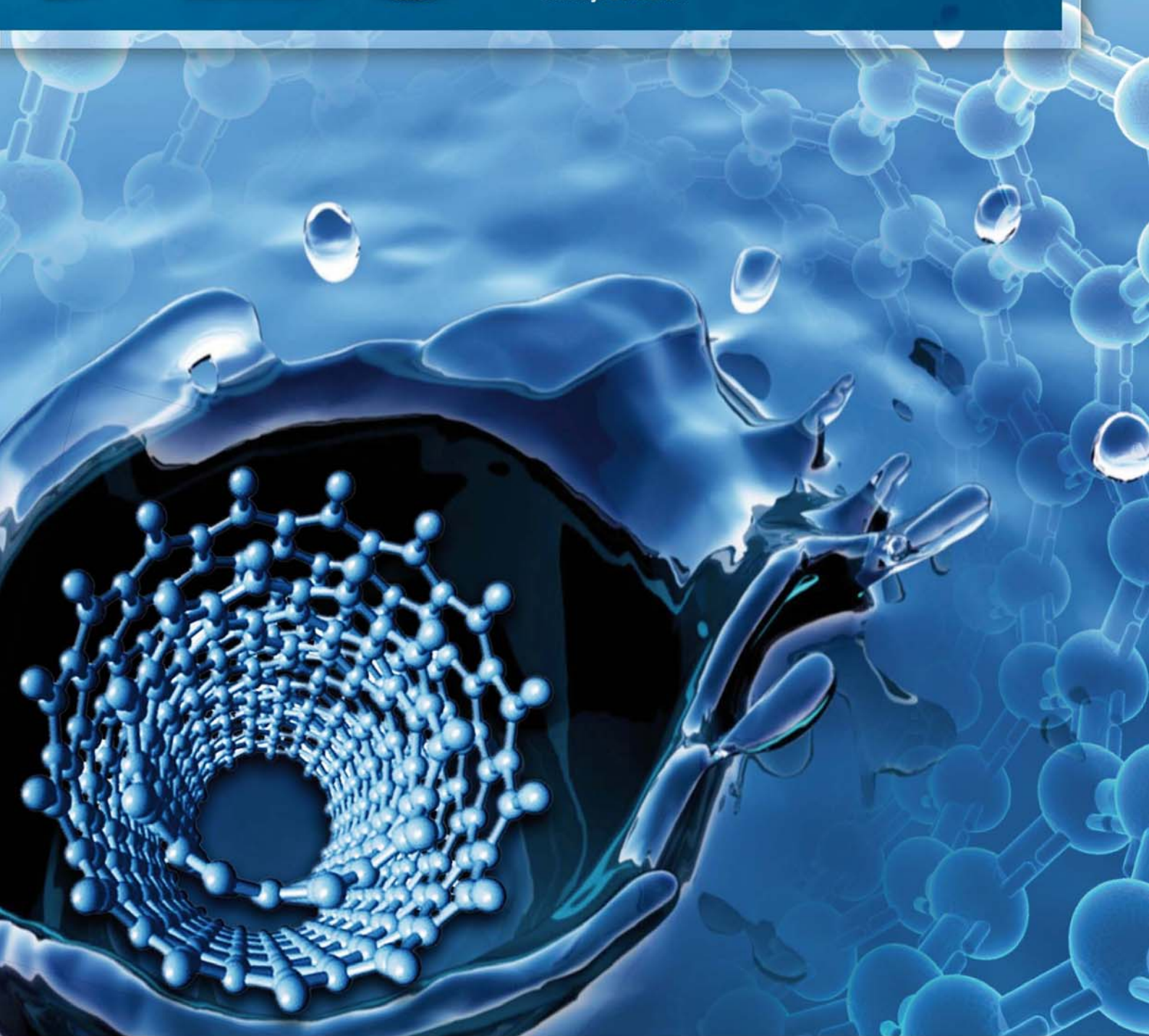


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Utilizing surfactants to control the sorption, desorption, and biodegradation of phenanthrene in soil-water system

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Abstract

An integrative technology including the surfactant enhanced sorption and subsequent desorption and biodegradation of phenanthrene in the soil-water system was introduced and tested. For slightly contaminated agricultural soils, cationic-nonionic mixed surfactant-enhanced sorption of organic contaminants onto soils could reduce their transfer to plants, therefore safe-guarding agricultural production. After planting, residual surfactants combined with added nonionic surfactant could also promote the desorption and biodegradation of residual phenanthrene, thus providing a cost-effective pollution remediation technology. Our results showed that the cationic-nonionic mixed surfactants dodecylpyridinium bromide (DDPB) and Triton X-100 (TX100) significantly enhanced soil retention of phenanthrene. The maximum sorption coefficient K_d^* of phenanthrene for contaminated soils treated by mixed surfactants was about 24.5 times that of soils without surfactant (K_d) and higher than the combined effects of DDPB and TX100 individually, which was about 16.7 and 1.5 times K_d , respectively. On the other hand, TX100 could effectively remove phenanthrene from contaminated soils treated by mixed surfactants, improving the bioavailability of organic pollutants. The desorption rates of phenanthrene from these treated soils were greater than 85% with TX100 concentration above 2000 mg/L and approached 100% with increasing TX100 concentration. The biodegradation rates of phenanthrene in the presence of surfactants reached over 95% in 30 days. The mixed surfactants promoted the biodegradation of phenanthrene to some extent in 10–22 days, and had no obvious impact on phenanthrene biodegradation at the end of the experiment. Results obtained from this study provide some insight for the production of safe agricultural products and a remediation scheme for soils slightly contaminated with organic pollutants.

Key words: surfactant; phenanthrene; sorption; desorption; degradation; soil-water system

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Introduction

The contamination of soil by toxic and/or hazardous organic pollutants is a widespread environmental problem, and residual hydrophobic organic compounds (HOCs) damage the soil environment and eventually impair human health through bio-accumulation and entering food-chain systems (Samsøe et al., 2002; Fismes et al., 2002; Gao and Zhu, 2004; Lin et al., 2004). Importantly, slightly contaminated lands are still in use for agricultural production due to cultivated-land shortage (Cai et al., 2008; Daly et al., 2007; Khan et al., 2008). This calls for immediate action to control the translocation and accumulation of contaminants in plants in order to obtain safe agricultural products and reduce human health risks.

The HOCs in contaminated soils enter plants principally via root uptake from soil solution, and the pathway is

profoundly influenced by the interfacial transfer of contaminants from the soil solid phase into soil solution (Collins et al., 2006; Li et al., 2005). An effective way to restrain the accumulation of HOCs in plants is to enhance their soil retention and then reduce their bioavailability. Several studies have reported that cationic surfactants can significantly enhance the sorption of HOCs onto soils and then reduce their concentrations and mobility in soil solution (Boyd et al., 1988; Lee et al., 1989; Smith and Galan, 1995; Zhu et al., 2000, 2010), because cationic surfactants can be strongly sorbed by soils and the sorbed surfactant acts as an effective sorbent for HOCs (Sheng et al., 1996). Cationic surfactants can also effectively reduce the plant uptake of HOCs from contaminated soils (Lu and Zhu, 2009). Research has reported that cationic-nonionic mixed surfactants are more effective in enhancing the soil retention of phenanthrene than a single cationic surfactant, since they are sorbed on soils and clays simultaneously

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without competition and thus provide higher organic matter content for sorption of HOCs (Zhao et al., 2010). Nonionic surfactant is cheaper and less toxic because it is more biodegradable, and it can also enhance the soils' retardation capabilities of HOCs to some extent (Lee et al., 2000, 2006; Zhou and Zhu, 2005). Using a small amount of nonionic surfactant to replace a portion of the cationic surfactant may reduce not only the cost but also the environmental risks. Thereby, cationic-nonionic mixed surfactants may be the optimum additive reagents for slightly contaminated soils to enhance soil retention and then reduce plant uptake of HOCs. On the other hand, the retained HOCs still need to be removed or remediated when HOC concentrations in contaminated soils reach a high level after several rounds of planting. However, information on the removal of HOCs from the surfactant-enhanced sorption zone is not sufficient.

Surfactant-aided soil-washing has been reported to be an effective approach in enhancing HOC removal from organic contaminated soils by increasing HOC solubilities in the aqueous phase via micelle solubilization, and then improving the mass-transfer of HOCs from solid into aqueous phases (Paria, 2008). Previous studies showed great solubilization enhancement by nonionic surfactants and high removal efficiency for HOCs from contaminated soils (Edwards et al., 1991; Peng et al., 2011). Hayworth and Burris (1997) also demonstrated that a nonionic surfactant (CO 730) (1977) could effectively remove HOCs from the cationic surfactant-enhanced sorbent zone. Nonionic surfactant may be an effective washing reagent for the removal of HOCs from the surfactant enhanced sorbent zone. Therefore, cationic-nonionic mixed surfactants and nonionic surfactant can be utilized to enhance sorption and desorption of HOCs in soils, respectively, and then regulate the bioavailabilities of HOCs in the soil-water system.

In a word, an integrative technology combining enhanced sorption by cationic-nonionic mixed surfactants and a subsequent desorption step by nonionic surfactant for phenanthrene in contaminated soils needs to be developed to regulate the sorption/desorption/degradation of HOCs in the soil-water system for an alternative scheme during or after planting. However, no research has been conducted on this aspect. The objective of this study was to evaluate the performance of cationic-nonionic mixed surfactants and nonionic surfactant in regulating the sorption/desorption/degradation of HOCs in the soil-water

system, with the aim of providing valuable information for the production of safe agricultural products and a remediation scheme for soils slightly contaminated with organic pollutants.

1 Material and methods

1.1 Chemicals

Clean soil was collected from the upper (0–10 cm) layer of a paddy rice field in Hangzhou, China. The soil was air-dried and sieved to obtain particles less than 100 mesh size in all experiments, which contained 0.97% organic carbon, 9.52% clay, and had a cation-exchange capacity (CEC) of 82.2 mmol/kg. Phenanthrene was selected as a representative polycyclic aromatic hydrocarbon (PAH) to model HOCs, and was obtained from Aldrich Chemical Co. (USA), with a purity of 98%. Triton X-100 (TX100), a nonionic surfactant, was purchased from Aldrich Chemical Corporation (USA). Dodecylpyridinium bromide (DDPB), a cationic surfactant, was purchased from Enterprise Group Co., Ltd. (China), and used without further treatment. DDPB and TX100 were used to compose cationic-nonionic mixed surfactants. Selected physicochemical properties of the compounds are listed in **Table 1**.

1.2 Sorption of surfactants onto soil

A 0.05 g soil sample was added into 20 mL surfactant solutions in glass tubes. Then, the samples were mixed for 24 hr and centrifuged at 3000 r/min for 15 min and filtered through 0.22 μm filter units for the analysis of surfactant concentration by a UV-spectrometer (UV-2401PC, Shimadzu, Japan). The supernatant of samples was analyzed at UV wavelengths of 259 and 275 nm for the equilibrium concentrations of DDPB and TX100, respectively, when used individually. In the combined systems of DDPB and TX100, the system of equations for dual-wavelength spectrophotometry, expressed by Eqs. (1) and (2), was employed to analyze and calculate the equilibrium concentrations of DDPB and TX100 in the supernatant of control samples:

$$A_{\text{DDPB}} = \varepsilon_{\text{DDPB1}} C_{\text{DDPB}} + \varepsilon_{\text{TX1001}} C_{\text{TX100}} \quad (1)$$

$$A_{\text{TX100}} = \varepsilon_{\text{DDPB2}} C_{\text{DDPB}} + \varepsilon_{\text{TX1002}} C_{\text{TX100}} \quad (2)$$

Table 1 Selected physicochemical properties for phenanthrene and surfactants*

Compound	Molecular formula	Molecular weight	log K_{ow}	S_{w} (mg/L)	CMC (mg/L)
Phenanthrene	C ₁₄ H ₁₀	178.2	4.46	1.18	–
Triton X-100	C ₈ H ₁₇ C ₆ H ₄ O(CH ₂ CH ₂ O) _{9.5} H	646.86	–	–	194.1
DDPB	C ₁₇ H ₃₀ BrN	328.3	–	–	3283

* PAH data are from Yaws (1999).

K_{ow} : micellar-water partition coefficient; S_{w} : water solubility; CMC: critical micelle concentration; –: no available data.

where, A_{DDPB} and A_{TX100} are the absorbance of DDPB and TX100 at the wavelengths of 259 and 275 nm, respectively; ε_{DDPB1} and ε_{TX1001} are the molar absorbance ratios of DDPB and TX100 respectively at the wavelength of 259 nm; ε_{DDPB2} and ε_{TX1002} are the molar absorbance ratios of DDPB and TX100 respectively at the wavelength of 275 nm; C_{DDPB} and C_{TX100} are the equilibrium concentrations of DDPB and TX100, respectively.

1.3 Mixed surfactant enhanced sorption of phenanthrene

Sorption experiments were conducted using duplicate samples by the batch equilibration technique at $(25 \pm 1)^\circ\text{C}$ in 22 mL glass centrifuge tubes with Teflon caps. 0.05 g soil was added into 20 mL solutions which contained various concentrations of phenanthrene and surfactants in the tubes. Then the tubes were shaken end-over-end for 24 hr to reach an apparent equilibrium. After centrifugation (3000 r/min and 25°C for 15 min), an appropriate aliquot of the supernatant was filtered through 0.22 μm filter units for further HPLC analysis (Zhu and Zhang, 2008). 0.01 mol/L of NaCl and 0.01% (W/W) NaN_3 were added in all experiments to maintain a certain ionic strength and suppress the growth of microorganisms. The sorbed amounts of phenanthrene onto soil were directly calculated from the difference between the initial and equilibrium concentrations of phenanthrene in the aqueous phase. The sorption isotherms of phenanthrene were drawn using the sorbed amount and the equilibrium concentration.

1.4 Nonionic surfactant enhanced desorption of phenanthrene

After the sorption experiment, the supernatant was removed and different concentrations of TX100 were added. The samples were mixed for 24 hr, then centrifuged at 3000 r/min for 15 min and filtered through 0.22 μm filter units for further HPLC analysis. Again, a sample without surfactant was defined as the control. From these data, the desorption rate of phenanthrene could be obtained.

1.5 Mixed surfactant enhanced biodegradation of phenanthrene in soil

The phenanthrene biodegradation was conducted using aboriginal microbes. Each beaker was filled with 50 g contaminated soils (initial value of phenanthrene was 86.8 mg/kg) and different amounts of surfactants. The same samples which contained 0.01% (W/W) NaN_3 were set as controls. These samples were covered with medical white gauze and placed in an incubator at 25°C . The moisture content of all the samples was kept around 25% during the experiment. After a freeze-dry process, triplicate samples containing 1.0 g contaminated soils of each beaker were extracted and analyzed by the method described by Gao and Zhu (2004). The values of residual phenanthrene in the soil could be obtained.

1.6 Analytical methods

Aqueous phenanthrene concentrations were quantified by an Agilent HPLC 1100 (Agilent Technologies Co., Ltd, USA) fitted with UV detector and an Agilent Eclipse XDB-C₁₈ column (4.6 mm \times 150 mm, 5 μm) using methanol-water (9:1, V/V) as the mobile phase at a flow rate of 1 mL/min. Chromatography was performed at 30°C . The UV wavelength was set at 250 nm for phenanthrene determination.

2 Results and discussion

2.1 Mixed surfactant enhanced sorption of phenanthrene onto soil

The sorption of HOCs onto soil in a surfactant-free soil-water system is generally governed by the mechanism where HOCs partitioned into the soil organic matter (SOM), which can be evaluated with the sorption coefficient of K_d . However, with the presence of surfactants, two additional competitive processes would affect the distribution and sorption of HOC in the soil-water system: (1) the partition of HOCs into aqueous phase surfactant micelles, and (2) the sorption of HOCs by the soil-sorbed surfactant. Thereby, the sorption of HOCs onto soil can be evaluated with the apparent sorption coefficient K_d^* (Edwards et al., 1994; Sun et al., 1995), which is expressed as Eq. (3)

$$K_d^* = (K_d + Q_{sm}K_{sm}) / (1 + C_{mic}K_{mic}) \quad (3)$$

where, Q_{sm} is the sorption amount of surfactant onto soil, K_{sm} is the solute distribution coefficient with the soil-sorbed surfactant, C_{mic} is the aqueous concentration of surfactant in micellar form, and K_{mic} is the micelle-water partition coefficient of solute in surfactant solution.

In this study, linear sorption isotherms were observed for the sorption of phenanthrene onto soil with or without surfactants (data not shown), and the values of K_d^* and K_d were obtained from the slope of the linear sorption isotherms, respectively. The obtained values were then used to evaluate the effect of surfactant on the sorption of phenanthrene onto soils. The K_d^* values are shown in **Fig. 1**, while the K_d value was approximately 86.2 mL/g. With the addition of the cationic surfactant DDPB, the K_d^* values dramatically increased with increasing DDPB concentration and then reached the maximum value of 1439.8 mL/g with the added DDPB dose of 1000 mg/L, which was about 16.7 times the K_d value. In comparison, a maximum K_d^* value of 133.2 mL/g for phenanthrene was obtained with the presence of nonionic surfactant TX100 at 200 mg/L, which was only about 1.5 times the K_d value. Thereby, cationic surfactants such as DDPB are more effective in enhancing phenanthrene sorption onto soil than nonionic surfactants such as TX100. Equation (3) can be used to describe the effect of the surfactant on the sorption of

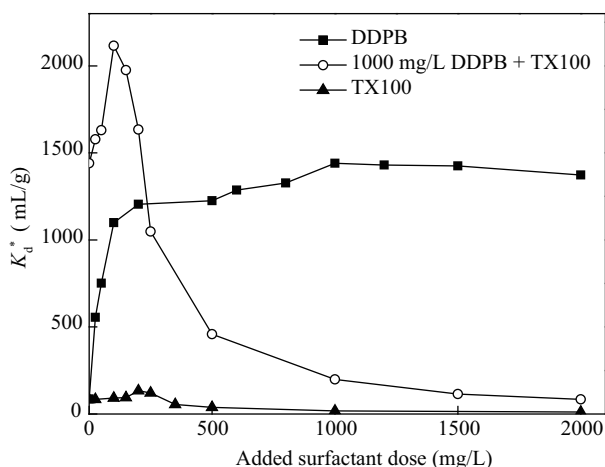


Fig. 1 Effect of surfactants on the measured apparent sorption coefficients (K_d^*) of phenanthrene in soil-water system.

phenanthrene onto soils. At low surfactant concentration, K_d^* values increased due to the rapid increase of soil-sorbed surfactant prior to the formation of surfactant micelles in the aqueous phase, and the sorbed surfactant on soils was a very effective sorbent for phenanthrene partitioning, leading to the enhanced sorption of phenanthrene onto soils. When the sorbed surfactant reached a plateau, the equilibrium concentration of surfactant in the aqueous phase reached its CMC and surfactant micelles in the aqueous phase became an important partition phase. As a result, surfactant micelles began competing for phenanthrene, thereby causing a decrease in K_d^* .

The effect of cationic-nonionic mixed surfactants on the sorption of phenanthrene onto soil was studied with a fixed DDPB concentration (1000 mg/L) together with a set of varied TX100 concentrations, and the corresponding K_d^* values for phenanthrene are also shown in **Fig. 1**. A similar changing tendency was observed for phenanthrene K_d^* with increasing TX100 concentration in mixed surfactants, and a maximum K_d^* of 2115.6 mL/g was obtained with the surfactant concentration of DDPB at 1000 mg/L and TX100 at 100 mg/L. This maximum K_d^* was about 24.5 times K_d and greater than the sum of the maximum K_d^* for individually applied DDPB and TX100. The maximum adsorbed amount of phenanthrene onto soil with DDPB-TX100 was also greater than the sum of the amounts with DDPB and TX100 separately. With an initial phenanthrene concentration of 0.8 mg/L in the aqueous phase, the adsorbed amounts of phenanthrene onto soil were 204.0 and 183.6 mg/kg with the presence of mixed surfactants and cationic surfactant, and the sorption rates were 84.4% and 80.6%, respectively. This result demonstrated the synergistic effect of cationic-nonionic mixed surfactants in enhancing sorption of phenanthrene onto soil compared to DDPB alone.

In general, cationic and nonionic surfactants are adsorbed onto soils by ion-exchange reactions and hydrogen bonding interactions, respectively. Therefore, DDPB and

TX100 in the mixture could be adsorbed onto soils simultaneously without sorption competition. The sorption of DDPB and TX100 onto soils from the individual or mixed surfactants is shown in **Fig. 2**. It can be observed that the added TX100 did not apparently change the sorption of DDPB onto soil. The coexisting DDPB greatly facilitated the sorption amount of TX100 onto soils, which increased from 4.5 to 40.0 mg/g, resulting in the result that more TX100 was adsorbed onto soils and acted as an effective organic medium for phenanthrene sorption. In addition, the adsorbed DDPB and TX100 on soils could also form a more effective partition phase for HOCs than DDPB and TX100 separately. Therefore, the cationic-nonionic mixed surfactant showed more capability in enhanced-sorption of phenanthrene onto soils than individually applied DDPB and TX100. The cost of the cationic-nonionic mixed surfactants for the same effectiveness was approximately reduced by 52%. As a result, the cationic-nonionic mixed surfactants could be used to enhance soil retention capabilities for organic contaminants by decreasing the applied surfactant level and thus the cost.

2.2 Desorption of phenanthrene by nonionic surfactant from contaminated soils treated by mixed surfactants

From the above results, the addition of cationic-nonionic mixed surfactants into a soil-water system could enhance HOCs sorption onto soils and the soil retention capabilities for organic contaminants, and then reduce the mobility and bioavailability of HOCs in the soil-water system, which could effectively restrict the plant uptake of HOCs. However, the retained HOCs still need to be removed or remediated when HOC concentrations in contaminated soils reach a high level. Nonionic surfactant is generally applied as an effective washing agent because of the higher solubilization capacity for HOCs compared to cationic or anionic surfactants. Thereby, TX100 could be used to

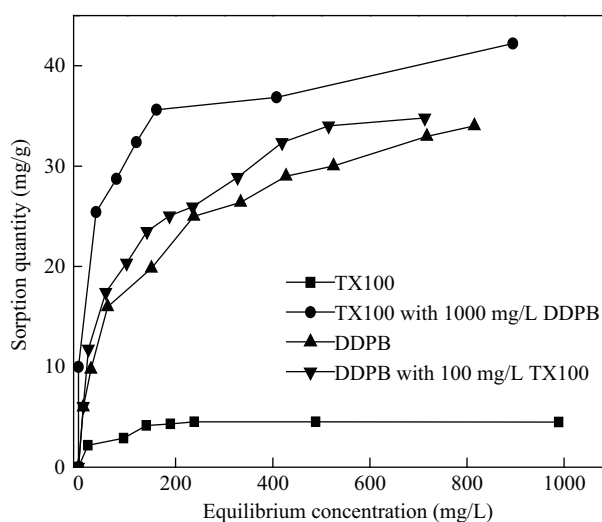


Fig. 2 Sorption isotherms of surfactants in the individual or mixed solutions.

remove phenanthrene from the contaminated soils treated by cationic-nonionic mixed surfactants.

Figure 3 shows the desorption of phenanthrene by TX100 from three contaminated soils treated by surfactant-free (soil 1) or DDPB alone (soil 2) or DDPB-TX100 mixed surfactant solutions (soil 3) in the same conditions. The phenanthrene concentrations in the three contaminated soils were 30.8, 161.9 and 179.4 mg/kg, respectively. With addition of TX100, the residual contents of phenanthrene decreased with increasing TX100 concentration. The desorption rates of phenanthrene had a rapid increase with TX100 concentration up to 2000 mg/L, then followed a gradual increase with higher TX100 concentration. With TX100 concentration at about 2000 mg/L, the phenanthrene desorption rate was 85%, and then approached 100% with increasing TX100 concentration. The desorption rate of phenanthrene from contaminated soil 3 was higher than that of soil 2, while the desorption rate of phenanthrene from soil 1 was the lowest with the same dose of TX100. This difference could be contributed to the different solubilization capability of TX100 for HOCs in the different soils. In addition, the removal rates of phenanthrene by TX100 from soil 3 were greater than those from soil 2. This might be attributed to the weaker sorption of TX100 onto soil 3 because the pre-sorption of TX100 in the sorption-enhancement step could decrease the sorption of TX100 onto soils in the desorption step. In a word, the application of cationic-nonionic mixed surfactants could not only enhance the retention of HOCs in the water-soil system, but also improve the subsequent desorption extent of HOCs by nonionic surfactant from organic pollutant-contaminated soils.

2.3 Mixed surfactant enhanced biodegradation of phenanthrene in soil

After the desorption step, a small amount of phenanthrene still remains in the soil and needs to be removed by biodegradation, and surfactants also remain in the

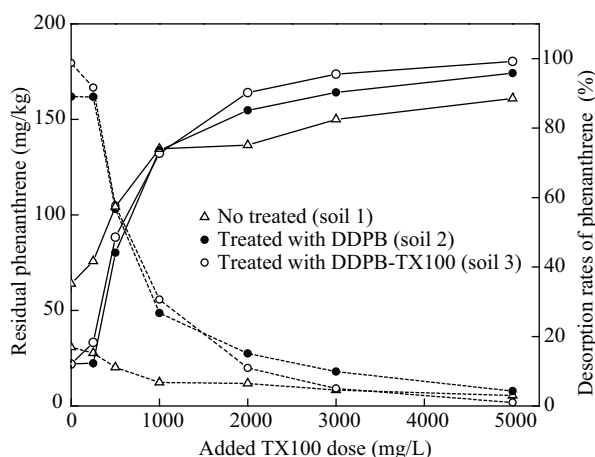


Fig. 3 Residual phenanthrene in soil (dashed lines) and the desorption rates of phenanthrene (solid lines) by TX100 from the contaminated soils with different treatments.

treated zone, which may affect the biodegradation of phenanthrene. Therefore, it is important to evaluate the potential impact of residual surfactants on phenanthrene biodegradation, and actions could be taken to control the concentration of residual surfactants to improve the removal efficiency of the residual phenanthrene from soils.

To investigate the effect of cationic-nonionic mixed surfactants on phenanthrene biodegradation, surfactants were directly injected into phenanthrene-contaminated soils with a fixed TX100 content of 0.5 mg/g and changing DDPB content of 0–1.0 mg/g, respectively. The biodegradation rates of phenanthrene in different periods are shown in **Fig. 4**. It can be observed that the residual phenanthrene in all soil samples decreased significantly during the biodegradation period, and more than 95% of phenanthrene was degraded within 30 days in all experiments. Moreover, the presence of DDPB-TX100 mixed surfactants promoted the biodegradation of phenanthrene to some extent in 10–22 days. This may attributed to the microbial activity being restrained for a short time and recovering quickly with its increasing mass (Domsch et al., 1993). And at the end of the experiment, there was no statistically significant difference between the surfactant systems and surfactant-free controls. The enhanced biodegradation of phenanthrene indicated that the microorganisms were capable of degrading phenanthrene in the cationic-nonionic mixed surfactant micelles because of the desorption of phenanthrene. Addition of TX100 into the cationic surfactant solution led to the formation of mixed micelles, and may change the interaction between microorganisms and surfactants. In other words, residual surfactants containing DDPB in the range of 0–1.0 mg/g in soils seemed to be non-toxic to this phenanthrene degrader. Therefore, this integrative approach can be used to regulate the interfacial behavior, i.e., sorption and desorption, of organic contaminants in the soil-water system, and thus provides an efficient and cost-effective technology for the

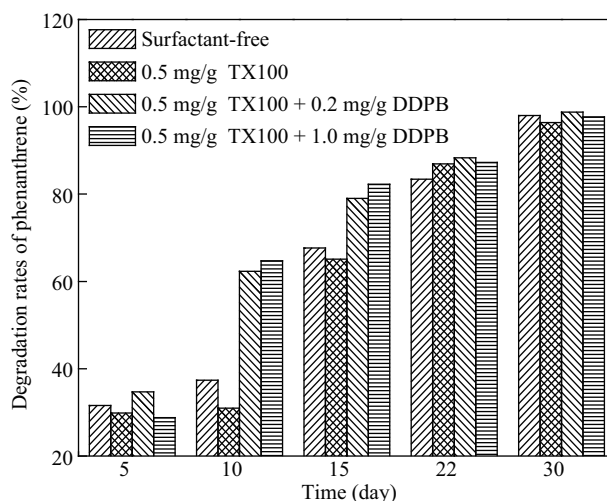


Fig. 4 Degradation rates of phenanthrene in the presence of mixed surfactants.

production of safe agricultural products and remediation for soils slightly contaminated with organic pollutants.

3 Conclusions

An integrative procedure including sorption/desorption/degradation steps enhanced by different surfactants for phenanthrene in the soil-water system was investigated in this study. DDPB-TX100 mixed surfactants showed great efficiency in enhancing soil retention capability for phenanthrene, and the maximum enhancement extent was about 24.5 times that of soil organic matter. Compared to individual cationic surfactants, the cost of the mixed surfactants was approximately decreased by 52% for the same effectiveness. In the subsequent desorption step, the sorbed phenanthrene could be significantly removed by TX100 from the contaminated soils treated by DDPB-TX100, and the desorption rates for phenanthrene were greater than 85% with TX100 concentration above 2000 mg/L, and then approached 100% with increasing TX100 concentrations, which were even greater than those from the solely DDPB treated contaminated soils. The biodegradation experiments for the residual phenanthrene in soil showed that all the biodegradation rates of phenanthrene increased during the experimental period and reached over 95% in 30 days, which indicated that the cationic-nonionic mixed surfactants did not have an obvious impact on phenanthrene biodegradation at the end of the experiment. Thereby, the surfactants can be used to regulate the interfacial behavior of organic contaminants in the soil-water system for an alternative scheme of enhancing sorption or removing organic contaminants, in order to safe-guard agricultural production and cost-effectively remedy these organic pollutant-contaminated soils.

Acknowledgments

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