Kinetics study of aqueous sorption of phenanthrene to humic acids and sediments

ZHOU Yan-mei[1,*], LIU Rui-xia[1], TANG Hong-xiao[1]

(1. State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: fox_55555@sohu.com)

Abstract: The sorption behavior was determined for a model polycyclic aromatic hydrocarbon (PAH), i.e., phenanthrene(PHN), from water to three humic acids(HAs) and three sediments in different reacting time. The chemical compositions of HA samples were measured using cross polarization magic angle spinning carbon-13 (CPMAS ^{13}C NMR along with elemental analysis. The dissolved humic substances dissociating from solid HAs and sediments were characterized by ^{1}H NMR. The experiments indicated that the sorption modes and mechanisms of natural sorbents for PHN varied significantly between short(< 7 d) and long contact time and the reaction time should be taken into consideration in studying the overall sorption process. The sorption capacity(K'_t) and exponent (n) might be relative to the properties of dissolved humic materials in initial stage but the solid aromatic organic matter after long time reaction. According to the experiments performed in this investigation and the previous researches, a conceptive sorption model was established.

Keywords: sorption; phenanthrene; humic acid; sediment; CPMAS ^{13}C NMR

Introduction

The sorption of hydrophobic organic contaminants (HOCs) on natural geosorbents plays a significant role in their transport, degradation and ultimate fate in the aquatic environment (Alexander, 1995; Luthy, 1997; Weber, 2001). Since the late 1970s, the organic matter(OM) has been considered to be a major component of soil and sediment with regard to the uptake of HOCs and the majority of sorption studies have indicated that the sorption of HOCs occurred largely by partition into OM (Lambert, 1967; Chiou, 1979). But it has recently been reported that the sorption of nonionic organics to some natural sorbents displays various extents of nonlinear and hysteretic (Chiou, 2000; Huang, 1998). To account for these observations, a dual-mode sorption model has been hypothesized. This model suggested that there exist both a fast partition domain and a slow adsorption domain in solid-phase organic matter(Luthy, 1997; Pignatello, 1996; Accardi-Dey, 2002; Xia, 2001). However, there is on technique that can nondestructively separate and characterize these two domains at present. More recently, several studies have determined the chemical composition of organic matter by nondestructive solid-state CPMAS ^{13}C NMR and found that the sorption capacities is fast connected with sorbent characteristics, such as polarity, aromaticity or aliphaticity (Chiou, 1998; Ahmad, 2001; Chefetz, 2000; Salloum, 2002; Kile, 1999). For instance, Ahmad et al. report that there is a good positive exponential correlation between aromaticity of OM and the sorption capacity of nonionic pesticides and consider that the aromatic

component has implications for prediction of a geosorbent's ability to adsorb nonpolar pesticides. But several researches on PAH sorption to natural organic matter consider that aliphatic-rich OM has the capability to associate as much or even more PAHs than aromatic-rich samples(Chefetz, 2000; Salloum, 2002).

It has been evidenced that the humic substances consist of separate hydrophobic and hydrophilic parts and form self-associating aggregates in solution by intermolecular hydrophobic interactions (Kubicki, 1999; Wershaw, 1993; Conte, 1999; Wong, 2002). On one hand, the hydrophobic region of dissolved humic substances is the excellent sorption site for low-palority organic contaminants. The solubility, volatilization, hydrolysis and stability of the organic contaminants change in the presence of dissolved humic materials and such modifications would consequently influence the sorption behavior on geosorbents(Uhle, 1999; Oesterreich, 1999). On the other hand, the hydrophilic groups have relatively strong affinity with mineral and organic surfaces. The dissolved humic molecules keep exchanging and solving equilibrium with water-wet surfaces of particle materials and the chemical property of dissolved humics represents at least part of the characteristics of organic matter on the surface of particles (Murphy, 1990; 1994; Avena, 1999; Oste, 2002). However, the majority of sorption investigations neglect the contribution of dissolved humics.

In the present investigation, the sorption behaviors of phenanthrene to humic acid and sediment sorbents in different reaction times were investigated. The hydrophobic indexes of dissolved organic matter dissociating from HAs and sediments

were measured by liquid-state ^{1}H NMR and the chemical compositions of solid HA samples were determined by solid-state CPMAS ^{13}C NMR along with element analysis. The objective is to determine the role of dissolved humic materials and solid organic matter in sorption process.

1　Experiment

1.1　Materials

The sediments used in this investigation were collected from Gui River and Guanting Reservoir (Beijing, China), respectively. One humic acid was extracted from Guanting Reservoir sediment (Beijing) according to the procedure recommended by the International Humic Substances Society (IHSS)(Schnitzer, 1982). The other two humic acids were purchased from Tianjin and Shanghai, respectively. The physicochemical properties of all the samples, including the total and dissolved organic carbon contents(TOC and DOC, Apollo 9000, Tekman-Dohrmann Co., USA), specific surface areas(SSA, APAS2000, Micromeritics Co., USA) and cation exchange capacities (CEC, ICP-AES ULTIMA, Jobin Yuon Emission Horiba Group, France) (Hendershot, 1986), were measured and the results are listed in Table 1. PYR (analytically pure) used in sorption experiments was purchased from China while the sorbate(HPLC grade) used in standard curve was purchased from the National Research Center of Standard Material, China.

Table 1　Physicochemical property of humic acids and sediments

	TOC, %, g/g	DOC, %, g/g	SSA, m²/g	CEC, cmol (+)/kg
Guanting HA	28.76	2.78	NA[a]	9.36
Tianjin HA	64.77	0.87	NA[a]	3.22
Shanghai HA	55.79	0.49	NA[a]	2.68
Gui sediment	0.55	0.0064	12.09	5.47
Guangting sediment 1	1.47	0.0277	47.21	18.28
Guanting sediment 2	1.42	0.0259	37.57	11.47

Notes: a. not analyzed

1.2　Elemental analysis and CPMAS ^{13}C NMR spectrometry of HA samples

Elemental analyses of three HA samples were performed by a Vario EL Elemental Analyzer (Elementar Co., Germany) and the results are listed in Table 2. The CPMAS ^{13}C NMR spectra were acquired on a Bruker Advance 300 MHz NMR-spectrometer(Breker Analytic GmbH, Germany). The spectrum was divided into the six major regions: alkyl (0—40 ppm), O-alkyl(40—100 ppm), aromatic(100—140 ppm), phenolic (140—165 ppm), carboxyl and amide (165—185 ppm), and aldehyde and ketone (185—220 ppm). The spectra of three humic acid samples are presented in Fig. 1 and the C-containing function group contents are reported in Table 3.

1.3　^{1}H NMR spectroscope of dissolved humic substances

0.02—0.2 g sorbent samples and 1 ml 99.9% D_2O containing 0.005 mol / L $CaCl_2$ and 100 mg / L NaN_3 were

Table 2　Carbon, hydrogen, nitrogen and oxygen contents and C/N, O/ C and H/C ratios of three studied humic acids

	Guanting HA	Tianjin HA	Shanghai HA
C[a], %	24.01	62.53	52.99
H[a], %	3.96	4.80	3.80
N[a], %	2.97	NA[c]	1.30
O[a], %	25.20	32.34	30.36
C/N[b]	9.43	—	47.56
O/C[b]	0.79	0.39	0.43
H/C[b]	1.98	0.92	0.86

Notes: a. values represent the mean of triplicate measurements with a coefficient of variation less than 5%; b. atomic ratio; c. not analyzed
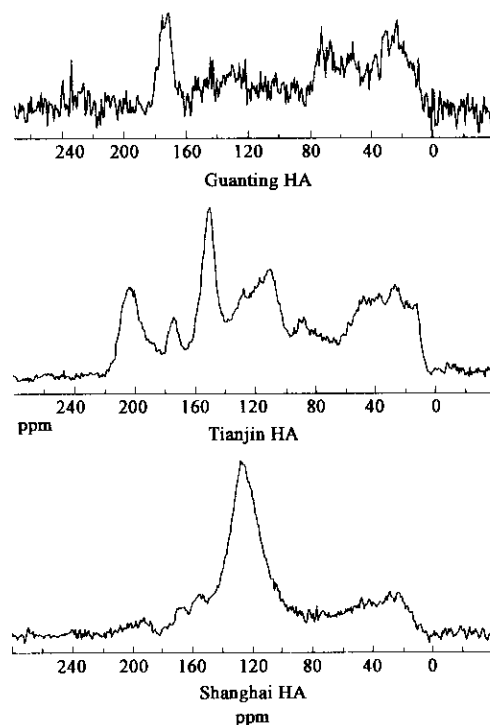

Fig. 1　Solid-state CPMAS ^{13}C NMR spectra of three studied humic acids

Table 3　Distribution of carbon intensity in different regions of CPMAS ^{13}C NMR spectra of humic samples as a present of total C

	Guanting HA	Tianjin HA	Shanghai HA
Alkyl(0—40 ppm), %	24.6	17.8	11.8
Alkyl-O(40—100 ppm), %	30.1	23.1	17.6
Aromatic(100—140 ppm), %	13.6	23.9	51.0
Phenolic(140—165 ppm), %	7.7	17.0	13.0
Carboxyl(165—185 ppm), %	15.0	5.3	3.1
Carbonyl(185—220 ppm), %	2.5	12.4	3.3
Hydrophobic index[a]	0.72	0.92	1.86
Aromaticity[b], %	21.8	41.1	64.2
Aliphabicity[c], %	55.9	41.1	29.5

Notes: a. [(0—40 ppm) + (100—140 ppm)]/[(40—100 ppm) + (140—185 ppm)]; b. (100—165 ppm)/(0—240 ppm); c. (0—100 ppm)/(0—240 ppm)

continuously mixed on shaker at 25 ℃ for 60 h, then the mixtures were centrifuged for 30 min at 2000 g. ^{1}H NMR spectra of the supernatants were obtained by Avance DPX 500 MHz NMR-spectrometer(Bruker Analytic GmbH, Germany). The spectra were approximately divided into the following chemical shift region: hydrocarbon chain (0—2.8 ppm),

polar group such as sugar, amino acid, aromatic methoxyl, and methylene unit adjacent to ether and ester (3.0—5.0 ppm), and aromatic moiety (7.0—8.5 ppm). ^{1}H NMR spectra of dissolved humic substances from solid sorbents investigated in this paper are presented in Fig. 2 and the integration results are listed in Table 4.
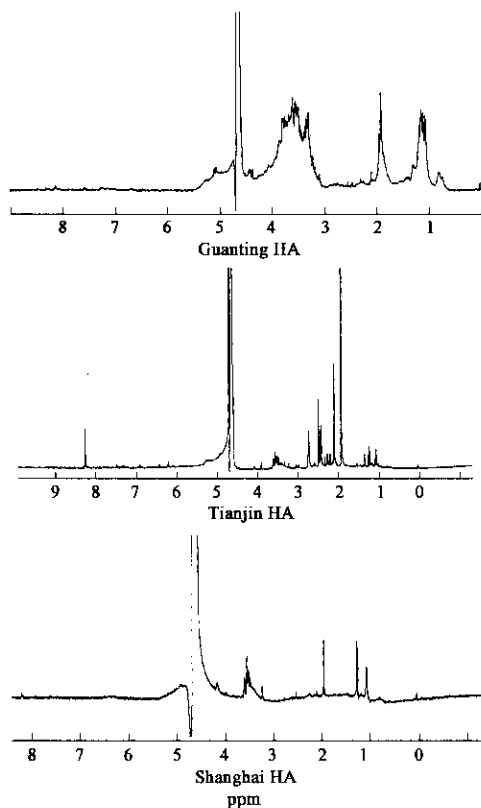

Fig.2 ^{1}H NMR spectra of dissolved fraction contained in solid humic acids and sediments

Table 4 ^{1}H NMR integration results of dissolved fraction contained in humic acid and sediments

	Guanting HA	Tianjin HA	Shanghai HA	Cui sediment	Guanting sediment 1	Guanting sediment 2
Hydrocarbon chain(0— 3.0 ppm), %	24.6	15.4	2.7	67.72	48.81	56.60
Polar group (3.0—6.5 ppm),%	75.4	84.1	97.3	27.90	47.20	38.38
Aromatic moiety (6.5—8.5 ppm), %	NA [b]	0.5	NA[b]	4.37	3.98	5.02
Hydrophobic index[a]	0.33	0.19	0.03	2.59	1.12	1.61

Notes: a. [(0—3.0) + (6.5—8.5)]/(3.0—6.5); b. not analyzed

1.4   Sorption experiments

The stock solution of PHN was prepared by ultrasonic treating excess amount of PHN in 0.005 mol/L CaCl$_2$ plus 100 mg/L NaN$_3$ solution for 1 h and then shaking overnight. The solution was subsequently filtered (GF/F filter paper, Whatman Co., England) to remove insoluble solutes. The different concentration solutions used in sorption experiments were prepared by diluting this original stock solution with 0.005 mol/L CaCl$_2$ and 100 mg/L NaN$_3$ solution. 0.2—2 g of sorbent samples was weighed into 50-ml flasks, and 10-ml

aliquot of PHN solution was added. The flasks were tightly sealed by parafilm immediately. The suspensions were continuously mixed on a shaker at room temperature for desired time and then centrifuged for 3—10 min at 12000 g by a refrigerated centrifuge (Bekman Co., German). The sorbate in supernatant was quantified by a high performance liquid chromatography (HPLC, 10A, Shimadzu Co., Japan) equipped with an Extend-C18 reversed-phase column (4.6 × 250 mm, Agilent Technologies, USA). The absorbance wavelength of 240 nm, the mobile phase of 90% methanol/ 10% water, a flow rate of 1 ml/min and an injection volume of 20 μl were used to determine PHN concentration.

2   Results and discussion

2.1   Chemical properties of solid humic acids and dissolved organic matter

CPMAS ^{13}C NMR spectrum connected with element analysis can provide useful information on the functional group composition of the natural organic matter. As shown in Table 2, of three HA samples Guanting HA presents the largest N content (2.97%) and the highest O/C ratio (0.79), and H/C ratio (1.98) is about 2, indicating high aliphaticity. Tianjin HA exhibits the highest C (62.53%) and O (32.34%) contents but the lowest N content (not analyzed), and H/C ratio (0.92) is close to 1. Shanghai HA has the lowest H/C ratio (0.86). The CPMAS ^{13}C NMR spectrum of Guanting HA reveals the following composition: the aliphatic carbons (0—34 ppm), the carbohydrates (72 ppm) and the amide and/or carboxyl carbon (171 ppm). According to large N content (2.97%) and high O/C ratio from elemental analysis, the strong resonance at 171 ppm can be attributed to proteinaceous materials. These data imply that Guanting HA is rich in polar groups and aliphatic compounds. Tianjin HA CPMAS ^{13}C NMR spectrum exhibits major peak at: long-chain aliphatic C (28 ppm), nonpolar aromatic C (110 ppm), O-substituted aromatic C (150 ppm), carboxyl or amide C (175 ppm) and aldehyde or ketone C (204 ppm). Considering that N content of Tianjin HA is not analyzed and O content (32.34 %) is very high, the signal at 175 ppm is likely due to carboxyl carbon. Shanghai HA spectrum contains an intense signal from C-substituted aromatic carbon (129 ppm). The strong resonance at 29 ppm can be attributed to long-chain aliphatic structures. Shanghai HA presents the largest hydrophobic index (1.86) in three HA samples. Combining with the elemental analysis, it is indicated that Shanghai HA contains a large percent of nonpolar aromatic compounds.

Comparison of ^{1}H NMR spectra of dissolved humic substances with CPMAS ^{13}C NMR of solid HAs showed that the chemical composition of dissolved fraction are greatly different from the solid. For three solid HA samples, the hydrophobic index is the highest for Shanghai HA (1.86) and the lowest for Guanting HA (0.72), but in dissolved fractions, the hydrophobic index of Guanting HA (0.33) is much higher than that of Shanghai HA (0.03). The dissolved

humics dissociating from Gui sediment present the highest hydrophobic index (2.59) of all sorbents studied in this investigation.

2.2   Role of dissolved and solid humic materials in sorption process

The sorption of HOCs on natural geosorbents is often described by Freundlich equation. In this paper, the modified Freundlich equation was utilized to carry out direct comparison of sorption data for different sorbents in various contact times(Carmo, 2000) :

$$\Gamma = K'_f C_r^n \quad , \tag{1}$$

where Γ is the adsorbance of sorbent, K'_f is the modified Freundlich coefficient indicating the sorption capacity of sorbent, n is the Freundlich exponent denoting the degree of deviation from isotherm linear, and C_r is the solubility-normalized equilibrium concentration of sorbate($C_r = C_e / S_w$, where C_e is the sorbate equilibrium concentration, S_w is the sorbate water solubility) and has no unit. To avoid crowding of the figure and table, only the sorption isotherms and parameters of 60 h (regarded as equilibrium time in most routine sorption experiments) for three humic acids and three sediments are presented in this investigation (Fig. 3 and Table 5, respectively).

Table 5 Modified freundlich parameters for sorption of phenanthrene to humic acids and sediments

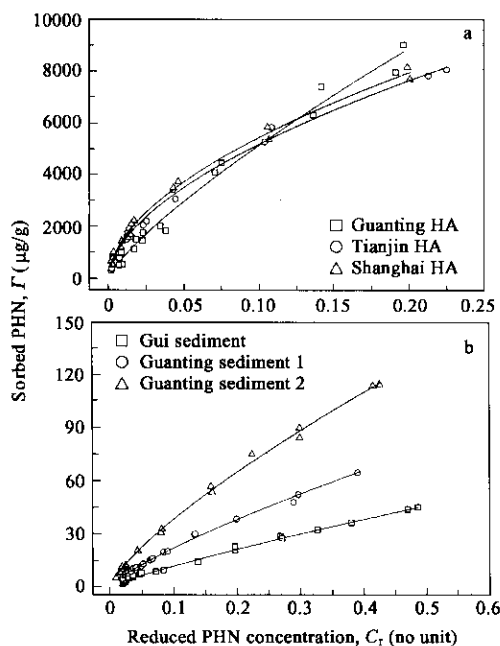|	K'_f, $\mu g/g$	n	R^2
Guanting HA	31862	0.802	0.967
Tianjin HA	21861	0.614	0.969
Shanghai HA	19048	0.550	0.978
Gui sediment	83.92	0.861	0.977
Guanting sediment 1	137.4	0.802	0.991
Guanting sediment 2	232.6	0.799	0.996

Fig.3 Sorption isotherms of phenanthrene to studied sorbents in 60 h contact time

Previous studies reported that the sum of nonpolar

components or individual aromatic or aliphatic compounds contained in natural organic matter may be responsible for the association of hydrophobic contaminants (Chiou, 1998; Ahmad, 2001; Chefetz, 2000; Salloum, 2002; Kile, 1999). However, our sorption experiments do not show such correlation between the sorption capacity and the chemical property of solid organic matter when contacting 60 h. Both Tianjin and Shanghai HA contain long-chain aliphatic and nonpolar aromatic carbon, while Guanting HA is rich in polar aliphatic materials (Table 2, 3 and Fig. 1). The sorption capacity of Guanting HA for PHN (31862 $\mu g/g$) is significantly higher than Tianjin and Shanghai HA(21861 and 19048 $\mu g/g$, respectively). Although the TOC content of Guanting sediment 1(1.47%) is closed to Guanting sediment 2(1.42%), the uptake capacity for Guanting sediment 1 (137.4 $\mu g/g$) is significantly less than Guanting sediment 2 (232.6 $\mu g/g$). As shown in Fig.4, the sorption coefficients and exponents vastly differ among different reaction times. For all sorbent samples, there exists a sharpened change rate of the sorption parameters K'_f and n between 1 and 7 d and the system is still far from the equilibrium after 60 h of reaction. These observations suggested that the sorption modes and mechanisms may be different between various sorption stages and the application of bulk organic matter properties to characterize the sorption behavior of one certain reaction time (generally fast sorption process in most researches) is not appropriate.
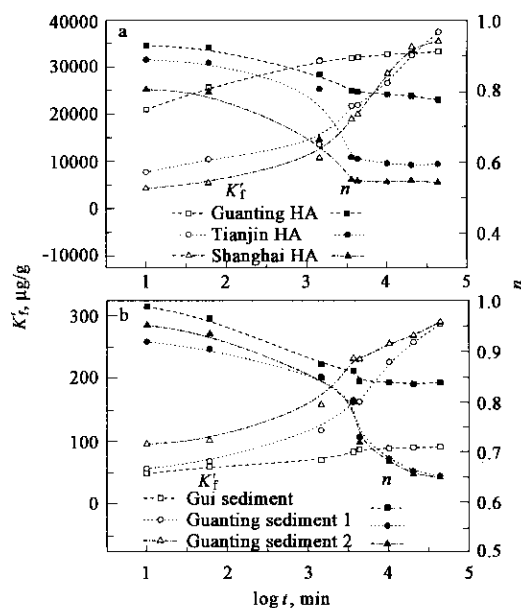

Fig. 4   Changes in sorption capacities (K'_f) and exponents (n) of phenanthrene for studied sorbents as a function of time

In initial sorption stage, nonpolar molecules first diffuse into the surface OM domains because these domains are highly hydrated and swollen by water and readily accessible. And the binding capacity is dependent on the chemical properties of this domain. The higher the hydrophobic index, the larger the sorption capacity is(Luthy, 1997; Pignatello, 1996; Wershaw, 1993). The dissolved organic matter dissociating from solid particles keeps exchanging and solving

equilibrium with water-solid interfaces, thereby reflects at least part properties of organic matter on water-wet surfaces of particulates (Wershaw, 1993; Simpson, 2001). Thus, in initial stage the sorption parameters may relate to the characteristics of dissolved humic substances dissociating from solid sorbents. Of three HA samples, the DOC content and hydrophobic index of dissolved humic substances are the highest for Guanting HA and the lowest for Shanghai sediment. At the beginning of sorption, Guanting HA exhibits the largest while Shanghai sediment presents the lowest K'_f and n values. The DOC content of Guanting sediment 1 (0.0277%) is slightly higher than Guanting sediment 2 (0.0259%), but Guanting sediment 1 presents lower K'_f values than Guanting sediment 2 in short contact time, presumably due to the less hydrophobic index of Guanting sediment 1 dissolved humics(1.12). Although Gui sediment exhibits significantly lower TOC and DOC contents (0.55% and 0.0064%, respectively) compared to Guanting sediment 1 (1.47% and 0.0277%, respectively), the sorption capacities of 10 min and 1 h are only slightly lower than Guanting sediment 1. It is possibly due to the much higher hydrophobic index of Gui sediment dissolved organic matter(2.59).

The sorption parameters for long time reaction may be connected with the aromaticity of solid organic materials. Solid Shanghai and Tianjin HA exhibit much higher aromaticity (64.2% and 41.1%, respectively) than Guanting HA (21.8 %) and they present larger sorption capacities when uptake 30 d. From organic geochemistry and petrography, the loose and highly amorphous humic materials gradually change into condensed and crystalline organic matter over geological times. After thousands years of equilibrium and diagenesis, the quality and quantity of aged and diagenetically altered organic materials contained in Guanting sediment 1 and 2 may be similar due to their nearby sampling sites. Contacting long time(such as 1 month), both K'_f and n values of Guanting sediment 1 and 2 for PHN tend to equivalence. These observations agree with the inferences of recent experimental work on HOC sorption that the aromatic materials may be the major component of the adsorption domains that are responsible for the nonlinear and hysteretic sorption behavior of long contact time (Weber, 2001; Huang, 1998; Accardi-Dey, 2002).

2.3 Concept sorption model for hydrophobic organic chemicals

During the long diagenetic processes, the organic matter contained in soils and sediments have formed two states;

amorphous and crystalline, and over the geological times the amorphous state continually and solely transforms into crystalline state (Tissot, 1984; Engel, 1993). The amorphous organic matter is swollen and the water solubility is high while the structure of crystalline substance is relatively condensed and it is almost insoluble in water. In sorption process the organic sorbates first diffuse into amorphous states, then reach crystalline humics, due to the loose structure of amorphous humic and the condensed conformation of crystalline region. Due to the repulsion between nonpolar sorbates and charged surface of solids, the initial sorption is not linear but agrees well with Freundlich equation. It is given:

$$[HOC]_a = K_1 [HOC]_w^{n_1} , \qquad (2)$$

where $[HOC]_a$ presents the concentration of HOC in OM amorphous state, $[HOC]_w$ presents the concentration of HOC in water phase, K_1 and n_1 are Freundlich sorption capacity and exponent of HOC on amorphous organic matter, respectively. Moreover, it is reported that the binding capacities of HOCs to dissolved humics are much higher than sorption capacities to solid-phase humics and the binding kinetics of dissolved humics is faster than the sorption kinetics of solid humics(Brunk, 1997; Laor, 1998; 2002). In water phase some sorbates are not existence by themselves but associated with dissolved humic substances. When dissolved humic acids interacting with the surface of particles, the bound HOC molecules is simultaneously "transported" into humic acids (Wershaw, 1993; Conte, 1999; Murphy, 1990). According to Laor(Laor, 2002), the sorption of PAHs to dissolved humics deviates from linear. It is given:

$$[HOC]_{HS} = K_2 [HOC]_w^{n_2} , \qquad (3)$$

where $[HOC]_{HS}$ presents the concentration of HOC in dissolved humics, K_2 and n_2 are Freundlich sorption capacity and exponent of HOC on dissolved humics, respectively. The sorption of humics to minerals can be well fitted by Langmuir equation:

$$[HS]_a = \frac{q_{max} K_3 [HS]_w}{1 + K_3 [HS]_w} , \qquad (4)$$

where $[HS]_a$ presents the concentration of humic substances in water-wet surface, $[HS]_w$ presents the concentration of humic substances in water phase, q_{max} and K_3 are the saturated adsorbance and sorption coefficient of humics on solid sorbents, repectively. Combining Equation (3), (4), (5) and (6) gives:

$$[HOC]_a = \frac{q_{max} K_2 K_3 [HS]_w + K_1 [HOC]_w^{n_1 - n_2} + K_1 K_3 [HOC]_w^{n_1 - n_2} [HS]_w}{1 + K_3 [HS]_w} [HOC]_w^{n_2} . \qquad (5)$$

The uptake of HOC on crystalline organic matter is nonlinear. It is given by:

$$[HOC]_c = K_4 [HOC]_a^{n_3} , \qquad (6)$$

where $[HOC]_c$ presents the concentration of HOC in crystalline humics, K_4 and n_3 are Freundlich sorption capacity and exponent of HOC on crystalline state,

respectively. In Equation(6), n_1 is fast closed to n_2 since the chemical structure of dissolved humic materials is similar to that of surface organic matter. Thus:

$$[HOC]_c = \left[\frac{q_{max} K_2 K_3 + K_1 + K_1 K_3 [HS]_w}{1 + K_3 [HS]_w} \right]^{n_3} \cdot$$
$$K_4 [HOC]_w^{n_2 n_3} \qquad (7)$$

The Freundlich equation can be used to describe the sorption

behavior of both short and long contact time. The concentration of humic substance in water phase ($[HS]_w$) and the chemical property of dissolved organic matter (determining the value of K_1, K_2, K_3, n_1 and n_2) are two crucial factors determining the sorption parameters, particularly in initial stage.

3 Conclusions

Of all sorbent samples studied in this investigation, the sorption behavior exhibits bimodal. These data demonstrated that there exist two different sorption domains in natural sorbents and the sorption modes and mechanisms on these two domains differ. It is apparent that characterization of the sorption behavior of one certain uptake time (generally fast sorption process in most researches) using the bulk organic matter properties, such as TOC content, polarity, aromaticity and aliphabicity, is problematic and the reaction time is a prerequisite in order to understand or predict behavior of organic contaminants in natural environment. The kinetics experiment indicated that in short contact time, the sorption capacity and exponent may be relative to the properties of dissolved humic substances in water phase since the dissolved humics are characteristic of water-wet surfaces of solid sorbents and strongly interact with hydrophobic sorbates. After long time reaction, the uptake parameters may be dependent on the OM aromaticity. The present research investigates both the influences of dissolved and solid organic components contained in natural sorbents on PHN sorption and put forward a conceptive sorption model, which also evidences the importance of dissolved organic matter.

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