

The Effect of the Mixture of Nonionic Surfactant and Bioactive Agent for Surfactant-enhanced Soil Flushing (SESF) of TCB Contaminated Soil

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ABSTRACT

The objective of this study was to find the effect of the mixture of the nonionic surfactant and bioactive agent that solubilizes trichlorobenzene (TCB) present as a contaminant for surfactant-enhanced soil flushing (SESF). Three different nonionic surfactants and two different bioactive agents were obtained from four companies. Separate funnel experiments and shaker table agitation / centrifugation experiments were used for the test. Based on the separate funnel experimental results, three suitable mixture agents (APG + OSE, Brij 35 + MOSE, T-Maz 60 + MOSE) were selected. In the shaker table agitation / centrifugation experiments, these three different mixture agents were reduced to one (T-Maz 60 + MOSE). The maximum removal (95%) of TCB was obtained using a mixture of the nonionic surfactant and bioactive agent. Therefore, the used test methods and results can be used for SESF.

Key words : SESF, TCB, Nonionic surfactants, Bioactive agents, Maximum removal

1. Introduction

Dense non-aqueous phase liquids (DNAPLs), such as trichlorobenzene (TCB), have posed a threat to the environment in industrial areas of Korea (Lee et al., 2001; Chung and Lee, 2012). 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 (Deshpande et al., 1999; Wang and Mulligan, 2004). Surfactants (surface active agents) and / or bioactive agents may aid in the remediation of subsoil and aquifers contaminated with DNAPL (Lee et al., 2001; Mulligan and Gibbs, 1993). Surfactants and /or bioactive agents can be used to vastly increase the solubility of the DNAPL in water as well as lower the interfacial tension at the water- DNAPL interface (Rosen, 1989; Rouse et al., 1993; Wang and Mulligan, 2004).

Surfactants can be classified according to the nature of the hydrophilic portion of the molecule: anionic, cationic, nonionic, and zwitterionic (Rosen, 1989). Nonionic surfactants generally have smaller critical micelle concentration (CMC)

values than ionic surfactants and are known to be good solubilizers of hydrophobic substances (Ang and Abdul, 1994). Generally, cationic surfactants are not selected in remediation works because of toxicity and strong complexation with anionic soil mineral surfaces (Paria and Khilar, 2004). Also, anionic surfactants may form precipitates with groundwater cations, and thereby cause reduction in soil hydraulic conductivity by blocking pores (Rouse et al., 1993; Lee et al., 2002; Chu and Kwan, 2003).

Abdul et al. (1990) evaluated the suitability of ten surfactants for washing automatic transmission fluid (ATF) from sand. They measured the surface tension of the surfactant and also conducted batch tests for solubilization capacity. The most effective surfactant was Witconol SN70 (alkyl polyoxyethylene glycol, a nonionic surfactant). DOSL (diphenyl oxide disulfonates, an anionic surfactant) was also a good surfactant for the removal of chlorinated hydrocarbon in the column test and the pilot test (Cort et al., 2002). In another surfactant selection study, using a separate funnel experiment of solubility, Fountain et al. (1991) evaluated 100 surfactants for washing PCE (tetrachloro-

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thylene) from sand. The most effective surfactant was the 1 : 1 volume mixture of Rexophos 25/27 (anionic) and T-Det N-9.5 (nonionic). These results show that the effectiveness of the surfactant differs depending on the specific organic contaminant.

The surfactant-enhanced soil flushing (SESF) extracts contaminants from soil matrices using a liquid medium such as an aqueous surfactant solution and/or bioactive agent solution (Fountain et al., 1991; Mulligan et al., 1999). SESF system is a combination of physical separation and chemical treatment, including physical separation techniques and extraction techniques. Also, SESF technology may be designed either to remove DNAPL or/and simultaneously act as an augmentation for existing technologies such as pump-and-treat systems (Wang and Mulligan, 2004). A major concern related to the effectiveness of SESF is surfactant losses. Nonionic surfactants seem to be less susceptible than ionic (anionic / cationic) surfactants to precipitation losses due to an increase in their solubility and steric constraints (Rosen, 1989; Lee et al., 2008). Therefore, the objective of this study was to find the effect of the mixture of the nonionic surfactant and bioactive agent that solubilizes TCB present as a contaminant for SESF.

2. Materials and methods

2.1. Materials

The three surfactants and two bioactive agents were used as received. The surfactants and bioactive agents, along with their relevant properties, are listed in Table 1 and Table 2, respectively. The used bioactive agents consist of lipopolysaccharides, phospholipids, and fatty acids. They are readily biodegradable and are used for general-purpose cleaning. Deionized water was used in preparing surfactant and bioactive agent samples.

The material used as model soil required high permeability, low cation exchange capacity (CEC), and low total organic carbon content. Ottawa sand was selected because it met these criteria and because of its uniformity and simple mineralogy. It was obtained from the U. S. Silica Company (Ottawa, IL). The mean grain diameter of Ottawa sand is 0.45 mm, and the specific surface area is 0.007 m²/g (Lee et al., 2001). 1,2,4-trichlorobenzene (TCB) was employed as a DNAPL model substance representative of aromatic chlorinated solvents, and is commonly reported as a groundwater contaminant (Lee et al., 2001). TCB is not effectively removed by water pump-and-treat cleanup technology because of its hydrophobic nature. TCB

Table 1. Properties of surfactants used in this study

Trade Name	Chemical Name	HLB ^a	CMC ^b	Molecular Formula	Type	Manufacturer
APG	Alkyl Polyglucoside	9	0.004	N/A	Nonionic	Henkel Korea, Korea
Brij 35	POE(23) Lauryl Ether	11	0.0099	C ₁₂ (CH ₂ CH ₂ O) ₂₃	Nonionic	Yakuri Chemicals, Japan
T-Maz 60	POE ^c (20) Sorbitan Monostearate	14	0.023	C ₁₈ H ₃₄ O ₂ C ₆ H ₁₀ O ₄ (CH ₂ CH ₂ O) ₂₀	Nonionic	PPG/Mazer Chemicals, USA

^a = Hydrophilic-lipophilic balance

^b = Critical micelle concentration (unit: mM). Data provided by the surfactant manufacturers

^c = polyoxyethylene

N/A = Not Available

Table 2. Properties of bioactive agents used in this study

Trade Name	Surface Tension	Interfacial Tension	Main Composition	Manufacturer
OSE	30 mN/m	1 mN/m	Lipopolysaccharides Phospholipids Fatty acids Nutrient	WISCO, Korea
MOSE	20 mN/m	1 mN/m	Lipopolysaccharides Phospholipids Fatty acids Enzyme Nutrient	WISCO, Korea

(spectrophotometric grade) was obtained from Aldrich Chemical. Characteristics of TCB are shown in Table 3.

Prior to use, the Ottawa sand (20-30 mesh) was rinsed with 0.1N HCl and deionized water. Contamination of soil was achieved by dissolving 5 mL of the TCB in 20 mL of hexane, and slowly adding the mixture to 100 g of the soil. After mixing by a shaker table for 10 minutes at 1000 rpm, the wet soil mixture was then placed in a hood at 30°C, and the hexane and TCB was allowed to evaporate for 10 minutes. The mixture was agitated several times during this process (Lee, 1999).

2.2. Separate funnel experiments

This series of experiments provided a rapid, qualitative, and fairly reliable means of determining which surfactant

and/or bioactive agent are good solubilizers. Experimental procedures were as follows: 100 mL of a 4% (v/v) or 4% (w/v) of each aqueous surfactant solution and/or bioactive agent were placed in a 250 mL separate funnel and an initial 1 mL of TCB was added. The funnel was then shaken gently for 60 seconds and left to settle for two hours. If the entire volume of TCB was solubilized, then another 1 mL of TCB was added and the funnel was shaken again. If any of the first 1 mL remained or if an emulsion was present, the funnel was shaken again for 60 seconds and then again set aside during for two hours (Lee et al., 2001; Lee et al., 2002).

This process continued for six hours, after which the funnels were left undisturbed for the remainder of the 24-hour period. The experiment ended after 24 hours, and the results recorded. This process was repeated three times for each eleven different cases (Table 4).

Table 3. Characteristics of the used contaminant

Chemical Name	1,2,4-Trichlorobenzene (TCB)
Formula	C ₆ H ₃ Cl ₃
Molecular Weight (g/mol)	181.45
Density (g/mL at 25°C)	1.454
Boiling Point (°C)	214
Melting Point (°C)	16
Purity	>99%
CAS Number	120-82-1
Aqueous Solubility (mg/L)	48.8
Log Kow(octanol-water partition coefficient)	4.02
Viscosity (cP)	0.83
Liquid-Water Interfacial Tension (dyne/cm)	45
Liquid-Air Interfacial Tension (dyne/cm)	25

2.3. Shaker table agitation / centrifugation experiments

These experiments were conducted to select suitable surfactants and/or bioactive agents which could solubilize/extract the TCB compound from contaminated Ottawa sand. The concentration of TCB of Ottawa sand was 5 mg/kg. Experimental procedures were as follows: 80 g of contaminated Ottawa sand with 250 mL of 4% (v/v) (or 2% (v/v) + 2% (v/v) in mixing) aqueous surfactant solutions and/or bioactive agent were placed in 500 mL Teflon screw cap jars. The contaminated Ottawa sand and aqueous surfactant solution and/or bioactive agent were mixed in a

Table 4. The results of separatory funnel experiments

Selected Agents Order	Amount TCB Added (ml)	Estimated Amount Solubilized (ml)	Characteristics after 24 hours, Decesion
APG	2.5	2.5	Very clear liquid formed, ineffective
Brij 35	2	2	Very clear liquid formed, ineffective
T-Maz 60	2.5	2.5	Light milky emulsion, ineffective
OSE	1	0.5	Very clear liquid formed, ineffective
MOSE	1.5	1	No foaming with milky color, ineffective
APG + OSE	3.5	3.5	Very clear liquid formed, passing
APG + MOSE	2.5	2.5	Little foaming, ineffective
Brij 35 + OSE	2.5	2.5	Light milky emulsion, ineffective
Brij 35 + MOSE	3.5	3.5	Very clear liquid formed, passing
T-Maz 60 + OSE	2.5	2.5	Light milky emulsion, ineffective
T-Maz 60 + MOSE	3.5	3.5	Very clear liquid formed, passing

shaker table at 200 rpm and 50 minutes. The jar was then centrifuged at 2000 rpm for 5 minutes to separate the aqueous and Ottawa sand phases. The liquid was decanted, 250 mL of deionized water was added to the soil, and the jar was shaken again for 50 minutes. The process was repeated until one surfactant and/or bioactive agent wash and two deionized water rinses were completed. Leachates were collected after each step and analyzed for the contaminant (Lee et al., 2001; Lee et al., 2002).

2.4. Analytical methods

The TCB in aqueous samples was extracted by solvent extraction with hexane using the standard separate funnel method 3510 and analyzed by gas chromatography with the split / splitless injection system (Hewlett Packard Model 5890 series II). The TCB was analyzed according to U.S. EPA standard methods using gas chromatography equipped with a flame ionization detector at the on-site laboratory. Prior to the analysis of sample extracts, the response factor and linearity of detection for the internal standard and contaminant were determined. The main criteria for selecting an internal standard are water solubility, chromatographic similarity to analyzed substance, and structure. The compound selected was ethyl benzene. 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 the sample peak areas were compared with those of their respective internal standards (Lee et al., 2001). New

standard curves were prepared after approximately 15-20 injections.

3. Results and Discussion

3.1. Separate funnel experiments

In these experiments, it was noted how much TCB was taken into an emulsion- solution before a separate phase was observed (e.g. TCB separated or a heavy emulsion / TCB phase separated from the rest of the solution). APG, Brij 35, T-Maz 60, OSE, MOSE, APG + MOSE, Brij 35 + OSE, and T-Maz 60 + OSE were not able to solubilize at least 3 mL of TCB and were considered ineffective, while those that solubilized more than this amount were given a "passing" grade and then subjected to further screening techniques (Table 4). APG + OSE, Brij 35 + MOSE, and T-Maz 60 + MOSE were relatively good solubilizer for TCB based on the separate funnel experiments. These eleven different surfactants and/or bioactive agents were reduced to three in the separate funnel experiments (Table 5). These were then used in a variety of other experiments, such as shaker table agitation / centrifugation experiments, which are discussed later. Emulsion and foam formation can create problems, but were not found in separate funnel experiments. Also, nonionic surfactants may undergo phase separation as the surfactant concentration increases (Rosen, 1989; Martel and Gelinas, 1996; Mulligan et al., 1999). This phase separation is related to the cloud point temperature of most nonionic surfactants. We did not

Table 5. The results of the TCB removal (%) in the shaker table and centrifugation experiments

Selected Agents Order	1 st Test by Agent	1 st Test by Agent + one rinsing	1 st Test by Agent + two rinsing
APG	60	62	63
Brij 35	65	66	67
T-Maz 60	65	65	68
OSE	40	40	40
MOSE	50	51	52
APG + OSE	70	75	78
APG + MOSE	70	75	76
Brij 35 + OSE	72	74	74
Brij 35 + MOSE	77	78	78
T-Maz 60 + OSE	70	73	74
T-Maz 60 + MOSE	86	88	95

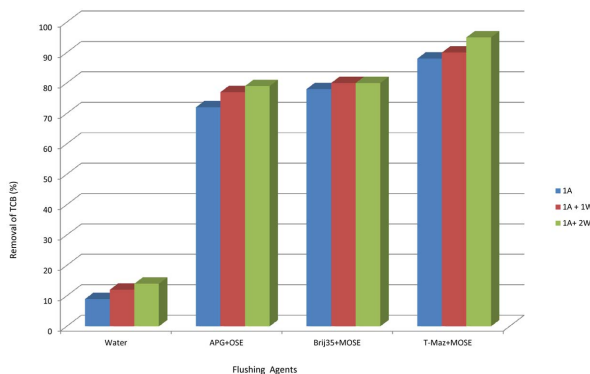


Fig. 1. The results of the TCB removal (%) in the shaker table and centrifugation experiments.

observe phase separation in this study.

3.2. Shaker table agitation / centrifugation experiments

Generally, removal of the TCB was found to increase with the number of washes and rinses. However, the greatest removal occurred with the mixture of surfactant and bioactive agent, and subsequent rinses with deionized water resulted in little additional removal (Fig. 1). The highest recovery of the TCB was 95% which was obtained by the using the mixture agent (T-Maz 60 + MOSE) (Fig. 1). Results of these experiments were compared to pure water results (Fig. 1). Mixtures of two different agents often show a “synergistic” interaction (Rosen, 1989; Lee, 1999; Lee et al., 2001). Mixed micelle formation in aqueous solution can be greater than that of the individual components, and explained by non-ideal solution theory and molecular environments (pH, temperature, and ionic strength of the solution) (Harwell, 1992). Attwood and Florence (1983) provided a partial explanation as stated: “a cosolubilization effect where one solubilize causes structural alterations in the micelle so enhancing its capacity for another.”

Encouraging results were achieved from laboratory demonstrations. However, as an innovative technology, there are many factors that need to be investigated with future development. Special attention needs to be paid to the selection of the most appropriate surfactant and/or bioactive agent, which are critical to the success of the implementation of the remediation process and have significant effects on the treatment costs.

4. Conclusion

In the shaker table and centrifugation experiment phase, the highest recovery of the TCB was 95% which was obtained by the using the mixture agent (T-Maz 60 + MOSE). The used test methods for SESF in this study may be very useful and are essential for reducing cost and time in the SESF remediation strategies. Also, the selected mixture of the nonionic surfactant and bioactive agent can be practically used for SESF remediation of TCB contaminated soil.

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References

- Abdul, A.S., Gibson, T.L., and Rai, D.N., 1990, Selection of surfactants for the removal of petroleum products from shallow sandy aquifers, *Ground Water*, **28**, 920-926.
- Ang, C.C. and Abdul, A.S., 1994, Evaluation of an ultrafiltration method for surfactant recovery and reuse during in situ washing of contaminated sites: Laboratory and field studies, *Ground Water Monit. & Remed.*, **14**, 160-171.
- Attwood, D. and Florence, A., 1983, *Surfactant systems: Their chemistry, pharmacy and biology*, Chapman and Hall, New York, 72-123.
- Chu, W. and Kwan, C.Y., 2003, Remediation of contaminated soil by a solvent / surfactant system, *Chemosphere*, **53**, 9-15.
- Chung, S.-L. and Lee, D.-H., 2012, Remediation of PCE-contaminated groundwater using permeable reactive barrier system with MOM-Bentonite, *J. Soil & Groundwater Env.*, **17**, 73-80.
- Cort, T.L., Song, M.-S., and Bielefeldt, A.R., 2002, Nonionic surfactant effects on pentachlorophenol biodegradation, *Water Res.*, **36**, 1253-1261.

- Deshpande, S., Shiau, B.J., Wade, D., Sabatini, D.A., and Harwell, J.H., 1999, Surfactant selection for enhancing ex situ soil washing, *Water Res.*, **33**, 351-360.
- Fountain, J.C., Klimek, A., Beikirch, M., and Middleton, T., 1991, The use of surfactants for in-situ extraction of organic pollutants from a contaminated aquifer, *J. Hazard. Mater.*, **28**, 295-311.
- Harwell, H.H., 1992, Factors affecting surfactant performance in groundwater remediation applications, *American Chemical Society Symposium Series*, **491**, 124-131.
- Lee, D.-H., 1999, Experimental investigation of the removal of hydrophobic organic compounds from two Iowa soils using food grade surfactants and recovery of used surfactants, Ph.D. dissertation, Iowa State Univ., 200pp.
- 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 Monit. & Remed.*, **21**, 49-57.
- Lee, D.-H., Cody, R.D., Kim, D.J., and Choi, S., 2002, Effect of soil texture on surfactant-based remediation of hydrophobic organic-contaminated soil, *Environ. Internation.*, **27**, 681-688.
- Lee, D.-H., Chang, H.-W., and Kim, C., 2008, Mixing effect of NaCl and surfactant on the remediation of TCB contaminated soil, *Geosci. J.*, **12**, 63-68.
- Martel, R. and Gelinas, P.J., 1996, Surfactant solutions developed for NAPL recovery in contaminated aquifers, *Ground Water*, **34**, 143-154.
- Mulligan, C.N. and Gibbs, B.F., 1993, Factors influencing the economics of biosurfactants, In: *Marcel Dekker* (Ed.), Surfactant Science Series, Biosurfactants: production, properties and applications, vol. **48**, Marcel Dekker, Inc., New York, pp. 329-371.
- Mulligan, C.N., Yong, R.N., and Gibbs, B.F., 1999, On the use of biosurfactant for the removal of heavy metals from oil-contaminated soil, *Environ. Prog.*, **18**, 50-54.
- Paria, S. and Khilar, K.C., 2004, A review on experimental studies of surfactant adsorption at the hydrophilic solid water interface, *Adv. in Colloid and Interface Sci.*, **110**, 75-95.
- Rosen, M.J., 1989, Surfactants and Interfacial phenomena, *John Wiley & Sons*, New York, pp. 125-431.
- Rouse, J.D., Sabatini, D.A., and Harwell, J.H., 1993, Minimizing surfactant losses using twin-head anionic surfactants in subsurface remediation, *Environ. Sci. & Technol.*, **27**, 2072-2078.
- Wang, S. and Mulligan, C.N., 2004, An evaluation of surfactant foam technology in remediation of contaminated soil, *Chemosphere*, **57**, 1079-1089.