

Rational Selection of Surfactant in Surfactant-Based Remediation

Dal-Heui Lee^{1*}, Dong-Ju Kim¹, Robert D. Cody² and Sangil Choi³

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

²Department of Geological and Atmospheric Sciences, 253 Science 1, Iowa State University, Ames, IA 50011, USA

³Department of Environmental Engineering, Kwangwoon University, Wolgye-dong, Nowon-ku, Seoul 139-701, Korea

오염복원에 있어서의 계면활성제의 선택

이달희^{1*} · 김동주¹ · Robert D. Cody² · 최상일³

¹고려대학교 지구환경과학과

²Department of Geological and Atmospheric Sciences, Iowa State University

³광운대학교 환경공학과

계면활성제는 소수성 화합물로 오염된 토양과 대수층을 복원하는데 사용할 수 있다. 본 연구의 목적은 톨루엔으로 오염된 사질토양을 복원하는데 사용될 수 있는 적당한 계면활성제들의 선택과 선택된 계면활성제들이 얼마나 효과적으로 톨루엔을 제거하는가를 연구하는데 있다. 사용된 토양은 Ottawa 사질 토양이며, 이용된 유기오염물질은 톨루엔이었다. 6종의 계면활성제의 선택은 독성도, 용해도 등에 따라 이루어졌으며, 이들을 이용한 계면활성제들의 선택실험 방법은 separatory funnel 실험과 shaker table agitation and centrifugation 실험이다. HLB 및 표면장력과 본 연구의 실험 결과에 의하여 6 종의 계면활성제 중 가장 효율적인 종으로 Sandopan JA36(an anionic surfactant)과 Pluronic L44(a non-ionic surfactant)가 선택되었다. 최고의 톨루엔 회수율 96%는 Sandopan JA36를 사용한 shaker table agitation and centrifugation 실험에서 얻었다.

주요어 : 톨루엔, 복원, 계면활성제선택, HLB, 표면장력

Surfactants may be used in remediation of subsoil and aquifer contaminated with hydrophobic compounds. The objectives of this study were to select potentially suitable surfactants that solubilize toluene present as a contaminant and to determine the effectiveness of toluene removal from Ottawa sand by the selected surfactants. Material used as the model soil was Ottawa sand and the organic used as model contaminant was toluene. Used experimental methods were separatory funnel experiment and shaker table agitation/centrifugation experiments. Based on the experimental results, the following conclusions were drawn; 1) In the surfactant selection, six different surfactants were chosen based on surfactant types, toxicity, and water solubility. These six were focused into two on the basis of HLB and surface tension study, separatory funnel experiment, shaker table and centrifugation experiments. The two most suitable surfactants were Sandopan JA36 (an anionic surfactant), and Pluronic L44 (a non-ionic surfactant). 2) In the shaker table agitation and centrifugation experiments, the highest recovery of the toluene was 96% which was obtained with one surfactant wash plus two water rinses using an anionic surfactant (Sandopan JA36).

Key words : toluene, remediation, surfactant selection, HLB, surface tension

1. INTRODUCTION

Removal of hazardous organic substances from soils and aquifers becomes increasingly important. The traditional remediation method, pump-and-treat, has been shown to be ineffective for

remediation soil or groundwater contaminated with nonaqueous phase liquids (NAPLs) (Deitsch and Smith, 1995). Hydrophobic organic compounds are immiscible in water and have a relatively large octanol-water partition coefficient ($k_{ow} > 10^2$) (Rajput *et al.*, 1994; Adeel and Luthy, 1995; Gonzalez and Ukrainczyk, 1996). These chemical comprise 30 percent of the total number

* Corresponding author: dalheui@korea.ac.kr

of organic compounds on the US EPA list of priority pollutants.

Surfactants (surface active agents) may aid in remediation of subsoil and aquifers contaminated with hydrophobic organic compounds (Ang and Abdul, 1994). Over 13,000 surfactants are commercially available. Some may become potential contaminants in soil or groundwater and might also be expected to influence the behavior of other pollutants. Therefore the establishment of criteria for a rational selection of surfactant type and dose is essential. Suitable surfactants should decrease the surface tension of the water and must be non-volatile and easily cleaned and recycled (Rosen, 1989). They must efficiently solubilize or mobilize NAPLs. Unsuitable surfactants may clog pore spaces by flocculating, forming excessively large micelles, or dispersing soil colloids. Pore clogging will prevent the surfactant solution from permeating the contaminated area (Deshpande *et al.*, 1999). Suitable surfactants also must be commercially available, inexpensive, and nontoxic. The parameters of surfactant selection used in this study were surfactant types, solubility in water, toxicity, HLB (Hydrophilic-Lipophilic Balance) number, CMC (Critical Micelle Concentration), settling behavior, and solubilization effectiveness. The objectives of this study were the following: 1) to select potentially suitable surfactants that solubilize toluene present as a contaminant on Ottawa sand, and 2) to determine the effectiveness of toluene removal from Ottawa sand by the selected surfactants.

2. MATERIALS AND METHODS

Material used as model soil required high permeability, low cation exchange capacity, and low total organic carbon content. Ottawa sand was selected because it met these criteria, and because of its uniformity, simple mineralogy, and availability. 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).

The organic used as model contaminant was toluene (C₆H₅CH₃). Toluene, a non-chlorinated aromatic hydrocarbon, is a major industrial hydrophobic organic compound and is commonly found at waste disposal site. It is not effectively removed by pump-and-treat cleanup technology. It is similar in properties to benzene but is less toxic and consequently more suitable for experimental studies than benzene. Toluene has been detected in both soils and underlying groundwater, and is sorbed to soil particles because of its hydrophobic nature.

Sixty different surfactants were obtained from 11 companies. From these surfactants, six were selected on the basis of type, toxicity, and water solubility (Table 1). They were generally clear liquids, non-odorous, readily pourable liquids at room temperature, and soluble in water. They are recommended for remediation of organic contaminated soil by their manufacturers.

2.1. Separatory funnel experiment

This series of experiments provided a rapid,

Table 1. The characteristics of the selected surfactants.

Trade Name	Company	HLB	Type	S.T.*	Solubility in Water	Toxicity
Triton X100	Union Carbide	13	Nonionic	32	Soluble	Nontoxic
Triton RW50	Union Carbide	14	Nonionic	34	Soluble	Nontoxic
Pluronic L44	BASF Crop	14	Nonionic	45	Soluble	Nontoxic
Sandopan JA36	Sandoz Chemical	14	Anionic	40	Soluble	Nontoxic
Sandopan MA18	Sandoz Chemical	19	Anionic	35	Soluble	Nontoxic
Aerosol GPG	American Cyanamid	26	Anionic	30	Soluble	Nontoxic

*=Surface Tension (dyne/cm)

qualitative and fairly reliable means of determining which surfactants are effective solubilizers. Experimental methods were as follow (Lee, 1999); 100 ml of a 2% of each aqueous surfactant solution were placed in a 250 ml separatory funnel and an initial 0.5 ml of toluene was added. The funnel was then shaken gently for 30 sec, and left to settle for one hour. Vigorous shaking in a separatory funnel experiment caused the formation of extremely persistent emulsions. If the entire volume of toluene has solubilized then another 0.5 ml of toluene was added and the funnel shaken again. If any of the first 0.5 ml remained or if an emulsion was present, the funnel was shaken again for 30 sec. and then again set aside during for one hour. 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 were recorded. This process was repeated three times for each surfactants.

2.2. Shaker table agitation and centrifugation experiments

These experiments were conducted to select surfactants which can solubilize/extract organic compounds from sand using toluene as a contaminant. Eighty grams of sand spiked with 5 ml (4.335 g) toluene with 250 ml of 2%(v/v) aqueous surfactant solutions were placed in 500 ml Teflon screw cap jars. Surfactants used were Triton X100, Triton RW50, Pluronic L44, Sandopan JA36, based on the HLB number study and separatory funnel experiments. The contaminated sand and aqueous surfactant solution were mixed on a shaker table at 200 rpm for 50 minutes. The jar was then centrifuged at 2000 rpm for 5 minutes to separate the aqueous and sand phases. The liquid was decanted, and 250 ml deionized water was added to the sand, and again shaken for 50 minutes. The process was repeated until one surfactant wash and two deionized water rinses were completed (Lee, 1997; Lee *et al.*, 2001). Leachates were collected after each step and analyzed for contaminant.

2.3. Analytical procedures

The analysis of toluene in aqueous leachate samples used solvent extraction and gas chromatography. Gas chromatographic analysis on all the extracts of aqueous leachate samples were per-

formed using a Hewlett Packard model 5890 series II gas chromatography with split/splitless injection system. The system was temperature programmable and has a Flame Ionization Detector (FID). Prior to the analysis of sample extracts, the response factor and linearity of detection for the internal standard and toluene was demonstrated. Retention times and response factors were recorded. After having calculated the response factor, a calibration graph was prepared. A calibration curve was prepared by using solutions containing known concentrations of toluene. In this study, the concentrations of toluene stock solutions for standard curves were 9.4×10^{-5} , 18.8×10^{-5} , 28.2×10^{-5} , 37.6×10^{-5} , 47.0×10^{-5} M (mol/L). The linear range of detection for the internal standard of ethyl benzene and the organic compounds of interest, toluene, was determined and all sample extracts were analyzed within this range. If an extract was concentrated or dilute, it was adjusted to a concentration within the linear detector response range.

3. RESULTS AND DISCUSSION

3.1. HLB and surface tension data

From sixty surfactants, six were selected on the basis of type, toxicity, and water solubility (Table 1). Each surfactant has an HLB number. This number is useful for preliminary surfactant selection (Currie *et al.*, 1992, Lee *et al.*, 2001) because maximum solubilization will occur at a specific HLB number within a given surfactant's chemical family (Rosen, 1989). Two surfactants with different functional groups but the same HLB value should show similar solubilities. When a combination of surfactants of different HLB value is used, the HLB number of the mixture is the weighted average of the individual HLB numbers. Generally, the more water soluble the surfactants, the higher the HLB number. A high HLB value indicates a large percentage of polar head groups, and a dominantly hydrophilic character. These surfactants will favorably partition into the water phase. If the HLB of the surfactant is high for the given substrate, however, then stable emulsions will not form because the surfactant will concentrate nearly exclusively in the water phase. For aromatic hydrocarbon contaminants the optimum HLB number is 12-15 (Rosen, 1989). In this study

HLB values were obtained from literature reviews, catalogs, and surfactant suppliers. The HLB number of studied surfactant is given in Table 1. Unsuitable surfactants based on HLB number in this study were Sandopan MA 18 and Aerosol GPG with HLB > 15.

The critical micelle concentration (CMC) is the aqueous concentration of surfactant at which surface tension of the solution is smallest. The CMC is determined by interpreting a plot of surface tension vs. log surfactant concentration (Rosen, 1989). As the concentration is increased, the surface tension decreases until the CMC is reached. The CMC is a significant parameter in solubilization, and mobility of contaminants can be expected to be highest and/or above the CMC of the aqueous surfactant solution (Deshpande *et al.*, 2000). A surfactant with a lower CMC value will be more desirable as it can begin to solubilize organic contaminant at lower concentrations with minimal toxic exposure to soil microbes (Knox *et al.*, 1997). Reduction of surface tension in aqueous solutions is a standard test for surface activity.

3.2. Separatory funnel experiments

In these experiments, it was noted how much toluene was taken into an emulsion solution before a separate phase was observed (e.g. toluene separated or a heavy emulsion/toluene phase separated from the rest of the solution). Sandopan MA18, Aerosol GPG were not able to solubilize at least 1 ml of toluene 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 2). Sandopan JA36, Pluronic L44, Triton X100, and Triton RW50 were relatively efficient solubilizers for toluene. Sandopan JA36 and Pluronic L44 had no emulsion. These were then used in a vari-

ety of other experiments, such as shaker table agitation and centrifugation experiments, which is discussed later.

Emulsion and foam formation created problems in the experiments. It was difficult to determine if an emulsion was present in a cloudy surfactant solution, and thus if solubilization was occurring. Because of this it is possible that some surfactants may have been considered more effective solubilizers than actually were.

3.3. Shaker table agitation and centrifugation experiments

As expected, removal of the toluene was found to increase with the number of washes and rinses. However, the greatest removal occurred with the surfactant wash, and subsequent rinses with deionized in little additional removal. The highest recovery of the toluene was 96% which was obtained with one surfactant wash plus two water rinses using the anionic surfactant, Sandopan JA36 (Fig. 1). Based on these experimental results, it was concluded that Triton X100, Triton RW50 were least effective, although more effective than distilled water (Lee, 1997; Lee *et al.*, 2001). Sandopan J36, and Pluronic L44 surfactants give high effectiveness for toluene removal based on the shaker table and centrifugation experiments. Consider the high volatility of toluene, some of the low recovery may be due to loss by volatilization occurring during vigorous shaking and centrifugation.

3.4. Surfactant selection study

Surfactant are widely used for solubilization purposes in various areas. They can be used to enhance the extractive power of water. The use of aqueous surfactant solutions for removal of organic contaminants from sand has been reported in lab-

Table 2. The results of separatory funnel experiments.

Trade Name	Amount Toluene Added (ml)	Estimated Amount solubilized	Characteristics after 24 hours
Triton X100	1.5	1.0	Heavy milky emulsion
Triton RW50	2.0	1.5	Light pink color formed
Pluronic L44	2.0	2.0	No foaming
Sandopan JA36	2.5	2.5	Moderation foaming formed
Sandopan MA18	1	0.5	Heavy milky emulsion
Aerosol GPG	1	0.5	Heavy milky emulsion

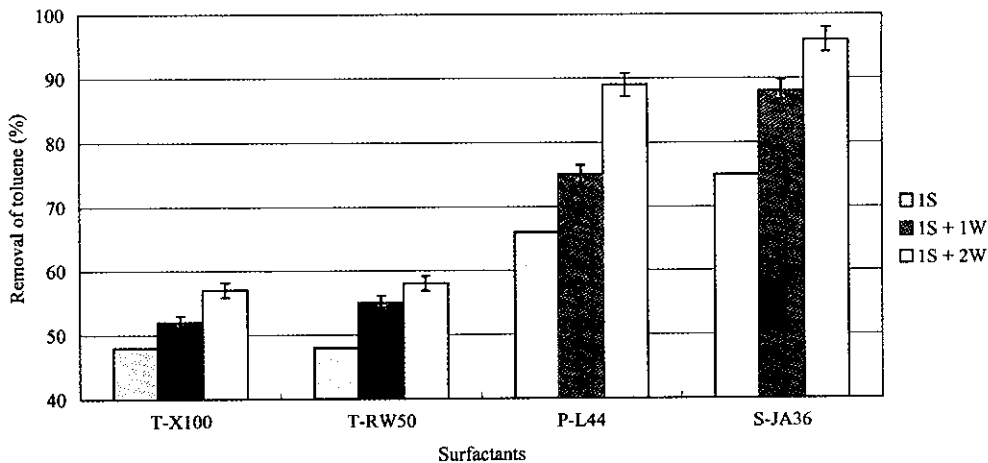


Fig. 1. The removal of toluene by different surfactant in shaker table and centrifugation experiments.

oratory column studies (Martel and Gelinas, 1996). Nash and Traver (1986) used 2% nonionic surfactant (Adsee 799) for removal of the anthracene from sand. Results indicated that aqueous surfactant solutions removed more than 90% of contaminants from sand in column experiments. Extractive efficiencies for hydrophobic organic compounds were seven to ten times greater than those which may be obtained by flushing with water alone. These prior studies showed that aqueous surfactant solutions significantly enhanced the removal of hydrophobic contaminants from sand. Abdul *et al.* (1990) evaluated the suitability of 10 surfactants for washing automatic transmission fluid (ATF) from sand. They measured the surface tension of the surfactant and also conducted batch test for solubilization capacity. The most effective surfactant was Witconol SN70 (alkyl polyoxyethylene glycol, a nonionic surfactant). In another surfactant selection study, using separatory funnel experiment of solubility, Fountain *et al.* (1991) evaluated 100 surfactant for washing PCE (tetrachloroethylene) 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 effectiveness of surfactant differs depending on the specific organic contaminant.

4. CONCLUSION

The following conclusions are drawn based on

the experimental work:

1. In the surfactant selection phase of the investigation, six different surfactants were chosen based on surfactant types, toxicity, and water solubility. These six were reduced to two on the basis of HLB and surface tension study, separatory funnel experiment, shaker table and centrifugation experiments. The two suitable surfactants were Sandopan JA36 (an anionic surfactant), and Pluronic L44 (a non-ionic surfactant).

2. In the shaker table and centrifugation experiment phase, the highest recovery of the toluene was 96% which was obtained with one surfactant wash plus two water rinses using the anionic surfactant, Sandopan JA36. The most suitable surfactant in this study was Sandopan JA36 (trideceth-19-carboxylic acid) based on shaker table and centrifugation experiments.

ACKNOWLEDGEMENTS

The first author has a scholarship of the Korean-American Association for the encouragement of scientific research in the university of USA. We would like to express our appreciation to Dr. William W. Simpkins of Iowa State University, USA for suggestions and encouragement during the study. We also like to express appreciation to the members of organic chemistry laboratory and soil physics laboratory in Iowa State University, USA. This research was partly supported by the Brain Korea 21 project fund of Korea University.

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*, v. 28, p. 920-926.
- Adeel, Z. and Luthy, R.G. (1995) Sorption and transport kinetics of a nonionic surfactant through an aquifer sediment. *Environmental Sciences and Technology*, v. 29, p. 1032-1042.
- 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. *Ground Water Monitoring and Remediation*, v. 14, p. 160-171.
- Currie, J.C., Bunge, A.L., Updegraff, D.M. and Batal, W.H. (1992) Surfactant enhanced remediation of creosote contaminated soils. *Hydrocarbon Contaminated Soils*, Lewis Publishers, London, p. 641-674.
- Deitsch, J.J. and Smith, J.A. (1995) Effect of Triton X-100 on the rate of trichloroethene desorption from soil to water. *Environmental Science and Technology*, v. 29, p. 1069-1080.
- 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.
- 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. *Journal of Hazardous Materials*, v. 28, p. 295-311.
- 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. *Ground Water 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.
- Nash, J.H. and Traver, R.P. (1986) Field evaluation of in situ washing of contaminated soils with water/surfactants. *Proceedings of the Twelfth Annual Research Symposium*, EPA/600/9-86/022, p. 208-217.
- Rajput, V.S., Higgins, A.J. and Singley, M.E. (1994) Cleaning of excavated soil contaminated with hazardous organic compounds by washing. *Water Environment Research*, v. 66, p. 819-827.
- Rosen, M.J. (1989) *Surfactants and interfacial phenomena*. John Wiley & Sons, k, p. 108-239.

2001년 6월 7일 원고접수, 2001년 8월 14일 게재승인.