Modelling the uptake of natural organic matter (NOM) by different granular sorbent media

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ABSTRACT

The removal of natural organic matter (NOM) by four different granular sorbent media, activated carbon, an anion exchange resin, activated alumina and granular ferric hydroxide, respectively, was investigated. Isotherm data, kinetic parameters and column breakthrough curves were determined. Adsorption analysis was applied to describe sorption equilibria, and the film-homogeneous surface diffusion model was used to predict NOM uptake in fixed-bed columns. The results show that NOM adsorption by activated carbon and activated alumina could be modelled quite well by the approach used. NOM uptake by the anion exchange resin could be predicted with respect to capacity while two kinetic parameters were obviously not sufficient to describe the rate of uptake correctly. NOM adsorption by granular ferric hydroxide proved to be a very slow process that could not be predicted using parameters derived from batch data.

Key words | activated alumina, activated carbon, adsorption, granular ferric hydroxide, humic substances, ion exchange resin, predictive model

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INTRODUCTION

Sorption behaviour of natural organic matter

Various sorbent media are applied in drinking water treatment in order to remove undesired compounds. In some cases the primary task is the reduction of natural organic matter (NOM) concentration, but most often the main focus is directed towards the removal of micropollutants. Since NOM is always present in natural waters it will then interfere with the uptake of the target compounds. Therefore, the behaviour of NOM must be taken into account when describing technical sorption processes.

Sorption equilibria need to be studied in order to estimate the ultimate capacity of the sorbent material for a given solute. For single substances the equilibrium data usually follow a single curve. NOM, however, representing a multi-solute system with unknown composition, can only be described using sum parameters like dissolved organic carbon (DOC) or UV-absorbance at 254 nm (SAC-254). Equilibrium data for a NOM sample relate the sum of the solid-phase concentrations to the sum of the liquid-phase concentrations of all NOM compounds. For activated carbon, such an overall isotherm shows two distinct differences compared with a single-solute isotherm: the shape and the influence of the initial concentration (Sontheimer *et al.* 1988).

In order to account for the heterogeneity of NOM with respect to carbon adsorption, Frick & Sontheimer (1983) suggested dividing such mixtures into a strongly adsorbable, a weakly adsorbable and a non-adsorbable pseudo-component. Overall isotherm data are then described as the result of competitive adsorption of the adsorbable fractions using the ideal adsorbed solution theory (IAST) as an adsorption model. Freundlich adsorption parameters K_i and n_i and the initial concentrations of the fictive components $C_{o,i}$ are determined from measured isotherm data by nonlinear regression. Although the parameter set obtained from this fictive-component analysis is not always unique, Johannsen *et al.* (1992) have proved that several characteristics of NOM adsorption on activated carbon, for example the effect of the initial concentration on the overall isotherm, can be predicted by this approach. In order to

avoid ambiguous solutions, Smith (1994) suggested a searching procedure for the adjustable parameters where the number of components is increased stepwise. An alternative modelling approach was proposed by Matsui et al. (1998) where normal distributions of the Freundlich isotherm coefficient K are assumed. Unfortunately it is quite difficult to use the resulting parameters for the comparison of different sorption systems.

The rate of NOM uptake by sorbent particles whose mean diameter is on the order of 1 mm, is assumed to be dependent on external (film) diffusion and internal mass transfer. Both the film-surface diffusion model and the film-pore diffusion model have been used to describe adsorption kinetics of NOM. Of the two kinetic parameters, a mean film transfer coefficient can be determined experimentally, for example by the short fixed-bed technique, without accounting for adsorption equilibria. This parameter depends on the bulk diffusivities of the adsorbable NOM species and thus on their average molecular size. Surface or pore diffusion coefficients must be determined by fitting the respective model to experimental data. When batch adsorption tests are evaluated, only average kinetic parameters can be obtained for the adsorbable species (Sontheimer et al. 1988), while an analysis of column data may yield individual intraparticle diffusivities (Smith 1994).

Uptake by activated carbon

Activated carbon is the sorbent material most widely used in drinking water treatment. There are several physical and chemical parameters that affect NOM adsorption on activated carbon. The ultimate capacity for NOM seems to be primarily dependent on the combined effects of pore structure and size of the NOM species; that is, size exclusion of large NOM molecules from micropores is likely to occur, as discussed by Johannsen et al. (1993), Newcombe et al. (1997) and Pelekani & Snoeyink (1999). This agrees with the observation of Kilduff et al. (1996) and Matsui et al. (1998) that smaller-sized compounds are adsorbed to a greater extent on an adsorbent mass basis. However, it is not possible yet to state definitely whether size exclusion is the only reason for the preferential removal of small NOM compounds, because these species might also compete more successfully for sorption sites accessible for all compounds.

Activated carbon is usually applied as a granular material (GAC) in fixed-bed columns with empty bed contact times (EBCT) of 5–30 min. From the kinetic parameters, Fettig & Sontheimer (1987) concluded that intraparticle diffusion is the rate-controlling process for NOM adsorption. Hubele (1985) could successfully predict NOM breakthrough curves for technical-scale adsorbers, based on fictive-component analysis parameters and kinetic coefficients determined from batch tests.

Uptake by anion exchange resins

Since a large fraction of NOM can be characterized as anionic polyelectrolytes, macroporous anion exchange resins are, in principle, well suited for NOM removal. Brattebø et al. (1987) found that strong base resins were superior to weak base resins with respect to capacity. Ion exchange is considered the dominant removal mechanism while surface adsorption only contributes to the removal of smaller NOM species to some extent (Fu & Symons 1990).

In several studies, the bottle point technique with 7–8 days of contact time was used to determine sorption isotherms. In one study, however, the resin was found not to be saturated even after 16 days (Fettig & Ødegaard 1989). Isotherms for the sorption of NOM on anion exchange resins have shown that there is a non-removable fraction ranging from <10% to about 40% that primarily consists of small NOM species (Fu & Symons 1990). In order to describe isotherm data, Brattebø et al. (1987) used the Freundlich equation, while Fettig & Ødegaard (1989) suggested applying the Langmuir equation modified by introducing a non-removable fraction.

Kinetic parameters for NOM uptake by resins have been determined from batch test data according to the description of activated carbon systems. Although internal mass transfer is rate controlling, the uptake of NOM by resins is significantly faster than NOM uptake by GAC in batch systems (Bolto et al. 2002).

Uptake by metal oxides

Both activated alumina (most often γ-Al$_2$O$_3$) and granular ferric hydroxide have been investigated with respect to sorption of NOM. In aqueous solution their surface is

generally covered with hydroxyl groups where weak organic acids are assumed to be bound according to a ligand exchange mechanism (Stumm & Morgan 1981). Davis & Gloor (1981) found that NOM removal by γ-Al$_2$O$_3$ was dependent on pH; maximum solid-phase concentrations were obtained for pH = 5–6.5. High molecular weight compounds were preferentially removed, while a portion of 20–60% with respect to DOC was regarded as non-adsorbable. Lambert & Graham (1995) found curved isotherms indicating different adsorbabilities of the organic species with respect to γ-Al$_2$O$_3$. Fettig (1999a) evaluated sorption equilibria of nine different NOM samples from Norway on γ-Al$_2$O$_3$ using fictive-component analysis. On average, 50% of the total NOM was characterized as strongly adsorbable, 30% as weakly adsorbable and 20% as non-adsorbable.

Korshin *et al.* (1997) showed with iron-oxide-coated sand and Gu *et al.* (1995) demonstrated with powdered iron oxide that a large fraction of NOM can be bound to iron oxide surfaces. Technical application of this material as a sorbent medium requires surface areas of $>100\,m^2\,g^{-1}$. Recently a granular ferric hydroxide product called GEH with a surface area of $280\,m^2\,g^{-1}$ became commercially available in Germany which has the formula β-FeOOH. Teermann & Jekel (1999) observed that NOM removal by this sorbent was only little dependent on pH. Higher molecular weight compounds were preferentially removed, while a fraction of about 5–10% with respect to DOC was regarded as non-adsorbable.

This study was conducted to compare the uptake of the same type of NOM by four different granular sorbent media, activated carbon, an anion exchange resin, activated alumina and granular ferric hydroxide, respectively, under controlled pH conditions, and to evaluate the applicability of existing models in order to describe equilibrium data and predict NOM removal in fixed-bed columns.

EXPERIMENTAL METHODS

NOM samples and reagents

NOM-rich water samples were collected from the Mecklenbruch swamp (Solling region, Northern Germany) in autumn 1998, 1999 and 2000 and stored in polyethylene tanks in a dark room for up to 2 months. Prior to the studies the water was filtered through $1\,\mu m$ filters (Schleicher&Schuell) and diluted with deionized water when needed, then $2\,mmole\,l^{-1}$ NaHCO$_3$ were added, and HCl or NaOH was used to adjust pH to the desired value. All reagents were of p.a. grade (Merck, Darmstadt).

Sorbent media

Some important parameters of the sorbent media studied are given in Table 1. The commercial brand ROW 0.8 S (Norit, The Netherlands) used as a carbon sorbent was washed in a Soxhlet apparatus for several days, dried at 110°C and stored in a desiccator. Powdered carbon (d < 0.05 mm) was obtained by crushing the granules in a ball mill.

As a strong base anion exchange resin, LEWATIT S 6328 A (Bayer AG, Germany) was chosen. The resin was

Table 1 | Sorbent parameters given by the suppliers or determined in this study

Sorbent	Activated carbon	Anion exchange resin	γ-Al$_2$O$_3$	β-FeOOH
Volume mean diameter (mm)	1.18	0.55	1.82	≈ 1.0
Void fraction of particles ($-$)	0.64	0.61	0.44	0.72–0.77
BET surface area ($m^2\,g^{-1}$) resp.	900–1000	–	≤ 300	280
total exchange capacity (eq l^{-1})	–	0.80	–	–
Water content (%)	0	58–63	0	45
Packed-bed density (g cm^{-3})	0.37	0.70	0.98	1.25

conditioned with 10% NaCl and 2% NaOH solutions according to the producer's recommendations, then washed with HCl (0.01 M), centrifuged at 4000 g for 5 min and stored in a closed box.

The product COMPALOX of Martinswerke (Germany) was selected as a γ-Al_2O_3 sorbent. Powdered material (d < 0.05 mm) was obtained by crushing the granules in a ball mill. It was used after pre-washing with HCl and NaOH solutions (1 M) in order to remove Na_2O from the surface. Afterwards it was washed batchwise with deionized water until the pH of the wash water remained about neutral.

The product GEH (GEH Wasserchemie, Germany) was used as a granular ferric hydroxide sorbent. A fraction of smaller particles (d < 0.1 mm) was obtained by manual crushing.

Equilibrium studies

NOM isotherm data were determined according to the bottle point technique with powdered material, except with the ion exchange resin. Different amounts of sorbent were added to 200 ml aliquots of NOM solution and equilibrated on a shaker at room temperature (22°C) for 70 h except with the ion exchange resin where a contact time of 14 days was required. Then samples were taken from the supernatant, filtered through 0.45 μm membrane filters (Sartorius) and analysed for DOC and SAC-254. Solid-phase concentrations were calculated from a mass balance. The overall isotherm data were evaluated using the ADSA software described by Johannsen *et al.* (1992) and Sontheimer & Johannsen (1992). This program determines fictive-component parameters by non-linear simultaneous regression of up to three isotherms, based on the IAST model. The regression criterion is minimization of the sum of deviations between measured and calculated overall liquid-phase and solid-phase concentrations.

Kinetic experiments

The short fixed-bed reactor technique was used to determine external mass transfer coefficients for NOM adsorption on granular activated carbon at 22°C. Since the ratio between effluent and influent concentration for short periods of operation is evaluated here, adsorption equilibria

are not relevant and data evaluation can be based on UV-absorbance as a concentration measure. From the results, effective diffusivities of the NOM samples were calculated using Gnielinski's empirical correlation (Sontheimer *et al.* 1988). The same correlation was then used to estimate mean film transfer coefficients for other flow rates and sorbent particle sizes, respectively. Details of this approach are given by Fettig & Sontheimer (1987).

Intraparticle diffusivities were determined from concentration-vs.-time curves measured in 2 l glass beakers where granular sorbent material was exposed to a high liquid flow rate in a basket impeller. Based on the results from fictive-component analysis, the homogeneous surface diffusion model was fitted to the experimental data assuming the same value of the surface diffusivity for the adsorbable components.

Column runs

The column tests were conducted with two glass columns, 3 cm in diameter and 50 cm high, which were operated in series. Each column was filled with 25 cm of sorbent material that was backwashed prior to the experiment in order to remove fines. The NOM solution was pumped to a constant head tank from where it was flowing through the columns at a constant rate. Influent and effluent samples were analysed for pH, DOC and SAC-254.

Analytical methods

pH was measured by a Type 539 pH-meter (WTW). Spectral absorption coefficients (SAC) at 254 nm were determined by a Type 1201 UV-spectrophotometer (Milton Roy) after acidifying the samples to pH <3, and DOC values were measured using the principle of low temperature oxidation (liqui-TOC, Elementar).

RESULTS AND DISCUSSION

NOM characterization

Some important characteristics of the NOM samples used are given in Table 2. While the data are similar for the 1998 and 1999 sampling periods, the NOM concentration was

Table 2 | NOM characteristics for the different sampling periods

Sampling date	14/10/1998	21/10/1999	3/11/2000
Conductivity ($\mu S\,cm^{-1}$)	64	75.5	92.5
pH ($-$)	3.6	3.4	3.7
Turbidity (NTU)	0.7	1.1	1.6
SAC-254 (m^{-1})	175	195	262
DOC concentration ($mg\,l^{-1}$)	33.9	43.9	55.5
Effective diffusivity ($10^{-10}\,m^2\,s^{-1}$)	0.93 ± 0.08	0.80 ± 0.07	0.64 ± 0.10

considerably higher in 2000. According to the effective diffusivities derived from kinetic experiments as described above, which were determined from six single tests each, the average molecular size had also increased. Since the water was taken from the same source it is assumed that the main NOM characteristics were yet similar.

Uptake by activated carbon

Figure 1 shows isotherms obtained with two different initial NOM concentrations from the first sampling period. Maximum solid-phase DOC concentrations of $>50\,mg\,g^{-1}$ were found while the isotherms' shape and the effect of the initial concentration indicate that NOM is adsorbed as a heterogeneous mixture. Fictive-component analysis was
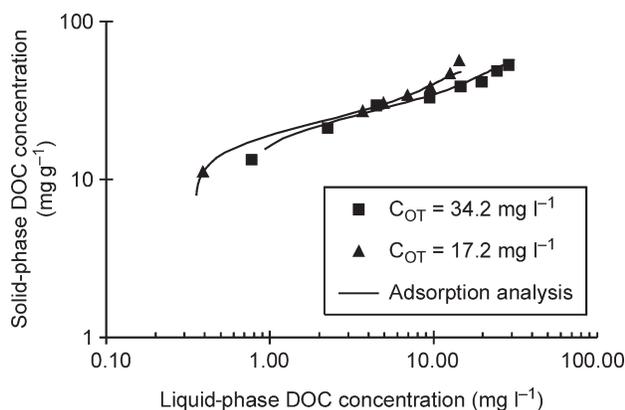
Figure 1 | Isotherms of NOM from the first sampling period on activated carbon for two initial concentrations at pH = 7.0.

applied assuming two adsorbable and one non-adsorbable component. In order to reduce the number of adjustable parameters, the n-values of the adsorbable components were assigned a value of n = 0.2. As demonstrated by Sontheimer *et al.* (1988) a good description of multi-component adsorption equilibria can be obtained by preadjusting n = 0.2 for both NOM and wastewater systems. Thus four parameters had to be determined when fitting the competitive adsorption model to the data of both isotherms simultaneously. The results are given in Table 3 together with the parameters obtained with the other sorbent media. The calculated isotherms shown in Figure 1 illustrate that the experimental data can be described reasonably well by this approach.

Figure 2 shows experimental and calculated data from an adsorption rate test. The calculated curve represents the best fit of the kinetic model to the data, while the intraparticle diffusivity determined here is given in Table 3. The uptake of NOM in activated carbon columns was only simulated in this study. For both fictive components the calculated Biot number was >50 indicating that intraparticle diffusion is the rate-controlling step.

Uptake by an anion exchange resin

Figure 3 shows isotherms obtained with three different initial NOM concentrations from the second sampling period. For high solid-phase concentrations the curves almost coincide while they split up for low residual liquid-phase concentrations. This finding can be attributed to a more homogeneous sorption behaviour of NOM with respect to the resin, except that a small fraction does not seem to be removable. Therefore, fictive-component analysis assuming only one adsorbable and one non-adsorbable component was applied. The results are given in Table 3, and the calculated isotherms shown in Figure 3 illustrate that a fairly good description of the experimental data is obtained by this approach.

Batch kinetic tests for two initial concentrations were conducted over a period of 350 h. Constant residual concentrations were reached after about 300 h (12.5 days). The intraparticle diffusivities derived from the rate data are given in Table 3. The uptake of NOM in a resin column was investigated for two bed depths, 25 cm and 50 cm. In

Table 3 | Results of fictive-component analysis (K_i, n are the Freundlich coefficients and $C_{O,i}/C_{OT}$ are the initial fractions of the fictive components), and kinetic parameters derived from batch test data

| Sorbent | Fictive components | | | Film transfer coefficient [at superficial velocity v_F] (10^{-5} m s^{-1}) | Surface diffusivity [for initial DOC concentration C_{OT}] (10^{-14} m^2 s^{-1}) |
	Non-adsorbable	Weakly adsorbable	Strongly adsorbable		
Activated carbon	$K_1 = 0$	$K_2 = 18$; n = 0.2	$K_3 = 33$; n = 0.2	0.41 [5.0 m h^{-1}]	1.2 [17.1 mg l^{-1}]
	$C_{O,1}/C_{OT} = 2\%$	$C_{O,2}/C_{OT} = 47.6\%$	$C_{O,3}/C_{OT} = 50.4\%$		
Anion exchange resin	$K_1 = 0$	–	$K_2 = 4.8$; n = 0.57	0.70 [4.6 m h^{-1}]	0.9 [41.1 mg l^{-1}]
	$C_{O,1}/C_{OT} = 3.6\%$	–	$C_{O,2}/C_{OT} = 96.4\%$		1.2 [9.7 mg l^{-1}]
γ-Al$_2$O$_3$	$K_1 = 0$	$K_2 = 4$; n = 0.2	$K_3 = 12$; n = 0.2	0.24 [2.1 m h^{-1}]	1.2 [32.6 mg l^{-1}]
	$C_{O,1}/C_{OT} = 16.4\%$	$C_{O,2}/C_{OT} = 33.2\%$	$C_{O,3}/C_{OT} = 50.4\%$		0.2 [8.2 mg l^{-1}]
β-FeOOH	$K_1 = 0$	$K_2 = 4$; n = 0.2	$K_3 = 12$; n = 0.2	0.30 [1.7 m h^{-1}]	0.4 [13.2 mg l^{-1}] *
	$C_{O,1}/C_{OT} = 1.9\%$	$C_{O,2}/C_{OT} = 23.4\%$	$C_{O,3}/C_{OT} = 74.7\%$		
β-FeOOH * *	$K_1 = 0$	$K_2 = 5.9$; n = 0.2	–	0.30 [1.7 m h^{-1}]	0.8 [13.2 mg l^{-1}] *
	$C_{O,1}/C_{OT} = 2.3\%$	$C_{O,2}/C_{OT} = 97.7\%$	–		

* evaluation of column data.
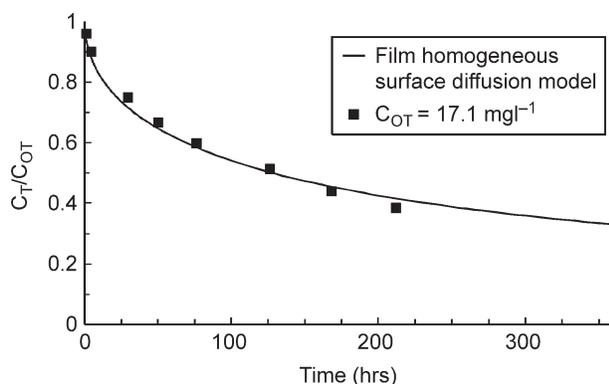* * derived from lower part of isotherms.

Figure 2 │ Rate test with NOM from the first sampling period on granular activated carbon at pH = 7.0: experimental data for a ratio of sorbent mass: solution volume of $0.587 \, \mathrm{g\,l^{-1}}$ and best fit of the kinetic model based on the fictive components given in Table 3.

Figure 4, measured and modelled breakthrough curves are compared. While NOM uptake seems to be slower than predicted in the beginning of the column operation, the measured effluent concentration eventually crosses the calculated curve. When trying to use lower intraparticle diffusivities this could only be compensated in part: though there was a better agreement during the first period of operation, the deviations became larger for the second part of the test. It might be concluded that a single-parameter intraparticle diffusion model is too simplified to describe the transport processes involved in NOM uptake by resins correctly. If one takes into account that counter diffusion of chloride ions occurs inside the resins, one may assume that the intraparticle diffusivity is somehow dependent on the local solid-phase concentration or on its radial gradient in
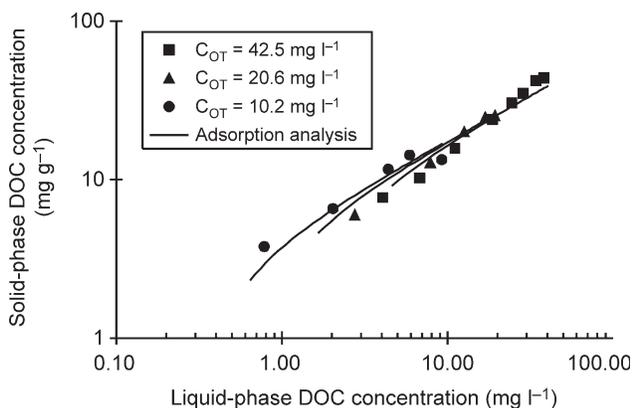

Figure 3 │ Isotherms of NOM from the second sampling period on an anion exchange resin for three initial concentrations at pH = 7.0.
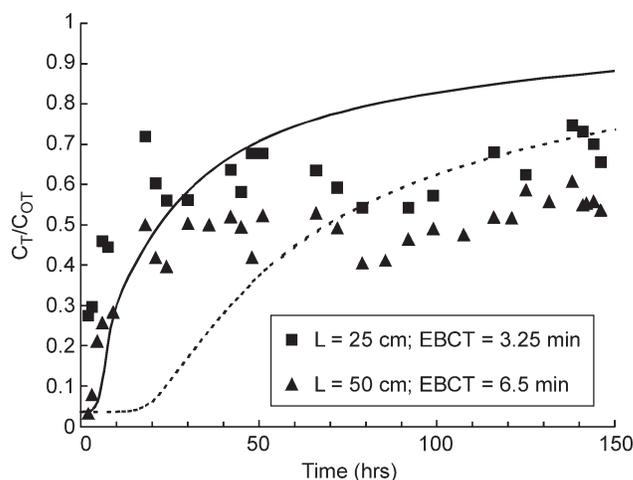

Figure 4 │ Breakthrough curves of NOM from the second sampling period in resin columns at pH = 7.0: experimental data for an influent DOC concentration of $10.15 \, \mathrm{mg\,l^{-1}}$ and predicted curves using the film homogeneous surface diffusion model and the fictive components given in Table 3.

the way that the diffusivity is lower when the mass flux is higher and vice versa.

Uptake by γ-Al$_2$O$_3$

Isotherms obtained with three different initial NOM concentrations from the first sampling period have been shown elsewhere (Fettig 1999b). They look very similar to isotherms found for NOM adsorption on activated carbon with respect to shape and effect of the initial concentration. Therefore, the same fictive-component approach as used for activated carbon above was applied. According to the results given in Table 3, the K_i values of the adsorbable components are considerably lower than for the carbon sorbent while a larger non-adsorbable fraction is obtained.

Batch kinetic data for two initial concentrations were evaluated by the homogeneous surface diffusion model. The intraparticle diffusivities given in Table 3 show the same influence of the initial concentration as found with activated carbon (Sontheimer et al. 1988). Data from the pilot column run conducted with bed depths of 25 cm and 50 cm are compared with the predicted breakthrough curves in Figure 5. During the first few hours the experiment was affected by residual Na$_2$O on the sorbent resulting in effluent pH >8 despite of thorough washing prior to the test run. This may explain the high initial breakthrough. For longer operation times there is a reasonable agreement between measured and
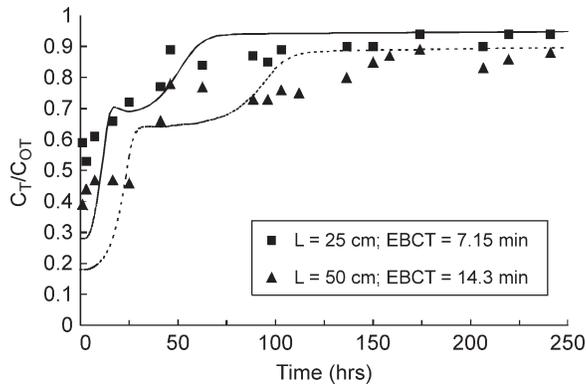
Figure 5 | Breakthrough curves of NOM from the first sampling period in γ-Al_2O_3 columns at pH = 7.0: experimental data for an influent DOC concentration of 8.75 mg l^{-1} and predicted curves using the film homogeneous surface diffusion model and the fictive components given in Table 3.

predicted data. The predicted curves illustrate with their two-step pattern the breakthrough of the two adsorbable components. The apparent plateau between 25 and 75 h for L = 50 cm is a result of the (calculated) substitution of weakly by strongly adsorbable NOM species at the γ-Al_2O_3 surface. The slight peak for L = 25 cm is caused by numerical deviations when the differential equations are solved.

Uptake by β-FeOOH

Isotherms obtained with two different initial NOM concentrations from the third sampling period are shown in Figure 6. Maximum solid-phase DOC concentrations close to 30 mg g^{-1} were found. The isotherms' shapes have more similarities with the results obtained with activated carbon
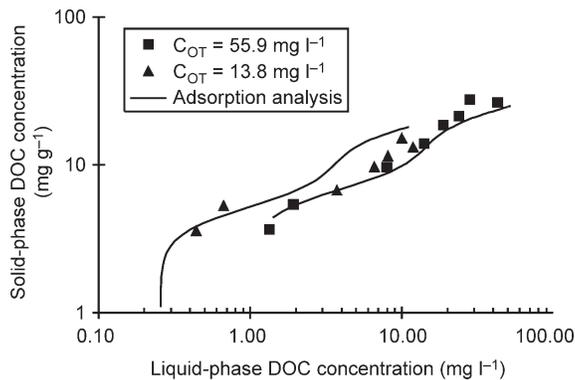

Figure 6 | Isotherms of NOM from the third sampling period on β-FeOOH for two initial concentrations at pH = 6.5.

and γ-Al_2O_3 than with the resin data. Since there is also evidence for an effect of the initial concentration, fictive-component analysis assuming two adsorbable and one non-adsorbable component was applied. For a better comparison of the results, the K_i values determined for γ-Al_2O_3 were chosen as fixed parameters. The calculated isotherms given in Figure 6 illustrate that the experimental data can be described with only minor deviations by this simplified approach. The parameters listed in Table 3 show that a fraction of <2% is considered non-adsorbable while the strongly adsorbable fraction is larger than for γ-Al_2O_3. From the isotherm data it could therefore be concluded that GEH is better suited for NOM uptake than the γ-Al_2O_3 sorbent.

Batch kinetic tests with supplier-sized GEH granules were not successful. NOM concentrations decreased very little, even after long contact periods. In another test where a mixture of NOM and ortho-phosphate was studied, phosphate ions were removed much faster than NOM. Therefore it was decided to focus on column tests and to evaluate NOM uptake from breakthrough data.

Results from a pilot column run conducted with a bed depth of 25.5 cm are shown in Figure 7. The predicted curve is based on the fictive-component parameters given in Table 3 and an intraparticle diffusivity that was fitted to the effluent data obtained after 30 h. There is a large deviation between measured and predicted effluent data during the
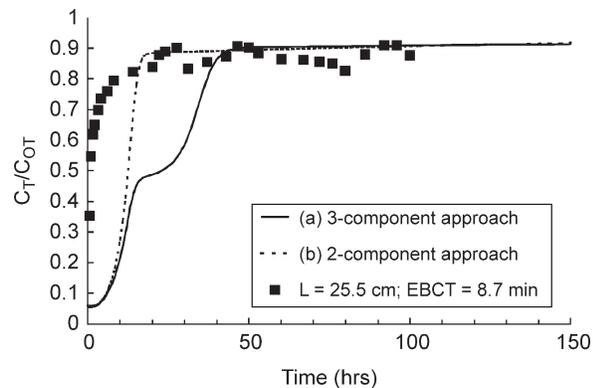

Figure 7 | Breakthrough curves of NOM from the third sampling period in a β-FeOOH column at pH = 6.5: experimental data for an influent DOC concentration of 13.2 mg l^{-1} and predicted curves using the film homogeneous surface diffusion model and the fictive components given in Table 3 with (a) three-component approach describing all of the isotherm data, (b) two-component approach describing the lower part of the isotherms.

first period of operation; that is, a much smaller portion of NOM is actually removed than should be expected. This phenomenon was also observed by Teermann & Jekel (1999) and attributed to the particular structure of GEH: the material consists of very small primary crystallites with pore diameters below 6 nm (to a large extent even below 3 nm), thus very slow intraparticle mass transfer or even size exclusion effects are likely to occur with large NOM molecules. When the GEH granules are crushed, extra surface area becomes more easily accessible resulting in larger solid-phase concentrations. However, since the formation of smaller particles would also occur in jar-test bottles because the intraparticle binding forces of GEH crystallites are quite weak, it does not seem to be possible to obtain reliable equilibrium data for high-molecular NOM samples from isotherm tests.

An attempt was made to evaluate only the lower parts of the overall NOM isotherms assuming that they might represent the true capacity of the sorbent. One adsorbable and one non-adsorbable component were chosen, and the parameters given in Table 3 were obtained. As shown in Figure 7 there is still a considerable deviation between measured and calculated breakthrough curves during the first 15 h. Hence the column capacity seems to be much lower than that derived from the bottle-point test with crushed sorbent material.

Prediction of average column capacities

Experimental and predicted breakthrough curves were evaluated by calculating the average column capacity (DOC accumulated per mass of sorbent media) at the end of each column run from a mass balance. The results shown in Table 4 illustrate the predictability of these capacities by the model approach used. For the resin and for γ-Al$_2$O$_3$, there is a fairly good agreement between experimental and predicted data. The deviations are smaller for 50 cm than for 25 cm of bed length, possibly because the initial phase of the breakthrough curves, which is most difficult to predict, has less impact when modelling longer columns. As noted earlier a similar good agreement can be expected for fixed-bed granular activated carbon adsorption. Meanwhile the data for the β-FeOOH product confirm that a model based on bottle-point isotherm data may not be suited to predict NOM uptake in packed-bed columns.

CONCLUSIONS

Activated carbon and anion exchange resins have proven to be efficient sorbent media for NOM in this study. The non-removable fractions of NOM were 2% with activated

Table 4 │ Comparison of experimental and predicted average column capacities

Sorbent	Bed depth (cm)	EBCT (min)	Bed volumes (m³ m⁻³)	Average column capacity	
				Experimental (mg g⁻¹)	Predicted (mg g⁻¹)
Activated carbon	25	3.0	2000	–	6.9
	50	6.0	1000	–	6.6
Anion exchange resin	25	3.25	2693	15.5	11.8
	50	6.5	1346	10.3	10.8
γ-Al$_2$O$_3$	25	7.15	2024	2.5	2.2
	50	14.3	1012	2.2	2.2
β-FeOOH (3 components)	25.5	8.7	689	0.92	2.2
β-FeOOH (2 components)	25.5	8.7	689	0.92	1.6

carbon and 3.6% with the exchange resin investigated. The latter, however, seemed to be more homogeneous with respect to the binding characteristics. The rate of NOM uptake by granular media was controlled by slow intra-particle mass transfer for both sorbents.

Activated alumina has shown the ability to remove a significant portion of NOM. The non-adsorbable fraction of 16% that was found here is smaller than that observed in other studies. Compared with activated carbon, the maximum solid-phase concentrations obtained were 2–3 times lower, which is about the difference between the BET surface areas. The rate of NOM uptake was clearly controlled by intraparticle diffusion.

Granular ferric hydroxide had a very low capacity for the NOM sample studied, which could not be predicted from isotherm data obtained with crushed material. Both size exclusion of NOM species and an extremely slow access into the micropore region of the sorbent are possible reasons for this behaviour.

Of the four media studied, the anion exchange resin had the highest average column capacity, followed by activated carbon. This finding confirms the applicability of resins for NOM removal in water treatment that is utilized in several plants in Scandinavia. With respect to activated carbon the removal of NOM might be an aim; however, when the medium is applied for the removal of micropollutants, uptake of NOM can have negative effects by causing so-called carbon fouling. The capacities of the metal oxides are too low to use these media for NOM removal on a technical scale. Their application so far is directed towards a selective removal of particular pollutants, for example the removal of arsenic by GEH, where NOM uptake is not needed nor desired.

ACKNOWLEDGEMENTS

NOMENCLATURE

$C_{O,i}$ initial DOC concentration of component i $(mg\,l^{-1})$

C_{OT} total initial DOC concentration $(mg\,l^{-1})$

d   diameter (mm)

K   Freundlich isotherm parameter $(mg\,g^{-1}\,[mg\,l^{-1}]^{-n})$

L   column bed depth (cm)

n   Freundlich isotherm parameter $(-)$

v_F superficial velocity $(m\,h^{-1})$

ABBREVIATIONS

DOC   dissolved organic carbon

EBCT   empty bed contact time

GAC   granular activated carbon

IAST   ideal adsorbed solution theory

NOM   natural organic matter

SAC   spectral absorption coefficient

UV   ultra violet

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