HPO_4), to achieve a final pH of 7.8 and final ionic strength of $1.75 \times 10^{-3} \text{M}$.

Three kinds of NOM were added separately to the Bromacil solutions at various concentrations (~ 2 to $\sim 25 \text{mg L}^{-1}$ as DOC): a commercially available humic acid and two NOM extracted from river water. Aldrich humic acid (A-HA, Lot No. 31620) is a terrestrial peat humic substance which is often used as a model adsorbate because it is commercially available and especially convenient to test the effects of high concentrations. This humic acid has a complex chemical structure and is polymeric and multifunctional, with a dominant acidic character [10]. Table 1 presents some physicochemical characteristics of A-HA derived from the literature. The studied natural organic matters were extracted by other researchers of our team (University of Poitiers), using a specific procedure [11]. The same surface water (collected at different periods of the year near Poitiers, France) was used: a river water called “Vienne” (VRW). Raw water was pre-filtered through a $0.45\text{-}\mu\text{m}$ cartridge filter, acidified at pH 2 (with HCl) and pumped through a macroporous XAD-8 resin (previously washed with NaOH and HCl), followed by passing through a macroporous XAD-4 resin (previously washed like XAD-8 resin). The humic substances retained on the XAD-8 resin are usually considered as being the most hydrophobic compounds, while the XAD-4 adsorbed part is less hydrophobic. Some authors [11,12] call these two experimental fractions “hydrophobic or HPO” and “transphilic or TPH”. After washing the resin columns with formic acid (0.1 M) to remove chlorides, the adsorbed organic compounds were then eluted from two separate XAD resins using an acetonitrile/water (75/25) mixture. Finally, the extracts were evaporated and freeze-dried. The HPO fraction of VRW (called “VRW-HPO”) and the TPH fraction of VRW (“VRW-TPH”) were used in this study. The obtained organic powders were characterized by various analytical techniques in their solid form (elemental analysis, pyrolysis/GC/MS) or in aqueous

Table 1
Some structural properties of the studied NOMs.

NOM	Elementary analysis		Size indexes		
	% Carbon ^a	% Nitrogen ^a	Scale of M_w^b (kDa)	M_w^c (kDa)	SUVA ^d ($m^{-1} L mg^{-1}$)
A-HA	38.7	–	~1 to ~7 ^e	–	6.3
VRW-HPO	52.8	1.55	~0.18 to ~5.7	0.6	5.1
VRW-TPH	48.9	2.7	~0.15 to ~1.5	0.5	2.7
NOM	Functional groups				
	% PHA ^f	% PS ^f	% PR ^f	% AS ^f	
A-HA	–	–	–	–	
VRW-HPO	16.3	25.3	15.0	3.0	
VRW-TPH	5.2	29.6	23.3	4.0	

PHA, polyhydroxyaromatics; PS, polysaccharides; PR, proteins; AS, aminosugars.

^a From Central Analysis Service in French National Centre for Scientific Research.

^b Molecular weight evaluated by high-performance size exclusion chromatography (HPEC) using suitable standards.

^c M_w = average molecular weight calculated from Chin et al.'s method [13].

^d Specific UV absorbance (SUVA) = UV_{254nm} absorbance/DOC.

^e From Ref. [15].

^f Functional groups evaluated by pyrolysis/gas chromatography/mass spectrometry, from Bruchet et al.'s method [14].

solution (HPSEC, SUVA). The findings revealed significant differences for the studied NOM (Table 1).

2.2. Powdered activated carbon

PAC Norit SA-UF powdered activated carbon was used in this study. It 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 main PAC SA-UF properties were mentioned in our previous studies [1,2].

2.3. Equilibrium and kinetic experiments

The same protocol as used in our previous studies in organic-free water (OFW), i.e. reverse osmosis buffered water [1,2], was used for all equilibrium and kinetic experiments (using the conventional bottle-point technique), with two different reactors according to the studied concentration ranges:

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

The final pH of the studied solutions was adjusted to 7.7–7.9.

To plot the adsorption isotherms, different PAC masses ($0.5\text{--}4\text{ mg L}^{-1}$) were added to the buffered Bromacil/NOM solution under mixing for a 24 h contact time. The PAC concentrations were selected to avoid that Bromacil adsorption would not exceed ~90% of the initial concentration.

For the kinetic experiments, the PAC dose was chosen to avoid Bromacil adsorption would not exceed ~90% of the initial concentration, under mixing for a contact time of 5–6 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 and DOC concentrations.

2.4. Analytical procedure

Before each analysis, a standard range was prepared to be able to accurately determine the initial and equilibrium Bromacil concentrations by HPLC coupled with a UV detector. Bromacil analyses were conducted with the following equipment set up: Waters 717 injector (200 μL), Hichrom column (reversed phase C_{18} , 5 μm , 250 mm \times 4.6 mm); Waters 510 pump (isocratic method), mobile

phase with 40% ultra-pure water (Milli RQ–Milli Q water) and 60% methanol at a flow rate of 0.7 mL min^{-1} , Waters 286 UV detector (277 nm), Millennium data acquisition.

A pre-concentration was sometimes necessary, especially for experiments conducted at low-initial concentration ($\sim 5\text{ }\mu\text{g L}^{-1}$). In this case, samples (100 mL) were extracted by cartridges (Oasis Waters) and Bromacil was eluted with 2 mL methanol and then diluted with the same amount of ultra-pure water. Extraction yields were above 97% and the repeatability (0.5–4.5%) was determined from solutions of different concentrations ($0.1\text{--}10\text{ }\mu\text{g L}^{-1}$) prepared in ultra-pure water. The detection limit obtained by this extraction method was $0.05\text{ }\mu\text{g L}^{-1}$ in OFW.

When specifically indicated, the dissolved natural organic material concentration was measured directly in terms of DOC content using a Shimadzu TOC 5000-A based on the principle of catalytic oxidation of organic matter at high temperature, followed by IR spectrometric detection of CO_2 formed. Each analysis was performed after acidification (2N HCl) and was then purged with synthetic air. 100 μL samples were injected into an oven (680°C) containing a platinum catalyst. The detection limit was about 0.1 mg CL^{-1} . The accuracy usually claimed by the manufacturer and the laboratory is about $\pm 2\%$ to 3%, provided that a minimum of five tests per sample are performed. Before each new use of the TOC analyzer, a sample of ultra-pure water was injected three times to rinse the device and a standard 10 mg CL^{-1} was analyzed to verify the validity of the analyzer response. Standards were prepared from a stock solution of potassium hydrogen phthalate ($\text{HOOC-C}_6\text{H}_4\text{-COOK}$, 1 g L^{-1}), kept for a maximum of 1 month at 4°C and protected from light. When approximately indicated, the DOC value was the product of the known NOM-weight concentration (in mg L^{-1}) by the NOM-carbon percentage given in Table 1.

3. Results and discussion

For experiments carried out in the presence of NOM, indexes 1 or 2 were added to symbols for Bromacil and NOM (in DOC), respectively (e.g. $C_{0,i}$ or $q_{e,i}$). For data and/or calculations derived from our previous studies on Bromacil adsorption in OFW [1,2], no index was added to symbols.

3.1. General

The eight isotherm experiments and six kinetic experiments were carried out with initial Bromacil and NOM concentrations ranging from $C_{0,1} \approx 5\text{ }\mu\text{g L}^{-1}$ to $80\text{ }\mu\text{g L}^{-1}$ and $C_{0,2} \approx 2\text{--}25\text{ mg CL}^{-1}$,

Table 2

Experimental conditions for Bromacil/NOM-adsorption isotherms in buffered solution (pH 7.7–7.9) on PAC Norit SA-UF.

Isotherm experiment	Bromacil initial concentration, $C_{0,1}$ ($\mu\text{g L}^{-1}$)	NOM kind: initial concentration, $C_{0,2}$ (mg CL^{-1})	Volume of solution, $V \pm 1\%$ (L)	PAC concentration, $m_s \pm 5\%$ (mg L^{-1})
# 1	77.3 ± 2.5	A-HA: ~ 25	15	1, 1.5, 2, 3, 4
# 2	74.0 ± 2.4	A-HA: ~ 12.5	15	1, 1.5, 2, 3, 4
# 3	39.6 ± 1.3	A-HA: ~ 12.5	15	2, 3
# 4	67.1 ± 2.5	A-HA: 2.71 ± 0.08	15	1, 1.5, 2, 3
# 5	38.0 ± 1.3	A-HA: 2.71 ± 0.08	15	0.5, 1.5, 3
# 6	5.05 ± 0.25	A-HA: 2.32 ± 0.07	100	1
# 7	4.82 ± 0.24	VRW-HPO: 2.10 ± 0.06	100	2
# 8	5.04 ± 0.25	VRW-TPH: 2.23 ± 0.07	100	2

Table 3

Experimental conditions for Bromacil/NOM-adsorption kinetics in buffered solution (pH 7.7) on PAC Norit SA-UF.

Kinetic experiment	Bromacil initial concentrations, $C_{0,1}$ ($\mu\text{g L}^{-1}$)	NOM kind: initial concentration, $C_{0,2}$ (mg CL^{-1})	PAC concentration, $m_s \pm 5\%$ (mg L^{-1})	Volume of solution, $V \pm 1\%$ (L)	Time period of model applications (min)
# 9	64.5 ± 2.1	A-HA: ~ 2.5	3	15	3–330
# 10	66.8 ± 2.2	A-HA: ~ 2.5	2	15	4–330
# 11	66.1 ± 2.2	A-HA: ~ 2.5	1.5	15	5–330
# 12	33.2 ± 1.1	A-HA: ~ 2.5	1.5	15	5–330
# 13	36.9 ± 1.2	A-HA: ~ 2.5	0.5	15	5–330
# 14	5.10 ± 0.25	A-HA: 2.60 ± 0.02	1	100	60 to $\sim 10,000$

respectively, in reverse osmosis water buffered at pH 7.7–7.9 (Tables 2 and 3).

3.2. Equilibrium parameters

As for Bromacil, i.e. the target compound (index 1), the results were processed in the following form, where $q_{e,1}$ vs ($C_{e,1}$):

$$q_{e,1} = \left(\frac{V}{m}\right) (C_{0,1} - C_{e,1}) \quad (1)$$

Fig. 1 shows all results obtained in the presence of A-HA, by isotherm plotting $q_{e,1}$ vs $C_{e,1}$ for experiments # 1–6. The dotted curve shows the “theoretical” isotherm in OFW at pH 7.8, derived from application of the two-site Langmuir (Eq. (2)) model, with the assumption of two different reactivity and concentration sites or pores (A and B) on the PAC [1]:

$$\frac{q_e}{q_m} = \left[\frac{f_A K_{LA} C_e}{1 + K_{LA} C_e} + \frac{f_B K_{LB} C_e}{1 + K_{LB} C_e} \right] \quad (2)$$

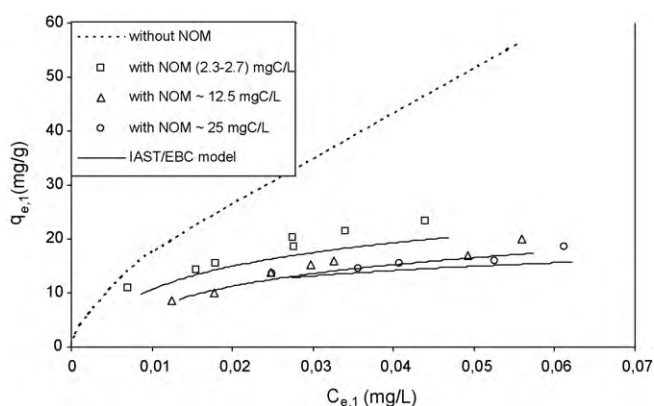


Fig. 1. Bromacil adsorption isotherm in OFW (dotted line) and in the presence of NOM (A-HA) on PAC Norit SA-UF at pH 7.7–7.9. Dotted line: single-solute isotherm derived from the two-site Langmuir model for Bromacil in OFW at pH 7.8 (Eq. (2)) with $K_{LA} \sim 1000 \text{ L mg}^{-1}$; $K_{LB} \sim 10 \text{ L mg}^{-1}$; $q_m = 151 \text{ mg g}^{-1}$; $f_A = 0.031 \pm 0.011$; $f_B = 0.956 \pm 0.023$; $r^2 = 0.986$ [1]. (\square , \triangle , \circ) experimental data for Bromacil/NOM adsorption (standard deviations for $C_{e,1}$ is comprised between 3.3% ($C_{e,1} > 0.01$) and 8% ($C_{e,1} < 0.01$), and 3% for $q_{e,1}$). Full lines: simplified IAST/EBC model fits for Bromacil/NOM adsorption (Eq. (7)) with $K_{F,1} = K_{F,2} = 218$; $n_{F,1} = n_{F,2} = 0.49$ and $q_{2,e} \gg q_{1,e}$.

Regardless of the different initial Bromacil concentrations ($C_{0,1} \approx 5\text{--}80 \mu\text{g L}^{-1}$) or initial A-HA concentrations ($C_{0,2} \approx 2\text{--}25 \text{ mg CL}^{-1}$), we noted very significantly lower experimental values in the presence of A-HA compared to the dotted curve in OFW. This revealed reduced Bromacil adsorption capacities due to competitive effects exerted by NOM. Moreover, this adsorption reduction was more marked for higher initial NOM concentrations. In OFW solutions [1], our initial objective was to find an isotherm equation able to model all of the experimental data from $C_e \approx 0.1 \mu\text{g L}^{-1}$ to $C_e \approx 360 \mu\text{g L}^{-1}$. Five two-parameter models (nonlinear and linear forms of Freundlich, Langmuir, Temkin, Elovich and Dubinin–Radushkevich), seven three-parameter models (Redlich–Peterson, Langmuir–Freundlich, Sips, Generalized, Tóth, Fritz–Schluender, Radke–Prausnitz) and the Langmuir-2 site model were tested. For all linear isotherm expressions, it was possible to obtain: (i) a right isotherm portion corresponding to higher equilibrium concentrations ($\sim 10 \mu\text{g L}^{-1} < C_e < \sim 360 \mu\text{g L}^{-1}$), with good linear regressions, (ii) a left isotherm portion for low equilibrium Bromacil concentrations ($\sim 0.1 \mu\text{g L}^{-1} < C_e < \sim 10 \mu\text{g L}^{-1}$), but with a less good linear regression. Regarding the application of models in their linear forms allowed us to define the studied PAC as related to active sites [1]:

- very reactive sites, called “A sites”, which are weakly present at the surface of PAC and which react in a first stage (these sites are the only ones that complex Bromacil at very low concentration);
- less active sites, called “B sites”, strongly present at the PAC surface, which react in a second stage when A sites are saturated (in the presence of high Bromacil concentrations, most reactions concern these B sites while masking the reaction of A sites).

Among the tested two-parameter isotherms (under linear form), Langmuir II and Temkin models (Eqs. (3) and (4)) gave the best results [1]. In Figs. 2 and 3, we thus present the application of these models in OFW (dotted line) in comparison with the experimental data in the presence of NOM (A-HA = 2.3–2.7 mg CL^{-1}) at different initial Bromacil concentrations:

$$\frac{C_e}{q_e} = C_e \frac{1}{q_m} + \frac{1}{q_m K_L} \quad (3)$$

$$q_e = B_T \ln K_T + B_T \ln C_e \quad \text{with } B_T = \frac{q_m R T}{\Delta Q} \quad (4)$$

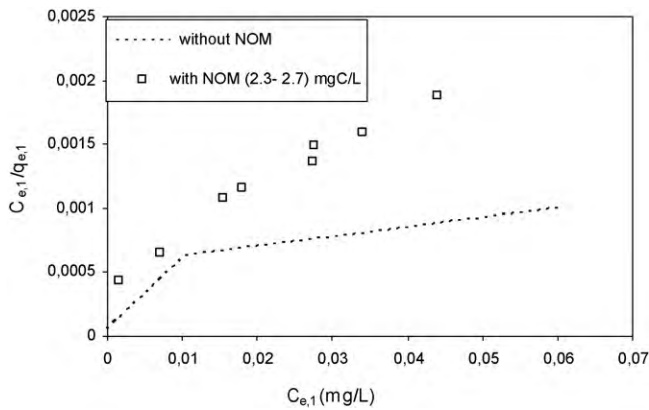


Fig. 2. Application of the Langmuir isotherm for Bromacil/NOM adsorption on PAC Norit SA-UF at pH 7.7–7.9. Dotted line: single-solute isotherm derived from the Langmuir model for Bromacil in OFW at pH 7.8 (Eq. (3)) with $K_L = 920 \text{ L mg}^{-1}$ and $q_m = 18.1 \text{ mg g}^{-1}$ for the left part; with $K_L = 11 \text{ L mg}^{-1}$ and $q_m = 151.5 \text{ mg g}^{-1}$ for the right part [1]. (□) Experimental data for Bromacil/NOM adsorption.

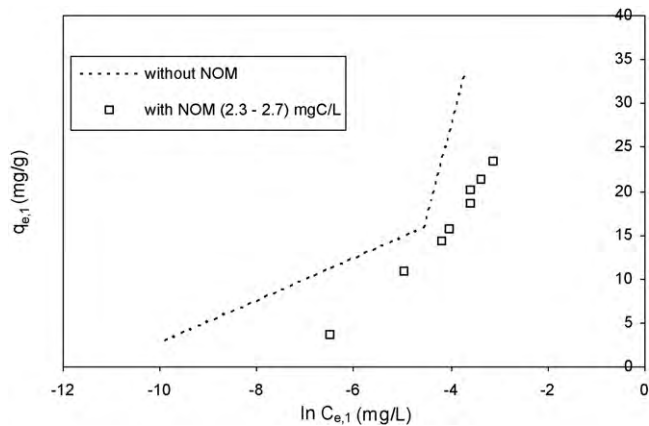


Fig. 3. Application of the Temkin isotherm for Bromacil/NOM adsorption on PAC Norit SA-UF at pH 7.7–7.9. Dotted line: single-solute isotherm derived from the Temkin model for Bromacil adsorption (Eq. (4)) with $K_T = 6.7 \times 10^4 \text{ L mg}^{-1}$ and $\Delta Q = 18.4 \text{ kJ mol}^{-1}$ for the left part; with $K_T = 117 \text{ L mg}^{-1}$ and $\Delta Q = 11.7 \text{ kJ mol}^{-1}$ for the right part [1]. (□) Experimental data for Bromacil/NOM adsorption.

Figs. 2 and 3 show that the two (right and left) portions of the isotherms were transformed into a (almost) single straight line when Bromacil adsorption was performed in the presence of NOM.

The Bromacil adsorption capacity measured by $q_{m,1}$ or $K_{F,1}$ of pseudo-single solute isotherms (Langmuir and Freundlich), for experiments # 4–6 in the presence of NOM (2.3–2.5 mg C L^{-1}), showed a very significant decrease over most of the right part of the isotherm (Table 4), as compared to experiments conducted in OFW at similar pH [1]. The presence of NOM therefore drastically

decreased the PAC capacity of highly reactive sites (or pores) into PAC (sites A) which appeared to be “blocked” by NOM adsorption.

3.3. Application of IAST combined with the EBC concept

Weber et al. [16] conducted important reference studies on NOM adsorption into activated carbon. These authors have shown that plotting “ $\log q_e$ vs $\log C_e$ ” (for equilibrium NOM concentrations from 0.1 mg to 4 mg L^{-1} in DOC) sometimes led to a change in the straight line slope with increasing C_e values. For example, three principal regions were noted in the Freundlich isotherm of humic acid adsorption: (i) an essentially vertical line indicating little or no adsorption at high activated carbon doses and low- C_e values; (ii) an intermediate region where middle-range doses of activated carbon weakly adsorb organic matter; (iii) a steep-sloped region corresponding to high adsorption for low doses of activated carbon and high- C_e values. These findings were confirmed in other studies [e.g. 7,17]. More recently, Ding et al. [4] mentioned, consistent with previous works [3], that NOM is divided into two fictive adsorbable fractions, i.e. a “strongly competing” fraction (SC) and a “pore-blocking” fraction (PB). For these authors, the SC fraction is the only fraction that affects the micropollutant isotherm (atrazine in this case), and can be treated as a single compound based on the equivalent background compound model (EBC) [4]. For these authors [4], the system can be modeled as a bi-solute system (trace organic compound, with index 1, and EBC, with index 2) and can be described by solving the ideal adsorbed solution theory (IAST) equations (Eqs. (5) and (6)) [7,8].

$$C_{0,1} - q_{e,1} m_s = \left[\frac{q_{e,1}}{q_{e,1} + q_{e,2}} \right] \left\{ \frac{[(q_{e,1}/n_{F,1}) + (q_{e,2}/n_{F,2})]}{K_{F,1}/n_{F,1}} \right\}^{1/n_{F,1}} \quad (5)$$

$$C_{0,2} - q_{e,2} m_s = \left[\frac{q_{e,2}}{q_{e,1} + q_{e,2}} \right] \left\{ \frac{[(q_{e,1}/n_{F,1}) + (q_{e,2}/n_{F,2})]}{K_{F,2}/n_{F,2}} \right\}^{1/n_{F,2}} \quad (6)$$

with $q_{e,i} = K_{F,i} C_{e,i}^{(n_{F,i})}$ (Freundlich isotherm).

Solving Eqs. (5) and (6) needed various assumptions by authors [4]:

- the EBC solid-phase concentration ($q_{e,2}$) is much greater than the solid-phase concentration of the target compound ($q_{e,1}$),
- NOM molecules competing with the micropollutant have the same molecular weight and adsorption properties as those of the target compound,
- Freundlich constants are similar for target compounds ($K_{F,1}$, $n_{F,1}$) and for the SC fraction of NOM ($K_{F,2}$ and $n_{F,2}$).

Incorporation of the above assumptions into Eq. (5) leads to Eq. (7), thus allowing us to easily calculate $q_{e,2}$ from the known values of

Table 4
Single Bromacil and pseudo-single Bromacil (with NOM) isotherm constants in buffered solution on PAC Norit SA-UF at pH 7.7–7.9.

Isotherms	Langmuir constants			Temkin constants			Freundlich constants		
	q_m (mg g^{-1})	K_L (L mg^{-1})	r^2	ΔQ (kJ mol^{-1})	K_T (L mg^{-1})	r^2	n_F	K_F ($\text{mg}^{(1-n)} \text{ L}^n \text{ g}^{-1}$)	r^2
Bromacil in OFW [1] (left part, sites “A”) $0.09 \leq C_{1,e} < 10.4 \mu\text{g L}^{-1}$	18.1	920	0.955	18.4	6.7×10^4	0.831	0.27	59	0.900
Bromacil in OFW [1] (right part, sites “B”) $10.4 \leq C_{1,e} \leq 364 \mu\text{g L}^{-1}$	151.5	11	0.981	11.7	117	0.972	0.49	218	0.966
Bromacil/NOM (a straight line alone) $1.6 \leq C_{1,e} \leq 44 \mu\text{g L}^{-1}$	29.5	67.8	0.976	12.4	1009	0.976	0.55	142	0.982

NOM: A-HA, DOC = 2.3–2.5 mg L^{-1} .

Table 5

Comparison of experimental data for Bromacil/NOM adsorption with calculated equilibrium values for bi-solute (Bromacil and NOM) and mono-solute (Bromacil alone) adsorption on PAC Norit SA-UF at pH 7.7–7.9, in very low-Bromacil concentration.

NOM	m_s in mg L^{-1} $C_{0,2}$ in mg C L^{-1} $C_{0,1}$ in $\mu\text{g L}^{-1}$	Experimental data		Calculated values by IAST/ EBC model ($n_{F,1} = 0.49$, $K_{F,1} = 218$)		Calculated values by IAST/ EBC model ($n_{F,1} = 0.27$, $K_{F,1} = 59$)		Calculated values by Freundlich isotherm [1], in organic-free water ($C_{0,2} = 0$)	
		$q_{e,1}$ (mg g^{-1})	$C_{e,1}$ ($\mu\text{g L}^{-1}$)	$q_{e,1}$ (mg g^{-1})	$C_{e,1}$ ($\mu\text{g L}^{-1}$)	$q_{e,1}$ (mg g^{-1})	$C_{e,1}$ ($\mu\text{g L}^{-1}$)	q_e (mg g^{-1})	C_e ($\mu\text{g L}^{-1}$)
A-HA	1 ± 0.05 2.32 ± 0.07 5.05 ± 0.25	3.47 ± 0.10	1.58 ± 0.08	3.32	1.73	2.92	2.13	4.95	0.095
VRW-HPO	2 ± 0.1 2.10 ± 0.06 4.82 ± 0.24	0.845 ± 0.025	3.13 ± 0.16	0.84	3.14	0.81	3.20	2.41	0.007
VRW-TPH	2 ± 0.1 2.23 ± 0.07 5.04 ± 0.25	1.10 ± 0.03	2.84 ± 0.14	1.09	2.85	1.04	2.95	2.52	0.008

$C_{0,1}$, $C_{e,1}$ and m_s :

$$C_{0,1} - q_{e,1} m_s = C_{e,1} = \left(\frac{q_{e,1}}{q_{e,2}} \right) \left(\frac{q_{e,2}}{K_{F,1}} \right)^{1/n_{F,1}} \quad (7)$$

Indeed, the experimental quantification of $q_{e,2}$ (by DOC measurement and $q_{e,2} = C_{0,2} - C_{e,2}/m_s$) is very fastidious because: (i) dissolved organic traces of NOM can be retained by sample filtration; which is indispensable before DOC analysis; (ii) small micro-particles of PAC can cross the filtration membrane; and (iii) some inaccuracy percentages may have a substantial effect on the calculated value.

To illustrate the validity of a simplified IAST/EBC model, Fig. 1 shows model fits for solutions of A-HA ($C_{0,2} \approx 2\text{--}25 \text{ mg L}^{-1}$ as DOC) and Bromacil ($C_{e,1} \approx 1\text{--}60 \mu\text{g L}^{-1}$), with $K_{F,1} = K_{F,2} = K_{F,B} = 218 \text{ mg}^{(1-n_{F,B})} \text{ L}^{(n_{F,B})} \text{ g}^{-1}$ and $n_{F,1} = n_{F,2} = n_{F,B} = 0.49$. These Freundlich constants, for Bromacil in OFW at pH 7.8, were determined in our previous studies [1] for weakly reactive sites (B) of the Norit SA-UF PAC, e.g. for $C_{e,1} > 10 \mu\text{g L}^{-1}$ in OFW. Note that for the two experimental $C_{e,1} < 10 \mu\text{g L}^{-1}$ (# 5, $m_s = 3 \text{ mg L}^{-1}$ and # 6, $m_s = 1 \text{ mg L}^{-1}$, Table 2), incorporation of Freundlich constants for low-equilibrium concentrations ($K_{F,1} = K_{F,2} = K_{F,A} = 59 \text{ mg}^{(1-n_{F,A})} \text{ L}^{(n_{F,A})} \text{ g}^{-1}$ and $n_{F,1} = n_{F,2} = n_{F,A} = 0.27$) led to less good fits with the simplified IAST/EBC model (Table 5).

In order to verify this observation, some experiments at very low-Bromacil concentrations (# 7 and 8) were carried out in the presence of other NOMs (VRW-HPO and VRW-TPH). The results (Table 5) verified the assumptions of the simplified IAST/EBC model, especially when the used Freundlich constants corresponded to the weakly reactive sites (sites "B") defined in our previous studies [1]. Application of the simplified IAST/EBC model thus provided further evidence that NOM adsorption would block the more reactive sites (sites "A") of the studied PAC, which in turn would become unavailable for Bromacil (i.e. target compound) adsorption.

Based on the data given in Table 5, the competing effect of VRW-HPO and -TPH (65% and 56% reduction of $q_{e,1}$ capacity, respectively) was found to be higher than that of A-HA (30%). As compared to the molecular weight of NOM (Table 1), the smaller molecules of aquatic NOM (VRW-HPO and -TPH) seemed to be more competitive than the higher-MW molecules of A-HA. This confirmed previous evidence [18] that the pore-blocking fraction of NOM is mostly in the 200–700 Da MW range. The slight difference observed between VRW-HPO and VRW-TPH effects (significant for $q_{e,1}$, but not significant for the $C_{e,1}$) could be explained by the greater polarity of VRW-TPH, as shown notably by functional groups (Table 1).

3.4. Kinetic parameters

Six experiments (Table 3) were conducted in the presence of NOM (A-HA: $\sim 2.5 \text{ mg CL}^{-1}$). An example of raw results is presented in Fig. 4.

Like in our previous studies [2], intra-particle diffusion models (Weber and Morris, Vermeulen), the HSDM-surface diffusion model and surface reaction (pseudo-first and pseudo-second order) models were tested. Suitable fits were obtained with the Weber–Morris, Vermeulen and HSDM models, but with a low-regression coefficient ($0.8 < r^2 < 0.9$) and scattered surface-diffusion coefficient values. As for the experiments in OFW [2], the pseudo-second order surface-reaction model fitted particularly well, under the linear expression given by Eq. (8). This model is a simplified form of a more general equation for cases when the adsorption kinetics are governed by the surface-reaction rate [2,19].

$$\left(\frac{1}{q_t} \right) = \left(\frac{1}{k_{\text{app}} q_e^2} \right) \frac{1}{t} + \left(\frac{1}{q_e} \right) \quad (8)$$

This almost perfect applicability (Table 6) of the pseudo-second-order model was mathematically confirmed by Azizian [20], showing that the kinetic so-called Langmuir model, i.e. Eq (9) with $n = 1$, leads to the same integrated expression as Eq. (8).

$$+\frac{d\theta_t}{dt} = k_{\text{ads}}(1 - \theta_t)^n C_t - k_{\text{des}} \theta_t^n \quad \text{with } \theta_t = \frac{q_t}{q_m} \quad (9)$$

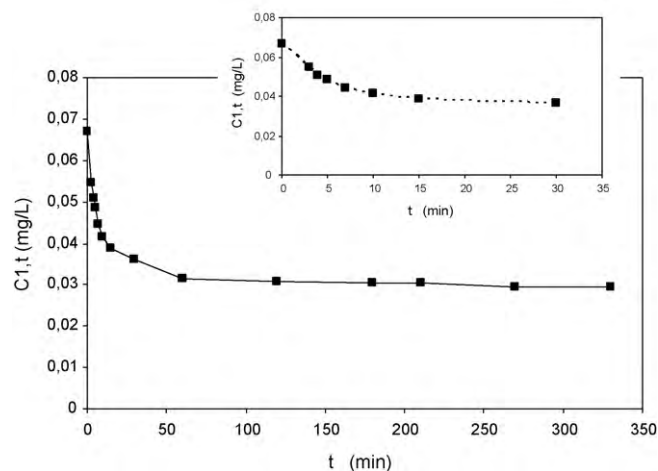


Fig. 4. Example of raw kinetic data for Bromacil adsorption on PAC Norit SA-UF at pH 7.7 in the presence of NOM (experiment # 10).

Table 6
Kinetic constants k_{app} . (pseudo-second order model, Eq. (8)) and k_{ads} . (Langmuir kinetic equation, Eq. (9)) for adsorption of Bromacil on PAC Norit SA-UF at pH 7.8 in the presence of NOM (A-HA \approx 2.5 mg CL⁻¹).

Experiment	$C_{0,1}$ and $C_{e,1}$ ($\mu\text{g L}^{-1}$)	$q_{e,1 \text{ calc.}}$ (mg g^{-1})	$q_{e,1 \text{ exp.}}$ (mg g^{-1})	$k_{app.}^a$ ($\text{g mg}^{-1} \text{min}^{-1}$)	r^2	$k_{ads.}^b$ ($\text{L mg}^{-1} \text{min}^{-1}$)
# 9	64.5–17.9	17.3	15.6 \pm 0.5	10.3 \times 10 ⁻³	0.991	1.33
# 10	66.8–27.5	19.2	19.8 \pm 0.6	9.2 \times 10 ⁻³	0.998	1.82
# 11	66.1–34.1	21.9	21.3 \pm 0.6	6.3 \times 10 ⁻³	0.988	1.43
# 12	33.2–15.5	13.2	12.0 \pm 0.4	9.2 \times 10 ⁻³	0.995	1.84
# 13	36.9–27.6	18.4	18.6 \pm 0.5	3.3 \times 10 ⁻³	0.999	1.08
# 14	5.1–1.5	3.4	3.5 \pm 0.1	13.3 \times 10 ⁻³	0.999	1.02

^a k_{app} . calculated from Eq. (8).

^b k_{ads} . calculated from Azizian approach [2,20] with $K_{L,1}$ = 67.8 L mg⁻¹ and $q_{m,1}$ = 29.5 mg g⁻¹.

From the rate constant of the pseudo-second order model, calculated by Eq. (8) (k_{app} ., Table 6) and the Langmuir-equilibrium constants for Bromacil/NOM adsorption (K_L and q_m ., Table 4), the Azizian approach allowed us to obtain k_{ads} ., corresponding to the surface-reaction rate of Bromacil adsorption (Table 6).

Without NOM (i.e. in OFW solution), we showed by a similar approach [2] that the surface-adsorption reaction rate was much higher for low Bromacil equilibrium concentrations (C_e) than for high- C_e values [2]. Indeed, for C_e over $\sim 10 \mu\text{g L}^{-1}$, the adsorption constants were relatively independent of C_e ($k_{ads.} = (0.31 \pm 0.16) \text{L mg}^{-1} \text{min}^{-1}$), while for $C_e \leq 10 \mu\text{g L}^{-1}$, the adsorption constants were significantly higher ($k_{ads.} = 2.73 \pm 0.95 \text{L mg}^{-1} \text{min}^{-1}$). In the presence of NOM (A-HA $\sim 2.5 \text{mg CL}^{-1}$), the k_{ads} . values for Bromacil adsorption were found to be independent of $C_{e,1}$ (Table 6). So our kinetic data confirmed the above observation: the high-reactivity sites available to the very low-Bromacil concentration ($C_{e,1} < 10 \mu\text{g L}^{-1}$) were probably blocked by NOM. However, for high- $C_{e,1}$ values, we noted a significant increase in k_{ads} . due to the presence of NOM ($k_{ads.} = 1.1\text{--}1.8 \text{L mg}^{-1} \text{min}^{-1}$ as compared to $k_{ads.} = 0.3 \text{L mg}^{-1} \text{min}^{-1}$ in OFW). Further experiments are required to explain this latter phenomenon, especially on possible reactions between Bromacil and NOM.

3.5. Practical approach

Our data show that prediction of Bromacil on PAC SA-UF adsorption with the pseudo-single solute isotherm is possible, regardless of the initial (or equilibrium) Bromacil concentration, when the NOM concentration is about 2.5mg L^{-1} as DOC. Indeed, from Figs. 2 and 3, it can be concluded that experiments carried out with relatively high aqueous equilibrium Bromacil concentrations (around $10 \mu\text{g L}^{-1}$) allow prediction of the PAC capacity for lower aqueous equilibrium concentrations ($0.1\text{--}10 \mu\text{g L}^{-1}$). Moreover, the Bromacil adsorption rate in the presence of NOM ($\sim 2.5 \text{mg L}^{-1}$ as DOC), was found to be independent of the initial target compound concentration. Note that this consistency in the equilibrium and kinetic constants, regardless of the initial Bromacil concentration, was due to the presence of NOM, which probably blocked some PAC sites or pores, especially the most reactive ones.

4. Conclusion

Adsorption on powdered activated carbon (PAC), combined with liquid–solid separation in specific reactor configurations, is commonly used for the removal of both organic micropollutants and natural organic matter, especially in drinking water treatment. We previously showed (by application of several mono-solute equilibrium models) that Bromacil (pesticide) adsorption in buffered pure water (pH 7.8) probably occurred at two types of site (part 1 of our studies). A kinetic study clearly confirmed this hypothesis (part 2).

Since competition between target trace compounds and natural organic matter is common in activated carbon processes, the

present study (part 3) was carried out to investigate the effect of natural organic matter (NOM) concentrations on Bromacil adsorption (equilibrium and kinetics) in the same experimental conditions as in our previous studies. Many isotherm and kinetic experiments were thus carried out under conditions similar to those found in pure water, but in the presence of various kinds of natural organic matter and concentrations.

Regardless of the different initial Bromacil concentrations ($\approx 5\text{--}80 \mu\text{g L}^{-1}$) and initial NOM concentrations ($\approx 2\text{--}25 \text{mg CL}^{-1}$), we noted a significant reduction in Bromacil adsorption capacities due to competitive effects exerted by NOM. Moreover, highly reactive sites (or pores) in PAC appeared to be “blocked” by NOM adsorption, as demonstrated by application of the simplified IAST/EBC model. The competing effect of low-molecular weight NOM was found to be higher than that of high molecular weight NOM.

The pseudo-second order surface-reaction model fitted particularly well for Bromacil adsorption, even in the presence of NOM. However, the adsorption–kinetic constant values were found to be independent of the Bromacil equilibrium concentration, contrary to that observed in pure water. The kinetic data thus confirmed high-reactivity sites on the studied PAC were blocked by NOM.

Concerning the practical approach, our data showed that prediction of Bromacil on PAC SA-UF adsorption with the pseudo-single solute isotherm was possible when NOM is present, regardless of the initial (or equilibrium) Bromacil concentration.

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References

- [1] F. Al Mardini, B. Legube, Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 1: Equilibrium parameters, *J. Hazard. Mater.* 170 (2009) 744–753.
- [2] F. Al Mardini, B. Legube, Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 2: Kinetic parameters, *J. Hazard. Mater.* 170 (2009) 754–762.
- [3] Q. Li, B.J. Marinas, V.L. Snoeyink, C. Campos, Three-component competitive adsorption model for flow-through PAC systems, 1. Model development and verification with a PAC/membrane system. 2. Model application to a PAC/membrane system, *Environ. Sci. Technol.* 37 (2003) 2997–3011.
- [4] L. Ding, B.J. Marinas, L. Schideman, V.L. Snoeyink, Q. Li, Competitive effects of natural organic matter: parametrization and verification of the three-component adsorption model COMPSORB, *Environ. Sci. Technol.* 40 (2006) 350–356.
- [5] L. Ding, V.L. Snoeyink, B.J. Marinas, Z. Hue, J. Economy, Effects of powdered activated carbon pore size distributions on the competitive adsorption of aqueous atrazine and natural organic matter, *Environ. Sci. Technol.* 42 (2008) 1227–1231.
- [6] S. Qi, L.C. Schideman, An overall isotherm for activated carbon adsorption of dissolved natural organic matter in water, *Water Res.* 42 (2008) 3353–3360.
- [7] B.R. Frick, H. Sontheimer, Adsorption equilibria in multisolute mixtures of known and unknown composition, *Adv. Chem. Ser.* (1983) 247–268.

- [8] J.C. Crittenden, P. Luft, D.W. Hand, J.L. Oravitz, S. Lopers, M. Ari, Prediction of multicomponent adsorption equilibria using ideal adsorbed solution theory, *Environ. Sci. Technol.* 19 (1985) 1037–1043.
- [9] D.W. Hand, J.C. Crittenden, M. Asce, W.E. Thacker, User-oriented batch reactors solutions to the homogeneous surface diffusion model, *J. Environ. Eng.* 109 (1983) 82–101.
- [10] F. Monteil-Rivera, E.B. Brouwer, S. Masset, Y. Deslandes, J. Dumonceau, Combination of X-ray photoelectron and solid-state ^{13}C nuclear magnetic resonance spectroscopy in the structural characterisation of humic acids, *Anal. Chim. Acta* 424 (2000) 243–255.
- [11] G. Aiken, J.A. Leenheer, Isolation and chemical characterization of dissolved and colloidal organic carbon, *Chem. Ecol.* 8 (1983) 135–151.
- [12] J.A. Leenheer, J.P. Croué, Characterizing aquatic dissolved organic matter, *Environ. Sci. Technol.* 37 (2003) 18A–25A.
- [13] Y. Chin, G.R. Aiken, E. O'Loughlin, Molecular weight, polydispersity, and spectroscopy properties of aquatic humic substances, *Environ. Sci. Technol.* 28 (1994) 1853–1858.
- [14] A. Bruchet, C. Rousseau, J. Malleval, Pyrolysis–GC–MS for investigating high-molecular-weight THM precursors and other refractory organics, *J. Am. Water Works Assoc.* 82 (1990) 66–74.
- [15] F.S. Li, A. Yuasa, H. Chiharada, Y. Matsui, Polydisperse adsorbability composition of several natural and synthetic organic matrices, *J. Colloid Interface Sci.* 265 (2003) 265–275.
- [16] W.J. Weber, T.C. Voice, A. Jodellah, Adsorption of humic substances: the effects of heterogeneity and systems characteristic, *J. Am. Water Works Assoc.* 75 (1983) 612–619.
- [17] E.H. Smith, Bench-scale tests and modelling of adsorption of natural organic matter by activated carbon, *Water Res.* 28 (1994) 1693–1702.
- [18] Q. Li, V.L. Snoeyink, B.J. Marinas, C. Campos, Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds, *Water Res.* 37 (2003) 773–784.
- [19] W. Rudzinski, W. Plazinski, Kinetics of solute adsorption at solid/solution interfaces: a theoretical development of the empirical pseudo-first and pseudo-second order kinetic rate equations, based on applying the statistical rate theory of interfacial transport, *J. Phys. Chem. B* 110 (2006) 16514–16525.
- [20] S. Azizian, Kinetic models of sorption: a theoretical analysis, *J. Colloid Interface Sci.* 267 (2004) 47–52.