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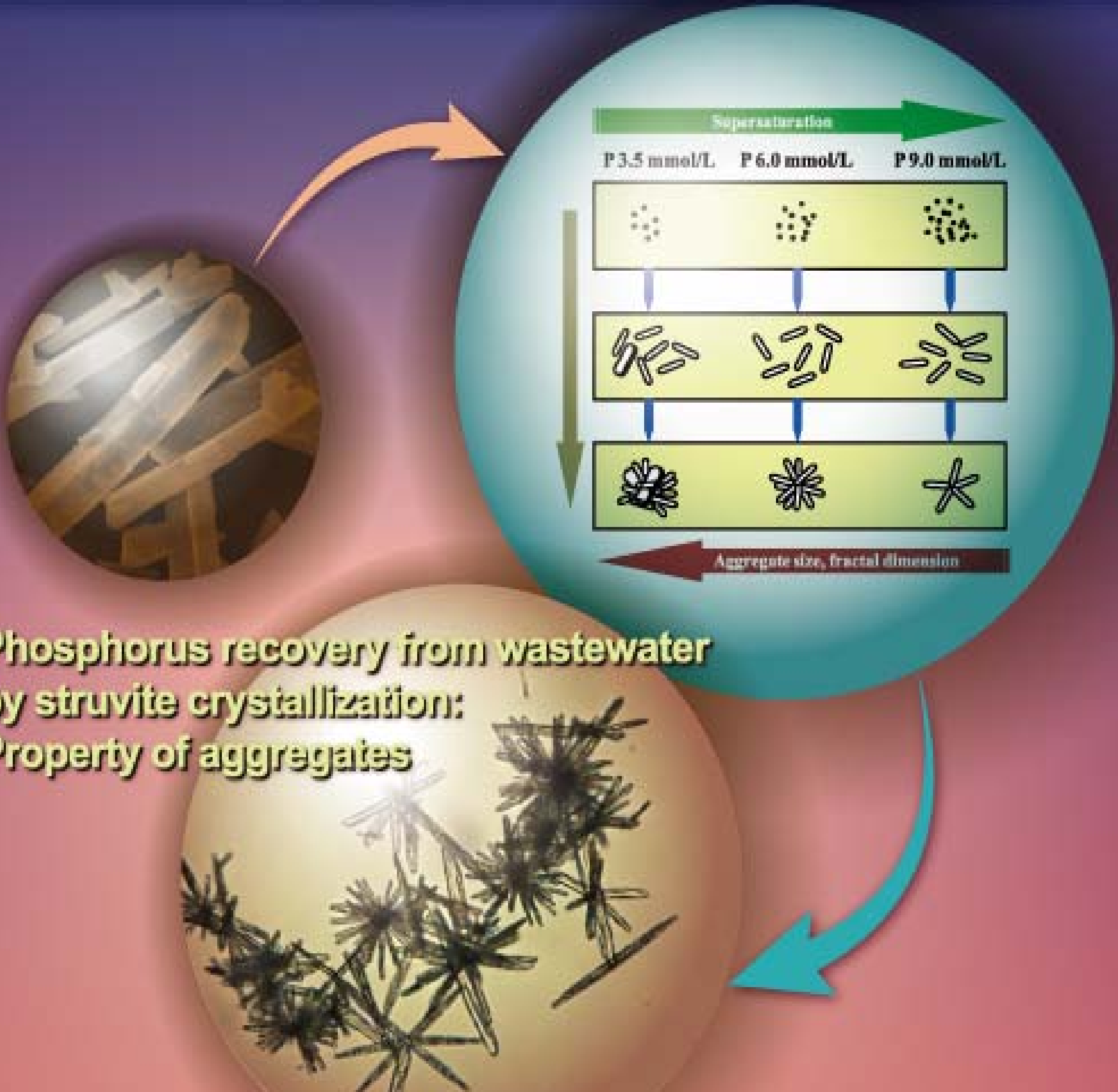


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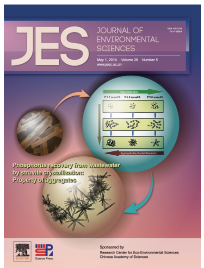


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# Enhancing plant-microbe associated bioremediation of phenanthrene and pyrene contaminated soil by SDBS-Tween 80 mixed surfactants

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ABSTRACT

The use of surfactants to enhance plant-microbe associated dissipation in soils contaminated with polycyclic aromatic hydrocarbons (PAHs) is a promising bioremediation technology. This comparative study was conducted on the effects of plant-microbe treatment on the removal of phenanthrene and pyrene from contaminated soil, in the presence of low concentration single anionic, nonionic and anionic-nonionic mixed surfactants. Sodium dodecyl benzene sulfonate (SDBS) and Tween 80 were chosen as representative anionic and nonionic surfactants, respectively. We found that mixed surfactants with concentrations less than 150 mg/kg were more effective in promoting plant-microbe associated bioremediation than the same amount of single surfactants. Only about (*m*/*m*) of mixed surfactants was needed to remove the same amount of phenanthrene and pyrene from either the planted or unplanted soils, when compared to Tween 80. Mixed surfactants (< 150 mg/kg) better enhanced the degradation efficiency of phenanthrene and pyrene via microbe or plant-microbe routes in the soils. In the concentration range of 60–150 mg/kg, both ryegrass roots and shoots could accumulate 2–3 times the phenanthrene and pyrene with mixed surfactants than with Tween 80. These results may be explained by the lower sorption loss and reduced interfacial tension of mixed surfactants relative to Tween 80, which enhanced the bioavailability of PAHs in soil and the microbial degradation efficiency. The higher remediation efficiency of low dosage SDBS-Tween 80 mixed surfactants thus advanced the technology of surfactant-enhanced plant-microbe associated bioremediation.

## Introduction

The contamination of soils and groundwater by toxic, hazardous organic pollutants is a widespread environmental problem. Research efforts have accordingly been directed towards degradation of polluting hydrophobic organic compounds (HOCs) to harmless compounds. Bioremediation, especially plant-microbe associated bioremediation, has attracted great interest for *in situ* treatment of HOC-contaminated soils and sediments for economic and environmental reasons (Franzetti et al., 2008; Wenzel, 2009). However, HOCs such as polycyclic aromatic hydrocarbons (PAHs) in soil usually exhibit low bioavailability to both microorganisms and plants due to their strong adsorption to the soil matrix (Chen et al., 2005; Collins et al., 2006). Therefore the low bioavailability of PAHs in soils is a key problem to solve for improving bioremediation efficiency of plant-microbe associated dissipation of PAHs.

Surfactants have been proposed to improve the bioavailability of PAHs in soil (Tiehm et al., 1997; Makkar and Rockne, 2003; Kim and Weber, 2005). Surfactants can decrease interface tension and increase the apparent aqueous solubility of PAHs, thus facilitating mass-transfer of PAHs from solid into aqueous phases so that they can be desorbed from contaminated soils (Bragg et al., 1994; Zhou and Zhu, 2007; Paria, 2008). Several studies have demonstrated that surfactants, especially nonionic surfactants, can stimulate

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microbial degradation of PAHs in soils or soil slurry by increasing their aqueous-phase concentrations (Kim et al., 2001; Bueno-Montes et al., 2011). Researchers have also applied nonionic surfactants to promote plant uptake of PAHs from aqueous solution (Gao et al., 2008; Cheney et al., 2009). However, little information is available for the effects of surfactants on plant-microbe associated bioremediation of PAH-contaminated soils. For the present study, we hypothesized that surfactants could improve plant-microbe bioremediation of PAH-contaminated soils.

It was previously thought that PAHs first were easily desorbed from soils by nonionic surfactants and then degraded by microbes and/or plants or accumulated by plants. However, nonionic surfactants can be strongly adsorbed onto soils (Yang et al., 2006). To desorb PAHs from polluted soil effectively, therefore, more surfactant needs to be added to the soil. This not only increases remediation cost, but also has deleterious environmental effects: increased toxicity due to disruption of bacterial cell membranes (Rosen et al., 2001); competitive degradation of surfactant and contaminants (Kim and Weber, 2005); and accumulation of inhibitory products of incomplete metabolism (Willumsen and Arvin, 1999). Consequently, desorption rates of PAHs are greater than their biodegradation rates, and fluids containing dissolved contaminants migrate dramatically, increasing the contaminated zone area, a highly undesirable consequence, especially where groundwater is of concern (Wang and Mulligan, 2004). Meanwhile, while considerable attention has been given to partitioning PAHs into surfactant micelles in soil solution using high concentrations, little effort has been directed towards finding surfactants that would be effective at low concentrations. To the authors' knowledge, the few studies of low surfactant concentrations reported low desorption rates (Aronstein et al., 1991; Richard et al., 1999).

Currently, to reduce soil adsorption loss of nonionic surfactants, some anionic-nonionic mixed surfactants are being used. Anionic surfactants can greatly reduce nonionic surfactant sorption (Thibaut et al., 2000; Yang et al., 2006). Anionic-nonionic mixed surfactants possess other synergistic advantages. They can form mixed micelles, and decrease the critical micelle concentration (CMC) to some extent (Guo et al., 2009; Shen et al., 2007), and have greater solubility than either individual anionic or nonionic surfactants (Zhu and Feng, 2003). Moreover, mixed anionic-nonionic surfactants can enhance the phenanthrene microdegradation in soil-water systems under certain conditions (Yu et al., 2007), or promote plant uptake of PAHs from aqueous solution (Sun and Zhu, 2009). Hence, using low concentrations of anionic-nonionic surfactants may combine these advantages to enhance plant-microbe associated dissipation of PAH-contaminated soil, and supply valuable information for high-efficiency, low-cost soil bioremediation technologies.

The objective of this study was therefore to investigate the effect of low concentrations of anionic-nonionic surfactant mixtures on plant-microbe associated dissipation of phenanthrene and pyrene in contaminated soil. It is hoped that the findings of this investigation will provide insights into enhancing plant-microbe associated bioremediation efficiency with a small surfactant dose.

## 1 Materials and methods

### 1.1 Materials

Phenanthrene, pyrene (purity 98%), and Tween 80 were obtained from J&K Chemicals (Germany). Sodium dodecyl benzene sulfonate (SDBS) (purity 95%) was purchased from Aladdin Chemicals (China). SDBS-Tween 80 mixed surfactant solutions with different mass ratios (SDBS:Tween 80 = 0:5, 1:4, 2:3, 5:0) were prepared by dissolving SDBS and Tween 80 in ultrapure water. Some physicochemical properties of the compounds are listed in **Table 1**.

### 1.2 Preparation of PAH-polluted soil

Clean soil was collected from the Zhejiang University farm at a depth of 0 to 20 cm. The soil contains 18.1% sand, 68.1% silt, and 13.8% clay, which was analyzed with a Laser Particle Analyzer (Malvern MAM-5005, England). The particle analyzer distribution identified the soil as a silty loam soil. Soil organic carbon content was determined to be 0.69%, and the pH of the soil solution was measured to be 6.6. Soil samples were air-dried, milled, and sieved through 2-mm-mesh sieve and then spiked with a solution

**Table 1** Some physicochemical properties of tested PAHs and surfactants*

| Compound | Molecular formula | Molecular weight (g/mol) | $\log K_{ow}$ | $S_w$ (mg/L) | CMC (mg/L) |
|---|---|---|---|---|---|
| Phenanthrene | $C_{14}H_{10}$ | 178.2 | 4.46 | 1.18 | – |
| Pyrene | $C_{16}H_{10}$ | 202.3 | 4.88 | 0.13 | – |
| Tween 80 | $C_{17}H_{35}COOS_6(OCH_2CH_2)_{20}OH$ | 1309 | – | – | 35 |
| SDBS | $C_{12}H_{25}C_6H_4SO_3Na$ | 348.48 | – | – | 522 |

* PAH data from Yaws, 1999.

$K_{ow}$: *n*-octanol-water partition coefficient; $S_w$: water solubility; CMC: critical micelle concentration; SDBS: sodium dodecyl benzene sulfonate; –: means no available data.

of phenanthrene and pyrene in acetone as described by Lu and Zhu (2009). The polluted soil was aged at 60% field water holding capacity (WHC). After two weeks of aging, six samples were randomly collected. Chemical analyses showed that PAHs were homogeneously distributed in soil at concentrations of 63.5 mg/kg phenanthrene and 160.2 mg/kg pyrene (dry weight).

### 1.3 Pot experiment

PAH-spiked soil (500 g dry weight) was packed onto a piece of clean plastic film (40 cm in length and width). The soil was further spiked with 60 mL SDBS-Tween 80 mixed surfactant solutions at different doses (0–200 mg/kg dry soil). Soil and surfactant solution were thoroughly mixed, and the soil then put on a clean non-woven fabric to adjust the soil moisture content to about 60% of field WHC. Finally, the soil was thoroughly crushed and transferred to a plastic pot (12 cm in diameter and 10 cm in height).

Ryegrass (*Lolium multiflorum* Lam) seeds were selected, germinated, and then sowed as 8 clusters of 6 seeds in every pot. Three treatments were used: (1) planted pots with spiked soil, (2) unplanted control pots with spiked soil, (3) microbe-inhibited unplanted control pots with spiked soil (0.1% (*m*/*m*) sodium azide ($NaN_3$) was used to inhibit the microbial activity). $NaN_3$ could result in cellular damage through pathology of whole systems and metabolic inactivation without disrupting the physical texture of the soils (Frederick and Babish, 1982). The pots were arranged randomly on a greenhouse benchtop with the day temperature at 28–32°C and night temperature at 20–25°C. Each treatment was performed in triplicate. The pots were watered as needed to maintain 60% WHC such that no leachate was produced. Soils and vegetation were sampled after forty days of cultivation. The aerial parts of ryegrass (stems and leaves) were carefully harvested from each pot. The topsoil (2–3 cm) was discarded and residual soil surrounding the roots was collected and mixed evenly. Root samples were carefully washed with tap water to remove any adhering soil particles, rinsed thoroughly with ultrapure water, and dried with filter paper. All samples were then freeze-dried and stored at –80°C to prevent further microbial degradation of PAHs. Soil and plant samples from three pots with the same surfactant treatment were analyzed and averaged values and standard errors were given in all the figures below.

### 1.4 PAH analysis for soil and plant samples

PAHs in soil and vegetation samples were treated with ultrasonic-assisted solvent extraction and determined using HPLC as described by Gao et al. (2005). For soils, the average recoveries of phenanthrene and pyrene through the whole analytical process were 95.6% ($n$ = 5, RSD < 2.48%) and 91.3% ($n$ = 5, RSD < 3.06%), respectively. For plant samples, the recoveries of phenanthrene and pyrene through the whole procedure averaged 91.4% ($n$ = 5, RSD < 2.61%) and 92.8% ($n$ = 5, RSD < 2.48%).

## 2 Results and discussion

### 2.1 Ryegrass biomass at the end of pot experiment

There were no significant differences in either ryegrass germination or growth in the presence of different surfactant treatments. Germination rates of ryegrass ranged from 83% to 85%, indicating that the various dosages of surfactants did not affect the germination of ryegrass in PAH-contaminated soil. Moreover, ryegrass grew well during the entire experiment. As shown in **Fig. 1**, the final dry masses of ryegrass shoot and root were (1.06 ± 0.05) and (0.27 ± 0.04) g, respectively.

Compared to the control, all surfactant treatments showed no inhibition of plant growth, and the biomass

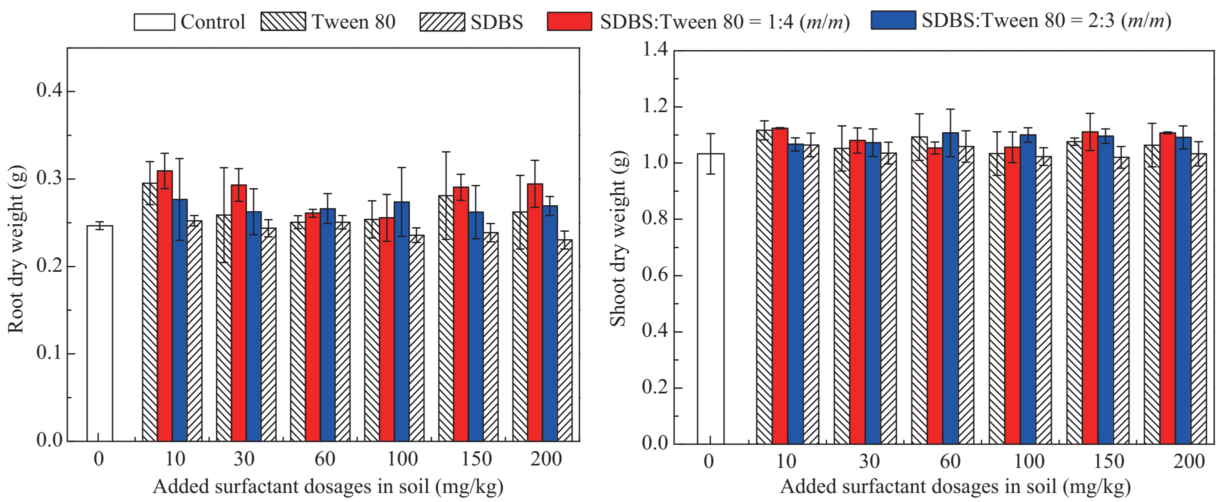


**Fig. 1** Biomass of ryegrass (40 days) as a function of surfactant dosages.

yields with Tween 80 alone and mixed surfactants were slightly higher than that with SDBS alone. This may be due to Tween 80 having potentially bioavailable carbon, whereas SDBS contains a bio-unavailable benzene ring. However, the low applied concentrations (⩽ 200 mg/kg) had no adverse effect on ryegrass growth.

### 2.2 Removal of phenanthrene and pyrene in ryegrass-planted soils without surfactants

At the end of the pot experiment, the concentrations of phenanthrene and pyrene remaining in the soils without surfactants were measured. The residues of phenanthrene and pyrene in unplanted soil without added $NaN_3$ were 16.88 and 46.73 mg/kg, respectively; and 3.79 and 6.88 mg/kg of phenanthrene and pyrene in planted soil, respectively. The results showed that phenanthrene and pyrene removal in vegetated soil was greater than that in non-vegetated soil.

Our study was contrasted with the previous reports that applied ryegrass to enhance the removal rate of PAH-spiked soil, as shown in **Table 2**. Here, spiked soils were used. The use of soil spiked with recalcitrant organic pollutants in solvent to produce contaminated soil has been frequently reported in the literature (Wang and Jones, 1994; Binet et al., 2000; Gao and Ling, 2006). The pollutants in the spiked soils are clear and homogeneous. Soils collected from PAH-contaminated field sites rarely contain only PAHs, but also contain other organic pollutants, possibly heavy metals, and usually are very heterogeneous. Such complex systems are inappropriate for study of the mechanisms involved in the biodegradation of PAHs in the rhizosphere (Binet et al., 2000).

Aging is an important factor in the remediation of spiked soil. In this study, the aging time of spiked soil was two weeks. At the end of the experiment (40 days), around 73.4% of phenanthrene and 70.8% of pyrene were removed from the unplanted soil. The spiked contaminants in the soil tend to be more available and more degradable than those in soils aged in the field. Studies have shown that freshly applied PAHs become less bioavailable during a period of a few months (Tang et al., 1998; Hwang and Cutright, 2002). Soil organic matter is the chief sorbent for hydrophobic molecules. For this study, the aging time was relatively short (**Table 2**) and the content of soil-organic matter (1.19%) was low. These factors may explain the high removal efficiency of phenanthrene and pyrene in unplanted soil.

As to the plant-assisted bioremediation, the enhancement in removal rate for phenanthrene and pyrene was 20.7% and 24.9%, respectively, in planted versus unplanted soil was greater than that of phenanthrene (20.7%). Similar results were observed by Xu et al. (2005, 2006). During aging, it is believed that hydrophobic organic chemicals, especially those with high molecular weight, slowly move into sites within the soil matrix and are often not available to even the smallest organisms, limiting their biodegradation (Alexander, 1995; Ling et al., 2010). It is worth mentioning that the 5–6-ring PAHs still decreased in the rhizospheric soil after 6-month aging while they did not in the non-rhizospheric soil (Binet et al., 2000). All of these results suggested that high-molecular-weight PAHs, especially after month-aging, were more resistant to microbial attack than low-molecular-weight PAHs, and in this case the use of plants may show more advantages.

### 2.3 Removal of PAHs from soils by plant-microbe associated bioremediation with surfactants

The residual amounts of phenanthrene and pyrene in soil after 40 days of cultivating ryegrass are shown in **Fig. 2a** and **b**. The residues of phenanthrene and pyrene in control soil without surfactants were 3.79 and 8.56 mg/kg, respectively. Adding Tween 80 only, the residues of phenanthrene and pyrene in planted soil gradually decreased (from initial values of 2.33 and 6.28 mg/kg to 1.17 and 3.26 mg/kg, respectively) with the increased concentration. SDBS, however, showed the opposite tendency. With increasing SDBS concentration, the residual amounts of phenanthrene and pyrene in soil gradually increased from the initial 1.20 and 3.61 mg/kg to 3.68 and 9.07 mg/kg, respectively. Compared with a single surfactant, mixed surfactants showed better performance, and furthermore, at a lower surfactant dosage of 150 mg/kg. Moreover, the 100 mg/kg dosage resulted in the minimum residual amounts of phenanthrene and pyrene, 0.856 mg/kg and 2.32 mg/kg respectively, for the mass ratio of 2:3 mixed surfactants.

The residual amounts of phenanthrene and pyrene in the unplanted and sterilized soils are shown in **Fig. 2c**, **d**, **e** and **f**. Compared to planted soil, surfactants had similar effects

**Table 2** Application of ryegrass in enhancing removal rate of PAH-spiked soil

| Soil texture | Organic matter (%) | Pollutant | Soil aging time (day) | Ryegrass (seedling per kg soil) | Growth (day) | Enhanced removal rate than unplanted soils (%) | Reference |
|---|---|---|---|---|---|---|---|
| Silty soil | 2.5 | Chrysene | 28 | – | 56 | 26.6 | Joner et al., 2001 |
| Loam soil | 2.36 | Phenanthrene/pyrene | 7 | 24 | 60 | 14.27/30.75 | Xu et al., 2005 |
| Loam soil | 2.36 | Phenanthrene/pyrene | 7 | 6 | 60 | 20.9/29.8 | Xu et al., 2006 |
| Sandy loam soil | 2.1 | Phenanthrene/pyrene | 42 | 20 | 65 | 2/11 | Cheema et al., 2010 |
| Silty loam soil | 1.19 | Phenanthrene/pyrene | 14 | 80 | 40 | 20.7/23.8 | This study |

–: means no available data.

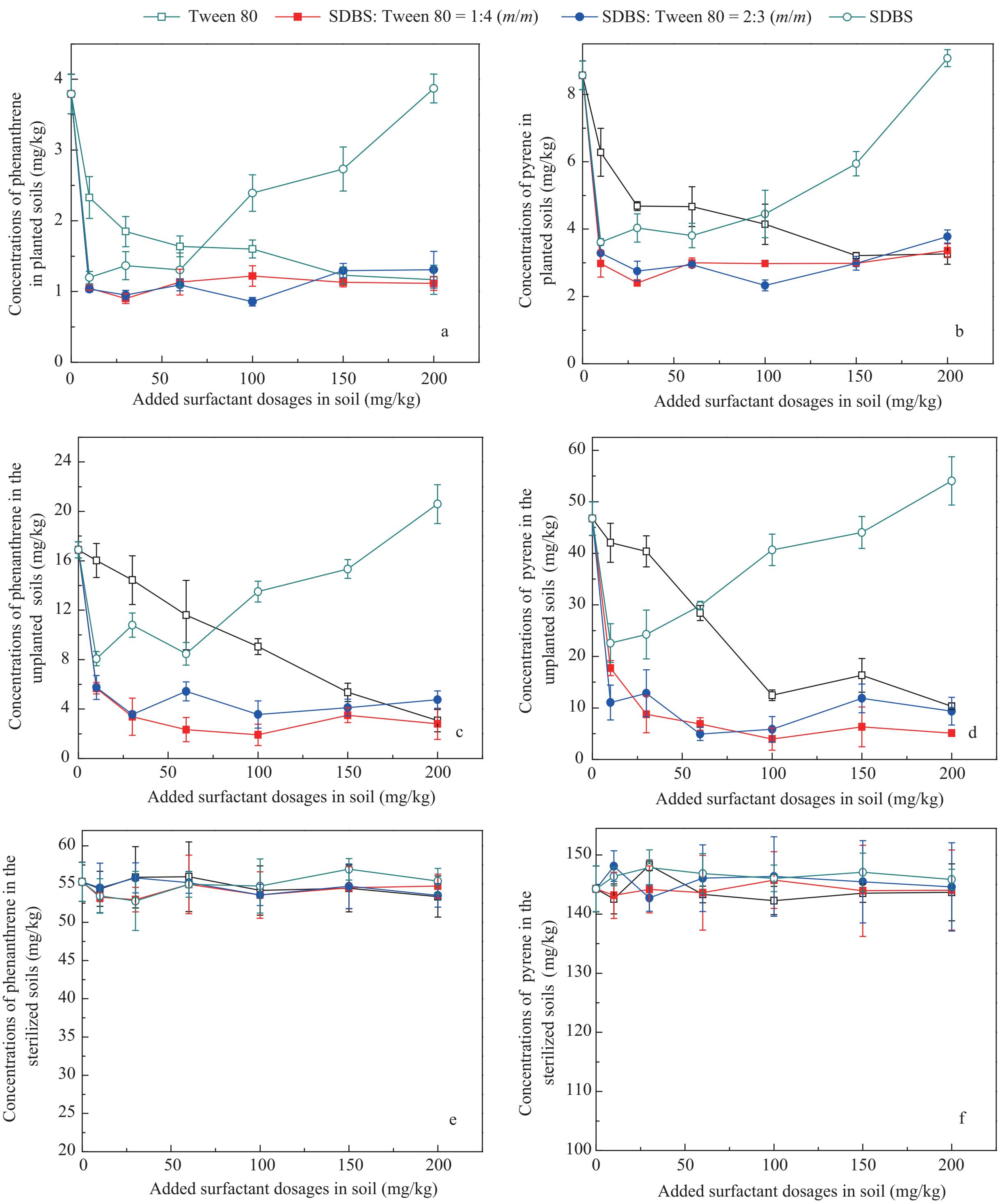


**Fig. 2** Concentrations of PAHs in planted ryegrass soil (a and b), unplanted and unsterilized soil (c and d), and sterilized soil (e and f) (40 days) as a function of surfactant dosages.

on the trend of dissipation of phenanthrene and pyrene in unplanted soil. The abiotic sterile control had 54 ± 2 and 145 ± 3 mg/kg of phenanthrene and pyrene respectively, indicating that the removal of PAHs in contaminated soil was mainly due to microbial/plant-microbe degradation.

The residual amounts of phenanthrene and pyrene in non-amended vegetated soils were lower than those of the unplanted and sterilized control, suggesting that the cultivation of ryegrass could significantly improve the overall removal of both phenanthrene and pyrene in soil.

When a low concentration of Tween 80 was used in soil, most surfactant was adsorbed onto soil particles. Surfactant molecules adsorbed at soil surfaces also led to a reduction of the interfacial tension, which may have improved contact between aqueous and solid phases (Volkering et al., 1998). With the increase of surfactant concentration, surfactant sorption onto soil surfaces led to the formation of single (hemimicelles) or double (admicelles) layers of surfactant molecules at the interface (West and Harwell, 1992; Nayyar et al., 1994). Meanwhile, more surfactant entered into the soil solution, which was beneficial for decreasing the surface tension of the soil particle pore water and facilitating PAH transport from adsorbed-to-soil to aqueous phase. This may explain the observation that the residues of phenanthrene and pyrene in soil decreased with the proportional increase of Tween 80 concentration in the range of tested concentrations. This is in accordance with the results reported by Cheng et al. (2008).

Several studies have shown that high concentrations of SDBS can inhibit the dissipation of PAHs. Chen et al. (2001) reported that 100 mg/L SDBS inhibited naphthalene and phenanthrene degradation by microorganisms. Similarly, when SDBS was applied at 80 mg/L, the removal ratio of phenanthrene was found to be significantly lower than that of the control group (Li and Zhu, 2012). The inhibition may be a result of inactivation of some cells (Li and Zhu, 2012), or impedance of microbial processes in soil (Kristiansen et al., 2003). This may explain the reason why the residues of phenanthrene and pyrene in soil increased with increased SDBS dosage.

For SDBS-Tween 80 surfactant mixtures, the amounts of Tween 80 sorbed onto soil decreased with increased SDBS concentration. Precipitation and sorption loss for SDBS have also been shown to decrease with increased Tween 80, resulting in an increase of the effective surfactant concentration in soil solution (Zhang and Zhu, 2010). Zhou and Zhu (2007) also observed that phenanthrene desorption by anionic-nonionic mixed solutions was more efficient than single surfactants, due to lower sorption and precipitation loss of mixed surfactants. Thus, these results suggested that SDBS-Tween 80 mixed surfactants increased the effective surfactant concentration in soil solution, reduced the surface and interfacial tension and then improved the PAHs desorption from soil, which facilitated bioavailability of PAHs. Moreover, biodegradation rates of phenanthrene and pyrene may be increased in the presence of mixed surfactants (Yu et al., 2007). Therefore, the enhanced removal of phenanthrene and pyrene in soil amended with SDBS-Tween 80 mixed surfactants could be due to the combined effects of increased transport of PAHs from soil to aqueous phase, which led to greater biodegradation of phenanthrene and pyrene.

In this experiment, the lowest residual concentrations of PAHs were observed when the dosage of mixed surfactants with mass ratio 2:3 was 100 mg/kg. The residual amounts of phenanthrene and pyrene in soil for addition of 150 mg/kg of Tween 80 alone approximated those mixed surfactants obtained using 10 mg/kg. These findings suggest that the combination of SDBS-Tween 80 surfactants could improve the performance of plant-microbe bioremediation of PAH-contaminated soil.

### 2.4 Ryegrass uptake of phenanthrene and pyrene from contaminated soils in the presence of surfactants

Ryegrass consists of underground and overground parts, roots and shoots. **Figure 3a** and **b** depict PAH concentrations in ryegrass roots (40 days) as a function of surfactant dosages. As expected, the amounts of pyrene absorbed in roots were much greater than those of phenanthrene in each treatment. This could be explained by the more hydrophobic nature of pyrene, as reflected in its higher octanol-water partition coefficient. **Figure 3a** and **b** also show that Tween 80 and SDBS used separately can both slightly increase the uptake of phenanthrene and pyrene by ryegrass root. However, SDBS-Tween 80 mixed surfactants clearly enhanced the uptake of phenanthrene and pyrene by roots, especially when mixed surfactant concentrations increased from 60 to 150 mg/kg. For example, the uptake of phenanthrene and pyrene by roots in the presence of SDBS-Tween 80 surfactants with 1:4 mass ratio at 100 mg/kg were about 2.7 and 2.0 times higher than that for Tween 80 alone, respectively, and 3.5 and 3.0 times that without surfactant, respectively.

Surfactants can be sorbed onto soil, which decreases the interfacial tension and thus plays an essential role in the facilitated transport of sorbed PAHs from soil to aqueous phase (West and Harwell, 1992). Also, surfactants can be sorbed on root surfaces and act as an adsorption surface film onto which phenanthrene and pyrene can be adsorbed (Gao et al., 2008). By either mechanism, surfactants would enhance uptake and accumulation of phenanthrene and pyrene by ryegrass roots.

There are significant differences in the capacity to form adsorption films and change the membrane permeability of plant roots in the presence of anionic-nonionic mixed surfactants compared with single surfactants, which greatly influence root uptake behavior (Sun and Zhu, 2009). Furthermore, mixed surfactants can increase the effective surfactant concentration in soil solution by the lower sorption and precipitation loss, and improve the bioavailability of PAHs. This may explain why mixed surfactants promoted ryegrass roots to accumulate 2–3 times the phenanthrene and pyrene as Tween 80 or no surfactant. It is worth mentioning that Lu and Zhu (2009) approached this issue from the opposite direction. They utilized cationic surfactant to enhance the sorption of PAHs onto soils, reduce the transfer of PAHs from soil to soil solution and thereby restrain subsequent plant uptake.

The effects of SDBS-Tween 80 mixed surfactants on ryegrass shoot uptake of phenanthrene and pyrene are shown in **Fig. 3c** and **d**. The concentrations of phenanthrene and pyrene in ryegrass shoots tended to increase

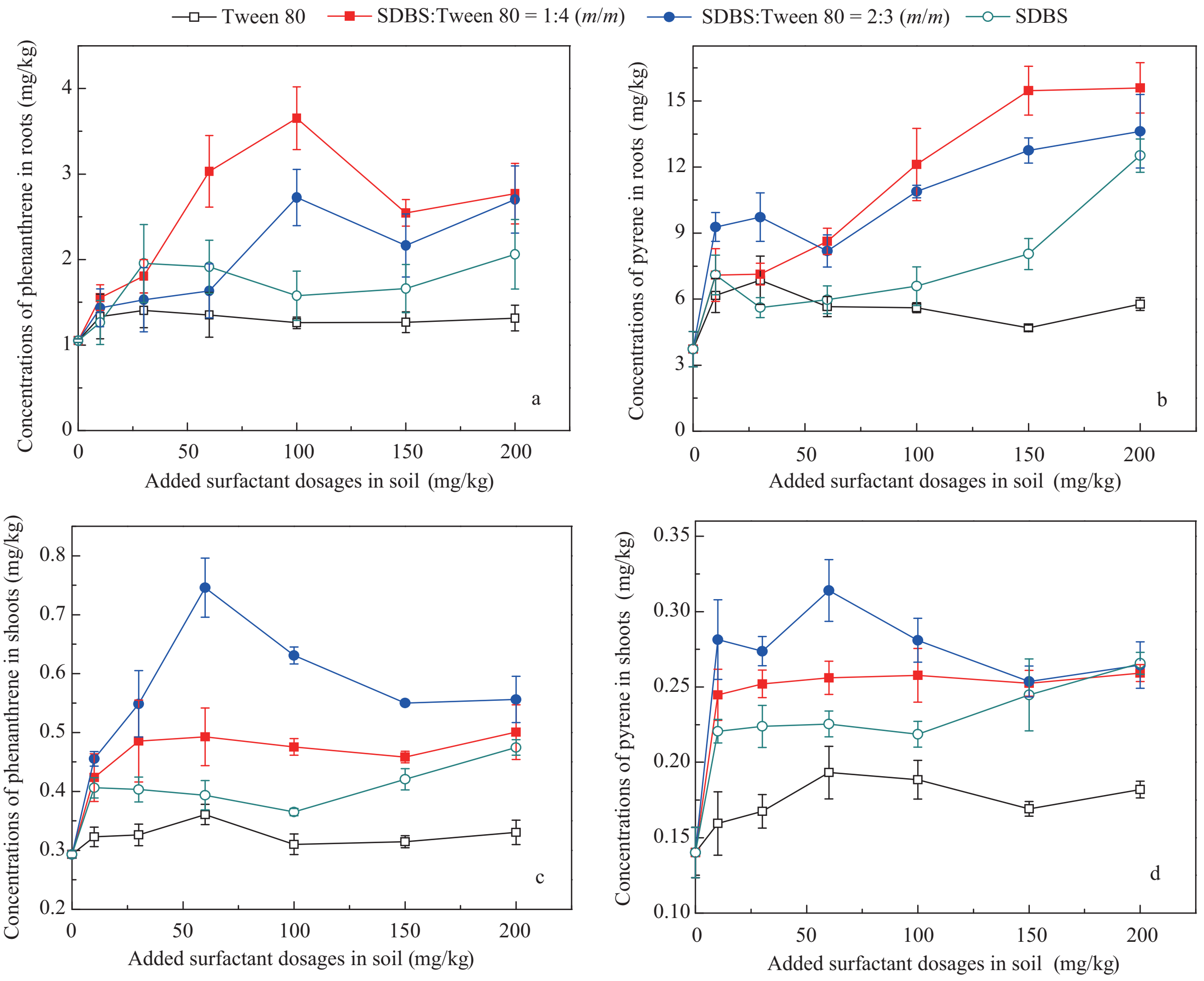


**Fig. 3** Concentrations of PAHs in ryegrass roots (a and b) and shoots (c and d) (40 days) as a function of surfactant dosages.

initially and then slightly decrease with increasing SDBS-Tween 80 concentrations. As expected, concentrations of these two PAHs in ryegrass shoot were considerably lower than those in root tissues, presumably due to a rate-limited translocation of these compounds from roots to shoots. Hydrophobicity of organic pollutants is an important determinant for plant uptake. Organic compounds with log$K_{ow}$ > 3.5 have a high potential for retention in plant roots, and they are more likely to be degraded or bound by plant roots (Schnoor et al., 1995). Additionally, the translocation by roots is greater for phenanthrene than that of pyrene because of phenanthrene's lower molecular weight and higher water solubility (**Table 1**), resulting in a higher shoot accumulation of phenanthrene than that of pyrene.

The contribution of plant accumulation of PAHs to plant-enhanced or surfactant-plant-enhanced remediation of soil phenanthrene and pyrene was calculated as described by Gao and Zhu (2004). Although plants definitely took up PAHs, the plant direct accumulation of phenanthrene and pyrene in planted soil without surfactants was 0.562 µg/pot for phenanthrene and 1.06 µg/pot for pyrene, which only accounted for less than 0.86% dissipation enhancement for phenanthrene and 0.53% for pyrene in planted versus unplanted soil. This concurred with the findings of Gao and Zhu (2004). In the presence of mixed surfactants with mass ratio 2:3 at 100 mg/kg, the plant direct accumulation amount of phenanthrene and pyrene was 1.39 µg/pot and 3.16 µg/pot, respectively, which both accounted for less than 2% dissipation enhancement in planted versus unplanted soil. In theory, part of these PAHs after plant uptake from the soil environment may have been metabolized during the experiment. Plant metabolism of PAHs has been directly observed (Wild et al., 2005); however, for PAHs of higher molecular weight and with more benzene rings, like phenanthene and pyrene, plant metabolism was not significant (Trapp et al., 1990). Phytovolatilization can be also a way of removing hydrophilic volatile organic pollutants. For phenanthrene and pyrene, the translocation of these compounds from root to shoot is known to be highly restricted, and phytovolatilization of phenanthrene and pyrene should be negligible. Therefore, on the whole, plant uptake and accumulation were a minor contribution, and plant-promoted or surfactant-plant-promoted biodegradation was the dominant contribution (more than 98%) to the remediation enhancement for soil contaminated with phenanthrene and pyrene.

## 3 Conclusions

This study focused on the effects of mixed surfactants (SDBS and Tween 80) on the plant-microbe associated bioremediation of phenanthrene and pyrene in contaminated soil relative to a single surfactant. Mixed surfactants appeared to promote plant-microbe associated biodegradation of phenanthrene and pyrene from soil with low concentrations ($\leqslant$ 150 mg/kg) compared with Tween 80 alone, and they reduced the nonionic surfactant adsorption and could avoid the groundwater contamination associated with high concentrations of surfactant. Results obtained from this study can provide methods to enhance bioremediation efficiency with optimal concentrations of mixed surfactants, and to supply valuable information for high-efficiency, low-cost soil remediation technologies in practical projects. Further studies are needed to investigate the effects of the mixed surfactants on the removal and fate of high-ring PAHs in soils, and on the microbial diversity in bulk soil and in the rhizosphere.

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