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Journal of Hazardous Materials 142 (2007) 354–361

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

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

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Received 18 May 2006; received in revised form 10 August 2006; accepted 11 August 2006
Available online 18 August 2006

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.

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

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doi:10.1016/j.jhazmat.2006.08.028

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 nonionic 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 nonionic 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	$C_8H_{17}C_6H_4O(OCH_2CH_2)_{9.5}H$	628	0.29
SDS	$C_{12}H_{25}SO_4Na$	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 mouths. 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): NaH_2PO_4 (500), KH_2PO_4 (850), K_2HPO_4 (1656), NH_4Cl (1000), $MgSO_4{\cdot}7H_2O$ (1.0), $FeSO_4{\cdot}7H_2O$ (1.0), $MnSO_4{\cdot}H_2O$ (0.36), $ZnSO_4{\cdot}7H_2O$ (0.3), $CoCl_2{\cdot}6H_2O$ (0.1), $CaCl_2{\cdot}2H_2O$ (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 ($7295 \times g$) 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 $25 \pm 1\,^{\circ}C$ 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 NaN_3 (100 g/L). Enclosed with two sheets of sterile gauze, the flask was shaken at $25 \pm 1\,^{\circ}C$ 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