

Enhanced Desorption of PAHs from Manufactured Gas Plant Soils Using Different Types of Surfactants^{*1}

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ABSTRACT

Surfactant enhanced remediation is thought to be an effective method for the remediation of soils polluted with hydrophobic organic compounds. Desorption of polycyclic aromatic hydrocarbons (PAHs) from an abandoned manufactured gas plant (MGP) soil was evaluated using four eluting agents including Triton X-100 (TX100), sodium dodecylbenzene sulfonate (SDBS), rhamnolipid water solution (RWS) and rhamnolipid fermentation broth (RFB). The weight solubilization ratios for acenaphthene and fluorene were in the order of TX100 > SDBS > RWS > RFB. The S_m value, which indicates the maximum amounts of surfactants adsorbed in the soil, was in the order of RWS > RFB > SDBS > TX100. By using 8 g L⁻¹ of TX100, SDBS and RWS and 100% of RFB, the T-PAHs removal for the MGP soil contaminated with 207.86 mg T-PAHs kg⁻¹ dry soil was 48.0%, 45.7%, 1.9%, and 8.6%, respectively, while that decreased to 41.6%, 37%, 0.38%, and 1.3% for the soil contaminated with 3494.78 mg T-PAHs kg⁻¹ dry soil. Only 8 g L⁻¹ TX100 could remove all types of the 16 PAHs partly in the MGP soil, and the removal efficiencies of different PAHs ranged from 13% to 77.8%. The results of this study herein provide valuable information for the selection of TX100 surfactant for remediating PAH-contaminated soils in MGP.

Key Words: adsorption, polycyclic aromatic hydrocarbons, remediation, soil washing, solubilization

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), which are distributed ubiquitously in soils and known to be carcinogenic, teratogenic and mutagenic, are toxic to humans and can be harmful to soil organisms and plants through trophic transfer (Zhang *et al.*, 2010). Some of PAHs have been classified as priority pollutants in the United States of America, China, and the European Union (Keith and Telliard, 1979; Zhou *et al.*, 1991; Wenzl *et al.*, 2006). Because of low water solubility and strong affinity to organic matter, PAHs are hard to remove from the soil environment and can be a long-term source of groundwater contamination (Zhang *et al.*, 2006).

Surfactant enhanced remediation (SER) is thought to be an effective, economic and quick method for the remediation of soils polluted with hydrophobic organic compounds (HOCs, including PAHs) (Intera

Inc. and NFESC, 2003; USEPA, 2004). Under suitable conditions, more than 80% of the PAHs in coal tar-contaminated soils could be removed by Tween 80 (TW80, a non-ionic surfactant) and Triton X-100 (TX100, a non-ionic surfactant) solutions (Peng *et al.*, 2011). Through column flushing experiments (Zhou and Zhu, 2008a), it has been found that 90% of the phenanthrene in the contaminated soil could be removed by an anionic-nonionic mixed surfactant (sodium dodecyl sulfate and TX100). The washing performances of four different non-ionic surfactants including Tween 40, TW80, Brij 30 and Brij 35 were compared in a phenanthrene-spiked soil at a concentration of 200 mg kg⁻¹ (Ahn *et al.*, 2008). Because of the highest solubilizing ability and lowest adsorption onto the soil, Brij 30 had the highest washing efficiency with 84.1% phenanthrene removal at a surfactant concentration of 2 g L⁻¹.

In addition to the common chemical surfactants,

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due to biodegradability, the biosurfactants have recently been preferred for remediation and thought to be a type of effective and environmentally friendly surfactant for removing HOCs in the contaminated soils and water (Shin and Kim, 2004; Ying, 2006; Daverey and Pakshirajan, 2011). However, the low production and high costs of their purification have limited the application of biosurfactants (Mulligan, 2005). Surfactant enhanced remediation is primarily effective based on two mechanisms: 1) molecules of the surfactant tend to concentrate at the interfaces, and decrease the interfacial tension between the HOCs and water (Paria, 2008), which facilitate the removal of the HOCs; and 2) when the surfactant is above a certain concentration (critical micelle concentration, CMC), micelles are formed that increase the solubility of HOCs (Zhou and Zhu, 2007). Fig. 1 shows the interactions among soils, PAHs, and surfactants.

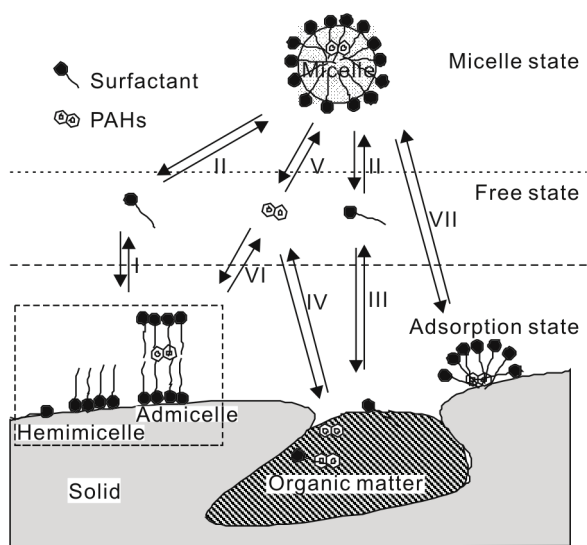


Fig. 1 Interactions among soils, polycyclic aromatic hydrocarbons (PAHs), and surfactants in soil washing process (West and Harwell, 1992; Edwards *et al.*, 1994; Wang and Keller, 2009). I = sorption of surfactants on inorganic surfaces; II = formation of the micelle; III = sorption of surfactant molecules onto soil organic matter; IV = partitioning of PAHs between water and soil organic matter; V = partitioning of PAHs between water and micelle; VI = partitioning of PAHs between micelle-like phase and water; VII = solubilization of PAHs.

Manufactured gas plants (MGPs) are one of the major sources of PAHs. The concentration of PAHs in the MGP soil can reach up to $10\text{--}30\text{ g kg}^{-1}$ (Khadoust *et al.*, 2000). The types of surfactant which have been used in remediation include anionic and non-ionic surfactants (classified depending on the head group type of the surfactant molecules), or the synthetic surfactant and biosurfactant (classified accor-

ding to production process). The properties of surfactant play a decisive role on the remediation (Gan *et al.*, 2009). However, for removing PAHs in the MGP soil, there are few comprehensive studies with different types of surfactants. Here, four types of eluting agents, including the nonionic/synthetic surfactant (TX100), the anionic/synthetic surfactant (sodium dodecylbenzene sulfonate, SDBS), the anionic/biological surfactant (rhamnolipid water solution, RWS), and the anionic/biological surfactant (rhamnolipid fermentation broth, RFB), were investigated systematically with regard to their desorption potential of PAHs in the MGP soil. The solubilization capacity for PAH and adsorption onto the soil of four eluting agents were also compared.

MATERIALS AND METHODS

Soil samples

Soil samples were taken from an abandoned MGP in Beijing, which had been previously producing gas for 50 years. Five samples sited evenly in vertical direction (from 0 to 5 m below the ground surface). The heavily PAH-contaminated (HPC) soil and the slightly PAH-contaminated (SPC) soil were chosen for study. Soils were air-dried and sieved through a 60-mesh sieve, which were used in the washing test. The physico-chemical properties of the two soils are listed in Table I, and some chemical properties of the 16 PAHs in the two soils are described in Table II. The pH was measured in a 1:2.5 solid-to-water suspension. The total organic carbon (TOC) was determined by a high-temperature combustion-based elemental analyzer (Elementar Vario EL, Germany). The cation exchange capacity (CEC) was determined by the ammonium acetate saturation method, and the particle size distribution was measured by laser diffraction (Malvern Mastersizer 2000, Malvern Instruments, UK).

Chemicals

Acenaphthene (Ace, purity > 98%) and fluorene (Flu, purity > 98%) were purchased from J&K Scientific Ltd., China. The deuterated surrogates (naphthalene-d₈, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂) and the internal standards (2-fluorobiphenyl, *p*-terphenyl) were obtained from AccuStandard Inc., USA. Three representative surfactants (TX100, SDBS and RWS) and the rhamnolipid fermentation broth (RFB) were used in this study and their properties are presented in Table III. The TX100 and SDBS were obtained from J&K Scientific Ltd., China.

TABLE I

Selected physico-chemical properties of the slightly polycyclic aromatic hydrocarbon (PAH)-contaminated (SPC) soil and the heavily PAH-contaminated (HPC) soil

Soil	pH	Total organic C	Cation exchange capacity	Particle size fraction (mm)		
				0.020–2.000	0.002–0.020	< 0.002
		g kg ⁻¹	cmol kg ⁻¹		%	
SPC	7.50	5.1	9.67	43.16	41.67	15.17
HPC	7.10	15.2	9.81	78.34	16.54	5.12

TABLE II

Some chemical properties of the 16 polycyclic aromatic hydrocarbons (PAHs) in the slightly PAH-contaminated (SPC) soil and the heavily PAH-contaminated (HPC) soil

PAH ^{a)}	Abbreviation	Rings	S_w ^{b)}	$\log K_{ow}$ ^{c)}	SPC soil		HPC soil	
					Concentration	Weight percentage	Concentration	Weight percentage
			mg L ⁻¹		mg kg ⁻¹	%	mg kg ⁻¹	%
Naphthalene	Nap	2	31.50	3.37	13.78	6.63	83.20	2.38
Acenaphthylene	Acy	3	3.93	3.72	3.07	1.48	22.43	0.64
Acenaphthene	Ace	3	3.93	3.92	104.41	50.23	1 658.44	47.45
Fluorene	Flu	3	1.98	4.18	70.47	33.90	1 300.60	37.22
Phenanthrene	Phe	3	1.15	4.46	11.80	5.68	345.08	9.87
Anthracene	Ant	3	0.08	4.45	1.44	0.69	47.33	1.35
Fluoranthene	Fla	4	0.21	5.30	1.15	0.55	22.77	0.65
Pyrene	Pyr	4	0.13	5.32	0.64	0.31	7.05	0.20
Benzo[a]anthracene	BaA	4	0.01	5.61	0.15	0.07	1.34	0.04
Chrysene	Chr	4	0.00	5.61	0.22	0.11	1.86	0.05
Benzo[b]fluoranthene	BbF	5	0.00	6.11	0.22	0.11	1.53	0.04
Benzo[k]fluoranthene	BkF	5	0.00	6.11	0.17	0.08	0.93	0.03
Benzo[a]pyrene	BaP	5	0.00	6.11	0.08	0.04	0.79	0.02
Dibenzo[a, h]anthracene	DaA	5	0.00	6.63	0.03	0.01	0.16	0.00
Indeno[1,2,3- <i>cd</i>]pyrene	IcP	6	0.00	6.69	0.12	0.06	0.74	0.02
Benzo[<i>g, h, i</i>]perylene	BgP	6	0.00	6.70	0.10	0.05	0.55	0.02
Low-molecular-weight PAHs	L-PAHs	2–3			204.97	98.61	3 457.08	98.92
Middle-molecular-weight PAHs	M-PAHs	4			2.17	1.04	33.01	0.94
High-molecular-weight PAHs	H-PAHs	5–6			0.73	0.35	4.69	0.13
Total PAHs	T-PAHs				207.86	100.00	3 494.78	100.00

^{a)} From the United States Environmental Protection Agency priority pollutant list (Keith and Telliard, 1979).

^{b)} Intrinsic solute solubility in pure water at 25 °C.

^{c)} Octane-water distribution (Mackay *et al.*, 2006).

TABLE III

Selected properties of the four eluting agents including Triton X-100 (TX100), sodium dodecylbenzene sulfonate (SDBS), rhamnolipid water solution (RWS) and rhamnolipid fermentation broth (RFB)

Eluting agent	Type	Molecular weight	Critical micelle concentration	Purity
		g mol ⁻¹	mg L ⁻¹	%
TX100	Nonionic/synthetic surfactant	646.85	201.3	> 90
SDBS	Anionic/synthetic surfactant	348.48	1 000.0	> 90
RWS	Anionic/biological surfactant	650.00	22.5	> 90
RFB	Anionic/biological surfactant	-	-	-

and the RWS was obtained from GemkingBio Scientific Ltd., China. The RFB was prepared using standard methodology (Pei *et al.*, 2009). The *P. aeruginosa* was provided by the College of Resources and Environmen-

tal Sciences of Nanjing Agricultural University, China. The rhamnolipid concentration of RFB was 3.72 g L⁻¹. All the reagents were used without further purification. Deionized water was used for preparing solutions.

Solubilization test

The concentrations of Ace and Flu were very high in the two contaminated soils, and made up more than 80% of the total PAHs (T-PAHs) present. Therefore, pure Ace and Flu were used for the solubilization tests. Each eluting agent (20 mL) at the various concentrations (from 0 to 8 g L⁻¹ of TX100, SDBS and RWS and from 0 to 100% of RFB) was added to a 40-mL Corex centrifuge tube with a Teflon-lined screw cap. An excess mass of PAH was added to each tube for dissolution. All aqueous solutions for the solubilization tests contained 0.01 mol L⁻¹ NaCl to keep a constant ionic strength and 0.5 g L⁻¹ HgCl₂ to inhibit microbial growth. The tubes were maintained in a reciprocating shaker at 150 r min⁻¹ at 25 ± 2 °C for 24 h. The undissolved solutes were separated by centrifugation at 1 647 × *g* for 30 min. An aliquot of the supernatant (5 mL) was carefully withdrawn for PAH analysis.

Soil washing test

Soil samples (2.0 g) were weighed into centrifuge tubes, to which a 20 mL solution with a series of surfactants (from 0 to 8 g L⁻¹ of TX100, SDBS and RWS and from 0 to 100% of RFB) were added. All tubes were maintained in a reciprocating shaker at 150 r min⁻¹ and 25 ± 2 °C for 24 h. The solution and solid phase were separated completely by centrifuging at 927 × *g* for 20 min. An appropriate aliquot (5 mL) of the supernatant was carefully withdrawn to analyze PAHs.

Surfactant analysis

The concentration of TX100 present was determined by the KI-I₂ spectrophotometry method (Chang *et al.*, 1988). The concentration of SDBS was determined by using the national standard of the People's Republic of China (GB 7494–1987). The concentration of rhamnolipid was determined by the phenol-sulfuric acid spectrophotometry method (Chandrasekaran and Bemiller, 1980).

PAH analysis

The PAHs in the soil were extracted with dichloromethane using the ultrasonic method. Soil samples (2.0 g) were placed into 40-mL Corex centrifuge tubes, and 10 mL dichloromethane was added. The samples were placed in a sonication bath for 60 min. Then, the solution and solid phase were separated completely by centrifugation at 927 × *g* for 20 min. The supernatant (2 mL) was cleaned using a chro-

matography column (10 mm × 300 mm) filled with 10 g of silica gel (activated by heating at 130 °C for 16 h) and 1 g of anhydrous sodium sulfate. First, 30 mL of hexane was used to remove the aliphatic hydrocarbons and then the eluate was discarded. Next, the column was eluted with 50 mL of dichloromethane/hexane (1:1, v/v) mixture. The eluate was exchanged into hexane by a rotary evaporator at 40 °C and concentrated to 1 mL with a gentle purified N₂ stream. Prior to transfer to a gas chromatography-mass spectrometer (GC-MS) vials, a known quantity of internal standard was added.

For PAHs in the eluting agent, the supernatant was extracted with hexane in a reciprocating shaker. The supernatant (5 mL) was added to 40-mL Corex centrifuge tubes, with 10 mL hexane. The tubes were maintained in a reciprocating shaker at 200 r min⁻¹ and at 25 ± 2 °C for 2 h, and then centrifuged at 1 647 × *g* for 30 min. The rest of the process was the same with the PAH extraction of the soil.

Sample extracts were analyzed for PAHs using a GC-MS (Agilent 5975C-Agilent 7890A, Agilent Company, USA). The PAHs were separated by using an HP-5MS 30 m × 0.25 mm fused silica column in selected ion mode. The GC-MS operating conditions were as follows: helium was the carrier gas at a flow rate of 37 cm s⁻¹; the injection port, interface line, and ion source temperature were maintained at 300 °C; and the column temperature was programmed to be 60 °C, increasing to 300 °C at a rate of 5 °C min⁻¹, and held for 20 min.

Removal efficiency of PAHs in soil

The PAH removal efficiency (*R*) can be calculated as:

$$R(\%) = (S \times V) / (S_i \times m) \times 100 \quad (1)$$

where *S* is the PAH concentration in the eluting agents (mg L⁻¹), *V* is the initial volume of the eluting agents (L), *S_i* is the original PAH concentration in the polluted soil (mg kg⁻¹), and *m* is the initial weight of the polluted soil (kg).

Quality control

Experiments were carried out in duplicate. The variations of PAHs and the surfactant concentrations of the duplicated samples were less than 10%. The results shown in each figure corresponded to mean values. Prior to extraction, more than 12 soil samples and eluting agents were added to known quantities of deuterated PAH recovery surrogate standards. Average

extraction recoveries of the deuterated PAHs were 95% (naphthalene-d8), 82% (phenanthrene-d10), 81% (chrysene-d12), and 119% (perylene-d12) from the soil, and 95% (naphthalene-d8), 81% (phenanthrene-d10), 91% (chrysene-d12), and 124% (perylene-d12) from the eluting agents.

Statistical analysis

Experimental data, including the PAH and surfactant concentrations, were expressed as means. All statistical analyses were performed using OriginPro 8.5 software (OriginLab Corporation, USA).

RESULTS

Solubilization of the eluting agents

The enhanced solubilization of Ace and Flu in the different eluting agents was expressed using the solubility enhancement factor of S'_w/S_w (Fig. 2) (Song *et al.*, 2008), where S'_w is the apparent solute solubility in the surfactant solution and S_w is the intrinsic solute solubility in pure water (Table II). The solubility of PAHs increased linearly with the surfactant concentration above CMC, which has been previously demonstrated (Edwards *et al.*, 1991). The solubilities of Ace

and Flu could be enhanced by surfactant addition, while the enhanced solubilization of Ace and Flu at the surfactant concentrations above 2 g L^{-1} was in the order of TX100 > SDBS > RWS. The solubilities of Ace in the 8 g L^{-1} of the three eluting agents were 149.2, 73.7 and 35.5 times those of the S_w , respectively. The S'_w/S_w for Flu was 200.9, 112.1 and 45.6, respectively. The solubilities of Ace and Flu in the pure RFB were 3.0 and 5.3 times those of the S_w , and the enhanced solubilization was limited. At the same concentration, the solubilization capacity of the eluting agent for Flu was higher than that for Ace.

The molar solubilization ratio (MSR) was proposed as a measure of the effectiveness of a particular surfactant in solubilizing a given solute (Edwards *et al.*, 1991). It was defined as the number of moles of organic compound solubilized per mole of surfactant micellized, and can be calculated as follows:

$$\text{MSR} = (S - S_{\text{cmc}})/(C_s - \text{CMC}) \quad (2)$$

where S is the apparent solubility of solute at a particular surfactant concentration greater than the CMC, C_s is the surfactant concentration at which S is evaluated, and S_{cmc} is the apparent solubility of PAH at the CMC. All concentrations are expressed in mol L^{-1} .

Using a weight solubilization ratio (WSR) to quantify the surfactant enhanced solubilization can be a more direct measure. The relationship between WSR and MSR can be defined as:

$$\text{WSR} = \text{MSR} \times M_{\text{PAH}}/M_{\text{surf}} \quad (3)$$

where M_{PAH} and M_{surf} are the molecular weights of the solute (PAH) and surfactant, respectively. The larger the WSR value of the surfactant, the greater its solubilization capacity.

The WSR of the TX100, SDBS, RWS and RFB for Ace were 0.0736, 0.0389, 0.0165 and 0.0024, respectively. In addition, the WSR of the TX100, SDBS, RWS and RFB for the Flu were 0.0497, 0.0297, 0.0210 and 0.0035, respectively. The values for both Ace and Flu were in the order of TX100 > SDBS > RWS > RFB. At the same concentration, the solubilization capacity of the nonionic surfactants was higher than that of the biosurfactants.

Adsorption isotherms of the surfactants

The adsorption isotherms of the four surfactants for the soils studied are shown in Fig. 3. The Langmuir-type isotherm is commonly used to describe adsorption from solutions of surfactants (Rosen, 2004):

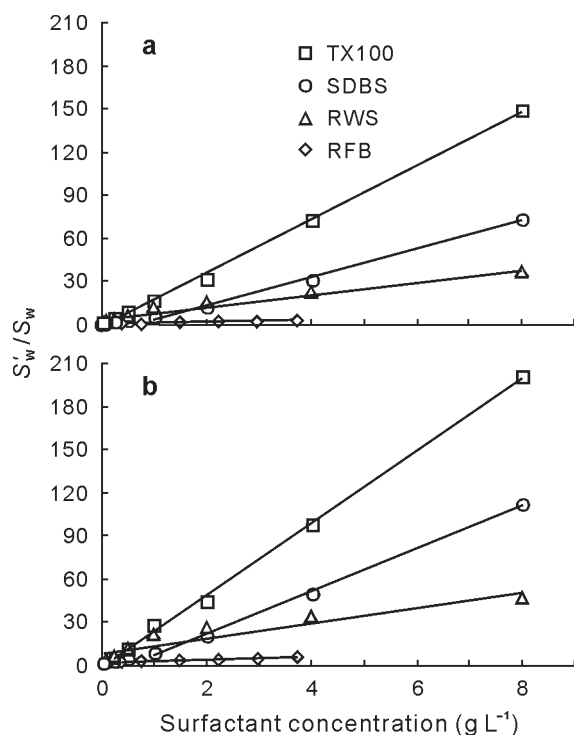


Fig. 2 The solubility enhancement of acenaphthene (a) and fluorene (b) by the surfactants Triton X-100 (TX100), sodium dodecylbenzene sulfonate (SDBS), rhamnolipid water solution (RWS) and rhamnolipid fermentation broth (RFB) at different concentrations. S'_w is the apparent solute solubility in the surfactant solution; S_w is the intrinsic solute solubility in pure water.

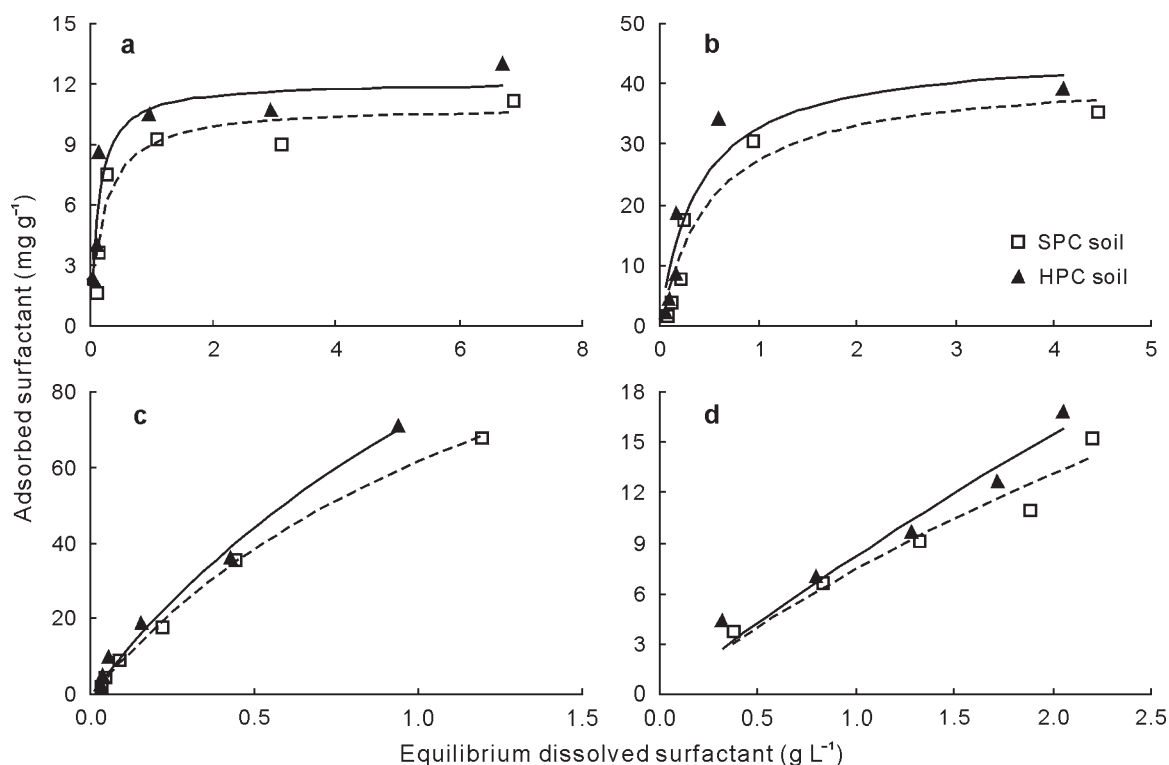


Fig. 3 Equilibrium adsorption isotherms for the surfactants Triton X-100 (a), sodium dodecylbenzene sulfonate (b), rhamnolipid water solution (c) and rhamnolipid fermentation broth (d) applied to the slightly polycyclic aromatic hydrocarbon (PAH)-contaminated (SPC) soil and the heavily PAH-contaminated (HPC) soil.

$$S_{\text{ads}} = b \times C_{\text{aqu}} \times S_{\text{m}} / (1 + b \times C_{\text{s}}) \quad (4)$$

where S_{ads} is the adsorbed surfactant mass (mg g^{-1}), b is the Langmuir constant (L mg^{-1}), C_{aqu} is the aqueous phase surfactant concentration at equilibrium (mg L^{-1}), and S_{m} is the maximum amounts of surfactants adsorbed in the soil (mg g^{-1}).

The parameters b and S_{m} for the four eluting agents are summarized in Table IV. The Langmuir isotherm gave a good fit to the data. The S_{m} value,

TABLE IV

The isotherm constants for the adsorption of Triton X-100 (TX100), sodium dodecylbenzene sulfonate (SDBS), rhamnolipid water solution (RWS) and rhamnolipid fermentation broth (RFB) onto the slightly polycyclic aromatic hydrocarbon (PAH)-contaminated (SPC) soil and the heavily PAH-contaminated (HPC) soil

Eluting agent	SPC soil			HPC soil		
	$b^{\text{a)}$	$S_{\text{m}}^{\text{b)}$	R^2	b	S_{m}	R^2
	L mg^{-1}	mg g^{-1}		L mg^{-1}	mg g^{-1}	
TX100	0.0018	10.94	0.8670	0.0082	12.12	0.8674
SDBS	0.0019	41.95	0.8980	0.0026	45.47	0.8638
RWS	6.6830×10^{-4}	153.78	0.9980	5.4759×10^{-4}	206.02	0.9883
RFB	1.5490×10^{-4}	55.55	0.9224	6.3681×10^{-5}	137.21	0.9322

^{a)}Langmuir constant.

^{b)}Maximum amounts of surfactants adsorbed in the soil.

which indicates the maximum amounts of surfactants adsorbed in the two soils, was in the order of $\text{RWS} > \text{RFB} > \text{SDBS} > \text{TX100}$. The maximum amounts of the surfactants adsorbed on soil were in the range of 10.94–206.02 mg g^{-1} .

Soil washing

The T-PAHs removal efficiencies of the two soils with the four eluting agents of different concentrations are shown in Fig. 4. The heavily T-PAHs removal efficiencies of the SPC soil and HPC soil occurred in the 8 g L^{-1} TX100 washing procedure, being 48% and 41.6%, respectively. The 8 g L^{-1} RWS washing treatment had the lowest T-PAHs removal efficiencies of the two soils, which were no more than 2%. The T-PAHs removal efficiency of the SPC soil was higher than that of the HPC soil when using the same concentration of surfactant. The variations in PAH removal efficiency with the different eluting agents were probably controlled by their solubilization and the adsorption of the surfactants onto the soil. With increasing surfactant concentration the T-PAHs removal efficiencies first decreased, and then increased. For the RWS, the T-PAHs removal efficiencies of the two soils decreased with increasing concentration (from 0 to 8 g L^{-1}) of the surfactants. Under the same concentration, the removal

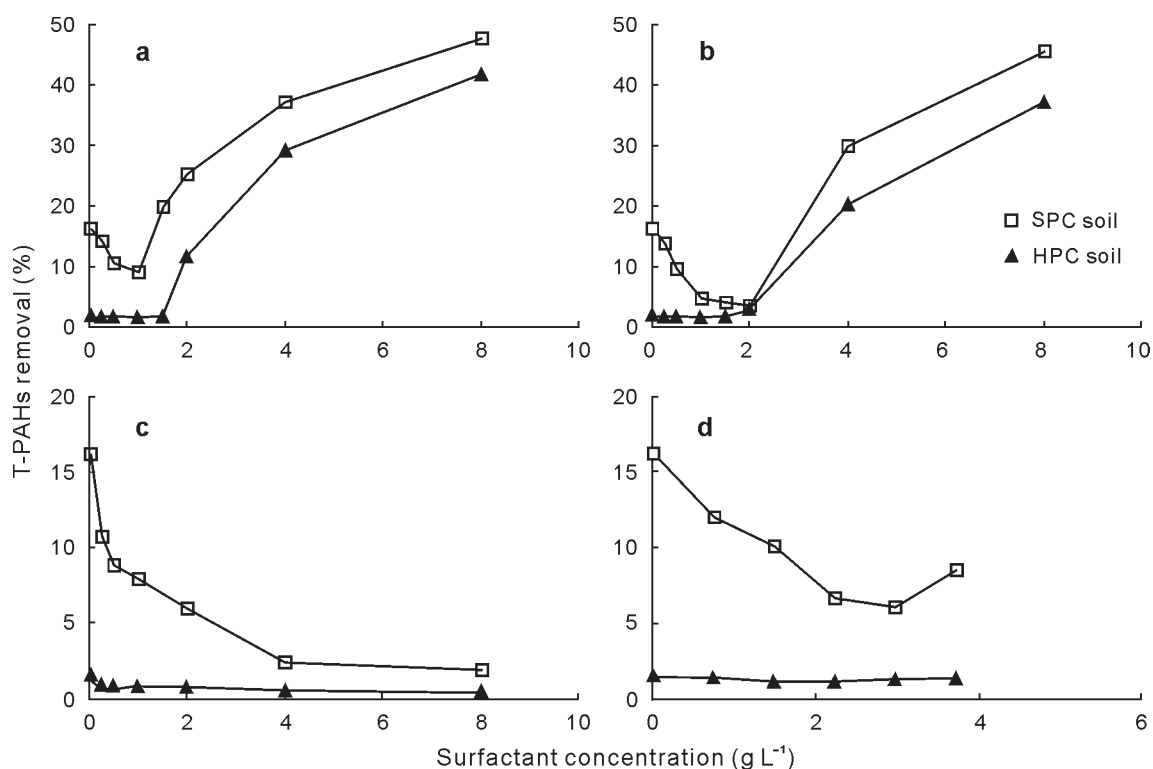


Fig. 4 Total polycyclic aromatic hydrocarbons (T-PAHs) removal efficiencies of the slightly PAH-contaminated (SPC) soil and the heavily PAH-contaminated (HPC) soil with the surfactants Triton X-100 (a), sodium dodecylbenzene sulfonate (b), rhamnolipid water solution (c) and rhamnolipid fermentation broth (d) at different concentrations.

efficiency of the T-PAHs in the two soils was in the order TX100 > SDBS > RFB > RWS, which was opposite to the order for the S_m (Table IV). The lowest T-PAHs removal efficiencies in the SPC and HPC soils occurred with TX100, SDBS and RFB between 1 and 2 g L^{-1} , 1 and 4 g L^{-1} , and 2 and 4 g L^{-1} , respectively.

Fig. 5 shows the removal efficiencies of the individual PAHs in the two soils with eluting agents of the

highest concentration, *i.e.*, 8 g L^{-1} of TX100, SDBS, and RWS, and 100% of RFB. The removal efficiencies of the 16 PAHs varied greatly among the four eluting agents. However, most of the removal efficiencies of the PAHs followed the order of TX100 > SDBS > RWS > RFB.

The TX100 had almost no effect on the removal of DaA, IcP and BgP in the SPC soil. The removal effi-

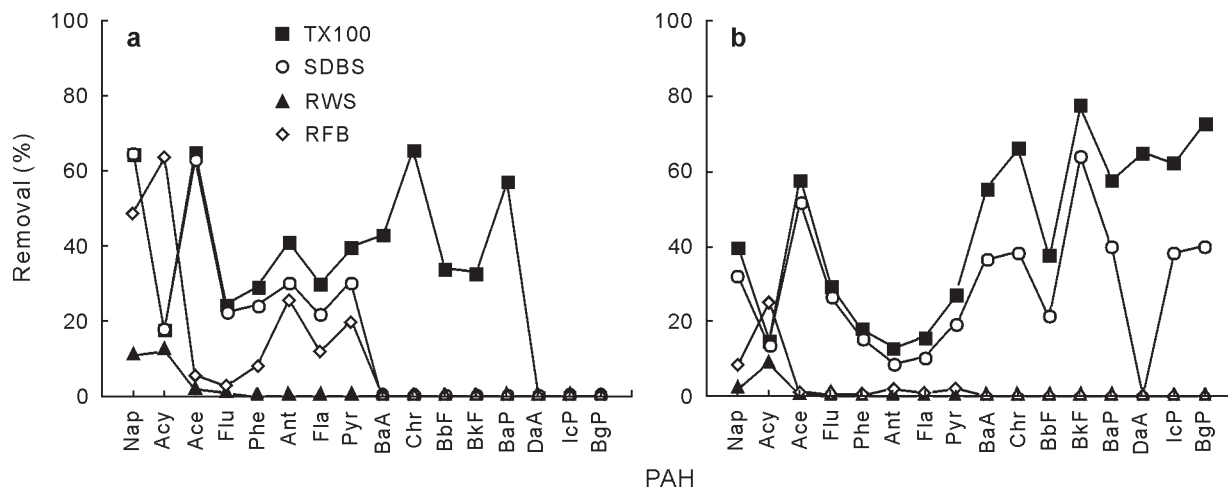


Fig. 5 The removal efficiencies of individual polycyclic aromatic hydrocarbons (PAHs) in the slightly PAH-contaminated soil (a) and the heavily PAH-contaminated soil (b) with 8 g L^{-1} of the surfactants Triton X-100 (TX100), sodium dodecylbenzene sulfonate (SDBS) and rhamnolipid water solution (RWS) and 100% of rhamnolipid fermentation broth (RFB). See Table II for the description of PAHs.

ciencies of the other 13 PAHs were between 17.8% and 65.8%. The greatest degree of removal among the 16 PAHs was seen with the Chr, and then the Ace. All types of the 16 PAHs in the HPC soil could be partly removed by the TX100 surfactant. The removal efficiencies ranged from 13% (Acy) to 77.8% (BkF). The SDBS could partly remove some low-molecular-weight PAHs (L-PAHs) and high-molecular-weight PAHs (H-PAHs) (Nap, Acy, Ace, Flu, Phe, Ant, Fla and Pyr) in the SPC soil. The removal efficiencies ranged from 17.8% (Acy) to 64.6% (Nap). For the HPC soil, only the DaA showed little obvious removal. The removal efficiencies of the other 15 PAHs ranged between 8.6% (Ant) and 64.3% (BkF).

Only the four L-PAHs (Nap, Acy, Ace, and Flu) in the two soils could be partly removed by the RWS. The order of removal efficiencies was $\text{Acy} > \text{Nap} > \text{Ace} > \text{Flu}$. The efficiencies ranged from 0.7% to 12.3% in the SPC soil, and from 0.2% to 8.7% in the HPC soil. The RFB partially removed the L-PAHs and middle-molecular-weight PAHs (M-PAHs) (Flu, Ace, Phe, Fla, Pyr, Ant, Nap and Acy) in the two soils.

DISCUSSION

The results obtained in the present study showed that the SER could effectively remove the PAHs in the MGP soil. The removal efficiency using the nonionic/synthetic TX100 was the greatest for the T-PAHs ($> 41\%$), followed by the anionic/synthetic surfactant SDBS ($> 36\%$). However, the removal efficiency of the biosurfactant eluting agent (RWS and RFB) was limited for the T-PAHs with a removal efficiency of no more than 9%. Besides surfactants, many other solvents have been studied for the purpose of extracting PAHs from MGP soils, such as organic solvents (Khodadoust *et al.*, 2000), cyclodextrins (McCray and Brusseau, 1999) and vegetable oils (Gong *et al.*, 2006) (Table V). The removal efficiencies of the PAHs using different solvents varied greatly, even with the same solvent. Using a rotating shaker with soil:solvent (g mL^{-1}) of 5:5 at 160 r min^{-1} and 30°C for 16 h (Gong *et al.*, 2010), the order of the degree of PAH removal from the soil was fatty acid methyl esters (FAME, $> 35\%$) $>$ TW80 (31%) $>$ methanol (28%) $>$ TX100 (22%) $>$ soybean oil (17%) $>$ hydroxypropyl- β -cyclodextrin (HPCD, $< 10\%$). The washing performance of biodiesel, HPCD, and TW80 has also been investigated (Wu *et al.*, 2010). It was discovered that the biodiesel solubilized a wider range of PAHs compared with HPCD and TW80. The removal efficiencies of the T-PAHs in biodiesel from both minimally and highly contaminated soil were greater than 80%. In total, the

removal efficiencies of the PAHs in the MGP soil using organic solvents, cyclodextrins, vegetable oil, and surfactants were 6%–100%, 10%–60%, 17%–97%, and 0%–100%, respectively. Compared with other solvents, the surfactants showed a wide range of removal efficiencies. Though the organic solvents had a high PAH removability, they were difficult to be reused (Yap *et al.*, 2010). Cyclodextrin and vegetable oils were thought to be more environment-friendly, but one molecule of cyclodextrin could only adsorb one molecule of HOCs (so for heavily polluted soils, such as MGP soils, more cyclodextrin would be needed to remove the PAHs than usual) and the removal efficiency with vegetable oil can be strongly affected by soil moisture (Gong *et al.*, 2005), and any residual oil in the soil could also result in a higher transient increase in toxicity (Li *et al.*, 2007). Therefore, using SER to remove PAHs in MGP soils looks promising, and choosing an appropriate surfactant for the type of contaminated soil will be a key factor.

The solubilization capacity and the degree of adsorption onto the soils of the surfactant are two important factors for choosing an appropriate surfactant. The surfactants and PAHs can be roughly divided into free state, micelle state and adsorption state. Desorption of PAHs in contaminated soils by surfactants was just part of the dynamics of the three PAHs-forms (Fig. 1). Solubilization capacity of the surfactant, which is quantified by the WSR, affected process V (partitioning of PAHs between the water and the micelle). The higher the WSR was, the more grams the PAHs were solubilized by per gram of surfactant micellized. Sorption of the surfactant by the soil, which can be quantified by the S_m , affects processes I (sorption of surfactants on inorganic surfaces) and III (sorption of surfactant molecules onto the soil organic matter) (Mata-Sandoval *et al.*, 2002; Laha *et al.*, 2009). Adsorption not only reduces the amount of surfactant (free state and micelle state) in soil solution, but also can cause some soluble PAHs to partition into the solid-sorbed surfactant (Zhou and Zhu, 2008b; Zhu and Zhou, 2008), which then becomes an adsorption-state PAH. Where there are low concentrations of eluting agent, the amount of adsorption-state surfactant increases with the concentration of eluting agent and the adsorption-state surfactant is very effective in partitioning of PAHs. When the sorption of the surfactant onto soil reaches saturation, the concentration of free-state surfactant reaches its CMC and then surfactant micelles are formed to compete for PAHs. In this study, the solubilization capacity for PAHs (Ace and Flu) with the four eluting agents was in the order of

TABLE V

Some solvent extraction studies on polycyclic aromatic hydrocarbons (PAHs) in manufactured gas plant (MGP) soils

Eluting agents ^{a)}	Location	Process details	Contaminants ^{b)}	Total contamination mg kg ⁻¹	Removal of total contamination %	Reference
1-pentanol-water-ethanol	Bedford, USA	Rotating shaker at 24 °C for 1 h	<i>Organic solvent</i> T-PAHs, 2-Men, Dib, BeP	10 000–30 000	65–90	Khodadoust <i>et al.</i> , 2000
Methanol, FAME	Beijing, China	Rotating shaker with soil:solvent (g mL ⁻¹) of 5:5 at 160 r min ⁻¹ and 30 °C for 16 h	Flu, Phe, Ant, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP, IcP	≈ 1 000	28–46	Gong <i>et al.</i> , 2010
Biodiesel	Beijing, China	Rotating shaker with soil:solvent (g mL ⁻¹) of 5:5 at 150 r min ⁻¹ for 16 h	Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP	52.8–996.9	> 80	Wu <i>et al.</i> , 2010
Ethanol	-	Soxhlet extract	Nap, 2-Men, Acy, Ace, Flu, Phe, Ant, 1-Mep, Flu, Pyr, BbF, BkF, BaP, BgP	2 517–29 828	≈ 100	Kilbane, 1998
Methanol	Iowa, USA	Column extraction with 10 pore volumes (PVs) of solvent in 5.5-cm columns	Nap, 2-Men, 1-Men, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, BaA, Chr, BbF, BkF, BaP, IcP, DaA, BgP	11 082	52	Chen <i>et al.</i> , 2005
MTBE	Iowa, USA	Column extraction with 10 PVs of solvent in 5.5-cm columns	Nap, 2-Men, 1-Men, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, BaA, Chr, BbF, BkF, BaP, IcP, DaA, BgP	11 082	6	Chen <i>et al.</i> , 2005
HPCD	Beijing, China	Rotating shaker with soil:solvent (g mL ⁻¹) of 5:5 at 150 r min ⁻¹ for 16 h	<i>Cyclodextrin</i> Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP	52.8–996.9	< 60	Wu <i>et al.</i> , 2010
BCD, HPCD, MCD	France	Column extraction	Phe, Ant, Nap	655	< 50	Vigilanti <i>et al.</i> , 2006
10% HPCD	Beijing, China	Rotating shaker with soil:solvent (g mL ⁻¹) of 2:20 at 160 r min ⁻¹ and 30 °C for 16 h	Flu, Phe, Ant, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP, IcP	≈ 1 000	< 10	Gong <i>et al.</i> , 2010
Sunflower oil	Berlin, Germany	Column extraction with soil:solvent (kg L ⁻¹) of 1:2 (or 4)	<i>Vegetable oil</i> Flu, Phe, Ant, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP, IcP	724–4 721	80–90	Gong <i>et al.</i> , 2006
Sunflower oil	Berlin, Germany	Rotating shaker with soil:solvent (g mL ⁻¹) of 150 (or 75):150 at 200 r min ⁻¹	Flu, Phe, Ant, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP, IcP	1 254.8	67–97	Gong <i>et al.</i> , 2005
Soybean oil	Beijing, China	Rotating shaker with soil:solvent (g mL ⁻¹) of 5:5 at 160 r min ⁻¹ and 30 °C for 16 h	Flu, Phe, Ant, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP, IcP	≈ 1 000	17	Gong <i>et al.</i> , 2010
TW80	Beijing, China	Rotating shaker with soil:solvent (g mL ⁻¹) of 5:50 at 150 r min ⁻¹ for 16 h	<i>Surfactant</i> Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP	52.8–996.9	< 90	Wu <i>et al.</i> , 2010
TX100, TW80	Beijing, China	Rotating shaker with soil:solvent (g mL ⁻¹) of 2:20 at 160 r min ⁻¹ and 30 °C for 16 h	Flu, Phe, Ant, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BgP, IcP	≈ 1 000	< 31	Gong <i>et al.</i> , 2010
TX100, TW80	Beijing, China	Stirred with a two-paddle-agitator at 20±2 °C	BaA, BbF, BkF, BaP, IcP	12.6	0–100	Peng <i>et al.</i> , 2011
TX100, TW80, Brij 35	New York, USA	End-on-end shaker with soil:solvent (g mL ⁻¹) of 2.5:25	Phe, Ant, Pyr, BaP	652	< 25	Yeom <i>et al.</i> , 1995

^{a)}FAME = fatty acid methyl esters; MTBE = methyl tert-butyl ether; HPCD = hydroxypropyl- β -cyclodextrin; BCD = β -Cyclodextrin; MCD = methyl- β -cyclodextrin; TW80 = Tween 80; TX100 = Triton X-100; ^{b)}See Table II for the description of PAHs; Men = methylnaphthalene; Dib = dibenzofuran; BeP = benzo[e]pyrene; Mep = methylphenanthrene.

TX100 > SDBS > RWS > RFB. The maximum amounts of surfactants adsorbed in the soil (S_m) followed the order RWS > RFB > SDBS > TX100. The synthetic surfactant TX100 had the strongest degree of solubilization and the least adsorption ability in our MGP soil, therefore the removal efficiency for the T-PAHs using TX100 was the greatest among all the surfactants tested. Although the solubilizing capacity of the RWS was higher than the RFB, the removal efficiency with RFB was higher than that with RWS. The reason could be that the complex compounds in the RFB, such as salts, could reduce the adsorption of the surfactants onto the soil and increase the solubilization capacity of the RWS (López *et al.*, 2004). On the whole, synthetic surfactants were better than biosurfactants for desorption of PAHs in the MGP soil. Meanwhile, the removal efficiency of the surfactants was determined mainly by the combined effect of solubilization capacity and adsorption.

For different PAHs, removal efficiency by each surfactant was very different. The L-PAHs could be removed partly by the four eluting agents, and the M-PAHs and H-PAHs just could be removed by the synthetic surfactants at high concentrations. The removal efficiencies of the individual PAHs between the TX100 and SDBS showed similar trends. For the L-PAHs in the two soils, the removal efficiency of Ace with synthetic surfactants was the highest (> 45%) and that of Acy was the lowest (< 20%). The removal efficiencies of almost all the PAHs with biosurfactants were lower than those with synthetic surfactants, except for Acy with the RFB. Meanwhile, we found that the removal of H-PAHs could be observed under high concentrations of synthetic surfactants (no less than 2000 mg kg⁻¹, data not shown) and the removal efficiencies were relatively high. Similar results have been found elsewhere where the removal of high molecular weight PAHs is greater than that of the lower molecular weight PAHs when using the synthetic surfactants of TW80 and TX100 (Gong *et al.*, 2010). In general, the octane-water distribution (K_{ow}) of PAH was in direct ratio to the solubilization capacity of the surfactant. Though the K_{ow} and WSR of the L-PAHs were higher than that of the H-PAHs, more L-PAHs could be partitioned into the soil-sorbed surfactant and therefore the removal efficiency of the L-PAHs was low. Such a situation results from competition among the different PAHs to partition into micelles and also the competitive sorption of PAHs and surfactants on to the soil (Grasso *et al.*, 2001). In addition, there was no obvious relationship between the concentration of PAH in the MGP soil and its removal efficiency. However, it is specu-

lated that one of the reasons leading to lower removal efficiency of L-PAHs could be their high contents in the soils.

CONCLUSIONS

In this comprehensive study on the removal of PAHs in MGP soils with different types of surfactant, a batch experiment with TX100, SDBS, RWS and RFB was implemented. The order of solubilization capacity for the PAHs was TX100 > SDBS > RWS > RFB. The adsorption isotherm for the surfactants in the four eluting agents was generally in good agreement with the Langmuir isotherm. Where there was no biodegradation, the removal of T-PAHs in the MGP soil with synthetic surfactants (TX100 and SDBS) was higher than that with biosurfactants. The removal efficiencies of the 16 PAHs varied greatly among the four eluting agents. Only 8 g L⁻¹ TX100 could remove all types of the 16 PAHs partly in the HPC soil, and the removal efficiencies of different PAHs ranged from 13% (Acy) to 77.8% (BkF). Therefore, we suggest that TX100 surfactant can potentially and successfully be used for the remediation of soils contaminated with PAHs in the industrial sites.

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