≪ **Technical note** ≫

A Pilot Study for Remediation of Groundwater by Surfactant -Enhanced Soil Flushing

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ABSTRACT

The removal of non-aqueous phase liquids (NAPLs) from groundwater using pure water, via pump and treat, is quite ineffective due to their low solubility and hydrophobicity. Therefore, the objectives of pilot tests were to select potentially suitable surfactants that solubilize tetrachloroethylene (PCE) and trichloroethylene (TCE) present as contaminants and to evaluate the optimal range of process parameters that can increase the removal efficiency in surfactant-enhanced soil flushing (SESF). Used experimental method for surfactant selection was batch experiments. The surfactant solution parameters for SESF pilot tests were surfactant solution concentration, surfactant solution pH, and the flow rate of surfactant solution in the SESF pilot system. Based on the batch experiments for surfactant selection, DOSL (an anionic surfactant) was selected as a suitable surfactant that solubilizes PCE and TCE present as contaminants. The highest recovery (95%) of the contaminants was obtained using a DOSL surfactant in the batch experiments. The pilot test results revealed that the optimum conditions were achieved with a surfactant solution concentration of 4% (v/v), a surfactant solution pH of 7.5, and a flow rate of 30 L/min of surfactant solution (Lee and Woo, 2015). The maximum removal of contaminants (89%) was obtained when optimum conditions were simultaneously met in pilot-scale SESF operations. These results confirm the viability of SESF for treating PCE and TCE-contaminated groundwater.

Key words : PCE, TCE, Groundwater, Remediation, Surfactant-enhanced soil flushing

1. Introduction

Groundwater contamination by hydrophobic organic compounds (HOCs) has caused concern in industrial areas of Korea (Heo et al., 2007). HOCs enter the subsurface as a separate organic phase or dense non-aqueous phase liquid (DNAPL). Under normal flow regimes, this DNAPL phase is immobile and often represents a long-term source of aquifer contamination as it slowly dissolves into the groundwater (Lee et al., 2001a). Pump-and-treat remediation methods are among the most widely used for contaminated groundwater (Adeel and Luthy, 1995; Martel and Gelinas, 1996). However, the traditional remediation method, pump-and-treat, has been shown to be ineffective for remediation groundwater contaminated with DNAPL (Lee et al., 2002; Kim et al., 2005). Tetrachloroethylene (PCE) and trichloroethylene (TCE) are among the most ubiquitous

chlorinated compounds found in groundwater contamination.

Many research papers showed that surfactants (surface active agents) may aid in remediation of subsoil and aquifers contaminated with PCE and/or TCE (Adeel and Luthy, 1995; Feng et al., 2001; Cases et al., 2002). These studies showed that aqueous surfactant solutions significantly enhanced the removal of PCE and/or TCE from soil and groundwater. The surfactant-enhanced soil flushing (SESF) extracts contaminants from aquifer matrices using a liquid medium such as aqueous surfactant solution (Joshi and Lee, 1996; Knox et al., 1997; Feng et al., 2001). Extractive efficiency of surfactant solution for PCE and/or TCE was seven to ten times greater than that which could be obtained by flushing and/or washing with water alone (Lee and Cody, 2001c). Surfactants can be used to vastly increase the solubility of the DNAPLs in water and also lower the interfacial tension at the water-DNAPLs interface (Chang and

Rosano, 1984; Kim et al., 2005).

However, the removal of HOC from groundwater using pure water by in-situ soil flushing is quite ineffective due to its low solubility and hydrophobicity. SESF appears to be effective in removing HOC from contaminated groundwater (Knox et al., 1997; Deshpande et al., 2000). When selecting a surfactant for groundwater remediation, one must consider the environmental conditions of contaminated aquifer. At this time aqueous surfactant solutions are affected by the surfactant solution conditions such as clay contents of aquifer area, surfactant concentration, and surfactant solution flow rate (Harwell, 1992; Lee and Cody, 2001c). Also a major concern relative to the effectiveness of SESF is surfactant losses. Therefore, the objectives of this study were to select potentially suitable surfactants that solubilize PCE and TCE present as contaminants and to evaluate the optimal range of process parameters that can increase the removal efficiency in SESF pilot tests.

2. Materials and Methods

2.1. Batch tests for surfactant selection

Batch tests were carried out to examine the surfactant selection. The procedure of batch tests was the same as the previous studies (Lee et al., 2001b). Four different surfactants were obtained from four companies. Table 1 shows the characteristics of the used surfactants in batch tests. To measure surfactant-assisted removal of the PCE and TCE from the groundwater, 125 mL of PCE and TCE -contaminated groundwater and 250 mL of the surfactant solutions were placed in 500 mL Teflon screw cap (inner-double cap) jars. The jars were shaken on a shaker table at 200 rpm for 120 min and then they were centrifuged at 2000 rpm for 12 min. The liquid was decanted, and 250 mL of deionized water was added to the jars, which were shaken and centrifuged as before (Rajput et al., 1994; Lee et al., 2001b). The deionized water wash was repeated once more. Each treatment was performed in triplicate. Samples of the supernatants were analyzed for PCE and TCE concentration.

PCE and TCE were analyzed according to U.S. EPA standard methods using gas chromatography equipped with a flame ionization detector. Dichloromethane extraction was done with a soxhlet's extractor. 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. 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 (Shiau et al., 1995; Lee et al., 2001a). New standard curves were prepared after approximately 15-20 injections.

2.2. Pilot tests by SESF

Pilot tests were carried out to examine the effect of surfactant solution conditions (concentration, pH, flow rate) on

**Table 1.** Properties of surfactants used in this study

Trade Name or Abbreviation Chemical Name	HLB[a]	CMC[b] (mM)	Molecular Formula (General Structure)	Type Manufacturer
DOSL Disodium n-hexadecyl diphenyloxide disulfonate	N/A	0.5	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	Anionic Dow Chemical
SDS Sodium dodecyl sulfate	N/A	0.8	$CH_3(CH_2)_{11}OSO_3Na$	Anionic Fisher Scientific
T-Maz 60 POE[c](20) sorbitan Monostearate	14	0.023	$C_{18}H_{34}O_2C_6H_{10}O_4(CH_2CH_2O)_{20}$	Nonionic PPG/Mazer Chemicals
Brij 35 POE(23) lauryl ether	N/A	0.0099	$C_{12}(CH_2CH_2O)_{23}$	Nonionic Yakuri Chemicals, Japan

a = Hydrophilic-lipophilic balance
b = Critical micelle concentration. Data provided by the surfactant manufacturers
c = polyoxyethylene
N/A = Not Available
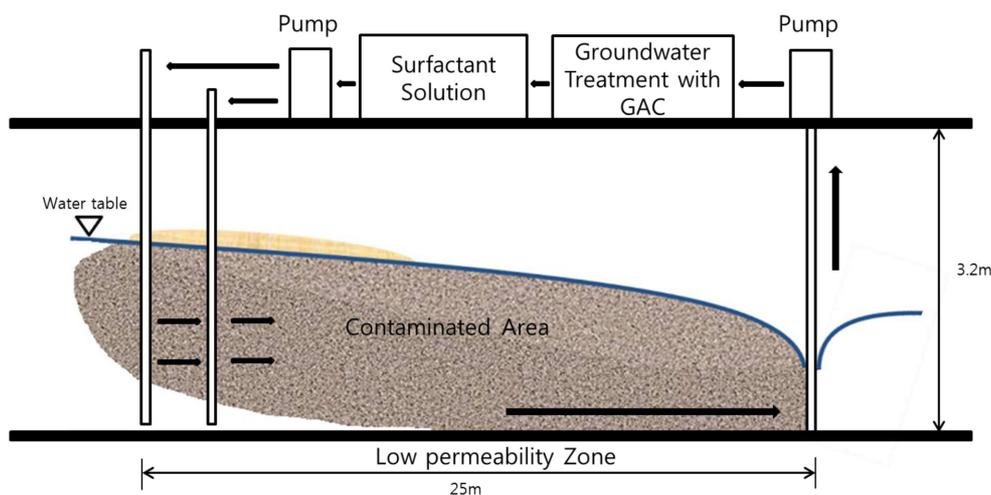
Fig. 1. The schematic diagram of surfactant-enhanced soil flushing (SESF) system at the demonstration site.

surfactant-enhanced soil flushing (SESF). The demonstration site is located about 33 km northwest of Seoul, Korea and has been contaminated with DNAPLs, especially PCE and TCE (Fig. 1). Soil texture and the hydraulic conductivity of the demonstration site are sandy soil, 2.7×10^{-5} cm/s, respectively. The procedure of pilot tests was the same as the previous study (Lee et al., 2001c) except for variations in surfactant solution parameters.

2.2.1. Surfactant solution concentration effects in SESF

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. The range of surfactant concentrations were selected based on cost effectiveness (Rouse et al., 1993; Kim et al., 2005). Therefore this test was essential for reducing cost in SESF. Surfactant concentrations used for the SESF pilot tests were 1, 2, 4, 6, 8% (v/v) and all tests were performed at a flow rate of 30 L/min. and pH 7.0.

2.2.2. Surfactant solution pH effects in SESF

In order to evaluate the effects of surfactant solution pH on SESF pilot tests, the pH of surfactant solutions was varied by adjusting pH with a 10% NaOH solution. The pH values of the aqueous surfactant solution were then adjusted to 6.5, 7.0, 7.5, 8.0, 8.5 (Lee et al., 2001a; Shiau et al., 1995). Tested the range of surfactant pH levels was selected based on prior studies (Lee et al., 2001a). The concentra-

tion of surfactant solutions used was 4% (v/v) and all tests were performed at a flow rate of 30 L/min.

2.2.3. The flow rate effects of surfactant solution in SESF

Flow rate variation in the SESF pilot test might significantly affect the removal efficiency of the surfactant used (Knox et al., 1997). Therefore, flow rate variation effects on removal of PCE and TCE from the groundwater were examined for surfactant solutions with various initial flow rates of 15, 20, 25, 30, 35 L/min., respectively. The flow rate ranges were selected based on a preliminary field study. The concentration of surfactant solutions used was 4% (v/v) and pH 7.0.
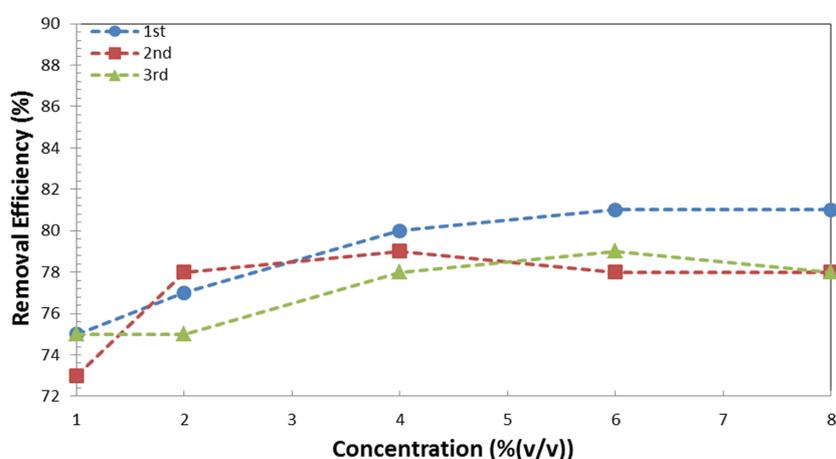
3. Results and Discussion

3.1. Batch tests for surfactant selection

The four candidate surfactants for surfactant selection were DOSL (anionic), SDS (anionic), T-Maz 60 (nonionic), and Brij 35 (nonionic). The highest recovery (95%) of the PCE and TCE was obtained using an anionic surfactant (disodium n-hexadecyl diphenyl oxide disulfonate (DOSL)) in the batch experiments (Table 2). Therefore, DOSL (trade name Dowfax 8390) surfactant was selected for SESF pilot tests. 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; Knox et

Table 2. The removal efficiency (%) of PCE and TCE in the batch tests

Trade Name or Abbreviation Chemical Name	1st (1 washing)	2nd (1 washing and 1 rinsing)	3rd (1 washing and 2 rinsing)
DOSL Disodium n-hexadecyl diphenyloxide disulfonate	88	92	95
SDS Sodium dodecyl sulfate	86	90	91
T-Maz 60 POE[c](20) sorbitan Monostearate	86	88	90
Brij 35 POE(23) lauryl ether	85	88	89

Fig. 2. The effect of surfactant solution concentration in SESF pilot tests.

al., 1997; Deshpande et al., 2000; Lee et al., 2002; Paria and Khilar, 2004). DOSL meets criteria as an indirect food additive under US FDA (Food and Drug Administration) Regulation 21CFR 178.3400 (Shiau et al., 1995). 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 et al., 2001a).

3.2. Pilot tests for process parameters in SESF

3.2.1. Effect of surfactant solution concentration

As expected, the lowest concentration of 1% (v/v) gave the least removal efficiency (Fig. 2). Removal efficiency of DOSL increased almost linearly from 1% (v/v) to 4% (v/v) and then leveled off (Fig. 2). As shown in Fig. 2, 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 concentrations (Chang and Rosano, 1984 ; Deshpande et al., 2000). 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-ionic surfactant OPEE (octylphenoxypolyethoxy ethanol), 4% (v/v) of surfactant also gave the highest removal efficiency, while concentration of 2% (v/v) gave only a slight decrease in effectiveness (Lee and Cody, 2001c). When using a surfactant for SESF, one must consider the concentration of the surfactant.

3.2.2. Effect of surfactant solution pH

Fig. 3 shows the variation of the removal efficiency with surfactant solution pH. A maximum removal of PCE and
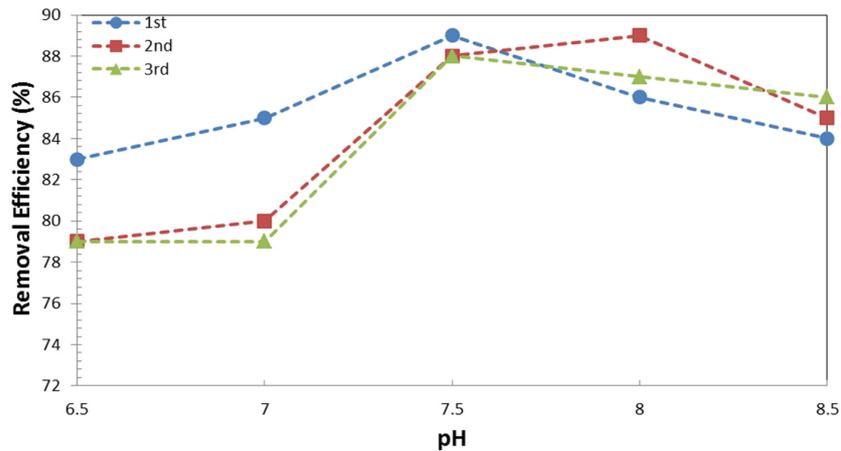
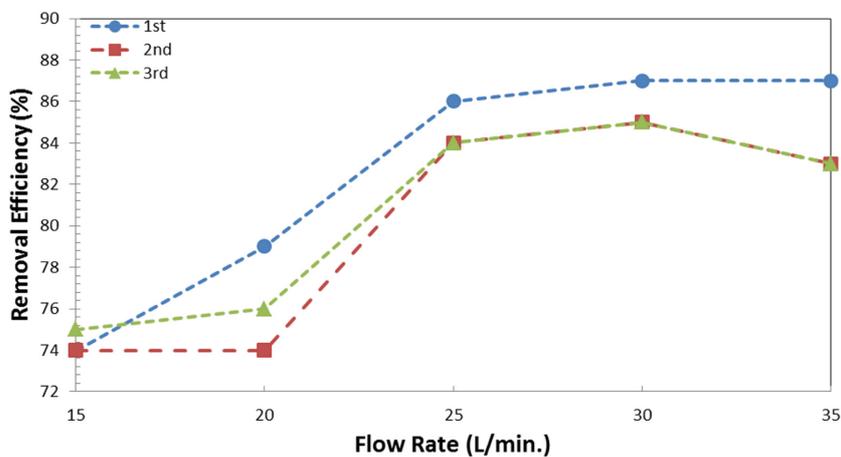**Fig. 3.** The effect of surfactant solution pH value in SESF pilot tests.

Fig. 4. The effect of surfactant solution flow rate in SESF pilot tests.

TCE was obtained at pH 7.5 (Fig. 3). The increased removal efficiency (%) of contaminants was about 8.8% when the pH varied from 6.5 to 7.5 (Fig. 3).

These increased removal efficiencies (%) were less than that observed for Ottawa sand column tests (Lee et al., 2001b). In a previous other study (Lee et al., 2008), 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 30%, an anionic surfactant (TDCA, trade name Sandopan JA36) by 34%, and water by 10% in a pure sand column. The effect of NaOH in changing effectiveness is not due to Na^+ counter-ion effects, but rather to the OH^- based on experimental results (Lee et al., 2008). Increased micelle formation and decreased surface

tension of surfactant solution at high pH may have affected our results (Lee and Cody, 2001c). However, near the higher end of the pH range (11-14) some of anionic sulphates can begin to hydrolyze and lose activity (Chang and Rosano, 1984, Adeel and Luthy, 1995; Cases et al., 2002; Kim et al., 2005). The cause of the lower effect obtained from this study compared to Lee et al. (2008) results might be attributed to the differences in model contaminants and soils. Also, hydrogen ion concentration in surfactant solution was an important factor in surfactant effectiveness (Lee et al., 2001c).

3.2.3. Effect of surfactant solution flow rate
Effect of surfactant solution flow rate is shown in Fig. 4. Remediation efficiencies by SESF did vary with flow rate,

and the greatest removal efficiency occurred at 30 L/min. The removal was lowest at the lowest flow rate of 15 L/min and increased with flow rate up to 30 L/min, and then slightly decreased to 35 L/min (Fig. 4).

3.3. Effect of optimal process parameters in pilot-scale SESF

The adjusted surfactant solution was essential to have an effect on PCE and TCE removal from groundwater. The maximum recoveries of PCE and TCE (89%) were obtained for a surfactant concentration of 4% (v/v), surfactant solution pH 7.5, and surfactant solution flow rate of 30 L/min in pilot-scale SESF (Lee and Woo, 2015). The maximum removal (89%) of contaminants was obtained when optimal conditions of each surfactant solution parameter were simultaneously met. The increased removal efficiencies by optimum conditions of PCE and TCE were about 13% greater than that which could be obtained by SESF with non-optimum conditions.

3.4. Additional recommendation for SESF in field work

Conducted SESF showed this remediation technology potentially can be adjusted in field. When selecting a SESF technology for groundwater remediation, one must consider the hydro-geochemical conditions of contaminated aquifer. At this time SESF remediation technology are affected by the soil texture such as clay contents of aquifer area, surfactant toxicity, and hydraulic conductivity. Also a major concern relative to the effectiveness of SESF is Eh value of the aquifer.

4. Conclusions

Performed surfactant-enhanced soil flushing (SESF) in this research showed potentially suitable technology for PCE and TCE-contaminated groundwater remediation. The process parameters for SESF were found to have a significant effect on contaminants (PCE and TCE) removal from groundwater. The test results revealed that optimal range for each surfactant solution parameter for SESF was: (i) Surfactant solution concentration: 4% (v/v), (ii) Surfactant solution pH: 7.5, (iii) Surfactant solution flow rate: 30 L/min. The optimal range was determined for each parameter

under given flushing conditions. The maximum removal (89%) of contaminants was obtained when optimal conditions of each surfactant solution parameter were simultaneously met. The results from this study may be useful for determining optimum condition of surfactant solution in SESF for the removal of PCE and TCE from groundwater.

Acknowledgements

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