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Remediation of groundwater contaminated with DNAPLs by biodegradable oil emulsion

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Abstract

Emulsion-based remediation with biodegradable vegetable oils was investigated as an alternative technology for the treatment of subsurface DNAPLs (dense non-aqueous phase liquids) such as TCE (trichloroethylene) and PCE (perchloroethylene). Corn and olive oil emulsions obtained by homogenization at 8000 rpm for 15 min were used. The emulsion droplets prepared with corn and olive oil gave a similar size distribution (1–10 μm) and almost all of initially injected oil, >90%, remained in a dispersed state. In batch experiments, 2% (v/v) oil emulsion could adsorb up to 11,000 ppm of TCE or 18,000 ppm of PCE without creating a free phase. Results of one-dimensional column flushing studies indicated that contaminants with high aqueous solubility could be efficiently removed by flushing with vegetable oil emulsions. Removal efficiencies exceeded 98% for TCE and PCE with both corn and olive oil emulsions. The results of this study show that flushing with biodegradable oil emulsion can be used for the remediation of groundwater contaminated by DNAPLs.
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1. Introduction

Human health is threatened by contaminated groundwater [1] and contamination by the non-aqueous phase liquids (NAPLs) is of particular concern. Contamination by NAPLs is particularly difficult to treat or remove because of their low aqueous solubility. Based on water density, NAPLs are divided into dense NAPLs (DNAPLs) and light NAPLs (LNAPLs). Removal of DNAPLs is complicated because DNAPLs are less water-soluble and denser than LNAPLs. When a spill occurs, DNAPLs are initially trapped in the form of immobile blobs or ganglia by capillary forces [2,3]. As time elapses, the DNAPLs migrate into the aquifer and form pools in its bottom. Due to their low aqueous solubility, DNAPLs can pollute groundwater continuously for a long period of time [4]. Most of DNAPLs detected in contaminated sites are chlorinated solvents, especially chlorinated ethylenes such as TCE (trichloroethylene) and

PCE (perchloroethylene). TCE and PCE are used as extracting solvents, dry cleaning fluids and chemical intermediates [2,5]. Chlorinated solvents are suspected carcinogens, and therefore their presence in groundwater is of considerable concern [6].

Surfactant-enhanced aquifer remediation (SEAR) is a proven technology that can be used for the remediation of subsurface DNAPLs. The aqueous solubility of DNAPLs increased by the use of surfactants and a number of researchers have studied SEAR in the laboratory and field [7–14]. In the application of SEAR for remediation of subsurface DNAPLs, the downward migration of the solubilized and mobilized DNAPLs can occur because the density of DNAPLs is higher than that of water. This downward migration of DNAPLs can lead to the secondary contamination of fresh aquifer [15]. Thus, the application of SEAR is restricted to those aquifers that have an impermeable layer at the bottom, even though SEAR is the cost-effective means of improving removal efficiency [16].

To overcome this limitation by the SEAR method, emulsion-enhanced remediation method was proposed [15,17,18]. Silicone oil emulsion was used as a flushing agent and it was found that the emulsion was able to solubilize DNAPL in both batch

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and column experiments. However, the residual silicone oil that would be left behind in the subsurface after the remediation process would be undesirable even though silicone oil is biocompatible. However, it was found that the in situ biodegradation of TCE and PCE can be greatly enhanced by the injection of electron donors such as vegetable oils and vegetable oil emulsions into contaminated aquifers. Vegetable oils are inexpensive and act as a slowly released electron donor [19,20]. The use of biodegradable vegetable oils has contributed to the removal of contaminants by enhancing microbial activities. In this study, the feasibility of remediation using a vegetable oil emulsion was investigated to remediate groundwater contaminated by chlorinated solvents, representative DNAPLs, without secondary contamination of fresh groundwater by dissolved DNAPLs and flushing agents.

2. Materials and methods

2.1. Preparation and characterization of emulsions

A homogenizer (HMZ-20DN; Global Lab., Korea) was used to make an emulsion with commercial corn and olive oil. The characteristics of corn and olive oil are summarized in Table 1. The concentrations of oil used were 0.5, 1, and 2% (v/v) and the homogenization rates were 5000 and 8000 rpm. Emulsions were prepared by homogenizing for 5, 10, and 15 min. The particle size distribution of the emulsions was analyzed by a particle size analyzer (Beckman Coulter LS230, Brea, USA). The amount of oil dispersed in the emulsion phase was measured after evaporation of water in a 105 °C oven.

2.2. Solubilization of TCE and PCE in batch system [21]

The batch test is necessary to determine the maximum solubilization capacity of the oil emulsion prepared. The physicochemical properties of TCE and PCE are shown in Table 2 and the partitioning of TCE and PCE into the oil emulsions was investigated using 20 ml vial. Initially 20 ml vial was filled with 10 ml emulsion solutions and then it was capped with Teflon-coated septa. After injection of contaminants into vials, the vials were shaken at 25 °C for 6 h to achieve phase equilibrium. A gas

tight syringe was used to obtain 100 μl of sample from the head space of the vial and the samples were immediately inserted into the GC injector. For quantification of TCE and PCE concentration, gas chromatography (Hewlett Packard 6890, USA) coupled with a flame ionization detector (FID) was employed. The chromatographic capillary column was a HP-5 (Hewlett Packard, 30 m × 0.25 mm). The GC conditions were as follows: injector temperature, 250 °C; column temperature, 40 °C for 4 min, followed by 40–190 °C at a rate of increase of 20 °C/min; detector temperature, 250 °C. The carrier gas was helium and the column flow rate was 1 ml/min without split.

2.3. Emulsion flushing of TCE and PCE

Column flushing experiments were performed in 30 mm × 160 mm column (Kontes, USA) containing 115 g of sieved Jumunjin filtered sand (20–30 mesh). The pore volume of sand in the column was 35 ml. Initially, 20 pore volumes of deionized water were pushed through the column in an upward direction at a flow rate of 1 ml/min. Next, the column was contaminated by injecting 1 pore volume of TCE and PCE individually at a flow rate of 1 ml/min. Since chlorinated solvents have high density than water, neat liquid was introduced in upward direction, from bottom to top, to achieve displacement of water from the column. After contamination, deionized water (>30 pore volume) was flowed in the opposite direction, from top to bottom, in order to remove any TCE or PCE that was free in the mobile phase. As a result, residual saturation was reached. For the flushing of contaminants from the column, emulsions, prepared with 2% (v/v) corn or olive oil by homogenization at 8000 rpm during 15 min, were pumped in an upward direction through the column at a flow rate of 1 ml/min. After the flushing procedure, any TCE or PCE that remained on the columns were recovered by washing the columns with 500 ml of methanol and its amount was analyzed by HPLC/UV. The flow rate was controlled by a peristaltic pump (Masterflex, USA). HPLC (high performance liquid chromatograph) was used to measure TCE and PCE concentration in the emulsion solutions. The HPLC is equipped with a symmetry C18 column (Waters, USA), a UV detector (Waters 490E, USA), and an autosampler (Waters 717 plus, USA). The HPLC was operated under the following conditions: a flow rate of 1.0 ml/min, the mobile

Table 1
Characteristics of oil (at 25 °C)

Oil	Specific gravity	Viscosity (cSt)	TCE solubility (ppm)	PCE solubility (ppm)
Corn	0.913	51	276,317	311,980
Olive	0.906	60	287,871	325,203

Table 2
Physicochemical properties of TCE and PCE

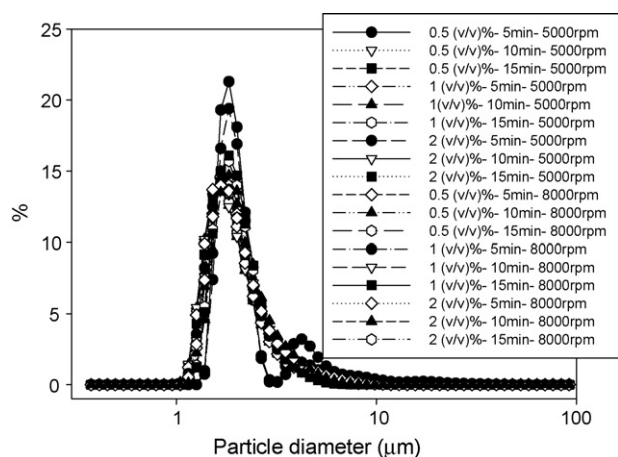|	Molecular weight	Density (g/cm^3)	Solubility (mg/l, 25 °C)	Vapor pressure (Pa)	log $1/H^a$ (25 °C)
TCE	131.3	1.463	1099.0	938.0	0.384
PCE	165.8	1.623	200.0	252.1	0.145

[a] Henry's law constant.

Fig. 1. Percent distribution of corn oil emulsion particles prepared using following conditions: homogenization rate of 5000 and 8000 rpm; homogenization time of 5, 10 and 15 min; oil contents of 0.5, 1 and 2% (v/v).

phase was acetonitrile/water (85/15, v/v) and detection was via a UV detector operated at a wavelength of 214 nm.

3. Results and discussion

3.1. Particle properties of corn and olive oil emulsions

The size distribution of corn oil emulsion particles prepared using different emulsification conditions is presented in Fig. 1. Most of the emulsion particles were distributed between 1 and 10 μm and all showed a similar distribution pattern. The effects of preparation parameters on the particle properties of the emulsion were analyzed by calculating the volume percentage of particles whose diameter is less than 10 μm because most particles were distributed between 1 and 10 μm. Fig. 2 shows the effect of homogenization rate and time on the particle distribution of corn oil emulsion. At a homogenization rate of 5000 rpm, the volume percentages of the particles (<10 μm) were below 40%. Change of the homogenization rate from 5000 to 8000 rpm resulted in an increase in the volume percentage of particles (<10 μm) of 20–30%. As the homogenization time increased, the emulsion particles became well-dispersed and consequently the volume percentage of the emulsion particles (<10 μm) increased. The volume percentage of particles (<10 μm) at 15 min is about 10% higher than that at 5 min (Fig. 2). To order to confirm the effect of homogenization rate and time on the olive oil emulsion, 2% (v/v) olive oil emulsion was prepared under the same conditions as with corn oil emulsion. Fig. 3 shows similar patterns to the previous corn oil emulsion, in which a key parameter in the preparation of emulsion was the homogenization rate. The volume percentage of particles (<10 μm) emulsified at 8000 rpm was 20% higher than that emulsified at 5000 rpm. Long homogenization time was effective in terms of yielding a well-dispersed emulsion. The stability of the emulsion was observed over a period of 7 days (Fig. 4). During this time, more than 90% of oil remained in a dispersed state. As a result, significant change in the particle size distribution and phase separation by coalescence was not detected over the 7 days incubation.
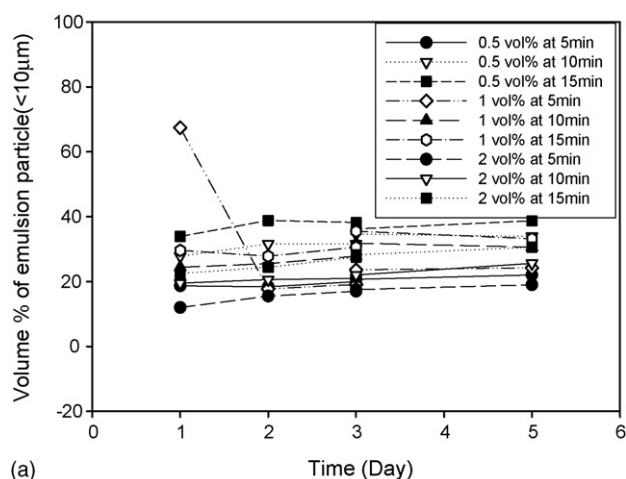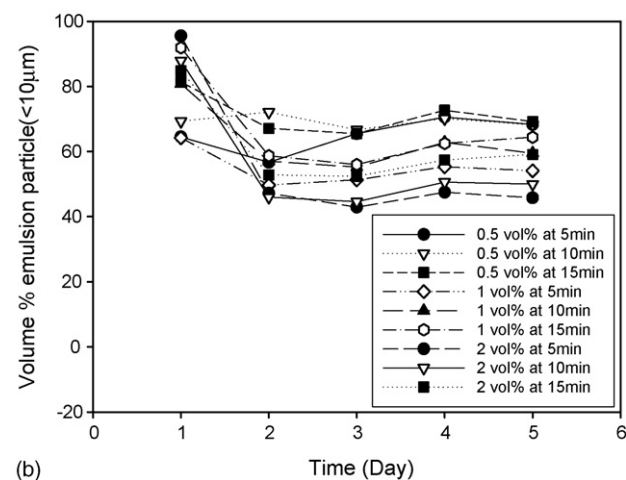
Fig. 2. Volume percentage of corn oil emulsion particles whose diameter is less than 10 μm: (a) at homogenization rate of 5000 rpm; (b) at homogenization rate of 8000 rpm.

3.2. Partitioning of TCE and PCE in batch system

Fig. 5 shows the effect of TCE concentration on its solubilization into the corn and olive oil emulsions. Similar solubilization
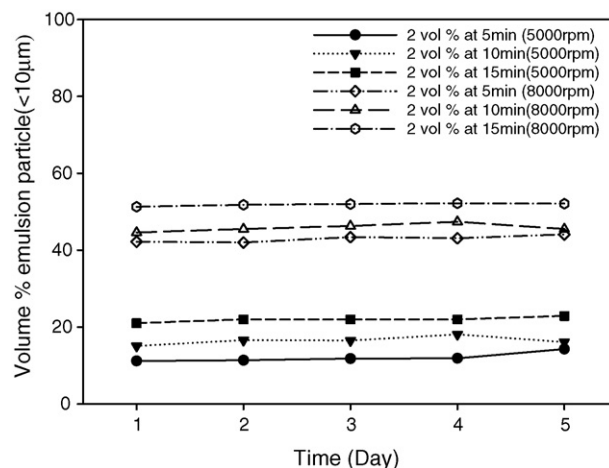

Fig. 3. Volume percentage of 2% (v/v) olive oil emulsion particles whose diameter is less than 10 μm.
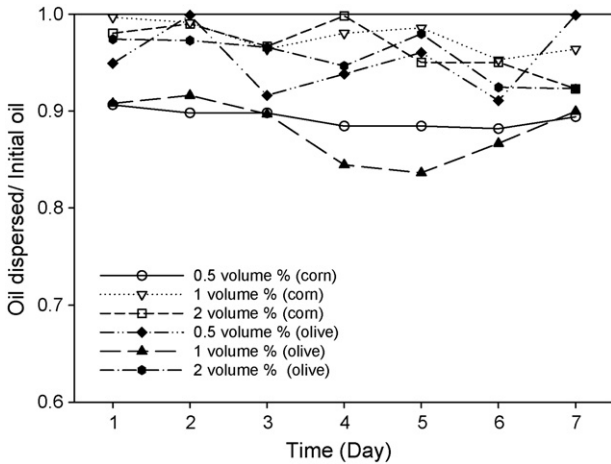
Fig. 4. The contents of corn oil and olive oil in dispersed state. Emulsions were prepared by homogenization at 8000 rpm for 15 min.

results were obtained with both emulsions because corn and olive oil have similar emulsifying ability and solubility for TCE (Table 1). When a 2% (v/v) oil emulsion was applied for the treatment of 11,000 ppm TCE, the residual concentration was less than the aqueous solubility of TCE (1099 ppm at 25 °C). Thus, 11,000 ppm TCE was treated by the emulsion without
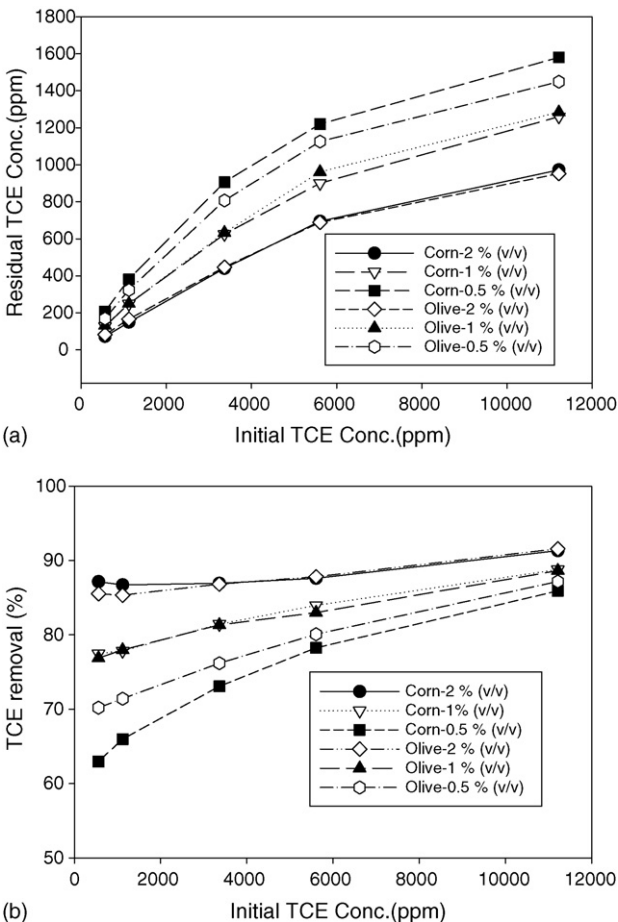

Fig. 5. Residual concentration (a) and solubilization efficiency (b) of TCE in 2, 1 and 0.5% (v/v) corn and olive oil emulsions.
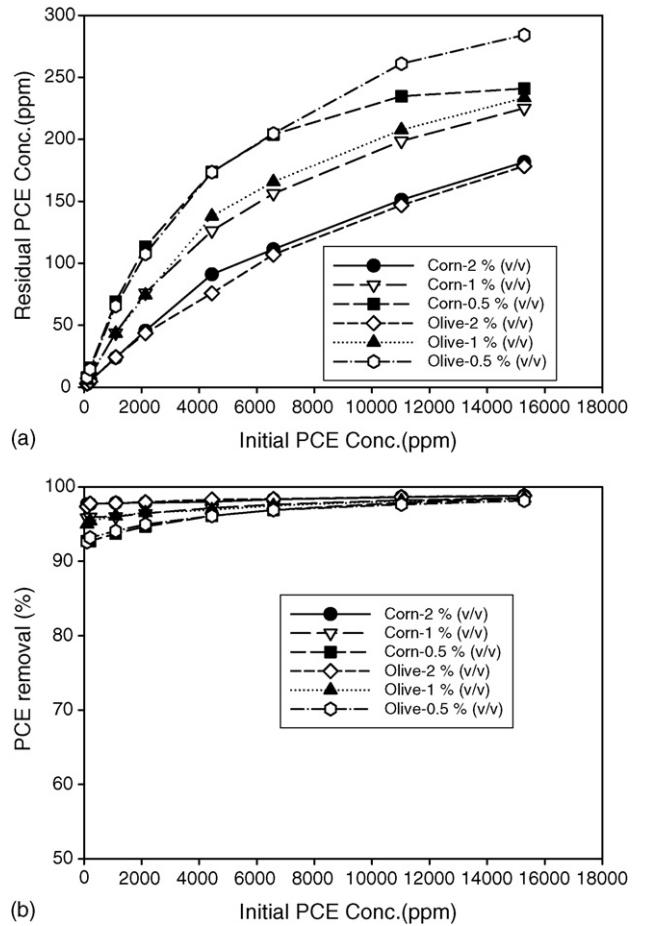

Fig. 6. Residual concentration (a) and solubilization efficiency (b) of PCE in 2, 1 and 0.5% (v/v) corn and olive oil emulsions.

the formation of a free TCE phase. When 0.5 and 1% (v/v) oil emulsions were used with high TCE concentration, however, free phase of TCE formed because the residual TCE concentration exceeded the aqueous solubility of TCE. Solubilization of PCE in corn and olive oil emulsions is described in Fig. 6. A 2% (v/v) oil emulsion could treat 18,000 ppm PCE without the formation of a free PCE phase. Compared to the results for TCE solubilization, the solubilization efficiency increased because the solubility of PCE in corn and olive oil is higher than that of TCE (Table 1). Free PCE phase formed when 0.5 and 1% (v/v) oil emulsion were used for PCE solubilization of high concentration.

3.3. Use of emulsions to flush TCE and PCE from sand column

The concentration of TCE in column effluents flushed with corn and olive oil emulsions is plotted in Fig. 7. Removal efficiencies of 98.2% with the corn oil emulsion and 99.1% with the olive oil emulsion were obtained. Corn and olive oil showed similar flushing performance because they have similar emulsifying ability and TCE solubility. In other studies where surfactant flushing was used, tails of low contaminant concentration were detected in the latter phases of the flushing procedure [7,8].
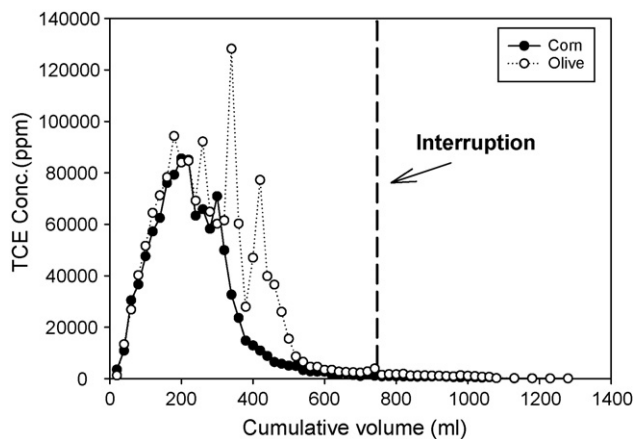
Fig. 7. TCE flushing with 2% (v/v) corn and olive oil emulsions. Flow was interrupted during 12 h after flow of 720 ml emulsion.

This phenomenon is caused by the low mass transfer between emulsion and contaminants because the small amount of contaminants exists within soils. Therefore an interruption of flow for 12 h was conducted to enhance mass transfer. However, effluent TCE concentration was not increased by interruption of flow because most of TCE had already been flushed out by the flow of 720 ml of 2% (v/v) oil emulsion before the interruption. Similar results were obtained with PCE. Removal efficiencies of 98% with the corn oil emulsion and 98.7% with the olive oil emulsion were obtained (Fig. 8). Corn and olive oil also showed similar removal tendencies for PCE. Interruption of emulsion flow increased the effluent PCE concentration, because mass transfer between PCE and the emulsion was enhanced during interruption. Compared with TCE flushing, the removal of PCE progressed slowly even though the solubility of PCE on corn and olive oil is higher than that of TCE (Table 1). The differences in the removal of TCE and PCE flushing were due to the difference in the aqueous solubility of TCE and PCE. TCE has a higher aqueous solubility (1099 ppm at 25 °C) than PCE (200 ppm at 25 °C). Therefore, TCE can be flushed from the column in a shorter period of time. The amounts of oil remaining in the soil columns were 5.217 g corn oil/kg sand and 4.348 g olive
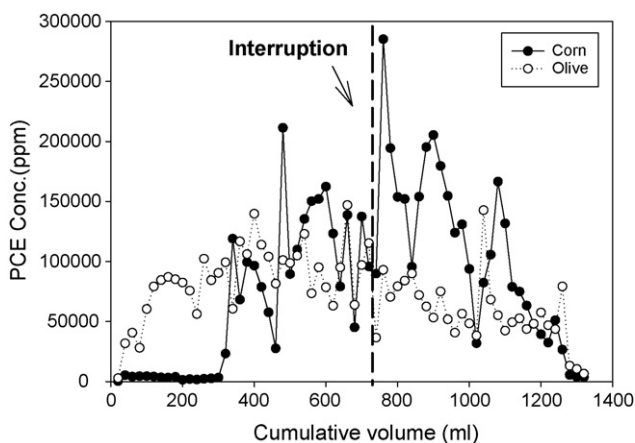
oil/kg sand (TCE flushing), and 6.967 g corn oil/kg sand and 6.522 g olive oil/kg sand (PCE flushing). These indicated that 2–3% of the total oil that flowed through column was sorbed on the sand, indicating that viscosity effect of oils on sorption was insignificant. Although some portion of oil emulsion containing contaminants may remain in soil after flushing, the results of bioremediation of chlorinated solvents using vegetable oils indicate that it does not cause secondary contamination [18–20].

4. Conclusions

The feasibility of emulsion-based remediation via the removal of trichloroethylene (TCE) and tetrachloroethylene (PCE) from groundwater was investigated. Homogenization rate was the most important parameter in preparation of the emulsion. As homogenization time increased, the portion of small emulsion particles increased and the emulsion stability was enhanced. Utilizing emulsification at 8000 rpm for 15 min, more than 90% of oil initially injected existed in a dispersed state. The emulsion prepared with 2% (v/v) corn oil could treat 89% of 11,000 ppm TCE and 98% of 18,000 ppm PCE. Similar solubilization results were obtained for the olive oil emulsion: 91% of 11,000 ppm TCE and 99% of 18,000 ppm PCE. In column flushing, most TCE and PCE (>98%) were removed by flushing with corn and olive oil emulsions. The important parameter in column flushing was the aqueous solubility of the contaminants.

In short, properties of the emulsion solution did not change during column flushing and the stability of emulsion was maintained. In addition to its biodegradability of emulsion phase, it is expected that residual contaminants would be degraded to nontoxic products by microbial activities. Therefore, remediation of groundwater contaminated with DNAPLs by a biodegradable oil emulsion can be practical through pilot-scale study along with economic feasibility.

References

[1] J.H. Harwell, D.A. Sabatini, R.C. Knox, Surfactants for ground water remediation, Colloid Surf. A. 141 (1999) 255–268.
[2] J.F. Pankow, J.A. Cherry, Dense Chlorinated Solvents, Waterloo Press, Portland, 1996.
[3] S.R.D. Lunn, B.H. Kueper, Manipulation of density and viscosity for the optimization of DNAPL recovery by alcohol flooding, J. Contam. Hydrol. 38 (1999) 427–445.
[4] T. Oolman, S.T. Godard, G.A. Pope, M. Jin, K. Kirchner, DNAPL flow behavior in a contaminated aquifer: evaluation of field data, Ground Water Monit. R. 15 (1995) 125–137.
[5] P.J. Squillace, M.H. Moran, W.W. Lapham, C.V. Price, R.M. Clawges, J.S. Zogorski, Volatile organic compounds in untreated ambient groundwater of the United States, 1985–1995, Environ. Sci. Technol. 33 (1999) 4176–4187.
[6] G.D. Hopkins, J. Munakata, L. Semprini, P.L. McCarty, Trichloroethylene concentration effects on pilot field-scale in-situ groundwater bioremedia-

Fig. 8. PCE flushing with 2% (v/v) corn and olive oil emulsions. Flow was interrupted during 12 h after flow of 720 ml emulsion.

tion by phenol-oxidizing microorganisms, Environ. Sci. Technol. 27 (1993) 2542–2547.

[7] T.P. Taylor, K.M. Rathfelder, K.D. Pennell, Effects of ethanol addition on micellar solubilization and plume migration during surfactant enhanced recovery of tetrachloroethene, J. Contam. Hydrol. 69 (2004) 73–99.

[8] T.P. Taylor, K.D. Pennell, L.M. Abriola, J.H. Dane, Surfactant enhanced recovery of tetrachloroethylene from a porous medium containing low permeability lenses: 1. Experimental studies, J. Contam. Hydrol. 48 (2001) 325–350.

[9] K.D. Pennell, M. Jin, L.M. Abriola, G.A. Pope, Surfactant enhanced remediation of soil columns contaminated by residual tetrachloroethylene, J. Contam. Hydrol. 16 (1994) 35–53.

[10] K.D. Pennell, G.A. Pope, L.M. Abriola, Influence of viscous and buoyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing, Environ. Sci. Technol. 30 (1996) 1328–1335.

[11] C.T. Miller, M.M. Poirier-McNeill, A.S. Mayer, Dissolution of trapped nonaqueous phase liquids: mass transfer characteristics, Water Resour. Res. 26 (1990) 2783–2796.

[12] A.S. Mayer, C.T. Miller, The influence of mass transfer characteristics and porous media heterogeneity on nonaqueous phase dissolution, Water Resour. Res. 32 (1996) 1551–1567.

[13] J.C. Fountain, A. Klimel, M.G. Beikirch, T.M. Middleton, The use of surfactants for in situ extraction of organic pollutants from a contaminated aquifer, J. Hazard. Mater. 28 (1991) 295–311.

[14] T.B. Boving, M.L. Brusseau, Solubilization and removal of residual trichloroethene from porous media: comparison of several solubilization agents, J. Contam. Hydrol. 42 (2000) 51–67.

[15] T.S. Kwon, J.S. Yang, K. Baek, J.Y. Lee, J.W. Yang, Silicone emulsion-enhanced recovery of chlorinated solvents: batch and column studies, J. Hazard. Mater. 136 (2006) 610–617.

[16] J.C. Fountain, R.C. Starr, T. Middleton, M. Beikirch, C. Taylor, D.A. Hodge, Controlled field test of surfactant-enhanced aquifer remediation, Ground Water. 34 (1996) 910–916.

[17] T.S. Kwon, K. Baek, Y. Ahn, J.Y. Lee, J.S. Yang, J.W. Yang, The solubilization characteristics of DNAPLs by oil-based emulsion, Sep. Sci. Technol. 40 (2005) 685–698.

[18] G.P. Streile, J.W. Cary, J.K. Fredrickson, Innocuous oil and small thermal gradients for in situ remediation, in: Proceeding of the National Research and Development Conference on the Control of Hazardous Materials, 1991, pp. 32–37.

[19] L. Zhengkai, B.A. Wrenn, A.D. Venosa, Anaerobic biodegradation of vegetable oil and its metabolic intermediates in oil-enriched freshwater sediments, Biodegradation 16 (2005) 341–352.

[20] P. Patricia, R.B. Angela, I. Tissa, H. Bruce, Partitioning of dissolved chlorinated ethenes into vegetable oil, Water Res. 39 (2005) 4521–4527.

[21] R. Nagarajan, M.A. Chaiko, E. Ruckenstein, Locus of solubilization of benzene in surfactant micelles, J. Phys. Chem. 88 (1984) 2916–2922.