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Multicomponent Adsorption of Pesticides onto Activated Carbon Fibers

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Abstract. The adsorption equilibria of pesticides and metabolites (atrazine, deethylatrazine, deisopropylatrazine and simazine) are studied onto activated carbon fibers –ACF– with a broad pore size distribution (32% mesopore volume, 68% micropore volume). Mono-and multi-component isotherms have been determined for low concentrations, from 0.23×10^{-6} to 9.52×10^{-6} mol L^{-1}. Single solute isotherms, modeled by Freundlich and Langmuir models, tend to prove the influence of the adsorbate's solubility in the adsorption capacity of activated carbon fibers. Binary solute isotherms confirm the strong influence of pesticide solubility on the competitive adsorption mechanism: the competition is higher in the case of adsorbates of different solubilities (atrazine and DEA or DIA for example). Multicomponent experimental data were modeled by extended Langmuir-based equations and the Ideal Adsorbed Solution theory. Whereas the first ones failed to model accurately binary adsorption due to restrictive hypothesis, the IAS model showed a good agreement between experimental and predicted data. It emphasised also the difficulty in satisfying the hypothesis of the model in the case of highly adsorbed compounds. Finally, the simultaneous adsorption of atrazine and NOM (in a natural water, DOC = 18.2 mg L^{-1}) shows no adsorption competition effects between natural organic matter and atrazine. This is due to the presence of secondary micropores (0.8–2 nm) and mesopores in the ACF, which limit a pore blockage phenomenon by NOM.

Keywords: liquid multicomponent adsorption, activated carbon fibers, pesticides, natural organic matter, extended Langmuir equation, IAS modeling

1. Introduction

The increase of use of phytosanitary products, due to intensive agriculture, non-respect of good agricultural practices and the existence of especially vulnerable sites has involved a pollution by pesticides of surface and groundwaters used for drinking water. This contamination of water resources is above the european regulations on drinking water quality, which set a maximum concentration of 0.1 μg L^{-1} for individual pesticides and some of their degradation products and 0.5 μg L^{-1} for total pesticides present in the sample (directive 80/778/CEE, decree 2001–1220). Some analysis projects have shown that surface and groundwater supplies are frequently polluted by atrazine, a triazine herbicide. Higher pollution levels are reached for water surfaces, but pollution in groundwaters is more permanent (Carabias-Martinez et al., 2003). Indeed, in anaerobic conditions, the atrazine degradation by microorganisms is very slow (Shapir et al., 1998) compared with aerobic conditions where 20% are removed in 3 weeks. A survey carried out in the State of Kansas has shown that, for an annual average concentration of atrazine lower than 3 μg L^{-1}, this concentration could reach 33.5 μg L^{-1} in the spring and the summer (Christensen and Ziegler, 1998). In France, a study was carried out in 2002 on the quality of groundwater designed for producing potable water. 38% of the sampled and quantified points were concerned by pesticides pollution and 8 French departments exceeded

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the regulatory limits: $>2\,\mu g\,L^{-1}$ per substance and $>5\,\mu g\,L^{-1}$ for all substances, meaning that water requires special permission from the French Ministery of Health before distribution (IFEN, 2004).

Pesticides have drawn particular public attention due to their potential effects on human health as well as terrestrial and aquatic ecosystems. Maximum contaminant levels (MCL) established by the U.S. Environmental Protection Agency is fixed at $3\,\mu g\,L^{-1}$ for atrazine. However, atrazine metabolites such as deethylatrazine (DEA) and deisopropylatrazine (DIA) are currently not considered in the risk analysis. These two metabolites, structurally similar to atrazine, are phytotoxic-like and 5 times less than atrazine (Winkelmann and Klaine, 1991). Liu et al. (1996) have demonstrated, from a large monitoring project, that the presence of atrazine is coupled with that of metabolites, the mean concentration of atrazine residue (atrazine + DEA + DIA) being 53% higher than that of atrazine alone.

In this context, the removal of pesticides and metabolites from aqueous solutions is of great interest in the environmental field. According to the literature survey, various treatment processes have been widely investigated to remove pesticides from waters, the most conventional being oxidation and adsorption. Concerning the oxidation process, chlorinated compounds (like chlorine or chlorine dioxide) have shown to be little reactive (Baldauf, 1993) compared with ozonation, with or without hydrogen peroxide. Furthermore, triazines are only partly oxidized under ozonation, involving the formation of by-products (Reynolds et al., 1989).

Adsorption onto activated carbon does not present the disadvantage of by-products formation. It is currently used in drinking water treatment in the form of powder (PAC), generally applied when needed as a crisis reagent, or in the form of granules (GAC) in large scale filters. From 30 years, a different activated carbon has been developed, in the form of fibers (ACF). Its adsorption properties have been demonstrated for various pollutants present in water: high adsorption capacities were found to adsorb microorganics like phenols (Economy and Lin, 1976; Petkovska and Mitrovic, 1989), aromatic compounds (Brasquet and Le Cloirec, 1999), methylene blue (Pimenov et al., 1995), compounds responsible for taste (Tajima and Tanaka, 1996), or trichloroethylene (Suzuki, 1991); in all cases, adsorption capacities obtained in a static or in a dynamic reactor are higher than those obtained with a GAC, up to $500\,mg\,g^{-1}$. Furthermore, the low diameter of fibers ($10\,\mu m$) enable high external surface area and thus initial adsorption rates 5 to 20 times higher than those obtained with a GAC (Brasquet et al., 2000). For the adsorption of macromolecules like humic substances (Starek et al., 1994) or dyes (Métivier-Pignon et al., 2003), ACF are efficient if their pore size distribution is large enough compared with that of solutes. In the case of pesticides, micro-column tests have showed that the performance of highly activated ACF ($1{,}700\,m^2\,g^{-1}$) was around 7 times better than a commercial GAC of specific surface $1.100\,m^2\,g^{-1}$, due to a wide-opened microstructure of ACF coupled with an appreciable contribution of the low size mesopores (Martin-Gullon and Font, 2001). Hopman et al. (1995) obtain also an adsorption capacity of ACF for diuron 10 to 20 times higher than the adsorption capacity of a GAC.

However, with the goal to use ACF for industrial processes, the multicomponent adsorption of pesticides needs to be studied. This work aims to assess the ability of ACF to remove from water a pesticide and its metabolites. With this goal, the monocomponent and multicomponent adsorption of atrazine, DEA and DIA is carried out in a static reactor to study the competitive adsorption of these pesticides of similar size. Furthermore, with an objective of use of this adsorbent in an industrial settling, the simultaneous adsorption of pesticides with natural organic matter (NOM) has to be studied. In the case of atrazine adsorption onto powdered activated carbon, Gicquel et al. (1997) obtain adsorption capacities 20 to 70% lower in a natural water compared with those obtained in pure water, the competition effect increasing with NOM concentration. The same authors show that adsorption decrease of atrazine because of the presence of NOM is more marked for low initial concentrations of atrazine ($<50\,\mu g\,L^{-1}$) than for higher initial concentrations (50–$500\,\mu g\,L^{-1}$). As demonstrated by Pelekani and Snoeyink (1999), when pores are large enough to admit the micropollutant but too small to admit NOM, pore blockage may be the dominant competition mechanism. When the pores are large enough to admit both micropollutant and NOM, direct sites competition becomes the important competition mechanism. However, as demonstrated by Li et al. (2003) with different model compounds, a broadening of the adsorbent pore size distribution (PSD) can reduce and even avoid pore blockage by NOM. The study of atrazine removal by pre-loaded NOM AC leads to the same conclusions than surveys carried out for simultaneous adsorption: in order to adsorb atrazine in the presence of NOM, AC must have a wide-opened structure (Martin-Gullon and Font, 2001). For these reasons, the ACF used in this work presents a high specific surface area coupled with a large pore size distribution (32% of mesopore volume).

2. Materials and Methods

2.1. Adsorbents

In this study, ACF used was supplied by Actitex Companies (Levallois, France). Fibers are woven in the form of cloth, and originate from the rayon activated by steam at 800°C. Main characteristics of ACF are shown in Table 1: micro (<2 nm) and mesopore (2–50 nm) characteristics were determined by N_2 adsorption at 77 K using a Micromeritics Asap 2010 analyzer. The theories of Brunauer et al. (1938), Horvath and Kawazoe (1983) and Barrett et al. (1951) were used to calculate specific surface, micropore volume and mesopore size distribution respectively. As presented in Table 1, the ACF possesses a high specific surface area (close to 1,500 $m^2\ g^{-1}$) coupled with a broad PSD (32% of mesopore volume). Figure 1 presents more precisely PSD of this fibrous adsobent: PSD in the domain of micropores (Fig. 1(a)) shows that our ACF develops primary micropores of diameter less than 0.8 nm (as defined by Pelekany and Snoeyink (1999)) and secondary micropores with diameters ranging between 0.8 and 2 nm. Furthermore, some mesopores are present (Fig. 1(b)) partly at the surface of fibers as presented in the Scanning Electron Micrograph (Jeol JSM-6400F) of Fig. 2. The point of zero charge (PZC), i.e. the pH above which the total surface of the carbon is negatively charged, was measured by the so-called pH drift method (Newcombe et al., 1993).

Before use, the activated carbon was washed with de-ionised water and dried at 105°C. More details on structure and properties of ACF have been published previously (Brasquet et al., 2000).

Table 1. Main characteristics of activated carbon fibers.

	Mesoporous ACF
Commercial name	RS 1301
Raw material	Rayon
Weave	3 twill
Activation (temperature °C/gaz)	900/H_2O
Specific surface area ($m^2 \cdot g^{-1}$)	1,461
Porous volume ($cm^3 \cdot g^{-1}$)	0.743
% microporosity volume	68
Median micropore diameter (Å)	7.3
Point of zero charge	9.5

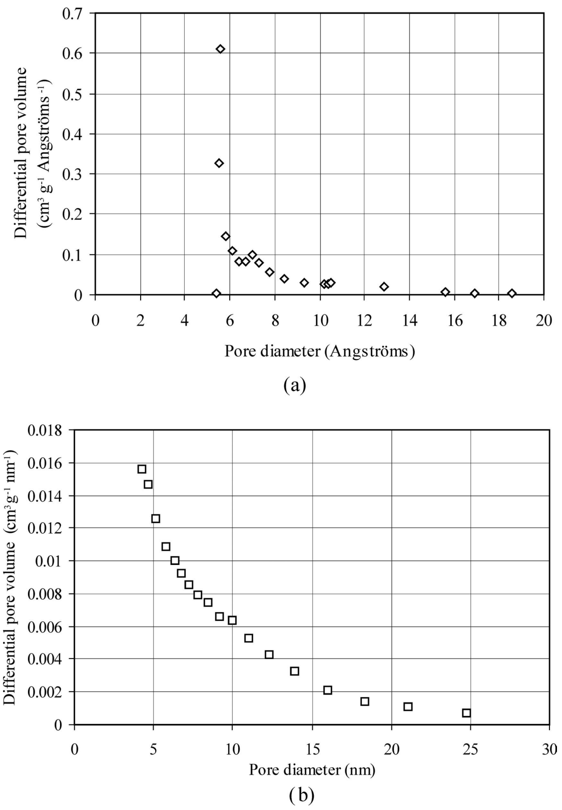
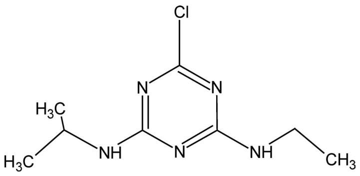
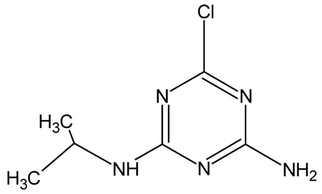
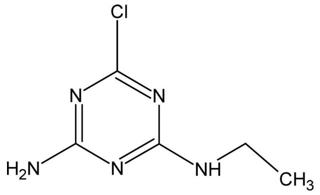
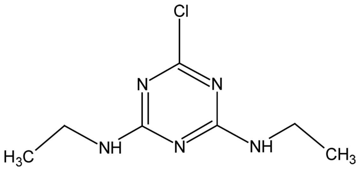


Figure 1. Pore size distribution of ACF in the domaine of (a) micropores and (b) mesopores.

2.2. Adsorbates

2.2.1. Pesticides. Atrazine and two metabolites, namely deethylatrazine (DEA) and deisopropylatrazine (DIA), and simazine were selected because they are frequently encountered in a case of a pollution by phytosanitary products (Bottoni et al., 1996). All chemicals were purchased from Riedel-de-Häen, their main properties are given in Table 2. Stock solutions were prepared with deionized water. All pesticides were analysed using a WATERS 600 High Performance Liquid Chromatograph, provided with a UV WATERS 486 detector and a NOVAPACK C_{18} non-polar column (150 mm length, 3.9 mm diameter), at a wavelength of 220 nm. Eluant is constituted by a ratio 75/25 of water/acetonitrile. Multisolute analyses were performed using an isocratic mode. In the case of low concentrations (less than 0.08 mM), a Solid Phase Extraction (SPE) preceded the HPLC analysis, carried out with a

Table 2. Main characteristics of pesticides.

Compound	Formula	Molecular weight ($g\,mol^{-1}$)	pKa	Solubility ($mg\,L^{-1}$)
Atrazine		215.7	1.68	34.7
DEA		187.6	1.00	3200
DIA		173.6	1.00	670
Simazine		201.7	1.65	5.0

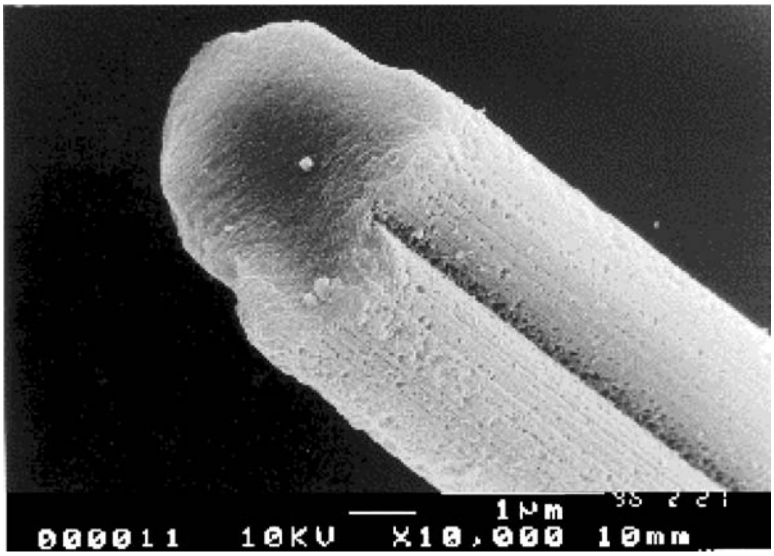


Figure 2. SEM observation of ACF (10,000 magnification).

Table 3. Characterization of NOM from Erdre River, Nantes, France.

pH	Suspended solids (mg L^{-1})	Turbidity (NTU)	DOC (mg L^{-1})	KMnO$_4$ oxidability (mg O$_2$ L^{-1})	Abs$_{254\text{ nm}}$
7.5	29.4	28	18.2	13.4	1.166

DOC: dissolved organic carbon.

CARBOSEP cartridge to reach a concentration factor up to 500.

2.2.2. Natural Organic Matter (NOM). To study the influence of NOM on pesticides adsorption onto activated carbon, a raw river water (Erdre River, Nantes, France) was collected and characterized. All characterization parameters of NOM are given in Table 3, where suspended solids concentration has been determined according to French normalization AFNOR T-90-105. Dissolved organic carbon was measured with a TOC-meter SHIMADZU TOC-5000A, after filtration at 0.45 μm. The absorbance at 254 nm was determined using a spectrophotometer SHIMADZU UV-1601. The turbidity was determined following international standard ISO-7027, using an AL 1000 turbidimeter (Aqualytic).

2.3. *Adsorption*

2.3.1. Monocomponent and Multicomponent Equilibrium Experiments of Pesticides. Equilibrium experiments were performed using the classical bottle-point method. A given weight (10 mg) of ACF is stirred at 20 ± 1°C and 300 rpm in 5 L of a monocomponent solution of pesticide. Initial concentrations range between 0.23×10^{-6} and 9.5×10^{-6} mol L^{-1}. The time needed to reach equilibrium is fixed at 48 h according to Brasquet et al. (1996) and Baup et al. (2000). To study the influence of competitive adsorption, adsorption isotherms of binary mixing (atrazine + DEA, DIA or simazine) were also performed in the same operating conditions, using equimolar initial concentrations.

2.3.2. Competition of Pesticides with NOM for Adsorption onto ACF. Activated carbon performance being highly dependent on the presence of NOM in water, the simutaneous adsorption of atrazine and NOM by ACF was studied in a natural water. Atrazine isotherm was carried out in a river water (Erdre River, France) in the same operating conditions than in a synthetic water (see Section 2.3.1).

3. Results and Discussion

3.1. *Monocomponent Adsorption of Pesticides*

Adsorption isotherms of the four pesticides onto ACF are given in Fig. 2. The different experimental isotherms were modelled according to two equations: the Freundlich and Langmuir models.

The Freundlich empirical model is represented by:

$$q_e = K_f \cdot C_e^{1/n} \tag{1}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e the amount adsorbed at equilibrium (mg g^{-1}) and K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) and $1/n$ are Freundlich constants depending on temperature and on the given (adsorbent-adsorbate) couple. Different authors consider Freundlich parameters constant for well defined and limited ranges of concentrations (Crittenden et al., 1985). For this reason, this empirical model may be used to represent pure-component isotherm data on a piecewise basis with a high degree of accuracy (Tien, 1994).

Langmuir's model, which is the simplest description of the adsorption process, is based on a physical hypothesis:

$$q_e = \frac{bq_m C_e}{1 + bC_e} \tag{2}$$

where b is the equilibrium adsorption coefficient (L mg^{-1}) and q_m the maximum adsorption capacity (mg g^{-1}).

All parameters calculated using both models are given in Table 4, where r^2 is the determination coefficient of the linearized equation. These values and the Fig. 3 show the dependence of adsorption properties on adsorbates solubility, the following order being obtained for adsorption capacities: DEA $<$ DIA $<$ atrazine $<$ simazine. Whereas the adsorption capacities of the compounds of low solubility (atrazine, 34.7 mg L^{-1} and simazine 5 mg L^{-1}) reach a plateau at high equilibrium concentrations, those of the most soluble compounds (DIA, 670 mg L^{-1}, and DEA, 3,200 mg L^{-1}) tend to increase over the whole range of concentrations. In other words, and as demonstrated by the values of the b parameters, the stronger

Table 4. Freundlich and Langmuir parameters of pesticides monocomponent adsorption onto the ACF.

		Freundlich			Langmuir		
Compund	Concentration range (μg L^{-1})	K (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	$1/n$	r^2	q_m (mg g^{-1})	b (L mg^{-1})	r^2
Atrazine	0 to 330	400.5	0.372	0.95	238.1	46.7	0.99
	330 to 980	253.8	0.049	0.91			
Simazine	0 to 940	387.8	0.131	0.89	370.4	45.0	0.91
DIA	0 to 1500	131.1	0.409	0.98	119.0	12.0	0.99
DEA	0 to 1200	123.1	0.500	0.97	303.0	0.7	0.96

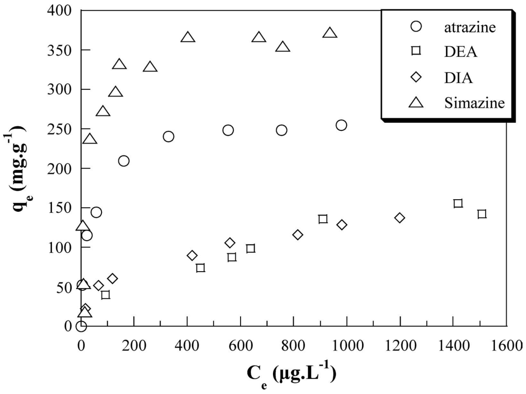


Figure 3. Adsorption isotherms ($T = 20 \pm 1$°C) of pesticides onto the ACF.

Table 5. Comparison of adsorption capacities q_e in monocomponent and binary systems.

Binary system 1/2	$q_{e\,\mathrm{bin}}(1)/q_{e\,\mathrm{mono}}(1)$	$q_{e\,\mathrm{bin}}(2)/q_{e\,\mathrm{mono}}(2)$	$q_{e\,\mathrm{bin}}(1)/q_{e\,\mathrm{bin}}(2)$
A/DEA	~1	~0.5	1.2–3.8
A/DIA	~1	1–0.4	1.2–4.9
A/S	0.2–0.8	0.4–0.6	0.8

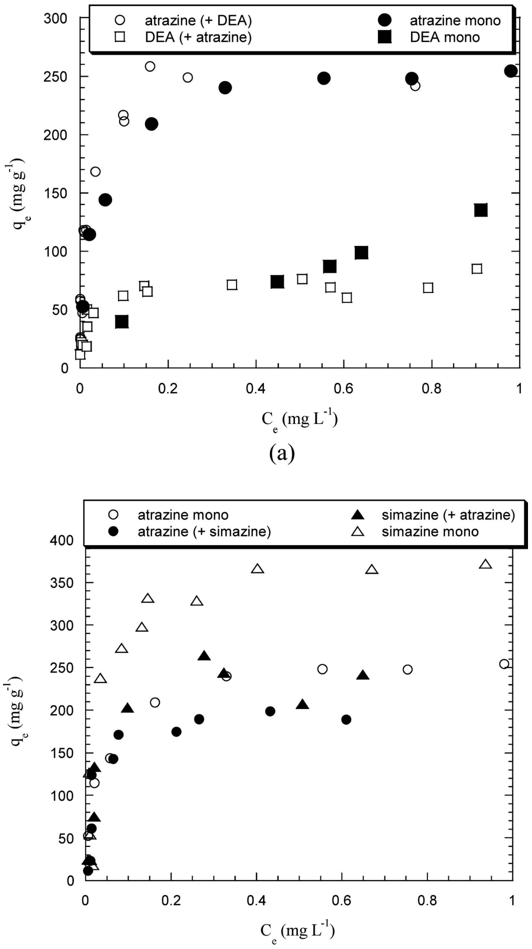
A: atrazine, DEA: deethylatrazine, DIA: deisopropylatrazine, S: simazine.

the affinity for the solvent, the lower the affinity for the adsorbent. Matsui et al. (1996) have also observed that adsorptive capacities of 6 pesticides were inversely related to their water solubility.

3.2. Competitive Adsorption of Pesticides

Binary adsorption of pesticides was studied in the same conditions than monocomponent adsorption. Three binary systems were studied: atrazine—DEA, atrazine—DIA and atrazine–simazine. Adsorption isotherms are given for the systems (atrazine—DEA) and (atrazine–simazine) in Fig. 4, compared with monocomponent results. The behavior observed for the couple (atrazine—DIA) was similar to that of (atrazine—DEA). The comparison of equilibrium adsorption capacities for both adsorbates in solution ($q_e(1)/q_e(2)$) and the comparison of equilibium adsorption capacities in mono and in binary solutions for a given adsorbate ($q_{e\,\mathrm{bin}}(i)/q_{e\,\mathrm{mono}}(i)$) is presented in Table 5.

The bahavior of binary systems may be related with the adsorbates monocomponent adsorption and thus solubility, as observed in the monocomponent study. In the case of a binary system where there is a strong differences of solubility between both compounds (atrazine—DEA or atrazine—DIA), the adsorbate of low solubility (atrazine) is favoured for the adsorption and the presence of the co-adsorbate has no influence (Fig. 4(a)): equilibrium adsorption capacities of atrazine are similar in mono and in multicomponent solutions in both cases. In return, a decrease of adsorption of the highly soluble compound (DEA or DIA) is observed compared with monocomponent adsorption ($q_{e\,\mathrm{bin}}/q_{e\,\mathrm{mono}} < 1$), this effect being more marked for high concentrations. Ayranci and Hoda (2004) obtain, for competitive adsorption of metribuzin and bromacil on a high surface area activated carbon cloth, ratio of mono and multicomponent adsorption capacities equal to 1.33 and 1.08 respectively. The adsorbate for which adsorption competition has less influence (bromacil) is that presenting the higher removal in single component solution. Gao et al. (1998) show also no influence of the presence of atrazine on bifenox removal whereas the presence of bifenox involves a decrease of atrazine adsorption, this last one being 2 times less adsorbed in a monocomponent solution.



(a)

(b)

Figure 4. Binary isotherms on the ACF of (a) atrazine—DEA; (b) atrazine–simazine.

As initial concentration decreases, solubility is no longer such a decisive factor so the multicomponent adsorption capacities become similar to the monocomponent ones and adsorption of the high solubility compound tends to that of atrazine: for initial concentrations ranging between 1.10 and 5.50 μmol L^{-1}, the ratio of adsorption capacities between atrazine and DEA or DIA ($q_{e\,\mathrm{atraz}}/q_{e\,\mathrm{DEA\,or\,DIA}}$) vary from 1.7 to 4.9, whereas it is close to 1.2 for concentrations lower than 1.10 μmol L^{-1}. This influence of solubility on multicomponent adsorption, in correlation with initial concentration, was observed by Monneyron et al. (2002) for organic micropollutants.

In the case of a binary system where adsorbates present slight difference of solubility (atrazine–simazine, Fig. 4(b)), the competition effects are not so obvious: the ratio of adsorption capacities of atrazine and simazine ($q_{e\,\mathrm{atraz}}/q_{e\,\mathrm{simaz}}$) is close to 0.8 for the whole concentrations range. In return, for both adsorbates a strong decrease of adsorption capacities may be observed compared with monocomponent solutions: it ranges between 20 and 80% for atrazine and 40–60% for simazine.

Among the various multicomponent equilibrium theories, the extended Langmuir equation was used by several authors because its simplicity offers a significant advantage in adsorption calculations (Darwish et al., 1998):

$$q_{e,i} = \frac{b_i q_{m,i} C_{e,i}}{1 + \sum_{j=1}^{N} b_j C_{e,j}} \tag{3}$$

where b_i (L mg^{-1}) and $q_{m,i}$ (mg g^{-1}) are Langmuir parameters obtained in monocomponent solution for the ith adsorbate, $C_{e,i}$ (mg L^{-1}) is the equilibrium concentration of the multicomponent adsorption of the ith compound, $q_{e,i}$ is the equilibrium adsorption capacity of the multicomponent adsorption of the ith compound (mg g^{-1}), and N the number of components. The extended Langmuir model is well adapted to competing adsorbates, which are adsorbed in a similar way in monocomponent solutions. When this is not the case, Jain and Snoeyink (1973) have proposed for binary systems another Langmuir-based equation, which assumes that a part of binary adsorption happens without competition for the more adsorbable compound (compound 1):

$$\begin{aligned} q_{e,1} &= \frac{(q_{m,1} - q_{m,2}) b_1 C_{e,1}}{1 + b_1 C_{e,1}} + \frac{q_{m,2} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \\ q_{e,2} &= \frac{q_{m,2} b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \end{aligned} \tag{4}$$

Figure 5 presents modelling results obtained with both Langmuir-based equations. For all bisolute systems, adsorption capacities predicted by the extended-Langmuir equation are underestimated. The restrictive hypothesis of this model (monolayer adsorption and homogeneity of adsorption sites) must be responsible for this poor agreement (Tien, 1984). For the system (atrazine/simazine), where both co-adsorbates present similar affinities for ACF, a multilayer adsorption phenomenon must happen which involves a lower competition. For both other systems, different affinities of DEA and DIA for ACF must traduce the non-homogeneity of adsorption energies.

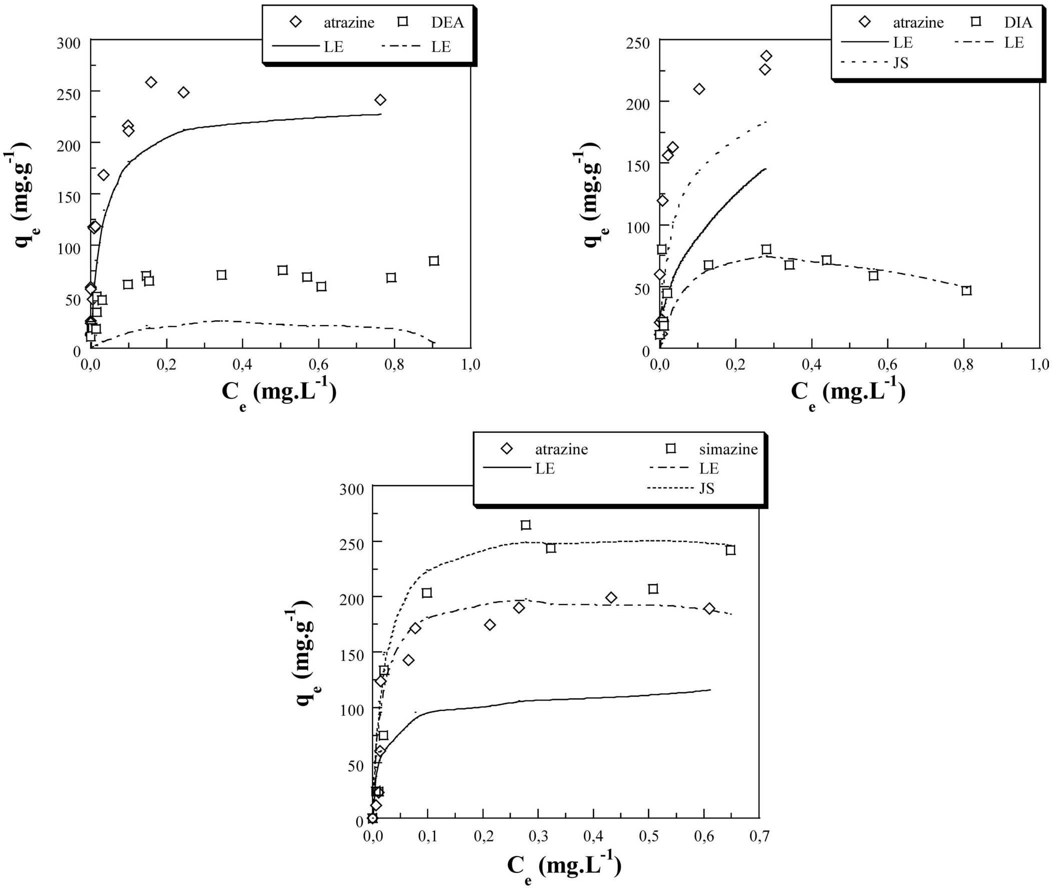


Figure 5. Modelling results of binary adsorption of pesticides with extended Langmuir model (LE) and Jain and Snoeyink equation (JE).

Compared with the extended Langmuir model, the Jain and Snoeyink equation can improve modelling only for the most adsorbable compound of binary systems as shown by the comparison of Eqs. (3) and (4). Whereas simazine adsorption is well predicted in the couple (atrazine–simazine), atrazine adsorption in system (atrazine—DIA) is better modelled than using the extended Langmuir equation but is always underestimated.

Because of low performances of based-Langmuir models to predict binary adsorption, a thermodynamic model, the Ideal Adsorbed Solution (IAS) theory, was applied to our experimental data. IAS is the most widely tested and used model (Tien, 1994), especially to model binary adsorption of organics onto activated carbon (Crittenden et al., 1985; Monneyron et al., 2002). IAS theory was first established for a mixed gas adsorption by Myers and Prausnitz (1965), and then extended to a multi-solute adsorption from dilute liquid solution by Radke and Prausnitz (1972). The model is based on the fundamental hypothesis that the multicomponent solution has the same spreading pressure π as that of the ideal single solution of the ith component, the spreading pressure being the difference between the interfacial tension of the pure solvent and that of the solution containing the solute. This hypothesis is described by the Gibbs equation:

$$\frac{\pi A}{RT} = \int_0^{C_i^0} \frac{q_i^0}{C_i^0} dC_i^0 \tag{5}$$

where A is the adsorbed surface area per unit mass of adsorbent (m^2 g^{-1}), π the spreading pressure, T the temperature (K), C_i^0 the equilibrium concentration of the pure component adsorption of the ith compound (mol L^{-1}), and q_i^0 the equilibrium adsorption capacity of the pure component adsorption of the ith compound (mol g^{-1}).

The following equations complete the system description:

$$q_{e,i} = q_t \cdot x_i \tag{6}$$

$$C_{e,i} = C_i^0(\pi, T) \cdot x_i \tag{7}$$

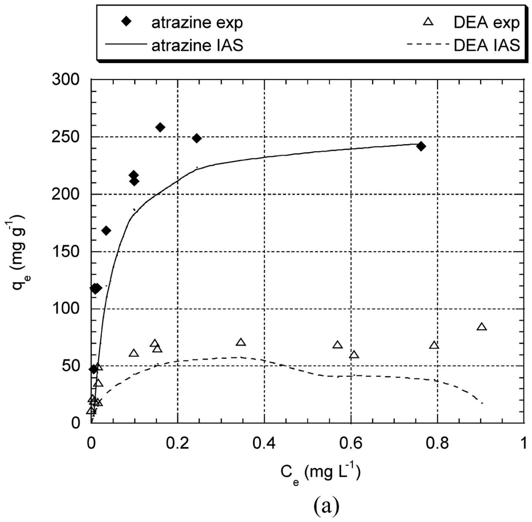
$$q_t = \left[\sum_{j=1}^{N} \frac{x_j}{q_j^0}\right]^{-1} \tag{8}$$

where $q_{e,i}$ and $C_{e,i}$ are expressed on a molar basis, q_t is the total adsorption capacity of the multicomponent system (mol g^{-1}) and x_i the mole fraction of the ith adsorbate in the adsorbed phase. The evaluation of the IAS model requires a precise determination of Eq. (6) subject to the constraint:

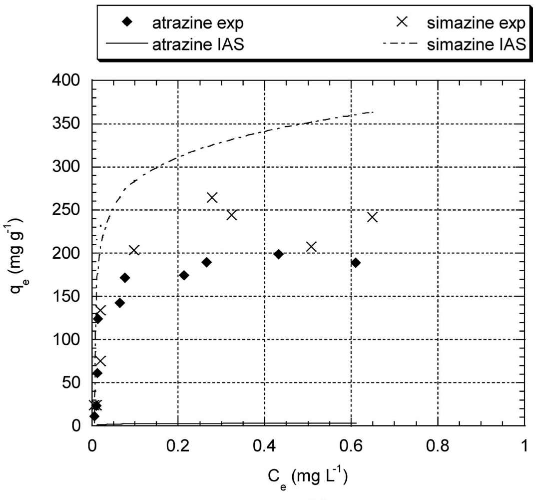
$$\sum_{i=1}^{N} x_i = 1 \tag{9}$$

which enables the calculation to be carried out using an iterative estimation of the spreading pressure. The determination of adsorption capacities in multicomponent solutions requires an appropriate description of the single solute isotherm. Freundlich's model was selected here, because it enables the division of isotherms into linear concentration ranges introduced by Tien (1994).

Calculations were performed using a program developed on Microsoft® Excel 97. The results obtained for two binary systems are presented in Fig. 6. From a global point of view, experimental adsorption of binary mixtures of atrazine and DEA (Fig. 6(a)) or DIA onto the ACC is well described by the IAS model. In return, in the case of the couple atrazine–simazine, adsorption capacities of atrazine are underestimated by the IAS model (q_e predicted ~3 mg g^{-1} for all values of C_e) whereas those of simazine are overestimated (Fig. 6(b)). In this case, the disagreement between experimental and predicted adsorption capacities may originate from a non-respect of model's hypothesis. Seidel and Gelbin (1988) notice that low solubility compounds may involve the non-ideality of the solution. Thus, the presence of two solutes of low solubility (simazine and atrazine) may induce a shift from the solution's ideality more important than with other pesticides. Furthermore, whereas the IAS theory is well adapted to compounds weakly adsorbed, Belfort (1981) has shown that the model is not suitable for highly adsorbed compounds. Indeed, the IAS model needs that monocomponent adsorption satisfies to the Henry law at low surface covering, which limits the use of the model to low concentrations (Jossens et al., 1978). Finally, Baudu et al. (2004) have demonstrated that if a pore blockage phenomenon happens during atrazine-simazine adsorption, the IAS model can't consider it and doesn't allow a satisfying modelling of data.



(a)



(b)

Figure 6. IAS modelling of binary adsorption of pesticides onto the ACF. (a) atrazine–deethylatrazine; (b) atrazine-simazine.

3.3. *Adsorption Competition Between Pesticides and Natural Organic Matter*

The adsorption competition between pesticides and NOM has been studied by various researchers. As demonstrated by Bernazeau et al. (1996) or Li et al.

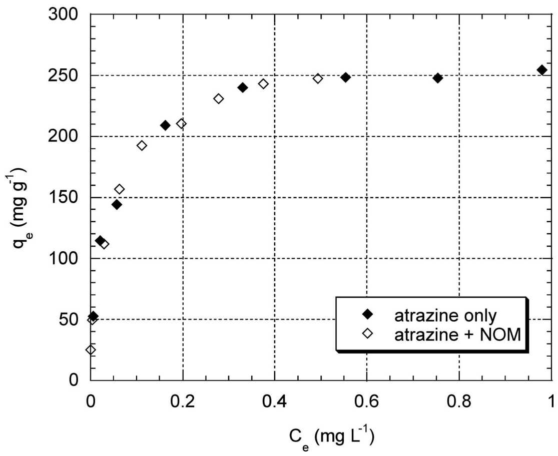


Figure 7. Comparison of atrazine adsorption isotherm in a synthetic water and in a river water containing NOM.

(2003), the NOM content, from a qualitative and quantitative point of view, can vary widely from one water to another. Combined to the dependence of adsorption competition on the sorbent pore size disbribution extensively studied by Pelekani and Snoeyink (1999, 2000, 2001), this result may explain variations observed in competition effects in these studies.

In this work, as presented in Fig. 7, the atrazine removal by ACF was not influenced by the presence of NOM. Furthermore, the NOM adsorption was quantified by DOC measurements, the adsorption capacities ranging between 45 and 58 mg DOC g^{-1}. These results enable to conclude that NOM is weakly adsorbed by the ACF and this adsorption does not disturb the atrazine removal. These results may originate from the ACF porous properties. Indeed, our adsorbent presents a quite broad PSD with 32% mesoporosity as presented in Fig. 1 and Table 1. Furthermore, micropores are divided into primary micropores (<0.8 nm) and secondary micropores (0.8–2 nm). Pelekanli and Snoeyink (2000, 2001) have studied simultaneous adsorption on various ACF of pesticides with similar molecular weight (MW) compounds as methylene blue and higher MW compounds as congo red. They have shown the strong influence of secondary micropores to decrease competition effects with both kinds of molecules: with highly microporous ACF, the inhability of high MW to acess the small micropores results in a pore blockage. Including secondary micropores leads to the elimination of any effect of congo red and to a large decrease of methylene blue effect on adsorption capacities of atrazine. In another study, Pelekani and Snoeyink (1999) observed also a decrease of pore blockage with ACF of larger pore size distribution but selectivity for the pesticide was not so high than in our work due to a mesopore volume less developped (0.038 cm^3 g^{-1} for a total pore volume of 0.339 cm^3 g^{-1}). Our large mesopore volume may enable NOM to be adsorbed, whereas secondary micropores may allow an elimination of pore blockage by NOM molecules and thus atrazine adsorption in primary and secondary micropores.

The high selectivity against dissolved organic molecules of our ACF is interesting in terms of selective adsorption of target molecules such as pesticides or hydrolized by-products. This non-competition enables a specific use of the porous volume to remove pesticides, inducing a larger life of ACF filters.

4. Conclusion

This work has studied the adsorption of pesticides onto activated carbons in the form of fibers, of high specific surface area (1,460 m^2 g^{-1}) and containing 32% mesoporous volume. Monocomponent adsorption of four pesticides and metabolites (atrazine, deethylatrazine, desisopropylatrazine, simazine) showed the influence of the adsorbate's solubility: ACF present a larger adsorption of pesticides of low solubility, with Langmuir maximum adsorption capacities reaching 370 mg g^{-1} for simazine (solubility of 5 mg L^{-1}). The effects of adsorbates solubility was confirmed for binary adsorption of pesticides, the competition effects being more marked when one co-adsorbate had a lower solubility than the other (as the couples atrazine—DEA or atrazine—DIA). In this case, experimental results were successfully modelled by the Ideal Adsorbed Solution theory, whereas the model underestimated adsorption capacities in the case of a binary mixture of pesticides with low and similar solubilities (atrazine–simazine), which shifted the solution from ideality. Finally, the adsorption competition of pesticides with NOM onto the mesoporous ACF was approached. The ACF showed an interesting behavior of selectivity for low molecular size compounds like pesticides in the presence of NOM because of a broad pore size distribution including secondary micropores and mesopores. This property enables a specific use of this fibrous adsorbent to remove pesticides and thus an increase of the life of ACF filters.

Nomenclature

A	adsorbed surface area per unit mass of adsorbent ($\mathrm{m^2\,g^{-1}}$)
b	Langmuir equilibrium adsorption coefficient ($\mathrm{L\,mg^{-1}}$)
b_i	Langmuir equilibrium adsorption coefficient of the ith component ($\mathrm{L\,mg^{-1}}$)
C_e	equilibrium concentration ($\mathrm{mg\,L^{-1}}$)
$C_{e,i}$	equilibrium concentration of the multicomponent adsorption of the ith compound ($\mathrm{mol\,L^{-1}}$)
C_i^0	equilibrium concentration of the pure component adsorption of the ith compound ($\mathrm{mol\,L^{-1}}$)
K_f	Freundlich constant ($\mathrm{mg^{1-1/n}\,L^{1/n}\,g^{-1}}$)
$1/n$	Freundlich constant
N	number of components
q_e	adsorption capacity at equilibrium ($\mathrm{mg\,g^{-1}}$)
$q_{e,i}$	equilibrium adsorption capacity of the multicomponent adsorption of the ith compound ($\mathrm{mol\,g^{-1}}$)
q_i^0	equilibrium adsorption capacity of the pure component adsorption of the ith compound ($\mathrm{mol\,g^{-1}}$)
q_m	Langmuir maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$)
$q_{m,i}$	Langmuir maximum adsorption capacity of the ith compound $\mathrm{mg\,g^{-1}}$
q_t	total adsorption capacity of the multicomponent system ($\mathrm{mol\,g^{-1}}$) Ttemperature (K)
x_i	mole fraction of the ith adsorbate in the adsorbed phase
π	spreading pressure

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