

## Effect of Surfactant Solution pH on Surfactant-Assisted Remediation

Dal-Heui Lee<sup>1\*</sup> and Robert D. Cody<sup>2</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, Korea University, Anam-dong, Sungbuk-ku, Seoul 136-701, Korea

<sup>2</sup>Department of Geological and Atmospheric Sciences, 253 Science I, Iowa State University, Ames, IA 50011

### 계면활성제를 이용한 오염복원에 있어서 계면활성제 용액 pH의 효과

이달희<sup>1\*</sup> · Robert D. Cody<sup>2</sup>

<sup>1</sup>고려대학교 지구환경과학과, <sup>2</sup>아이오와 주립대학교 지질대기과학과

계면활성제를 이용한 오염복원에 있어서 제거효율에 영향을 주는 계면활성제 용액 pH의 최적 범위를 조사하기 위하여 주상실험이 수행되었다. 톨루엔과 1,2,4-trichlorobenzene이 소수성 유기화합물로서 선택되었다. 4%(v/v)의 sodium diphenyl oxide disulfonate(DOSL), trideceth-19-carboxylic acid(TDCA), octylphenoxypoly ethoxyethanol(OPEE)을 사용하여 두 종류의 아이오와 토양(Fruitfield sand, Webster clay loam)에 대한 용출실험을 수행하였다. 실험결과, 톨루엔과 1,2,4-trichlorobenzene의 최대 제거효율은 계면활성제 용액 pH 10에서 나타났고, Fruitfield 사질토양에서 DOSL을 이용한 경우 최대 제거효율은 각각 94%, 97%였다. Fruitfield 사질토양에서 DOSL을 사용한 경우, pH 조절에 의하여 증가된 톨루엔과 1,2,4-trichlorobenzene의 제거효율은 각각 16%와 20%였다. Webster clay loam에서 DOSL을 이용한 경우 최대 제거효율은 각각 89%, 93%였다. Webster clay loam에서 DOSL을 사용한 경우, pH 조절에 의하여 증가된 톨루엔과 1,2,4-trichlorobenzene의 제거효율은 각각 26%와 19%였다. 이러한 실험결과는 NAPLs로 오염된 토양을 복원하는데 있어서 계면활성제 용액의 pH를 높게 유지하는 것이 바람직하다는 것을 의미한다.

**주요어 :** 계면활성제, pH, 제거효율, 최적조건, 복원

Column tests were conducted to investigate the optimal condition of surfactant solution pH that can affect the removal efficiency in surfactant-assisted remediation. Toluene and 1,2,4-trichlorobenzene were chosen as the model hydrophobic substances. Two Iowa soils, Fruitfield sand and Webster clay loam, were leached with solutions of 4%(v/v) sodium diphenyl oxide disulfonate (DOSL, trade name Dowfax 8390), or 4%(v/v) trideceth-19-carboxylic acid (TDCA, trade name Sandopan JA36), or 4% (v/v) octylphenoxypoly ethoxyethanol (OPEE, trade name Triton X100). The test results revealed that a maximum removal of toluene and 1,2,4-trichlorobenzene was obtained at pH 10 of surfactant solution, and maximum recoveries of added toluene (94%) or 1,2,4-trichlorobenzene (97%) were obtained for DOSL surfactant solution in Fruitfield sandy soil column. Increased removal efficiency by pH control of both toluene and 1,2,4-trichlorobenzene was 16% and 20% for DOSL with Fruitfield sandy soil, respectively. In addition, the maximum recoveries of added toluene or 1,2,4-trichlorobenzene were 89% and 93% for DOSL surfactant solution in Webster clay loam soil column. The maximum increase of toluene and 1,2,4-trichlorobenzene removal was 26% and 19% for DOSL with Webster clay loam soil, respectively. These experimental results indicate that maintaining a high pH surfactant solution in surfactant-assisted remediation is desirable for efficient removal of NAPLs from contaminated soils.

**Key words :** surfactant, pH, removal efficiency, optimal condition, remediation

## 1. INTRODUCTION

Soil and groundwater contamination by hydrophobic organic substances has caused significant

concern in industrial areas. The aromatic fraction of petroleum products (benzene, toluene, and the xylene) is the single largest source of groundwater contamination, and evokes the most concern from an environmental point of view. Petroleum-based organic products enter the subsurface as a separate

\* Corresponding author: dalheui@korea.ac.kr

organic phase or nonaqueous phase liquid (NAPL). Under normal flow regimes, this NAPL phase is immobile and often represents a long-term source of aquifer contamination as it slowly dissolves into the groundwater (Pennell *et al.*, 1997).

Removal of NAPLs from contaminated soils often confronts with difficulties because they possess low solubilities and high interfacial tensions. Currently the common method for remediation of aquifers contaminated with hydrophobic organic substances is pump-and-treat. This method is neither effective nor economical (Sabatini *et al.*, 1997). Extensive researches on soil and groundwater remediation have demonstrated that surfactant (surface active agents) flushing is a viable alternative for improving the efficiency of pump-and-treat remediation (Chen and Knox, 1997; Knox *et al.*, 1997). These studies showed that aqueous surfactant solutions significantly enhanced the removal of NAPLs from soil and groundwater.

Surfactants are amphiphilic molecules with a hydrophobic portion and a polar hydrophilic head group. Surfactants may aid in remediation by decreasing the surface tension of the water and efficiently solubilizing or otherwise mobilizing NAPLs (Lee, 1997; Deshpande *et al.*, 1999). As the surfactant concentration increases, the surface tension of the solution decreases until the critical micelle concentration is reached. Remediation of aquifer contamination requires a combination of injection wells and withdrawal wells, which will continuously flood a contaminated zone with remediation solutions. At this time optimization of aqueous surfactant solution pH is one of the essential subjects for remediation of contaminated groundwater. More laboratory work is needed to understand the pH of surfactant solution affecting the removal of hydrophobic organic compounds. Therefore, the objective of this study is to evaluate the pH of surfactant solution that can affect the efficiency of maximum removal in surfactant-assisted remediation.

## 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

Reagent grade toluene was obtained from Fisher Scientific (Chicago, IL), and spectrophotometric grade 1,2,4-trichlorobenzene was obtained from Aldrich Chemical (St. Louis, MO). As a component of gasoline, toluene is one of the most common light NAPL contaminants in soil and groundwater. An aromatic hydrophobic 1,2,4-trichlorobenzene (TCB) was also chosen as the model contaminant of DNAPL (denser-than-water nonaqueous phase liquid) because it has been frequently detected in soil and groundwater contaminated at industrial sites.

### 2.3. Surfactant selection

4%(v/v) sodium diphenyl oxide disulfonate (DOSL, trade name Dowfax 8390), 4%(v/v) trideceth-19-carboxylic acid (TDCA, trade name Sandopan JA36), and 4%(v/v) octylphenoxypolyethoxyethanol (OPEE, trade name Triton X100) surfactants were selected for this study. Anionic surfactants (DOSL, TDCA) are usually chosen for soil flushing procedures because of their lower degree of adsorption on soil than that by cationic and nonionic surfactants, and their recoverability for reuse (Rouse *et al.*, 1993). DOSL meets criteria as an indirect food additive under FDA Regulation 21CFR 178.3400 and is rapidly biodegradable. TDCA and OPEE are non-food additive surfactant and are also selected in this study in order to compare its effectiveness to the food additive chemicals (Lee *et al.*, 2001). OPEE is a nonionic surfactant and is usually used for remediation research by other scientists. They were obtained from Dow Chemical, Sandoz Chemicals, Union Carbide, respectively. Characteristics of used surfactants are listed in Table 1.

### 2.4. Column tests with various surfactant solutions

Column tests were similar to those performed in

**Table 1.** The characteristics of used surfactants.

Trade Name	DOSL (Dowfax 8390)	TDCA (Sandopan JA36)	OPEE (Triton X100)
Chemical Name	Diphenyl Oxide Disulfonates	Trideceth-19-Carboxylic Acid	Octylphenoxypoly Ethoxyethano
Molecular Weight	642	N/A	624
<sup>a</sup> HLB	<sup>c</sup> N/A	14	13
<sup>b</sup> CMC (mM)	0.5	0.6	N/A
Molecular Formula	C <sub>16</sub> H <sub>33</sub> C <sub>12</sub> H <sub>7</sub> O(SO <sub>3</sub> Na) <sub>2</sub>	<sup>d</sup> M/S	C <sub>33</sub> H <sub>60</sub> O <sub>10</sub>
Type	Anionic	Anionic	Nonionic
Company	Dow Chemicals	Sandoz Chemicals	Union Carbide

<sup>a</sup>HLB=Hydrophile-Lipophile Balance<sup>b</sup>CMC=Critical Micelle Concentration<sup>c</sup>N/A=Not Available<sup>d</sup>M/S=Mixture in Sulfuric Acid

previous researches (Lee, 1997; Lee, 1999; Lee *et al.*, 2001) except that surfactant solution pH conditions varied as listed in Table 2. Glass wool and glass beads were placed at the column's base, and Fruitfield soil or Webster soil was placed over the beads, respectively. Compaction of the dry soil in 0.5cm 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<sup>3</sup> and porosity of 0.49. Pore volume of this column was about 126 cm<sup>3</sup>. 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<sup>3</sup> and porosity of 0.58. Pore volume of this column was about 223 cm<sup>3</sup>. 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 toluene or 1,2,4-trichlorobenzene) 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. Then ten pore volumes of 4%(v/v) surfactant solutions was pumped to the top of the column with various pH. All tests in this study were run duplicately.

In order to evaluate the effects of pH on surfactant-based remediation, the pH of surfactant

solutions was varied by adjusting pH with a 10% NaOH (2.5 M) solution. The surfactant 4% (v/v) DOSL had an unadjusted pH of 8.7. The pH values of the aqueous surfactant solution (4%(v/v) DOSL) were adjusted to 10, 11 (Table 2). The unadjusted pH values of 4%(v/v) TDCA and 4%(v/v) OPEE were 3 and 7.2, respectively. The pH values of the 4%(v/v) TDCA were adjusted to 7.2, 8.7, 10, 11 and pH values of the OPEE were adjusted to 8.7, 10, 11 (Table 2).

## 2.5. Chemical analysis

Analysis of toluene or 1,2,4-trichlorobenzene was conducted by solvent extraction and gas chromatography (Hewlett Packard Model 5890 series II) (Lee, 1999). Ethylbenzene or 1,2-dichloroben-

**Table 2.** pH value of 4%(v/v) surfactant solution based on added NaOH volume.

Surfactant	Volume (mL)	Added NaOH vol-ume (mL) <sup>a</sup>	Measured pH value of surfactant solution
DOSL	125	0 <sup>b</sup>	8.7
DOSL	125	140	10.0
DOSL	125	540	11.0
TDCA	100	0	3.0
TDCA	100	650	7.2
TDCA	100	750	8.7
TDCA	100	770	10.0
TDCA	100	940	11.0
OPEE	100	0	7.2
OPEE	100	30	8.7
OPEE	100	120	10.0
OPEE	100	450	11.0

<sup>a</sup>=10% NaOH (2.5 M)<sup>b</sup>=No added NaOH

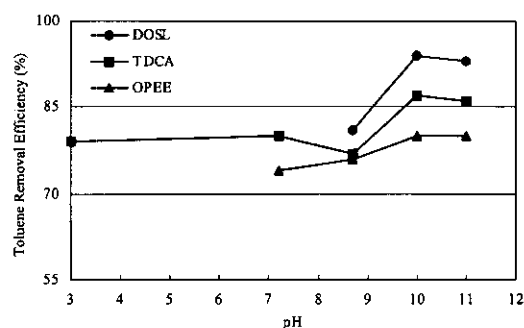
zene was used as an internal reference standard. Prior to the analysis of sample extracts, the response factor and linearity of detection for the internal standard and contaminant were determined. After having calculated the response factor, a calibration graph was prepared. During analysis of a sample, the sample mass or volume was determined and a known amount of ethylbenzene or 1,2-dichlorobenzene was added to the sample. The quantitative determination of contaminant concentration was based on these internal standard reference compounds, so that sample peak areas were compared with those of their respective internal standards (Lee, 1997; Lee, 1999; Lee *et al.*, 2001). New standard curves were prepared after approximately 15-20 injections. The standard curves were constructed using concentrations ranging from 8.7 to 43.3 mg/L for toluene and from 26.8 to 71.6 mg/L for 1,2,4-trichlorobenzene. Solutions were diluted if necessary to fit within the range of this line. All tests were conducted at room temperature.

### 3. RESULTS AND DISCUSSION

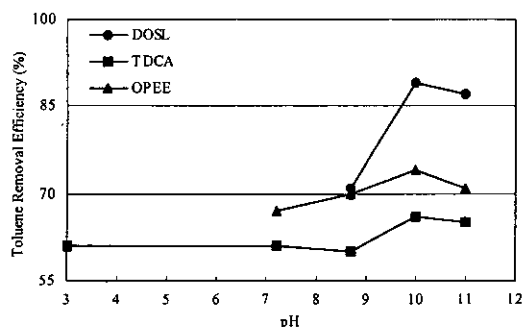
Monitored pH values of effluent solutions during experiments were nearly the same as the initial solution pH at the start of each test. The pH value of nonionic OPEE was constant throughout the tests. The pH values of anionic surfactants (DOSL and TDCA) were slightly varied (Table 3) and this is considered to be insignificant in terms of influ-

**Table 3.** Monitored pH values of the effluent from the soil column.

4%(v/v) Surfactants	Initial	After 10 pore volumes effluent passed in sandy soil column	After 10 pore volumes effluent passed in clay loam soil column
DOSL	8.7	8.9	8.9
DOSL	10.0	10.0	10.2
DOSL	11.0	11.1	11.1
TDCA	3.0	3.1	3.3
TDCA	7.2	7.0	7.3
TDCA	8.7	9.0	9.0
TDCA	10.0	10.1	10.5
TDCA	11.0	11.2	11.3
OPEE	7.2	7.2	7.1
OPEE	8.7	8.7	8.9
OPEE	10.0	10.0	10.0
OPEE	11.0	11.0	11.3



**Fig. 1.** Effect of surfactant solution pH on leaching of toluene from Fruitfield sandy soil.



**Fig. 2.** Effect of surfactant solution pH on leaching of toluene from Webster clay loam soil.

encing degree on pH effects.

Fig. 1 and Fig. 2 show the variation of the removal efficiency with pH for the three surfactants used in case of toluene. The pH of surfactant solution affected clearly toluene removal from contaminated soil columns. For all surfactants a maximum removal of toluene was obtained at pH 10 and toluene removal efficiency between pH 10 and pH 11 was slightly varied. The maximum recoveries (94%, 89%) of added toluene were obtained for DOSL surfactant solution in Fruitfield sandy soil and Webster clay loam soil, respectively. The maximum increase of toluene removal was 16% for DOSL in Fruitfield sandy soil, and was 26% for DOSL in Webster clay loam soil when the pH varied from 8.7 to 10. The percentage increase was 10% for TDCA when the pH varied from 3.0 to 10 in both soils, and was 9%, 10% for OPEE when the pH varied from 7.2 to 10 in Fruitfield sandy soil and Webster clay loam soil, respectively.

Fig. 3 and Fig. 4 show the variation of the removal efficiency with pH for the three surfac-

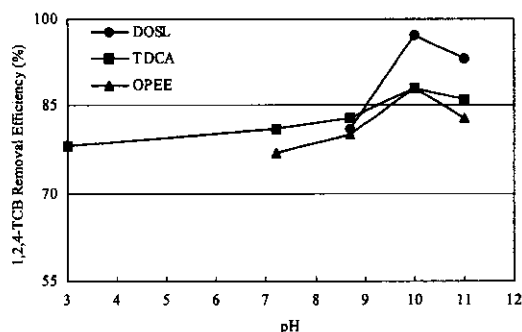


Fig. 3. Effect of surfactant solution pH on leaching of 1,2,4-TCB from Fruitfield sandy soil.

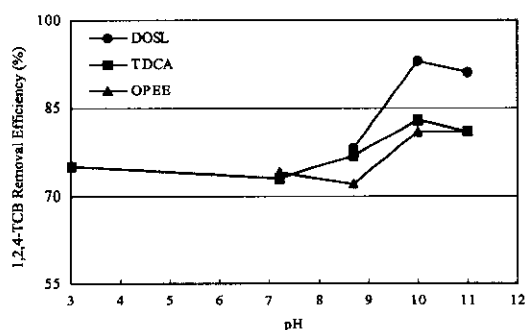


Fig. 4. Effect of surfactant solution pH on leaching of 1,2,4-TCB from Webster clay loam soil.

tants used in case of 1,2,4-trichlorobenzene. The pH of surfactant solution had also a clear effect on 1,2,4-trichlorobenzene removal from contaminated soil columns. For all surfactants a maximum removal of 1,2,4-trichlorobenzene was obtained at pH 10. Also, 1,2,4-trichlorobenzene removal efficiency between pH 10 and pH 11 was slightly varied. The maximum recoveries (97%, 93%) of added 1,2,4-trichlorobenzene were obtained for DOSL surfactant solution in Fruitfield sandy soil and Webster clay loam soil, respectively. The maximum increase of 1,2,4-trichlorobenzene removal was 20% for DOSL in Fruitfield sandy soil, and was 19% for DOSL in Webster clay loam soil when the pH varied from 8.7 to 10. The percentage increase was 13%, 10% for TDCA when the pH varied from 3.0 to 10 in Fruitfield sandy soil and Webster clay loam soil, respectively. The percentage increase was 14%, 9% for OPEE when the pH varied from 7.2 to 10 in Fruitfield sandy soil and Webster clay loam soil, respectively.

These increased values were less than that observed for Ottawa sand column tests (Lee,

1997). Laboratory experiments showed the effectiveness of highly alkaline surfactant solutions in leaching toluene from Ottawa sand (Lee, 1997; Lee *et al.*, 2001). In previous study (Lee, 1997), 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. In addition, the mixture of surfactant and NaOH was most effectively extracted by solvents during leaching tests for recycled surfactant solution (Lee, 1997). The effect of NaOH in changing effectiveness is not due to  $\text{Na}^+$  counter-ion effects, but rather to the  $\text{OH}^-$  based on experimental results (Lee, 1999; Lee *et al.*, 2001). 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. However, the cause of the lesser effect obtained from this study compared to Lee's (1997) results might be attributed to the differences in model contaminants and soils. Hydrogen ion concentration in solution was an important factor in surfactant effectiveness. The cause of the pH effect on a nonionic surfactant (OPEE) is unknown, but perhaps OPEE may contain minor amount of a charged molecular species (Lee, 1999). 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.

Based on results of these column experiments, DOSL can be a good candidate for surfactant-based soil or groundwater remediation. In addition to the high percentage removal of toluene and 1,2,4-trichlorobenzene observed in our column experiments, DOSL has good solubilizing abilities for phenanthrene, naphthalene and related substances (Rouse *et al.*, 1993; Deshpande *et al.*, 1999; 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; Deshpande *et al.*, 2000). Because of low sorption to soil particle and resistance to precipitation with cations, DOSL should show minimal loss during surfactant flushing of an aquifer compared to nonionic and other anionic single polar head surfactants.

#### 4. CONCLUSION

We performed laboratory column tests to investigate the effect of surfactant solution pH on the removal efficiency of toluene and 1,2,4-trichlorobenzene from two different soils, Fruitfield sandy and Webster clay loam soils. The pH of surfactant solution was essential to have effect on toluene and 1,2,4-trichlorobenzene removal from contaminated soil columns. The test results revealed that, in each surfactant a maximum removal of toluene and 1,2,4-trichlorobenzene was obtained at pH 10 of surfactant solution. The maximum recoveries of added toluene or 1,2,4-trichlorobenzene were 94% and 97%, and maximum increase of toluene and 1,2,4-trichlorobenzene removal were 16% and 20% for DOSL with Fruitfield sandy soil. Also, the maximum recoveries of added toluene or 1,2,4-trichlorobenzene were 89% and 93%, and maximum increase of toluene and 1,2,4-trichlorobenzene removal were 26% and 19% for DOSL with Webster clay loam soil. These experimental results indicate that maintaining a high pH surfactant solution in surfactant-assisted remediation is desirable for efficient removal of NAPLs from contaminated soils.

#### ACKNOWLEDGEMENTS

We are grateful for support of this research from Iowa Academy Sciences. We also wish to acknowledge the helpful review comments and invaluable suggestions provided by Dr. Michael L. Thompson

of the Department of Agronomy at Iowa State University.

#### REFERENCES

- Chen, L. and Knox, R.C. (1997) Using vertical circulation wells for partitioning tracer tests and remediation of DNAPLs. *Groundwater Monitoring and Remediation*, v. 17, p. 161-168.
- Deshpande, S., Shiau, B.J., Wade, D., Sabatini, D.A. and Harwell, J.H. (1999) Surfactant selection for enhancing ex situ soil washing. *Water Research*, v. 33, p. 351-360.
- Deshpande, S., Wesson, L., Wade, D., Sabatini, D.A. and Harwell, J.H. (2000) Dowfax surfactant components for enhancing contaminant solubilization. *Water Research*, v. 34, p. 1030-1036.
- Gonzalez, J.M. and Ukrainczyk, L. (1996) Adsorption and desorption of nicosulfuron in soils. *Environmental Quality*, v. 25, p. 1186-1192.
- Knox, R.C., Sabatini, D.A., Harwell, J.H., Brown, R.E., West, C.C. and Griffin, C. (1997) Surfactant remediation field demonstration using a vertical circulation well. *Ground Water*, v. 35, p. 948-953.
- Lee, D.H. (1997) The effect of surfactants in leaching hydrophobic organic compounds from sand. M.S. Thesis. Iowa State University, Ames, IA.
- Lee, D.H. (1999) Experimental investigation of the removal of hydrophobic organic compounds from two Iowa soils using food grade surfactants and recovering of used surfactants. Ph.D. Dissertation. Iowa State University, Ames, IA.
- Lee, D.H., Cody, R.D. and Hoyle, B.L. (2001) Laboratory evaluation of the use of surfactants for ground water remediation and the potential for recycling them. *Groundwater Monitoring and Remediation*, v. 21, p. 49-57.
- Martel, R. and Gelinas, P.J. (1996) Surfactant solutions developed for NAPL recovery in contaminated aquifers. *Ground Water*, v. 34, p. 143-154.
- Pennell, K.D., Adinolfi, A.M., Abriola, L.M. and Diallo, M.S. (1997) Solubilization of dodecane, tetrachloroethylene, and 1,2-dichlorobenzene in micellar solutions of ethoxylated nonionic surfactants. *Environmental Science and Technology*, v. 31, p. 1382-1389.
- Rouse, J.D., Sabatini, D.A. and Harwell, J.H. (1993) Minimizing surfactant losses using twin-head anionic surfactants in subsurface remediation. *Environmental Science and Technology*, v. 27, p. 2072-2078.
- Sabatini, D.A., Knox, R.C., Harwell, J.H., Soerens, T., Chen, L., Brown, R.E. and West, C.C. (1997) Design of a surfactant remediation field demonstration based on laboratory and modeling studies. *Ground Water*, v. 35, p. 954-963.

2001년 3월 15일 원고접수, 2001년 6월 15일 게재승인.