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原著

톨루엔으로 오염된 토양에서 DOSL 계면활성제를 이용한 최적의 정화 조건 규명

이 달 희 · 김 동 주 · Robert D. Cody*

고려대학교 지구환경과학과

Optimization of DOSL Surfactant Solution Conditions in Surfactant-Enhanced Remediation of Soil Contaminated by Toluene

Dal-Heui Lee, Dong-Ju Kim, Robert D. Cody*

Department of Earth and Environmental Sciences, Korea University, Anam-dong, Sungbuk-ku, Seoul, 136-701, Korea
**Department of Geological and Atmospheric Sciences, 253 Science 1, Iowa State University, Ames, IA 50011, USA*

ABSTRACT

Column tests were carried out to examine the effect of surfactant solution conditions on the surfactant-enhanced remediation of soil columns contaminated by toluene. The conditioned parameters of the surfactant solution for the column tests were concentration, pH, temperature and flow rate. The test results revealed that an optimum condition was achieved for 4 %(v/v) of concentration, 10 of pH, 20℃ of temperature and 4 mL/min of flow rate respectively. The removal of 95 % of toluene was obtained when optimal conditions of each surfactant solution parameter were simultaneously met. This was a marked improvement and removal efficiency increased by 6-19 % compared to that with unadjusted conditions. The optimum range of these parameters may be useful for a surfactant-based remediation in the aquifer contaminated by toluene.

Key words : Toluene, Surfactant solution, Remediation, Optimum conditions

요 약 문

본 주상실험은 오염된 토양에서의 계면활성제 용액상태에 따른 복원 효과를 조사하기 위하여 실행되었다. 농

도, pH, 온도, 그리고 용액의 유속을 달리하여 실험을 수행하였다. 실험에 사용된 오염물질은 톨루엔, 토양시료는 Iowa Fruitfield sandy soil, 그리고 계면활성제는 Sodium diphenyl oxide disulfonate(DOSL)이었다.

실험결과, 최적 조건은 다음과 같이 구해졌다. 계면활성제의 농도는 4 %(v/v), pH는 10, 온도는 20℃, 그리고 유속은 4 mL/min이었다. 이 조건이 모두 만족하는 상태에서는 95 %의 톨루엔이 제거되었으며 이는 다른 조건에서보다 6~19 %의 상승효과를 보인 것이다.

본 실험에서 보여준 계면활성제 조건은 톨루엔으로 오염된 대수층의 복원에 매우 유용한 자료가 될 것이다.

주제어 : 톨루엔, 계면활성제, 복원, 최적조건

1. INTRODUCTION

Hydrophobic organic compounds are immiscible in water and may be sorbed on soil particles, and also may be present as discrete phases in the subsurface. These organic compounds frequently enter the subsurface as a separate 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[1,2].

Removal of NAPLs from contaminated soils is difficult because they have low solubilities and high interfacial tensions. Currently the common method for remediation of soils and aquifers contaminated with NAPL organic substances is a pump-and-treat method. This method, however, is neither effective nor economical[2]. According to Mackay and Cherry, contaminant concentrations rapidly decrease after initiation of pumping and then level off at a still high asymptotic concentration. Recently, extensive research on soil and ground water remediation has demonstrated a surfactant(surface active agents) flushing to be a viable alternative for improving the efficiency of pump-and-treat remediation.

Remediation of a contaminated aquifer in a pump-and-treat method requires a combination of injection wells and withdrawal wells, which will continuously flood a contaminated zone with remediation solutions. At this time aqueous surfactant solutions are affected by the conditions such as surfactant solution concentration, pH, temperature and flow rate[3,4]. Optimization of surfactant dose, pH, temperature and flow rate for the efficient NAPL organic removal is an essential subject for the remediation of contaminated ground water. Therefore, objectives of this study were (i) to examine NAPL organic dissolution based on surfactant solution conditions and (ii) to evaluate the optimal range of the conditions that can significantly increase the removal efficiency.

2. MATERIALS AND METHODS

2.1 Soil and chemicals selection

One Iowa Fruitfield soil was used for this study. The soil is classified as a sand(USDA classification), and consists of 86.3 % sand, 10 % silt, 3.7 % clay and 0.2 % organic carbon. Prior to use it was air-dried and passed through a 2 mm sieve.

Toluene was selected as the LNAPL(lighterthan-water nonaqueous phase liquid) model substance because benzene, toluene, ethylbenzene, and xylene(BTEX) are probably the most common LNAPL contaminants in soil and ground water, and it is representative of non-chlorinated solvents. Reagent grade toluene was obtained from Fisher Scientific(Chicago, IL).

Sodium diphenyl oxide disulfonate(DOSL) that is an anionic surfactant was selected in this study because DOSL surfactant showed a good solubilization for hydrophobic organic, and DOSL(C16-DOSL, $C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$) is food additive and rapidly biodegradable according to FDA(Food and Drug Administration) of USA. The structure of DOSL is a straight chain of diphenyl oxide disulfonates with molecular weight of 642 and the critical micelle concentration of 0.5 mmol/L. This surfactant was obtained from Dowfax Chemical and used without further purification.

2.2 Column tests with various surfactant solution conditions

Column tests were carried out to examine the effect of surfactant solution conditions on the surfactant-enhanced remediation. A porous ceramic plate was placed beneath the soil column to prevent loss of soil during leaching. Compaction of the dry soil in 0.5 cm layers was standardized by tapping the side of the column 25 times, which minimizes the preferential liquid channeling. The soil column length was 15.4 cm and the soil column radius was 2.3 cm. When packed in columns, the soil medium had a bulk density of 1.24g/cm^3 corresponding to a porosity of 0.40. 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. Five mL of toluene was then injected into the middle of the column by a long syringe. This method of contamination is closely analogous to field contamination in which a mass of contaminant is transported to the subsurface from a localized contaminant source such as leaking underground storage tank. Ten pore volumes(1 pore volume = 125 mL) of surfactant solutions were then pumped into the top of the column with various surfactant solution conditions. Each column experiment was duplicated for evaluation. Operating variables used in this study were surfactant solution concentration, pH, temperature and flow rate.

2.2.1 Case 1: Surfactant solution concentration effects

Surfactant concentrations ranging from 1 %(v/v) to 10 %(v/v) were tested to determine the one which gives the best removal efficiency. Surfactant concentrations used for the column tests were 1, 2, 4, 6, 8, and 10 %(v/v) for the fixed solution pH of 8.5 and the flow rate of 2.5 mL/min. This test was essential for reducing cost in a surfactant-enhanced remediation[5,6].

2.2.2 Case 2: 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(2.5M) solution. The surfactant 4 %(v/v) DOSL had an unadjusted pH of 8.5. The pH values of the aqueous surfactant solution were then adjusted to 9, 9.5, 10, 10.5, and 11 for a constant flow rate of 2.5 mL/min.

2.2.3. Case 3: Surfactant solution temperature effects

Temperature variation during the column test might significantly affect the removal efficiency of the surfactant used. Therefore, temperature effects on removal of toluene from the Fruitfield sandy soil were examined for surfactant solutions with various initial temperatures of 5, 10, 15, 20, 25, and 30℃, respectively. In all column tests, the soil column was initially at a room temperature of 20℃ and the temperatures of surfactant solutions were controlled by heating or cooling before injected into the soil column. Concentration of surfactant used was 4 %(v/v) based on the results of case 1 and solution pH was 10 based on the results of case 2 for constant solution flow rate of 3 mL/min.

2.2.4 Case 4: Surfactant solution flow rate effects

In order to investigate the effect of surfactant solution flow rate on surfactant-based remediation, various flow rate of 0.5, 1, 2, 4, 8, and 16 mL/min was applied to the column using a pump. In this case, solution concentration was 4 %(v/v) and surfactant solution temperature of 20℃ was used based on the test results of case 1, and 3 while surfactant solution pH was 10 based on the results of case 2.

2.2.5. Soil column test using optimal surfactant solution conditions

To see the effect of optimal surfactant solution conditions, parameters selected from individual case studies were used. The result was then compared with non-optimal surfactant solution conditions for removal efficiency.

2.3 Analysis

Toluene was extracted from liquid samples with hexane in separatory funnels according to EPA Method 3510, and concentrations were measured using gas chromatography (Hewlett Packard Model 5890 series II). The system was temperature programmable and has a Flame Ionization Detector (FID). Ethylebenzene was used as internal reference standard. Prior to the analysis of extracted samples, the response factor (R = 0.998) and linearity of detection for the internal standard and contaminant were determined. After calculating the response factor, a calibration graph was prepared. The quantitative determination of contaminant concentration was based on these internal standard reference compounds such that sample peak areas were compared with those of their respective internal standards. New standard curves were prepared after approximately 15-20 injections. Solutions were diluted if necessary to fit within the range of this line. All tests were conducted at a room temperature of 20℃.

3. RESULTS AND DISCUSSION

3.1 Case 1: Surfactant solution concentration

Removal efficiency increased almost linearly

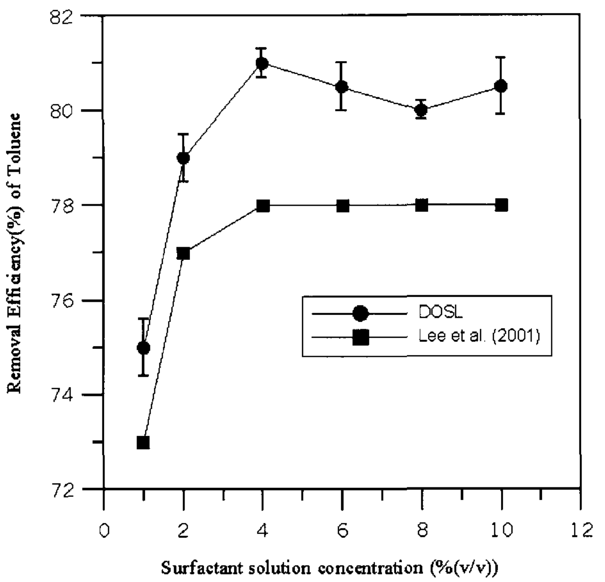

Fig. 1. Effect of surfactant solution concentration on leaching of toluene from soil column

from 1 %(v/v) to 4 %(v/v) and then leveled off(Figure 1). In order to compare the effects of concentration for a non-food grade surfactant, we used a data for which Sandopan JA36 surfactant was tested at the same concentrations[7, 8, 9)]. Removal efficiency of DOSL and Sandopan JA36 increased with surfactant concentration between 1 %(v/v) and 4 %(v/v) (Figure 1). For DOSL and Sandopan JA 36, removal efficiency slightly decreased between 6 %(v/v) and 10 %(v/v). Surfactant solutions may undergo a phase change at high concentration range so that the system may not be isotropic. For example, ionic or nonionic surfactants may form liquid crystals which clog pores at high concentration. Based on these results, a surfactant concentration of 4 %(v/v) was found to give the best removal efficiency. For non-food grade Sandopan JA36, 4 %(v/v) of surfactant also gave the highest removal efficiency, while concentration of 2 %(v/v) gave only a slight decrease in effectiveness(Figure 1). This result gives the guidence for cost effectiveness in an surfactant-enhanced field remediation.

3.2 Case 2: Surfactant solution pH

Monitored pH values of effluent solutions during column tests were nearly the same as the initial solution pH at the start of each test. Figure 2 shows the variation of the removal efficiency with pH for the DOSL surfactant. The pH of surfactant solution affected clearly toluene removal from contaminated soil columns. A maximum removal of toluene was obtained at pH 10, and toluene removal efficiency between pH 10 and 10.5 was slightly varied. The pH of subsurface water-sediment systems depends on the nature of the recharge water and geochemistry of the aquifer.

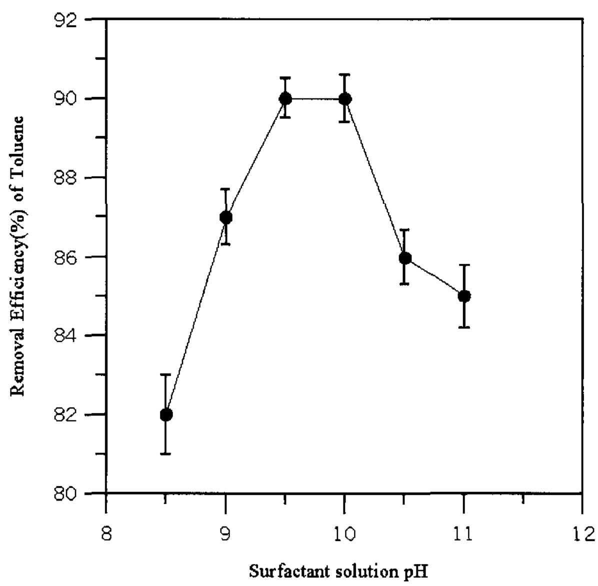

Fig. 2. Effect of surfactant solution pH on leaching of toluene from soil column

The maximum recovery of 90 % of added toluene was obtained for DOSL surfactant solution in Fruitfield sandy soil. The maximum increase of toluene removal was 20 % for DOSL in Fruitfield sandy soil when the pH varied from 8.5 to 10. These results show the effectiveness of highly alkaline surfactant solutions in leaching toluene from Fruitfield sandy soil, although the increased values were less than that observed for Ottawa sand column tests[9].

3.3 Case 3: Surfactant solution temperature

Monitored temperatures of effluent solutions during column tests were nearly the same as the initial solution temperature at the start of each test due to facilities for controlling column temperatures[10, 11]. Effect of solution temperature is shown in Figure 3. Remediation efficiencies did vary with temperature, and the greatest removal efficiency occurred at 20℃ in this study. The removal was lowest at the lowest temperature of 5℃ and increased with temperature up to 20℃, and then slightly decreased above 25℃ (Figure 3). Joshi and Lee[11] reported that the ionic surfactant is more soluble at higher temperature(not extreme temperature). These results are consistent with our test results.

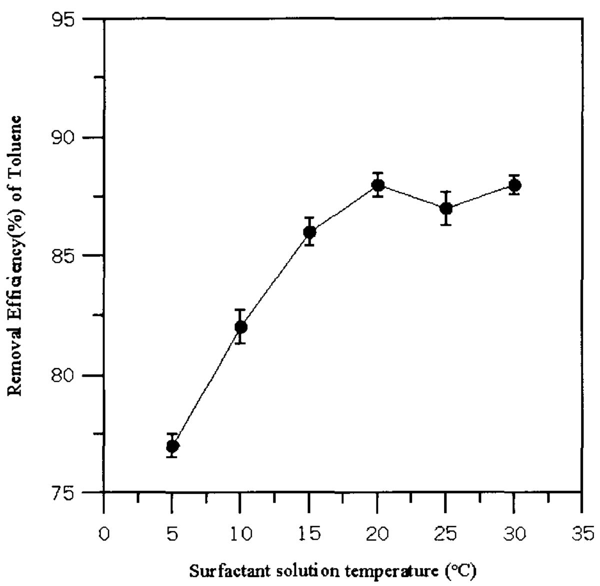

Fig. 3. Effect of surfactant solution temperature on leaching of toluene from soil column

For extremely low temperature, phase separation of surfactants may occur(e.g. precipitation, liquid crystals). Generally, the more hydrophobic organic, the more sensitive temperature for removal effectiveness. Temperatures in USA are generally low corresponding to the mean annual air temperature and at depths of 30-60 ft fluctuates from 3 ℃ to 25 ℃[11]. Temperature fluctuation of soil and ground water is less than that at the surface. Temperature dependency of surfactant solution will depend on the specific solute-soil system.

3.4 Case 4: Surfactant solution flow rate

Figure 4 shows the effect of surfactant solution flow rate on removal of toluene. An optimum flow rate of surfactant exists, which yields maximum removal efficiency of toluene. It was observed that a pumping rate of 4 mL/min gives the highest recovery of toluene in the column tests(Figure 4). The removal was lowest at the lowest flow rates of 0.5 mL/min, and increased with flow rates up to 4 mL/min and then leveled off(Figure 4). This is attributed to the fact that below 2 mL/min little foaming of surfactant occurs which reduces efficiency, and above 4 mL/min much more foaming occurs. This result shows somewhat a higher value of pumping rate

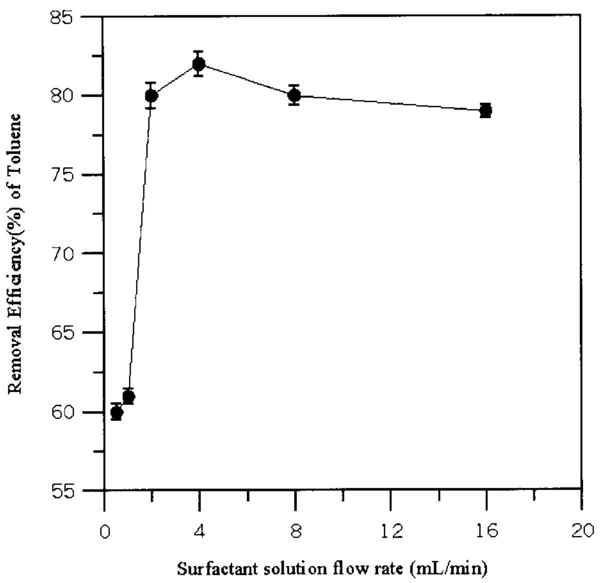

Fig. 4. Effect of surfactant solution flow rate on leaching of toluene from soil column

than the study of Lee et al[9]. who found that a pumping rate of 3 mL/min of non-food grade surfactants gave the maximum efficiency.

3.5 Soil column test at optimal surfactant solution conditions

Figure 5 summarizes removal results for

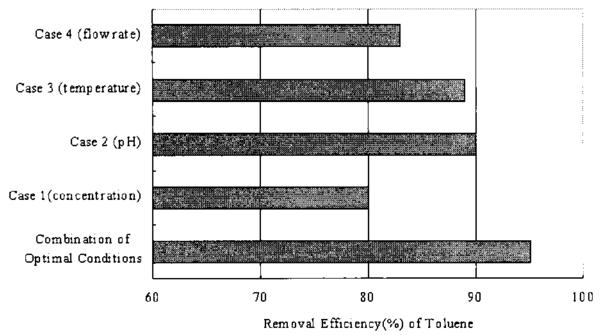

Fig. 5. Effect of optimal surfactant solution conditions on leaching of toluene from soil

toluene at adjusted surfactant solution conditions. The removal of 95 % contaminant(toluene) was obtained for a surfactant concentration of 4 %(v/v), surfactant solution pH of 10, surfactant solution temperature of 20℃ with a surfactant solution flow rate of 4 mL/min. The effectiveness of optimal surfactant solution conditions was significant because removal efficiency increased by 6-19 % compared to experimental results with non-optimal environmental conditions(Figure 5).

4. CONCLUSIONS

Laboratory coloumn tests were performed for various surfactant solution parameters to investigate the effects of these different parameters on surfactant-enhanced remediation of soil columns contaminated by toluene. Surfactant solution conditions were found to have a significant effect on toluene 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℃, (iv) Surfactant solution flow rate: 4 mL/min. The removal of 95 % of toluene was obtained with combination of optimal conditions of surfactant solution. This was a marked improvement and removal efficiency increased by 6-19 % compared to that with unadjusted surfactant solution conditions. The results from this study may be useful for determining optimum condition of surfactant solution for surfactant-based remediation in aquifer system.

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