Fixed-bed adsorption in drinking water treatment: a critical review on models and parameter estimation

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ABSTRACT

A review is given on the state of modelling of fixed-bed adsorption processes in drinking water treatment with special consideration of parameter estimation. In particular, the Homogenous Surface Diffusion Model (HSDM) and the Linear Driving Force Model (LDF model) are compared and evaluated with respect to availability of the required model parameters. In this context, methods for predicting equilibrium and mass transfer parameters are critically discussed under particular consideration of the specific drinking water characteristics. Feasibilities and limits of different approaches for estimating equilibrium parameters are exemplarily shown. In particular, Polanyi's potential theory, a modified Freundlich equation, and the adsorption analysis for complex mixture solutions are considered. Furthermore, empirical correlations for predicting mass transfer coefficients for single-solute and multi-component adsorbate systems are presented and evaluated.

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NOMENCLATURE

A	empirical parameter in Equation (11)
a	empirical parameter in Equation (19)
a_V	area available for mass transfer per reactor volume, m^2/m^3
B	empirical parameter in Equation (11)
b	empirical parameter in Equation (19)
c	concentration, mg/L or mmol/L
c_s	concentration at the external particle surface, mg/L or mmol/L
c_0	inlet concentration, mg/L or mmol/L
D_L	liquid phase diffusion coefficient, m^2/s
D_P	pore diffusion coefficient, m^2/s
D_S	surface diffusion coefficient, m^2/s
d_P	particle diameter, m
E	adsorption potential, J/mol
K	parameter of the Freundlich isotherm, $(mg/g)/(mg/L)^n$ or $(mmol/g)/(mmol/L)^n$
K^*	parameter of the normalized Freundlich isotherm, mg/g

k_F	film diffusion mass transfer coefficient, m/s
$k_F a_V$	volumetric film diffusion mass transfer coefficient, 1/s
k_S	intraparticle (surface) diffusion mass transfer coefficient, m/s
$k_S a_V$	volumetric intraparticle (surface) diffusion mass transfer coefficient, 1/s
M	molecular weight, g/mol
N	normalizing factor of the characteristic curve
n	exponent of the Freundlich isotherm, dimensionless
n^*	exponent of the normalized Freundlich isotherm, dimensionless
q	mass adsorbed (loading), mg/g or mmol/g
q_s	mass adsorbed in equilibrium with c_s, mg/g or mmol/g
q_T	total mass adsorbed, mg/g or mmol/g
q_0	mass adsorbed in equilibrium with c_0, mg/g or mmol/g
R	gas constant, $R = 8.314\,J/(K\,mol)$

Re	Reynolds number, dimensionless
r	radial coordinate, m
r_P	particle radius, m
S	aqueous solubility, mg/L
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
$SPDFR$	solid-to-pore diffusion flux ratio
T	absolute temperature, K
t	time, s
V_{ads}	volume adsorbed, cm^3/g
V_m	molar volume, cm^3/mol
V_0	maximum volume adsorbed, cm^3/g
v_l	linear filter velocity, m/s
z	axial coordinate, m
z	adsorbed phase mole fraction, dimensionless
ε_b	bed porosity, dimensionless
η	dynamic viscosity, Pa s
Φ	spreading pressure term in the IAS theory, mmol/g
ρ	adsorbate density, g/cm^3
ρ_b	bed density, g/cm^3
τ	tortuosity

ABBREVIATIONS

BTC	breakthrough curve
DOM	dissolved organic matter
DOC	dissolved organic carbon
GAC	granular activated carbon
HSDM	homogeneous surface diffusion model
IAST	ideal adsorbed solution theory
LDF	linear driving force
LFER	linear free energy relationship
RSSCT	rapid small-scale column test

INTRODUCTION

Granular activated carbon (GAC) adsorbers are widely used in drinking water treatment in order to remove taste and odour compounds as well as synthetic organic micropollutants. Dissolved organic matter (DOM) generally present in raw water will also be removed by GAC and acts as a competitor during micropollutant adsorption. The available capacity of a fixed-bed adsorber until the breakthrough point depends on both adsorption equilibrium and adsorption kinetics. The adsorption rate can be limited by the mass transfer processes film diffusion (external diffusion), pore diffusion (internal diffusion in the pore fluid) or surface diffusion (diffusion along the internal surface). In order to describe the breakthrough curve (BTC) of a single adsorbate or an adsorbate mixture, an adequate model is required. Furthermore, the characteristic equilibrium and kinetic parameters must be known. In general, the number of parameters required for calculation increases with increasing complexity of the BTC model. Therefore, in view of model selection for practical purposes, a compromise has to be found between the accuracy of process description and the effort for determining the model parameters.

In practice, the acceptance of a BTC model depends on the availability of the required parameters. Although a lot of BTC models were proposed during the last decades, up to now such models have been rarely used in adsorber design for drinking water treatment, not least due to problems in parameter estimation. In particular, problems result from the composition of drinking water which is not a defined single-solute system but a complex multi-component system of – at least partly – unknown composition. It consists of micropollutants and (natural) dissolved organic matter, where DOM itself is a multi-component mixture of fractions with different adsorption behaviour. The composition of this multi-component mixture is unknown, only collective parameters such as dissolved organic carbon (DOC) can be measured.

In the following, the state of fixed-bed adsorber modelling will be discussed with special regard for parameter estimation. Experimental bench-scale methods to assess GAC performance such as the rapid small-scale column tests (RSSCT) which can be used as an alternative prediction tool for DOM and micropollutant adsorption (Crittenden *et al.* 1991; Summers *et al.* 1995; Hopman *et al.* 1996) will not be considered here.

While references are made to studies published by others, the paper is not intended as a global review but rather as a comprehensive description and critical assessment of the results from a sequence of studies carried out in the authors' group during the last years.

BREAKTHROUGH CURVE MODELS: HSDM VS. LDF

In general, most of the published BTC models consist of three components: the differential mass balance equation, the equilibrium relationship (isotherm in case of single solute adsorption or an appropriate mixture model in case of competitive adsorption), and a set of equations describing the external and internal mass transfer (Sontheimer *et al.* 1988; Kümmel & Worch 1990). Under the typical hydrodynamic conditions existing in water works dispersion effects can be neglected and the mass balance equation reads

$$v_l \frac{\partial c}{\partial z} + \varepsilon_b \frac{\partial c}{\partial t} + \rho_b \frac{\partial q}{\partial t} = 0 \qquad (1)$$

where v_l is the linear filter velocity, c is the concentration, z is the distance, t is the time, q is the loading (mass adsorbed), ε_b is the bed porosity, and ρ_b is the bed density.

Single-solute adsorption from aqueous solutions can be described in most cases by the Freundlich isotherm

$$q = Kc^n \qquad (2)$$

where K and n are the isotherm parameters. For mixture adsorption, special models are needed which will be discussed later.

Although models including all three mass transport processes (film, pore, and surface diffusion) were proposed in the literature (e.g. Crittenden *et al.* 1987), their applicability is restricted in terms of availability of internal transport parameters. Pore diffusion and surface diffusion act in parallel in the interior of the adsorbent particle and the related diffusion coefficients, D_P and D_S, cannot be determined independently. The proposed method of calculating D_P from the liquid-phase diffusion coefficient, D_L, and the tortuosity, τ, of the adsorbent with subsequent calculation of D_S from D_P using a solid-to-pore diffusion flux ratio, *SPDFR*, as suggested by Crittenden *et al.* (1987) and Sontheimer *et al.* (1988) do not solve this problem, because not only D_S and D_P but also τ and *SPDFR* cannot be determined independently.

Therefore, models considering only one single internal transport mechanism additionally to the external film diffusion are often preferred. In this case, the internal transport coefficient exhibits the character of an effective parameter. In the following only this type of BTC model will be considered.

There are two different approaches to describe a uniform internal mass transport: the homogeneous surface diffusion model (HSDM) based on Fick's law and the linear driving force (LDF) model based on a simplified mass transfer equation. In both cases the internal mass transport is assumed to be surface diffusion. In the case of HSDM (Hand *et al.* 1984) the surface diffusion is written as

$$\frac{\partial q}{\partial t} = D_S \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \qquad (3)$$

where D_S is the surface diffusion coefficient and r is the radial coordinate.

The successful application of the linear driving force approach was demonstrated in numerous papers (e.g. Hashimoto & Miura 1976; Moon & Lee 1986; Worch 1991*a,b*). In the LDF model, the transport equation for internal (surface) diffusion reads

$$\frac{dq}{dt} = k_S a_V (q_s - q) \qquad (4)$$

where $k_S a_V$ is the volumetric mass transfer coefficient for surface diffusion (product of mass transfer coefficient, k_S, and external adsorbent surface area per reactor volume, a_V), q_s is the loading at the external particle surface, and q is the mean loading of the particle.

In both models the external film diffusion is described in the same way by the linear mass transfer equation

$$\frac{dq}{dt} = \frac{k_F a_V}{\rho_b} (c - c_s) \qquad (5)$$

where $k_F a_V$ is the volumetric mass transfer coefficient for film diffusion.

If the particles assumed to be spherical, a_V can be calculated by

$$a_V = \frac{3}{r_p} (1 - \varepsilon_b) \qquad (6)$$

where r_p is the particle radius.

To answer the question if there are significant differences in the quality of BTC calculations between both models, single-solute adsorption simulations were

performed using process parameters typically for drinking water treatment (Tables 1 and 2). In order to make the results comparable, the Glueckauf approach (Glueckauf 1955) was used to find equivalent values for volumetric mass transfer coefficient, $k_F a_V$, and surface diffusion coefficient, D_S.

$$k_S a_V = \frac{15 D_S}{r_p^2} \tag{7}$$

Figure 1 shows the results of the BTC simulations. Under the given practice-oriented process conditions there is no difference between the solutions of HSDM and LDF. It has to be noted that larger but still negligible deviations will be found at very high Biot numbers (very high ratios of film to surface diffusion rate), e.g. if surface diffusion is extremely slow. Given that the computing time on modern computers is very short for both models and the number of the required mass transfer parameters is the same ($k_F a_V$ and D_S vs. $k_F a_V$ and $k_S a_V$) none of the models exhibit a significant advantage over the other.

Generally, the BTC models described above can also be used to calculate mixture adsorption processes. In this case, the single-solute isotherm has to be substituted by a mixture adsorption model. The ideal adsorbed solution theory (IAST) originally developed by Myers & Prausnitz (1965) for gas phase adsorption and later applied to liquid-phase adsorption by Radke & Prausnitz (1972) is widely accepted as the standard model for mixture adsorption modelling. The IAST is based on a thermodynamic approach and allows predicting mixture equilibrium data from concentrations and isotherm parameters of the mixture components. If the single-solute adsorption of the mixture

Table 1 │ Process parameters for BTC simulation

Process parameter	Unit	Value
Inlet concentration	mg/L	1
Bed diameter	m	2
Bed length	m	2
Adsorbent mass	kg	3,140
Empty bed contact time	min	20
Filter velocity	m/h	6
Particle diameter	mm	2
Bed porosity	–	0.4

Table 2 │ Adsorbate properties for BTC simulation

Adsorbate property	Unit	Value
K	$(mg/g)/(mg/L)^n$	60
n	–	0.3
D_S	m^2/s	2.67×10^{-13}
k_F	m/s	1.37×10^{-5}

components is described by the Freundlich isotherm, the following set of equations can be derived from the IAST:

$$\sum_{i=1}^{N} z_i = \sum_{i=1}^{N} \frac{c_i}{\left(\frac{\Phi n_i}{K_i}\right)^{1/n_i}} = 1 \tag{8}$$

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{\Phi n_i}\right]^{-1} \tag{9}$$

$$q_i = z_i q_T \tag{10}$$

where z_i is the adsorbed phase mol fraction of component i, c_i is the concentration of i, n_i and K_i are the isotherm parameters of i, q_T is the total amount adsorbed, and q_i is the adsorbed amount of i. Φ is a spreading pressure term originating from the thermodynamic approach.

Equation (8) has to be solved for Φ and z_i by an iteration procedure. From these data the total adsorbed amount q_T can be calculated by using Equation (9). Finally, the individual loadings of the mixture components result from Equation (10). As can be seen from the given equations, only the concentrations c_i and the isotherm parameters K_i
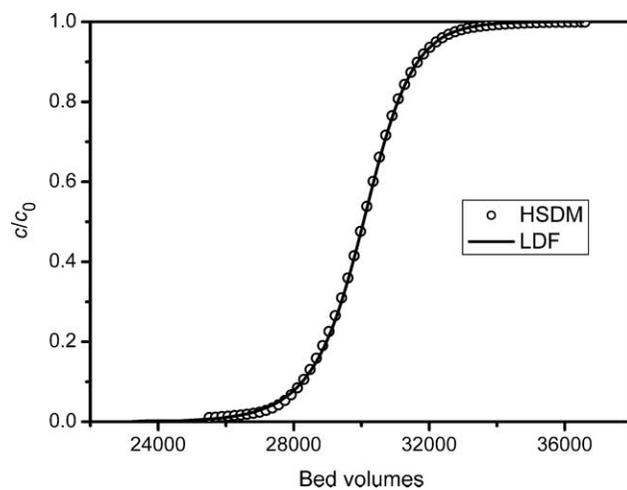

Figure 1 │ BTC simulation: Comparison of HSDM and LDF model. Input data are given in Tables 1 and 2.

and n_i of the mixture components are required to calculate all equilibrium loadings. It has to be noted that in case of fixed bed adsorption the equilibrium concentrations c_i in Equation (8) can be set equal to c_{0i} whereas for batch processes inlet and equilibrium concentrations are not identical and the mass balance equation has to be additionally included.

The use of the IAST in BTC modelling was described e.g. by Kuennen et al. (1989) for HSDM and by Moon & Lee (1986) and Worch (1991a,b) for LDF.

ESTIMATION OF EQUILIBRIUM PARAMETERS

Single-solute adsorption

In case of single-solute adsorption the isotherm parameters of the adsorbate are required as equilibrium data for BTC calculation. Single-solute isotherm parameters are also needed for predicting mixture adsorption by IAST.

It is known from experience that in most cases the adsorption of organics from aqueous solutions can be satisfactorily described by using the two-parameter Freundlich Equation (Equation (2)). The isotherm parameters have to be determined experimentally by batch isotherm tests. Up to now there is no method which allows an exact prediction of isotherm parameters. For an only rough estimation Polanyi's potential theory can be used. The basic equation of the potential theory reads

$$\ln V_{\text{ads}} = \ln\left(\frac{q}{\rho}\right) = A\left(\frac{E}{N}\right)^B + \ln V_0 \tag{11}$$

where V_{ads} is the adsorbed volume, ρ is the adsorbate density, E is the adsorption potential, N is a normalizing factor, V_0 is the maximum adsorbed volume, and A and B are empirical parameters.

The adsorption potential is given by

$$E = RT \ln\left(\frac{S}{c}\right) \tag{12}$$

where R is the gas constant, T is the absolute temperature, and S is the solubility of the adsorbate.

Equation (11) describes the so-called characteristic curve which theoretically should be the same for all

adsorbates. The parameters A, B and V_0 have to be determined from experimental data. In most cases the molar volume V_{m} is used as a normalizing factor (e.g. Kuennen et al. 1989; Speth & Adams 1993), but other factors such as LFER (linear free energy relationship) parameters were also proposed (Crittenden et al. 1999). If the parameters of the characteristic curve are once known, it should be possible to calculate isotherms for all other adsorbates. If, furthermore, the parameter B is 1 as found in many cases, the Freundlich parameters K and n can be directly calculated from the parameters of the characteristic curve.

$$\ln K = \frac{ART}{V_{\text{m}}} \ln S + \ln V_0 + \ln \rho \tag{13}$$

$$n = \frac{-ART}{V_{\text{m}}} \tag{14}$$

In most practical cases the isotherms of different adsorbates do not fall exactly on a single characteristic curve. Frequently, better correlations can be found for single substance classes (e.g. Crittenden et al. 1999). Exemplarily, these findings are shown in Figure 2 for the substance groups of phenols and aromatic amines adsorbed onto activated carbon F 300 (Börnick 1998; Eppinger 2000; Slavik 2006). While the class-specific characteristic curves for both adsorbate groups show acceptable correlations they do not coincide to one single curve. Furthermore, it
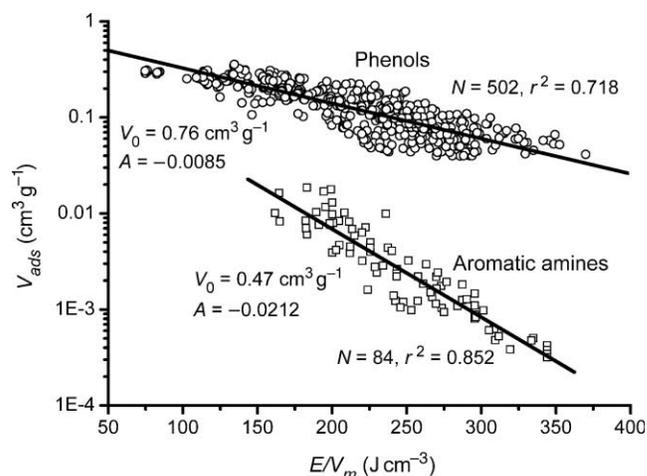

Figure 2 | Potential theory: Characteristic curves for phenols and aromatic amines adsorbed onto activated carbon F 300 (N-number of data points).

can also be seen from Figure 2 that deviations of experimental data from the characteristic curve exist even for the same substance group. Tables 3 and 4 compare experimental isotherm parameters with parameters calculated from the characteristic curves. In some cases these deviations of the calculated from the experimental n and K values compensate each other resulting in smaller errors in the predicted loadings. This can be seen from a comparison of calculated and experimental loadings for a given concentration shown in the last two columns of the tables. The mean deviation of calculated from experimental loadings was found to be 32.2% for amines (at $c = 0.01$ mg/L) and 29.6% for phenols (at $c = 0.5$ mg/L), respectively.

In general, there are numerous problems connected with the application of the potential theory. The problems result from the model itself (e.g. choice of an appropriate normalizing factor) and from the uncertainties in the substance property data needed for calculation (adsorbate solubilities and densities). These uncertainties and the fact that the characteristic curve is only valid for a defined adsorbent are the main factors limiting the applicability of the potential theory as a prediction tool.

In our own investigations, for the substance groups of phenols and aromatic amines an alternative approach was

found to give results which are comparable to the results of the potential theory. This approach is based on a normalized Freundlich equation written as

$$q = K^* \left(\frac{c}{S}\right)^{n^*} \tag{15}$$

where K^* is a modified Freundlich coefficient and n^* is a mean Freundlich exponent valid for all considered adsorbates. The latter implies that the adsorption characteristics of the included adsorbates are not extremely different. The quality of the correlation and the prediction errors can be seen from Figure 3, Table 5, and Table 6. The mean deviation of calculated from experimental loadings were found to be 40.5% for amines (at $c = 0.01$ mg/L) and 22.3% for phenols (at $c = 0.5$ mg/L), respectively.

Table 3 | Application of the potential theory to adsorption of phenols onto activated carbon F 300: Comparison of experimental and calculated Freundlich isotherm parameters and loadings at $c = 0.5$ mg/L. K in (mg/g)/(mg/L)^n, q in mg/g

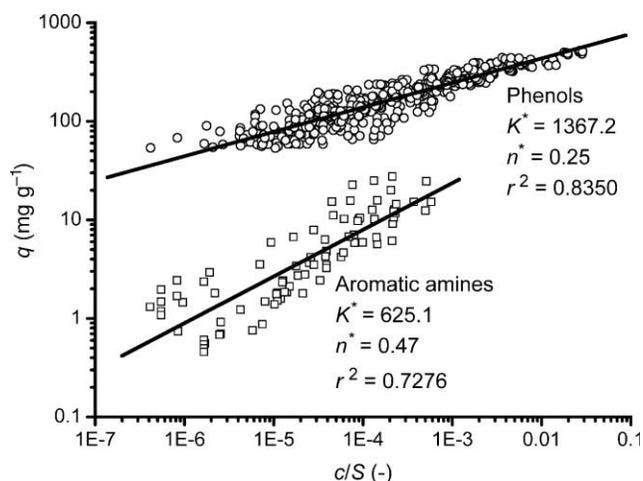| Adsorbate	K_{exp}	K_{calc}	n_{exp}	n_{calc}	q_{exp}	q_{calc}
Phenol	75.7	55.0	0.26	0.24	63.2	46.7
2-Chlorophenol	201.9	143.0	0.18	0.20	178.2	124.3
2-Nitrophenol	140.7	195.5	0.31	0.22	113.5	167.3
2-Methylphenol	192.4	101.3	0.13	0.20	175.8	88.0
3-Chlorophenol	113.9	118.1	0.25	0.21	95.8	102.3
3-Nitrophenol	119.1	134.3	0.24	0.22	100.8	114.9
4-Chlorophenol	127.7	115.6	0.22	0.21	109.6	99.7
4-Nitrophenol	125.8	139.5	0.27	0.22	104.3	119.6
4-Methylphenol	192.4	106.7	0.18	0.20	169.8	92.8
2,4-Dichlorophenol	269.3	236.0	0.15	0.18	242.7	208.6
2,4-Dinitrophenol	189.2	280.2	0.27	0.19	156.9	245.4
2,4,6-Trichlorophenol	279.4	388.4	0.20	0.18	243.2	343.4

Table 4 | Application of the potential theory to the adsorption of aromatic amines onto activated carbon F 300: Comparison of experimental and calculated Freundlich isotherm parameters and loadings at $c = 0.01$ mg/L. K in (mg/g)/(mg/L)^n, q in mg/g

Adsorbate	K_{exp}	K_{calc}	n_{exp}	n_{calc}	q_{exp}	q_{calc}
2-Nitroaniline	24.0	14.1	0.61	0.55	1.45	1.14
2,5-Dichloroaniline	92.7	31.1	0.74	0.50	3.07	3.14
3,4-Dichloroaniline	56.3	36.4	0.47	0.43	6.46	4.94
2-Chloro-5-nitroaniline	99.0	86.5	0.59	0.46	6.54	10.46
4-Methyl-2-nitroaniline	73.5	71.9	0.55	0.45	5.84	8.97

Figure 3 | Adsorption isotherms of phenols and aromatic amines plotted according to the normalized Freundlich Equation (N-number of data points). Adsorbent: Activated carbon F 300.

Table 5 | Normalized Freundlich isotherm for phenols adsorbed onto activated carbon F 300: Comparison of experimental and calculated loadings at $c = 0.5$ mg/L. $K^* = 1367.2$ mg/g, $n^* = 0.25$

Adsorbate	q_{exp} (mg/g)	q_{calc} (mg/g)
Phenol	63.2	67.9
2-Chlorophenol	178.2	111.5
2-Nitrophenol	113.5	162.6
2-Methylphenol	175.8	90.6
3-Chlorophenol	95.8	90.5
3-Nitrophenol	100.8	106.7
4-Chlorophenol	109.6	92.4
4-Nitrophenol	104.3	110.3
4-Methylphenol	169.8	94.9
2,4-Dichlorophenol	242.7	140.4
2,4-Dinitrophenol	156.9	158.2
2,4,6-Trichlorophenol	243.2	216.2

Mixture adsorption

In principle, mixture equilibria can be predicted from single-solute isotherm data by using the IAS theory as discussed above. But in the case of drinking water treatment, problems arise from the fact that DOM is not a defined mixture. Therefore, neither the concentrations nor the isotherm parameters of the different DOM components (fractions) are known. In order to apply the IAS theory to such a system, it must be formally transformed into a mixture of a limited number of components with known concentrations. This can be done by using the so-called adsorption analysis (Sontheimer et al. 1988; Johannsen & Worch 1994). The principle of adsorption analysis consists in defining DOM fractions (mostly 3 to 5) with different adsorption behaviour characterized by assigning isotherm

Table 6 | Normalized Freundlich isotherm for aromatic amines adsorbed onto activated carbon F 300: Comparison of experimental and calculated loadings at $c = 0.01$ mg/L. $K^* = 625.1$ mg/g, $n^* = 0.47$

| Adsorbate	q_{exp} (mg/g)	q_{calc} (mg/g)
2-Nitroaniline	1.45	2.55
2,5-Dichloroaniline	3.07	3.67
3,4-Dichloroaniline	6.46	3.24
2-Chloro-5-nitroaniline	6.54	8.24
4-Methyl-2-nitroaniline	5.84	7.62

parameters (different K values, constant n value). Then, for the water under consideration an isotherm has to be determined using DOC as a concentration measure. Finally, a search routine based on the IAS theory is used to find that concentration distribution of the DOM fractions which allows the best description of the experimental data. In numerous studies this approach was successfully applied to characterize raw water (e.g. Müller et al. 1996). As an example, the results of the adsorption analysis of Elbe River water are shown in Figure 4. Results of adsorption analysis can be used as input parameters for DOC breakthrough curve prediction as will be shown later.

The typical situation in GAC systems is that both trace pollutants and DOM are simultaneously adsorbed onto activated carbon. In general, the presence of DOM decreases the capacity for micropollutants as exemplarily shown in Figure 5 for atrazine adsorbed onto activated carbon F 300. In this context it has to be noted that the DOM concentration measured as DOC is much higher (mg/L level) than the typical micropollutant concentrations (μg/L or ng/L level). Therefore, competition effects can be expected even for strongly adsorbable micropollutants.

It would seem at first consideration a simple matter to add the trace pollutant to the fictive-component mixture as a further component and to apply the IAST to this system in order to characterize the pollutant adsorption in presence of DOM. However, this kind of prediction fails in many cases. There are manifold reasons for this failure, e.g.
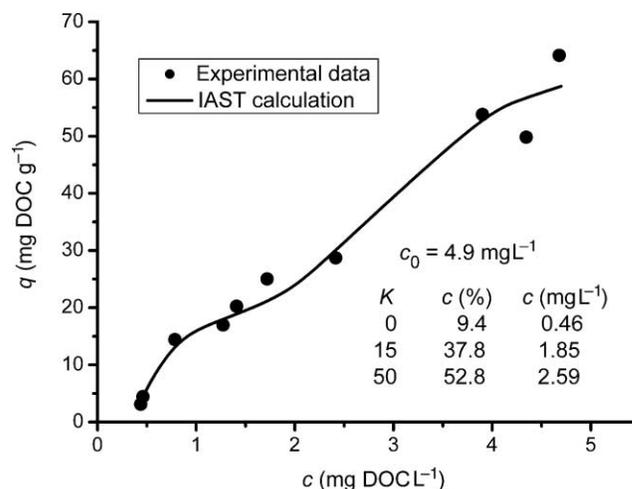
Figure 4 | Results of an adsorption analysis of Elbe River water (K in $(mg/g)/(mg/L)^n$, $n = 0.2$ for all adsorbable components). Adsorbent: Activated carbon F 300.
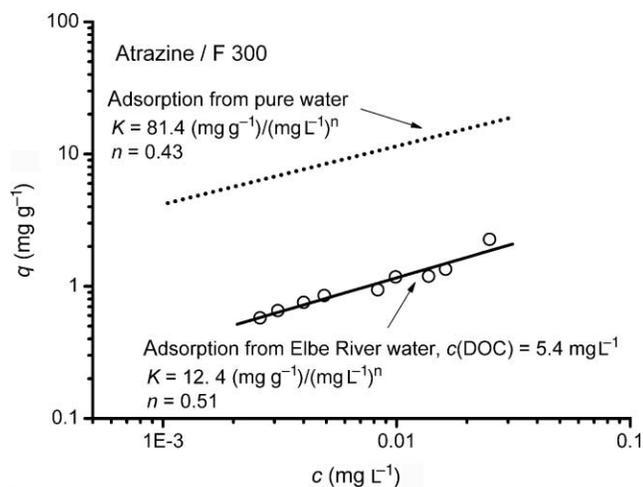
Figure 5 | Isotherms of atrazine adsorbed from pure water and Elbe River water onto activated carbon F 300.

(i) The thermodynamic IAST requires the use of molar concentrations, but this is not possible for DOM because of the unknown structure and molecular weights of the DOM fractions. As long as only fictive components are considered, the use of DOC concentrations (= mass concentrations) is not problematic because the same error but in reverse direction occurs in backward (adsorption analysis) and forward (IAST prediction) calculations. In contrast, in the case of mixture adsorption of a micropollutant and different fictive DOM components the use of mass concentrations instead of molar concentrations can lead to erroneous IAST predictions, even when micropollutant concentration is given as DOC.

(ii) The IAST postulates the absence of intermolecular interactions (ideal behaviour), but it cannot be excluded that micropollutants interact with DOM to form complexes. Moreover, adsorbed organic matter can also act as adsorbent for hydrophobic molecules.

(iii) The IAST postulates further that there is no full or partial exclusion of components from the adsorption sites at the inner adsorbent surface. The latter condition might not be fulfilled in the case of larger DOM molecules (size exclusion).

(iv) In the case of sequential loading of GAC with DOM and trace pollutant, the latter can be excluded from pores by pore blockage caused by DOM. A detailed discussion on the effects of DOM preloading on

micropollutant adsorption can be found in the paper of Weber (2004).

To overcome most of these problems a simple approach was developed which is based on the correction of the IAST input parameters, in particular on the correction of the isotherm parameters of the micropollutant (Rabolt et $al.$ 1998). To do this correction, a micropollutant isotherm has to be measured using the water under consideration as matrix. A subsequent IAST fitting procedure under variation of the micropollutant Freundlich parameters yields "corrected" isotherm parameters which can be used in further IAST predictions for the same adsorbate-adsorbent system.

This principle is shown in Figure 6 for atrazine adsorption from Elbe River water. If using the single-solute isotherm parameters determined for adsorption from pure water ($K = 52$ (mg/g)/(mg/L)^n, $n = 0.43$) together with the results of the adsorption analysis of the Elbe River water, the predicted mixture isotherm of atrazine is about one order of magnitude lower than the experimental data. Using a parameter set of $K = 39$ (mg/g)/(mg/L)^n and $n = 0.16$ found by the proposed correction method, the experimental data can be described satisfactorily by the IAST. It has to be noted that all concentrations and K values are related to C to get the same basis as for the DOC concentration.

A stronger adsorption of micropollutants in comparison to the conventional IAST prediction was experimentally found not only for atrazine but also for other adsorbates, such as
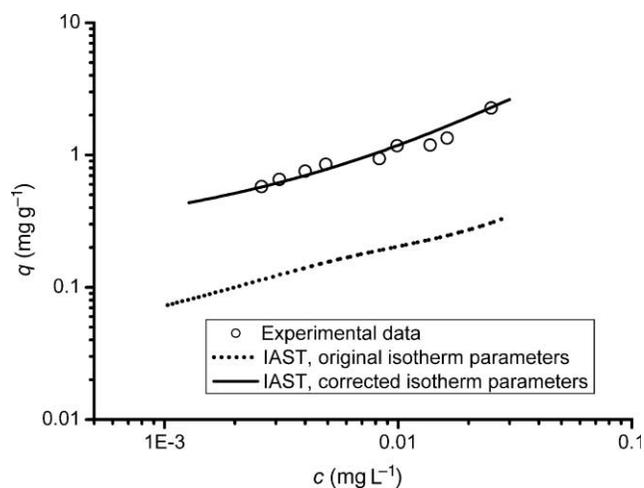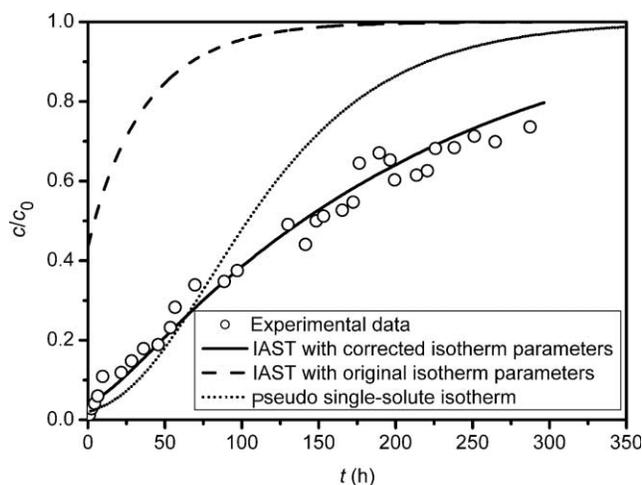

Figure 6 | Adsorption of atrazine from Elbe River water onto activated carbon F 300: Prediction of mixture adsorption by IAST with different input data sets.

trichloroethene, 1,1,1-trichloroethane, naphthaline-2,7-disulfonate, 4-aminonaphthalene sulfonate, and diurone (Rabolt 1998). In all these cases the IAST markedly overestimates the competition between micropollutants and DOM. That means that the conventional IAST provides a conservative estimate of micropollutant adsorption. Up to now, this effect is not fully understood and requires further research.

The corrected parameter set can also be used in BTC calculations for the same mixture adsorbate system. This is demonstrated in Figure 7. In this figure, an atrazine BTC determined in a lab-scale adsorber is compared with BTCs calculated using the LDF model with different approaches for equilibrium calculation. The kinetic parameters were estimated by methods presented in the next section of this paper. According to the overestimation of the competitive effect by the conventional IAST as shown for the isotherm in Figure 5, a very early breakthrough is predicted by using the original isotherm parameters of atrazine in the mixture equilibrium calculation. On the other hand, the proposed modification of Freundlich parameters within the IAST framework as presented above allows a much better prediction of the micropollutant breakthrough in presence of DOM.

In this context, it is worthwhile to evaluate the use of a pseudo single-solute isotherm for micropollutant adsorption in presence of DOM within a single-solute BTC model. In principle, the mixture isotherm of atrazine shown in Figure 5 can be described by the Freundlich isotherm

Figure 7 | Experimental and calculated breakthrough curves of atrazine adsorbed from Elbe River water onto activated carbon F 300: Comparison of pseudo single-solute model and different IAST approaches.

equation. In this case the parameters would be $K = 12.4$ and $n = 0.51$. As can be seen in Figure 7, this pseudo single-solute approach provides better results as the BTC model with the conventional IAST but cannot describe the BTC as good as the multi-solute BTC model with corrected isotherm parameters. This finding clearly indicates that the consideration of DOM presence only by modified single-solute isotherm parameters and neglecting all competitive effects in the BTC model is a too strong simplification of the complex processes in the GAC bed.

PREDICTION OF RATE PARAMETERS

As shown before, two mass transfer parameters are required to calculate breakthrough curves by using the described models. Since D_S can be calculated from $k_S a_V$ and vice versa by Equation (7), the following discussion is restricted to the LDF model with the mass transfer parameters $k_F a_V$ and $k_S a_V$.

Mass transfer coefficients for film diffusion can be calculated with adequate accuracy from empirical correlations. The general form of these correlations is

$$Sh = f(Re, Sc) \tag{16}$$

where Sh is the Sherwood number, Re is the Reynolds number, and Sc is the Schmidt number.

Table 7 lists a selection of equations which can be used for predicting film diffusion mass transfer coefficients. Additionally to several process parameters the liquid-phase diffusion coefficient of the adsorbate is needed for using these correlations. If this adsorbate-specific parameter is not available from data bases, it can be estimated by an empirical equation proposed in a previous paper (Worch 1993):

$$D_L = \frac{3.595 \times 10^{-14} T}{\eta M^{0.53}} \tag{17}$$

where T is the absolute temperature, η is the dynamic viscosity of water (in Pa s), and M is the molecular weight.

In principle, the given equations can also be used in adsorbate systems containing DOM. Since all other data are known, the only problem arises from the uncertainties regarding the diffusion coefficients of the DOM fractions and the molecular weight of these fractions, respectively.

Table 7 │ Correlations for estimating film diffusion mass transfer coefficients (adapted from Smith & Weber 1989, extended)

Authors	Correlation	Validity range
Williamson *et al.* (1963)	$Sh = 2.4\varepsilon_b Re^{0.34}Sc^{0.42}$	$0.08 < Re < 125; 150 < Sc < 1,300$
Wilson & Geankoplis (1966)	$Sh = 1.09\varepsilon_b^{-2/3}Re^{1/3}Sc^{1/3}$	$0.0016 < \epsilon_b Re < 55; 950 < Sc < 70,000$
Kataoka *et al.* (1972)	$Sh = 1.85[(1-\varepsilon_b)/\varepsilon_b]^{1/3}Re^{1/3}Sc^{1/3}$	$Re\,[\varepsilon_b/(1-\varepsilon_b)] < 100$
Dwivedi & Upadhyay (1977)	$Sh = (1/\varepsilon_b)[0.765(\varepsilon_b Re)^{0.18} + 0.365(\varepsilon_b Re)^{0.614}]Sc^{1/3}$	$0.01 < Re < 15,000$
Gnielinski (1978)	$Sh = \left[2 + (Sh_L^2 + Sh_T^2)^{0.5}\right][1 + 1.5(1-\varepsilon_b)]$	$Re\,Sc > 500; Sc < 12,000$
	$Sh_L = 0.644Re^{1/2}Sc^{1/3}$	
	$Sh_T = (0.037Re^{0.8}Sc)/1 + 2.443Re^{-0.1}(Sc^{2/3} - 1)$	
Ohashi *et al.* (1981)	$Sh = 2 + 1.58Re^{0.4}Sc^{1/3}$	$0.001 < Re < 5.8$
	$Sh = 2 + 1.21Re^{0.5}Sc^{1/3}$	$5.8 < Re < 500$
	$Sh = 2 + 0.59Re^{0.6}Sc^{1/3}$	$Re > 500$
Vermeulen *et al.* (1973)	$k_F a_V = 2.62(D_L v_l)^{0.5}/d_P^{1.5}$	$\varepsilon_b \approx 0.4$

$Re = v_l d_p/\varepsilon_b \nu$, $Sh = k_F d_p/D_L$, $Sc = \nu/D_L$, d_P–particle diameter, ν-kinematic viscosity.

Therefore, assumed values have to be used to calculate diffusion coefficients by Equation (17). Although the molecular weight of DOM generally exhibits a broad distribution, the main fraction seems to fall into the range of about 500 to 1,500 g/mol. Therefore, values in this order of magnitude should be used for D_L estimation.

The use of assumed molecular weight values for DOM fractions can be accepted because it is known from the experience that the BTC curves under typical process conditions are not very sensitive to small $k_F a_V$ changes. Table 8 compares $k_F a_V$ values calculated for 500 and 1,500 g/mol using the Wilson-Geankoplis correlation together with Equation (17). For the conditions given in Table 1, the increase of molecular weight from 500 g/mol to 1,500 g/mol would decrease $k_F a_V$ about 30%. Under the conditions used in the BTC simulation (Tables 1 and 2) the breakthrough time for a defined normalized concentration of $c/c_0 = 0.1$ would decrease only about 4%.

Table 8 │ Influence of DOM molecular weight on calculated diffusion coefficient D_L and volumetric film diffusion mass transfer coefficient $k_F a_V$ (calculated using Equation (17) and Wilson-Geankoplis correlation, process parameters from Table 1)

Molecular weight, M (g/mol)	Diffusion coefficient, D_L (m²/s)	Film diffusion mass transfer coefficient, $k_F a_V$ (1/m)
500	2.9×10^{-10}	1.6×10^{-2}
1,500	1.6×10^{-10}	1.1×10^{-2}

In contrast to $k_F a_V$, $k_S a_V$ is typically determined from kinetic experiments under conditions where only surface diffusion is rate-limiting (high stirrer velocity in batch experiments or high flow rate in differential fixed-bed reactors). In order to avoid this very time-consuming determination, an empirical equation based on the results of more than 100 kinetic experiments with single sorbates and different activated carbons was developed as described in previous papers (Heese & Worch 1997a,b; Sierig 1999).

$$k_S a_V = 0.00129\sqrt{\frac{D_L c_0}{r_P^2 q_0}} \qquad (18)$$

The empirical factor in the Equation (18) is valid in case of using the units m²/s for D_L, mg/L for c_0, mg/g for q_0, and m for r_P. The correlation according to Equation (18) is shown in Figure 8. In combination with Equation (7) this empirical correlation can also be used for estimating D_S.

In general, this correlation gives acceptable results for defined micropollutants. In contrast, the calculated values for DOM fractions are often too high in comparison with parameters estimated by BTC fitting. Figure 9 shows a DOC breakthrough curve of Elbe River water determined in a lab-scale adsorber filled with 4.4 g activated carbon F 300 ($r_P = 0.225$ mm, $v_l = 8$ m/h). Assuming a DOM molecular
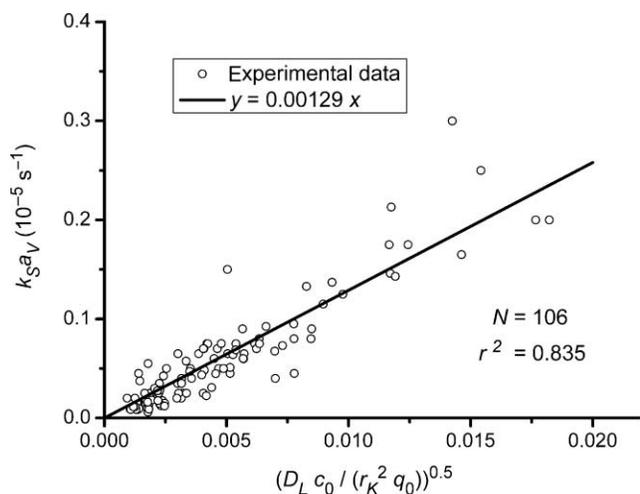
Figure 8 │ Correlation of internal mass transfer coefficients according to Equation (18).

weight of 1,000 g/mol and assuming the same DOM fractions and percentage concentration distribution as shown in Figure 4, mass transfer coefficients $k_S a_V$ of 3.4×10^{-5} 1/s and 2.1×10^{-5} 1/s respectively, are found from Equations (17) and (18) for the adsorbable components 2 and 3. These $k_S a_V$ values are nearly one order of magnitude higher than the mass transfer coefficients found by curve fitting (see Figure 9). Comparable results were also found for other water samples. Therefore, a specific correlation was proposed for DOM under the assumption that the mass transfer coefficients are the same for all DOM fractions (Hess 2001). The correlation found from kinetic
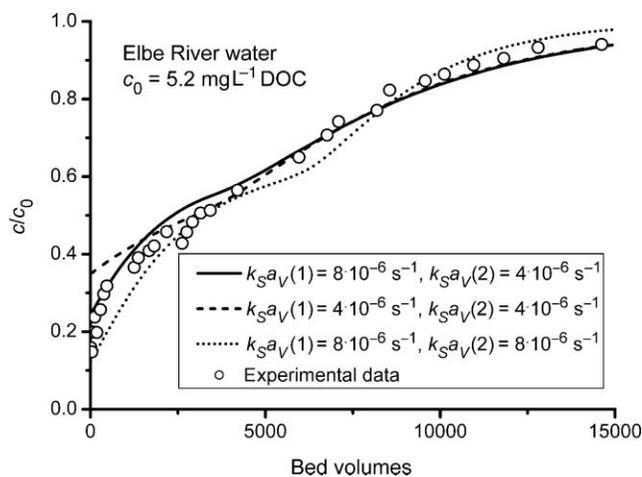

Figure 9 │ DOC breakthrough curve calculation for Elbe River water: Variation of the intraparticle mass transfer coefficients of the fictive components.

and column experiments with DOM containing water samples from different sources is given by

$$k_S a_V = a + b \frac{c_0}{r_P^2} \qquad (19)$$

where c_0 is the total concentration of all adsorbable DOM fractions expressed as DOC and r_P is the adsorbent particle radius. The empirical parameters were found to be $a = 3 \times 10^{-6}$ 1/s and $b = 3.215 \times 10^{-14}$ (m² L)/(mg s).

For the example discussed above the correlation provides a $k_S a_V$ of 6.0×10^{-6} 1/s. The order of magnitude of this $k_S a_V$ is in better agreement with the fitted values than the data from Equation (18). On the other hand, the model calculations presented in Figure 9 show clearly that graduated mass transfer coefficients with higher value corresponding to lower adsorbability describe the BTCs better than an uniform coefficient for both components. Nonetheless, Equation (19) can be used to find approximate $k_S a_V$ values for DOM.

In view of interactions between DOM and micropollutants during mass transfer different observations were made. As can be derived from our own experiences (e.g. Figure 7) and published results (e.g. Smith & Weber 1989) the influence of DOM on micropollutant mass transfer is often negligible. Therefore, the mass transfer coefficients measured or calculated for single-solute adsorption can be used for mixture systems, too. On the other hand, there are indications that preloading of activated carbon with DOM decreases the external and internal mass transfer rates of micropollutants (Weber 2004). The slowdown factors found in this study for trichloroethylene after 4 weeks preloading time were about 3 for film diffusion and 5 to 10 for intraparticle diffusion. It can be expected that the magnitude of this effect depends on the preloading time, the adsorbent type, and the nature of the DOM/micropollutant system. But up to now there are not enough data available to allow drawing general conclusions or integrating this effect into the prediction tools.

CONCLUSIONS

The evaluation of published adsorption models clearly shows that the main question in applying mathematical models for adsorber design is not the question which model has to be used but rather how to get the input parameters

required for calculation. In the case of equilibrium parameters there is up to now no satisfactory way to avoid the experimental determination of isotherms. The potential theory allows only a rough estimation of single-solute isotherm parameters whereby class-specific correlations are often of higher quality than general correlations. This advantage of class-specific correlations is suspended by the higher effort to find characteristic curves for each substance group. Results comparable to the potential theory can be found by using a normalized Freundlich isotherm. This approach is easier to handle, but underlies the same limitations as the potential theory.

The IAS theory allows predicting mixture adsorption equilibrium but requires isotherm parameters of the mixture components. In the case of DOM, the unknown mixture has to be formally transformed to a "known mixture" by applying the adsorption analysis to an experimental DOC isotherm. That means that in each case the raw water has to be characterized by the adsorption analysis prior to BTC calculation for DOM. In the case of simultaneous adsorption of micropollutants and DOM the IAST often fails for several reasons. A correction of micropollutant isotherm parameters used in IAST calculation can improve the description of micropollutant adsorption in presence of DOM.

In contrast to the equilibrium data, mass transfer coefficients for single solutes and approximately also for DOM can be predicted from empirical correlations without any additional experiments. But it has to be noted that the extent of experience with predicting film and internal mass transfer coefficients is very different. Whereas correlations for film diffusion are well-known and widely used, up to now only little studies have dealt with prediction of intraparticle mass transfer coefficients. To verify the proposed correlations for single micropollutants as well as for DOM, more experimental studies with different adsorbate-adsorbent systems are necessary. In particular, more research on preloading effects is required.

ACKNOWLEDGEMENTS

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