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Breakthrough of natural organic matter from fixed bed adsorbers: investigations based on size-exclusion HPLC

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Abstract Fixed bed adsorption experiments were performed using four granular activated carbon (GAC) columns designed by packing two size ranges of pulverized and sieved Filtrasorb 400 ($d = 0.5$-0.59 and 1.0-1.19 mm) to two bed depths ($L = 10$ and 20 cm), respectively. Continuous supplying of river water containing a lower content of natural organic matter (NOM) allowed investigation of the breakthrough of aqueous natural organic matrices assessed with lumped quality indices of total dissolved organic carbon (DOC) and ultraviolet absorbance at 260 nm (UV260). The capability of GAC columns in dealing with sudden rise in the load of influent NOM was also displayed by intermittently adding to the influent river water a peaty field groundwater that contained a higher content of NOM. Besides, assisted by the size-exclusion HPLC (SEHPLC), changes in the apparent molecular weight distribution of NOM along the bed depth of GAC columns were evaluated, and an important finding revealing relatively even adsorption for adsorbable NOM constituents within the entire molecular weight range of 1000-5200 g mol^{-1} as PSS (polystyrene sulfonates) detected for the river and groundwater NOM was obtained. Furthermore, using a previously proposed hypothetical multi-component approach incorporating the ideal adsorbed solution theory and a plug flow homogeneous surface diffusion model, the observed concentration profiles of the river water NOM were predicted.

Keywords NOM · Molecular weight distribution · Activated carbon · Adsorption · Breakthrough

1 Introduction

Most drinking water sources contain natural organic matter (NOM) consisted mainly of polydisperse humic molecules. Besides forming trihalomethanes during disinfection with chlorine, humic molecules adversely affect the adsorption performance of activated carbon for specifically-targeted organic compounds (SOCs). For instance, humic molecules are capable of competing with small SOCs for adsorption sites and of hindering the access of SOCs to small pores where their adsorption takes place more efficiently (Crittenden et al. 1985; Pelekani and Snoeyink 1999; Ebie et al. 2001). Characterization of NOM based on its adsorbability and major physicochemical features is thus important for better understanding the adsorption behavior of NOM. It is also important for establishment of more efficient and reliable modeling techniques that could better predict the removal of SOCs by fixed bed activated carbon adsorbers.

The performance of activated carbon in removing polydisperse NOM is affected by a variety of factors. Using natural and synthetic organic materials, several researchers have found that physical size and chemical features (including the functional group, charge density and aromaticity, etc.) are important factor affecting the adsorption capacity of such macromolecules by activated carbon (Summers and Roberts 1988a, 1988b; Karanfil et al. 1996). Based on the

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adsorption results with extracted organic macromolecules from such materials as soil, peat and coal, a few researchers have further pointed out that the molecular size impact may dominate the competitive adsorption among constituting compounds and chemical effects would play only minor roles (Newcombe et al. 2002; Karanfil et al. 1996). In addition to inherit physicochemical features, the solution chemistry of NOM, represented by variables such as pH and ionic strength, as well as the surface and pore characteristics of activated carbon also affect the uptake of NOM from aqueous systems (Randtke and Jepsen 1982; Weber et al. 1983; Summers and Roberts 1988a, 1988b; Li et al. 2002; 2003a, 2003b).

The broad distribution of NOM in molecular size is one of its most important features and its relations with the adsorption capacity onto activated carbon have been investigated by several researchers (Lee et al. 1981; Summers and Roberts 1988a, 1988b; Newcombe et al. 2002; Karanfil et al. 1996). However, in regard of the likely impacts of molecular size on the breakthrough of NOM, literature information is limited and findings related to the shift of NOM composition in molecular sizes along the depth of the fixed granular activated carbon (GAC) beds are not found.

In the present study, the removal of NOM by fixed activated carbon beds was investigated and the changing trend of NOM along the bed depth was presented with the aid of the size-exclusion high performance liquid chromatography (SEHPLC). Furthermore, by accounting for the polydisperse adsorbability of NOM with a hypothetical multi-component approach proposed before by incorporating the ideal adsorbed solution theory (IAST) and a plug flow homogeneous surface diffusion model (PFHSDM), the breakthrough of NOM and its hypothetical constituents were predicted.

2 Materials and methods

2.1 Water samples

Nagara River water (NRW) and a ground water (GW), which contain relatively lower and higher content of organic matter, respectively, were used as two NOM sources for the present study. NRW was used because, located within the territory of Gifu Prefecture, it is one of the well-known and relatively well-conserved rivers on the main Honsyu island of Japan and is less polluted by human and social activities (the dissolved total organic carbon is averaged as 0.53 $\mathrm{mg\,L^{-1}}$ over the past two years). With a main-stream length of 166 km, the basin area developed along this river extends for 1985 $\mathrm{km^2}$ and is rich with vegetation resources. The higher density of forest distribution (approximately 80% of the whole area is covered by a variety of forest types) is a major reason attributive to relatively better water qualities through the years. The ground water (GW) was collected from a shallow well at Kitamura village of Hokkaido. The use of this water was made because organic matter contained is mainly from peat (the total dissolved organic carbon is 8.2 $\mathrm{mg\,L^{-1}}$) and such water samples are frequently chosen for characterizing the behavior of naturally-occurring humic substances during water treatment with different physicochemical approaches.

The NRW was sampled once for every two weeks and was stored refrigerated at 5 °C in the dark to prevent biological activities after being filtered through 0.45 μm membrane filters (Toyo Roshi, Japan) prior to addition into the influent water reservoir (in most cases once a day). For the GW, however, the stock solution stored refrigerated at 5 °C in the dark after filtration through 0.45 μm membrane filters was used. The GW was used only at times when adsorption for relatively higher NOM influent was scheduled, which was achieved by intermittently adding pre-weighted quantities of GW to the NRW. Throughout this study, NRW was used as the base influent water and disruption was made only when backwashing was conducted.

2.2 Granular activated carbon

Filtrasorb 400 (Calgon Co., USA), a coal-based granular activated carbon (GAC) used widely in advanced water treatment applications and laboratory research works, was used as the adsorbent. Major physical characteristics of this adsorbent are reported elsewhere (Kilduff et al. 1996). The representative carbon particles of this GAC were pulverized and sieved in order to collect two GAC categories with sizes in the size ranges of 0.5-0.59 mm and 1.0-1.19 mm, respectively. The collected carbon categories were then washed and rinsed with distilled water to remove fines, dried at 105 °C overnight before packed into relative columns.

2.2.1 Fixed bed adsorption experiments

The schematic setup of the laboratory scale fixed bed adsorption system is displayed in Fig. 1. Four polyvinyl-chloride columns having an internal diameter of 2.5 cm were used. The weighted GAC category having the size in 0.5-0.59 mm was immersed in a glass beaker containing Milli-Q water and packed into two columns for the designated bed depths of 10 cm and 20 cm, respectively (referred hereafter as GAC-1 and GAC-2). Similarly, into the remaining two columns, the larger GAC category having size in 1.0-1.19 mm was packed to reach the bed depths of GAC-1 and GAC-2, respectively (referred hereafter as GAC-3 and GAC-4). During packing, all four columns were tapped to achieve a stable bed structure that allowed restoration of the bed depths even after backwashing. Soon after packing, all

Table 1 Fixed bed conditions for granular activated carbon columns used in this study

Column	GAC size (mm)	GAC weight (g)	Bed depth (cm)	Apparent porosity (%)	Empty bed contact time (min)
GAC-1	0.5-0.59	25	10	32.1	19.5
GAC-2	0.5-0.59	50	20	32.1	39.0
GAC-3	1.0-1.19	32	10	13.0	19.5
GAC-4	1.0-1.19	64	20	13.0	39.0

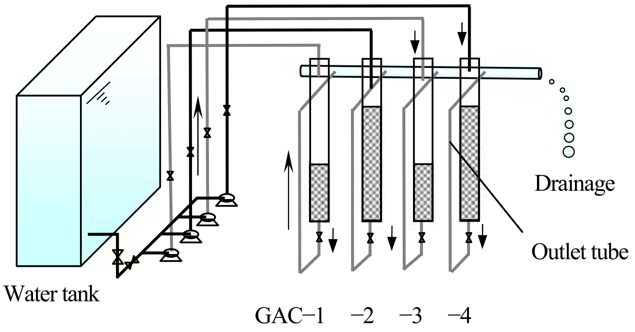

Fig. 1 The schematic setup of the laboratory scale fixed bed adsorption system

columns were backwashed for about 30 minutes to eliminate fines probably produced during packing with de-ionized tap water. The influent water was supplied to all columns at a constant flow rate of 2.5 ml min^{-1} in the down-flow mode from its storage tank (with a volume of about 50 L). The content of water within the storage tank was supplemented on a daily basis. Since water pumped into all columns contained no suspended particles (achieved by pre-filtration through 0.45 µm membranes), head loss development was retarded and backwashing was thus performed for about every two months. The fixed bed conditions for all GAC columns are briefly described in Table 1. Different from expectation, for GAC-3 and GAC-4 packed with the larger GAC particles, the apparent porosity was rather lower (13%) as compared to GAC-1 and GAC-2 (32.1%). A greater change in the shape of the GAC particles probably occurred as a result of pulverization performed for collecting two categories of GAC with relatively uniform sizes for examination of the size effect as well as for better model simulations.

The effluent from the outlet of each column was sampled and filtration was performed using 0.45 µm membrane filters before subjected to analysis. To generate information related to the vertical distribution of NOM within the columns, samples from designated bed levels were also collected using a special sampler that allowed insertion of a sampling needle (with a diameter of 0.3 mm and a length of 50 cm) into the packed bed. A total organic carbon (TOC) analyzer (model TOC-Vws, Shimazu Co., Japan) was used for measurement of total dissolved organic carbon (DOC) and a UV-visible spectrophotometer (model U-3210, Hitachi Co., Japan) was used for measurement of the UV-absorbance at 260 nm (UV260). The index of UV260 was used because, like UV-absorbance at 254 nm (UV254), it is capable of reflecting the presence of humic molecules present in water environment systems, and the specific ultraviolet absorption (SUVA), a calculated parameter of UV260 or UV254 divided by DOC, has thus been used as an indicator of the humic content.

2.3 Size-exclusion high performance liquid chromatography (SEHPLC)

SEHPLC was performed to measure the apparent molecular weight distribution of NOM contained in samples collected before and after adsorption through different levels of the packed GAC beds. A packed silica column (GL-W520-X 10.7 mm × 450 mm, Hitachi Co., Japan) and a UV-visible detector (Model LC-10AV, Shimadzu Co., Japan) set at 260 nm (UV260) were used. The mobile phase solution made up of Milli-Q water was buffered with phosphorus salts (0.02 M-Na_2HPO_4 + 0.02 M-KH_2PO) and was supplied to the chromatographic column at 0.5 ml min^{-1}. To calibrate the SEHPLC system, three polystyrene sulfonates (PSS) with known molecular weight of 1430, 4950 and 6530 g mol^{-1} were used and a good correlation ($R^2 = 0.998$) described by $MW = 106816 \cdot \exp(-0.1096t)$ was obtained, in which t is the elution time given in minutes.

3 Results and discussion

3.1 Adsorption behavior of NOM contained in the Nagara River water

The observed concentration profiles of the NOM in the NRW assessed with the quality index of UV260 are displayed in Fig. 2. Similarly, the concentration profiles assessed with the index of DOC are displayed in Fig. 3. In both figures, data are plotted in the format of influent and effluent UV260 or DOC versus the bed volume, with the latter being defined as the treated water volume divided by the packed GAC bed volume. For all columns, compared to the differences between the influent and effluent NOM levels assessed by DOC, those assessed by the UV260 index were more significant. This thus indicated that for all

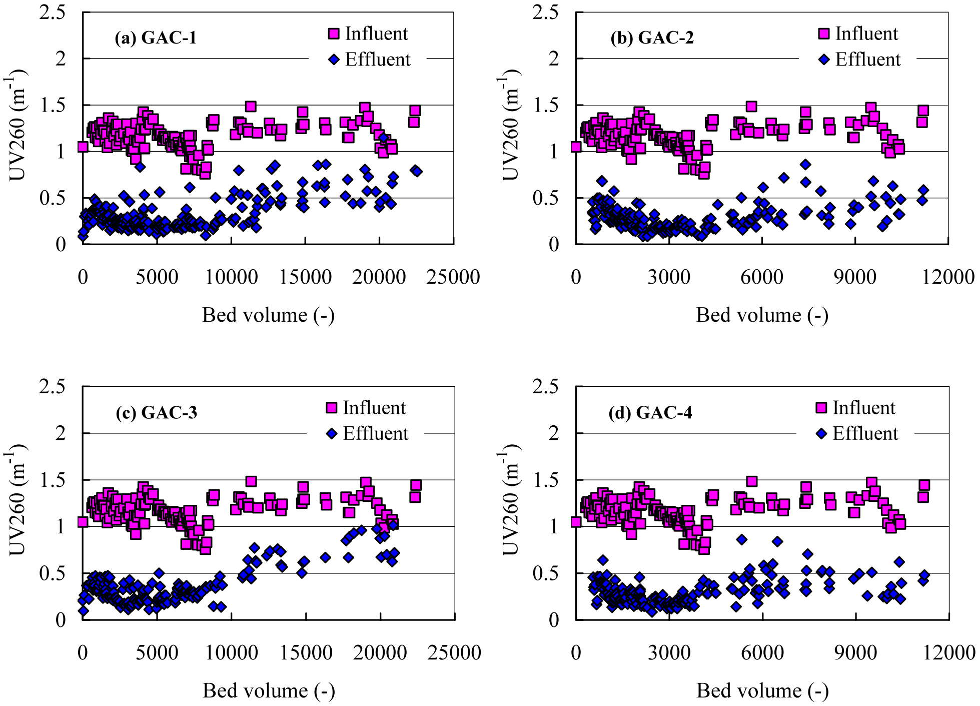

Fig. 2 The observed concentration profiles of the NOM in the NRW assessed with the quality index of UV260

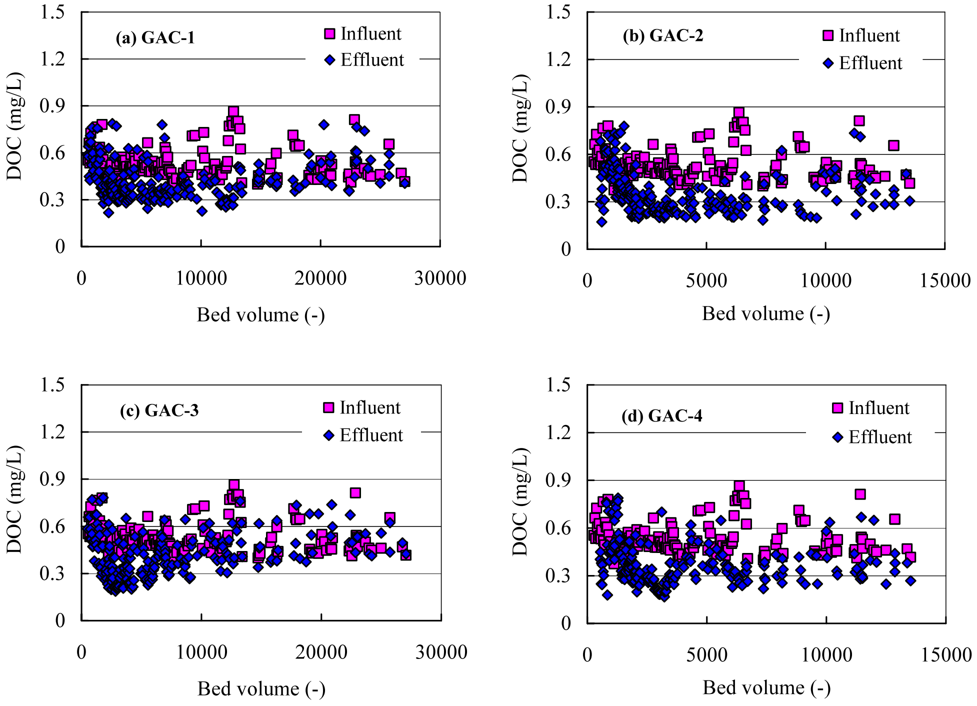

Fig. 3 The observed concentration profiles of the NOM in the NRW assessed with the quality index of DOC

organic constituents contained in the river water source, UV260 constituents were effectively adsorbed, and some constituents not detected by UV260 were less favorably adsorbed. This indication is conceivable, taking into consideration that while UV260 is an index reflective of the portion of organic compounds having UV absorbing features, the index DOC measures all organic molecules dissolved in water solutions including those not detectable with a UV-visible spectrophotometer.

With respect to the whole organic constituents detected by UV260, the observed profiles for all GAC columns in Fig. 2 revealed that averagely about 20% of the constituents were not adsorbable by activated carbon. This was true as could be estimated by comparing the initial concentra-

Table 2 Removals of NOM when groundwater containing the higher content of NOM was added into the influent Nagara River water for a short period (about 5 hours each time) after different running time lengths

Running time length (hrs)	Influent UV260 (m^{-1})	Influent DOC ($mg\,L^{-1}$)	Removal of UV260 (%) GAC-1	GAC-2	GAC-3	GAC-4	Removal of DOC (%) GAC-1	GAC-2	GAC-3	GAC-4
1363	9.544	3.128	97.4	98.1	96.4	97.5	91.6	91.6	86.1	90.6
2352	9.482	3.495	93.5	97.6	97.5	97.0	57.0	87.8	81.6	89.2
4889	9.316	1.696	93.6	95.3	83.0	94.2	77.2	81.5	63.3	78.9
5343	12.828	2.91	93.4	89.6	82.1	93.5	85.8	85.8	68.6	86.7
5821	12.874	2.802	94.8	94.8	85.3	95.9	84.2	77.7	63.9	85.4
7477	9.532	3.385	92.4	96.6	82.7	95.9	82.3	88.4	74.7	91.0

Table 3 Removals of NOM contained in the Nagara River water after different running time lengths

Running time length (hrs)	Influent UV260 (m^{-1})	Influent DOC ($mg\,L^{-1}$)	Removal of UV260 (%) GAC-1	GAC-2	GAC-3	GAC-4	Removal of DOC (%) GAC-1	GAC-2	GAC-3	GAC-4
1358	1.032	0.505	79.3	82.8	81.6	75.2	25.0	−5.7	21.4	42.2
2348	1.148	0.464	83.4	82.1	76.1	79.6	36.2	44.0	22.4	40.1
4884	3.306	0.624	93.7	81.5	40.2	68.8	21.8	50.0	20.5	47.8
5338	2.138	0.453	62.1	6.5	42.9	2.2	4.4	32.9	−2.0	37.1
5816	1.424	0.596	67.7	39.6	50.4	78.5	35.4	25.7	−6.9	48.7
7472	1.026	0.541	36.1	68.0	31.8	78.2	−13.3	13.7	1.7	43.6

tion profiles observed for GAC-1 and GAC-3 (or GAC-2 and GAC-4) having two different bed depths. In regard of GAC-1 and GAC-3, for example, even if the packed bed for the latter column ($L = 20$ cm) is twice as long as that for the former ($L = 10$ cm), the effluent from the latter (GAC-3) showed no further reduction in observed effluent UV260 levels. The existence of non-adsorbable constituents in this river water source was also confirmed in a previous batch study of the adsorption isotherms of the river water NOM collected before, during and after a heavy storm of rain (Li et al. 2003b). In this previous study, for six water samples subjected to batch adsorption experiments, whose UV260 changed in the range of 1.76-4.89 m^{-1} and DOC in 0.85-1.89 $mg\,L^{-1}$, the non-adsorbable fraction was estimated as 0-1.9% and 12.1-21.9% for the quality indices of UV260 and DOC, respectively.

3.2 Adsorption responses of GAC columns to short increases in the influent load of NOM

Over the total running period of about 350 days so far, the peaty field groundwater containing higher content of NOM was added into the influent Nagara river water for several times for investigation of the GAC bed responses to short time NOM increases induced probably by such natural phenomena as rainfall, typhoon, snow-thawing, etc. For each addition which lasted for about 5 hours, since changes in the effluent NOM content from each GAC column were less apparent, average UV260 and DOC values were computed. Average removals of UV260 and DOC computed accordingly are summarized in Table 2. For comparison, the removals of the river water NOM measured for samples collected just hours before addition of the groundwater NOM were also computed, as shown in Table 3.

In reflectance of gradual decline in the adsorption capacity of GAC caused by continuous adsorption of NOM, for all GAC columns, a general trend of decreases in the removal of UV260 with increases in the running time length was revealed, although there were several exceptional points. Besides, compared to the removal values shown in Table 3, the values in Table 2 were apparently higher, thus indicating that the intermittently added higher content of NOM contained in the groundwater was favorably adsorbed. The broader removal margins with the DOC index, rather than the UV260 index, observed between both influent samples containing lower and higher content of NOM, respectively, further indicated that the peaty groundwater contained larger percentages of organic constituents that could be removed through activated carbon adsorption. In a previous study, Li et al. (2005) analyzed the batch isotherms of the organic matrices contained in water samples of both the NRW and the peaty GW collected at a time earlier than those used in the present study. With the powdered species of the same activated carbon type (Filtrasorb 400) as the adsorbent, the non-adsorbable DOC fraction in the peaty GW was determined

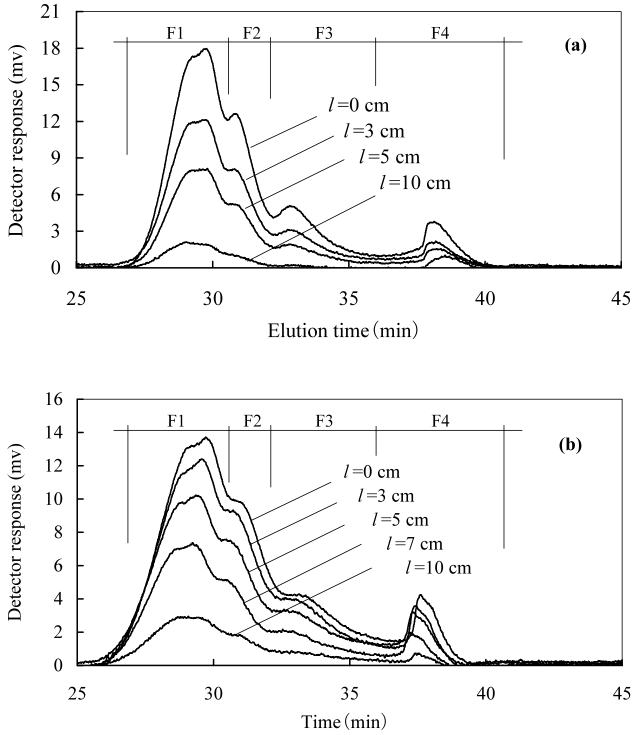

Fig. 4 Changes in the apparent molecular weight distribution of NOM along the bed depth of GAC-3 when groundwater containing higher content of NOM was added to the river water influent after consistent running of the column for consecutively (**a**) 120 days, and (**b**) 250 days

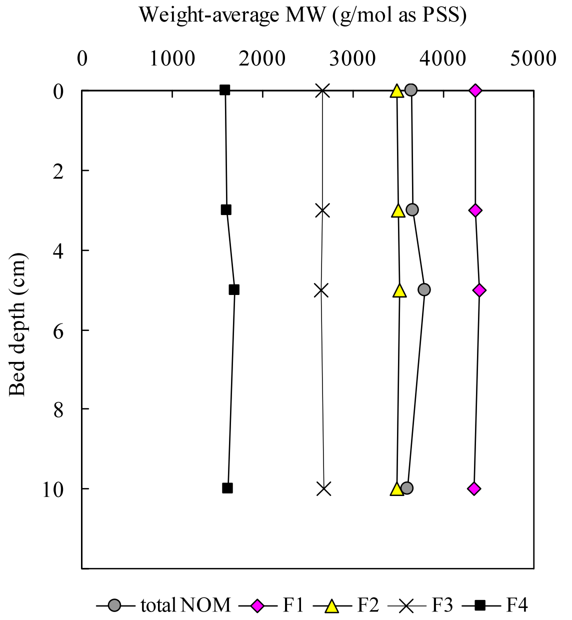

Fig. 5 The changing trend of the weight-average molecular weight of total NOM and its four fractions with the bed depth of GAC-3 when groundwater containing higher content of NOM was added to the river water influent after consistent running of the column for consecutively 120 days. The molecular weight values are: total NOM = 3640, F1 = 4350, F2 = 3500, F3 = 2700 and F4 = 1600 g/mol as PSS

as about 4%, a value being apparently smaller than the value of 15% determined for the NRW.

3.3 Breakthrough dependency on apparent molecular weight of NOM

The changes in the apparent molecular weight distribution of NOM along the fixed bed of GAC-3 are displayed in Fig. 4. The results displayed corresponded to SEHPLC measurements for samples collected at several different levels of the fixed bed during two short running times when GW was added to the base NGW after the GAC column had been consistently operated for about 120 and 250 days, respectively. By introducing the elution time of organic constituents into the calibration expression given earlier, the molecular weight range of the NOM studied was determined as about 1000-5200 $\mathrm{g\,mol^{-1}}$. For organic matrices in water and wastewater sources, if smaller organic constituents are adsorbed preferentially, a shift of the molecular weight distribution towards the larger molecular weight side should appear as the water flowed downwards. Over the broader molecular weight range of the studied NOM, such a shift was not obvious, thus suggesting that organic constituents in the river and ground water sources were adsorbed in a relatively even manner, where distinctly preferential adsorption for either larger molecules or smaller molecules did not occur.

For further examination, the whole molecular weight distribution was divided into four fractions (referred hereafter as F1, F2, F3 and F4) based on the number of peaks appearing in the chromatogram of the NOM before adsorption (i.e., $l = 0$ cm). The weight-average molecular weight (M_w) of these fractions was determined as 4350, 3500, 2700 and 1600 $\mathrm{g\,mol^{-1}}$ as PSS based on the expressions documented (Chin et al. 1994; Karanfil et al. 1996). In these expressions, MW(t), h(t) and Δt, which represent the molecular weight (MW) as a function of the elution time t, the UV detector response as a function t and the elution time interval, respectively, were involved. The relations between the computed M_w and the bed depth of the GAC column are displayed in Fig. 5. An apparent trend of either increasing or decreasing of the Mw as water flowed through the bed depth was not revealed. The removals of all four molecular weight fractions at different bed depths are displayed in Fig. 6. As illustrated, no matter which molecular weight fraction was concerned, as water flowed downwards the removal of NOM increased. For all bed depth levels examined, distinct differences in the removal were not found either among all divided molecular weight fractions.

The results obtained through this breakthrough study resembled those obtained through batch isotherm studies for aqueous organic matrices contained in river water sources and wastewater sources after biological degradation (Li et

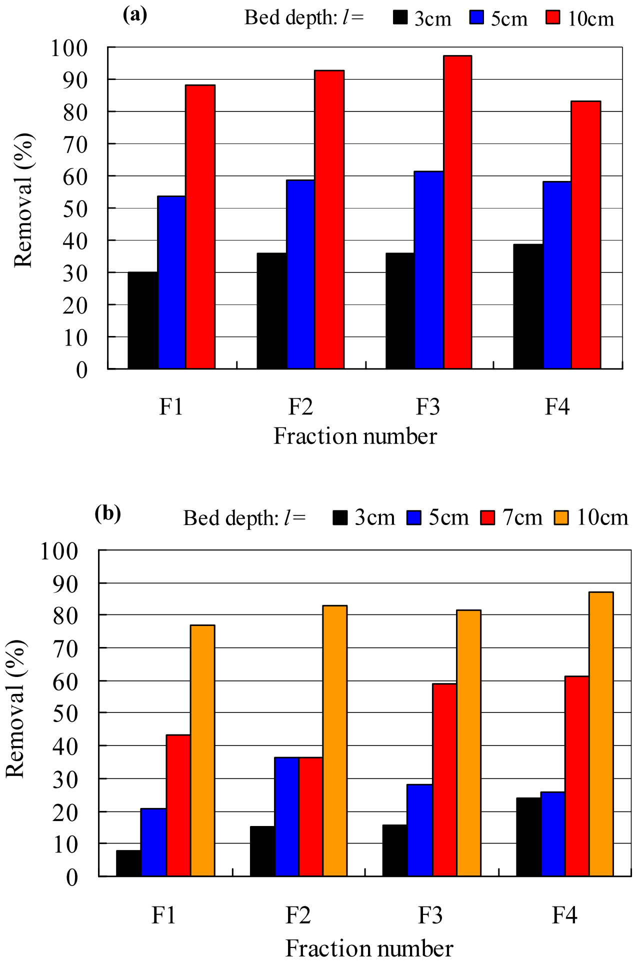

Fig. 6 Removals of divided molecular weight fractions based on the SEHPLC chromatograms of NOM along the bed depth of GAC-3 when groundwater containing higher content of NOM was added to the river water influent after consistent running of the column for consecutively (**a**) 120 days, and (**b**) 250 days. The molecular weight values are: F1 = 4350, F2 = 3500, F3 = 2700 and F4 = 1600 g/mol as PSS

al. 2005), thus supporting a previous indication made by the authors that for aqueous organic matrices with molecular weights ranging from several hundreds to several thousands, adsorption took place evenly for all constituting adsorbable constituents. However, caution has to be paid as others have demonstrated apparent dependency of NOM adsorption on the molecular weight of its constituting components. For instance, Kilduff et al. (1996) investigated the batch adsorption behavior of the Huron River water NOM on the carbon type Filtrasorb 400 and found that smaller molecular size components adsorbed to a greater extent on the adsorbent mass basis. For commercial humic acids or some macromolecular organic matters obtained by undergoing extraction or synthesis procedures from such materials as soil, peat and coal, a shift of the molecular weight distribution towards the larger side with increases of the activated carbon dose was also observed by researchers including the authors of the present study (Summers and Roberts 1988a, 1988b; Kilduff et al. 1996; Li et al. 2005).

3.4 Model prediction of the breakthrough of the NOM

To investigate the reliability of a previously proposed mathematical approach for description of the breakthrough of organic matrices in water and wastewater sources, the breakthrough data observed so far through the present study were described based on a multi-component approach proposed by incorporating the ideal adsorbed solution theory (IAST) and a plug flow surface diffusion model (Li et al. 1999). In addition to equilibrium parameters (Freundlich K_i and $1/n_i$), the model description also requires the external mass transfer coefficient (k_{fi}) and the surface diffusion coefficient (D_{si}) for all hypothetical adsorbable components.

In the present study, the total NOM was represented by five adsorbable components and a non-adsorbable one, and the equilibrium parameters for all adsorbable components were determined by analysis of observed isotherm data with the documented hypothetical multicomponent method (Yuasa et al. 1997; Li et al. 2005). For D_{Si}, documented values generated by model fitting of micro-column data observed for the organic matrix in the groundwater sampled at a different time were adopted (Li et al. 1999). The adoption of the D_{Si} values generated for the groundwater NOM was made because it exhibited an adsorption capacity very close to that of the organic matrix in the NRW. The MW distribution of the groundwater NOM and the NRW NOM was also similar: the weight-average MW (M_w) and the MW polydispersity ($= M_w/M_n$, where M_n is the number-average MW) computed using the documented expressions (Chin et al. 1994; Karanfil et al. 1996) were 3640 g mol^{-1} and 1.101, and 3400 g mol^{-1} and 1.124, respectively. The external mass transfer coefficient k_{fi} was considered identical for all hypothetical components and was computed based on the estimation procedure documented earlier by using the mean molecular weight of the NOM and packing and flow conditions of the columns (Li et al. 1999). The values for all parameters needed for making the breakthrough predictions are summarized in Table 4 for easy reference.

Comparisons of the model predictions with the observed breakthrough data for GAC-3 and GAC-4 are displayed in Figs. 7a, 7b. Although further running of the GAC columns is necessary in order to generate breakthrough data close to complete depletion in the adsorption capacity of the packed GAC, the obtained data so far were fairly well described. Figure 8 shows the predicted concentration profiles of all five adsorbable hypothetical components through the GAC-3 column. Although D_{Si} differed by several orders of mag-

Table 4 Adsorption equilibrium and kinetic parameters of all hypothetical components used for predictions of NOM breakthrough through GAC-3 and GAC-4 columns

Component (i)	C_{i0}/C_{t0} (%)	k_i ($\mathrm{m}^{1/n-1}\,\mathrm{L\,g}^{-1}$)	$1/n_i$	D_{Si} ($\mathrm{cm}^2\,\mathrm{s}^{-1}$)	k_{fi} ($\mathrm{cm\,s}^{-1}$)
1	3.46	36.8		1.47×10^{-10}	
2	23.90	65.7		3.60×10^{-11}	
3	45.28	117.3	0.29	8.55×10^{-12}	1.0×10^{-3}
4	23.90	209.6		2.11×10^{-12}	
5	3.46	374.4		5.83×10^{-13}	
6	17.63	non-adsorbable fraction			

The average influent concentration (C_{t0}) used for model predictions is 1.27 m^{-1}

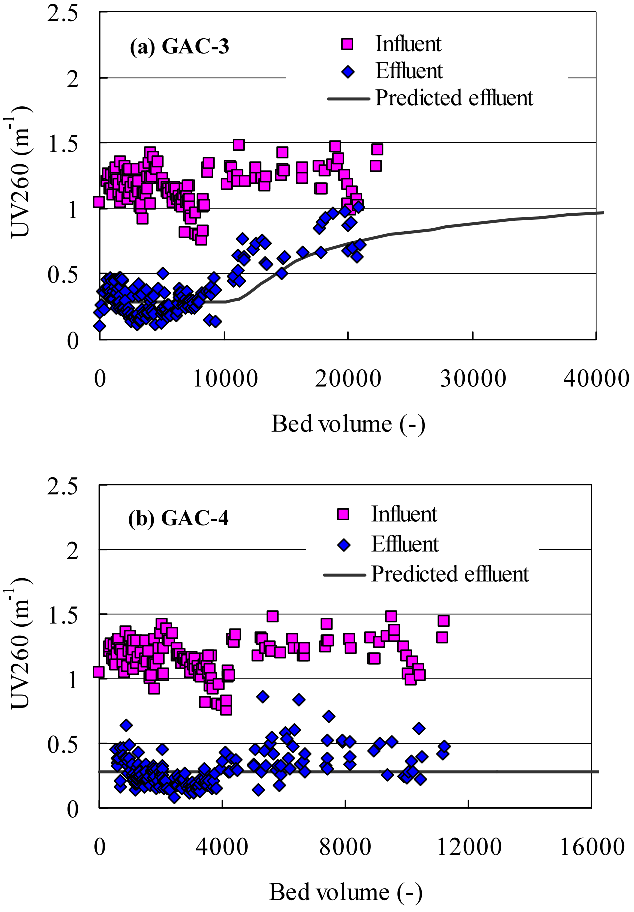

Fig. 7 Comparison of model predictions with observed breakthrough profiles for river water NOM with respect to (**a**) GAC-3 and (**b**) GAC-4

nitude for the respective components as shown in Table 4, the markedly different breakthrough behavior of the hypothetical adsorbable components in the mixture seemed to be controlled more by the adsorption capacity than by the uptake rate. For this, future experimental verification is necessary.

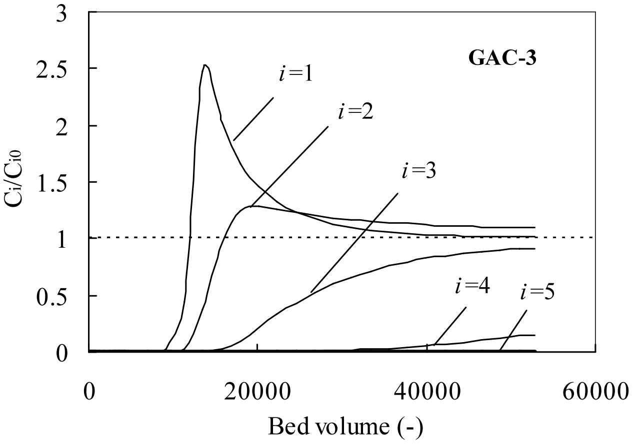

Fig. 8 Simulated breakthrough profiles for adsorbable hypothetical organic constituents of the river water NOM with respect to the column of GAC-3

4 Conclusions

Four granular activated carbon columns were designed by packing pulverized Filtrasorb-400 (Filtrasorb/USA) having particle size of 0.5-0.59 mm and 1.0-1.19 mm to two bed depths of 10 cm and 20 cm, respectively. River water that contains relatively a lower content of NOM was consistently pumped into the columns for investigation of its breakthrough behavior. In addition, a peaty groundwater containing a higher content of NOM was added intermittently into the river water influent to examine the column responses to short intervals of sudden NOM load increases.

The results showed that compared to the river water NOM, the organic matrix in the groundwater was adsorbed more effectively. Measurement of the molecular weight distribution of NOM for water samples collected at different bed levels clearly revealed that activated carbon uptake for NOM took place evenly for all adsorbable constituents having different molecular weight. Preferential adsorption for smaller molecular constituents within the detected whole molecular weight range of 1000-5200 g mol^{-1} as PSS for the natural aqueous organic matrices investigated in the study was confirmed inexistent, a behavior apparently different from extracted or synthetic macromolecular matrices and is of great significance. Furthermore, by accounting for the polydisperse adsorbabilities of NOM constituents with a hypothetical multi-component approach incorporating the ideal adsorbed solution theory and a plug flow homogeneous surface diffusion model, the breakthrough of NOM observed so far was reasonably predicted.

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