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Batch solubilization and washing of chlorobenzene from loess soil by mixed surfactant solutions

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ABSTRACT

Surfactant-enhanced remediation (SER) is a promising technology for the removal of hydrophobic organic contaminants in subsurface. Because chlorinated hydrocarbons are prevalent contaminants in soils and ground, much attention has been paid to the ways and techniques to remove them. In this paper, the water solubility enhancements of chlorobenzene by solutions of an anionic surfactant, sodium dodecyl sulfate (SDS), a nonionic surfactant, Brij 35, and their mixture SDS-Brij 35 were conducted and compared. Batch washing of chlorobenzene from loess soil was studied using single SDS, Brij 35, the mixed SDS-Brij 35, another nonionic surfactant Tween 80 and its mixtures with SDS. It was found that the apparent solubility of chlorobenzene in solutions was linear with the surfactant concentration. The values of the mass solubilization ratios (SR) were 0.0728, 0.0921, 0.0961, 0.144 and 0.193 of single SDS, Brij35, 1:3, 1:1 and 3:1 SDS-Brij35 (w/w), respectively. The mixed SDS-Brij 35 exhibited a large solubilization capability for chlorobenzene. In soil-water systems, the water phase concentrations of chlorobenzene increased with the initial concentration of surfactants at large and varied with the kinds of surfactant and ratios. The mixed surfactants at the given mass ratios of anionic to nonionic one exhibited a relative high washing efficiency for chlorobenzene-spiked loess while single ones did poorly. This paper indicated that the mixed anionic-nonionic surfactant could be an alternative ways to clean up the soils and groundwater contaminated by chlorinated solvents.

KEYWORDS

Chlorobenzene;
Surfactant;
Solubilization;
Soil washing;
Soil remediation.

INTRODUCTION

Chlorinated hydrocarbons are widespread contaminants and prevalently found in subsurface. Due to their serious environmental effect, they are termed as the prior contaminants by EPA and much attention has been paid on their clean-up from soils and groundwater. US EPA estimates that about 60% of Superfund sites have a medium to high likelihood of containing chlorinated solvents[1].

Many researches have indicated that in situ flushing and ex situ washing using surfactant solution become promise for the remediation of soils and aquifers contaminated with nonaqueous phase liquids (NAPLs) and are more effective than the traditional pump-and-treat method[2-4]. In general, the flushing and washing technologies involve the addition of surfactants to accelerate the dissolution or displacement of NAPLs from contaminated sites. Surfactant-enhanced flushing and washing is through micellar solubilization and mobilization[3,4]. The mobilization mechanism involves the immiscible removal of NAPLs as free product, due to the adsorption of surfactant molecules (monomers) at the interface between oil and water and reduction in the interfacial tension (IFT), which are derived from enhanced oil recovery[3]. Because chlorinated solvents are denser than the surrounding water, the risk of downward migration of them as free product into uncontaminated regions of aquifers has been a limitation for the implementation of this method for chlorinated solvents remediation[5]. In the meanwhile, reducing IFT would allow the displaced free products enter smaller pores that may be less readily accessible during remediation efforts[6]. Solubilization is usually to use the micellar surfactant solutions to increase the aqueous apparent solubilities of contaminant in a single phase microemulsion[3,4]. This method has been shown to be effective in numerous examples[7-13], which poses less risk of uncontrolled migration and are less complex to design.

The common surfactants used in remediation study are ethoxylated nonionic and anionic ones. The former such as Triton X-100, Tween 80, etc. have received much attention due to their relative high solubilization capacity[14,15]. However, their adsorption onto subsurface mediums[16] and partitioning from water phase into organic solvent phase[17-19] are concerns with the use of them for remediation application, which could result in large losses of surfactant and reducing the efficiency for dissolution removal of contaminants. In general, anionic surfactants do not adsorb onto soils much because of the repulsion force of negative charges between surfactant ions and soil surfaces[16] and partition into the organic phase[20]. However, they can solubilize less organic compounds than nonionic ones in unit mass[14,15]. Anionic and nonionic surfactants usually form mixed micelles in aqueous phase, whose properties are often different from those of the individual ones[21,22]. This may leads to a better flushing and washing efficiency for chlorinated hydrocarbons in soils and groundwater.

To our knowledge, few studies have been conducted for dissolution of chlorinated hydrocarbons in soil mediums by mixed anionic-nonionic surfactant. In this paper, Brij 35, Tween 80 and sodium dodecyl sulfate (SDS) were used as the representative nonionic and anionic surfactants and chlorobenzene (CB) as the chlorinated solvents. The objectives are to test and compare the apparent solubilization extents in aqueous solution and the dissolution of CB from spiked loess soil by single and mixed surfactant, using batch experiment. The results may demonstrate an implication for the remediation of soils and groundwater contaminated by chlorinated solvents.

EXPERIMENTAL

Chemicals

Sodium dodecyl sulfate (SDS) with analytical grade was purchased from Laiyang Chemical Company, China. Both of Tween 80 and Brij 35 were obtained from Acros Organics, USA and used as received. Chlorobenzene with analytical grade was obtained from Tianjin Suzhuang Chemical Company, China. The physical and chemical parameters of reagents are listed in TABLE 1. Methanol was analytical grade and purified water was used for all tests.

Material preparation

A vadose zone loess soil collected from Lanzhou, China was airdried and sieved through a 0.28-mm sieve. The soil has a pH of 8.14 and organic matter of 0.20%. This soil was then spiked with chlorobenzene and mixed homogeneously in reagent bottle sealed with Parafilm (Parafilm M, USA).

Solubilization tests

The procedures were similar to those in the previous report[22]. Surfactants were used as single or mixed with the following concentration, 100, 500, 1000, 2000, 4000 and 6000 mg/L. The mixed surfactant solutions were used at the initial mass ratios of 3:1, 1:1 and 1:3 of SDS to nonionic one. A series of surfactant solutions

TABLE 1: Physical and chemical parameters of reagents

Reagents	Molecular formula	Molar weight g/mol	Solubility[a] mg/L, 25 °C	CMC[b] mg/L
Chlorobenzene	C_6H_5Cl	112.56	390.7	-
Tween 80	$C_{17}H_{35}COOS_6(OCH_2CH_2)_{20}OH$	1309	-	73.76
Brij 35	$C_{12}(CH_2CH_2O)_{23}$	1198	-	66.0
SDS	$C_{12}H_{25}OSO_3Na$	288.38	-	1586

a. Water solubility[23]; b. The critical micellar concentration[22] were transferred into 250-mL flasks. Chlorobenzene was separately added to each flask in an amount slightly more than required to saturate the solution. The samples were tapped and sealed with Parafilm. Duplicate samples were prepared. Then these samples were equilibrated on a reciprocating shaker (CHA-S Shaker, Jintan Danyang Instrumental Company, China) for 24 h at a speed of 120 rpm and a temperature of 25±1^{0}C. The samples were subsequently centrifuged for 30 min at a speed of 3000 rpm. An appropriate aliquot of the supernatants was then carefully transferred and diluted to 25 mL in flasks with methanol and water. The absorbance of diluted samples was tested at 210 nm on spectrophotometer (Model 752, Shanghai Spectrum Instrumental Company, China) with 1.0 cm quartz cell. The concentrations of chlorobenzene were quantified from the calibration.

Soil washing tests

Batch soil washing experiments were conducted by placing a constant ratio (1 g to 20 mL) of soil to surfactant solution while the dissolution of chlorobenzene was evaluated. A series of 1 g of chlorobenzene-spiked loess soil was added and 20 ml of surfactant solutions with the initial concentrations mentioned above were placed into flasks. The controls were prepared using chlorobenzene-free soil. These samples and controls were shaken, centrifuged and quantified using method mentioned above.

RESULTS AND DISCUSSION

Solubilization

Figure 1 shows the relationship of the apparent solubilities of chlorobenzene (S*) as a function of surfactant concentration of SDS, Brij 35, 3:1, 1:1 and 1:3 SDS-Brij35, respectively. The linear relation was observed between the apparent solubilities and surfactant concentrations. The figure indicates that there is no significant difference of chlorobenzene solubility by single and mixed surfactant when their concentrations were low. Below 1000 mg/L, the molecules of SDS could not aggregate to form micelle due to its critical micelle concentration is 1586 mg/L. The effects of surfactant monomers on solubility enhancement of organic compounds are negligible[14]. Although Brij35 has formed micelle above its CMC (66.0 mg/L), the solubility enhancements of those organic compounds with high intrinsic water solubility (i. e. water solubility of chlorobenzene is 390.7 mg/L) are not significant yet[15]. On the basis of ideal mixing principle of mixed anionic-nonionic surfactants[20], the CMC of mixed Brij35-SDS are between that of single anionic and nonionic one. Thus, no obvious solubility enhancement by mixed Brij35-SDS was observed at lower surfactant concentrations.

However, when the surfactant addition were much more (i.e. 1000-6000 mg/L), the obvious solubility enhancements were observed and the difference of solubilization capacity by tested surfactant occurred, which are the results of partitioning of hydrophobic compounds from aqueous phase into pseudo-micellar phase. From the slopes of the solubilization curves, it was observed that the extents of solubilization by the surfactants followed the order 3:1 SDS-Brij 35 > 1:1 SDS-Brij 35 >1:3 SDS-Brij 35 ~ Brij35 > SDS. To compare the solubilization efficacy, the mass solubilization ratio (SR) is introduced, which are the measurement of the effectiveness of a particular surfactant in solubilizing a given solute[24]. The SR is defined as:

$$\mathbf{SR} = \frac{\mathbf{S^*_{mic} - S^*_{cmc}}}{\mathbf{C_{surf} - CMC}} \qquad \mathbf{(1)}$$

where S^*_{cmc} is the apparent solubility of organic compound at the CMC of surfactant; S^*_{mic} is the total apparent solubility of organic compound in micellar solution at a particular surfactant concentration at which S^*_{mic} is evaluated. SR can be obtained from the slope of solubilization curves. The calculated values of SR

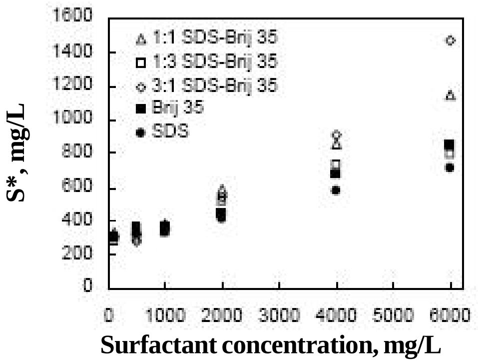

Figure 1: Relationship between the apparent solubilities of chlorobenzene (S*) and SDS, Brij 35 and mixed SDS-Brij 35 concentrations

TABLE 2: Calculation of mass solubilization ratios of SDS, Brij 35 and SDS-Brij 35

Surfactant	Regression equation	R^2	SR
SDS	$S^*_{mic} = 0.0728C_{surf} + 277.28$	0.9946	0.0728
1:3 SDS-Brij35	$S^*_{mic} = 0.0961\ C_{surf} + 269.86$	0.9499	0.0961
1:1 SDS-Brij35	$S^*_{mic} = 0.1444\ C_{surf} + 279.51$	0.9945	0.1444
3:1 SDS-Brij35	$S^*_{mic} = 0.1928\ C_{surf} + 220.86$	0.9477	0.1928
Brij35	$S^*_{mic} = 0.0921\ C_{surf} + 289.90$	0.9909	0.0921

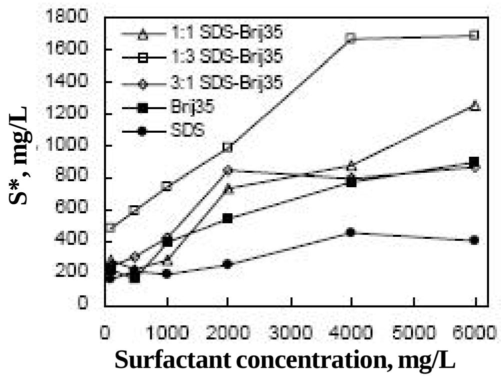

Figure 2: The concentration of chlorobenzene in aqueous phase (C^*) versus SDS, Brij 35 and the mixed SDS-Brij35 concentrations in soil-water system

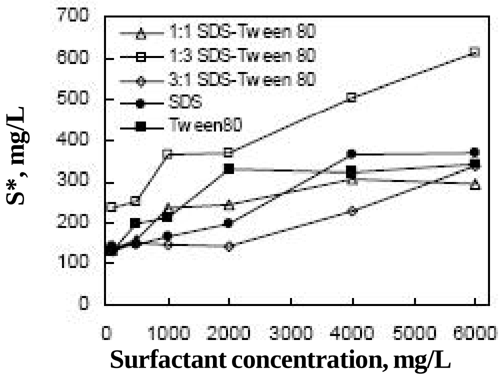

Figure 3; The concentration of chlorobenzene in aqueous phase (C^*) versus SDS, Tween80 and the mixed SDS-Tween 80 concentrations in soil-water system

are shown in TABLE 2. The SR by single SDS was less than those by the mixed SDS-Brij 35, which indicated SDS had a low solubilization capacity for chlorobenzene. The SR values by single Brij 35 was approximately equivalent to that by 1:3 SDS-Brij 35 but much less than those by 1:1 and 1:3 SDS-Brij 35, which demonstrated that mixed SDS-Brij 35 had relatively high solubilization capacity in proper ratios, compared with single nonionic and anionic surfactant.

In our previous study[25], the solubilization of chlorobenzene by mixed SDS-Tween 80 was investigated with a similar equilibrium method. The solubilization effects of chlorobenzene by mixed SDS-TW80 were significant compared with the single SDS. The values of SR by SDS, TW80 and mixed SDS-TW80 followed the order TW80 > 1:3 SDS-TW80 > 1:1 SDS-TW80 > 3:1 SDS-TW80 > SDS, which are some different from the order by SDS-Brij 35. Solubilization capacity is related to structure of surfactant, properties of solubilizates, effects of additives, temperature, and so on[20]. The solubilization extent by mixed anionic-nonionic surfactant for a given organic compound is also related to the solubilization capacity of each component surfactant, the ratios of surfactant, the mixed CMC, and the synergistical solubilization effects[20]. The synergism can be presented as the mixed surfactant solubilize more solutes than single one and partially depends on matching of the structure of anionic and nonionic surfactant molecules. The research indicated that the synergistical solubilization of phenanthrene by mixed SDS-Brij 35 were larger than that by mixed SDS-TW80[22]. At same conditions, the synergism by Triton X-100 mixed with SDS was little. Thus, the high solubilization capacity of chlorobenzene by mixed SDS-Brij 35 is probably due to the synergism.

Soil washing

Soil washing tests were conducted to evaluate the extent of surfactant solutions to dissolve chlorobenzene from loess soil. The mixed surfactant solutions were employed in the washing process at the same experimental conditions as the single surfactant solutions. For each surfactant system, chlorobenzene concentration in water phase (C*) was quantified as a function of the initial surfactant concentrations. Figure 2 shows the relations between chlorobenzene concentration in water phase and the initial SDS, Brij 35, and mixed SDS-Brij 35 concentration from 100 mg/L to 6000 mg/L. As the plots indicted, the clorobenzene concentration in water phase increased with the surfactant concentration increasing, at large. When the surfactant concentrations were large, a leveling off of the chlorobenzene concentration occurred. However, the washing efficiencies by various surfactants were different. The washing extent using single Brij35 was between that of single SDS and of mixed SDS-Brij 35. The mixed SDS-Brij 35 exhibited high capacity to wash chlorobenzene, among which 1:3 SDS-Brij 35 was the best one. The results demonstrated that the mixed SDS-Brij 35 at special mass ratios could solubilize more organic compound, which could reduce expenditure and the operation cost in remediation application. Figure 3 shows the aqueous concentration of chlorobenzene as a function of SDS, TW80 and mixed SDS-TW80 concentrations. A similar result were observed, i. e. a largest aqueous concentration of chlorobenzene occurred when the 1:3 SDS-TW80 was used.

In general, surfactant-enhanced soil washing results from two mechanisms[26]. Surfactant monomers are responsible for the soil roll-up mechanisms. Firstly, monomers accumulated at the soil-contaminant and soil-water interfaces and increase the contact angle (i. e. enhancing the wettability of the systems). Surfactant molecules adsorbed on the surface of the contaminant cause repulsion between the head group of surfactant molecule and the soil particles, thereby, promoting the separation of the contaminant from soil particles. Secondly, micellar solubilization is the main mechanism. Surfactant-enhanced solubilization results in contaminant partitioning into the hydrophobic core of surfactant micelles. Thus, concentration well above the CMC is necessary for this enhancement to be significant. However, the water soubilization capacity of surfactant in soil-water system is somewhat different from that in solution system. Many factors such as inorganic salts (existing in soil and groundwater), adsorption of surfactant onto soil particles and precipitation of anionic surfactant by hard water (i.e containing Ca^{2+}, Mg^{2+}) could significantly affect the solubilization efficiency of surfactant. Na^{+}, Mg^{2+} and Ca^{2+} could increase the apparent solubility of chlorobenzene in the mixed SDS-TW80 solutions[25]. In the presence of anionic surfactant (SDS), the adsorption of nonionic surfactant (Triton X-100) onto soil matrix decreased while the precipitation of SDS also decreased in the presence of TX100[16]. Therefore, the mixing of anionic and nonionic surfactants was conductive to solubilizing and washing organic contaminants. The results from a few researches also demonstrated this conclusion[27,28]. Laboratory experimental results showed that the sorption of TX100 onto soils was severely restricted in the presence of SDS in batch and column systems and decreased with the increasing mass fraction of SDS in mixed surfactant solutions. The enhancing solubilization of phenanthrene by SDS-TX100 was greater than that by individual surfactant[28]. The column flushing and batch washing showed that desorption efficiencies for phenanthrene-contaminated soil by SDS-TX100 was greater than that by individual surfactant[27,28].

CONCLUSION

The work presented here demonstrates that the SDS-Brij 35 at mass ratios of 1:1 and 1:3 enhanced the aqueous solubility of chlorobenzene to a much greater extent than single SDS or single Brij35. In soil washing, the water phase concentrations of clorobenzene increased with the initial concentration of surfactants at large and varied with the kinds of surfactant and ratios. The mixed anionic-nonionic surfactants at a given ratio exhibited a relative high washing efficiency while single ones did poorly. This paper indicated that the mixed anionic-nonionic surfactant could be an alternative ways to clean up the soils and groundwater contaminated by chlorinated solvents.

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