

Enhanced desorption and biodegradation of phenanthrene in soil–water systems with the presence of anionic–nonionic mixed surfactants

Haisu Yu, Lizhong Zhu*, Wenjun Zhou

Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310028, PR China

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Abstract

The effects of anionic–nonionic mixed surfactants, sodium dodecyl sulfate (SDS) mixed with Triton X-100 (TX100), on the desorption and biodegradation of phenanthrene in soil–water system were investigated in an aim to improve the efficiency of surfactant bioremediation technology. Results indicated that the presence of SDS not only increased the solubilization of TX100 for phenanthrene, but also reduced the sorption of TX100 onto soils. As a result, the desorption efficiency of phenanthrene from the contaminated soil was greatly enhanced by mixed surfactant solutions compared with that by single TX100 solution and appeared to be positively related with the mole fraction of SDS in solution. Mixed surfactants with relatively smaller ratio promoted phenanthrene biodegradation, for example, the biodegradation percentage of phenanthrene in 1:9 SDS–TX100 mixed solutions was about 165% of that in the single TX100 solution at the same TX100 concentration of 1.6 mmol/L in 24 h. But the biodegradation was inhibited with larger ratio of SDS in the mixed solutions, which may be due to the preferential utilization of SDS by phenanthrene degraders. Thus, the selection of mixed surfactants should consider simultaneously the effects of SDS on desorption and biodegradation. The experimental results can be used to provide valuable information in designing the surfactant bioremediation technology for contaminated soils.

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Keywords: Desorption; Biodegradation; Phenanthrene; Mixed surfactants; Soil remediation

1. Introduction

The contamination of soil and groundwater with toxic and/or hazardous hydrophobic organic compounds (HOCs) is a widespread environmental problem. Various physical, chemical, biological, and their combined technologies have been attempted to remediate HOCs contaminated soils and groundwater. Pump-and-treat remediation methods were often ineffective due to the low solubility of these compounds in water and their slow desorption from soils in old contamination sites [1]. Biotreatments were also affected due to the contaminants partitioning onto the soil, which made the contaminant unavailable to the microorganisms for biodegradation. Since surfactant can increase the HOCs aqueous-phase concentration via micelle solubilization [2–6] and the mobilization of HOCs from solid into aqueous phases [7–10]. Micellized HOCs may have increased bioavailability to microorganisms and may thereby improve the biodegradation

rate [11–16]. Surfactant enhanced remediation (SER) technology, containing surfactant enhanced bioremediation (SEBR) and other chemical–biological combined technologies, has been suggested as a promising technology for the remediation of contaminated soils and groundwater [17,18]. Desorption of HOCs is the precondition and biodegradation of HOCs is the key factor in SEBR.

Most of earlier studies were performed with a single anionic or nonionic surfactant. Several factors can influence the efficiency of soil remediation with single surfactant. Anionic surfactants may precipitate in soil, while nonionic surfactants were more likely to adsorb onto clay fractions [17,19] and thereby led to HOCs partitioning into immobile sorbed surfactants and thus, enhanced HOCs retardation [20,21]. The sorption of nonionic surfactant onto soil would reduce the remediation efficiency and result in an increase in remediation time and costs. Meanwhile, the environment factors, temperature, salinity and pH, had obvious effects on the solubilization of individual anionic or nonionic surfactant solution for HOCs. Thus, an improved strategy for SEBR is to enhance the desorption of HOCs from contaminated soils and then to improve the biodegradation rate of HOCs in

* Corresponding author. Tel.: +86 571 88273733; fax: +86 571 88273733.
E-mail address: zlz@zju.edu.cn (L. Zhu).

order to obtain optimal remediation efficiency with the minimum surfactant dose.

Surfactants mixtures, rather than individual surfactants, are often used in scientific and industrial applications. Mixed surfactants could be employed over a wider range of temperature, salinity and hardness conditions than the individual surfactant [22]. The synergistic solubilization of anionic-nonionic mixed surfactants for HOCs were observed in some studies [23,24]. Especially, some researchers [25] found that the sorption of non-ionic surfactant at the hydrophilic silicon surface was strongly restricted with the presence of anionic surfactant as the formation of mixed micelle. Thus, anionic–nonionic mixed surfactants may improve the efficiency of desorption and thereby enhance the biodegradation. But, little information is available about the effect of mixed surfactants on HOCs biodegradation in soil–water system. Therefore, a further understanding for the performance of mixed surfactants in soil–water system and the details in sorption, desorption and biodegradation are desirable.

The objectives of the present study are (1) to quantify the effect of anionic surfactant on the sorption of nonionic surfactant onto soil; (2) to evaluate the efficiency of anionic–nonionic mixed surfactants on the desorption of HOCs from contaminated soil; (3) to assess the effect of anionic–nonionic mixed surfactants on the biodegradation of HOCs in solution and soil–water systems. The experimental results can be used to understand the performance of anionic–nonionic mixed surfactants in the remediation of HOCs-contaminated soils and to provide valuable information in designing the surfactant bioremediation technology for contaminated soils.

2. Experimental

2.1. Chemicals

Phenanthrene was selected as representative polycyclic aromatic hydrocarbons (PAHs) to model the hydrophobic organic contaminants and obtained from Aldrich Chemical Company, with purity >98%. Sodium dodecyl sulfate (SDS) (purity >98%), an anionic surfactant, was obtained from Acros Organics and used without further purification. Triton X-100 (TX100), a non-ionic surfactant, was purchased from Sigma Chemical Company. Mixed surfactants were prepared by dissolving SDS and TX100 in deionized water with different mole ratios and the composition of mixed surfactants was expressed with the mole ratios of SDS to TX100. Selected physicochemical properties of compounds were presented in Table 1.

Table 1
Physicochemical parameters of compounds

Compounds	Molecular formula	MW	CMC (mmol/L)
Phenanthrene	C ₁₄ H ₁₀	178.23	–
TX100	C ₈ H ₁₇ C ₆ H ₄ O(OCH ₂ CH ₂) _{9,5} H	628	0.29
SDS	C ₁₂ H ₂₅ SO ₄ Na	288.38	7.8

2.2. Microorganisms and media

The microorganisms used in this study were derived from activated sludge of the wastewater treatment facility, Hangzhou Coking Plant, China. Before being utilized in biodegradation experiments, the microorganisms in the mixed culture were acclimated to phenanthrene for three months. The mixed culture was fed at 4 days intervals with phenanthrene and medium solution. The mineral basal medium used to cultivate the microorganisms was as following (mg/L): NaH₂PO₄ (500), KH₂PO₄ (850), K₂HPO₄ (1656), NH₄Cl (1000), MgSO₄·7H₂O (1.0), FeSO₄·7H₂O (1.0), MnSO₄·H₂O (0.36), ZnSO₄·7H₂O (0.3), CoCl₂·6H₂O (0.1), CaCl₂·2H₂O (1.0). Phenanthrene was added at an initial concentration of 0.1 mg/L, which increased to 0.5 and 1.0 mg/L. The resultant mixed culture was capable of degrading phenanthrene completely. The phenanthrene-acclimatized microorganisms were collected from the mixed culture by centrifugation at 5000 rpm (7295 × g) for 15 min and washed three times with physiological saline. The harvested microorganisms were suspended in the potassium phosphate buffer solution (0.1 mmol/L, pH 7.0), with an optical density of 0.1 at 600 nm before being used as inoculums.

2.3. Soil treatment

A clean natural soil was collected from Hangzhou city, China. The soil was air-dried and sieved to obtain particles less than 1 mm in all experiments. The soil contained 3.9% sand, 71.5% silt and 24.6% clay, respectively. The organic carbon content of soil sample was 0.52%. The contaminated soil was prepared by dissolving an appropriate quantity of phenanthrene in petroleum ether and a known weight of soil was added slowly with continuous mixing. This slurry was mixed thoroughly and the solvent was allowed to evaporate slowly. The dry contaminated soil was transferred into a bottle and tumbled for about a week before the experiments. The resulting contaminated soil had final concentration of 6.5 mg/kg of phenanthrene, which was used directly in the biodegradation and desorption experiments.

2.4. Biodegradation test

The biodegradation experiments in solution systems were performed in 150-mL flasks on the shaker and conducted in the dark to avoid photooxidation of phenanthrene. Surfactant solution and fine phenanthrene in the sealed flasks were shaken for 48 h at 25 ± 1 °C and then filtered to separate the crystalline particles. A 50 mL of the filtrate was transferred into 150 mL flask. A 5.0 mL of mineral basal medium solution was added. Duplicate samples were prepared for each solution. The killed control samples were prepared by adding 0.1 mL of NaN₃ (100 g/L). Enclosed with two sheets of sterile gauze, the flask was shaken at 25 ± 1 °C with the speed of 150 rpm. The reaction solutions were harvested at periodic intervals, diluted with methanol and filtered through 0.22 μm syringe filter. Phenanthrene and TX100 in solutions were analyzed by HPLC.

The biodegradation experiments in soil–water systems were performed in 25-mL Corex centrifuge tubes with Teflon-lined

screw caps on the shaker and conducted in the dark to avoid photooxidation of phenanthrene. The tubes contained 2 g of soil and 20 mL of solution containing mineral basal medium, microorganism and surfactant. Duplicate samples were prepared for each solution. The blank samples were prepared as the same except for using purified water instead of surfactant solution. The killed control samples were prepared by adding 0.1 mL of NaN_3 (100 g/L). The tubes were shaken at $25 \pm 1^\circ\text{C}$ with the speed of 150 rpm. The reaction solutions were harvested at periodic intervals. The aqueous phase was separated from cells and soil by centrifugation at 25°C and 5000 rpm for 20 min. A 2 mL of supernatant was sampled, diluted with methanol and filtered through 0.22 μm syringe filter. Phenanthrene and TX100 in solutions were analyzed by HPLC.

The rest soil part was further dealt with anhydrous Na_2SO_4 to remove moisture and sonication in 10 mL of acetone for 1 h followed by centrifugation. Then 3 mL of supernatant was filtered through 2 g of silica gel column with 11 mL 1:1 (v/v) elution of hexane and dichloromethane. The solvent fractions were then evaporated, and exchanged by methanol with a final volume of 5 mL. After filtration, phenanthrene and TX100 in solutions were analyzed by HPLC. Recovery rates of phenanthrene for soil samples through the complete analytical processes were 92.5–98.7%.

2.5. Solubilization test

Procedures for sample equilibration and solubility determination were essentially the same as described earlier [2]. A series of single/mixed surfactant solutions were placed in 25-mL Corex centrifuge tubes with Teflon-lined screw caps. The phenanthrene was separately added to each tube in an amount slightly more than required to saturate the solution. Duplicate tests were prepared for each surfactant concentration; these samples were then equilibrated on a reciprocating shaker for 24 h at $25 \pm 1^\circ\text{C}$. The aqueous phase was separated from undissolved phenanthrene by centrifugation at 25°C and 5000 rpm for 20 min. An appropriate aliquot of the supernatant was then carefully withdraw with a volumetric pipette and diluted to appropriate volume with methanol. Phenanthrene in solution was analyzed by HPLC.

2.6. Sorption of TX100 onto soil and phenanthrene desorption experiments

Batch experiments were conducted in duplicate to determine TX100 equilibrium sorption isotherm and the desorption percentage of phenanthrene using centrifuge tubes (Corex, 25 mL) with Teflon-lined screw caps. A weight of 2.0 g of contaminated soil sample was weighed into each centrifuge tube, to which 20 mL of TX100 solution was added. All aqueous solution for soil tests contained 0.1 mL of NaN_3 (100 g/L) to inhibit microbial growth. The initial TX100 concentration spread over a large range of values below and above the nominal CMC. These samples were equilibrated on a reciprocating shaker for 24 h at $25 \pm 1^\circ\text{C}$. The solution and solid phase were separated by centrifugation at 5000 rpm for 30 min. An appropriate aliquot of the supernatant was removed and analyzed for TX100 and

phenanthrene by HPLC. The sorbed amount of TX100 on soil was computed simply from the difference of the initial and final TX100 concentrations. The phenanthrene desorption percentage was computed from the difference of the initial and final phenanthrene concentrations.

2.7. Analytical methods

Phenanthrene and TX100 concentrations were quantified by a Agilent HPLC fitted with UV detector and a Agilent Eclipse XDB-C8 column (4.5 mm \times 150 mm, 5 μm) using methanol–water (75:25) as the mobile phase at a flow rate of 1 mL/min. Chromatography was performed at 30°C . The UV wavelengths were set at 250 and 224 nm for phenanthrene and TX100, respectively.

3. Results and discussion

3.1. Solubilization of phenanthrene

Fig. 1 shows the solubilization of phenanthrene by SDS–TX100 mixed surfactants with different solution composition. The solubilities of phenanthrene were enhanced by each of surfactant solutions, in which the solubilities increased linearly with the surfactant concentration above the CMC. The linear enhancements in solubility were consistent with solubilization data reported for other nonionic surfactants or HOCs of environmental concern [2–6]. The behavior was generally attributed to the incorporation or partitioning of organic solutes within surfactant micelles.

It was observed that the apparent solubilities of phenanthrene in mixed surfactant solutions were higher than those in single TX100 solutions at comparable surfactant concentrations and positively related with the mole fraction of SDS in mixed surfactant solutions. For example, with a same TX100 concentration of 4 mmol/L, the apparent solubilities of phenanthrene in SDS–TX100 mixed surfactants, in which the mole ratios of SDS to TX100 were 1:9, 1:4, 1:2, 1:1 and 2:1, were about 112,

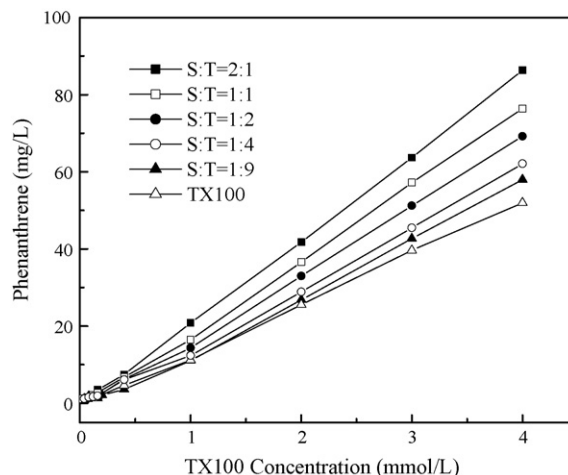


Fig. 1. The apparent solubilities of phenanthrene by different surfactant systems with various mole ratios of SDS (S) to TX100 (T).

120, 131, 147 and 166% of that with the single TX100 solution, respectively. With a larger solubilization capacity, aqueous phase would accept more phenanthrene desorbed from soil.

In this study, most concentrations of SDS in mixed surfactants were less than the CMC values and the solubilization enhancement of SDS in mixed solution for phenanthrene was neglectable. But, when SDS was mixed together with TX100, the critical micelle concentration of TX100 decreased and then the micelle concentration in the aqueous phase increased. At the same time, the formation of mixed micelle enhanced the partition of phenanthrene into surfactant micelle [2,23].

3.2. Effect of SDS on the sorption of TX100 onto soil

The sorption isotherms of TX100 onto soil from different surfactant systems were shown in Fig. 2, which illustrated the effect of SDS on the sorption of TX100 onto soil. The sorption isotherm of TX100 from single surfactant solution was nonlinear and typical S-shape curves, reaching a plateau in sorption amount at surfactant equilibrium concentration around the CMC, which was in accord with the results of other experimental studies for the sorption of nonionic surfactant [20,21,26]. A conceptual model based on numerous experimental observation can accounts for the sorption of nonionic onto hydrophilic surface. At low surfactant concentration, the nonionic surfactants are sorbed as monomers and lie parallel to the solid surface through surface interactions with both types of surfactant moieties. With the increase in the surfactant concentration, the sorption increases dramatically as the surface micelle (admicelle) or bilayers form on the adsorbent through association or hydrophobic interactions between the hydrocarbon chains of the surfactants, and a plateau is reached corresponding to a maximum sorption amount.

Similar sorption isotherms was obtained for TX100 from mixed surfactant solutions, in which the mole ratios of SDS to TX100 were 1:9, 1:4, 1:2, 1:1 and 2:1, respectively. But the presence of anionic surfactant, SDS, strongly affected the sorption amount of pure TX100. The amount of TX100 in mixed surfac-

tant solutions was significant higher than that in single TX100 solution. The addition of 10 mol% SDS to TX100 resulted in a 25% decrease in the maximum sorption amount for TX100, from 14.68 to 10.88 mmol/kg. When the mole ratio of SDS to TX100 in mixed surfactant solutions was 2:1, the maximum sorption amount of TX100 onto soil only was about 30% of the value for single TX100 solution. Thus, the higher the mole fraction of SDS in mixed surfactant solutions, the greater the decrease in the maximum sorption amount for TX100. These results showed that, when SDS was mixed together with TX100, the sorption of nonionic surfactant onto soil was severely restricted and a higher mole fraction of SDS in surfactant solution meant that a lower plateau sorption can be reached with a smaller TX100 concentration in surfactant solution. Reduction of sorption loss in mixed-surfactants indicated that mixed surfactant could increase available concentration of the surfactant quantities and then reduce the costs and the level of surfactant pollution in remediation.

3.3. Phenanthrene desorption studies

Desorption studies were used to evaluate the efficiency of surfactant solution to desorb phenanthrene from contaminated soil. Fig. 3 shows the desorption percentage of phenanthrene from the contaminated soil by single TX100 solution and SDS–TX100 mixed surfactants with different composition. It was observed that the phenanthrene desorption percentage decreased gradually until reaching a minimum and then increased dramatically in both single TX100 solution and mixed systems. But the phenanthrene desorption percentages with mixed surfactants were obviously greater than that with single TX100 solution and positively related with the mole fraction of SDS in mixed surfactant solutions. For example, using the same TX100 concentration in 3.5 mmol/L, the desorption percentage of phenanthrene were 46% with single TX100 solution and 58, 62, 75, 83 and 93% with mixed surfactants, in which the mole ratios of SDS to TX100 were 1:9, 1:4, 1:2, 1:1 and 2:1, respectively. From the trendy in Fig. 3, to reach a same phenanthrene desorption rate of 50%

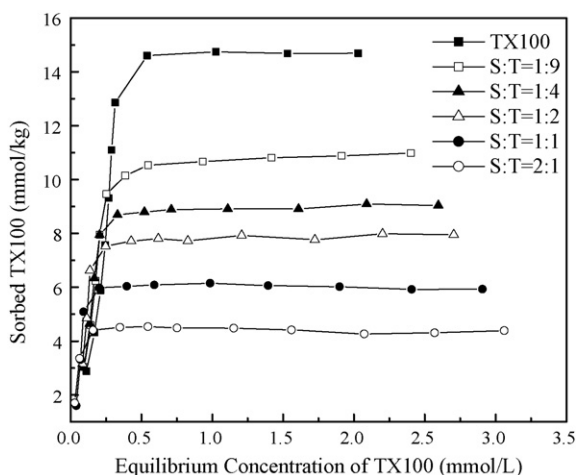


Fig. 2. The sorption isotherms of TX100 onto soil from different surfactant systems with various mole ratios of SDS (S) to TX100 (T).

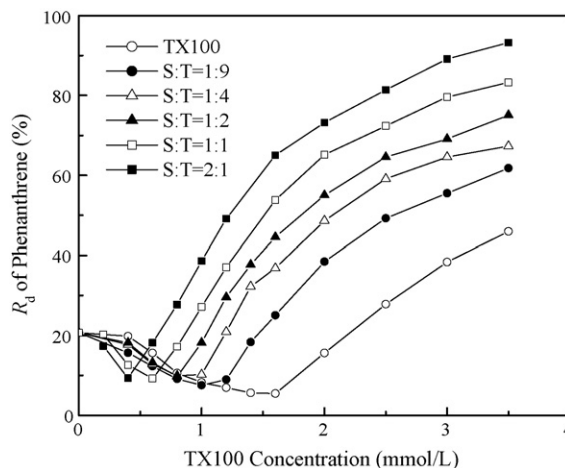


Fig. 3. The desorption percentage (R_d) of phenanthrene by different surfactant systems with various mole ratios of SDS (S) to TX100 (T).

from the contaminated soil, the corresponding concentration of TX100 was about 4 mmol/L for single TX100 solution and 2.7, 2.2, 2.0, 1.5 and 1.3 mmol/L for mixed solutions with the composition of 1:9, 1:4, 1:2, 1:1 and 2:1, respectively.

The corresponding TX100 concentration when desorption percentage of phenanthrene was equal to the initial desorption percentage with water can be defined as the critical desorption concentration (CDC). The CDC values of TX100 for phenanthrene with mixed surfactants were less than that with single TX100 solution and inversely related with the mole fraction of SDS in mixed solutions. The CDC values of single and mixed solutions for phenanthrene, in which the mole ratios of SDS to TX100 were 1:9, 1:4, 1:2, 1:1 and 2:1, were 2.2, 1.5, 1.2, 1.0, 0.8 and 0.6 mmol/L, respectively. The sharp increase and the CDC can be rationally explained with the sorption of TX100 onto soil from surfactant solution and were attributed to the formation of surfactant micelles in aqueous phase. Before the minimum of desorption percentage, TX100 was sorbed onto soil and the sorbed TX100 increased phenanthrene sorption, TX100 existed in aqueous as monomer and there were not surfactant micelles in aqueous phase, therefore, phenanthrene concentration in aqueous was decreased. With the sorption of TX100 in plateau, the surfactant micelle began to form in aqueous phase, which enhanced the solubilities of phenanthrene in aqueous phase and thus increased the desorption percentage. For SDS–TX100 mixed surfactant systems, the sorption of nonionic surfactant onto soil was severely restricted. The higher mole fraction of SDS in surfactant solution, the lower sorption plateau can be reached and then the lower the CDC values of TX100 for phenanthrene. These results indicated that SDS–TX100 mixed solution was more effective for the desorption of phenanthrene from the contaminated soil than the single TX100 solution.

3.4. Biodegradation of phenanthrene in solutions

Fig. 4 shows phenanthrene biodegradation in solution with the presence of single or mixed surfactants. In the first 24 h, there

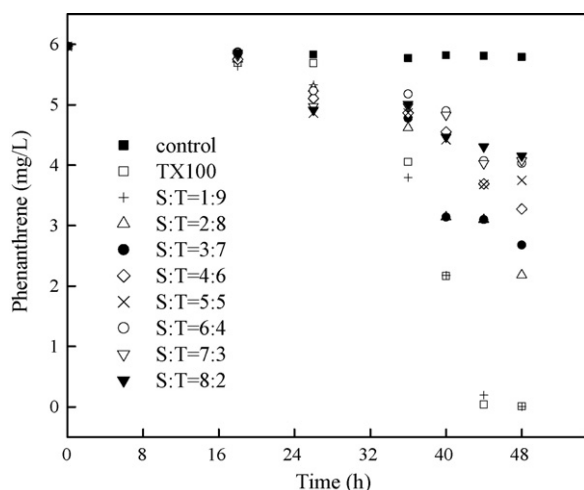


Fig. 4. Degradation of phenanthrene with the presence of single- and mixed-surfactant solutions (1.6 mmol/L of TX100).

was a plateau and little phenanthrene was degraded, which may be explained that the microorganisms needed time to acclimatize the surfactant solution. In the following 24 h, phenanthrene dissolved in micelle phase and aqueous phase was rapidly biodegraded. The killed control data showed that a loss of volatility of phenanthrene was negligible throughout the experiment. In the mixed systems, similar trend was observed in 1:9 mixed solution, a plateau was observed in the first 24 h and then phenanthrene was biodegraded in the next 24 h. But a distinct inhibitory effect was observed in other mixed systems, in which TX100 concentrations were the same as single TX100 solution and the mole ratios of SDS to TX100 were 2:8, 3:7, 4:6, 5:5, 6:4, 7:3 and 8:2. In general, the slopes of concentration–time plots indicated the rates of phenanthrene degradation. The higher the mole fraction of SDS in mixed surfactant solutions, the greater the decrease in phenanthrene degradation rates.

The continuous disappearance of phenanthrene throughout the experiment duration indicated that the phenanthrene-acclimatized microorganisms were capable of degrading phenanthrene in single TX100 solution, which was in accord with the result of other experimental studies for the surfactant enhanced biodegradation [27,28]. Combination of small ratio of SDS with nonionic surfactant, such as 1:9 SDS–TX100 mixed systems, exhibits little inhibition on phenanthrene degradation. Addition of SDS into nonionic surfactant led to the formation of mixed micelle and resulted in the change of interaction between microorganisms and surfactant. As to the inhibitory in other ratio mixed systems, it may be attributed to the inhibitory of SDS. It was reported that the addition of SDS decreased the biodegradation rate of PAHs, presumably because of the preferential utilization of surfactants by PAHs degraders [29,30].

3.5. Biodegradation of phenanthrene in soil–water system

Phenanthrene concentration in the soil phase, aqueous phase and the total residual amount in soil–water systems were examined and shown in Fig. 5 as a function of time. Phenanthrene concentration in the soil phase of the soil–water system decreased gradually in the blank sample, in which no surfactant was added. Meanwhile, phenanthrene concentration decreased faster in both single and mixed surfactant solutions and the degradation appeared to be positively related to the mole fraction of SDS in mixed surfactant solutions. Phenanthrene concentration in the aqueous phase of the soil–water system increased at first and then decreased. The maximum of the phenanthrene concentration in blank sample appeared in 24 h. The reason was that the desorption rate of the phenanthrene was higher than the biodegradation rate during the first 24 h. Similar trend of phenanthrene concentration was observed in either single TX100 solution or mixed solutions, but the maximum appeared in 12 h and the concentration of phenanthrene was lower than that in blank sample.

The residual amount was the total amount of phenanthrene in both solid and aqueous phase of the soil–water system. The residual amount decreased gradually and only one third of phenanthrene disappeared in 96 h in the blank sample. Meanwhile, in both single and mixed surfactant solutions, phenanthrene concentrations decreased faster than that in blank sam-

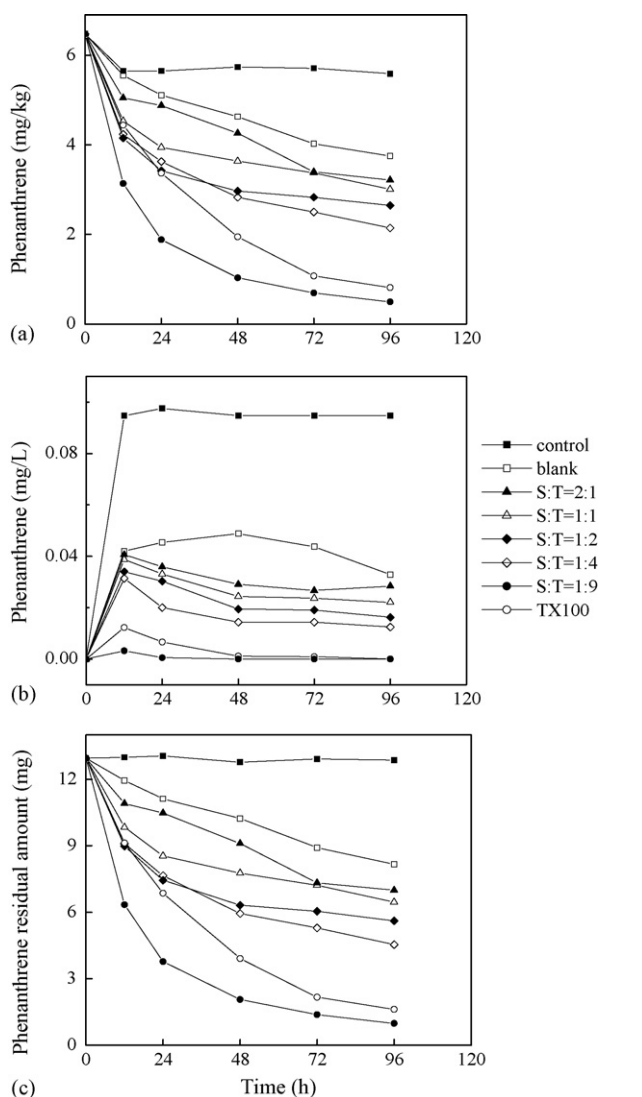


Fig. 5. Degradation of phenanthrene with the presence of single- and mixed-surfactant in soil–water system (a: phenanthrene concentration in soil phase; b: phenanthrene concentration in aqueous phase; c: total residual amount of phenanthrene).

ple, and what was more, the residual amount was positively related with the mole fraction of SDS in surfactant solutions. For example, the residual amount of phenanthrene in 96 h with SDS–TX100 mixed surfactants, in which the mole ratios of SDS to TX100 were 1:9, 1:4, 1:2, 1:1 and 2:1, were 0.99, 4.54, 5.62, 6.46 and 7.00 mg, respectively. The continuous disappearance of phenanthrene in the experiments duration indicated that the phenanthrene-acclimatized microorganisms were capable of degrading phenanthrene in soil–water system.

TX100 concentrations in Fig. 5 were 1.6, 1.2, 1.0, 0.8 and 0.6 mmol/L and the mole ratios of SDS to TX100 were 1:9, 1:4, 1:2, 1:1 and 2:1, the desorption in such condition was equal to that in water. The same desorption showed that the addition of surfactant accelerated the biodegradation of phenanthrene. The reason was that the addition of surfactant reduced the surface and interfacial tension and then increased the contact between the microorganisms and phenanthrene. When the

phenanthrene in aqueous phase decreased continual by biodegradation, phenanthrene was continual desorbed from soil. The biodegradation was inhibited with the increasing of SDS concentration, because that SDS may be preferential utilized by microorganisms [29,30], phenanthrene would have a competitive effect with SDS. It was also possible that the surfactant increased the instantaneous rate, rather than the extent, of desorption and that the microorganisms thus had more substrate continuously made available to them as they transformed the phenanthrene [31]. It was reported that the equilibrium concentration of the chemical in the aqueous phase in the presence of the surfactant was not important but rather the rate of removal the substrate from the soil solids determined the rate the degradation of the aromatic hydrocarbon [31]. Furthermore, it was also possible that the surfactants altered the strength of sorption or complex the substrate in some way that the phenanthrene became more available to microorganisms [31].

It could be seen from Fig. 5 that the phenanthrene degradation only in the 1:9 mixed system was better than in single TX100 solutions. Therefore further experiments focusing on single and 1:9 mixed surfactants at a series of concentrations were conducted. From Table 2, it was observed that phenanthrene in most samples degraded in 168 h. In the first 96 h, the degradation rate was fast and then slows down. In general, the degradation rates in 1:9 SDS–TX100 mixed surfactants were faster than that in single TX100 solution. Almost 50% of phenanthrene disappeared in 12 h in 1:9 SDS–TX100 mixed surfactants at the concentration of 1.6 mmol/L. The degradation rates in 24 h for 1:9 SDS–TX100 mixed surfactants at concentrations of 1.0, 1.3, 1.6 and 1.9 mmol/L were about 115, 223, 165 and 132% of that for the single TX100, respectively. The degradation rates in single TX100 solution increased at first and then decreased with the surfactants concentration increasing, and the maximum appeared at 2.2 mmol/L of TX100. Meanwhile, in the 1:9 SDS–TX100 mixed systems, similar change trendy was observed, and the maximum appeared at 1.6 mmol/L of TX100. In this study, the desorption percentage of phenanthrene from soil in 1:9 mixed SDS–TX100 solutions was greater than that in single TX100 solution and the desorption was the rate-limiting step, therefore the degradation rates in 1:9 SDS–TX100 mixed system were larger than that in single TX100 solution. In another hand, with the concentration of surfactants increasing, the inhibition of high concentration surfactant to microorganisms was emerged. It was reported that the biodegradation of phenanthrene was increased first and then decreased with increasing surfactant concentration [32,33]. The inhibition may be a result of a physical–chemical effect of the surfactant micelles interfering with substrate transport into the cell, or with the activity of enzymes and other membrane proteins of the cell [32,33]. The inhibition may also be a result of limited bioavailability of micellized phenanthrene, as it was reported that the addition of surfactant increased the degradation of PAHs, but the bioavailable fraction of micellar-phase phenanthrene decreased with the increasing of surfactant concentration [15]. Taking one with another, the selection of mixed surfactants should consider the effects of SDS on desorption and biodegradation simultaneously. It was important to choose proper ratio

Table 2
Biodegradation percentage of phenanthrene in single TX100 and 1:9 SDS–TX100 in the soil–water systems (%)

TX100 (mmol/L)	Time (h)							
	12	24	48	72	96	120	144	168
Single TX100								
Blank	0.45	7.33	14.74	25.70	32.02	43.69	49.38	53.17
1	13.48	20.57	31.29	41.76	53.28	65.16	68.79	74.47
1.3	18.21	24.93	39.02	57.06	70.05	81.26	86.03	88.68
1.6	20.03	41.65	61.65	72.42	80.58	88.58	91.84	92.82
1.9	28.92	42.68	65.96	75.49	83.25	87.04	90.39	91.45
2.2	24.71	42.58	66.87	81.69	85.98	91.31	92.73	94.32
2.5	23.91	37.38	52.08	63.95	74.58	85.39	90.17	93.18
1:9 SDS–TX100								
1	18.91	23.82	41.20	41.02	65.86	77.44	89.21	93.24
1.3	31.27	55.55	74.28	85.23	91.86	88.98	91.50	93.23
1.6	47.61	68.69	82.75	88.36	91.87	91.75	92.35	94.73
1.9	36.01	56.41	75.02	81.48	85.87	91.58	91.77	93.83
2.2	24.79	36.96	57.37	62.37	76.18	82.37	93.01	90.95

and concentration of anionic–nonionic mixed surfactants in remediation.

4. Conclusions

This study focused on the effects of anionic–nonionic mixed surfactants, SDS–TX100, on the desorption and biodegradation of phenanthrene in soil–water system. The apparent solubilities of phenanthrene in mixed surfactants appeared to be greater than that of in single TX100 solution and were positively related with the mole fraction of SDS in mixed surfactant solutions. The sorption amount of TX100 onto soil from the mixed solutions was less than that of single TX100 solution and inversely related with the mole fraction of SDS in solution. Both of the results induced that the desorption percentage of phenanthrene from the contaminated soil with mixed surfactant solutions was greater than that with single TX100 solution and appeared to be positively related with the mole fraction of SDS in solution. The mixed surfactants with relatively smaller ratio (e.g. 1:9 SDS–TX100) promoted phenanthrene biodegradation, but with the mole fraction of SDS in mixed surfactant solutions increasing, the phenanthrene biodegradation was inhibited, which may be due to the preferential utilization of SDS by phenanthrene degraders. Thus, the effects of SDS on desorption and biodegradation should be taken into account in the applications of surfactant enhanced bioremediation for contaminated soils.

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