Mixed surfactant washing of petroleum contaminants from the soils and sediments in the unsaturated zone

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Abstract: A laboratory study was conducted to evaluate the suitability of a mixed surfactant for washing oil from soils in the unsaturated zone. The commercial surfactant used for making mixed surfactant were alcohol polyethoxylate (AEO-9, nonionic) and sodium alcohol polyethoxylated ethers sulfate (AES, anionic). Based on the properties (critical micelle concentration, hydrophilic/lipophilic balance and surface tension) of individual surfactants and the mixed surfactant, the preferred composition of an aqueous mixed surfactant solution was determined which consisted of 0.5% AEO-9 and 0.1% AES. The batch washing experiments have shown that the removal efficiency of oil from soils with mixed surfactant was higher than that with individual surfactants. Soil column washing results have shown that the sequence of oil removal efficiency was mixed surfactant (0.5% AEO-9 and 0.1% AES)>AEO-9 (0.1%)>AES (0.2%)>water, and the ratio was 1:0.84:0.66:0.06. Biodegradation experiments by growth cells and resting cells were carried out to evaluate the environmental acceptability of the test surfactants. The results have shown that the surfactants were able to serve as sole carbon source for strains *Pseudomonos sp.* 52 and *Weeksella sp.* 6 which were isolated from petroleum contaminated soil. More than 90% of the parent mixed surfactants disappeared in two weeks under growth cell conditions.
Key words: surfactant; petroleum contaminants; the unsaturated zone; remediation
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Introduction

In recent years, remediation of petroleum-contaminated groundwater and soil has attracted much attention of scientists in various countries. Among the methods proposed for cleaning the contaminants in the environment (Calabrese, 1991), surfactant-enhanced washing has been studied and satisfactory results have been reported (Pennell, 1993; Abdul, 1992). Column washing studies showed that more than 85% of PCBs were removed from soil after 105 pore volume washings (Abdul, 1994). However, the precipitation, sorption and formation of coacervate phases in soil lead to the reduction of the activity of the cleaning agents and affects the costs of remediation. Rouse and Satatinl (Rouse, 1993) demonstrated that disulfonates were significantly less susceptible to precipitation and sorption than monosulfonates. Furthermore, it is hypothesized that mixed surfactants will exhibit lower losses in the subsurface as compared to individual surfactants while maintaining high solubilization, and using mixed surfactants has been suggested for subsurface remediation (West, 1992).

The keys to successful application of mixed surfactants reside in the prediction of the behavior and ultimate fate of these surfactants in the environment. Therefore, this research is aimed at: (1) determining the proper composition of a nonionic-anionic mixed surfactant and, (2) comparing the washing efficiency of individual surfactants and mixed surfactant for petroleum contaminants from the soils of unsaturated zone and (3) clarifying environmental behavior and ultimate fate of these surfactants including the biodegradability and sorption.

1   Materials and methods

1.1   Sampling

Samples of soil and sediments in the unsaturated zone in the vicinity of a petroleum-contaminated site in the central part of Shandong Province of China were collected including brown soil (alfisol, 1# soil) and the subsurface Quaternary deposits of yellow clay (2# sediment) and red clay (3# sediment). Physical and chemical properties of the samples were analyzed (Table 1).

Table 1   Physical and chemical properties of soil and sediments

Soil and sediments	Clay content, <0.001mm, 100%	Texture	pH	Organic content, 100%
1# soil	20.8	Silt	8.3	0.55
2# sediment	71.3	Clay	7.9	0.29
3# sediment	90.0	Clay	7.7	0.30

1.2   Surfactant selection

A previous study had been carried out to select surfactants from 20 commercial products of three categories: (1) ethoxylated alcohol; (2) ethoxylated nonylphenol; (3) sulfate (Zhu, 1996). The selection was based on the solubility, emulsification, critical micelle concentration (cmc) and their effects on soil dispersion. According to the experimental results, AEO-9 and AES were relatively suitable for oil clean-up. The properties of these two surfactants are shown in Table 2. AEO-9 and AES were used to make mixed surfactant for this study.

Table 2   The properties of the test surfactants

Surfactant commercial name	Chemical name	Nonionic(N) anionic (A)	Molecular formula	HLB	pH water solution	cmc, %	Lowest surface tension, 10^3N/m
AEO-9	Alcohol polyethoxylate	N	$RO(CH_2CH_2O)_9H$, $R=C_{10}-C_{13}$	11	7—8	0.073	31
AES	Sodium alcohol polyethoxylated ethers sulfate	A	$RO(CH_2CH_2O)_nOSO_3Na$, $R=C_{12}-C_{18}$, $n=2-4$	13	7.5—8.5	0.1	40.9

1.3   Washing experiments

Air dried soil and sediments were grounded, passed through an 0.84 mm sieve and treated with oil (the properties are shown in Table 3), so as to reach the concentration of 10000 mg/kg (oil/soil). Washing experiments were carried out by the following procedures.

Table 3   Properties of oil used in the experiment

Physical properties	
Viscosity (kinematic), 100℃	12.5—16.3 mm²/s
Flash point	>210℃
Solidifying point	< -20℃
Water solubility, 15℃	<40 mg/L
Composition	Approximate percentage
Hydrocarbon	90%

1.3.1   Batch washing

In these washing studies, 50 ml aqueous surfactant solution was added to 5g contaminated soil in a beaker and stirred on a magnetic stirrer for 1h. After settling for 30 minutes, the supernatant was decanted and analyzed for oil concentration, then the amount of the washed oil was calculated. Duplicate experiments were conducted.

1.3.2   Column washing

In these studies, 1.3 kg contaminated soil with the oil concentration of 10000 mg/kg (oil/soil) was packed into a plastic column which was 6 cm in diameter and 50 cm in height with broken stone at the bottom as filters. The level of surfactant solution was adjusted to maintain the cleaning agent passing through the soil column at a rate of 0.5 ml/min. Then, the effluent was collected and analyzed. Most of the column washing experiments were carried out at 25℃, however, in order to study the effect of temperature on the oil removal efficiency, one specific column washing experiment was carried out for mixed surfactant washing at 17℃.

In the washing tests, oil concentrations of the supernatant (batch washing tests) and effluent (column washing tests) were analyzed using the standard method (National Environmental Protection Agency of China, 1989). Oil in the solution was extracted with benzinum for two times, and the water phase was discarded. Tannic acid was used to eliminate the emulsion in the benzinum phase caused by nonionic surfactant (Zhu, 1996). When mixed surfactant existed in the solution, sulfuric acid was added to the organic phase after the addition of tannic acid to eliminate the emulsion caused by nonionic and anionic surfactants. Then oil concentration in the extraction was determined by measuring the absorbency at 225 nm wave length with a UV spectrophotometer (DU-8B).

1.4   Sorption experiments

2g of soil samples was added to each of 40 ml surfactant solution with concentrations in the range of 0 to 2.5% in the beaker and stirred on a magnetic stirrer for 4h at a constant temperature. After settling for 30 minutes, the supernatant was decanted and analyzed for surfactant concentration through measuring the surface tension of solution on the basis that surface tension decreases with the increase of surfactant concentration within the range of cmc.

1.5   Biodegradation experiments

1.5.1   Media

The synthetic media with the following constituents were used in the experiments: $K_2HPO_4 \cdot 3H_2O$ (0.1 g/L); KH_2PO_4(0.1 g/L), ammonium acetate (0.1 g/L), $MgSO_4 \cdot 7H_2O$ (0.005 g/L), $CaCl_2$(0.002 g/L), $FeCl_3$ and a certain amount of surfactants. The media were sterilized by autoclaving. Phosphate buffer was prepared by mixing solutions of 0.067 mol/L Na_2HPO_4 and 0.067 mol/L KH_2PO_4 to obtain the required pH.

1.5.2   Growth cell experiments

Bacteria, *Pseudomonos sp*. 52 (P. Strain 52) and *Weeksella sp. strain* 6 (W. Strain 6), possessing petroleum-degrading and surfactant-degrading capability, were isolated from petroleum-contaminated soils. The strains were transferred into fresh media with containing test surfactants for adaptation. They were acclimated in 50 ml basic media certain concentration of surfactant and incubated for 48h. Their growth was monitored by measuring the optical density of the culture liquid at 460 nm with a spectrophotometer (721 model). In this experiment, factors influencing the surfactant biodegradation including pH, temperature and surfactant concentration were studied. The effect of pH was tested between pH 5 and pH 9 at 28℃ with the media containing 5000 mg/L surfactant. The influence of temperature (5℃, 15℃, 28℃ and 37℃) was examined at pH 7. The effect of surfactant concentration (5000 mg/L, 10000 mg/L, 20000 mg/L and 30000 mg/L) in the media was determined at pH 7 and 28℃. Controls of the steriled media containing the surfactant ran as blanks.

1.5.3   Resting cell experiments

Resting cell experiments were conducted for AEO-9 and mixed surfactant. The strains were grown at 28℃ in 250 ml Erlenmeyer flask containing 50 ml media with 5000 mg/L AEO-9 or with mixed surfactant (1000 mg/L AEO-9 and 200 mg/L AES). The cells were harvested at the exponential growth phase by centrifugation at a rate of 10000 r/min for 30 minutes and washed

three times with 0.067 mol/L phosphate buffer solution (pH 7). The cells were then suspended in 10 ml phosphate buffer solution containing 5000 mg/L AEO-9 or the mixed surfactants and were incubated at 30℃ for a specific time period. The cells were removed by centrifugation at a rate of 10000 r/min for 20 minutes for analysis of the substrate (surfactant) in the supernatant.

In the biodegradation experiments, surfactant concentrations were determined by measuring surface tension. Therefore, the biodegradation efficiency implied the disappearance of parent compound.

2   Results and discussion

2.1   Determination of the preferred composition of the mixed surfactant

Surfactants may be precipitated and/or be absorbed to the solid phase during soil washing, which tends to reduce the cleaning efficiency. The adsorption of anionic surfactant is generally less than that of the nonionic ones because most soil colloids possess negative charges and they are subjected to losses by precipitation. Nonionic surfactants are not easily precipitated, but they are also subjected to sorptive losses, because the carbon atom in the polyethoxyl radical of surfactant tend to bound with soil colloid (Zhao, 1985). However, the precipitation and sorption tendency of surfactant can be reduced by using mixture of nonionic and anionic surfactants. In this study, an approach was made to determine the preferred composition of surfactant mixture of nonionic and anionic surfactants (AEO-9 and AES). Their optimal proportions in the mixture depend on the following factors (Zhao, 1985):

(1) The hydrophilic/lipophilic balance (HLB) of mixed surfactant

$$HLB_{mix} = X_1 \cdot Y_1\% + X_2 \cdot Y_2\% .$$

X_1, X_2 are the HLB of the two surfactants to be mixed; Y_1, Y_2 are the proportions of the two surfactants to be mixed.

According to the previous study (Zhao, 1985), the optimal HLB value of surfactant for oil emulsification is about 10—12. Since the HLB of AEO-9 is 11, and that of AES is 13, the proportion of AES should be less than 50%.

(2) The cmc of mixed surfactant

$$\frac{1}{C_{mix}} = \frac{Y_1}{C_1} + \frac{Y_2}{C_2},$$

C_1, C_2 are the cmc of the two surfactants to be mixed; Y_1, Y_2 are the mole proportion of the two surfactants to be mixed.

In order to obtain high washing efficiency, the cmc of the surfactant mixture should be as low as possible. Since the cmc of AEO-9 is lower than that of AES, the proportion of AEO-9 in the mixture should be higher than that of AES.

(3) Surface tension of mixed surfactant

Surface tension of mixed surfactant should be as low as possible. Based on factor (1) and (2), a series of mixed surfactant solutions with various mixed proportions was prepared and analyzed (Fig.1). The results showed that minimum surface tension of mixed solution occurred when the proportion of AEO-9 to AES was 5:1 and the mixed solution formed Winsor Type I systems (Zhao, 1985). Therefore, taking the previous experimental results into
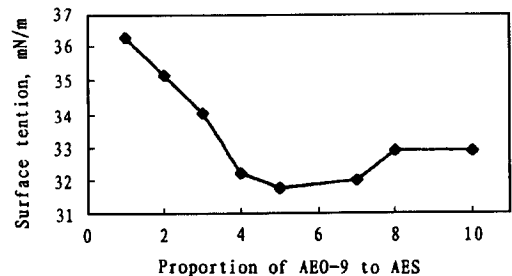

Fig. 1   Surface tension curve of surfactant solution

account, i.e., the concentration of surfactant solution with the best suitability for oil washing was 1% for AEO-9 and 0.2% for AES (Zhu, 1996), it was determined that the concentration of AEO-9 was 0.5% and AES was 0.1% in the surfactant mixture. This mixture was used to conduct the following experiments.

2.2 Washing experiments

2.2.1 Batch washing experiments

The washing efficiency of the surfactant solution was much higher than that of water (Table 4). The oil removal efficiencies of 0.2% AES, 1% AEO-9 and mixed surfactant (0.1% AES and 0.5% AEO-9) were about two times, three times and five times of that of water respectively. The removal efficiency of oil from the three soils (sediments) using mixed surfactant was higher than that using single type surfactant. The sequence of that was mixed surfactant > AEO-9 > AES > water, and the ratio was 1:0.52:0.41:0.04. If the concentration of AES decreases from 0.2% to 0.1%, and the concentration of AEO-9 decreases from 1% to 0.5% as their concentration in the mixed surfactant, their oil removal efficiencies will decrease coincidently. So both the oil removal efficiencies of 0.5% AEO-9 and 0.1% AES will be much less than that of the mixed surfactant.

Table 4   Removal efficiency of batch washing ($T = 25°C$)

Washing solutions	0.2% AES		1% AEO-9		0.5% AEO-9 0.1% AES		Water	
	Washing efficiency*	Standard deviation	Washing efficiency*	Standard deviation*	Washing efficiency*	Standard deviation	Washing efficiency*	Standard deviation
1# soil, %	30.8	3.02	42.3	2.56	75.1	2.78	3.14	1.06
2# sediment, %	28.0	2.03	35.6	2.03	68.2	3.07	2.94	0.92
3# sediment, %	3.01	1.01	9.24	0.350	12.7	0.23	1.60	0.61

* average of washing efficiency(%)

The removal efficiency of oil decreased with increased clay content in the material of the unsaturated zone. When the clay content of the material was 20.8%, the removal efficiency with mixed surfactant was 75.1%, and it was 12.7% while the clay content was 90%. Therefore, oil in the clay is more difficult to remove than in sandy soils.
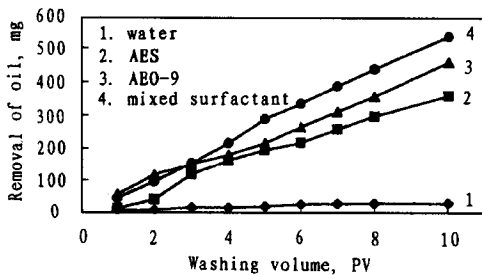
2.2.2 Column washing experiments

Fig.2   Soil column washing curve

When the temperature was 25°C, the sequence of washing efficiency was mixed surfactant > AEO-9 > AES > water, and the ratio was 1:0.84:0.66: 0.06. This was different from the ratio observed in the batch studies (1:0.52:0.41:0.04). Fig.2 shows the amount of oil removed from the soil column as a function of pore volume washing. 0.542g (4.2% of the total oil in the soil column) was removed by the mixed surfactant solution in 10 pore volume washings, while 0.464g oil (3.5%) and 0.361g oil (2.7%) was removed by 1% AEO-9 and 0.2% AES solution in 10 pore volume washings respectively. When the temperature was 17°C, 0.482g (3.7%) oil was removed by mixed surfactant solution in 10 pore volume washings, which was less than the removal efficiency (4.2%) at 25°C. The efficiencies of all the column washing were much lower than that of the corresponding batch washing.

2.3 Factors influencing oil removal efficiency

Properties of surfactants and environmental characteristics both influence the removal efficiency of oil. The former mainly include surface tension, *HLB*, cmc and solubility. The latter imply soil properties, sorption of surfactant on soils, temperature and the flow velocity of

surfactant solution. The fact that removal efficiency of oil was higher in 1# soil than in 3# sediment results from the lower clay content in 1# soil. The main reason of higher washing efficiency of oil by mixed surfactant than that by nonionic surfactant (AEO-9) was that the adsorption of the former on soil(sediment) was less than that of the latter. As shown in Fig. 3, the sorption of AEO-9 on 3# sediment and 2# sediment respectively fits to the Freundlich isotherm (1) and (2), and the sorption of mixed surfactant on 2# sediment fits to the Langmuir isotherm (3).
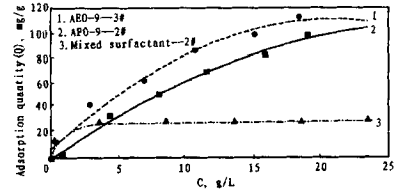
Fig. 3 Adsorption curves of surfactants on soils

$$Q = 10^{1.368}C^{0.554} \quad R^2 = 0.9920, \tag{1}$$

$$Q = 10^{0.526}C^{1.184} \quad R^2 = 0.9846, \tag{2}$$

$$Q = \frac{118.123C}{1 + 3.840C} \quad R^2 = 0.9968, \tag{3}$$

in which Q is the adsorption quantity, mg/g; C the surfactant concentration, g/L; R^2 the coefficient of determination; $T = 20°C$.

In addition, the temperature is an important factor influencing washing efficiency. When the temperature raises, the space in micella where solubilization takes place enlarges due to the enhanced thermal motion. Furthermore, the hydration of polyethoxyl decreases which enhances the formation of micella (Zhao, 1985). Therefore, increased temperature can promote the solubility of surfactants.

2.4 Biodegradation of test surfactant
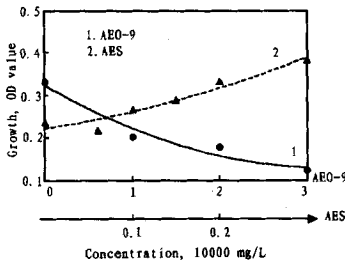### 2.4.1 Factors influencing surfactant biodegradation

Fig. 4 The influence of various surfactants on the growth of P. strain 52

It was observed that the two strains of bacteria were able to use AEO-9 and AES as sole carbon source and adapted to a wide range of temperature and pH. With AEO-9 as carbon source, the optimal growth temperature for P. strain 52 and W. strain 6 were all at 30°C. Good growth was observed between 20°C—37°C, and weak growth was observed between 5°C—15°C. The optimal initial pH was 9 and 7 for W. strain 6 and P. strain 52 respectively. As shown in Fig. 4, after being incubated for 48h, P. strain 52 could grow well in the media containing 30000 mg/L AEO-9, and the growth was promoted by the increase of AEO-9 concentration but inhibited by that of AES. The growth of P. strain 52 as a function of surfactant concentration fits to multinomial formula, which were expressed as formula (4) for AEO-9 and formula (5) for AES.

$$Y = 0.0078C^2 + 0.0317C + 0.226 \quad R^2 = 0.9343, \tag{4}$$

$$Y = 0.0188C^2 - 0.1218C + 0.328 \quad R^2 = 0.9617, \tag{5}$$

in which Y is the growth of strain (OD value); C is the concentration of surfactant, the unit is 10000 mg/L in (4) and 1000 mg/L in (5) respectively; R^2 is coefficient of determination.

2.4.2 Degradation efficiency of surfactants by bacteria
2.4.2.1 Growth cells

The growth of bacteria and degradation of surfactants were monitored continuously in the course of incubation under optimal conditions. It was found that the growth rates of the two strains utilizing AEO-9 as sole carbon source were different. The growth of P. strain 52 was faster than that of W. strain 6 in the initial period but slower in the later period. Corresponding with the fact, the required time for 50% removal of the test surfactant (5000 mg/L) was 4h for P. strain 52 and

8h for W. strain 6. Surfactant complex containing AEO-9 5000 mg/L and AES 1000 mg/L was inoculated with the mixture of P. strain 52 and W. strain 6 and incubated at 28℃ for two weeks. The results showed that 93% of the mixed surfactant could be degraded within two weeks. It is obvious that these two strains could degrade not only individual surfactants but also mixed surfactants.
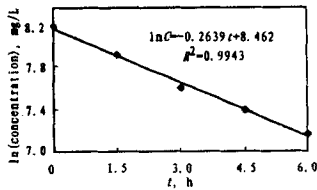
2.4.2.2 Resting cells

Fig.5   Kinetic curve of AEO-9 biodegradation

When the initial concentration of AEO-9 was 5000 mg/L, 50% of the surfactant could be degraded by resting cells of P. strain 52 with a cell density of 200 mg/ml within 3.9h under the optimal condition (Fig.5). When the initial concentration of mixed surfactant was 1000 mg/L for AEO-9 and 200 mg/L for AES, 50% of the mixed surfactant could be degraded within 4.5h under the same conditions. The results indicated that the surfactant-degrading bacteria could not only utilize surfactants as sole carbon source for growth but also produce active enzyme degrading it in the resting state.

3   Conclusion

The mixed surfactant has a higher washing efficiency than either nonionic (AEO-9) or anionic (AES) surfactant alone because it has a preferred *HLB* for oil emulsification, a lower cmc level and weaker tendency of adsorption. In addition, it could be degraded by the strains derived from the petroleum contaminated soil. Therefore, it is environmentally acceptable.

Surfactants are able to solubilize hydrocarbon contaminants in soil and sediments of the unsaturated zone and enhance their mobilization, leading to higher probability for microorganisms to attach and to degrade contaminants. Moreover, the surfactants can strength the osmosis of microorganism membrane, causing the acceleration of biodegradation of hydrocarbon contaminants. It is proposed that the combination of surfactant-enhanced washing and biodegradation can be adopted in the remediation of petroleum contamination in the unsaturated zone. When a large portion of petroleum in the contaminated zone has been removed with surfactants, microorganism should be used to degrade the residual surfactants and petroleum.

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