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The Solubilization Characteristics of DNAPLs by Oil-Based Emulsion

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Abstract: Because of its large surface area and hydrophobicity, a microsized oil emulsion can solubilize dense nonaqueous phase liquids (DNAPLs). When DNAPLs are solubilized by emulsion, they can be removed from the aquifer and their downward migration in the aquifer can be delayed or prevented due to the buoyancy force of the emulsion. Solubilization of DNAPLs was investigated in this study by using an oil-based emulsion prepared via mechanical homogenization of silicone oil. The emulsion droplets that were produced showed similar microsized distribution: the particles in the range of 1–10 μm in diameter were 99% in number distribution and 80% in volume distribution. The oil-based emulsion effectively solubilized trichloroethylene (TCE) and 1,2-dichlorobenzene (DCB) as target pollutants. The

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emulsion prepared with 2% silicone oil that had been homogenized at 8000 rpm for 15 min could solubilize 99.7% of 7800 ppm DCB and 90.7% of 10,000 ppm TCE. Even the emulsion prepared with a low concentration (0.5%, v/v) of silicone oil removed 99.0% of 7800 ppm DCB from the aqueous phase. Taken together, the results of this study show the potential of the oil-based emulsion as an effective alternative to treat DNAPLs in the aquifer.

INTRODUCTION

One of the most common types of groundwater contamination arises from spills of hydrocarbon fuels (1), which leak from underground storage tanks or pipelines. When a large fuel spill occurs, leaked liquid can reach the water table (1). While the light portion of hydrocarbons (light nonaqueous phase liquids, LNAPLs) stops its downward migration, the dense portion of hydrocarbons (dense nonaqueous phase liquids, DNAPLs) continues to migrate downward in the aquifer until it reaches the impermeable area (1). Although both LNAPLs and DNAPLs cause serious contamination, the latter are a more pernicious pollutant. In the aquifer, DNAPLs act as long-term sources of contamination by dissolving into flowing groundwater and pose a significant threat to the environment, especially to our drinking water.

Conventional pump-and-treat processes are inefficient to remove DNAPLs from the aquifer because of their low solubilities, high interfacial tensions, and mass-transfer limitations (2). Thus, surfactant-enhanced aquifer remediation (SEAR) was developed as an alternative to remove DNAPLs in the groundwater remediation process (1). However, the downward migration of dissolved DNAPLs has limited the application of SEAR (3).

Emulsions, which consist of droplets of one liquid dispersed in another immiscible liquid (4, 5), have various characteristics depending on preparation conditions. Microemulsions have especially high interfacial areas, thermodynamic stability, and ability to solubilize otherwise immiscible liquids, leading to their use in various fields such as cosmetics, pharmaceutics, lubrication, food technology, coatings, and environmental remediation (6). The large surface areas and hydrophobicity of emulsions can enhance the solubilization of hydrophobic chemicals. In groundwater remediation, emulsions could be used to solubilize DNAPLs in the aquifer and subsequently remove them. Moreover, the buoyancy force of emulsions could reduce or prevent the downward migration of the solubilized DNAPLs. The purpose of this study was to characterize oil-based microemulsions and to investigate their potential to treat DNAPLs. For development of microemulsions for use in aquifer remediation, research on several additional factors, such as pH, ionic strength, presence of humic materials, and surface charge of soil particles, is required.

MATERIALS AND METHODS

Preparation and Characterization of Emulsions

A homogenizer (HMZ-20DN; Global Lab., Seoul, Korea) was employed to prepare the emulsion using silicone oil (dimethylpolysiloxane, 5 cS; Sigma, St. Louis, MO, USA) in deionized water. Silicone oil was selected because of its biocompatibility, solubilizing potential, viscosity, and buoyancy (7, 8). Since silicone oil has low viscosity (5 cS) and density (0.98 g/cm^3) compared with other oils, emulsions prepared with silicone oil can have sufficient buoyancy force and little adsorption onto soil. The concentrations of silicone oil used were 0.5, 1, and 2% (v/v), and the homogenization rates were 5000 and 8000 rpm. The homogenization times were as follows: 2, 5, and 10 min at 5000 rpm and 5, 10, and 15 min at 8000 rpm.

Analysis of Emulsion

The mean diameter and size distribution of the particles in the emulsion were measured using a particle size analyzer (Beckman Coulter LS230, Brea, USA). The emulsion (20 mL) was sampled periodically to test its stability. After evaporation of water at 105°C for 2 days, the silicone oil in the sample was mixed with 3 mL *n*-hexane (Merck, Darmstadt, Germany). The solvent fraction of the sample was analyzed by a high-performance liquid chromatograph/refractive index detector (HPLC/RI) (Waters, Milford, CT, USA) with Petro XL column (250 × 4.6 mm, Genesis, Hengoed, UK). Elution was performed using 100% hexane at a flow rate of 1.0 mL/min..

Solubilization of DNAPLs (9)

TCE (Sigma) and DCB (Sigma) were used as target pollutants. Batch experiments were conducted with 20-mL vials to investigate the solubility of the DNAPLs by the emulsion. The DNAPL concentration was analyzed using a gas chromatograph (GC) (HP 6890, Hewlett Packard, Palo Alto, CA, USA) coupled with a flame ionization detector (FID). The chromatographic capillary column was an HP5 (30 m × 0.25 mm, Hewlett Packard, Palo Alto, CA, USA). The GC conditions were as follows: injector temperature: 200°C; column temperature: 40°C for 2 min, then ramped from 40 to 190°C at a rate of 20°C/min.; detector temperature: 250°C. Helium was used as a carrier gas, and the column flow rate was 1 mL/min without split. The headspace analysis was performed using 20-mL open-top vials equipped with a Teflon-coated septum. Each of the vials contained 10 mL of sample consisting of DNAPL and emulsion. The emulsion was used 1 h after preparation. Vials were shaken at 25°C for 6 h to achieve phase equilibrium. A gastight syringe was used to obtain 100 μL of sample from the headspace of the vial and immediately inserted into the GC injector.

RESULTS AND DISCUSSION

Mean Diameter and Size Distribution of Emulsion Particles

Figure 1 shows the mean diameter of emulsion particles prepared in this study. While emulsions were prepared with various parameters, such as different oil

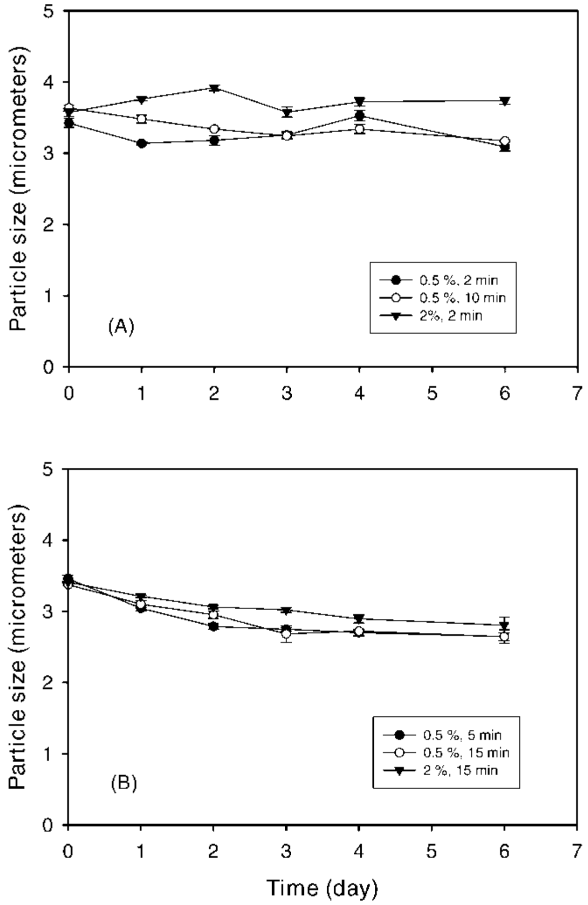

Figure 1. Mean diameter of emulsion particles prepared at the homogenization rates of (A) 5000 rpm and (B) 8000 rpm.

concentrations, homogenization rates, and homogenization times, the mean diameter of the emulsions was not affected by these parameters. The mean diameters were approximately 3.5 μm after preparation and remained constant for 6 days.

As was the case with mean diameter, emulsions prepared under various conditions also showed similar size distributions (Fig. 2). The pattern of

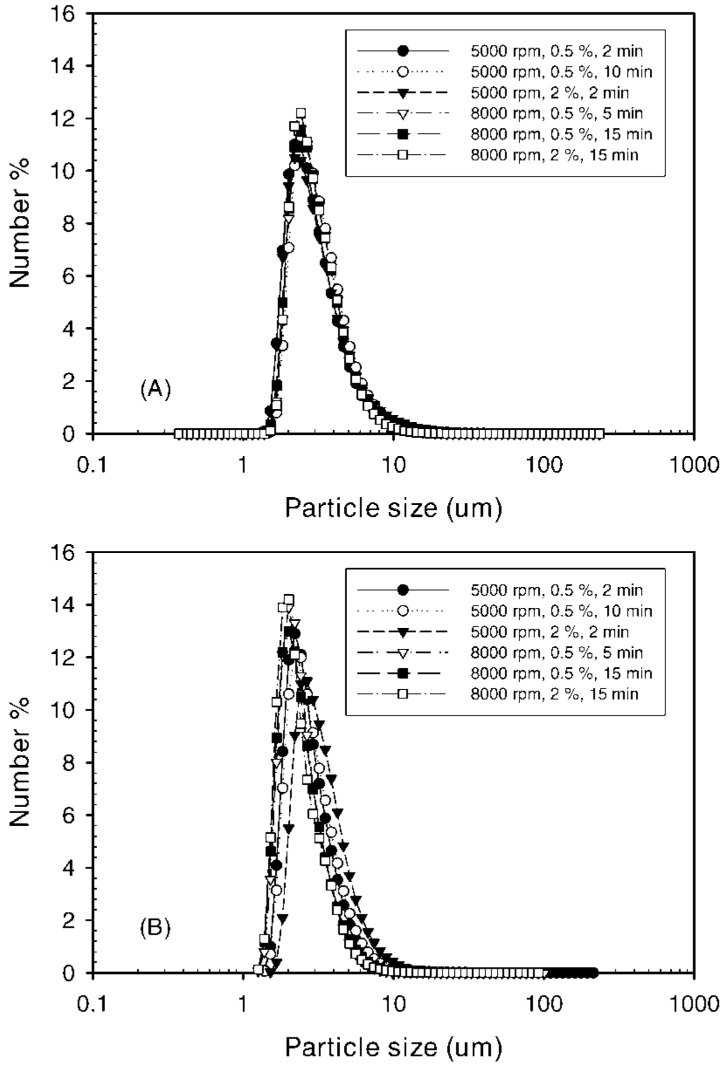

Figure 2. Size distribution of emulsion particles (A) immediately after formation and (B) after 6 days.

size distributions remained constant even up to 6 days. However, variations in homogenization rate resulted in differences in volume percentages of emulsion particles that were less than 10 μm in diameter (Fig. 3). High homogenization rates increased the volume percentages of emulsion particles with

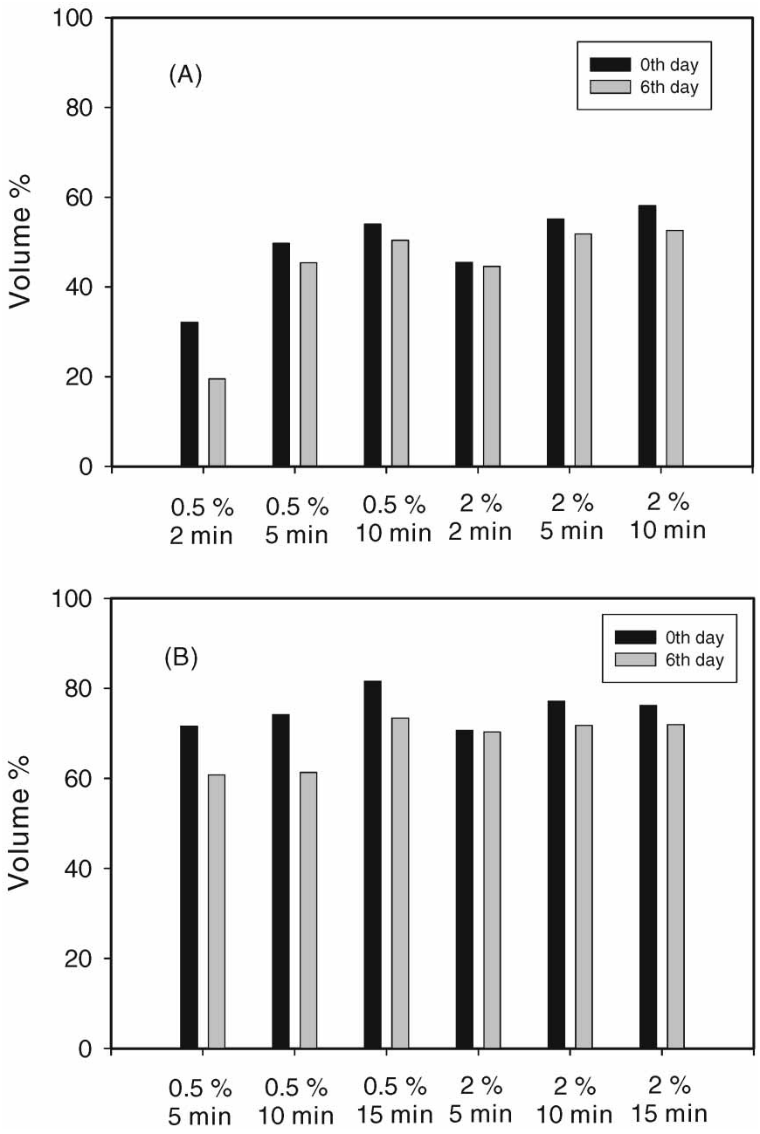

Figure 3. Volume percentage of emulsion particles with diameters less than 10 μm for homogenization rates of (A) 5000 rpm and (B) 8000 rpm.

diameters less than 10 μm, suggesting an increased number of emulsion particles in the dispersed state. The particles prepared at 8000 rpm showed volume percentages in the range of 70–80%. The values decreased to 60–70% on day 6.

Figure 4 shows the oil content as it existed in the dispersed state when the emulsion was prepared at 8000 rpm for 15 min. Initially, the amount of dispersed oil was approximately 10–20% of the injected oil. This amount decreased slightly after 4 days.

Dispersity of Emulsion

The distribution of the emulsion is the important factor that affects its stability. The similar-sized particles of a monodispersed emulsion led to greater stability, because such particles do not aggregate well (10). Also, a monodispersed emulsion has many advantages in characteristics such as interfacial area, thermodynamic property, and buoyancy force. The dispersed degree of emulsion is determined by polydispersity P_a, defined as

$$P_a = \frac{\delta a}{\bar{a}}$$

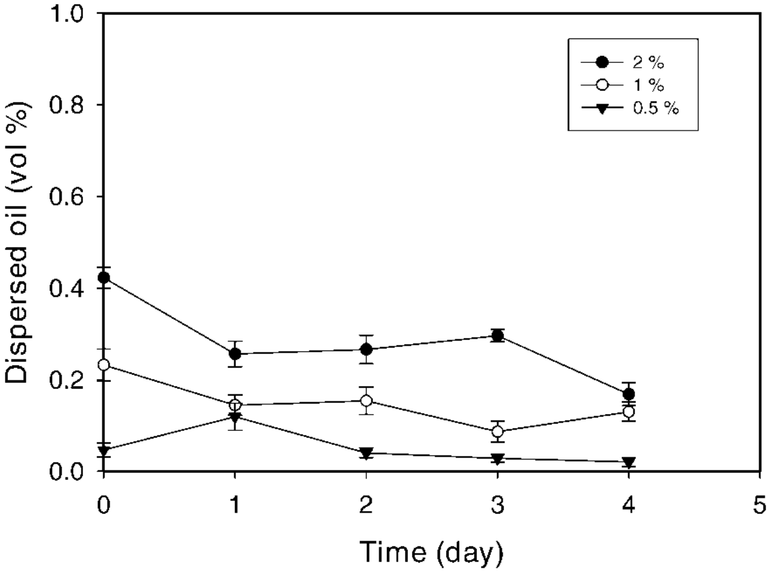

Figure 4. Content of oil in dispersed state when homogenization was performed at 8000 rpm for 15 min.

where $\bar{a}$ is the average droplet radius and δa is the standard deviation. Alternately, dispersion may be described by the uniformity factor U, defined as

$$U = \frac{1}{\bar{d}} \frac{\sum_i N_i d_i^3 |\bar{d} - d_i|}{\sum_i N_i d_i^3}$$

where $\bar{d}$ is the median size of distribution, that is, the diameter for which the cumulative undersized volume fraction is 50% and N_i is the total number of droplets with diameter d_i (4, 11). An emulsion with $P_a \approx 0.1$ or $U < 0.2$ is termed "monodisperse" (4, 11). Considering polydispersity values and uniformity factors of emulsions prepared in this study (Figs. 5 and 6, respectively), an 8000-rpm homogenization rate produced emulsions closer to monodisperse than did 5000 rpm. Emulsions prepared at 5000 rpm showed P_a values in the range of 0.5–0.6 and U factors more than 0.5, while those prepared at 8000 rpm showed P_a values of 0.4–0.5 and U factors less than 0.5. Although the values of P_a and U for the emulsions prepared in this study do not fall within the accepted range for monodispersity, the emulsions showed a certain degree of monodispersity since they had uniform distributions with more than 99% of emulsion particles in the range of 1–10 μm in diameter (Fig. 2).

Solubilization of DNAPLs

In the experiment with 0% silicone oil, <90% of initially injected DCB and 65–70% of initially injected TCE were dissolved into deionized water. These values coincide with those predicted using Henry's law constant (Fig. 7). Figures 8 and 9 show the removal efficiency and residual concentration of DCB and TCE, respectively, in oil-based emulsions prepared at 8000 rpm. Solubilization efficiency was expressed as removal efficiency since solubilization of DNAPLs into the emulsion resulted in their removal from the aqueous phase. The oil-based emulsions prepared in this study effectively solubilized maximum concentrations of DCB (7800 ppm) and TCE (10,000 ppm), showing residual concentrations of the chemicals lower than their water-solubility concentrations in the aqueous phase. The concentrations of DCB and TCE were more than 60 and 10 times higher, respectively, than their water solubilities at 25°C. The water solubilities of DCB and TCE at 25°C are 156 and 1099 ppm, respectively. More than 90% of DCB was solubilized effectively into emulsions prepared with 0.5, 1, and 2% (v/v) silicone oil. Emulsions prepared with 2% silicone oil could remove 99.7% of 7800 ppm DCB, showing less than 20 ppm of residual DCB in the aqueous phase. Even emulsions prepared with a low concentration (0.5%, v/v) of silicone oil removed 99.0% of 7800 ppm DCB from the aqueous phase.

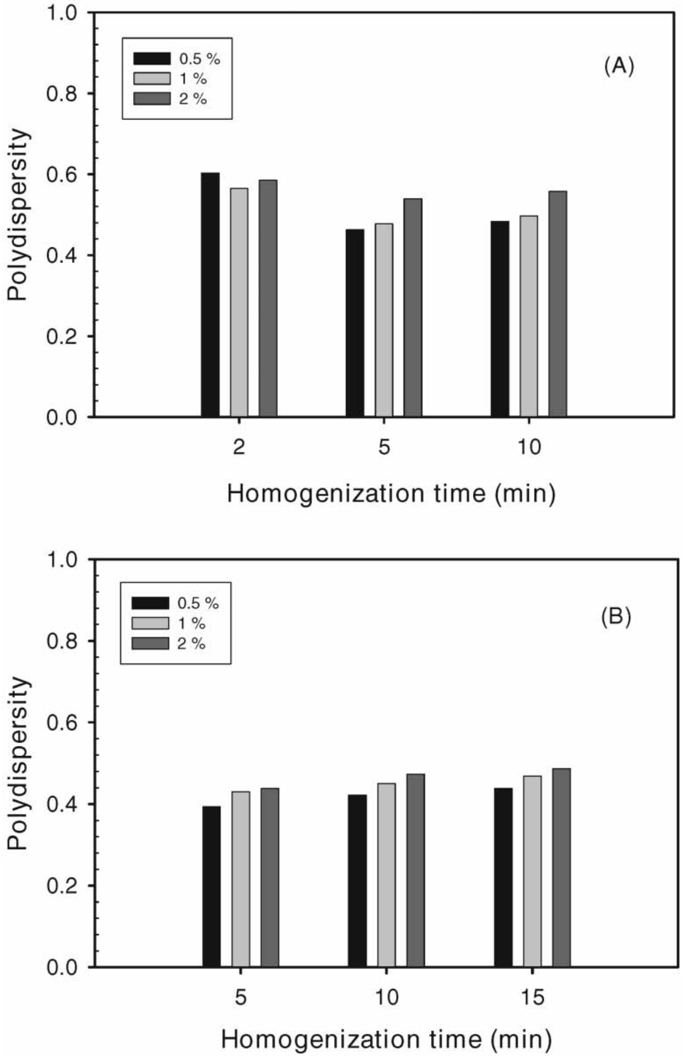

Figure 5. Polydispersity values of emulsions prepared at the homogenization rates of (A) 5000 rpm and (B) 8000 rpm.

When the emulsions used for DCB were applied to TCE, less efficiency in solubilization was observed. Emulsions prepared with 2% silicone oil could solubilize 90.7% of 10,000 ppm TCE. Despite the high removal efficiency, when the emulsion was employed for 10,000 ppm or more of TCE, residual concentrations of TCE in the aqueous phase were higher than its water solubility (1099 ppm at 25°C).

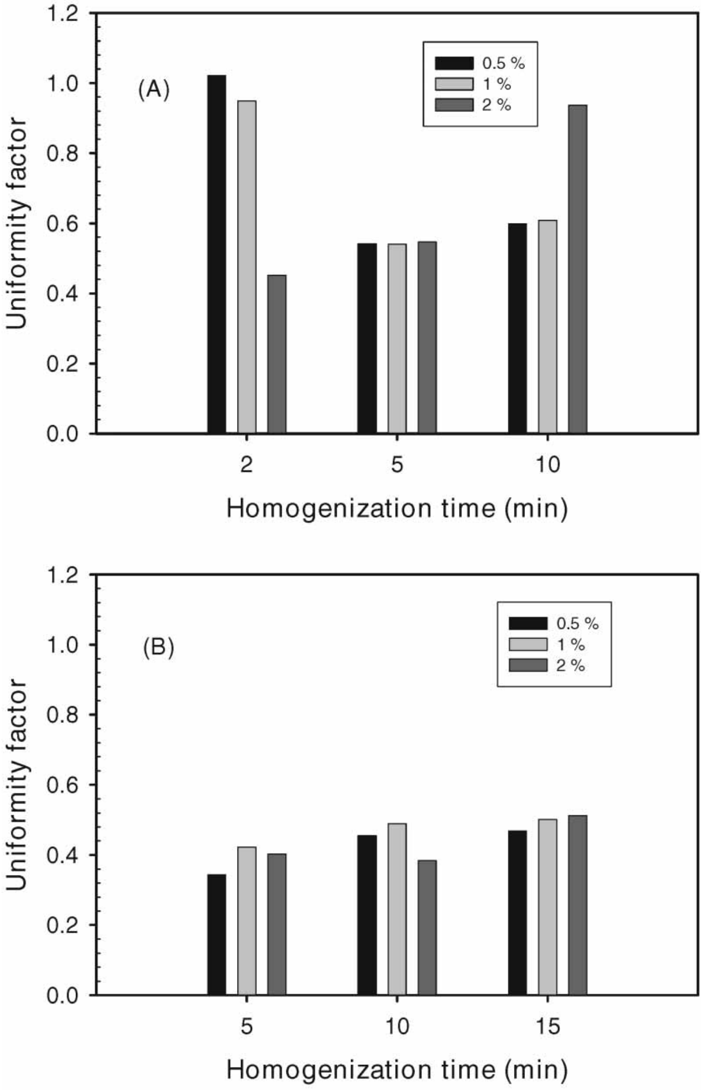

Figure 6. Uniformity factors of emulsions prepared at the homogenization rates of (A) 5000 rpm and (B) 8000 rpm.

After solubilization of DCB and TCE, the density of oil emulsion changed to 0.992 (DCB) and 1.04 (TCE). Although the density of the oil emulsion increased, it was similar to the initial density of the emulsion (0.98). Therefore the addition of DCB and TCE did not affect the droplet characteristics of the emulsion.

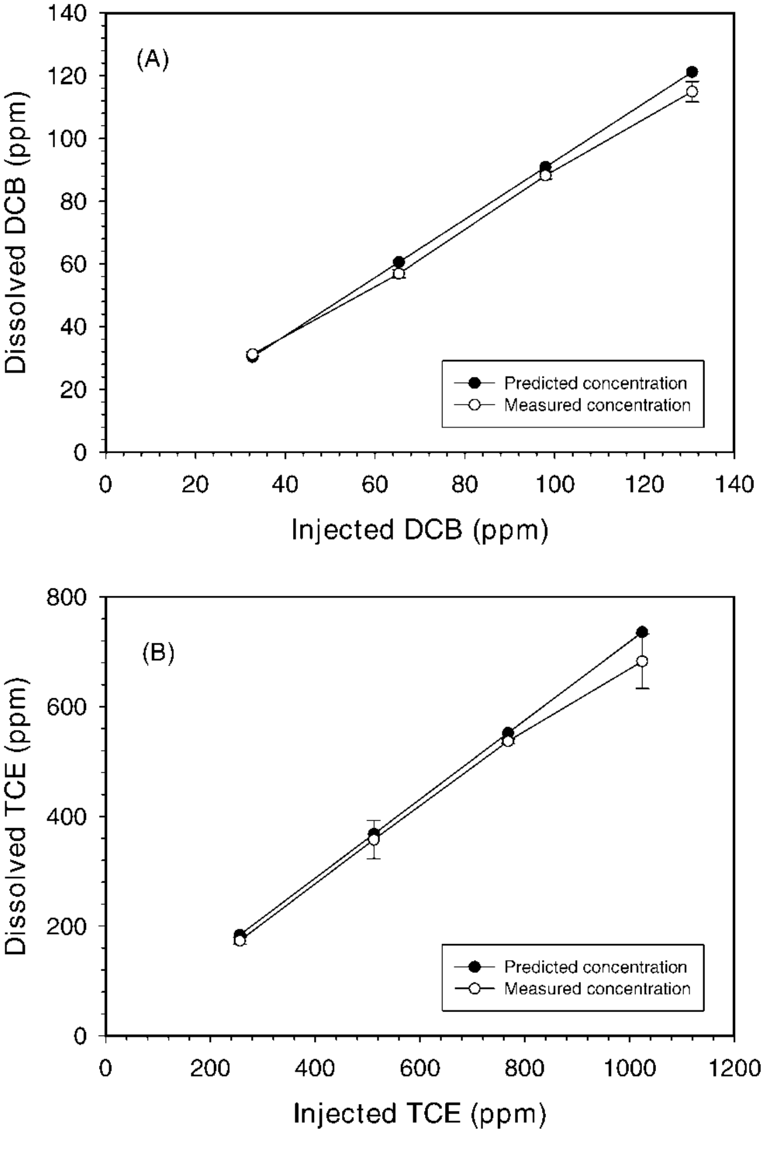

Figure 7. Comparison of dissolved concentration and concentration predicted using Henry's law constant in the experiment with 0% silicone oil and deionized water for (A) DCB and (B) TCE.

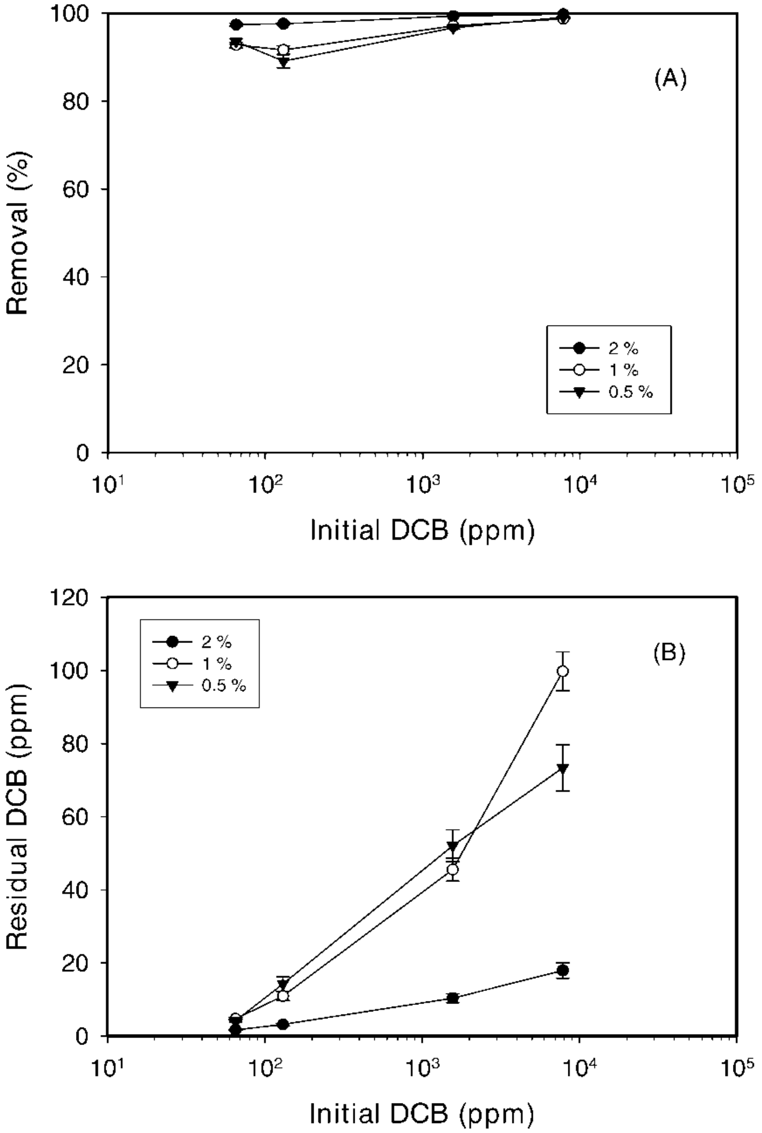

Figure 8. (A) Solubilization efficiency and (B) residual concentration of DCB in emulsions prepared with different concentrations of silicone oil. Homogenization was performed at 8000 rpm for 15 min. Because solubilization of DCB into the emulsion caused removal of DCB from the aqueous phase, solubilization efficiency was expressed as removal percentage.

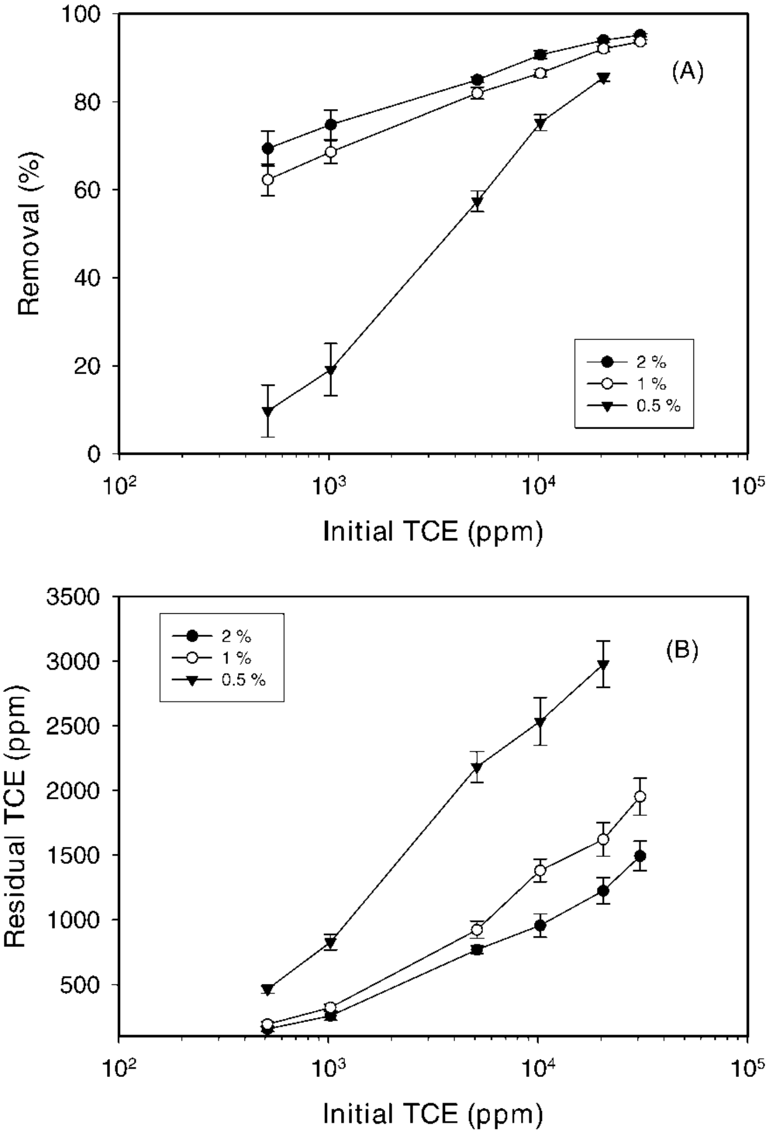

Figure 9. (A) Solubilization efficiency and (B) residual concentration of TCE in emulsions prepared with different concentrations of silicone oil. Homogenization was performed at 8000 rpm for 15 min. Because solubilization of TCE into the emulsion caused removal of TCE from the aqueous phase, solubilization efficiency was expressed as removal percentage.

CONCLUSIONS

Homogenization rate was the most important parameter in obtaining the most effective emulsion from an oil solution. A high rate of homogenization produced a well-dispersed emulsion, which enhanced its properties. The emulsions prepared in this study showed a certain degree of monodispersity as determined by the observation that more than 99% of emulsion particles were well distributed between 1 and 10 μm in diameter. However, considering the polydispersity value and uniformity factor of the emulsions, the state of the present emulsion needs to be improved. Nevertheless, the potential of the emulsions to remove DNAPLs has been demonstrated with DCB and TCE in this study. The emulsion prepared in this study was especially effective for the removal of DCB. A high concentration (7800 ppm) of DCB was fully solubilized by the emulsion. Currently under investigation for more effective remediation of DNAPLs is the enhancement of emulsion properties and solubilization of DNAPLs via use of surfactant at levels below the critical micelle concentration.

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