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Polydisperse Adsorption Characteristics of Aqueous Organic Matrices in Water and Wastewater Sources

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Abstract. Batch adsorption isotherms of fourteen dissolved organic matrices (DOMs) from river water, ground water, wastewater and commercial sources were measured using lumped quality indices of DOC and UV260, and analyzed using a distributed fictive component method. By accounting for the heterogeneity of DOM constituents with a log-normal distribution of Freundlich K, the adsorption equilibrium of each DOM was characterized by searching for only three parameters. Indicating strong adsorbability dependency upon the sources and types of DOMs, the distribution ranges of the Freundlich K differed markedly. Compared to a river water DOM that had a K range in 10.8–190 (mg/g)/(mg/l)$^{1/n}$, a commercial humic acid was found most heterogeneous: K varied in 0.01–1494.3 (mg/g)/(mg/l)$^{1/n}$. In addition, based upon chromatographic results measured using a HPSEC system for all DOMs before and after adsorption, preferential adsorption of small molecular weight constituents was revealed for commercial humic acids; for aquatic organic matrices, however, such a trend was not found.

Keywords: NOM, humic matter, adsorption, molecular weight distribution, isotherm

1. Introduction

Activated carbon adsorption applied for advanced water and wastewater treatment has to deal with two categories of organic adsorbates: macromolecular organic matrices and small synthetic organic compounds. Arising from the decay of plant and animal residues and other biological activities of microorganisms, the macromolecular organic matrices consisted of mainly humic molecules and/or similar organic polyelectrolytes are highly polydisperse in their physicochemical features (including molecular size, functional group, charge density, aromaticity, etc.). Characterization of their composition in terms of adsorbabilities is important for better understanding their adsorption behavior. It is also central for modeling the adsorption equilibrium and kinetics of specially targeted trace organic compounds whose adsorption

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extent is markedly affected by coexisting organic macromolecules (Crittenden et al., 1993; Warta et al., 1995; Pelekani and Snoeyink, 1999; Ebie et al., 2001).

Fictive component method (FCM), which involves a series of hypothetical components (HCs) and a competitive adsorption model, in many cases the ideal adsorbed solution theory (IAST), is an approach developed for description of the adsorption equilibrium of organic matrices with unknown composition (Fettig and Sontheimer, 1987; Crittenden et al., 1993; Warta et al., 1995). However, this approach has the drawback of requiring search for a large number of variables (the equilibrium parameters and initial concentrations of all HCs) and in many cases, the searched values are not unique (Harrington and DiGiano, 1989). Different from the common practice of using a discrete number of fictive components, we proposed a distributed fictive component method (DFCM), in which a straightforward equation derived from the IAST-Freundlich model was used (Yuasa et al., 1997; Matsui et al., 1998; Li et al., 2003). By accounting for the heterogeneity of organic constituents with a log-normal distribution of the Freundlich parameter (K), the total number of parameters regulating the overall adsorption isotherms of a given organic matrix is reduced to five (including only three fitting ones).

In this paper, the polydisperse adsorption characteristics of fourteen organic matrices from different river water, ground water, wastewater and commercial sources are analyzed and presented based on the DFCM proposed. Moreover, by examining the changing trends of HPSEC chromatograms measured before and after adsorption at variable activated carbon dosages, the likely role of molecular sizes of constituting components and its dependency on the sources and types of organic matrices are discussed.

2. Materials and Methods

2.1. *Batch Isotherm Experiments*

Twelve dissolved organic matters (DOMs) contained in nine river water samples, a ground water and two biological process effluents of a wastewater treatment plant were used along with two commercial humic acids, as illustrated in Table 1. The nine river water samples were collected from Tokoro River water (TRW), Nagara River water (NRW) at the upper, middle and down streams (NRW-US, NRW-MS, NRW-DS), and the down-stream NRW during a Typhoo-induced storm event [NRW-DS (1), (2), (3), (4) and (5)], respectively. TRW and NRW were chosen because

Table 1. Molecular weight information, along with adsorption parameters determined for all DOMs used in the study.

	DOC basis				UV260 basis				MW information		
	(mg/g)/(mg/l)$^{1/n}$				(m$^{1/n-1}$)/(g/l)				Dalton		
DOM source	K_M	σ	1/n	C_{non}/C_{TO}	K_M	σ	1/n	C_{non}/C_{TO}	M_w	M_n	Polydispersity
TRW	40.4	0.30	0.26	0.15	125.2	0.22	0.20	0.02	3456	3174	1.089
KGW	37.0	0.40	0.35	0.04	123.6	0.22	0.27	0.00	2865	2603	1.101
NRW-US	45.3	0.22	0.33	0.38	94.6	0.11	0.29	0.00	3391	2972	1.141
NRW-MS	62.2	0.39	0.29	0.14	141.1	0.25	0.27	0.00	3326	2928	1.136
NRW-DS	48.2	0.41	0.20	0.15	115.2	0.27	0.18	0.00	3392	3033	1.118
NRW-DS (1)	49.5	0.25	0.29	0.20	135.9	0.20	0.41	0.00	2880	2524	1.141
NRW-DS (2)	51.5	0.27	0.27	0.22	125.0	0.21	0.31	0.00	2897	2513	1.153
NRW-DS (3)	47.5	0.30	0.25	0.13	111.1	0.20	0.32	0.00	3236	2849	1.136
NRW-DS (4)	46.5	0.31	0.24	0.13	115.0	0.25	0.30	0.02	3326	2958	1.124
NRW-DS (5)	50.7	0.22	0.18	0.12	98.5	0.17	0.29	0.00	3326	2958	1.124
WBT (1)	42.5	0.43	0.35	0.02	122.0	0.42	0.33	0.02	2371	2026	1.170
WBT (2)	50.5	0.36	0.25	0.02	134.5	0.34	0.25	0.00	2347	1977	1.187
AHA	4.0	0.72	0.20	0.00	22.2	O.6O	0.18	0.00	3667	3185	1.152
WHA	2.5	0.97	0.21	0.00	20.0	0.79	0.20	0.00	3161	2510	1.259

they are representative of most drinking water sources in Hokkaido and the central-Japan Gifu and Aichi prefectures. The ground water (KGW) was collected from a shallow well at the Kitamura Village of Hokkaido, which contains mainly aquatic humic molecules originated from peat soil. Two wastewater samples after biological treatment (WBT-1 and WBT-2) were collected from a wastewater treatment plant in Gifu Prefecture. As model organic macromolecules often used to characterize the behavior of natural organic matters in aquatic environment, Wako humic acid (WHA) and Aldrich humic acid sodium salt (AHA), two commercial products extracted from coal and peat, respectively, were taken directly as received from Wako Pure Chemicals Co., Japan and Aldrich Co. Ltd., USA. The stock solutions of aqueous DOMs were prepared by filtering collected water samples through 0.2-μm membrane filters (Toyo Roshi, Japan) by following adjustment of pH to 7.0 as necessary. The stock solution of WHA was prepared by dissolving the material in Milli-Q water raised to pH 11 with 0.5 M NaOH, lowering water pH to 7.0 with 0.5 M HCl and filtering the solution through 0.2-μm membrane filters. The stock solution of AHA was obtained by dissolving the material in Milli-Q water, adjusting water pH to 7.0 and filtering the solution through 0.2-μm membrane filters.

Batch adsorption experiments were conducted according to the bottle-point method of variable adsorbent doses. Granular activated carbon (Filtrasorb 400; Calgon Co., USA) pulverized and sieved to a size below 47 μm was used as the adsorbent, the specific physicochemical features of which were documented (Kilduff et al., 1996). For each DOM, to measure the isotherm dependency on its initial concentrations, two or three working solutions were prepared by diluting the stock solution with Milli-Q water as necessary. To minimize the influence of changes in solution chemistry caused by dilution, for working solutions of each DOM, pH was adjusted to 7.0 and the ionic strength was adjusted with 0.5 M NaCl. Equilibration was reached by shaking for seven days at 20°C. The liquid phase DOMs were quantified using lumped quality indices of total dissolved organic carbon (DOC) and UV-absorbance at 260 nm (UV260), as commonly practiced. The apparent molecular weight (MW) distribution was measured using a HPSEC system calibrated with three polystyrene sulfonates with known MWs of 1430, 4950 and 6530 g/mol, respectively ($\log_{10} MW = -0.110t + 5.03$, $R^2 = 0.998$; t is the elution time in minute) (Li et al., 2003).

2.2. *Model Analysis of Observed Batch Isotherm Data*

To describe the adsorption isotherms of DOMs, the distributed fictive component method (DFCM) proposed by the authors was used (Yuasa et al., 1997; Matsui et al., 1998). This method involves the uses of a straightforward equation derived from the IAST-Freundlich model (Crittenden et al., 1993) and a distribution function of Freundlich K, $f(K)$, devised to account for the heterogeneity of a given organic matrix in adsorbabilities:

$$\int_0^{\infty} \frac{f(K)\,dK}{(q_T^n/(C_{T0} - C_{\mathrm{non}})) \cdot K^{-n} + 1 - (C_T - C_{\mathrm{non}})/(C_{T0} - C_{\mathrm{non}})} = 1 \tag{1}$$

where, K is the Freundlich parameter and C_{T0} the initial concentration of the whole organic matrix assessed using the index of either DOC or UV260, C_T the relative liquid phase equilibrium concentration, C_{non} the non-adsorbable component concentration and q_T the overall solid phase equilibrium concentration. Eq. (1) is an extended version of the IAST-Freundlich model, which can be generated by assuming identical Freundlich exponent ($1/n$) for all adsorbable constituents (i.e., $1/n_i = 1/n$). This assumption is well used when dealing with organic matrices with unknown composition (Harrington and DiGiano, 1989; Yuasa, 1993; Smith, 1994).

To find a distribution function suitable for application, a large number of distribution patterns defined by several functions were tested (Li, 1998). Simulations confirmed that the log-normal distribution function, as given below, was most suitable since it could generate isotherm shapes most close to observed ones and involves the least number of explanatory variables: the mean value (K_M) and the standard deviation (σ) of $\log_{10}(K)$:

$$f(K) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{[\log_{10}(K/K_M)]^2}{2\sigma^2}\right) \tag{2}$$

Using this distribution function, the overall isotherms (q_T vs. C_T) of a given DOM described by Eq. (1) are regulated by: K_M, σ, $1/n$, C_{T0} and C_{non}. Since C_{T0} and C_{non} can be measured independently, unknown parameters are limited to only three: K_M, σ and $1/n$, which can be logically searched by fitting observed data (C_T vs. C_{AC}) for two or more C_{T0}. Details of this method are documented (Li et al., 2003).

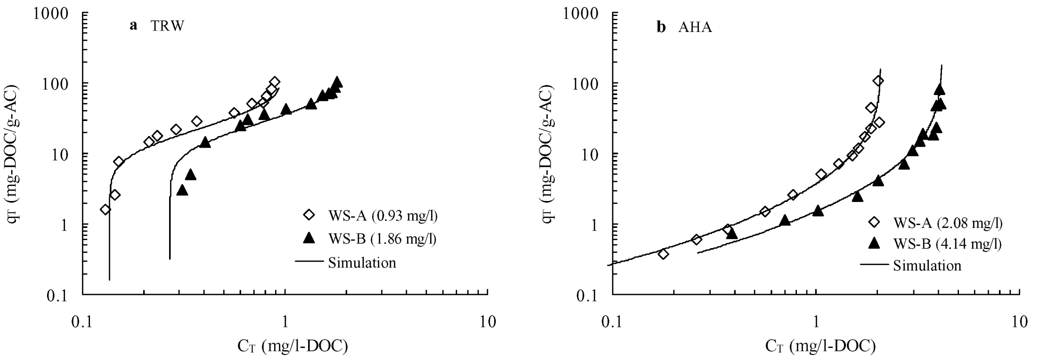

Figure 1. Description of DOC-based overall isotherms for organic matrices using DFCM. Symbols used are observed data and the solid lines are model simulations. The values in parentheses are initial DOC concentrations.

3. Results and Discussion

3.1. Adsorption Isotherms

Batch adsorption isotherms assessed by DOC for the river water DOM in TRW and the commercial AHA are displayed in Fig. 1. In reflective of the polydisperse adsorbabilities of organic constituents, the observed isotherm changed its position according to the initial concentration (C_{T0}) and exhibited a shape that could not be described by single-solute adsorption models. For all organic matrices studied, the simulations described isotherm data with reasonably high accuracies: the error defined by an objective function (Li et al., 2003) fell in 2.97–10.7%. Similarly, for all UV260-based isotherms, good agreement between simulations and observations was also confirmed: the error was in the range of 2.48–9.16%. As evidence, these results further proved the effectiveness of the DFCM in describing the overall adsorption equilibrium of organic matrices of unknown composition.

3.2. Polydisperse Adsorbabilities

Four parameters (K_M, σ, $1/n$ and C_{non}) determined for all DOMs are summarized in Table 1. Reflecting the differences in mean adsorbabilities, K_M differed considerably with respect to the sources and types of DOMs: 2.5–62.2 $(\text{mg/g})/(\text{mg}/l)^{1/n}$ and 20.0–141.1 $\text{m}^{1/n-1}/(\text{g}/l)$ for DOC and UV260, respectively. The largest K_M difference was found between the aquatic DOM of NRW-MS and the commercial WHA, with the DOC and UV260-based K_M of the former being about 25 and 7 times as large as that of the latter.

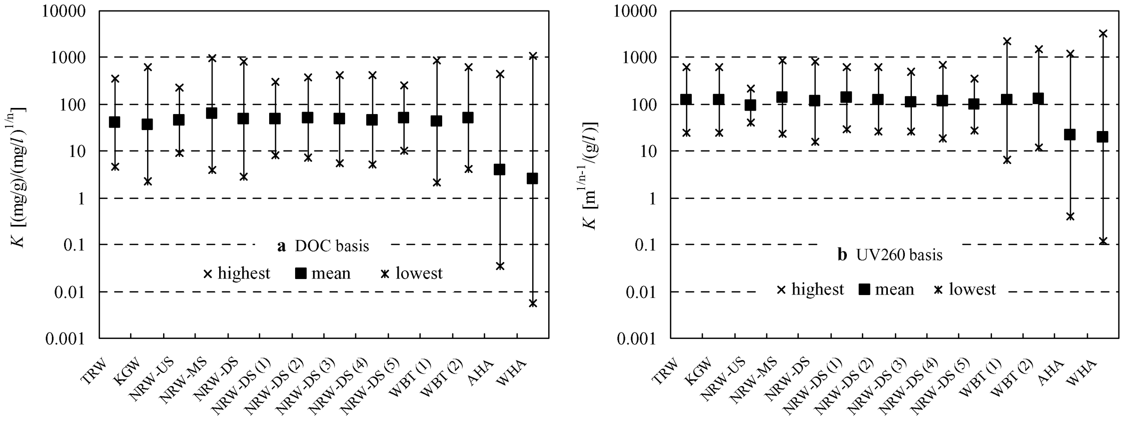

Figure 2. Ranges of Freundlich K of adsorbable fractions of all organic matrices: (a) DOC basis and (b) UV260 basis.

As an important parameter devised to assess the polydispersity of organic constituents in adsorbabilities, the magnitude of the DOC-based σ changed in 0.22–0.97, and that of the UV260-based one in 0.11–0.79, by following a general decreasing order: WHA > AHA > WBT-1 > NRW-DS > PW > NRW-MS > WBT-2 > TRW > NRW-US. The distribution ranges of the Freundlich K generated by simply introducing the determined K_M and σ values into Eq. (2) are depicted in Fig. 2. WHA and AHA displayed ranges of K much broader than aqueous DOMs, suggesting that these two commercial humic products were most heterogeneous with respect to their constituents' adsorption strengths: 0.01–1494.3 and 0.03–463.7 $(\mathrm{mg/g})/(\mathrm{mg}/l)^{1/n}$ for the index of DOC, and 0.11–3717.5 and 0.42–1165.1 $\mathrm{m}^{1/n-1}/(\mathrm{g}/l)$ for the index of UV260, respectively.

For the Nagara River DOM, it was interesting to see that, for both quality indices, the magnitude of σ followed the increasing order: NRW-US < NRW-MS < NRW-DS, indicating expanded polydispersity in adsorbabilities as the river flowed downstream. This trend was likely because, besides organic constituents from the upstream, some new ones having much stronger and weaker adsorbabilities from the river's tributaries were probably merged along the river line. A broader DOC-based K range was also revealed for the NRW-DS (4) (6.3–345.9) than the reference sample NRW-DS (1) (9.6–256.4) in $(\mathrm{mg/g})/(\mathrm{mg}/l)^{1/n}$ collected during and hours before the rainstorm, respectively. This result was also likely and interpretable as the storm-water probably brought into the river water some new components from its catchment area having adsorbabilities different from those in normal weather conditions.

3.3. Molecular Weight Impact on Adsorption

Changes in the HPSEC chromatograms of the river water (TRW) and groundwater (KGW) DOMs and the commercial AHA are displayed in Fig. 3 as examples. For a given organic matrix, if smaller organic constituents are adsorbed preferentially, a shift of the MW distribution towards larger molecular sizes should be observed in the solution as C_{AC} is increased. Such a shift was not obvious for the TRW and KGW DOMs (Fig. 3(a) and (b)), and was not observed for all remaining DOMs in the WBT and the NRW sources either. For commercial humic acids, however, although incomplete, a shift of the MW distribution towards the larger size side eluted earlier in the chromatograms was shown existent (Fig. 3(c)).

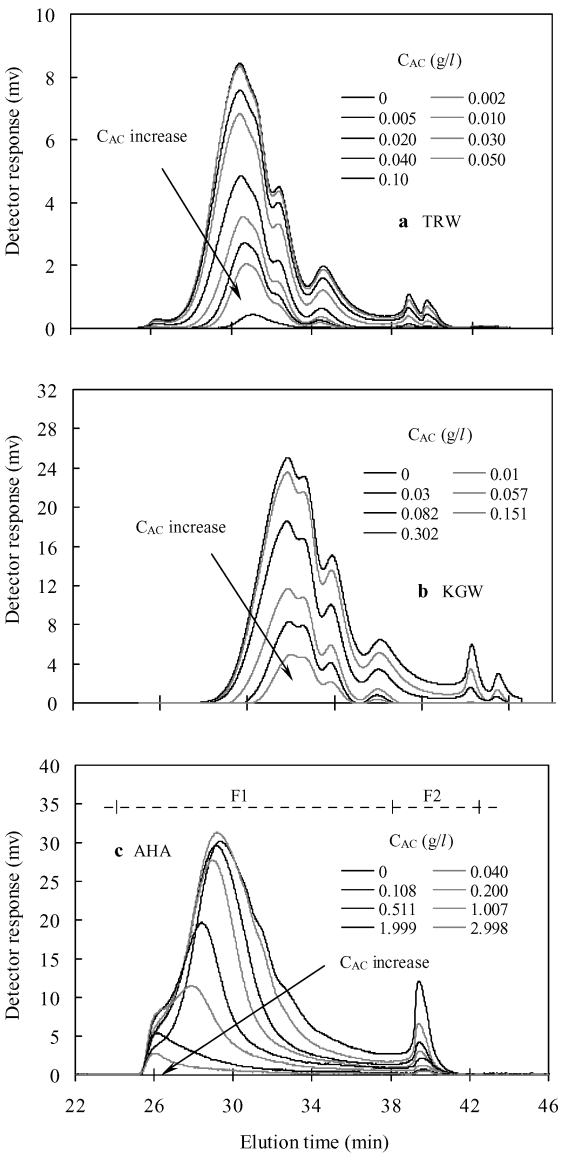

Figure 3. Changes of HPSEC chromatograms after adsorption. (a) for TRW ($C_{\mathrm{T0}} = 4.26\ \mathrm{m}^{-1}$ as UV260, =1.86 mg/l as DOC) (b) for KGW ($C_{\mathrm{T0}} = 15.12\ \mathrm{m}^{-1}$ as UV260, =4.12 mg/l as DOC) (c) for AHA ($C_{\mathrm{T0}} = 33.59\ \mathrm{m}^{-1}$ as UV260, =4.14 mg/l as DOC).

The changing trends of the weight-averaged MW (M_w) and the MW polydispersity (M_w/M_n) (M_n is the number-averaged MW) computed using relative expressions documented (Kilduff et al., 1996) are displayed in Fig. 4. The relative values determined for all DOMs before adsorption are summarized in Table 1. In reflective of the preferential adsorption of smaller constituents, the magnitude of M_w for the AHA remaining in solution increased with the increases of

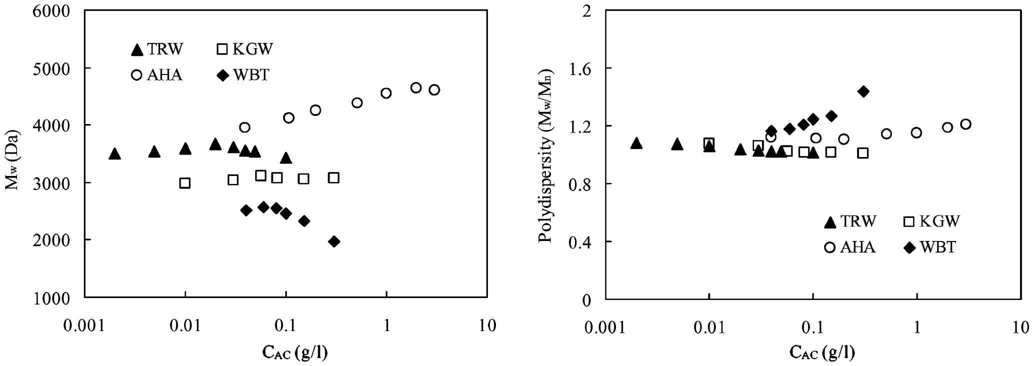

Figure 4. Changes of the weight-averaged MW (M_w) and polydispersity (M_w/M_n) with activated carbon dosage (C_{AC}).

C_{AC}. However, since the preference was not complete, as illustrated by the remaining of the smaller fraction (F2) even at higher C_{AC}, an expected decreasing trend in the MW polydispersity of the commercial humic acid was not exhibited. In contrary, for the wastewater DOM, parametric trends showing decreased M_w and increased polydispersity with the increases of C_{AC} were revealed due to unfavorable adsorption observed for some of its small molecules. The results of AHA and WHA support the idea that molecular size is probably the most important feature controlling adsorption of organic macromolecules, as proposed by others using the results of extracted or synthetic macromolecular organic matters from such materials as soil, peat and coal (Summers and Roberts, 1988; Kilduff, 1996). However, the results measured for all aqueous DOMs do not. These findings have significant means because they serve as strong evidence to stress that extracted or synthetic organic macromolecules are less representative of organic matrices present in water and wastewater sources, and that the potential impacts of chemical features (including the functional group, charge density and aromaticity, etc.) should be investigated especially for organic matrices contained in aqueous solutions.

4. Conclusions

Adsorption characteristics of fourteen organic matrices from different river water, ground water, wastewater and commercial sources were studied. The source and type dependency of the composition of organic matrices in adsorbabilities was clearly demonstrated, so was the role of molecular sizes of constituting components. All findings obtained have significant implications for better understanding the fundamentals of adsorption of organic matrices in water environmental systems. Problems of using extracted humic products as model substances for characterizing aqueous ones in solutions, a practice that has been frequently adopted, were also raised.

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