Effect of biosurfactant on the sorption of phenanthrene onto original and H$_2$O$_2$-treated soils

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Abstract

The objective of this study was to examine the effect of biosurfactant on the sorption of phenanthrene (PHE) onto the original or H$_2$O$_2$-treated black loamy soil (typic isohumisols) and red sandy soil (typic ferralisols). The sorption isotherms were performed with the original and "soft" carbon-removed soils in the presence and absence of biosurfactant (200 mg/L). The sorption and degradation of biosurfactant were investigated. The result showed that organic matter played an important role in PHE sorption onto the black loamy and red sandy soils, and the PHE sorption isotherms on the "soft" carbon-removed soils exhibited more nonlinearity than those on the original soils. The values of partition coefficient (K_d) on the original black loamy soil with or without 200 mg/L biosurfactant were 181.6 and 494.5 mL/g, respectively. Correspondingly, in the red sandy soil, K_d was 246.4 and 212.8 mL/g in the presence or absence of biosurfactant, respectively. The changes of K_d suggested that biosurfactant inhibited PHE sorption onto the black loamy soil, but facilitated PHE sorption onto the red sandy soil. The nonlinearity of PHE sorption isotherm was decreased in the presence of biosurfactant. Site specific sorption might occur during PHE sorption onto both the original and the "soft" carbon-removed soils in the presence of biosurfactant. It was noted that biosurfactant could also be sorbed onto soils. The maximal sorption capacity of the red sandy soil for biosurfactant was (76.9 ± 0.007) μg/g, which was 1.31 times that of black loamy soil. Biosurfactant was degraded quickly in the two selected soils, and 92% of biosurfactant were mineralized throughout the incubation experiment for 7 d. It implied that biosurfactant should be added frequently when the remediation of polycyclic aromatic hydrocarbon (PAH)-contaminated soils was conducted through PAH desorption approach facilitated by biosurfactant.

Key words: biosurfactant; phenanthrene; sorption; "soft" carbon; soil

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) constituted by hundreds of individual substances have been recognized as priority pollutants in many countries owing to their high toxicity and carcinogenic properties (Sun *et al*., 2002). Over 90% of PAHs in the environment reside in soils (Nelson, 1983). Therefore, the removal of PAHs from the contaminated sites is of major environmental concern.

Of all the remediation methods, biodegradation and its combination with other methods are believed to be a major removal process (Ding *et al*., 2008). In the removal process of PAHs, sorption is the rate-limiting step controlling both the rate and extent of bioremediation (Yang *et al*., 2005). Thus, the investigations on the sorption behavior of PAHs on soils are of great importance in assessing and predicting their mobility, bioavailability, transport and fate in the environment (Karickhoff *et al*., 1979; Nelson *et al*., 1998).

To enhance the mobility and bioavailability of PAHs sorbed on soils, the application of surfactant is a common practice (Wong *et al*., 2002). Some researchers found

that surfactants could effectively enhance mobilization, desorption and biodegradation of PAHs (Mulligan *et al*., 2001; Gao *et al*., 2007). Chemical surfactants are environmentally unfriendly due to the formation of foams on the surface of water with blocking the sunlight and oxygen, and their low biodegradability. Recently, biosurfactant produced from yeast or bacteria has gained increasing attention because of its biodegradability and low toxicity with comparison to chemical surfactant (Shin *et al*., 2006).

It has been well documented that sorption of PAHs is primarily regulated by soil organic matter (SOM) (McGinley *et al*., 1993; White *et al*., 1997; Walter and Weber, 2002). Chiou *et al*. (1983) demonstrated that sorption isotherms of PAHs by SOM were linear, and the partition model could interpret the observed phenomena adequately. However, some researchers observed nonlinear sorption of PAHs and introduced the concepts of "soft" and "hard" carbon representing two broad categories of expanded and condensed SOM domains (Weber *et al*., 1992). The "hard" carbon domain exhibits nonlinear sorption behavior, and the "soft" carbon domain may display linear sorption behavior, faster uptake rates, and no solute-solute competition (Weber *et al*., 1992; Xing and Pignatello, 1997).

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Moreover, Xing *et al*. (1996) reported that site specific sorption had taken place in SOM when atrazine and other organic compounds were selected as solute.

Up to now, the study on PAHs and biosurfactant has mainly focused on the sorption of PAHs onto the soils and PAHs solubility enhanced by surfactant in aqueous circumstance. Little information is available on biosurfactant impact on sorption behavior of PAHs onto "soft" carbon-removed soils. In particular, it is also unclear whether site specific sorption occurs during sorption of PAHs in the presence of biosurfactant.

Phenanthrene (PHE), one of the 16 PAHs selected as priority pollutants by the American Environmental Protection Agency, has been used as a model compound of PAHs owing to the most widespread in environment (Huang *et al*., 1998; Xiao *et al*., 2004).

In this study, we investigated the sorption and biodegradation of biosurfactant onto the selected soils and also the effect of biosurfactant on the sorption of PHE onto the soils with or without "soft" organic carbon. Such insights are beneficial for interpreting the sorption mechanism of PAHs onto soils in the presence of biosurfactant, and selecting a suitable biosurfactant to improve the remediation efficiency for PAH-contaminated soils.

1 Materials and methods

1.1 Chemicals

PHE, a three-ring polycyclic aromatic hydrocarbon with octanol-water partition coefficient ($\log K_{ow}$) of 4.57 and water solubility of 0.71–2.67 mg/L (Maagd *et al*., 1998; Mackay *et al*., 1992), was purchased from Fluka Company with a purity of 97%. Milli-Q water with a specific resistivity of 18.2 MΩ/cm was used throughout the experiment. PHE stock solution (1000 mg/L) was made through dissolving PHE in methanol and kept at 4°C prior to tests. The other chemicals in this study were analytical grade.

1.2 Soils

A black loamy soil (typic isohumisols) and a red sandy soil (typic ferralisols) were collected from the topsoil (0–15 cm) in Changchun, Jilin Province (hereinafter called "Jilin soil") and Yingtan, Jiangxi Province (hereinafter called "Jiangxi soil") in China, respectively. Soil samples were air-dried, grounded and passed through a 2-mm sieve. Preliminary physico-chemical properties of soils are presented in Table 1. Two soils differ greatly in the

amount of organic matter (OM), particle size and pH value. Jiangxi soil is a kind of iron-rich (laterite) and aluminous (bauxite) deposit which develops in heavily leached area with intensive rainfall and high temperature. Intensive leaching removes soluble H$_4$SiO$_4$ from soils and causes enrichment in aluminum and iron in soils showing low Si:(Al+Fe) ratio. OM of Jilin soil is higher than that of Jiangxi soil. The value of surface area is 2.55 m^2/g for Jilin soil and 21.2 m^2/g for Jiangxi soil.

In terms of the definition of "hard" carbon (Pan *et al*., 2007), a sequential separation procedure was employed in this study to obtain the soils without "soft" carbon. The soils were extracted by 1.0 mol/L sodium acetate at pH 5.0 adjusted by acetic acid for 6 h in shaker and then left to settle overnight. After supernatant was discarded, soil sample was thoroughly washed with Milli-Q water for several times and then dried at 60°C. Thirty percent of H$_2$O$_2$ solution was added dropwise to the above treated soil sample, intermittently agitated at 40°C water bath, and then evaporated to dryness. The H$_2$O$_2$ treatment was repeated six times in 48 h to remove "soft" organic matter completely. After treatment with H$_2$O$_2$, SOM was reduced by 90.0% for Jilin soil and by 74.6% for Jiangxi soil. It was noted that the surface area was reduced by 12.3% for Jilin soil and increased by 1.25% for Jiangxi soil. The residual soil was called as the H$_2$O$_2$-treated soil or "soft" carbon-removed soil.

1.3 Biosurfactant preparation

The biosurfactant was harvested and prepared from the culture medium of microorganism which was previously isolated from an oil-contaminated soil. The mineral basal medium at pH 7.0–7.5 used to cultivate the microorganisms is as follows (g/L): KH$_2$PO$_4$ 3.4, K$_2$HPO$_4$ 4.4, (NH$_4$)2SO$_4$ 10, KCl 1.1, NaCl 1.1, MgSO$_4$·7H$_2$O 0.5 and yeast extract 0.5, and soybean oil 10 mL/L as the sole carbon, and 10 mL/L trace element solution. The composition of the trace element solution was (g/L): ZnSO$_4$ 0.29, CaCl$_2$ 0.24, CuSO$_4$ 0.25, MgSO$_4$ 0.17. Biosurfactant was harvested by centrifuging at 12000 ×*g*, 4°C for 20 min to shear off microbial cells according to the method described by Liu *et al*. (2006). The supernatant was placed in 3000 molecular weight cut-off dialysis tubing and concentrated by excessive polyglycol with constant mixing for 3 d at 4°C. After concentration, biosurfactant was lyophilized and stored at 4°C in a sealed glass tube prior to test (Hisashi *et al*., 2009).

The harvested biosurfactant could lower the surface

Table 1 Basic physico-chemical properties of tested soils

Soil	Surface area (m^2/g)	pH	OM (g/kg)	CEC (cmol/kg)	Particle size (g/kg)			
					Clay (0–2 μm)	Silt (2–20 μm)	Fine sand (20–200 μm)	Coarse sand (200–2000 μm)
Jilin soil	2.55	6.10	22.1	26.5	101	416	451	31.8
Jiangxi soil	21.2	4.60	8.66	14.2	333	281	344	42.2

Soil texture was determined by using the pipette method (Gee and Bauder, 1996). Soil pH was detected using a suspension of 1:1 (solid to water, *w/w*), particle size form of the soils was introduced according to the international standardization (Huang, 2002).
CEC: cation exchange capacity was obtained by exchanging the samples with NH$_4$OAc at pH 7 (Sumner and Miller, 1996); OM: organic matter was determined by the Walkley and Black wet dichromate oxidation method (Nelson and Sommers, 1996).

tension of water from 74.2 to 49.2 mN/m at 25°C. Its critical micelle concentration (CMC) was about 10.0 mg/L at 25°C (Fig. 1), which was much lower than those obtained by others (Kim *et al.*, 2002). The biosurfactant in this study was recognized as rhamnolipid (Fig. 2) with 353 Dalton for average molecular weight (data not shown).

1.4 Biosurfactant sorption experiment

Biosurfactant sorption experiment was conducted in 20 mL capped vitreous centrifugal tubes. One gram of the soil sample (Jilin soil or Jiangxi soil) and 4 mL of Milli-Q water were added into the tubes and shaken on a reciprocal shaker for 2 h, and then a series of 4 mL of the biosurfactant solution with different concentrations were added into the tubes to produce seven different initial biosurfactant concentrations ranging from 0 to 40 mg/L. The suspension pH was adjusted to 4.60 for Jiangxi soil and 6.10 for Jilin soil by adding diluted H_2SO_4 or NaOH. The centrifuge tubes were sealed with Teflon stoppers and stirred for 16 h which was found to be sufficiently long for sorption equilibrium in our preliminary trials. The samples were centrifuged at 3000 ×g for 30 min, and then filtered through 0.45 μm membrane filters. The filtrates were analyzed for dissolved organic carbon (DOC). The difference between the DOC derived from biosurfactant treated soil and DOC of soil origin (the control) was regarded as DOC from the free surfactant. Furthermore, the adsorbed surfactant was calculated using calibration curves with standard solutions (Zhang *et al.*, 2004). All experiments were carried out at 25°C in triplicates.
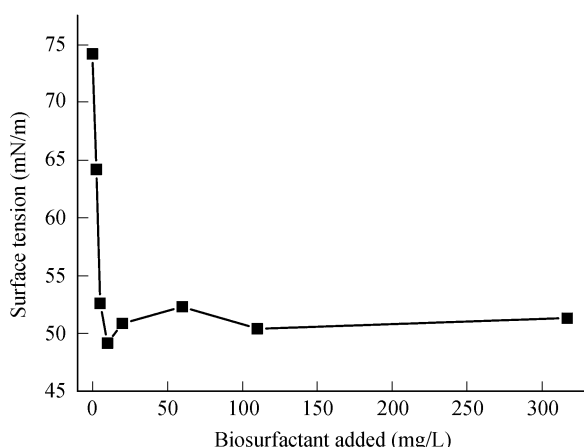

Fig. 1 Surface tension of aqueous solution with different biosurfactant concentrations.
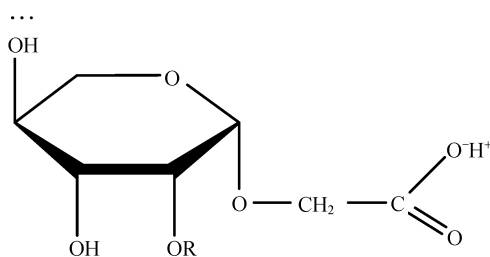

Fig. 2 Structure of biosurfactant in the experiment produced by a strain from College of Resources and Environmental Sciences in Nanjing Agricultural University, China. R: rhamnosyl.

1.5 Biosurfactant biodegradation experiment

Biosurfactant biodegradation experiments were conducted in a 25 mL plastic centrifuge tubes. Eight milliliters of 15 mg/L biosurfactant solutions were mixed with 0.5 g of selected soil. All samples were incubated in the dark at 25°C in triplicates. The water loss in tubes by evaporation during incubation was replenished with sterile water by periodically weighing throughout the incubation. The control with sterile soil and biosurfactant solution was also performed in present study. At day 0, 1, 2, 3, 4, 5, 6, and 7, six plastic centrifuge tubes including three tubes from the control were withdrawn, centrifuged at 12500 ×g for 10 min, and filtrated through 0.45 μm membranes. The percentage of biosurfactant decomposition (*R*%) was calculated as follows (Zhou *et al.*, 2004).

$$R\% = \frac{DOC_{control} - DOC_{biodegradation}}{DOC_{initial}} \times 100\% \qquad (1)$$

where, $DOC_{control}$, $DOC_{biodegradation}$, and $DOC_{initial}$ are DOC in the filtrates of the control, biodegradation experiment, and initial DOC concentration, respectively.

1.6 PHE sorption experiments in the presence and absence of biosurfactant

Batch experiments of PHE sorption onto the selected soil samples were performed. Original and H_2O_2-treated soil samples were used in the study. Two grams of tested soil sample were weighted into glass centrifuge tubes and shaken for 24 h at 25°C in the dark with 25 mL of 0.01 mol/L KCl solution consisting of PHE (0–1.0 mg/L) and 0.001 g/L of NaN_3 (in order to inhibit biodegradation of PHE and biosurfactant) in the presence or absence of 200 mg/L of biosurfactant. The tubes were then centrifuged at 3500 ×g for 30 min. An appropriate aliquot of the supernatant (1–2 mL) was withdrawn and analyzed for PHE. All treatments were done in triplicates. Meantime, the controls without addition of soils were also performed at each concentration level to assess the losses of PHE by photochemical decomposition, volatilization, and sorption to tubes. It was found that the losses of PHE were negligible under the experimental conditions. The amount of PHE sorbed was calculated as:

$$PHE_{sorbed} = PHE_{total} - PHE_{equilibrium} \qquad (2)$$

where, PHE_{sorbed}, PHE_{total}, and $PHE_{equilibrium}$ are the amount of PHE sorbed on the soils, the total amount of PHE added initially, and PHE in equilibrium solution, respectively.

1.7 Analytical methods

The concentration of PHE in solution was quantified by high performance liquid chromatography (HPLC, Waters, USA) fitted with a binary high-pressure pump (Waters 1525), a UV detector (Waters 2487), a fluorescence detector (Waters 2475) and a reverse phase C18 column (∅ 4.6 mm×150 mm, 5 μm particle size), using methanol/water (80:20, *V/V*) as the mobile phase at a flow rate of 1.0 mL/min. The UV wavelength was set at 254 nm, and

fluorescent excitation and emission wavelengths were set at 294 and 365 nm, respectively.

Surface tension was determined with a tension meter (JZHY-180, Chengde Experimental Instrument Co., China). DOC was determined by total organic carbon analyzer (TOC-5000A, Shimaduz, Japan). Surface area was measured by an auto nitrogen adsorption surface area analyzer (JW-004, Beijing JWGB Sci. and Tech. Co., China).

2 Results and discussion

2.1 Sorption isotherm of biosurfactant onto soils

Sorption of biosurfactant onto the soil is an important factor affecting environmental behavior of PHE in contaminated soils amended with biosurfactant. Figure 3 depicts the sorption of the biosurfactant onto tested soils. It was found that the amount of biosurfactant sorbed onto soils increased with the increase in equilibrium concentration of biosurfactant and eventually achieved a plateau value at high equilibrium concentrations. The amount of biosurfactant sorbed onto Jilin soil was much less than that onto Jiangxi soil at the same equilibrium concentration of biosurfactant.

The equilibrium isotherm could be described with Freundlich and Langmiur equation, respectively. The calculated parameters are listed in Table 2. The values of K_f and $1/n$ exhibited clearly that the affinity of Jiangxi soils with biosurfactant was stronger than that of Jilin soil. In the light of Langmiur equation, the maximal sorption capacity of Jiangxi soil for biosurfactant was (76.9 ± 0.007) μg/g, which was 1.31 times that of Jilin soil. The higher surface negative-charge density, pH and the lower

Fe- or Mn-oxides content in Jilin soil might be responsible for the lower sorption capacity of biosurfactant on Jilin soil. Because the biosurfactant tested was of negative-charge, it was easy to bind strongly with weathered oxisols like the tested acidic sandy loam with lower negative-charge density and higher Fe- or Mn-oxides content (Shen *et al.*, 2000; Zhang *et al.*, 2004).

2.2 Biodegradability of biosurfactant in soils

As shown in Fig. 4, biosurfactant was degraded quickly in the two selected soils during incubation for 7 d. It was noted that there was a relative slow degradation for biosurfactant in the first 3 d, but followed by a great reduction of biosurfactant in the soils until the end of the incubation experiment. After incubation for 1, 3 and 7 d, 10%, 20% and 92% of biosurfactant were mineralized for Jilin soil,
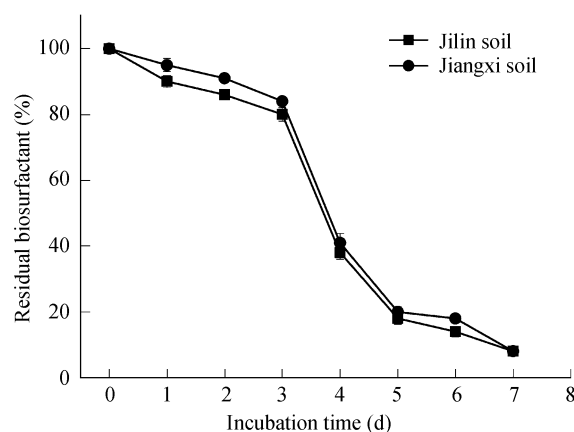

Fig. 4 Biodegradation of biosurfactant at the concentration of 15 mg/L in Jilin soil and Jiangxi soil at 25°C.
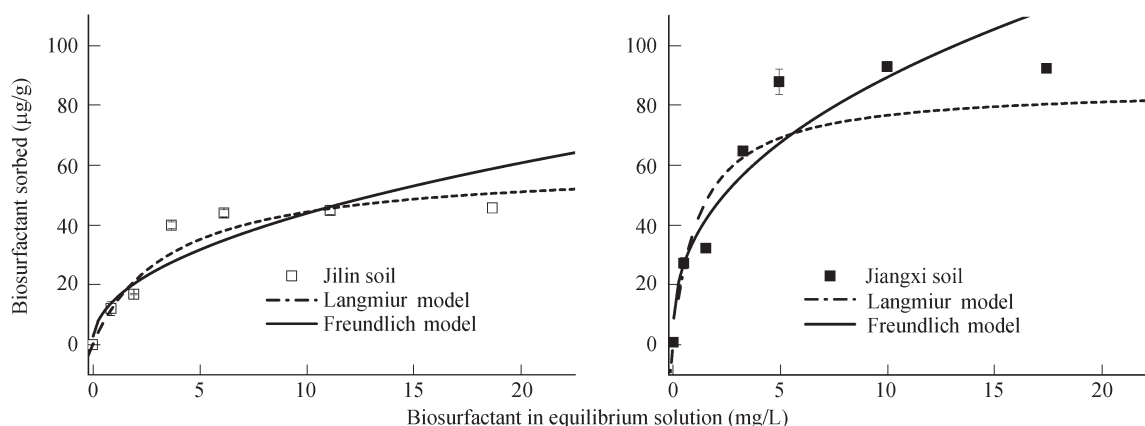

Fig. 3 Biosurfactant sorption isotherms on Jiangxi soil or Jilin soil after sorption equilibrium at 25°C.

Table 2 Calculated parameters of Langmuir and Freundlich equations for biosurfactant sorption onto the studied soils at 25°C

Soil	Langmuir equation			Freundlich equation		
	Q^0 (μg/g)	$1/K$ (mg/L)	r^2	K_f ((mg/g)/(g/L)$^{1/n}$)	$1/n$	r^2
Jilin soil	58.8 ± 0.008	59.38 ± 0.007	0.9317	14.95 ± 1.63	0.47 ± 0.12	0.8188
Jiangxi soil	76.9 ± 0.007	15.94 ± 0.006	0.8062	31.56 ± 1.39	0.41 ± 0.10	0.8724

Q^0: amount of sorbate per unit weight of sorbent to form a complete monolayer on the surface; K: constant related to the energy of sorption; $1/n$ represents the mutual interaction of adsorbed species; K_f is positively related to biosurfactant sorption capacity of soils.
Data are expressed as mean ± standard error.

respectively, and the biodegradation rates of biosurfactant were 5%, 16% and 92% for Jiangxi soil, respectively. It appeared that the degradation rate of biosurfactant on Jilin soil was slightly higher than that on Jiangxi soil during the first three days of incubation. The relative strong sorption of biosurfactant onto Jiangxi soil instead of Jilin soil might inhibit the attack of microorganisms because the "free" biosurfactant in aqueous solution was able to act readily as substrate for soil microorganisms. Therefore, to counteract the adverse effect of biodegradation, biosurfactant should be added frequently when the remediation of PAH-contaminated soils was conducted through PAHs desorption approach facilitated by biosurfactant.

2.3 PHE sorption onto the original soils in the presence or absence of biosurfactant

The sorptions of PHE onto Jiangxi soil and Jilin soil with or without the addition of biosurfactant are presented in Figs. 5 and 6, respectively. Generally, a partition coefficient (K_d) is introduced to describe PAH sorption onto organic particles:

$$K_d = \frac{P_{ads}}{P_{eq}} \tag{3}$$

where, P_{ads} (μg/g) is the pollutant content sorbed on the sorbent and P_{eq} (μg/L) is the concentration in the aque-

ous phase or equilibrium solution. For nonpolar organic sorbates, the partition coefficient and the organic carbon content (f_{oc}) are usually linked to calculate the normalized sorption coefficient (K_{oc}) through the following Eq. (2):

$$K_{oc} = \frac{K_d}{f_{oc}} \tag{4}$$

To investigate the sorption mechanism of PHE, the experimental isotherm equations including Freundlich equation and partition coefficient were selected in the present study. The related parameters with respect to partition coefficient and Freundlich model obtained from the experimental data with SPSS 16.0 software are listed in Table 3.

According to Figs. 5 and 6, it was found that the amount of PHE sorbed onto Jiangxi soil was lower than that onto Jilin soil at the same equilibrium concentrations of PHE. It was well known that, for soil suspensions of the same mass, the surface area and SOM content of soil sample might be the main factors which controlled the overall sorption characteristics of PHE by the soil. Usually, the amount of PHE sorbed was higher for the soil with larger surface area and SOM. As shown in Table 3, the values of K_d and K_{oc} were different in the tested soil samples. The K_d value of Jilin soil was larger than that of Jiangxi soil. Taking into account of SOM in each
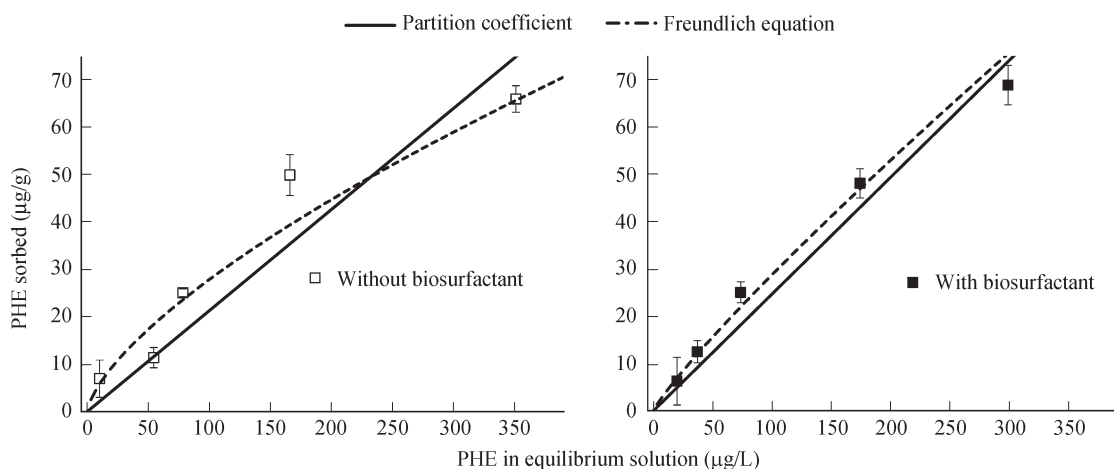

Fig. 5   PHE sorption isotherms on Jiangxi soil in the presence or absence of biosurfactant. Initial biosurfactant concentration: 200 mg/L.
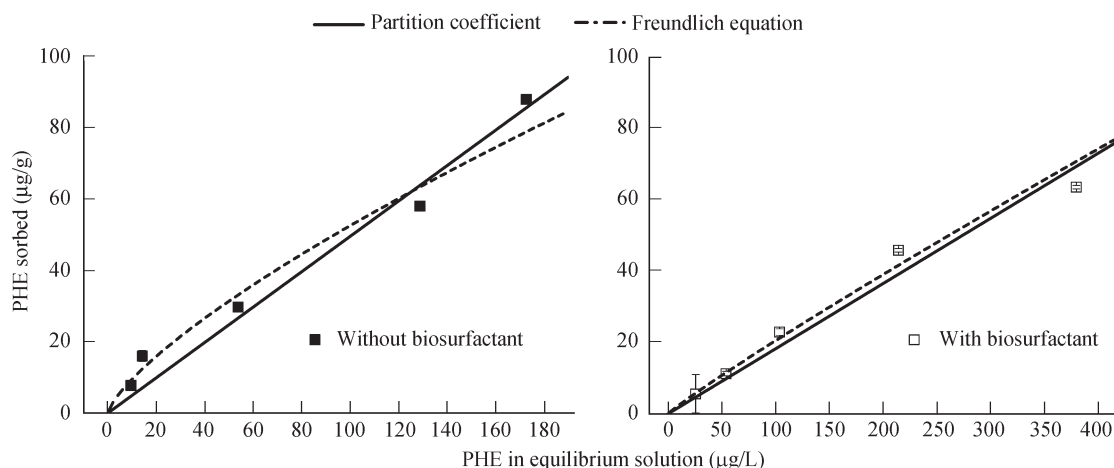

Fig. 6   PHE sorption isotherms on Jilin soil in the presence or absence of biosurfactant. Initial biosurfactant concentration: 200 mg/L.

Table 3   Parameters for PHE sorption on original and H$_2$O$_2$-treated soils in the presence or absence of biosurfactant

Soil	Treatment	Partition coefficient			Freundlich model		
		K_d (mL/g)	K_{oc} (mL/g)	r^2	$1/n$	K_f ((mg/g)/(g/L)$^{1/n}$)	r^2
Jilin soil	Original	495	22376	0.9681	0.742 ± 0.09	1.72 ± 0.04	0.9658
	Original + biosurfactant	182	8235	0.9590	0.927 ± 0.04	0.29 ± 0.02	0.9926
	H$_2$O$_2$ treated	29.3	1326	0.8059	0.415 ± 0.13	1.18 ± 0.07	0.8346
	H$_2$O$_2$ treated + biosurfactant	0	0	1.000	–	–	–
Jiangxi soil	Original	213	24572	0.8508	0.682 ± 0.14	1.21 ± 0.06	0.9126
	Original + biosurfactant	246	28406	0.9598	0.881 ± 0.04	0.50 ± 0.03	0.9898
	H$_2$O$_2$ treated	40.4	4665	0.8165	0.430 ± 0.12	1.11 ± 0.09	0.7318
	H$_2$O$_2$ treated + biosurfactant	67.1	7748	0.9366	0.813 ± 0.04	0.21 ± 0.04	0.9833

Data are expressed as mean ± standard error. "–": not be applied. Initial biosurfactant concentration: 200 mg/L.

soil, the amount of PHE sorbed onto the soil with more SOM was considerably larger than that with low SOM content, which might result in a decrease in bioavailability of PAHs. SOM plays an important role in the sorption of PAHs, which has been demonstrated by other researchers (Chiou *et al.*, 1983; White *et al.*, 1997; Walter and Weber, 2002). In addition, it was noted that the differences in K_d and K_{oc} between the two soils were 282 and 2196 mL/g, respectively, and the relative deviation of K_{oc} was smaller than that of K_d. This phenomenon had also been reported in other literatures (Spark and Swift, 2002; Gao *et al.*, 2007). The K_{oc} values are expected to be relatively constant when the effect of clay content and nature of SOM are taken into account during PHE sorption process (Brion and Pelletier, 2005).

The K_d values of Jilin soil with and without biosurfactant were 182 and 495 mL/g, respectively. It was decreased by 63.3% in the presence of biosurfactant. In other words, the amount of PHE partition into Jilin soil was apparently decreased in the presence of biosurfactant. However, the inhibit effect of biosurfactant on PHE sorption was much lower in Jiangxi soil than that in Jilin soil, as indicated by that the values of K_d of Jiangxi soil with and without biosurfactant were 246 and 213 mL/g, respectively. Generally, more attentions were paid to solubility of PAHs enhanced by biosurfactant in liquid phase. Practically, biosurfactant could also be sorbed by soils, thereby decreasing the concentration of biosurfactant micelles and the extent of solubilization of PHE in water (Brownawell *et al.*, 1997). On the other hand, PHE could be accumulated via partitioning into immobile sorbed biosurfactant. Thereby, the behave of PHE on the water-soil interface in the presence of biosurfactant was governed by the processes that the PHE molecules partitioned into the SOM and biosurfactant. They included (a) PHE sorbed on SOM and organic appearance formed by sorbed biosurfactant, (b) PHE partitioned into biosurfactant micelles and monomer, and (c) PHE dissolved into the water (Karickhoff *et al.*, 1979). The PHE sorption on soil in the presence of surfactant was a combined result of the two reverse effects. Undoubtedly, the properties of biosurfactant and the physico-chemical characteristics of SOM might be responsible for the different effects of the same biosurfactant on PAH sorption (Liu and Luthy, 1995; Grathwohl, 1990). All PHE sorption isotherms of the original fitted Freundlich model with $1/n$ values being smaller than 1, therefore, the sorption of PHE on the two soils were con-

sidered nonlinear. Xing and Pignatello (1997) also pointed out that sorption of PAHs was nonlinear because the sorption of PAHs in "soft" carbon occurred by dissolution, while in "hard" carbon by concurrent dissolution and hole filling mechanisms. For both Jilin and Jiangxi soils, the $1/n$ values increased in the presence of biosurfactant, implying that the isotherm nonlinearity decreased with the addition of biosurfactant because the lower the $1/n$ value is, the higher the nonlinearity presents. It was assumed that the reduction of nonlinearity was caused by competitive sorption between biosurfactant and PHE due to limited specific sites at soil surface. Furthermore, the K_f of Freundlich model along with their 95% confidence levels was the equilibrium partition coefficient positively related to PHE sorption capacity of soils. As shown in Table 3, K_f values of Jilin soil and Jiangxi soil were 1.72 ± 0.04 and 1.21 ± 0.06, indicating a higher sorption capacity of PHE onto Jilin soil with the comparison to Jiangxi soil. Moreover, the addition of biosurfactant to the reaction medium greatly reduced K_f values for both Jilin and Jiangxi soils. For example, K_f values were only 0.29 ± 0.02 for Jilin soil and 0.50 ± 0.03 for Jiangxi soil, suggesting that the presence of biosurfactant significantly decreased the sorption capacity of PHE onto two selected soils. Competition for sorption site of SOM between biosurfactant and PHE caused the expansion of organic matrix, reduction in the tortuosity and rearrangement of the soil structure during PHE sorption process on two soils (Xu *et al.*, 2006). Salloum *et al.* (2001) also demonstrated that the molecular structure was rearranged during sorption course. Because competitive sorption was an indicator for the occurrence of site specific sorption, site specific sorption might have taken place during PHE sorption in the presence of biosurfactant (Xing *et al.*, 1996).

2.4 PHE sorption onto the H$_2$O$_2$-treated soils in the presence or absence of biosurfactant

The sorptions of PHE onto H$_2$O$_2$-treated Jilin soil and Jiangxi soil with or without the addition of biosurfactant were given in Figs. 7 and 8, respectively. The parameters of the sorption of PHE along with their 95% confidence levels were also listed in Table 3 in terms of Freundlich model and partition coefficient.

All sorption isotherms of PHE onto two H$_2$O$_2$-treated soils were nonlinear and could be fitted with Freundlich model (Table 3). The values of $1/n$ of the H$_2$O$_2$-treated Jilin and Jiangxi soils were 0.415 and 0.430, respectively,
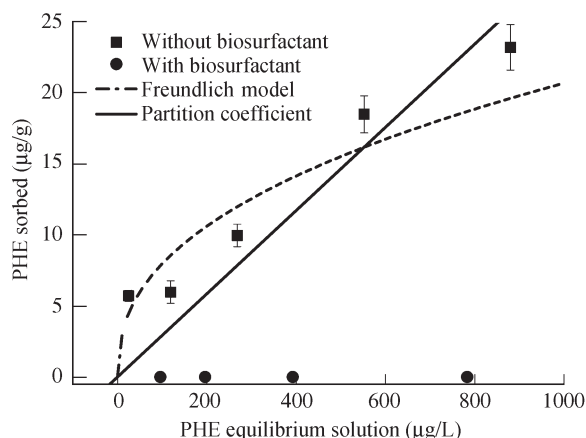
Fig. 7 PHE sorption isotherms on the H_2O_2-treated Jilin soil in the presence or absence of biosurfactant. Initial biosurfactant concentration: 200 mg/L.

suggesting a strong nonlinearity of PHE sorption on two H_2O_2-treated soils. Pan *et al*. (2007) validated that "hard" carbon was remained after treating soils by H_2O_2 to remove "soft" carbon. The increase in nonlinearity of PHE sorption on two H_2O_2-treated soils was also reported in some publications (Weber *et al*., 1992; Xing *et al*., 1996) in which the "soft" carbon domain might display linear sorption behavior.

The sorptions of PHE onto the original or H_2O_2-treated soils were influenced by biosurfactant, as indicating that the $1/n$ values of sorption isotherm according to Freundlich model increased with the addition of biosurfactant (Table 3). It was noted that PHE was entirely dissolved into solution when the H_2O_2-treated Jilin soil was tested as sorbent in the presence of biosurfactant. However, for the H_2O_2-treated Jiangxi soil, PHE sorption was not influenced significantly by biosurfactant. The differences in K_d and K_{oc} between two H_2O_2-treated soils were similar to those of the original soils, which were 11.1 and 3339 mL/g for K_d and K_{oc}, respectively. Like the original soils, clay content and SOM nature of two H_2O_2-treated soils also played an important role in PHE sorption. For the H_2O_2-treated Jilin soil, the K_f value was 1.18 ± 0.07 in the absence of biosurfactant, and the sorption of PHE was

inhibited completely in the presence of biosurfactant. The K_f value of the H_2O_2-treated Jiangxi soil was 1.11 ± 0.09 and 0.21 ± 0.04 in the absence and presence of biosurfactant, respectively. This demonstrated that the molecular structure was rearranged during PHE sorption onto the H_2O_2-treated soils in the presence of biosurfactant. Furthermore, site specific sorption had taken place during the sorption process in the presence of biosurfactant.

The amount of PHE partitioned into the original soils was larger than that into the H_2O_2-treated soils according to the value of K_d. For Jilin soil, the K_d value was 495 mL/g, which was reduced by 94.1% after treatment with H_2O_2. For Jiangxi soil, the K_d value was 213 mL/g, and it was reduced by 81.0% after treatment with H_2O_2. Therefore, the "soft" carbon of the soils affected significantly PHE sorption. Furthermore, the differences in K_f values between the two original and corresponding H_2O_2-treated soils also implied that the "soft" carbon in SOM played an important role in the PHE sorption.

3 Conclusions

The sorption of PHE was, to a great extent, governed by SOM, in which "soft" organic matter played a key role in sorption of PHE onto soil in spite of its low content in soil, as indicating that the sorption of PHE was reduced greatly for the H_2O_2-treated soils. In addition, PHE sorption was significantly inhibited in the presence of biosurfactant according to the parameters of Freundlich model and partition coefficient, especially for the H_2O_2-treated soils. However, the inhibit effect of biosurfactant on PHE sorption was much lower in Jiangxi soil than that in Jilin soil. This was contributed to the physico-chemical characteristics of the selected soil and biosurfactant. It was also found that biosurfactant itself could be sorbed and biodegraded in the soils, which decreased biosurfactant efficiency in improving the dissolution of PHE sorbed onto soils thereby inhibiting PHE sorption. It implied that biosurfactant should be added frequently when the remediation of PAH-contaminated soils was conducted through PAHs desorption approach facilitated by biosurfactant.
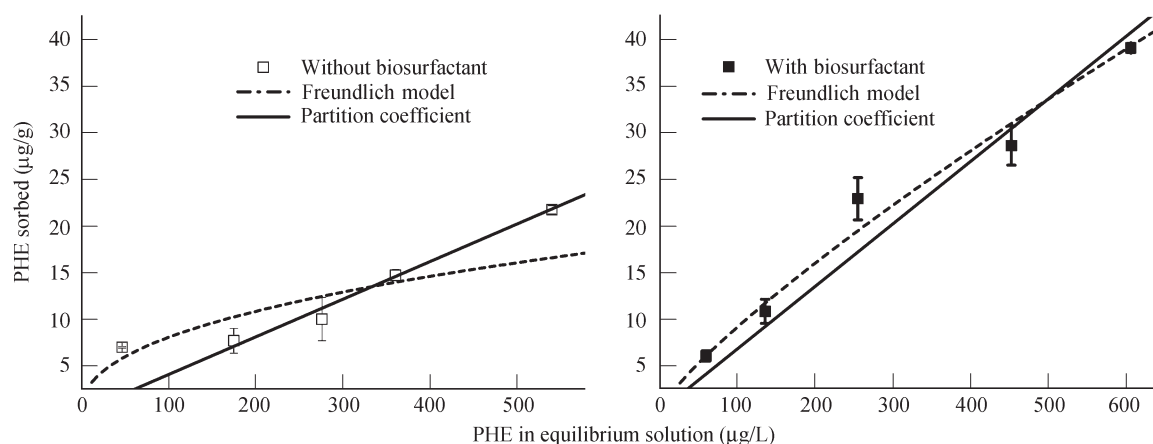

Fig. 8 PHE sorption isotherms on the H_2O_2-treated Jiangxi soil in the presence or absence of biosurfactant. Initial biosurfactant concentration: 200 mg/L.

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