Silicone emulsion-enhanced recovery of chlorinated solvents: Batch and column studies

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Abstract

Batch and column experiments were conducted to investigate the feasibility of flushing with silicone oil emulsion for the removal of chlorinated solvents, including trichloroethylene (TCE), perchloroethylene (PCE) and 1,2-dichlorobenzene (DCB). In the batch experiments, solubilization potentials of emulsion and effects of surfactants as additives were examined. The emulsion prepared with 2% (v/v) silicone oil could solubilize 90.7% of 10,000 ppm TCE, 97.3% of 4000 ppm PCE and 99.7% of 7800 ppm DCB. Results of one-dimensional column studies indicated that aqueous solubility and sorption of contaminants determined the flushing efficiency. The addition of surfactants below their critical micelle concentration (CMC) did not affect the removal of chlorinated solvents in batch and column experiments. The results of this study show that flushing with oil-based emulsion can be applied to treat the chlorinated solvents.
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1. Introduction

Organic pollutants such as chlorinated solvents in the aquifer have been a serious threat to human health because they are very toxic to human beings and mostly non-biodegradable. Therefore, the removal of chlorinated solvents from the subsurface environment has been investigated by many researchers. Pump-and-treat methods, traditional technique for cleanup of aquifers contaminated by organic pollutants, have proven to be ineffective due to rate-limited dissolution, spatial variability of subsurface, non-uniform contaminant distribution, and high density, hydrophobicity and low aqueous solubility of chlorinated solvents [1–7]. To improve the performance of pump-and-treat method, other alternatives have been proposed. Currently, surfactant enhanced aquifer remediation (SEAR), also called surfactant flushing, is

regarded as the most feasible technology to recover the chlorinated solvents from the aquifer. The apparent solubility and mobility of contaminants in the subsurface significantly increase by the use of surfactants as flushing agents.

The effectiveness of these technologies is ultimately controlled by the ability to deliver flushing fluids to zones of contamination and to capture the resulting dissolved contaminant plume, and in some cases, displaced free product [8]. Numbers of researchers have performed one-dimensional or two-dimensional laboratory studies to observe the effect of delivery or mass transfer limitation in the subsurface conditions [8–15]. In two-dimensional flushing of tetrachloroethylene [9], the 4% Tween 80 solution, which was slightly denser (1.002 g/ml at 20 °C) than the resident pore water (0.998 g/ml at 20 °C), flowed preferentially along the bottom of the box. Mobilization was observed in the some laboratory studies [10–12]. The preferential flow of a surfactant solution and mobilization would not be desirable because secondary contamination of aquifer can happen by migration of dense contaminant-swollen micelle

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or free product [8]. Besides, the sorption of surfactants on soils is severe due to their amphiphilic property. The loss of surfactants by sorption is environmentally and economically unacceptable.

To overcome the problems of SEAR, the emulsion-enhanced remediation was proposed in our previous study [16]. The silicone oil of low viscosity (5 cS) was selected as a solubilizing agent because the emulsion made with oils of high viscosity showed severe sorption on soil. The emulsion was well dispersed by mechanical homogenization. The results in the preliminary batch test revealed that the chlorinated solvents could be treated by emulsion. However, uncertain factors still exist within the soil or sand, and the flow of solubilizing agents is difficult to predict. The flow path in the subsurface is important for the effective mass transfer. Therefore, the feasibility of solubilizing agents should be confirmed for the application in contaminated sites. In this study, the detailed solubilizing characteristics of emulsion and one-dimensional flushing were investigated for the further application.

2. Materials and methods

2.1. Chemicals

Silicone oil (dimethylpolysiloxane, 5 cS), trichloroethylene (TCE), perchloroethylene (PCE), 1,2-dichlorobenzene (DCB), Brij 30, 35, 56 and sodium dodecyl sulfate (SDS) were purchased from Sigma–Aldrich (St. Louis, USA). Emulsion was prepared by dispersing oil in deionized water with homogenizer (HMZ-20DN, Global Lab., Korea). Homogenization was conducted at 8000 rpm during 15 min.

2.2. Solubilization in batch system [17]

TCE, PCE and DCB were used as target pollutants. Batch experiments were conducted with 20-ml vials to investigate the solubility of contaminants in emulsion. Concentrations were analyzed using a GC (HP 6890, Hewlett Packard, USA) coupled with FID. The chromatographic capillary column was a HP5 (30 m × 0.25 mm, HP). The GC conditions was as follows; injector temperature was set at 200 °C, and the GC oven was after an initial hold for 2 min at 40 °C increased to 190 °C at a rate of 20 °C/min and the detector temperature was set at 250 °C. Helium was used as a carrier gas and the column flow rate was 1 ml/min without split. The head space analysis was performed using 20-ml open-top vials equipped with a Teflon-coated septum. Each of the vials contained 10 ml of solution which consisted of contaminants and emulsion. 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 immediately inserted into the GC injector.

2.3. One-dimensional flushing

The used soil was Jumunjin filtered sand which was sieved to obtain 20–30 mesh size fractions. Flushing experiments were performed in a column (30 mm × 160 mm, Kontes, USA). The column was filled under vibration with the Jumunjin filtered sand of 115 g, and the pore volume of the sand in the column was 35 ml. The soil column was oriented vertically. Initially, the deionized water (>20 pore volumes) was injected from bottom of the column at a flowrate of 1 ml/min to remove the air from the column. After the soil column was saturated with water, the contamination was carried out by injecting TCE, PCE and DCB individually at a flowrate 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. To observe the contamination visually, the contaminants (TCE, PCE and DCB) were dyed as red color with a dying agent (Oil red-O, Sigma, USA). After the contaminant of 1 pore volume was injected, the flow was reversed and the deionized water (>30 pore volumes) was flowed to remove the mobile free pollutants. As a result, the residual saturation was reached. For the flushing of contaminants, emulsion prepared with 2% (v/v) silicone oil was passed in upward direction from the bottom of column at 1 ml/min. The column effluents were collected in 20 ml glass vials periodically. After emulsion flushing, the residual contaminants and oil were recovered by flow of methanol. Each experiment was conducted at least two times. The flowrate was controlled by a peristaltic pump (Masterflex, USA). The concentration of chlorinated compounds was measured by HPLC (Waters, USA) with C18 column (4.6 mm × 250 mm, Waters) at a wavelength of 214 nm. Elution was carried out with 85% (v/v) acetonitrile at a flow rate of 1.0 ml/min. The concentration of silicone oil was analyzed by HPLC/RI (Waters) with C18 column (4.6 mm × 250 mm, Waters).

3. Results and discussion

3.1. Solubilization of chlorinated solvents in batch system

The removal efficiency and residual concentration of TCE, PCE and DCB in emulsions are described in Figs. 1–3, respectively. The 2% (v/v) oil emulsion could treat TCE of 10,000 ppm, PCE of 4000 ppm and DCB of 7800 ppm, showing residual concentration of contaminants less than their aqueous solubilities (TCE, 1099 ppm; PCE, 200 ppm; DCB, 156 ppm). This means that TCE, PCE and DCB are removed by solubilizing into emulsion particle without making free phase. However, when TCE (>10,000 ppm) and PCE (>4000 ppm) were applied into emulsions, residual concentration of TCE and PCE exceeded their water solubility and free phase of TCE and PCE existed. Compared to the results of TCE and PCE, 99.7% of 7800 ppm DCB was removed by 2% (v/v) oil emulsion, resulting in a residual concentration of less than 20 ppm. Emulsion prepared with very low oil contents (0.5%, v/v) could remove 99.0% of 7800 ppm DCB. The differences in solubilization efficiency are partially explained by solubility and hydrophobicity of chlorinated solvents (Table 1). PCE and DCB have higher solubility in silicone oil than TCE. DCB is more hydrophobic and TCE is less hydrophobic among the used contaminants. These led to the lowest removal efficiency of TCE.
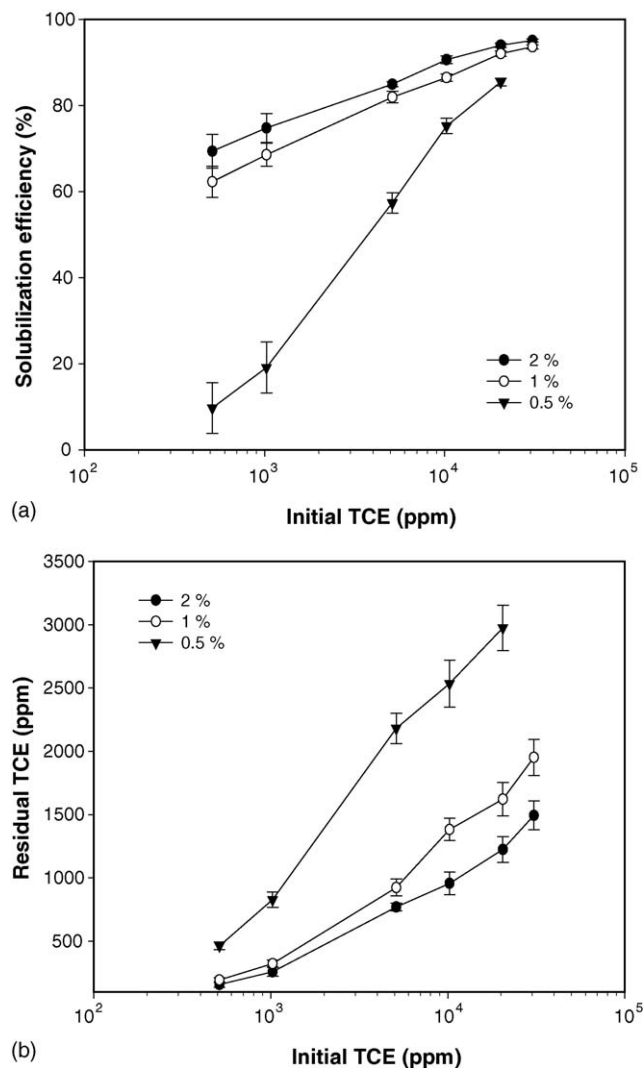
Fig. 1. Solubilization efficiency (a) and residual concentration (b) of TCE in 2, 1 and 0.5% (v/v) silicone oil emulsion.

3.2. Effects of surfactants on the solubilization of chlorinated solvents

Brij 30, 35 and 56 as non-ionic surfactants and sodium dodecyl sulfate (SDS) as a anionic surfactant were applied to enhance the solubilization by increasing the amount of dispersed emulsion. The surfactant of small amount (<critical micelle concentration) was employed because the use of surfactant could increase density of emulsion and the main solubilizing agent was oil. The properties of surfactants are summarized in Table 2.
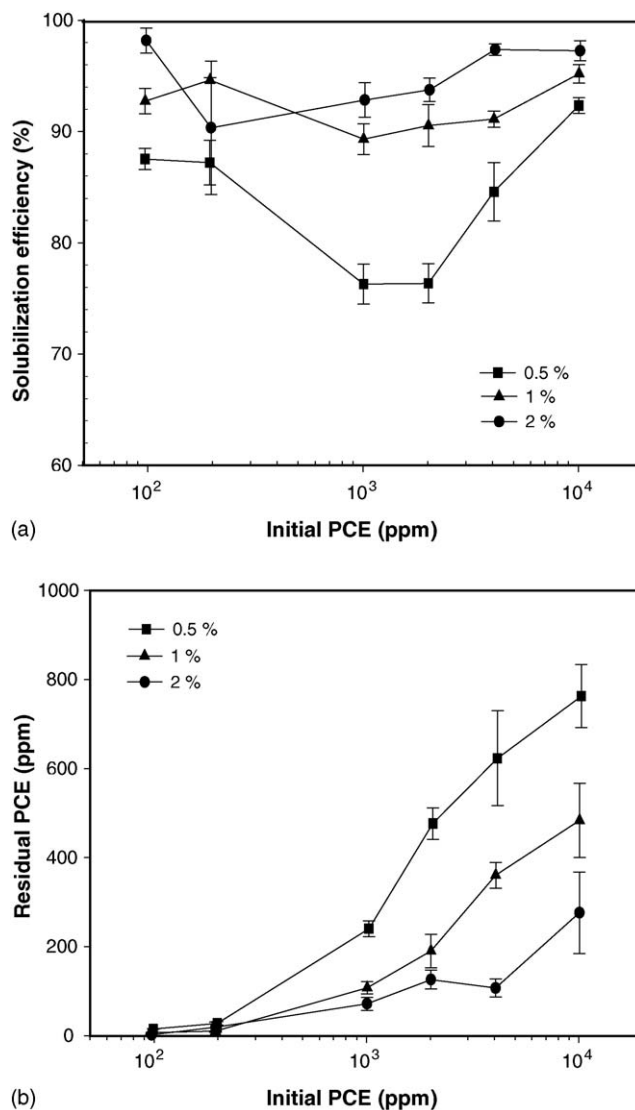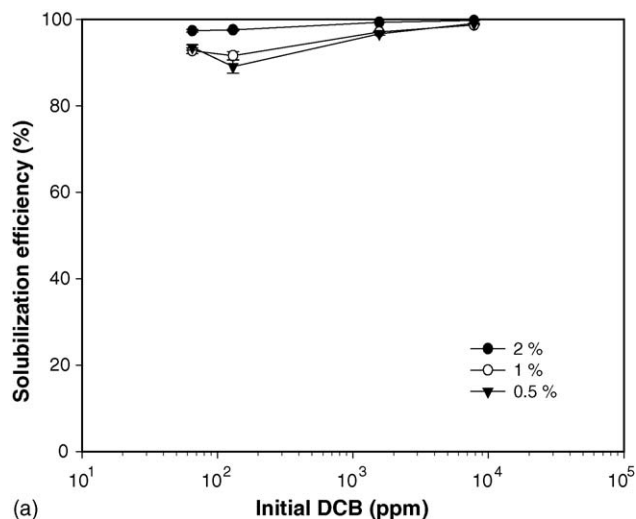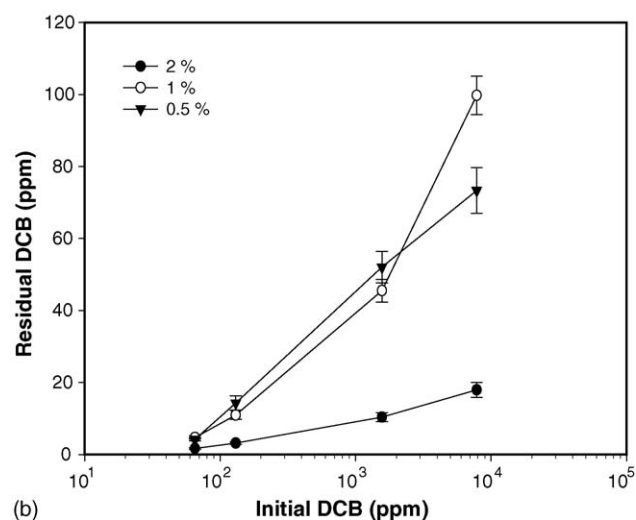

Fig. 2. Solubilization efficiency (a) and residual concentration (b) of PCE in 2, 1 and 0.5% (v/v) silicone oil emulsion.

With the addition of surfactants below their critical micelle concentration (CMC), the amount of dispersed oil increased remarkably (Fig. 4). Considering the dosage of each surfactant, non-ionic surfactant was more suitable than anionic surfactant as a emulsifying agent. It was also due to low CMC of non-ionic surfactant. In the non-ionic surfactant, hydrophile–lipophile balance (HLB) represents the relative strength of the polar head group to non-polar tails of a surfactant molecule. As HLB

Table 1
The physico-chemical properties of trichloroethylene, perchloroethylene and 1,2-dichlorobenzene from [18]

	Molecular weight	Density (g/cm^3)	Solubility (mg/l, 25 °C)	Vapor pressure (mmHg)	log K_{ow}[a]	K_{oc}[b] (l/kg)	log $1/H$[c] (25 °)
TCE	131.3	1.463	1099.0	69.0	2.29	125.9	0.384
PCE	165.8	1.623	200.0	18.5	3.40	660.7	0.145
DCB	147.0	1.306	156.0	1.5	3.83	1148	1.110

[a] Octanol/water partition coefficient.
[b] Organic carbon partition coefficient.
[c] Henry's law constant.

Fig. 3. Solubilization efficiency (a) and residual concentration (b) of DCB in 2, 1 and 0.5% (v/v) silicone oil emulsion.

Fig. 4. Contents of oil in dispersed state when the surfactants were added as the concentration below their CMC: (a) 2% (v/v) oil emulsion and (b) 1% (v/v) oil emulsion.

increases, the surfactant is stabilized and dispersed easily in water due to the increase of hydrophilic polyoxyethylene groups. Therefore, oil can be well emulsified by adding non-ionic surfactant of high HLB number. Compared with the results using Brij 30 (HLB no. of 9.7), the use of Brij 56 (HLB no. of 12.9) increased the portion of dispersed oil by two-fold. However, Brij 35 (HLB no. of 16.9) had similar dispersive effects to the case of Brij 56. These indicate that the certain optimum range of HLB number exists in the dispersion system.
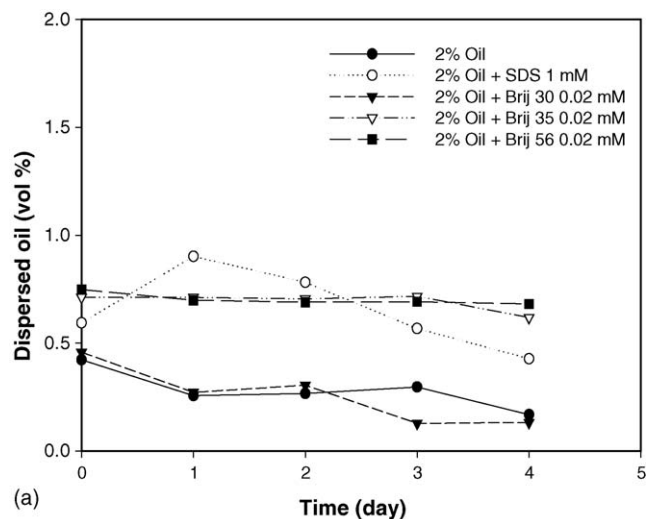
To confirm the effects of surfactants on solubilization, the experiments with 0.02 mM Brij 30, 35, 56 and 1 mM SDS were conducted in a batch system. As shown in Fig. 5, the results were opposite to the anticipation. The increase in solubilization efficiencies was not observed although the amount of dispersed oil increased by addition of surfactants. This could be explained by hydrophilicity of emulsion surface. The non-ionic surfactant of high HLB number enhanced the degree of emulsification by

Table 2
Properties of surfactants used in this study

Trade name	Chemical name	Formula	MW[a] (g/mol)	CMC[b] (mM)	HLB[c]
SDS	Sodium dodecyl sulfate	$CH_3(CH_2)_{11}OSO_3Na$	288	8.1	–
Brij 30	POE(4) lauryl ether	$C_{12}H_{25}(OCH_2CH_2)_4OH$	362	0.055	9.7
Brij 35	POE(23) lauryl ether	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$	1198	0.046	16.9
Brij 56	POE(10) cetyl ether	$C_{12}H_{25}(OCH_2CH_2)_{10}OH$	683	0.023	12.9

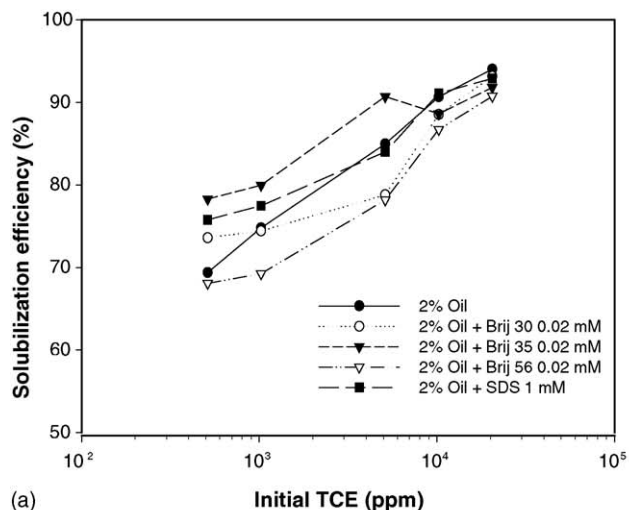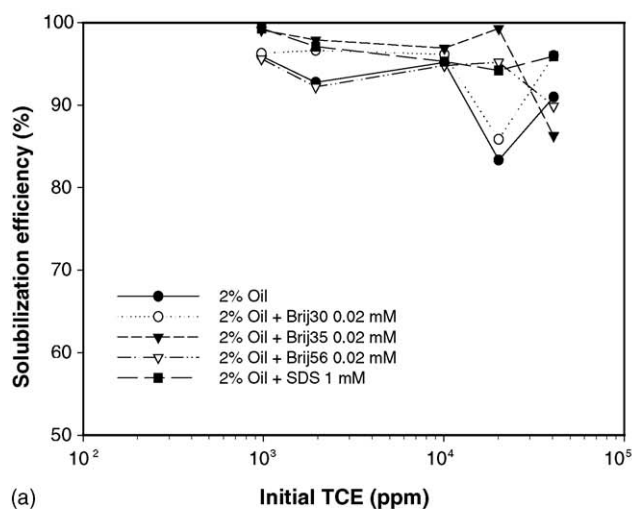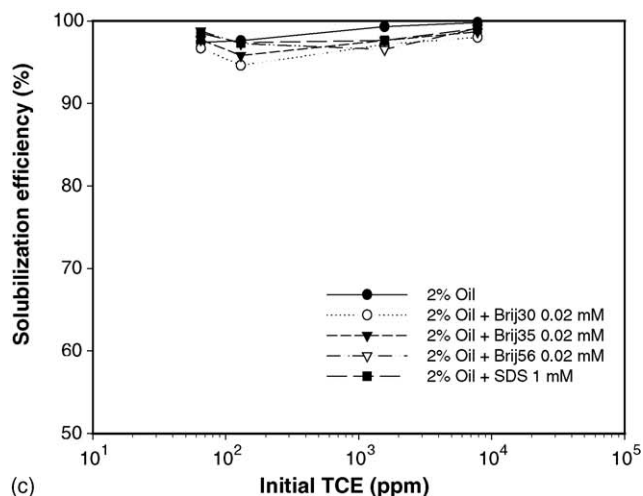[a] Molecular weight.
[b] Critical micelle concentration.
[c] Hydrophile–lipophile balance.

(a)

(a)

(b)

Fig. 6. Flushing of TCE using 2% (v/v) silicone oil emulsion: (a) flushing without surfactants and (b) flushing with addition of 0.02 mM Brij 35.

3.3. One-dimensional flushing of chlorinated solvents

Effluent TCE concentration is plotted in Fig. 6. During the initial phase of flushing (<200 ml or 6 pore volume), even though the effluent concentration was above the aqueous solubility of TCE (1099 ppm at 25 °C), solubilization of TCE slowly progressed. Most of TCE was eliminated when additional 600 ml (17 pore volume) emulsion solution was passed through column. TCE of 98.4 and 95.1% were removed by flowing the emulsions of 30 pore volume (Table 3). As reported in other studies on surfactant flushing, tails of low TCE concentration were detected in the latter phase of flushing [8,9,19,20]. These phenomena are due to the low mass transfer. After most of contaminants are flushed out, the small amount of contaminants exists within the soil. The mass transfer between residual contaminants and emulsion decreases because of limited contact of contaminants with emulsion. Therefore, low concentration of contaminants is detected in the effluents and that phenomena continue for a long time. To enhance the mass transfer in the latter phase of flushing, the flow was interrupted during 12 h after the flow of 600 ml emul-
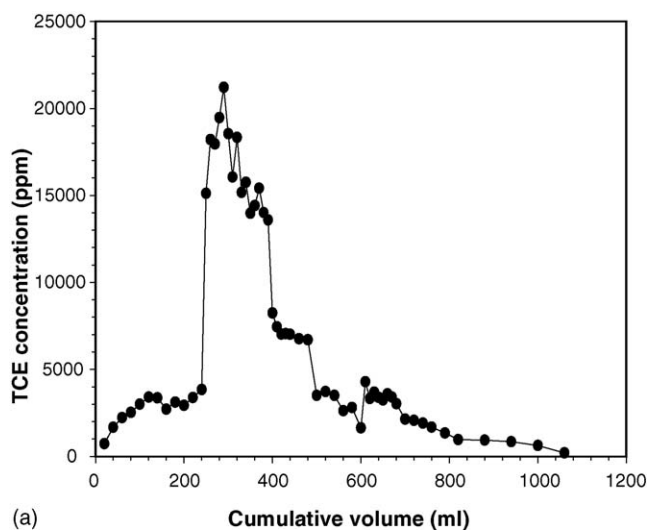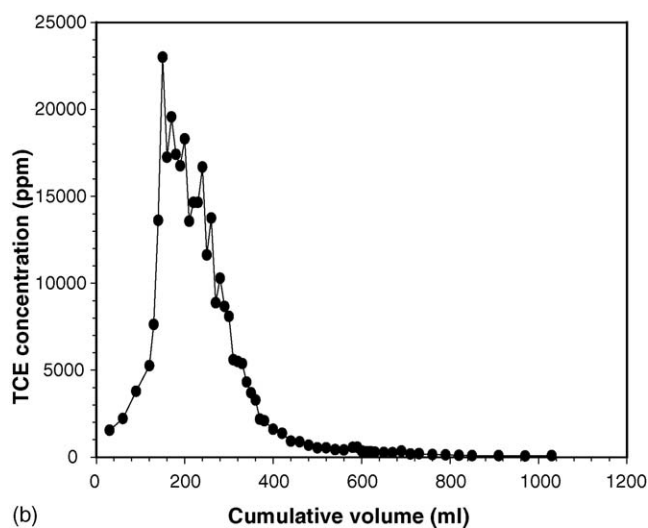

Fig. 5. Solubilization efficiency of TCE (a), PCE (b) and DCB (c) in 2% (v/v) emulsions stabilized by surfactants below their CMC.

making emulsion surface more hydrophilic. The mass transfer between TCE and emulsion surface, however, was inhibited by the increased hydrophilicity of emulsion surface. As a result, the use of surfactants in emulsification process did not affect the solubilization of chlorinated solvents.

Table 3
Mass balance in one-dimensional flushing experiments

	Initial (mg)	Removed (mg)	Residual (mg)	Removal efficiency (%)
TCE flushing #1 (w/o surfactant)	4831	4754	77	98.4
TCE flushing #2 (w/o surfactant)	5027	4781	245	95.1
TCE flushing #3 (with 0.02 mM Brij 35)	3518	3469	49	98.6
PCE flushing #1 (w/o surfactant)	5265.5	4480.9	784.6	85.1
PCE flushing #2 (w/o surfactant)	5014.6	4081.9	932.7	81.4
PCE flushing #3 (with 0.02 mM Brij 35)	5212.1	4466.8	745.3	85.7
DCB flushing #1 (w/o surfactant)	5121.8	3969.4	1152.4	77.5
DCB flushing #2 (w/o surfactant)	5578.9	4178.6	1400.3	74.9
DCB flushing #3 (with 0.02 mM Brij 35)	5487.2	4049.1	1438.1	73.8

sion. As a result, the effluent concentration increased to about 5000 ppm due to the enhanced mass transfer during interruption of flow. The use of 0.02 mM Brij 35 accelerated the initial mass transfer (Fig. 6). Flushing was finished within a shorter time by use of Brij 35.

Similar to the results of TCE flushing, the effluent concentration in the initial lag phase of PCE and DCB flushing was between 200 and 1000 ppm (Figs. 7 and 8). After that lag phase, PCE and DCB of high concentration were detected in the effluents. Most of contaminants removed by emulsion flushing were flushed out during the flow of 400 ml after lag phase. Then, the tails of low concentration were observed. Removal efficiencies of avg. 83.3% and avg. 76.2%, for PCE and DCB, respectively, were obtained with the flow of 32 pore volume emulsion (Table 3). To enhance the flushing performance at tails, the emulsion flow was interrupted during 12 h. The interruption of flow increased the effluent concentration to about 5000 ppm. 65–70% (PCE) and 55–60% (DCB) of contaminants removed were flushed out before interruption of flow and the rest of contaminants were flushed out almost completely after interruption. The differences in removal efficiency of TCE, PCE and DCB are due to the differences in aqueous solubility. TCE has extraordinarily high aqueous solubility (1099.0 mg/l at 25 °C) among the chlorinated compounds (PCE, 200 mg/l at 25 °C; DCB, 156.0 mg/l at 25 °C). Therefore, flushing of TCE showed the highest removal efficiency. Other presumable explanation is possible by the organic carbon partition coefficients (K_{oc}). High organic carbon partition coefficient of a pollutant leads to a strong sorption onto soil surface, which makes the pollutant removal difficult. The organic carbon partitioning coefficients of TCE, PCE and DCB are 125.9, 660.7 and 1148 l/kg, respectively. To confirm the effects caused by organic carbon partition coefficients of contaminants, experiments with soils of high organic contents are required.

With use of 0.02 mM Brij 35, the effluent concentration in initial lag phase increased above 2000 ppm (Figs. 7 and 8). This means that the existence of surfactants accelerated the mass transfer in the initial phase of flushing. However, PCE and DCB of high concentration were detected after the flow of about 400 ml emulsion. The mass balance of surfactant-enhanced flushing was same with that of surfactant-free flushing (Table 3). As a result, the addition of surfactants below their CMC did not enhance the flushing performance.

Compared to the results of surfactant flushing [8–10,19,20], the removal of contaminants progressed a little slowly in the emulsion flushing. This is due to particle size difference between emulsion and micelle. However, contaminants of high concentration exceeding their water solubility were detected in the initial effluent of 400 ml and most of contaminants, especially
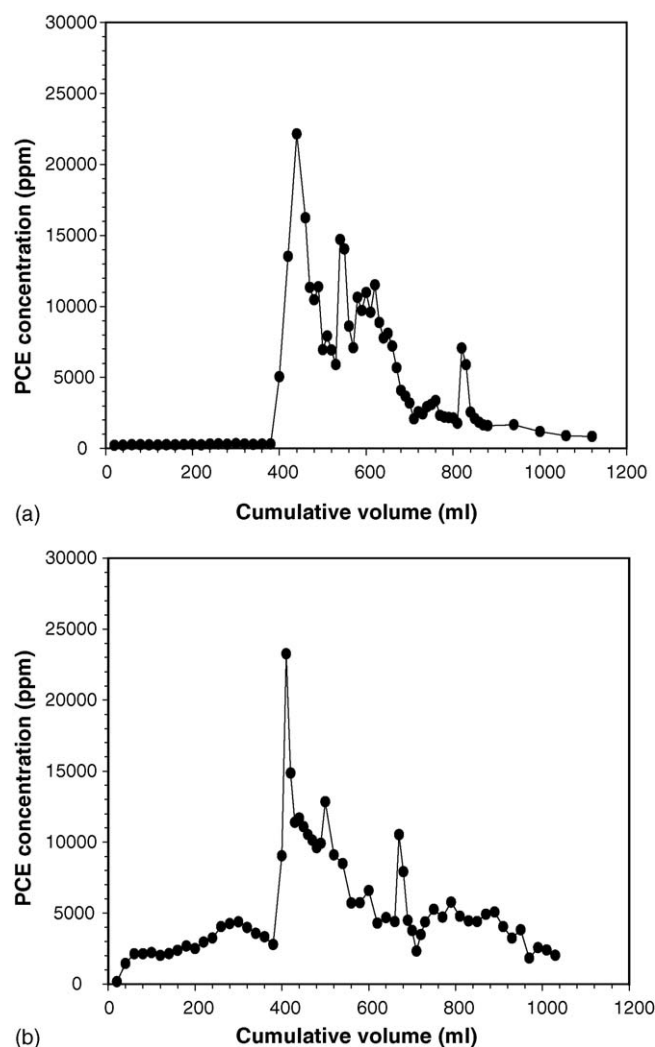

(a)

(b)

Fig. 7. Flushing of PCE using 2% (v/v) silicone oil emulsion: (a) flushing without surfactants and (b) flushing with addition of 0.02 mM Brij 35.
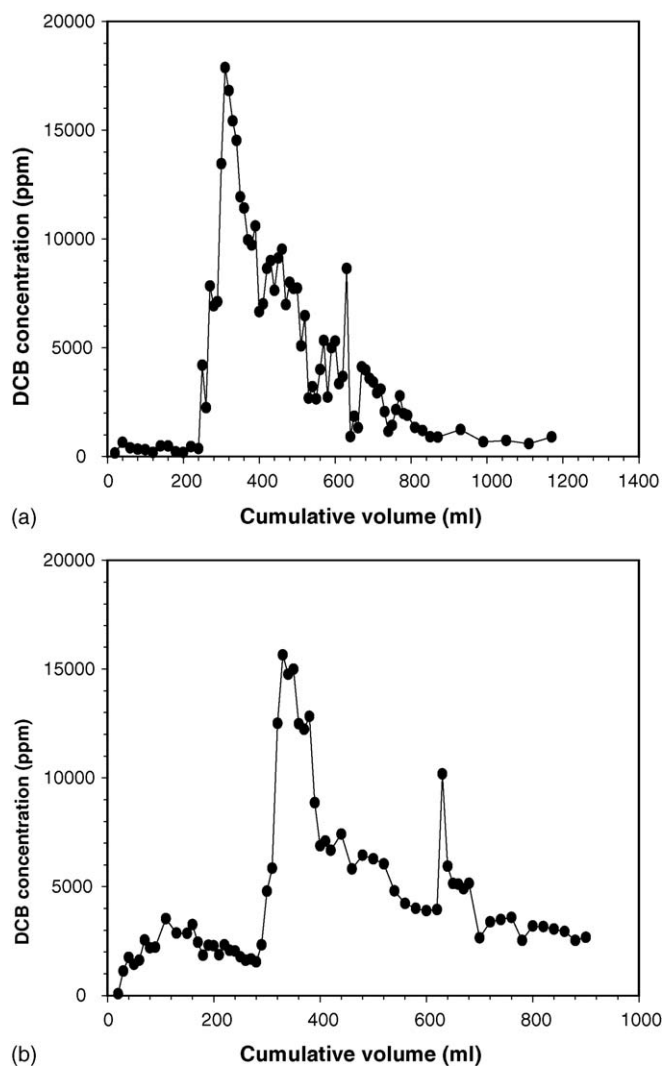
Fig. 8. Flushing of DCB using 2% (v/v) silicone oil emulsion: (a) flushing without surfactants and (b) flushing with addition of 0.02 mM Brij 35.

TCE, were well removed. That limited mass transfer was helpful to maintain the density of emulsion below water density. Therefore, these results mean that the remediation without secondary contamination could be possible.

Dissolution of chlorinated solvents in oil emulsion happens by contact of chlorinated solvents with emulsion surface. It is similar to solubilization in surfactant-enhanced remediation. The results revealed from surfactant-enhanced remediation involving batch, column and field experiments can contribute to the understanding of dissolution of chlorinated solvents in emulsion solutions [4–6,10]. However, further studies are needed for detailed dissolution mechanism because used emulsion particle is bigger than micelle and factors such as soil properties, contaminant distribution, etc. should be considered in field flushing.

4. Conclusions

The emulsion prepared with 2% (v/v) silicone oil could treat 90.7% of 10,000 ppm TCE, 97.3% of 4000 ppm PCE and 99.7% of 7800 ppm DCB without making free phase. DCB, more sol-

uble in silicone oil and hydrophobic, was almost completely removed in a batch experiment. Non-ionic surfactant of low CMC and high HLB number was effective for the stabilization of oil emulsion. However, the solubilization efficiencies did not increase because the emulsion surface became more hydrophilic by surfactant of high HLB number, thereby inhibiting the mass transfer. In the column flushing, TCE of high aqueous solubility and low organic carbon coefficient showed the highest removal efficiency. The interruption of flow was helpful for the reduction of solution usage.

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