Effects of temperature and surfactants on naphthalene and phenanthrene sorption by soil

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Abstract

Adsorption experiments were carried out to investigate the sorption behaviors of naphthalene and phenanthrene in six different soils and to determine the effects of temperature, linear alkylbenzene sulfonate (LAS) and cetylrimethyl ammonium bromide (CTAB) on sorption. The results show that for a given sorbent phenanthrene exhibited greater nonlinear and stronger sorption than naphthalene. There was a strong negative correlation for the K_{oc} values with organic carbon content (f_{oc}). The increase of temperature was not favorable to sorption. Sorption decreased along with the increasing aqueous LAS concentration from 0 to 1000 mg/L. At low CTAB concentration (< 100 mg/L), the adsorption increased as CTAB hemimicelles formed on the soil surface. At high concentration, CTAB decreased the adsorption by occupying active hydrophobic adsorption sites and solubilization of naphthalene and phenanthrene.

Key words: naphthalene; phenanthrene; sorption; soil; temperature; linear alkylbenzene sulfonate; cetylrimethyl ammonium bromide
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Introduction

The petroleum hydrocarbons contamination is one of the most common problems in soils and sediments. In the past ten years, soils were heavily polluted by oil leaching accidents occurred in gas stations in Beijing, China. Gasoline and diesel oil are two widely used fuels extracted from crude oil. Gasoline comprises low molecular weight alkanes (C5–C10) and aromatics (mainly benzenes and naphthalenes) with very little polycyclic aromatic hydrocarbons (PAHs). Diesel, however, contains a high percentage of aromatics (mainly naphthalene, 1-ethyl naphthalene, 2,5-dimethyl naphthalene, phenanthrene, anthracene, pyrene, and chrysene), and 3% PAHs (Adam et al., 2002). PAHs are environmental concern as they are persistent and some of them have adverse effects for human health. Therefore, due to their known toxicity, and mutagenic and carcinogenic effect, the remediation of oil-contaminated soils is an important environmental issue.

Sorption of PAHs is a key process controlling mobility, bioavailability, toxicity and fate of their compounds in soils. PAHs sorption is primarily regulated by soil organic matter (SOM). Temperature may also be an important parameter influencing distribution, sorption and other fate processes in the environment. The influences of temperature on Henry's law constant (H) for several PAHs, polychlorinated biphenyl (PCB) and chlorobenzenes have

been reported by Ten Hulscher et al. (1992), in which the H value is doubled with every 10°C temperature increment. Temperature influences both the sorption equilibrium and the sorption kinetics of hydrophobic organic compounds (HOCs) (Ten Hulscher and Cornelissen, 1996; Enell et al., 2005). In a review of the temperature effect on sorption equilibrium, Ten Hulscher and Cornelissen (1996) reported the values for the change in enthalpy (ΔH) in the range of 3.8–17.7 kJ/mol for naphthalene and fluoranthene. Values for ΔH are usually negative and close to zero when desorption of "fresh" contaminant or discussion of pure compounds is considered (negative value indicates that desorption is favored as temperature increasing). However, when desorption of PAHs from aged contaminated soil is considered, the temperature effect on sorption equilibrium is remarkably increased.

PAHs are commonly coexisted with surfactants in environmental matrixes. The fate and transport (leaching to groundwater, biotic and abiotic degradation, volatilization, bioavailability or plant uptake and accumulation in soil) of PAHs in plant-soil system is consequently affected by the coexistent surfactants by means of solubilization and mobilization. Generally, surfactants can increase the solubility of PAHs by partitioning them into the hydrophobic cores of surfactant micelles above the critical micelle concentration (CMC) (Edwards et al., 1991; Jafvert et al., 1994) and then enhancing the desorption and flushing of PAHs from solid into aqueous phase, which would

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improve the bioavailability of PAHs for microbial remediation and phytoremediation. However, some recent studies have indicated that surfactants can be adsorbed by the solid matrix, thereby leading to PAHs partitioning into immobile adsorbed surfactants (Edwards *et al.*, 1994; Sun and Inskeep, 1995; Zhou and Zhu, 2007). The sorbed surfactant, on a carbon-normalized basis, is more effective as a sorbent for PAHs than humic matter and can enhance PAHs sorption to soils. Surfactant-enhanced remediation has been suggested as a promising technology for the remediation of contaminated soils (Mulligan *et al.*, 2001). Therefore, only if the effect of surfactants on PAHs sorption is thoroughly understood, effective schemes for remediation of oil-contaminated soils can be accurately developed.

The aims of the present study were: (1) to examine the sorption behavior of naphthalene and phenanthrene to the six soils from Beijing, China; (2) to analyze the effect of temperature on sorption; (3) to investigate the effects of different surfactants on sorption.

1 Materials and methods

1.1 Soils

Six surface (0–20 cm) soil samples were collected from the Changping District of Beijing, China, in October 2004. The samples were selected considering their different total organic carbon (TOC) content and soil texture. After collection, the soils were airdried, passed through a 100-mesh sieve and then stored in pre-cleaned brown glass bottles. The TOC of the samples was determined by a high-temperature combustion-based elemental analyzer (elementar Vario EL, Germany). TOC of the six soils ranged from 0.29% to 5.26%. Sample pH were determined at the solids:water ratio 1:2.5 (g:mL). Physiochemical characteristics of the six soils are listed in Table 1.

1.2 Reagents

Naphthalene and phenanthrene (> 98%; Aldrich Chemical Co., USA) were directly used without further purification. They were chosen as the two PAH probes because

they are petroleum-, coal- and chemical industry-related organic contaminants and are frequently found in surface and subsurface environments. Some physicochemical properties of the two sorbates are given in Table 2 (Karickhoff *et al.*, 1979; Mackay *et al.*, 1992). LAS (> 90%; an anionic surfactant) and CTAB (> 90%; a cationic surfactant) were purchased from Sigma Chemical Co., USA. The CMC of LAS and CTAB is 1000 and 335 mg/L, respectively. Aqueous LAS and CTAB stock solutions were prepared in deionized water. Primary naphthalene and phenanthrene stock solutions were prepared by dissolving appropriate amounts of solutes in methanol (HPLC grade), and sequentially diluted with methanol to make a series of stock solutions with varying concentrations. A desired volume of stock solution was mixed with a background solution (0.01 mol/L $CaCl_2$ and 200 mg/L NaN_3) in a volumetric flask to make an initial aqueous solution for sorption experiments. The volumetric fraction of methanol in each initial solution was less than 0.2%. At this level, methanol had no measurable cosolvent effect on the sorption of organic pollutants (Wauchope and Koskinen, 1983).

1.3 Sorption experiments

In this study, 50-mL glass tubes with Teflon-lined caps were used as batch reactors. A mixture of 0.01 mol/L $CaCl_2$ and 200 mg/L NaN_3 was used as background solution in all sorption experiments to prevent biological degradation of naphthalene and phenanthrene. According to our preliminary sorption rate and equilibrium studies, an equilibration time of 48 h was used for all sorbent-solute systems. Preliminary tests were run to determine an appropriate solid/solution ratio for each sorbent-solute system to achieve 30%–85% reduction of the initial aqueous phase concentrations. Reactors filled with sorbent and initial aqueous solution (20 mL) were sealed and mixed completely at 125 r/min at 25 ± 0.5°C for 48 h. After centrifugation at 4000 r/min for 20 min, naphthalene and phenanthrene in the supernatant solution was determined by high performance liquid chromatograph (HPLC). Soil 2 with the highest TOC content was used for the sorption experiments to determine the effect of temperature

Table 1 Mechanical composition and major characteristics of the soil samples

Sample	Soil texture	pH	TOC (wt.%)	Grain size distribution (wt.%)			
				> 2 mm	2–0.01 mm	0.01–0.001 mm	<0.001 mm
Soil 1	Clay loam	8.12	0.46	0.0	51.2	36.1	12.7
Soil 2	Silt loam	8.05	5.26	20.7	53.5	12.8	12.9
Soil 3	Sandy clay loam	8.33	1.09	12.0	50.4	18.6	19.0
Soil 4	Sandy loam	8.45	1.30	36.4	45.8	9.9	7.7
Soil 5	Clay	8.28	4.05	0.0	48.2	27.5	24.3
Soil 6	Sand	8.14	0.29	0.0	90.5	0.6	8.9

Table 2 Physicochemical properties of the sorbates

Compound	MW (g/mol)[a]	S_w (mg/L)[b]	T_m (°C)[a]	S_{sci} (mg/L)[a]	$\log K_{ow}$[a]	K_{oc} (K_{ow})[c]	V_m (cm³/mol)[a]
Naphthalene	128.2	31.7	80	106.4	3.37	1130	111
Phenanthrene	178.2	1.29	101	5.18	4.57	17906	152

MW: molecular weight; S_w: aqueous solubility; T_m: melting points; S_{sci}: subcooled liquid-state solubility; K_{ow}: octanol-water coefficient; V_m: molecular volume. [a] Mackay *et al.*, 1992 ; [b] Karickhoff *et al.*, 1979 ; [c] $\log K_{oc} = \log K_{ow} - 0.317$.

and surfactants on sorption. Sorption of naphthalene and phenanthrene on Soil 2 was carried out at different temperatures (15, 25, 35°C) and in the presence of LAS (0, 50, 500, 1000 mg/L) and CTAB (0–500 mg/L) using the batch equilibrium method as described above, respectively. Two replicates for each point were performed in all sorption experiments. Control reactors prepared similarly but without any sorbent were run simultaneously to assess the loss of solutes to reactor during sorption test. Results showed that the average system loss was consistently less than 4% of initial concentration, indicating that microbial degradation and volatilization during the sorption and the uptake to the glass walls was negligible. Hence, no correction was made during the reduction of sorption data.

1.4 Solute analysis

The concentrations of phenanthrene and naphthalene were determined using a reversed-phase HPLC (C18 column, 4.6 mm × 25 mm, Waters, U.S.) with a fluorescence detector (model Waters 474, UV excitation/emission wavelengths at 292/366 nm for phenanthrene and at 250/364 nm for naphthalene). Isocratic elution was performed at 1.0 mL/min using the mobile phase methanol:water (90:10, V/V). The concentrations of solid phase were calculated by mass balance.

The solid phase sorbate concentration (q_e) (µg/g) at equilibrium condition was calculated as the following Eq. (1).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where, C_e (mg/L) is the liquid phase equilibrium concentration. C_0 (mg/L), V (mL), and m (g) are the initial solution phase solute concentration, volume of the solution phase, and sorbent mass introduced to each reactor, respectively.

1.5 Sorption model

Sorption of HOCs in soils has been described by the Freundlich model (Weber and Huang, 1996; Xing et al., 1996; Weber et al., 1992):

$$q_e = K_f \times C_e^n \tag{2}$$

$$\log q_e = \log K_f + n \log C_e \tag{3}$$

where, K_f ((μg/g)/(mg/L)$_n$) is the sorption capacity-related parameter and n is the isotherm nonlinearity index. When $n = 1$, Eq. (2) becomes a linear form:

$$q_e = K_d \times C_e \tag{4}$$

where, K_d (mL/g) is the linear sorption coefficient, and related to sorption capacity. Equation (4) has been often used in literature (Schwarzenbach et al., 1993). This equation is applicable for narrow solute concentration range or when partitioning is a only sorption mechanism (Weber et al., 1992; Xing and Pignatello, 1996).

2 Results and discussion

2.1 Sorption isotherms

Sorption isotherms of naphthalene and phenanthrene by the six soils are shown in Fig. 1. Both linear and Freundlich models were used to fit sorption data with fitting parameters listed in Table 3. The data show that the n values for naphthalene by the six soils ranged from 0.870 to 0.953, higher than those reported previously (Xiao et al., 2004; Chen et al., 2007), which may be caused by the difference of the soil characteristics. The sorption isotherm n values for phenanthrene in this study varied from 0.637 to 0.844, close to that for three soils in Guangzhou, China (Ran et al., 2007). The nonlinearity factor n is related to the sorption site energy distribution and has been related
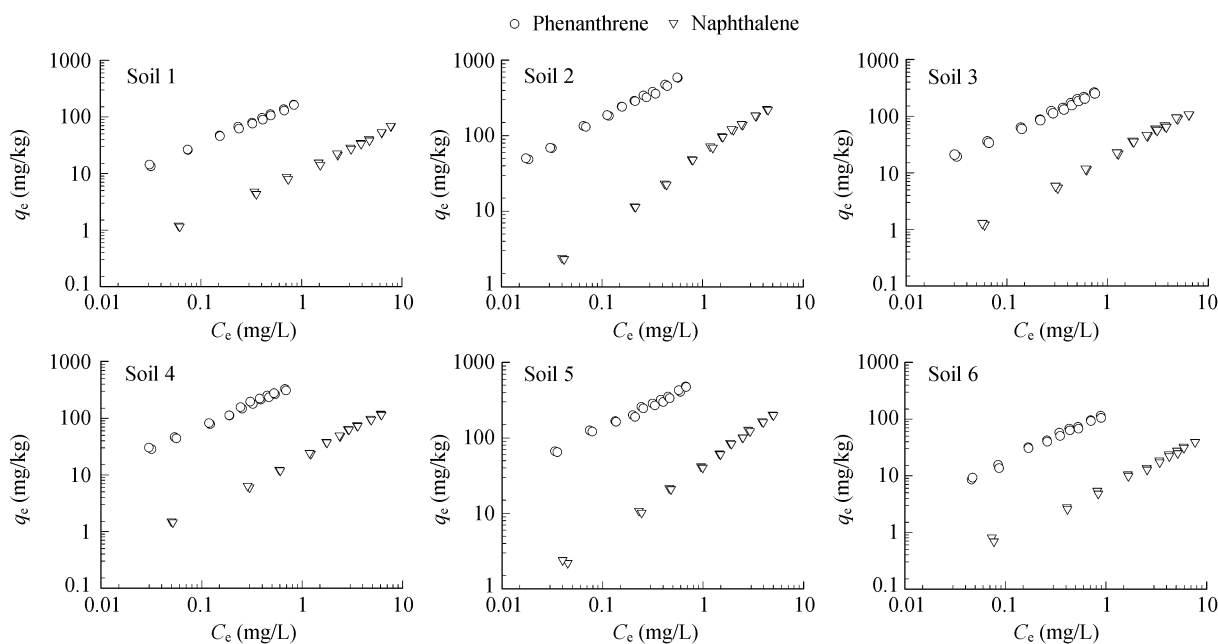

Fig. 1 Sorption isotherms of naphthalene and phenanthrene by six soils.

Table 3 Fitting parameters of Linear and Freundlich models

Sorbent	Linear			Freundlich					Single-point K_{oc}[b] (mL/g)		
	K_d (mL/g)	r^2	K_{oc}	n	r^2	K_f	$\log K_{foc}$[a]	N[d]	$C_e = 0.05$ mg/L	$C_e = 0.1$ mg/L	$C_e = 0.5$ mg/L
Naphthalene											
Soil 1	8.51 ± 0.13[c]	0.995	1850	0.953 ± 0.026	0.995	9.54 ± 0.43	3.32	20	2386	2310	2142
Soil 2	52.0 ± 1.36	0.988	988	0.870 ± 0.024	0.994	62.8 ± 1.76	3.08	20	1761	1610	1306
Soil 3	17.1 ± 0.44	0.988	1566	0.905 ± 0.031	0.991	20.3 ± 0.98	3.27	20	2479	2321	1991
Soil 4	19.6 ± 0.37	0.994	1510	0.923 ± 0.022	0.996	22.5 ± 0.75	3.24	20	2180	2067	1826
Soil 5	41.1 ± 0.63	0.996	1015	0.952 ± 0.021	0.996	44.4 ± 1.21	3.04	20	1264	1223	1132
Soil 6	5.07 ± 0.09	0.995	1748	0.936 ± 0.026	0.995	5.83 ± 0.26	3.30	20	2436	2330	2102
Phenanthrene											
Soil 1	179.8 ± 5.06	0.988	39087	0.747 ± 0.018	0.995	183.4 ± 2.55	4.60	18	85033	71366	47510
Soil 2	949.7 ± 30.8	0.982	18055	0.712 ± 0.021	0.992	858.9 ± 21.0	4.21	20	38742	31722	19943
Soil 3	331.8 ± 8.02	0.990	30440	0.844 ± 0.027	0.992	328.2 ± 6.94	4.48	20	48000	43090	33538
Soil 4	455.8 ± 16.4	0.977	35062	0.766 ± 0.027	0.989	437.0 ± 11.0	4.53	20	67795	57637	39537
Soil 5	600.4 ± 20.7	0.980	14825	0.637 ± 0.014	0.989	583.0 ± 13.3	4.16	20	42658	33177	18510
Soil 6	118.9 ± 4.39	0.980	41000	0.793 ± 0.030	0.988	121.3 ± 2.54	4.62	18	77850	67426	48290

[a] $K_{foc} = K_f/f_{oc}$, the unit of K_{foc} is (μg/g OC)/(mg/L)^n; [b] $K_{oc} = K_{foc} C_e^{n-1}$; [c] standard deviation; [d] number of data.

to heterogeneous glass, hard, or condensed soil organic matter (SOM) domain and to the maturation degree of SOM (Weber *et al.*, 1992; Pignatello and Xing, 1996; Xing *et al.*, 1996).

Lower n values indicate a more heterogeneous sorption site energy distribution and a higher degree of SOM maturation. For a given sorbent, phenanthrene exhibited a more nonlinear sorption than naphthalene.

As shown in Table 3, the concentration-dependent OC-normalized sorption coefficients K_{oc} at three selected concentrations ($C_e = 0.05$, 0.1, and 0.5 mg/L) were employed to compare the sorption capacity. In general, K_{oc} decreased as a function of C_e because of isotherm nonlinearity. At $C_e = 0.1$ mg/L, K_{oc} ranged from 1223 to 2330 mL/g for naphthalene and from 31722 to 71366 mL/g for phenanthrene. These values were higher than that for four soil/sediment samples from Guangzhou, China (Xiao *et al.*, 2004). At a given C_e, K_{oc} for phenanthrene are much higher than those for naphthalene, suggesting that phenanthrene exhibits much higher sorption capacities than naphthalene. Thus, sorption site heterogeneity and affinity of a specific sorbent are different for each HOC, and greater for phenanthrene, which may be related to the molecular and chemical properties of HOCs. Phenanthrene has larger MW, V_m and $\log K_{ow}$ (or lower S_w) value than

naphthalene. Similar results were reported for naphthalene and phenanthrene by Xing (2001) for several soil humic acids. It can be concluded that n seemed negatively correlated with MW, V_m and $\log K_{ow}$ while sorption affinity increased with the increase of these parameters.

The linear model was selected to derive K_d and K_{oc} for the purpose of comparison between soils. K_d of the six soils decreased in the order: soil 2 > soil 5 > soil 4 > soil 3 > soil 1 > soil 6, reflecting the different sorption capacities of soils with different soil textures. The above results also suggest the predominance of SOM for the sorption of naphthalene and phenanthrene. This observation is consistent with the work by other researchers (Means *et al.*, 1980; Xing, 1997). K_{oc} was in the range of 988–1850 mL/g for naphthalene and 14825–41000 mL/g for phenanthrene. The correlation of K_{oc} for naphthalene and phenanthrene to organic carbon (f_{oc}) in soils are presented in Fig. 2. There was a strong negative correlation of K_{oc} for naphthalene vs. f_{oc} ($r^2 = 0.941$, $p < 0.01$) and for phenanthrene vs. f_{oc} ($r^2 = 0.883$, $p < 0.01$). K_{oc} decreased with increasing f_{oc} for the two HOCs. This can be explained by that, when f_{oc} is the lowest, all organic matter molecules on the particle surfaces are fully accessible for HOC sorption. When f_{oc} increases, organic matter may adopt interfacial configuration that reduce the further HOC sorption.
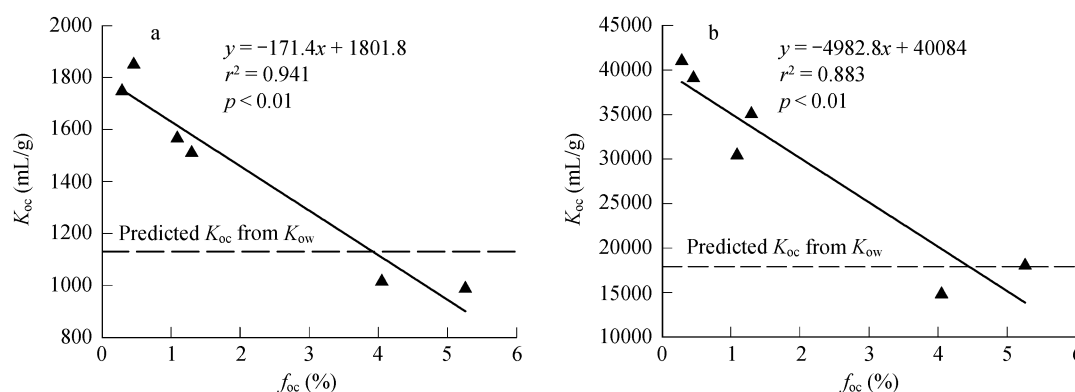
Fig. 2 Correlation of K_{oc} for naphthalene (a) and phenanthrene (b) to organic carbon (f_{oc}) in soils.

In Fig. 2, K_{oc} was also compared with K_{oc} calculated from K_{ow} using K_{oc}-K_{ow} equation derived by Mean *et al.* (1980). K_{oc} was not constant and either higher or lower than K_{oc} predicted from K_{ow}. However, the results differed to that by Karickhoff (1984), in which K_{oc} was relatively constant for a single organic compound. The results are complementary rather than contradictory to other findings, as both reveal the extremely important roles played by SOM. Uniformity of K_{oc} was expected from SOM of similar origin and structure. The variations in K_{oc} reflected in this study illustrated that even subtle differences in SOM composition, such as polarity and aromaticity, could modify the functionality of organic matter in pollutant binding.

2.2 Effect of temperature on sorption

Sorption isotherms of naphthalene and phenanthrene by soil 2 at different temperatures are shown in Fig. 3. Fitting parameters of the Freundlich model were listed in Table 4. As shown in Table 4, n increased with increasing temperature, ranging from 0.713 to 0.893 for naphthalene and from 0.557 to 0.756 for phenanthrene. Sorption of naphthalene and phenanthrene was inversely related to temperature. The Freundlich coefficient K_f dropped from 106.8 to 42.5 for naphthalene and from 932.7 to 568.9 for phenanthrene with an increase of temperature from 15 to 35°C. At C_e = 0.5 mg/L, K_{oc} varied from 869 to 2479 mL/g for naphthalene and from 12807 to 24104 mL/g for phenanthrene. This suggested that temperature may influence SOM structure and the characteristics of the sorbates. At a given C_e, K_{oc} decreased with increasing temperature, illustrating that high temperature was not

favorable to sorption. With temperature increase from 15 to 35°C, K_{oc} at C_e = 0.1 mg/L decreased from 3935 to 1033 mL/g for naphthalene and from 49166 to 18964 mL/g for phenanthrene.

Our finding is consistent with several prior studies. For example, Schwarzenbach *et al.* (1993) reported that for most HOCs, such as PAHs, there existed an inverse relationship between temperature and sorption equilibrium coefficient. He *et al.* (1995) studied the adsorption of fluoranthene on soil and found that the sorption coefficients decreased by a factor of 1.6 when the temperature increased from 5 to 25°C. For most organic micropollutants sorption partition coefficients decreased with increasing temperature (Ten Hulscher and Cornelissen, 1996). The effect of temperature on sorption is mainly caused by the temperature effect on HOCs water solubility. Increased temperature will lead to a higher solubility and thus lower sorption coefficient (K_{oc}). Mackay *et al.* (1992) reported that the water solubility of phenanthrene decreases by a factor of 2, with a temperature decrease from 20 to 2°C. We conclude that the release rates of the contaminants and their leachable concentrations will likely be further reduced in a cold climate.

2.3 Effect of LAS and CTAB on Sorption

Sorption isotherms of naphthalene and phenanthrene by soil 2 in the presence of LAS at various concentrations are shown in Fig. 4. The Linear model was used to fit sorption data with fitting parameters listed in Table 5. The data indicated that the adsorption of naphthalene and phenanthrene decreased with increasing aqueous LAS concentration from 0 to 1000 mg/L. K_d decreased in the
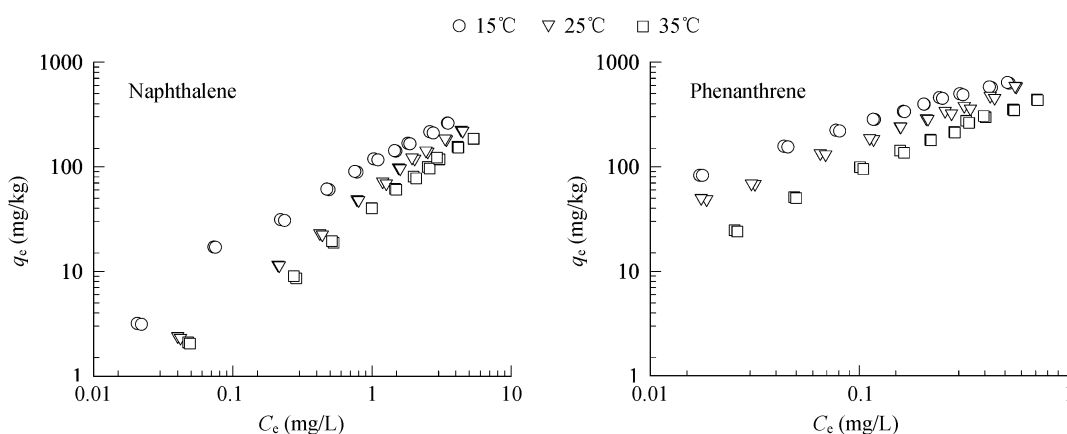

Fig. 3 Sorption isotherms of naphthalene and phenanthrene on soil 2 at 15, 25 and 35°C.

Table 4 Freundlich sorption parameters of naphthalene and phenanthrene at different temperatures

Temperature (°C)	n	r^2	K_f ((μg/g)/(mg/L)^n)	$\log K_{foc}$	Single-point K_{oc} (mL/g)		
					C_e = 0.05 mg/L	C_e = 0.1 mg/L	C_e = 0.5 mg/L
Naphthalene							
15	0.713 ± 0.014	0.997	106.8 ± 1.42	3.31	4802	3935	2479
25	0.870 ± 0.024	0.994	62.8 ± 1.76	3.08	1761	1610	1306
35	0.893 ± 0.023	0.995	42.5 ± 1.35	2.91	1113	1033	869
Phenanthrene							
15	0.557 ± 0.013	0.994	932.7 ± 16.7	4.25	66832	49166	24104
25	0.712 ± 0.021	0.992	858.9 ± 21.0	4.21	38742	31722	19943
35	0.756 ± 0.023	0.991	568.9 ± 12.6	4.03	22457	18964	12807

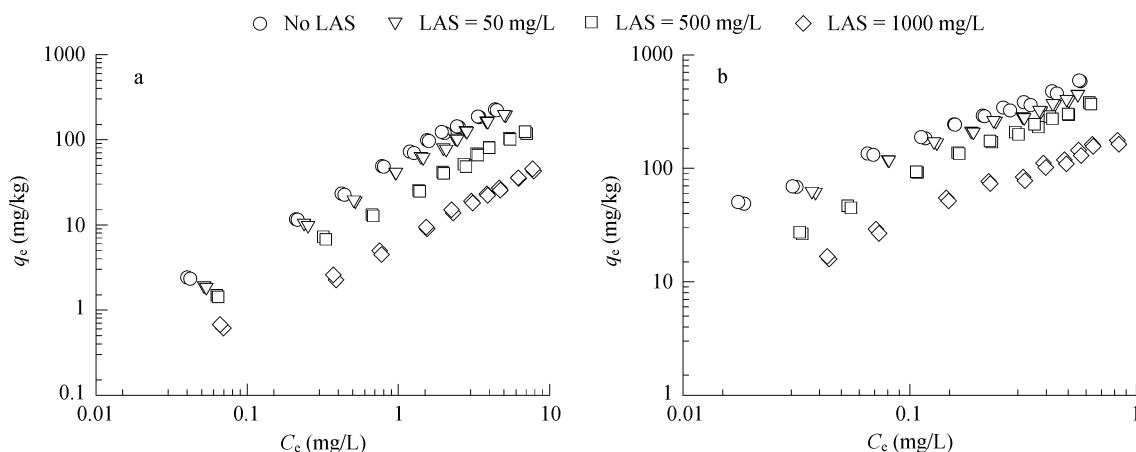○ No LAS ▽ LAS = 50 mg/L □ LAS = 500 mg/L ◇ LAS = 1000 mg/L

Fig. 4 Sorption isotherms of naphthalene (a) and phenanthrene (b) on soil 2 with or without LAS.

presence of LAS for both naphthalene and phenanthrene. A similar effect has been also observed by Qu *et al.* (1995), in which a decline of K_d was caused by LAS. $\log K_{oc}$ ranged from 2.03 to 3.00 for naphthalene and from 3.58 to 4.26 for phenanthrene with or without LAS. According to Valsaraj and Thibodeaus (1989), LAS-micelle-water partition coefficient (K_m) of hydrophobic organic compounds (HOCs) can be estimated from their K_{ow} using Eq. (5) (Table 2).

$$\log K_m = 0.865 \log K_{ow} + 0.92 \qquad (5)$$

As shown in Table 5, $\log K_m$ for naphthalene and phenanthrene are higher than $\log K_{oc}$ in the presence of LAS, which suggests that LAS does enhance the solubility of naphthalene and phenanthrene in the studied suspension concentration and their affinity to LAS micelles is higher than that to the studied soils.

Table 5 Linear sorption parameters of naphthalene and phenanthrene with or without LAS

LAS concentration (mg/L)	K_d (mL/g)	r^2	$\log K_{oc}$
Naphthalene			
0	52.0 ± 1.36	0.988	3.00
50	40.6 ± 0.95	0.990	2.89
500	18.0 ± 0.46	0.988	2.53
1000	5.60 ± 0.08	0.996	2.03
Phenanthrene			
0	949.7 ± 30.8	0.982	4.26
50	698.1 ± 22.8	0.981	4.12
500	570.6 ± 16.9	0.984	4.04
1000	199.5 ± 9.80	0.978	3.58

In a system with the coexistence of HOCs, surfactant, soil and water, the following interactions may occur simultaneously: (1) competition for active hydrophobic adsorption sites on soil surface between HOCs and surfactant, (2) equilibria of surfactant among monomers, micelles and hemimicelles (monomers adsorbed on soil surface), (3) partition of HOCs among soil hydrophobic adsorption sites, surfactant micelles (i.e., solubilization) and organo minerals (hemimicelles formed on soil surface), and (4) interaction of HOCs with surfactant monomers (Valsaraj and Thibodeaus, 1989; Jafvert, 1991; West and Harwell, 1992). Among them, the apparent adsorption of HOCs depends

on the extent and competition of each interaction, and the interaction between HOCs and surfactant monomers is usually very weak and negligible (Edwards *et al.*, 1991; Liu *et al.*, 1991).

When LAS concentration is low, e.g., less than 50 mg/L, which is much lower than CMC, there is no obvious solubilization of HOCs (Edwards *et al.*, 1991). Therefore, the apparent adsorption of HOCs mainly depends on the results of competition for active hydrophobic adsorption site on soil surface between HOCs and LAS, the formation of LAS hemimicelles on soil surface, and the partition of HOCs to LAS hemimicelles, which is weaker than the competition between HOCs and LAS. Thus, in low LAS concentrations (< 50 mg/L), adsorption of naphthalene and phenanthrene decreased due to the LAS occupation of active hydrophobic adsorption sites on the soil surface. For high concentrations (> 50 mg/L), LAS increased solubility of naphthalene and phenanthrene due to their partitioning into LAS micelles, which resulted in the decrease of the adsorption on soil. A slightly more rapid decline of naphthalene and phenanthrene adsorption was observed in LAS concentration range 500–1000 mg/L. The rapid decrease of sorption due to the significant solubilization of naphthalene and phenanthrene when CMC was approached (Liu *et al.*, 1991).

The effect of CTAB concentration on adsorption of naphthalene and phenanthrene is illustrated in Fig. 5. The adsorption of naphthalene and phenanthrene increased with the increasing aqueous CTAB concentrations from 0 to 100 mg/L but decreased almost linearly with the increase of CTAB concentration above 100 mg/L. For low CTAB concentration (< 100 mg/L), the solubilization is very weak.

As CTAB had a greater sorption affinity than LAS, the adsorbed CTAB onto soil surface can adsorb more naphthalene and phenanthrene (Park and Jaffe, 1993). The amount of naphthalene and phenanthrene adsorption increased via this mechanism is more than decreased due to the CTAB occupation of active hydrophobic adsorption sites, resulting in an increase of apparent adsorption of naphthalene and phenanthrene. For high CTAB concentration (> 100 mg/L), CTAB competition for active
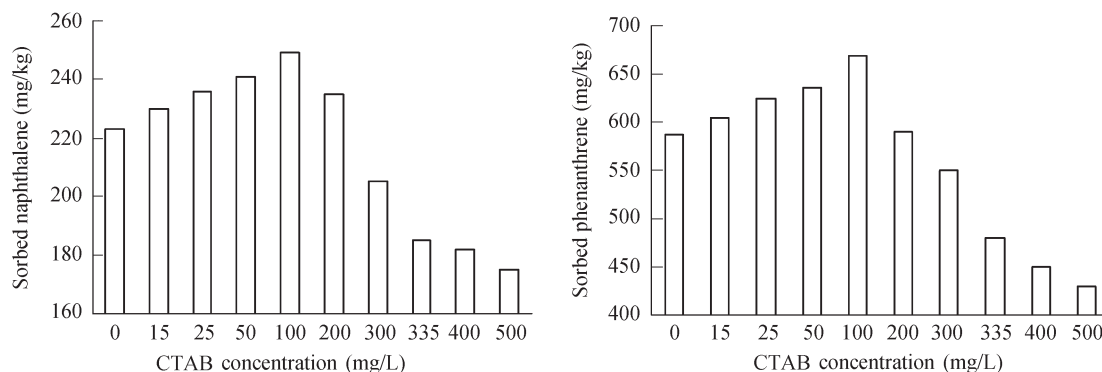
Fig. 5 Effect of CTAB concentration on sorption of naphthalene and phenanthrene by soil 2.

hydrophobic adsorption sites and solubilization of naphthalene and phenanthrene both increase. When CTAB concentration exceed 100 mg/L, rapid and significant increase of CTAB adsorption on soil due to cooperative adsorption was measured which made active hydrophobic adsorption sites much less available to naphthalene and phenanthrene. These interactions caused the less naphthalene and phenanthrene adsorption onto soils. Adsorption decreased almost linearly with the increasing CTAB concentrations from 100 to 500 mg/L. It is likely that CTAB micelles form in these concentrations and the solubilization of naphthalene and phenanthrene considerably increase due to its partitioning into CTAB micelles. This is consistent with the results obtained in high aqueous LAS concentration.

The results suggest that the high level of LAS and CTAB can increase the mobility of HOCs in soils. A significant increase in desorption and consequent mobility commences when LAS and CTAB approach CMC. Results from this study can provide valuable information for the development of effective and safe surfactant remediation technologies.

3 Conclusions

This study has shown that phenanthrene exhibits a more nonlinear and stronger sorption by soils than naphthalene with n range 0.637–0.844. This may be caused by the high values of MW, V_m and $\log K_{ow}$ for phenanthrene than those for naphthalene. Sorption of the two sorbates decreased with the increase of temperature. The Freundlich coefficient (K_f) dropped from 106.8 at 15°C to 42.5 at 35°C for naphthalene and from 932.7 at 15°C to 568.9 at 35°C for phenanthrene.

The adsorption behavior of naphthalene and phenanthrene by soils is significantly influenced by LAS and CTAB. Sorption decreased with increasing aqueous LAS concentrations from 0 to 1000 mg/L. At low CTAB concentration (< 100 mg/L), the adsorption of naphthalene and phenanthrene increased by partitioning into CTAB hemimicelles formed on the soil surface. While, a more rapid decline of adsorption was observed in CTAB concentration range 100–500 mg/L due to the solubilization of naphthalene and phenanthrene.

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