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Adsorption of clofibric acid and ketoprofen onto powdered activated carbon: Effect of natural organic matter

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The adsorption of two acidic pharmaceutically active compounds (PhACs), clofibric acid and ketoprofen, onto powdered activated carbon (PAC) was investigated with a particular focus on the influence of natural organic matter (NOM) on the adsorption of the PhACs. Suwannee River humic acids (SRHAs) were used as a substitute for NOM. Batch adsorption experiments were conducted to obtain adsorption kinetics and adsorption isotherms with and without SRHAs in the system. The adsorption isotherms and adsorption kinetics showed that the adsorption of clofibric acid was not significantly affected by the presence of SRHAs at a concentration of 5 mg (as carbon) L^{-1}. An adsorption capacity of 70 to 140 mg g^{-1} was observed and equilibrium was reached within 48 h. In contrast, the adsorption of ketoprofen was markedly decreased (from about 120 mg g^{-1} to 70–100 mg g^{-1}) in the presence of SRHAs. Higher initial concentrations of clofibric acid than ketoprofen during testing may explain the different behaviours that were observed. Also, the more hydrophobic ketoprofen molecules may have less affinity for PAC when humic acids (which are hydrophilic) are present. The possible intermolecular forces that could account for the different behaviour of clofibric acid and ketoprofen adsorption onto PAC are discussed. In particular, the relevance of electrostatic forces, electron donor-acceptor interaction, hydrogen bonding and London dispersion forces are discussed

Keywords: adsorption, powdered activated carbon, pharmaceutically active compounds, humic acids

Introduction

The detection of pharmaceutically active compounds (PhACs) in surface and groundwater has raised public concerns about their potential toxicity towards aquatic biota and human beings, and their fate in either natural or engineered systems [1–3]. Pharmaceutically active compounds in wastewater include antibiotics, painkillers, tranquilizers and beta-blockers [4]. Their relatively slow biodegradation means that some PhACs will enter the receiving water from the discharge of sewage treatment plants and will pose environmental and health risks. This problem is expected to increase with the current push for water reuse [3].

Studies have shows that the removal of PhACs during traditional sewage treatment relies on two mechanisms: biodegradation and adsorption to both activated sludge and suspended mineral matter [4]. Because the PhACs in wastewater often exist at ng L^{-1} or low μg L^{-1} levels [3], the use of PhACs as primary substrate by microorganisms is unlikely, and cometabolic biodegradation probably accounts for the largest part of the biological transformation. Some PhACs can also readily adsorb to activated sludge; however acidic PhACs such as clofibric acid and ketoprofen do not adsorb well because activated sludge is usually negatively charged at near neutral pH [5]. Research simulating the transport of clofibric acid through soil columns (at pH = 7) showed that clofibric acid behaves as a conserved tracer, i.e. without any retardation [6]. This explains why the removal of clofibric acid in primary sedimentation and in the activated sludge process is marginal.

Because the biodegradation of PhACs is often slow, several physicochemical techniques are being evaluated for PhAC treatment from secondary or tertiary effluents [7–11]. Ultraviolet (UV) treatment is promising. Direct UV oxidation [7], and UV coupled with hydrogen peroxide [7] or Fenton [8] were examined and were found to achieve satisfactory removal. High removal of PhACs was observed with large ozone doses [9]. Nanofiltration also shows promise, with sometimes close to 100% treatment efficacy [10]. Still, low cost and simple treatment techniques are needed. Compared with the above techniques, adsorption on activated carbon is often cheaper and requires simpler equipment.

Extensive data exist on the adsorption of single aqueous organic pollutants, including PhACs, by adsorption onto various kinds of activated carbons [12]. But little is known about possible interferences from natural organic matter (NOM). Therefore, an understanding of the mechanisms of adsorption in multicomponent systems and the definition

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of the interactions between the solutes and activated carbon are needed. The present work focuses on the adsorption of two acidic PhACs, clofibric acid and ketoprofen, onto powdered activated carbon (PAC). The emphasis was on the influence of humic acids (used as a mimic of NOM) on the adsorption characteristics.

Materials and methods

Conditions

Stock solutions of clofibric acid (MP Biomedicals, Solon, OH, USA) and ketoprofen (TCI America, Portland, OR, USA) were prepared in pure ethanol at a concentration of 20 mmol L^{-1} and stored in a refrigerator (<0°C) until used. For the adsorption experiments, a known volume of the stock solution was pipetted into an empty test flask. Ethanol was then evaporated in a vacuum oven (40 min, ~70 °C). Next, the PhAC compounds were redissolved in nanopure water adjusted to a desired ionic strength or pH as described below. This method allowed for accurate production of a broad range of clofibric acid or ketoprofen concentrations. All bottles were placed on a shaker (~140 rpm) for one day to ensure complete dissolution of the PhACs. The maximum initial concentration of clofibric acid and ketoprofen was 1400 μmol L^{-1} and 200 μmol L^{-1}, respectively. The chemical structures and additional information on the two compounds can be found in Table 1. The ionic strength of the solutions was adjusted to 0.01 mol L^{-1} using NaCl. The pH was adjusted to 7.00 (Oakton pH meter, Ion 510 series) by adding NaOH (5 M) or HCl (1 M) as needed. When humic acids were added, the initial pH was around 3–4; it was adjusted to 7.00 after the humic acid stock solution was added.

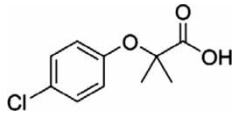
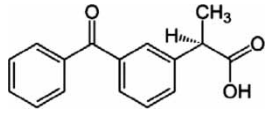
Suwannee River Humic Acids standard II (SRHAs) was supplied from the International Humic Substances Society (IHSS, St. Paul, MN, USA). The SRHA stock solution was prepared by mixing a know amount (~40 mg) of humic acids with 10 mL of nanopure water. Dissolution of humic acids was assisted by adding NaOH (5 M) until the pH value was 7.0. The solution was stabilized for six hours and then the total organic carbon (TOC) was measured by a Shimadzu TOC analyser 5000. The residual concentration of humic acids during adsorption experiments was not measured because of the complexity of the analysis and the low concentrations that were used.

Adsorbent

The PAC used in this study was obtained by pulverizing granular activated carbon, which were purchased by Sterm Chemical (CAS# 7440-44-0; Newburyport, MA, USA), using a coffee grinder (Hamilton Beach 80365). The powdered form was selected to avoid or limit possible internal mass transfer limitations. The particle size distribution of the PAC was narrowed to between 53 μm and 106 μm using two sieves (US Standard). After sieving, the carbon was washed with nanopure water until the supernatant of the H_2O-carbon mixture was clear and the powder settled rapidly. The PAC was then boiled for 30 min to remove potential volatile organic components, dried in oven at 110 °C for two two days and subsequently stored in a desiccator until use.

To characterize the surface charge of the PAC, the point of zero charge (PZC) of the PAC was determined using a titration method [13]. In short, PAC suspensions with different mass fractions ranging from 0.05% to 10% by weight were made with solutions of preadjusted pH (3, 6 and 11 using 0.1 M HNO 3 and 0.1 M NaOH). Sodium nitrate was used for ionic strength control. The flasks (200 mL with 100 mL solution) were placed on a rotary shaker (~140 rpm) at room temperature for 24 hours, after which the equilibrium pH was measured and reported. As shown in Figure 1, the PZC of the activated carbon used in these experiments was about 10. The BET surface area and pore size distribution were determined by an outside laboratory (Pacific Surface Science Inc, Ventura, CA, USA). The BET surface area was 982 ± 35 m^2 g^{-1}.

Table 1. Properties of the two PhACs used in this study[a].

Compound name	Clofibric acid	Ketoprofen
Structure		
Chemical formula	$C_{10}H_{11}ClO_3$	$C_{16}H_{14}O_3$
Water solubility (mg L^{-1})	583 (25 °C)	51 (22 °C)
Molecular weight(g mol^{-1})	214.7	254.3
Log K_{ow}	2.57	3.12
p*K*a	2.5 or 3.18[b]	3.98[c], 4.29[d] or 4.45
Molecular dimensions (nm)	0.5 × 0.58 × 1.9[e] 0.41 × 0.66 × 0.95[g]	0.39 × 0.61 × 0.77[f]

Sources: [a]http://www.syrres.com/, [b][31], [c][32], [d][26], [e][17], [f][33], [g][34].

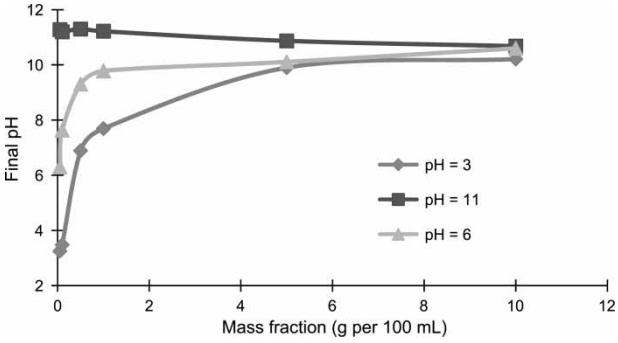


Figure 1. Point of zero charge determination. Final pH as a function of PAC mass fraction in the solution.

PhAC measurement

High-pressure liquid chromatography (HPLC)-UV absorption using a Varian HPLC was used for the analysis of PhACs following a published method [14]. Absorption at 260 nm and 230 nm was used for ketoprofen and clofibric acid quantification, respectively. The detection limit was 0.5 μmol L^{-1}. Potential interference from humic acids with the UV detection of PhACs was tested and no interference was found. The analysis method was calibrated by analysing standard solutions (five different concentrations within the range of interest) and conducting a least square regression for the concentration vs peak area.

Adsorption experiments

Kinetics experiments were conducted to find the time necessary for the adsorption systems to reach equilibrium. Only one initial concentration was used for each compound: 100 μmol L^{-1} for ketoprofen and 200 μmol L^{-1} for clofibric acid. The pH values and ionic strength were adjusted as mentioned above. The carbon dose used was 0.20 g L^{-1} (0.04 g per 200 mL) for all experiments. This carbon dose is close to the maximum dose commonly used for organic carbon removal [15] and was selected based on the study of Ternes *et al.* [16], who used an initial PhAC concentration of 100 μg L^{-1}. Upon adding PAC, all the bottles were laid horizontally on the shaker (~140 rpm). Samples were taken using 3 mL plastic syringes (BD, Luer-Lok, Franklin Lakes, NJ, USA) and filtered through 0.2 μm polypropylene syringe filter (VWR, Westchester, PA, USA). Each data point consists of at least two replicates and each sample was measured three times on the HPLC.

Adsorption isotherms were obtained by varying the initial solution concentration at a constant PAC dose (0.20 g L^{-1}). The initial concentration for clofibric acid ranged from 200 to 1400 μmol L^{-1} and from 80 to 200 μmol L^{-1} for ketoprofen. The bottles were shaken (~140 rpm) usually for four to seven days depending on the experiment. Controls flasks without PAC were included and no removal was found in absence of PAC for up to two weeks. Flasks were stored in the refrigerator (4 °C) for one hour prior to sampling to allow the PAC to settle. The brief temperature change had a negligible effect on the results.

Modelling of adsorption data

The fitting of experimental data to three frequently used isotherms was conducted [12,17,18]. These were the Langmuir, Freundlich and Koble–Corrigan isotherms as briefly summarized below.

The Langmuir isotherm is based on the assumption that the adsorption is confined to a monolayer and that there is no interaction between adsorbed molecules. The mathematical expression of this isotherm is:

$$q_e = \frac{K_l C_e}{1 + a_l C_e} \tag{1}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of sorbate adsorbed (mg g^{-1}), K_l and a_l are isotherm constants.

The Freundlich isotherm is an empirical formula describing the adsorption equilibrium as follows:

$$q_e = K_f C_g^n \tag{2}$$

where K_f and n are isotherm constants, K_f represents the adsorbed amount when $C_e = 1$, and n is related to the enthalpy of adsorption and indicates how adsorption changes with the adsorbed amount.

The Koble–Corrigan Model (KC) is a three-parameter empirical model representing equilibrium adsorption. It is a combination of the Langmuir and Freundlich models and is given by Equation (3). Compared with the Langmuir isotherm, the additional parameter g can be regarded as characteristic of the heterogeneity of the adsorption system [18].

$$q_e = \frac{AC_e^g}{1 + BC_e^g} \tag{3}$$

where A, B, and g are the Koble–Corrigan parameters.

Similarly, the adsorption kinetics data were fitted to three widely used models [18]: the pseudo-first-order equation, pseudo-second-order equation and an intraparticle diffusion kinetics equation. The expressions of these three models are shown below.

Pseudo-first-order (PFO) model:

$$q_t = q_e - q_e e^{K_l t} \tag{4}$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the adsorption capacity at time t and maximum adsorption capacity, respectively, and K_l (h^{-1}) is the PFO rate constant.

Pseudo-second-order (PSO) equation:

$$\frac{t}{q_t} = \frac{K_2}{q_e^2} + \frac{t}{q_e} \tag{5}$$

where K_2 (mg·h g^{-1}) is the PSO rate constant.

Intra-particle diffusion (IPD) kinetics:

$$q_t = Kt^{1/2} + C \tag{6}$$

where K (mg·$h^{-1/2}$ g^{-1}) and C (mg g^{-1}) are the IPD rate constants.

In all cases, isotherm or kinetic equations were fitted to experimental data by least-square regression, which was performed using the Solver function from Excel 2007. The best-fit parameters were determined and the correlation coefficient (R^2), residual sum of squares error (SSE) and the standard error (SE) were calculated to test the goodness of fit.

Results and discussion

Adsorption kinetics

The kinetics of adsorption of clofibric acid and ketoprofen on PAC are reported in Figures 2 and 3. Adsorption equilibrium for ketoprofen took about 24 hours, whereas about twice this time was required for clofibric acid. Examination of Figure 2 shows that the adsorption behaviour of clofibric acid in the presence of humic acids is virtually indistinguishable from the behaviour in the absence of humic acids, whereas a marked difference in the adsorption capacity can be observed for ketoprofen (Figure 3). Thus ketoprofen's adsorption capacity onto PAC is affected by the presence of humic acids. The contact time required to reach equilibrium found here is longer than the time found in several other studies [17,19] but is comparable with the one obtained by Ternes *et al.* [16]. Most probably, the differences in the types of activated carbon and in solution composition are responsible for the differences in adsorption rates. In this study, the reason why the ketoprofen–PAC system needed less time to reach equilibrium may be because of the smaller solute molecular size (see values in Table 1). It is known that smaller molecular sizes enhance the rate adsorbate transfer from the liquid phase to the macropores, and further the transfer to the mesopores and micropores, where the largest adsorption energy can be achieved [20].

Fitting of the adsorption dynamics to the pseudofirst and second order models and the intra-particle diffusion model was conducted and the results are tabulated in Table 2. The figures of the kinetics fittings are provided in the supplementary online material. It was found that the kinetic data for clofibric acid, either with or without humic acids, were

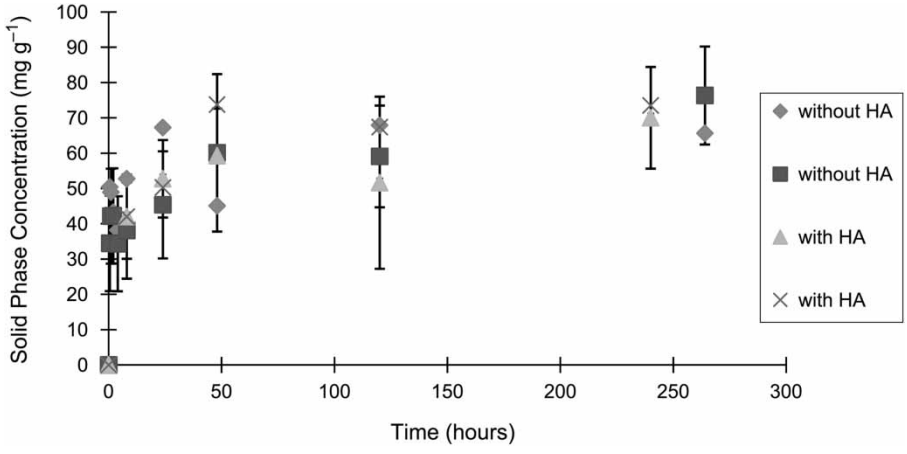


Figure 2. Adsorption kinetics of clofibric acid with and without humic acids in the solution. Error bars show one standard deviation from means. The different symbols are for two different experiments.

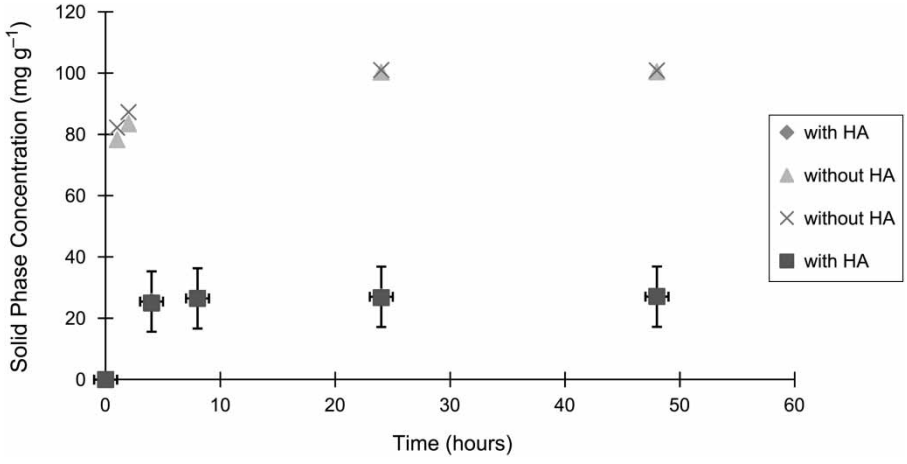


Figure 3. Adsorption kinetics of ketoprofen with and without humic acids in solution. Error bars show one standard deviation from means of one replicate. The different symbols are for two different experiments. Error bars or symbols that are not discernible are behind other symbols.

Table 2. Model constants for adsorption kinetics.

Isotherm	Model parameter	Clofibric acid (alone)	Clofibric acid (with humics)	Ketoprofen (alone)	Ketoprofen (with humics)
Pseudo-first-order	K_1 (h^{-1})	1.92	0.14	1.32	32.3
	q_e ($mg\,g^{-1}$)	51.1	59.2	100	26.7
	R^2	0.17	0.54	0.80	0.98
	SSE	1335	198	119	1.91
	SE	12.9	7.04	4.46	0.62
Pseudo-second-order	K_2 ($mg{\cdot}h\,g^{-1}$)	20.4	267	33.6	6.29
	q_e ($mg\,g^{-1}$)	53.8	63.1	101	27.1
	R^2	0.29	0.64	0.97	0.997
	SSE	1144	154	17.4	0.25
	SE	12	6.2	1.9	0.25
Intra-particle diffusion	K ($mg\,h^{-0.5}\,g^{-1}$)	0.042	0.028	0.96	0.038
	q_e ($mg\,g^{-1}$)	59.9	59.9	1.22	1.80
	C ($mg\,g^{-1}$)	34.82	41.32	85.80	26.2
	R^2	0.90	0.68	0.58	0.99
	SSE	164	139	253	1.26
	SE	7.4	6.8	8.0	0.65

best fitted by the intra-particle diffusion model. In contrast, the kinetics data for ketoprofen adsorption with humic acids were fitted well by all three kinetics models ($R^2 = 0.978$, 0.997, 0.986), while the data of ketoprofen without humic acids were best fitted by the pseudo-secondorder model. In some cases, discrimination between the different models was difficult because of the low number of data points and some scattering of the data in the unsteady-state phase, in particular for ketoprofen.

Adsorption isotherms

The adsorption isotherms for clofibric acid and ketoprofen obtained with PAC, with and without humic acids, are shown in Figures 4 and 5. In the case of clofibric acid (Figure 4), the adsorption capacity of PAC falls in the range of 70 to 140 $mg\,g^{-1}$. Much scattering of the experimental data was observed, which added significant difficulty in analysing the adsorption isotherms. The source of the data scattering was not identified. Even so, no important difference can be distinguished between the adsorption characteristics in the presence or absence of humic acids, suggesting that the presence of humics has little or no role in the adsorption of clofibric acid. This is also consistent with the findings of adsorption kinetics presented in the previous section.

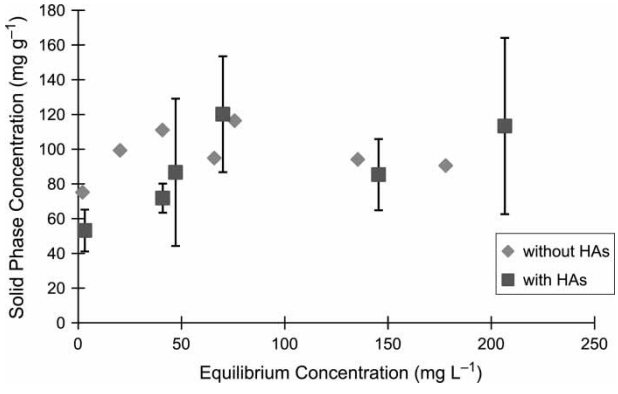


Figure 4. PAC adsorption capacity for clofibric acid in the presence and absence of humic acids. The error bars represent the standard error.

Only a few reports exist on the adsorption isotherms of PhACs [11,16,17,19,21,22]. Ternes *et al.* [16] reported an adsorption capacity of 10–50 $mg\,g^{-1}$ at residual concentrations of 1 to 100 $\mu g\,L^{-1}$ of clofibric acid and near neutral pH condition. Mestre *et al.* [17] conducted clofibric acid adsorption experiments using four kinds of activated carbon, some with a similar PZC to the one used in the present study. They found a maximum adsorption capacity of around 250 $mg\,g^{-1}$ at pH = 3.6, i.e. a capacity close to twice our value. The reasons for the differences are unknown, but could be linked to the different conditions (pH of 3.5, i.e. the pKa of clofibric acid, and 30 °C).

The PAC adsorption characteristic for ketoprofen is shown in Figure 5. In contrast to the results of clofibric acid, a negative effect of humic acids on the adsorption of ketoprofen is clearly visible. The adsorption capacity was decreased from around 120 $mg\,g^{-1}$ to 70–100 $mg\,g^{-1}$.

Some discussion of the differences observed between clofibric acid and ketoprofen is warranted. The different effects of humic acids on the adsorption of clofibric acid and ketoprofen can be attributed to (1) the different chemical properties, especially hydrophobicity of the two pharmaceuticals, and (2) the relative concentrations of PhACs to the humic acids (initial concentration of humics was 5 mg (as carbon) L^{-1}) in all experiments. As mentioned, the PAC used in this study had a PZC value of about 10. Therefore, despite some negative charges, the net charge of the carbon surface should be positive at the current experimental condition (pH = 7.0). In other words, the electrostatic force

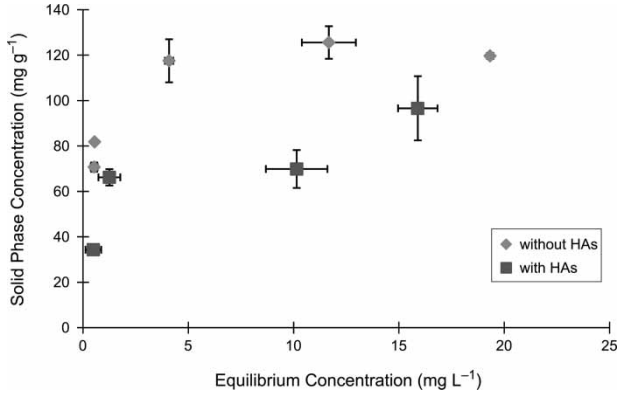


Figure 5. PAC adsorption capacity for ketoprofen in the presence and absence of humic acids. The error bars represent the standard error.

or attraction between clofibric acid or ketoprofen and the activated carbon should be significant because both PhACs are in their deprotonated forms at this pH. This phenomenon has been investigated by others, e.g. in the adsorption of ionic dyes on activated carbon with a charged surface; adsorption was favoured when the net surface charge of the carbon was positive [23]. Meanwhile, humic substances are always negatively charged at pH values from 4.5 to 8.0 [24]. Thus, once the negatively charged humics adsorb on the carbon surface, the adsorption of negatively charged PhACs should decrease as a result of repulsion from the residual negative charges of the humic acids. Nevertheless, considering the larger molar ratio of PhACs to humic acids in this study, which was 80–560 for clofibric acid and 32–80 for ketoprofen (assuming a molecular weight of 3820 g mol^{-1} for the humic acids), the repulsion of clofibric acid should be smaller. The lower molar ratio for ketoprofen should result in a greater influence of electrostatic effects; indeed the adsorption capacity of ketoprofen decreased significantly in the presence of humic acids.

In addition, ketoprofen is more hydrophobic (log D = 0.41, pH = 7.0, pKa = 4.29) than clofibric acid (log D = −1.25/ − 1.93, pH = 7.0, pKa = 3.18/2.5) [25,26], where log D is a pH-dependent octanol water partition number (K_{ow}) and is defined by the equations below. An increasing log D value indicates an increase in hydrophobicity.

$$\text{Acids(negatively charged): } \log D = \log K_{ow} - \log(1 + 10^{(pH-pKa)}) \quad (7)$$

$$\text{Bases(positively charged): } \log D = \log K_{ow} - \log(1 + 10^{(pKa-pH)}) \quad (8)$$

Thus ketoprofen is expected to be more affected by the formation of a relatively hydrophilic surface of humic acid aggregates [27]. This effect of hydrophobicity in adsorption was reported by Ahnert *et al.* [28], who used cyclohexane, a non-polar solvent, to study the influence of hydrophobicity of the carbon surface on the adsorption of several organic compounds including benzene and xylene, which have similar log K_{ow} (2.13 and 3.15, respectively) to the PhACs in this study. They found that the adsorption of benzene and xylene decreased as the surface polarity/acidity increased. Thus, considering the abundant acidic functional groups of humic acids, the enhanced acidity after binding of humic acids to the PAC surface can be expected to results in a decrease of ketoprofen adsorption, following the same mechanisms.

Although the residual concentrations of humic acids were not measured in the present experiments, a semi-quantitative prediction of the partition of PhACs to dissolved humic acids can help in interpreting the experimental data. The approach is as follows. First, one assumes that the humic acids are totally dissolved in water (i.e. no adsorption of humic acids on PAC). Then, based on the Karickhoff empirical relationship [29], which is shown below (Equation (9)), the log D values of ketoprofen (0.41) and clofibric acid (−1.25) are used to calculate the K_{oc} values of ketoprofen and clofibric acid. This makes possible the estimation of the amount of clofibric acid or ketoprofen that would adsorb to humics. In the case where there is 5 mg-C L^{-1} as humic acids in solution, the calculated equilibrium concentration of ketoprofen and clofibric acid in solution are 20 mg L^{-1} and 100 mg L^{-1}, respectively, and the amount of PhACs partitioned to the humic acids are 3.45×10^{-12} mol and 1.25×10^{-10} mol, for clofibric acid and ketoprofen, respectively. These results are tabulated in Table 3.

$$\log K_{oc} = \log D - 0.21 \quad (9)$$

Based on the above calculations, it appears that ketoprofen would partition more to humic acids than would clofibric acid, which could in part explain the differences in adsorption to PAC. However, consistent with our results, such reasoning is limited, since part of the humic acids will be adsorbed on the surface of the activated carbon.

In addition to electrostatic interactions, which are expected to play a major role, interactions between organic compounds containing phenyl groups and the activated carbon surface include: (1) donor–acceptor complexation, which involves surface electron–donating groups (e.g. carbonyl oxygen) and aromatic ring as electron acceptor; (2) London dispersion forces between the aromatic rings of the sorbate and the aromatic rings of the carbon surface, also called π-π dispersion; and (3) hydrogen bond formation between the heteroatoms (chlorine and oxygen) and the hydrogen atoms on the carbon surface [12].

Typically, a high PZC corresponds to a large content of basic groups such as pyrone-type and chromene-type groups (see Table S1 in supplementary material), either in absolute or relative terms [30]. These basic groups can be regarded as Lewis basic active sites, which have a high content of electrons [23]. Therefore, they could act as electron donor and interact with the electron acceptors,

Table 3. Calculation of partition of PhACs to humic acids.

Compound	Log D	Log K_{oc}	K_{oc} (L kg^{-1} OC)	Equilibrium concentration in liquid (μmol L^{-1})	Equilibrium concentration on solid (μmol kg^{-1})	Moles of PhAC partitioned to humic acids (μmol)	Moles of PhACs in liquid, 200 mL (μmol)
Clofibric acid	−1.25	−1.46	0.0074	466 ($\cong$100 mg L^{-1})	3.45	1.72×10^{-5}	93.2
Ketoprofen	0.41	0.2	1.59	78.7 ($\cong$20 mg L^{-1})	125	6.23×10^{-4}	15.7

which are the aromatic rings of clofibric acid or ketoprofen, whose π-system's electron density is reduced by the electron-withdrawing groups such as chlorine and oxygen (keto function). Besides, the existence of heteroatoms such as oxygen and chlorine makes it possible to have hydrogen bonds. A better characterization of surface functional groups is needed to better understand the magnitude of the intermolecular interactions that affect the adsorption of clofibric acid and ketoprofen on PAC.

The fitting of the adsorption isotherms for the two PhACs, with and without humic acids, using three widely used models is presented in Figures 6 and 7 and the parameters are tabulated in Table 4. Not surprisingly, the three-parameter model (Koble–Corrigan) fits the data best when considering only the standard errors or correlation coefficients in Table 4. However, examination of the figures reveals that the differences between the simulated isotherms of the three models are relatively trivial in the case of clofibric acid adsorption (both with and without humic acids). For ketoprofen adsorption, in particular in the presence of humics, the three different models resulted in relatively different behaviours. Visual observation suggests that the Langmuir isotherm is probably most appropriate as it adequately predicts saturation of the PAC. The

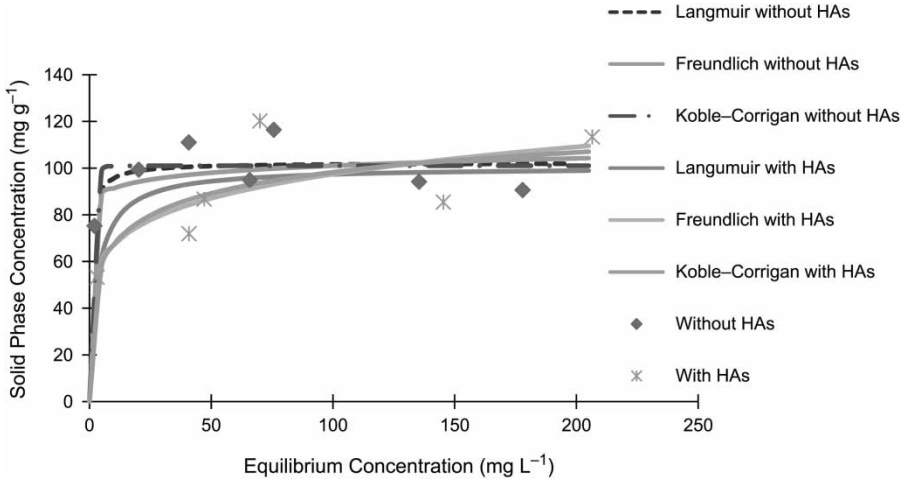


Figure 6. Adsorption isotherms for clofibric acid in absence of SRHAs using three widely used models.

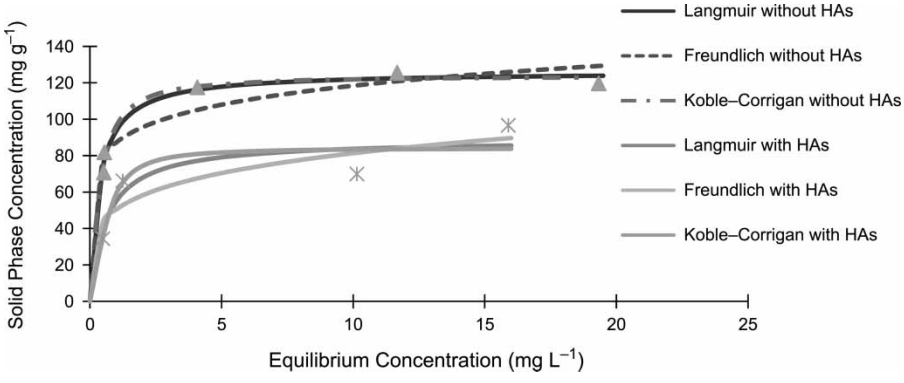


Figure 7. Adsorption isotherms for ketoprofen in the presence and absence of SRHAs using three widely used models.

Table 4. Isotherm constants for clofibric acid and ketoprofen adsorption onto PAC (SSE = residual sum of squares error, $mg^2\ g^{-2}$; SE = standard error, $mg\ g^{-1}$).

Isotherm	Model parameter	Clofibric acid (alone)	Clofibric acid (with humics)	Ketoprofen (alone)	Ketoprofen (with humics)
Langmuir	K_l	146	31.1	362	144
	a_l	1.42	0.31	2.87	1.62
	R^2	0.49	0.60	0.97	0.80
	SSE	563	1477	77	383
	SE	16.8	27.2	6.2	13.8
Freundlich	K_f	82.6	46.1	87.2	50.5
	n	0.044	0.16	0.13	0.21
	R^2	0.23	0.64	0.86	0.77
	SSE	851	1301	356	447
	SE	20.62	25.5	13.3	15.0
Koble–Corrigan	A	34.0	52.5	433	200
	B	0.34	0.34	3.49	2.38
	g	3.01	0.35	1.26	1.67
	R^2	0.52	0.65	0.99	0.82
	SSE	533	1269	68	348
	SE	16.3	25.2	5.8	13.2

isotherms also indicate that further experiments at the low end of the concentration scale, i.e. below $5\ mg\ L^{-1}$, are required.

Conclusion

The adsorption of clofibric acid and ketoprofen as two model PhACs onto powdered activated carbon was investigated and used to develop a better understanding of the mechanisms of adsorption of these compounds. In particular, the potential influence of humic acids, as a surrogate of NOM, was determined. Batch adsorption experiments were conducted with clofibric acid and ketoprofen in water at a pH of 7.00 ± 0.05 and constant ionic strength of 0.01 M as NaCl and with PAC as the adsorbent. The results demonstrated that PAC has relatively high adsorption capacity for clofibric acid and ketoprofen. The solid-phase concentrations obtained were around $70–120\ mg\ g^{-1}$ for concentrations of clofibric acid and ketoprofen greater than $40\ mg\ L^{-1}$ and $5\ mg\ L^{-1}$, respectively. The presence of humic acids had no effect on clofibric acid adsorption, whereas both the capacity and kinetics of ketoprofen adsorption to activated carbon was negatively affected by the humic acids.

The difference between the two compounds' behaviours was attributed to the different molar ratio of PhACs to humic acids in the solution and the stronger hydrophobicity of ketoprofen.

The adsorption kinetics of clofibric acid was best fitted by the intra-particle diffusion model, whereas ketoprofen adsorption in the absence of humics was best fitted to the pseudo-second-order kinetics model. In the presence of humic acids, ketoprofen adsorption kinetics could be well fitted by the pseudo-first-order, pseudosecond-order and intra-particle diffusion models.

A discussion of the molecular interactions between the carbon surface and the solutes highlighted that electrostatic forces between the carbon surface and solute molecules, electron donor–acceptor interaction, hydrogen bonding, London dispersion forces and possibly hydrophobic interactions could play an important role in the adsorption process.

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