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Effect of Surfactant Concentration and pH on Surfactant-Enhanced Remediation in Iowa Soil Contaminated by TCB

Dal-Heui Lee[1]* and Robert D. Cody[2]

[1]*Korea Biosystems, KIST Venture Town 945B, Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Korea*
[2]*Department of Geological and Atmospheric Sciences, 253 Science I, Iowa State University, Ames, IA, USA 50011*

삼염화벤젠으로 오염된 아이오와토양의 복원시 계면활성제의 농도와 pH의 영향

이달희[1]* · Robert D. Cody[2]

[1]한국바이오시스템, [2]미국 아이오와 주립대학교 지구대기과학과

오염된 토양의 복원에서 계면 활성제 용액의 조건에 따른 영향을 조사 하기 위하여 주상실험이 실행되었다. 계면 활성제 용액의 조건에는 농도와 pH가 선택되었으며 모델 소수성 유기화합물은 삼염화벤젠, 그리고 DOSL과 OPEE 계면 활성제가 본 연구에 사용 되었다. 또한 미국의 아이오와 토양이 본 연구에 이용 되었다. 실험 결과, 계면 활성제 용액의 최적 조건은 농도 4%(v/v), pH 10 이며, 이러한 최적 조건이 적용될 때 93-98%의 삼염화벤젠이 오염된 토양으로부터 회수 되었다. 규명된 최적 조건은 계면 활성제를 이용하여 삼염화벤젠으로 오염된 토양 복원에 유용하게 사용 될 수 있다.

주요어 : 계면활성제, 삼염화벤젠, 복원, 최적조건, 토양

Column tests were carried out to examine the effect of surfactant solution conditions on surfactant-enhanced remediation of contaminated soil. The selected conditions of the surfactant solution were concentration and pH. 1,2,4-trichlorobenzene (TCB) was chosen as the model hydrophobic organic substances. Sodium diphenyl oxide disulfonate (DOSL) and octylphenoxypoly ethoxyethanol (OPEE) surfactants were selected for this study. Two Iowa soils, Fruitfield sand and Webster clay loam, were leached with surfactant solution. The test results revealed that an optimum condition was achieved for 4 %(v/v) of concentration and 10 of pH, respectively. The maximum recoveries of added TCB (93-98%) were obtained when optimal conditions of each surfactant solution parameter were simultaneously met. The optimum conditions of these parameters may be useful for surfactant-assisted remediation in soil contaminated by TCB.

Key words : surfactant, TCB, Remediation, Optimum conditions, Soil

1. INTRODUCTION

Hydrophobic organic compounds enter the subsurface as a separate organic phase or nonaqueous phase liquids (NAPLs) (Pennell *et al.*, 1997; Deshpande *et al.*, 2000). Extensive research on soil remediation has demonstrated that surfactant (surface active agents) flushing is a viable alternative for improving the efficiency of traditional remediation (Chen and Knox, 1997; Sabatini *et al.*, 1997; Lee *et al.*, 2001). These studies showed that aqueous surfactant solutions significantly enhanced the removal of NAPL from soil. However, a major concern relative to the effectiveness of a surfactant-enhanced remediation project is surfactant losses. Twin head group ionic surfactants seem to be less susceptible than single head group surfactants to precipitation losses due to increased their solubility and steric constraints (Rouse *et al.*, 1993; Lee, 1999). Also, Lee *et al.* (2001) reported that maintaining a high pH sur-

*Corresponding author: dalheui@hanmail.net

factant solution in surfactant-enhanced remediation is desirable for efficient removal of hydrophobic organic from contaminated soils. They showed that the effect of NaOH in changing effectiveness is not due to Na^+ counter-ion effects, but rather to the OH^- based on experimental results.

The hypotheses of this research were (i) optimization of surfactant concentration and pH for efficient hydrophobic organic removal is an essential for remediation of contaminated soil and (ii) surfactants with twin head groups are more effective than single head group surfactants at the same concentration. Therefore, the objective of this study was to examine surfactant-enhanced TCB dissolution based on surfactant solution parameters (concentration, pH).

2. MATERIALS AND METHODS

2.1. Soil selection

Two Iowa soils, Fruitfield sand and Webster clay loam, used for this study were obtained from the Department of Agronomy at Iowa State University (Gonzalez and Ukrainczyk, 1996). Fruitfield soil is classified as a sand, and consists of 86.3% sand, 10% silt, 3.7% clay, and 0.2% organic carbon with the measured soil pH of 6.2. Webster soil is classified as a clay loam, and consists of 22.9% sand, 43% silt, 34.1% clay, and 0.61% organic carbon with the measured soil pH of 8.2. Prior to use they were air-dried and passed through a 2 mm sieve.

2.2. Contaminant selection

Spectrophotometric grade TCB ($C_6H_3Cl_3$) was obtained from Aldrich Chemical (St. Louis, Missouri, USA). TCB is often detected in contaminated soil (Joshi and Lee, 1996). The characteristics of TCB are listed in Table 1.

Table 1. Characteristics of TCB.

Name	TCB
Formula	$C_6H_3Cl_3$
Molecular Weight (g/mol)	181.4
Liquid Density (g/cm^3)	1.454
Aqueous Solubility[a] (mg/L)	48.8
Log Octanol-Water Partition Coefficient[b]	4.02
Liquid-Air Interfacial Tension (dyne/cm)	25
Liquid-Water Interfacial Tension (dyne/cm)	45
Total Gas Density (kg/m^3)	1.87
Viscosity (cP)	0.83

[a]=20°C-25°C, Atmospheric Pressure
[b]=from EPA Technical Fact Sheets, 1988
Data come from manufacturers

2.3. Surfactant selection

Sodium diphenyl oxide disulfonate (DOSL, trade name Dowfax 8390), and Octylphenoxypoly ethoxyethanol (OPEE, trade name Triton X100) surfactants were selected for this study. Anionic surfactant DOSL was selected for soil flushing procedures because of its lower degree of adsorption on soil (Knox *et al.*, 1997; Deshpande *et al.*, 1999). DOSL meets criteria as an indirect food additive under FDA (Food and Drug Administration) Regulation 21CFR 178.3400. Nonionic surfactant OPEE is non-food additive surfactant and was also selected in this study in order to compare its effectiveness to the food additive surfactant. DOSL is a double head surfactant and OPEE is a single head surfactant. They were obtained from Dowfax Chemical (Midland, Michigan, USA) and Fisher Scientific (Chicago, Illinois, USA), respectively. Characteristics of the surfactants used are listed in Table 2.

2.4. Column tests

Column tests were carried out to examine the effect of surfactant solution conditions (concentration and pH) on surfactant-enhanced remediation. The procedure of column test was the same as the previous study (Lee *et al.*, 2001) except variations in surfactant solution parameters. A porous ceramic plate was placed beneath the soil column to prevent loss of soil during leaching.

Table 2. The characteristics of used surfactants.

Trade Name	DOSL (Dowfax 8390)	OPEE (Triton X100)
Chemical Name	Sodium Diphenyl Oxide Disulfonate	Octylphenoxypoly Ethoxyethanol
Molecular Weight	642	624
[a]HLB	[c]N/A	13
[b]CMC (Mm)	0.5	N/A
Molecular Formula	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	$C_{33}H_{60}O_{10}$
Type	Anionic	Nonionic

[a]HLB = Hydrophile-Lipophile Balance
[b]CMC = Critical Micelle Concentration
[c]N/A = Not Available

Compaction of the dry soil in 0.5 cm layers was standardized by tapping the side of the column 25 times; this degree of compaction minimizes preferential liquid channeling (Martel and Gelinas, 1996). The Fruitfield soil column length was 15.4 cm, soil column radius was 2.3 cm, and the packed soil had a bulk density of 1.36 g/cm^3 and porosity of 0.49. Pore volume of this column was about 126 cm^3. The Webster soil column length was 14.7 cm, soil column radius was 3.2 cm, and the packed soil had a bulk density of 1.10 g/cm^3 and porosity of 0.58. Pore volume of this column was about 223 cm^3.

After a column was packed, deionized water was pumped at a rate of 3 mL/min into the column for three hours to saturate the soil. The contaminant (5 mL of TCB) was then injected by long syringe into the middle of the column. This method of contamination is closely analogous to field contamination in which a mass of contaminant leaches into the subsurface from a localized contaminant source such as leaking underground storage tank. Ten pore volumes of surfactant solutions were then pumped to the top of the column with various surfactant solution conditions. Each treatment was evaluated in duplicate columns.

Surfactant solution concentration effects : In this study, surfactant concentrations ranging from 1%(v/v) to 8%(v/v) were tested to determine the one which gives the best removal efficiency. Tested the range of surfactant concentrations were selected based on cost effectiveness (Rouse *et al.*, 1993). Surfactant concentrations used for the column tests were 1, 2, 4, 6, 8%(v/v) for fixed solution pH 8 and flow rate of 4 mL/min. Column tests performed at a room temperature of 22°C. This test was essential for reducing cost in surfactant-assisted remediation.

Surfactant solution pH effects : In order to evaluate the effects of surfactant solution pH on surfactant-based remediation, the pH of surfactant solutions was varied by adjusting pH with a 10% NaOH or HCl solution (Lee, 1999). The surfactant of 4%(v/v) DOSL had an unadjusted pH of 8.7. The pH values of the aqueous surfactant solution were then adjusted to 7.2, 10, 11, 12. The unadjusted pH values of 4%(v/v) OPEE was 7.2. The pH values of the 4%(v/v) OPEE was adjusted to 8.7, 10, 11, 12. Tested the range of surfactant pH levels were selected based on prior studies (Lee, 1999). Concentration of surfactant used was 4%(v/v) based on the results of case 1 for constant solution flow rate of 4 mL/min. Column tests were performed at a room temperature of 22°C.

2.5. Chemical analysis

Analysis of TCB was conducted by solvent extraction and gas chromatography (Hewlett Packard Model 5890 series II) (Lee, 1999). 1,2-dichlorobenzene was used as an internal reference standard. Prior to the analysis of sample extracts, the response factor and linearity of detection for the internal standard and contaminant were determined. After having calculated the response factor, a calibration graph was prepared. During analysis of a sample, the sample mass or volume was determined and a known amount of 1,2-dichlorobenzene was added to the sample. The quantitative determination of contaminant concentration was based on these internal standard reference compounds. New standard curves were prepared after approximately 15-20 injections. The standard curves were constructed using concentrations ranging from 26.8 to 71.6 mg/L for TCB. Solutions were diluted if necessary to fit within the range of this line.

3. RESULTS AND DISCUSSION

3.1. Surfactant solution concentration

As expected, the lowest concentration of 1 %(v/v) gave the least removal efficiency (Fig. 1 and Table 3). Removal efficiency of DOSL and OPEE increased almost linearly from 1%(v/v) to 4%(v/v) and then leveled off (Fig. 1). For DOSL and

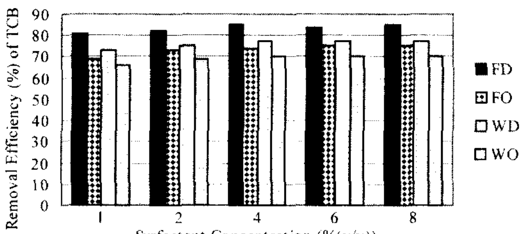

Fig. 1. Effect of surfactant concentration on removal of TCB, FD: DOSL with Fruitfield soil; FO: OPEE with Fruitfield soil; WD: DOSL with Webster soil; WO: OPEE with Webster soil.

OPEE, removal efficiency was almost same between 6%(v/v) and 8%(v/v). Surfactant solutions may undergo a phase change at high concentration range so that the system may not be isotropic (Joshi and Lee, 1996). For example, ionic or nonionic surfactants may form liquid crystals which clog pores at high concentration (Rosen, 1989). However, we did not observe liquid crystals in this system. Based on these results, a surfactant concentration of 4%(v/v) was found to give the best removal efficiency. For non-food grade OPEE, 4%(v/v) of surfactant also gave the highest removal efficiency, while concentration of 2%(v/v) gave only a slight decrease in effectiveness (Fig. 1 and Table 3). This result gives the guidance for cost effectiveness in surfactant-assisted field remediation.

3.2. Surfactant solution pH

The pH of effluent solution was the same as the influent pH to the column throughout the each column tests. Fig. 2 and Table 3 show the variation of the removal efficiency with surfactant solution pH. For DOSL and OPEE surfactants a maximum removal of TCB was obtained at pH 10. The increased removal efficiency (%) of TCB was 7% for DOSL in Fruitfield sandy soil, and was 19% for DOSL in Webster clay loam soil when the pH varied from 7.2 to 10 (Table 3).

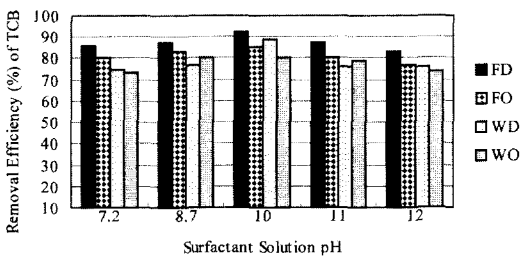

Fig. 2. Effect of surfactant pH on removal of TCB, FD: DOSL with Fruitfield soil; FO: OPEE with Fruitfield soil; WD: DOSL with Webster soil; WO: OPEE with Webster soil.

These increased removal efficiency (%) was less than that observed for Ottawa sand column tests (Lee *et al.*, 2001). Laboratory experiments showed the effectiveness of highly alkaline surfactant solutions in leaching toluene from Ottawa sand. In previous study (Lee *et al.*, 2001), much greater effectiveness was observed using surfactant solutions containing NaOH. In that study we found that NaOH increased the effectiveness of a nonionic surfactant (POE, trade name Pluronic L44) by 50%, an anionic surfactant (TDCA, trade name Sandopan JA36) by 57%, and water by 10% in a pure sand column. Another research results showed that a maximum removal of 84% of TCB occurred at pH 10 with NaOH (Harwell, 1992). The relatively high unexpected loss of the compound from the soil could be attributed to volatilization of the compound during the test. Rosen (1989) and Harwell (1992) observed that micelle formation of surfactant is also enhanced by high pH conditions. Rosen (1989) showed that generally the higher pH, the lower surface tension of a surfactant solution. Near the higher end of the pH range (11-14) some of anionic sulphates and nonionic acid esters can begin to hydrolyze and lose activity (Rosen, 1989; Adeel and Luthy, 1995).

Rosen (1989) showed that micelle formation in surfactant solution was enhanced by high pH and the surface tension of surfactant solutions was decreased by high pH. Increased micelle formation in high pH and decreased surface tension of surfactant solution in high pH may have affected our results (Harwell, 1992). However, the cause of the lesser effect obtained from this study compared to Lees (1999) results might be attributed to the differences in model contaminants and soils. Hydrogen ion concentration in solution was an important factor in surfactant effectiveness (Rosen, 1989). The cause of the pH effect on an nonionic sur-

Table 3. Effect of surfactant solution parameters on removal efficiency (%) of TCB.

Soil	Surfactant	Concentration (%(v/v))					pH				
		1	2	4	6	8	7.2	8.7	10	11	12
Fruitfield Soil	DOSL	81	82	85	84	85	86	87	92	87	83
	OPEE	69	73	74	75	75	80	83	85	80	77
Webster Soil	DOSL	73	75	77	77	77	75	77	89	76	76
	OPEE	66	69	70	70	70	73	80	80	79	74

Table 4. TCB removal efficiency (%) in combination of optimal conditions[a].

Soil	Surfactant	TCB removal (%)
Fruitfield Soil	DOSL	98
	OPEE	95
Webster Soil	DOSL	94
	OPEE	93

[a]concentration=4%(v/v), pH=10, temperature=22°C, flowrate=4 mL/min

factant (OPEE) is unknown, but perhaps OPEE may contain minor amount of a charged molecular species (Lee *et al.*, 2001). Subsurface aquifers will rarely contain such high pH waters, and buffering of pH in surfactant solutions to pH 10 may prove difficult and expensive for many aquifers. If possible, however, maintaining a high pH surfactant solution in field remediation is desirable because it will enhance contaminant removal.

3.3. Soil column test at optimal surfactant solution conditions

Table 4 summarizes removal results for TCB at adjusted surfactant solution conditions. The adjusted surfactant solution was essential to have effect on TCB removal from contaminated soil. The maximum recoveries of added TCB (93-98%) were obtained for a surfactant concentration of 4%(v/v), surfactant solution pH 10 with a surfactant solution flow rate of 4 mL/min. The increased removal efficiency (%) by optimum conditions of TCB was 15% for DOSL with Fruitfield sandy soil. In addition, the increased removal efficiency (%) by optimum conditions of TCB was 22% for DOSL with Webster clay loam soil. This was a marked improvement compared to other research results (Deshpande *et al.*, 2000).

Based on results of all tests, DOSL can be a good candidate for surfactant-based soil remediation. In addition to the high percentage removal of TCB observed in our column experiments, DOSL has good solubilizing abilities for phenanthrene, naphthalene (Rouse *et al.*, 1993; Deshpande *et al.*, 2000). Effectiveness of DOSL may be due to exceptionally small adsorption of the twin-head sulfate polar heads onto soil particles, or to minor amounts of surfactant loss by precipitation with soil components (Rouse *et al.*, 1993; Deshpande *et al.*, 1999). Also, DOSL is relatively cheaper than other surfactants.

4. CONCLUSIONS

Surfactant solution conditions were found to have a significant effect on TCB removal from contaminated soil columns. The test results revealed that optimal range for each surfactant solution parameter was: (i) Surfactant solution concentration: 4%(v/v), (ii) Surfactant solution pH: 10, (iii) Surfactant solution temperature: 20°C, (iv) Surfactant solution flow rate: 4 mL/min. The maximum recoveries of added TCB (93-98%) were obtained when optimal conditions of each surfactant solution parameter were simultaneously met. The increased removal efficiency (%) by optimum conditions of TCB was 22% for DOSL with Webster clay loam soil. The results from this study may be useful for determining optimum condition of surfactant solution for surfactant-assisted remediation in soil contaminated by TCB.

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