

Description of adsorption of hydrophobic organic compounds on sediment using multi-component adsorption model

QUAN Xie^{*}, LIU Zhen-yu, XUE Da-ming, ZHAO Ya-zhi, YANG Feng-lin

(School of Environmental Science and Technology, Dalian University of Technology, Dalian 116012, China. E-mail: xiequan@mail.dlptt.cn)

Abstract: A chemical sequential separation procedure for sediment has been developed for the adsorptive investigation of hydrophobic organic compounds (HOCs) including four fractions: carbonate, hydrous metallic oxide (ferric oxide, manganese oxide and alumina), clay and organic matter. Adsorption isotherms of these hydrophobic solute probes, such as hexachloroethane, lindane and 1,2,4,5-tetrachlorobenzene were measured for model sorbents, model and natural sediment, and the latter of which was pretreated with the simplified sequential separation method. The linear and Langmuir models are applied to correlate the experimental data of humic substance and other model sorbents respectively. Multi-component Adsorptive Model (MCAM) was used to simulate adsorption isotherms of model and natural sediment. The results reveal that (1) the separation efficiencies of carbonate, organic matter, ferric oxide, manganese oxide and alumina are 98.1%, 72.5%, 82.6%, 93.5% and 83.3%, respectively; (2) except for removing metallic oxide, the external structure of sediment is not changed greatly after separation; (3) the MCAM correlates the data of adsorption isotherm rather well with the maximal relative deviations of 9.76%, 6.78% and 9.53% for hexachloroethane, lindane and 1,2,4,5-tetrachlorobenzene in model sediment, respectively. The MCAM can clearly give expression to the different adsorptive mechanisms for HOCs in organic and inorganic matter, though the experimental data in each component are not very accurate due to the sequential separation efficiency.

Keywords: hydrophobic organic compounds; sediment; adsorption; model

Introduction

The transport and fate of HOCs in the environment is highly dependent upon their sorptive behavior on soil and sediment. Many studies have been reported that the predominant sorbent of HOCs in soil/sediment is normally the soil/sediment organic matter (SOM) fraction, and the sorption of HOCs occurs largely by partition (dissolution) into SOM (Chiou, 1979; 1998; Karickhoff, 1979; Kile, 1995; Piat, 1996). However, numerous studies have revealed that sorption on natural solids yields nonlinear sorption isotherms (Weber, 1991; 1992; McGinley, 1993; Grathwohl, 1993; Young, 1995; Weber, 1996; Xing, 1996a; 1996b; 1997; LeBoef, 1997; Huang, 1997). These results are inconsistent with the partition or linear model in which all sorption in the sorbents can be attributed to SOM.

To explain the results, it has been proposed that SOM may comprise two principal types of heterogeneous organic domains, a "hard" carbon domain and a "soft" carbon domain (Weber, 1992; 1996; Young, 1995; Xing, 1996a; 1997; LeBoef, 1997; Huang, 1997; Carroll, 1994; Pignatello, 1996), analogous to glassy and rubbery regions, in which the sorption on natural solids can be interpreted by the known respective sorption behaviors of the rubbery and glassy of polymers (Young, 1995; Xing, 1996a; LeBoef, 1997; Huang, 1997). The glassy domain of SOM would be expected to exhibit nonlinear sorption behavior, solute-solute competition. On the contrary, the rubbery domain should exhibit linear sorption behavior, no solute-solute competition. Thereby, Weber and coworkers (Weber, 1992; McGinley, 1993) introduce the distributed reactivity model (DRM), in which sorption of HOCs shows a combination of partitioning and adsorption depending on the nature of SOM. They correlated nonlinear behavior with the fraction of hard organic carbon. In recent studies (LeBoef, 1997; Huang, 1997), they advanced the limiting case form of DRM, the dual reactive domain model (DRDM), for characterizing soil and sediment domains (Weber, 1996).

Nevertheless, the sorbent nature of SOM cannot be determined unambiguously from studies of low-organic soils/sediments by virtue of the possible role of the minerals in the observed behavior (Xing,

1996a). While some information is available on organic matter colloids, sorption in these materials is difficult to quantitate, and it is not clear to what degree colloids represent solid-phase SOM (Xing, 1996a). Xing and his coworkers (Xing, 1996a; 1996b; 1997) described competitive sorption on natural and model sorbents. They introduced dual-mode model (DMM) and suggested that sorption in SOM, like glassy polymers, yields partition (dissolution) and hole-filling mechanisms. According to the DMM (Xing, 1996a; 1997), the total sorption to SOM is the sum of sorption in the dissolution domain $S(D)$ and sorption in the hole-filling domain $S(H)$. The DMM for the glassy polymer can be written as:

$$S = S(D) + S(H) = K_p C + \sum_{i=1}^n a_i \frac{S_i^0 b_i C}{1 + b_i C} \quad (1)$$

Where C is the solute concentration and K_p is the partition domain coefficient, and b and S^0 are the affinity constant and maximum capacity, respectively, for each of n unique holes. Despite the model sorbents are analogous to those components of soil and sediment, sorbents cannot completely substitute for components. However, relatively few attempts have been made to evaluate directly the contribution of each component in natural solids (Laird, 1994), especially in sediments. Laird and coworkers (Laird, 1994) used chemical extraction techniques to treat soil clay for the removal of organic matter and free Fe compounds, and then quantified the relative contributions of organic matter, free Fe and silicate clay to the sorption of atrazine.

Chemical extraction techniques are a traditional approach for soil chemical analysis and used in determination of speciation of trace metals in natural solids (Tessier, 1979; Rapin, 1986; Niss, 1993; Martens, 1997). Tessier and coworkers (Tessier, 1979; Rapin, 1986) firstly proposed the use of sequential extractions for the investigations of speciation of particulate trace metals in fluvial bottom sediment. They divide sediments into five fractions: (1) exchangeable; (2) bound to carbonates; (3) bound to iron and manganese oxides; (4) bound to organic matter; (5) residual. The five fractions were sequentially extracted with chemicals. Tang and his coworkers (Tang, 1982) advanced a sequential chemical separation procedure to study the heavy metal adsorption on multi-component adsorption model of aquatic sediments and obtained good results. Since the adsorption of HOCs is also presented in the clay mineral, hydrous metallic oxide and other inorganic matter (Xing, 1996a; LeBoef, 1997; Laird, 1994; Murphy, 1990; 1994; Gu, 1994), the method of sequential separation may be used to study the adsorption of HOCs in components of sediments after modified.

The objectives of this study are focused on the followings. First, to introduce the sequential separation method of sediment for the adsorptive isotherm of HOCs. Second, to investigate the single solute adsorption isotherms of hexachloroethane, lindane and 1,2,4,5-tetrachlorobenzene on model sorbents and sequential separated sediment. Finally, to introduce the MCAM that is analogous to DRDM (LeBoef, 1997; Huang, 1997) and DMM (Xing, 1996a; 1996b; 1997) to correlate adsorptive data.

1 Materials and methods

1.1 Sample

Sediment samples were collected at two sampling stations, Xinghai and Laohutan bay located in the south offshore of Dalian City of China. The samples were air-dried. Subsequently, they were gently and slowly grinded and homogenized in a mortar, and particles larger than 200 mesh were removed by a sieve, and stored at 4°C. Two pretreated sediments were mixed with 1 + 1 as the original separated sample. Each sample was analyzed for the following properties. Carbonate is determined by gasometric method. Organic matter is determined by $K_2Cr_2O_7$ oxidation method. Free iron, manganese and aluminum are determined by 1, 10-phenanthroline colorimetric method, ammonium persulfate method, and pyrocatechol violet colorimetric method respectively. Clay is determined by sedimentation-extraction-gravimetric method

(INSCAS, 1978).

1.2 Model sorbents

Illite, kaolinite and montmorillonite were purchased from Nanjing Soil Research Institute of Chinese Academy of Sciences (> 90%). Ferric oxide, manganese oxide, alumina and calcium carbonate were purchased from Reagent Corporation of Dalian (analytical pure). Humic substance was extracted from lignite by our own laboratory (> 98%).

1.3 Chemicals and reagents

Hexachloroethane, lindane and 1,2,4,5-tetrachlorobenzene were used as the target or probe solutes for the adsorption isotherm measurements, that these chemicals were purchased from Environmental Monitor Stations of China (standard samples of SEPA). Solvent benzene was purchased from Beijing Chemical Plant (GC pure). Ligroin was purchased from Dongfeng Chemical Plant of Dalian (analytical pure), which was redistilled until the interference peak of chromatographic solvent disappeared.

1.4 Sequential separation procedure

Numerous studies have showed that the organic matter, mineral matter in sediment exhibit distinct contributions to the sorption of HOCs (Chiou, 1979; Karickhoff, 1979; 1998; Laird, 1994; Murphy, 1990; Gu, 1994). Therefore, the effective components of sediments can be divided into three segments: i.e. organic matter, clay mineral and hydrated metal oxide. The sequential separation procedure is to remove effective components of sediments sequentially according to the research demand. Then the residues are used in the adsorption experiment. The adsorptive mechanism and capacity of each component can be obtained by mathematical deduction. The sequential separation procedure is performed as follows:

1.4.1 Carbonate removal

The reason to remove carbonate as the first procedure is that those reagents in the process of removing hydrated metal oxide may decompose carbonate. Carbonate was removed from separated sediment (400g) at room temperature by using 1000 ml of 1 mol/L sodium acetate (NaAc) adjusted to pH 5.0 with acetic acid (HAc). The sample was continuously agitated about 6h and settled for 24h. The supernatant was discarded, and then the sample was thoroughly diluted with enough distilled water and centrifugalized. The wet sample was dried at 50°C by infrared lamp.

1.4.2 Organic matter

The sample (about 80g) after the removal of carbonate was transferred into 500 ml beaker and treated with 30% H_2O_2 to remove organic matter.

1.4.3 Fe-Mn-Al oxides

The residual sample was extracted with 50 ml of 1.2 mol/L oxalic acid ($H_2C_2O_4$) and 0.8 mol/L ammonium oxalate ($(NH_4)_2C_2O_4$; pH 3.2) and thoroughly shaken for about 1h. The sample was settled for 24h and the supernatant was discarded. The above-mentioned process was repeated for five times. The sample was centrifugalized and diluted with distilled water.

1.4.4 Residue

The components of residual sample were mainly clay, sand, silt and other inorganic compounds.

After sequential separation, each sample was analyzed for its physical and chemical properties just like the initial mixed sample. Furthermore, all samples were scanned with electron microscope (KV KY-1000B).

1.5 Adsorption of model sorbents

Illite, kaolinite and montmorillonite were mixed with the proportion of 1:1:1 as the clay components. Ferric oxide, manganese oxide, and alumina were mixed with 1:1:1 as the metallic oxide components. Carbonate, humic substance, metallic oxide and clay were mixed with the proportion of 3.16:2.54:0.12:

17.7 to model the components of natural sediment. The model clay(1g), metallic oxide (1g), carbonate (1g), humic substance (0.5g) and model sediment were put into 150 ml ground glass triangular bottle respectively. Each bottle was added into 30 ml Kester artificial seawater(Xue, 1988) and sealed, shaken for 2h (25℃). And then hexachloroethane, 1,2,4,5-tetrachlorobenzene and lindane were added into different bottles with different concentration. The bottle was sealed and shaken for 8h (25℃) to attain adsorption equilibrium. They were subsequently transferred into centrifuge tubes and centrifuged (10000 r/min, 15 min) and decanted. The supernatant(10ml) was extracted with benzene and ligroin(1:1, 5ml) for two times. Raffinate was dried with anhydrous sodium sulfate and analyzed with GC/ECD (Japanese SHIMADZU 9A, Ni^{-63} electron capture detector).

1.6 Adsorption of sequentially separated sediments

Natural mixed sediment was only divided into two parts, organic matter and inorganic matter, and separated according to above organic matter separated procedure. The method of adsorptive experiment was the same as that of the adsorption of model sorbents.

1.7 Multi-component adsorptive model

It was assumed that the initial natural sediment was sequentially separated to n stages. HOCs were adsorbed with sequentially separated sediments sample including initial sediment. We hypothesized that components of sediment are mechanically mixed and their adsorptive property is not destroyed by sequential separation. Thereby, we could obtain equations according to the law of mass-conservation.

$$q_{12\Delta n} = a_{n1} q_1 + a_{n2} q_2 + \Delta + a_{nn} q_n, \quad (2)$$

$$q_{12\Delta n-1} = a_{n-1,1} q_1 + a_{n-1,2} q_2 + \Delta + a_{n-1,n-1} q_{n-1}, \quad (3)$$

$$\vdots$$

$$q_{12} = a_{2,1} q_1 + a_{2,2} q_2. \quad (4)$$

Where, $q_{12\cdots n}$ is the adsorbance of unit mass of initial sediment, and $q_{12\cdots n-1}$ is the adsorbance of unit mass of the first sequential separated sediment, and q_1 is adsorbance of unit mass of the final sequentially separated sediment. a_{nn} is percentage of the component compared with total sediment. The quantity of $q_1, q_{12} \cdots q_{12\cdots n}$ can be obtained from adsorptive experiment, and $q_2 \cdots q_n$ can be calculated with Equation (1), (2) and (3). The adsorption isothermal equation ($q_i = f_i(C)$) of each component can be developed with a group of equilibrium data. Besides, the total adsorbance (q_T) is equal to $q_{12\cdots n}$. In summary, the adsorptive model of sediment can be shown with the sum of components.

$$q_T = \sum_{i=1}^n a_{n,i} f_i(C). \quad (5)$$

Equation (5) shows the adsorptive capacity and curve forms of components of sediment to adsorb HOCs.

2 Results and discussion

2.1 Sequential separation procedure

The physicochemical characterization of sequentially separated sediments is listed in Table 1. The results revealed that the percentage of residual components did not change greatly after separation. The removal percentage of carbonate, organic matter, ferric oxide, manganese oxide and alumina is 98.1%, 72.5%, 82.6%, 93.5% and 83.3% respectively (Table 2). The scanning electron micrographs (SEM) (Fig. 1) of mixed sediment (A) indicated that the majority of particles are aggregated and come into existence with massive, amorphous state. The superficial state of the removed sediment for carbonate (B) and organic matter (C) did not change significantly in comparison with that of the mixed sediment. However, The SEM of metallic oxide sediment revealed that many finely ground particles existed and the dispersity of particles increased greatly. X-ray energy spectrum analysis showed that the surface of blocky

matter was mainly composed of Fe, Al and Mn metallic elements in the first three kinds of sediments. Thus, particles are supposed to be connected with metallic oxide. Although there has been limited research into problems of separation efficiency and variation of superficial structure (removed metallic oxide sediment), the method of sequential separation can be effectively used for obtaining informations concerning the adsorption of HOCs.

Table 1 Component of sorbents

Sorbent	Carbonate, %	Organic matter, %	Fe ₂ O ₃ , %	MnO, mg/kg	Al ₂ O ₃ , %	Clay, %
Xinghai Bay sediment	4.39	2.43	0.073	53.1	0.047	16.6
Laohutan Bay sediment	1.62	3.25	0.075	25.6	0.042	30.1
Mixed sediment	3.01	2.84	0.074	39.4	0.045	23.3
Carbonate removed sediment		2.90	0.073	38.7	0.041	23.9
Organic matter removed sediment			0.075	37.6	0.042	24.4
Metallic oxide removed sediment						24.5

2.2 Model sorbents

The adsorption isotherms of hexachloroethane, 1,2,4,5-tetrachlorobenzene and lindane are linear in humic substance, and nonlinear in metallic oxide, carbonate and clay (Figs. 2 – 4). All sets of equilibrium adsorption data were fitted with Langmuir model or linear model:

(1) the linear model:

$$q_e = K_{DL} C_e.$$

(6)

(2) the Langmuir model:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}.$$

(7)

Model parameters, for which with 95% confidence intervals, observation number and the proportion of components are presented in Table 3.

The Multi-component adsorption model can be derived from the summation of individual adsorption equation:

$$q_{e,T} = q_{e,L} + q_{e,NL} = a_L K_{DL} C_e + \sum_{i=1}^3 a_i \frac{Q_i^0 b_i C_e}{1 + b_i C_e}.$$

(8)

Fig. 5 shows adsorption isotherm data of model sediment and the results predicted by MCAM. Where, q_e and C_e are the equilibrium solid-phase and aqueous-phase solute concentrations (expressed as $\mu\text{g/g}$ and $\mu\text{g/L}$, respectively); K_{DL} is the distribution coefficient of the linear model; $q_{e,T}$, $q_{e,L}$ and $q_{e,NL}$ in Equation (8) are the total, linear contribution, and nonlinear contribution of solid-phase concentrations to the MCAM respectively; a_L and a_i are respectively the percentage of the linear and nonlinear components in model sediment; b_i and Q_i^0 are the Langmuir site energy and capacity factor for the nonlinear components of MCAM; the subscript i denotes nonlinear components.

Table 2 The removing efficiency of sequential separation procedure of mixed sediment

Sequential separation procedure	Removing efficiency, %				
	Carbonate	Organic matter	MnO	Fe ₂ O ₃	Al ₂ O ₃
Carbonate removed	98.1	1.2	4.6	4.3	10.0
Organic matter removed		72.5	4.7	-2.2	0
Metallic oxide removed			93.5	82.6	83.3

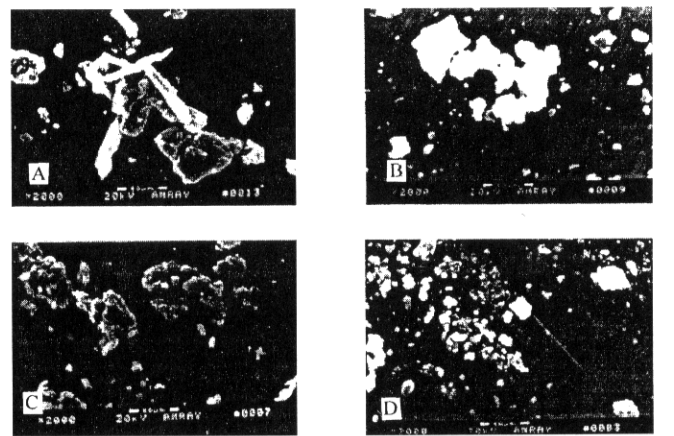


Fig.1 Scanning electron micrographs of mixed sediment (A); carbonate removed sediment (B); organic removed sediment (C) and metallic oxide removed sediment (D)

Table 3 Sorption isotherm parameters

Sorbent	$a_1, \%$	Adsorbate	Linear model		Langmuir model			
			$K_{D,L}$	R^2	$Q_{\infty 0}$	b	R^2	n
Model sorbents								
Carbonate	10.3	I			127.1 ± 20.5	16.92 ± 3.82	0.996	6
		II			9.742 ± 0.851	251.3 ± 28.1	0.999	6
		III			2.581 ± 0.178	82.76 ± 10.04	0.997	6
Metallic oxide	0.4	I			121.6 ± 6.6	9.369 ± 0.834	0.998	6
		II			5.111 ± 1.115	271.9 ± 76.3	0.996	6
		III			4.293 ± 0.158	93.01 ± 5.72	0.999	6
Clay	79.6	I			162.5 ± 20.4	10.42 ± 2.01	0.995	6
		II			6.878 ± 2.158	458.8 ± 169.7	0.997	6
		III			5.416 ± 0.933	145.1 ± 36.0	0.994	6
Humic substance	9.7	I	17.43 ± 0.19	0.998				6
		II	2.602 ± 0.032	0.997				6
		III	1.194 ± 0.018	0.997				6
Natural mixed sediment								
Organic matter	2.84	I	23.93 ± 0.21	0.998				7
		II	2.868 ± 0.055	0.991				7
		III	1.182 ± 0.025	0.991				7
Inorganic matter	95.27	I			105.9 ± 20.1	11.53 ± 3.05	0.993	7
		II			2.538 ± 0.189	55.40 ± 8.35	0.992	7
		III			26.85 ± 11.88	400.9 ± 208.9	0.994	7

Notes: I: Hexachloroethene; II: lindane; III: 1,2,4,5-tetrachlorobenzene

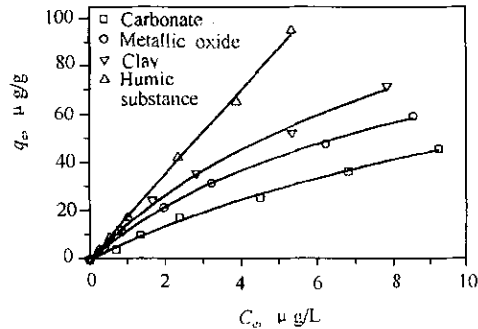


Fig.2 Adsorption isotherm of hexachloroethane by model sorbents

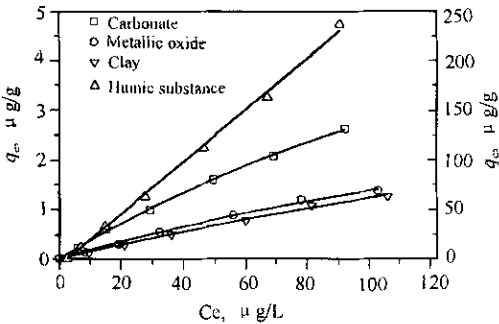


Fig.3 Adsorption isotherm of lindane by model sorbents

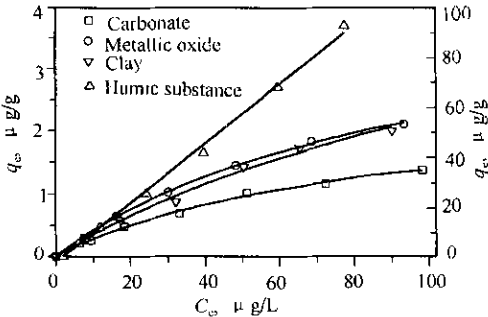


Fig.4 Adsorption isotherm of 1, 2, 4, 5 - tetrachlorobenzene by model sorbents

From the information presented in Figs. 2 – 4 and Table 3, it is evident that adsorption isotherms of hexachloroethane, lindane and 1,2,4,5-tetrachlorobenzene are correlated very well with linear model for humic substance, and with Langmuir model for carbonate, metallic oxide and clay mineral ($R^2 > 0.994$).

Fig. 5 demonstrates that the MCAM correlates the isotherm data of model sediment rather well. The maximal relative deviations for hexachloroethane, lindane and 1,2,4,5-tetrachlorobenzene are 9.76%, 6.78% and 9.53%, respectively. The results show

that adsorptive capacity of model sorbents changes little after mixing. The hypothesis that all components of sediment are mechanically mixed has been verified, though the change may occur (INSCAS, 1978; Gu, 1994).

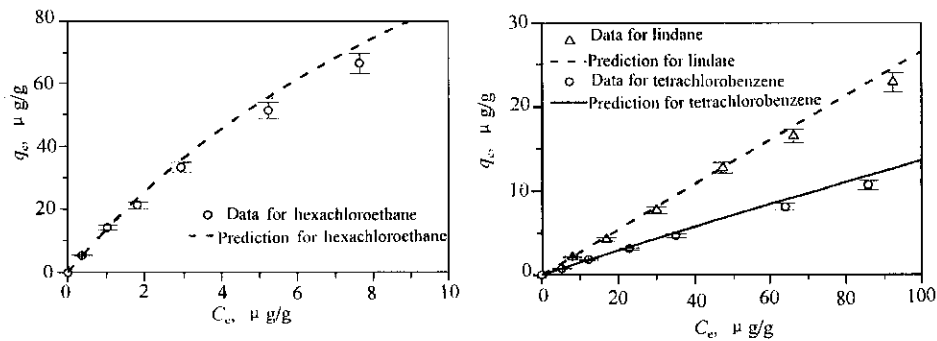


Fig.5 Adsorptive isotherm of hexachloroethane, lindane and 1,2,4,5-tetrachlorobenzene by model sediment(data point is 5% relative deviation)

Table 4 shows the proportions of adsorptive capacity for hexachloroethane, lindane and 1,2,4,5-tetrachlorobenane in model sorbents. It is evident that the adsorptive capacity of inorganic sorbents cannot be neglected for the adsorptive isotherm of hexachloroethane, 1,2,4,5-tetrachlorobenane. Furthermore, clay is the predominant group in inorganic sorbents for the adsorptive isotherm of the above-mentioned HOCs.

Table 4 The proportion of adsorptive capacity of sorbents in model sediment

	Organic matter, %	Carbonate, %	Metallic oxide, %	Clay, %
Hexachloroethane	11.66 – 17.97	5.23 – 5.66	0.30 – 0.34	76.07 – 82.77
Lindane	94.15 – 95.13	1.10 – 1.44	0.02 – 0.03	3.74 – 4.38
1,2,4,5-tetrachlorobenzene	78.42 – 85.06	1.16 – 2.05	0.07 – 0.12	13.71 – 19.42

2.3 Sequential separation sediment

The results in Table 4 indicated that the carbonate and metallic oxide can be neglected in the adsorption of HOCs in this study. To simplify the experimental procedure, the mixed sediment is divided into organic and inorganic matter. Therefore, the sequential separation procedure is only to remove organic matter. The removal percentage of organic matter is 74.5% that is slightly higher than the above-mentioned result. The two-component adsorptive model is deduced according to the above method (Eq. (2) – (5)) and the model parameters are shown in Table 3. The adsorptive isotherms of hexachloroethane, lindane and 1,2,4,5-tetrachlorobenane in mixed sediment, organic and inorganic matter are shown in Fig. 6 to Fig. 8 according to the proportion of components in sediment. From Figs. 6 – 8, it is evident that the predominant fraction of adsorption is inorganic matter for hexachloroethane and 1, 2, 4, 5-tetrachlorobenane and organic matter for lindane. Furthermore, the adsorptive capacity of inorganic matter for lindane is from 33.4% to 16.3% in total sediment that is significant and cannot be neglected. The reason is that the proportion of inorganic matter is absolutely dominant in sediment (95.27%). On the contrary, the organic matter is only 2.84%. However,

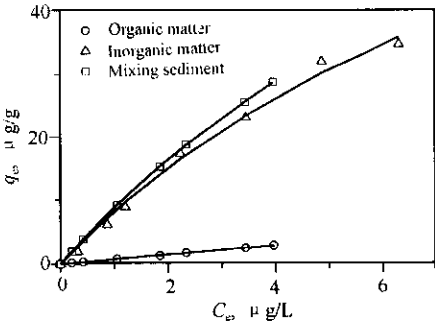


Fig.6 Adsorption isotherm of hexachloroethane by sequential separation sediments

the proportion of adsorptive capacity of organic matter is enhanced with the increasing of equilibrium concentration of solute (Figs. 6 – 8). Besides, when the product of langmuir site energy (b) and equilibrium concentration (C_e) is about half of the numerical value one, the adsorptive isotherm of inorganic matter shows linear or constant (Q^0). Therefore, the adsorptive isotherm of sediment will show linear in very low or high solute concentration that does not prove that the adsorptive mechanism is completely partition or dissolution.

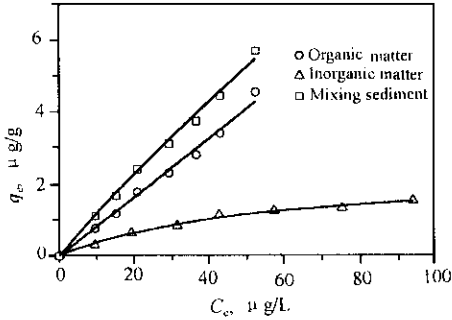


Fig.7 Adsorption isotherm of lindane by sequential separation sediments

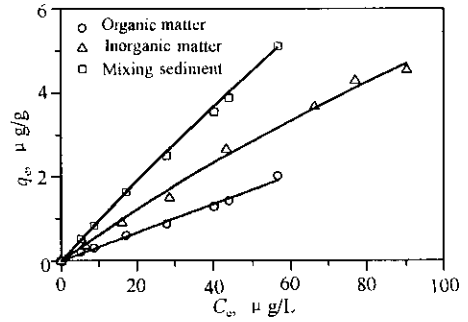


Fig.8 Adsorption isotherm of 1, 2, 4, 5-tetrachlorobenzene by sequential separation sediments

In summary, though the adsorptive isotherm data of each component are not adequately accurate because of the effect of separate efficiency and the change of external structure, the sequential separation method and MCAM of sediment can clearly explain some adsorptive phenomena and give expression to different adsorptive curve forms.

References:

- Chiou C T, Peter L J, Freed V H, 1979. A physical concept of soil-water equilibrium for nonionic organic compounds[J]. *Science*, 206: 831—832.
- Chiou C T, McGroddy S E, Kile D E, 1998. Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments[J]. *Environ Sci Technol*, 32: 264—269.
- Carroll K M, Harkness M R, Bracco A A, 1994. Application of a permeant/polymer diffusional model to the desorption of polychlorinated biphenyls from Hudson River sediments[J]. *Environ Sci Technol*, 28: 253—258.
- Grathwohl P, Reinhard M, 1993. Desorption of trichloroethylene in aquifer material. Rate limitation at the grain scale[J]. *Environ Sci Technol*, 27: 2360—2366.
- Cu B, Schmitt J, Chen Z *et al.*, 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanism and model[J]. *Environ Sci Technol*, 28: 38—46.
- Huang W, Young T M, Schlautman M A *et al.*, 1997. A distributed reactivity model for sorption by soils and sediments. 9. General isotherm nonlinearity and applicability of the dual reactive domain model[J]. *Environ Sci Technol*, 31: 1703—1710.
- Institute of Nanjing Soil of Chinese Academy of Sciences, 1978. Physics and chemistry analysis of soil[M]. Beijing: The Agriculture Publishing Company (China).
- Karickhoff S W, Brown D S, Scott T A, 1979. Sorption of hydrophobic pollutants on natural sediments[J]. *Water Res*, 13: 241—248.
- Kile D E, Chiou C T, Zhou H *et al.*, 1995. Partition of nonpolar organic pollutants from water to soil and sediment organic matters[J]. *Environ Sci Technol*, 29: 1401—1406.
- LeBoef F J, Weber W J Jr, 1997. A distributed reactivity model for sorption by soils and sediments. 8. Sorbent organic domains: discovery of a humic acid glass transition and an arguments for a polymer-based model[J]. *Environ Sci Technol*, 31: 1697—1702.
- Laird D A, Yen P Y, Koskinen W C, 1994. Sorption of atrazine on soil clay components[J]. *Environ Sci Technol*, 28: 1054—1061.
- Murphy E M, Zachara J M, Smith S C, 1990. Interaction of hydrophobic organic compounds with mineral-bound humic substances[J]. *Environ Sci Technol*, 24: 1507—1516.
- McGinley P M, Katz L E, Weber W J Jr, 1993. A distributed reactivity model for sorption by soils and sediments. 2. Multicomponents systems and competitive effects[J]. *Environ Sci Technol*, 27: 1524—1531.
- Murphy E M, Zachara J M, Smith S C *et al.*, 1994. Interaction of hydrophobic organic compounds with mineral-bound humic substances[J].

- Environ Sci Technol, 28: 1291—1299.
- Martens D A L, Suarez D L, 1997. Selenium speciation of soil/sediment determined with sequential extractions and hydride generation atomic absorption spectrophotometry[J]. Environ Sci Technol, 31: 133—139.
- Niss N D, Schabron J F, Brown T H, 1993. Determination of selenium species in coal fly ash extracts[J]. Environ Sci Technol, 27: 827—829.
- Piatt J J, Backhus D A, Capel P D *et al.*, 1996. Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments[J]. Environ Sci Technol, 30: 751—760.
- Pignatello J J, Xing B, 1996. Mechanisms of slow sorption of organic chemicals to natural particles[J]. Environ Sci Technol, 30: 1—11.
- Rapin F, Tessier A, Campbell P G C *et al.*, 1986. Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure[J]. Environ Sci Technol, 20: 836—840.
- Tessier A, Campbell P G C, Blsson M, 1979. Sequential extraction procedure for the speciation of particulated trace metals[J]. Anal Chem, 51: 844—851.
- Tang H X, Xue H B, Tian B Z *et al.*, 1982. Study on multi-component adsorption model of aquatic sediments with a sequential chemical separation procedure[J]. Acta Scientiae Circumstantiae, 2: 279—292.
- Weber W I Jr, McGinley P M, Katz L E, 1991. Sorption phenomena in subsurface systems concepts, models, and effects on contaminant fate and transport[J]. Water Res, 25: 499—528.
- Weber W I Jr, McGinley P M, Katz L E, 1992. A distributed reactivity model for sorption by soils and sediments 1. Conceptual basis and equilibrium assessments[J]. Environ Sci Technol, 26: 1955—1962.
- Weber W I Jr, Huang W, 1996. A distributed reactivity model for sorption by soils and sediments. 4. Intraparticle heterogeneity and phase-distribution relationships under nonequilibrium conditions[J]. Environ Sci Technol, 30: 881—888.
- Xing B, Pignatello J J, Gigliotti B, 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents for sorption mechanism[J]. Environ Sci Technol, 30: 2432—2440.
- Xing B, Pignatello J J, 1996. Time-dependent isotherm shape of organic compounds in soil organic matter: implications for sorption mechanism [J]. Environ Toxicol Chem, 15: 1282—1288.
- Xing B, Pignatello J J, 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter[J]. Environ Sci Technol, 31: 792—799.
- Xue W S, Zeng B W, 1988. Analytical handbook of environmental monitoring[M]. Taiyuan: Science and Education Publishing Company of Shanxi Province(China). 321—322.
- Young T M, Weber W I Jr, 1995. A distributed reactivity model for sorption by soils and sediments. 3. Effects of diagenetic processes on sorption energetics[J]. Environ Sci Technol, 29: 92—97.

(Received for review January 11, 2001. Accepted June 7, 2001)