

Cyclodextrin-Enhanced Solubilization and Removal of Residual-Phase Chlorinated Solvents from Porous Media

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The development of improved methods for remediation of contaminated aquifers has emerged as a significant environmental priority. One technology that appears to have considerable promise involves the use of solubilization agents such as surfactants and cosolvents for enhancing the removal of residual phase immiscible liquids. We examined herein the use of cyclodextrin, a glucose-based molecule, for solubilizing and removing residual-phase immiscible liquid from porous media. Batch experiments were conducted to measure the degree of trichloroethene (TCE) and tetrachloroethene (PCE) solubilization induced by hydroxypropyl- β -cyclodextrin (HPCD) and methyl- β -cyclodextrin (MCD). These studies revealed that the solubilities of TCE and PCE were enhanced by up to 9.5 and 36.0 times, respectively. Column experiments were conducted to compare water and cyclodextrin-enhanced flushing of Borden sand containing residual saturations of TCE and PCE. The results indicate that solubilization and mass removal were enhanced substantially with the use of cyclodextrins. The effluent concentrations during the steady-state phase of the HPCD (5% and 10%) and MCD (5%) flushing experiments were close to the apparent solubilities measured with the batch experiments, indicating equilibrium concentrations were maintained during the initial phase of cyclodextrin flushing. Mobilization was observed for only the TCE-MCD (5% and 10%) and PCE-5%MCD experiments.

Introduction

While pump-and-treat systems may work very well for plume containment, they have not been successful for complete remediation of sites contaminated with immiscible liquids. As a consequence, the development of improved methods for complete remediation of contaminated aquifers has emerged as a significant environmental priority. One technology that appears to have considerable promise involves the use of solubility enhancing agents such as surfactants, cosolvents, and complexing agents. The use of surfactants and cosolvents for enhanced-solubilization of immiscible liquids has been discussed by several researchers (1–7).

Cyclodextrins, glucose-based toroidal-shaped molecules, are produced at commercial scales from the enzymatic

transformation of starch by bacteria. Cyclodextrins have a low-polarity cavity within which organic compounds of appropriate shape and size can form inclusion complexes. This unique property provides cyclodextrins with a capacity to significantly increase the apparent solubilities of low-polarity organic contaminants such as polyaromatic hydrocarbons and organic solvents.

The application of cyclodextrins as solubility enhancing agents has recently been investigated (8–13). Most of this research has focused on solubilization in batch systems and on enhancing the removal of sorbed-phase contaminants. The focus of this study is the use of two cyclodextrins for the enhanced solubilization and removal of residual-phase chlorinated solvents from porous media, which has not yet been examined in detail.

Materials and Methods

Materials. Analytical-grade trichloroethene (TCE; >99%) and tetrachloroethene (PCE; >99%) were purchased from Aldrich Chemical Co., Inc. Hydroxypropyl- β -cyclodextrin (HPCD; 90%) and methyl- β -cyclodextrin (MCD; >99.8%) were supplied by Cerestar USA, Inc., Hammond, IN. The average molecular weights of HPCD and MCD are 1365 and 1303 g mol⁻¹, respectively. All aqueous solutions were prepared with deionized water free of measurable quantities of organic contaminants.

The porous media used in the study was a subsoil collected from the Canadian Air Force base in Borden, Ontario, and is identical to that used by Brusseau et al. (8). The sandy material (98% sand-fraction) has a porosity of 36%, a bulk density of 1.70 g cm³, and an organic carbon content of 0.29%. The intrinsic permeability ($k = 7.2 \times 10^{-8}$ cm²) was estimated based on reported hydraulic conductivity values (14). The soil was dry sieved (<2 mm) prior to use. Preparative chromatography columns made of precision-bore borosilicate glass (2.5 cm i.d., 5.0 cm length, Kontes Co.) were used in the experiments. The columns were designed to have minimum void volume in the end plates. All connections and tubing were made of Teflon.

Experimental Procedures. The columns were packed in incremental steps with dry porous medium to establish uniform bulk density. The column was weighed before and after packing to determine the dry mass of the soil. After packing, the columns were slowly saturated from the bottom with electrolyte solution (0.01 N CaCl₂) using a single-piston pump (Scientific Systems Inc., Model 300 LC). After saturation was achieved, about 100 pore volumes of solution were pumped through the column to condition the porous medium to the electrolyte solution, which was used to maintain a typical ionic strength. The pore volume of a column was calculated by measuring the mass of water retained in the column after complete saturation, corrected for dead volume (see Table 1).

The method used to establish residual saturation of TCE and PCE was similar to those used by Pennell et al. (1) and Bai et al. (15). The immiscible liquid was injected through the bottom of the electrolyte-saturated column using a syringe pump (Sage Instruments Syringe Pump Model 335). A vertical, upward flow regime was used to maintain stable conditions during displacement of water from the column by the denser-than-water organic liquids. The flow rate was 0.1 cm³ min⁻¹, which is equivalent to a darcian velocity of 0.02 cm min⁻¹. A total volume of approximately 6–7 mL of organic liquid was pumped into the column. The exact amount of injected liquid was determined gravimetrically by measuring the mass difference of the syringe before and after injection. Organic

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TABLE 1. Experimental Conditions of the Column Experiments

property	water	5% HPCD horizontal	5% HPCD vertical	10% HPCD	5% MCD	10% MCD
TCE						
column pore volume (cm ³)	11.0	11.0		9.9	11.0	10.0
initial NAPL mass (g)	1.64	1.63		1.80	2.44	2.70
saturation (%)	10.2	10.1		12.7	15.1	18.4
av flow rate (cm ³ min ⁻¹)	0.63	0.64		0.70	0.71	0.75
PCE						
column pore volume (cm ³)	10.0	10.4	10.4	10.4	11.0	11.0
initial NAPL mass (g)	2.20	2.56	1.78	2.18	2.36	1.96
saturation (%)	13.6	15.1	10.5	12.9	13.2	11.0
av flow rate (cm ³ min ⁻¹)	0.70	0.69	0.70	0.74	0.71	0.70

TABLE 2. Summary of the Physicochemical Properties of the Flushing Agents

property	water	5% HPCD	10% HPCD	5% MCD	10% MCD
density (ρ_L ; g cm ⁻³)	1.000	1.010	1.027	1.010	1.028
TCE-interfacial tension ($\sigma_{TCE-agent}$; dynes cm ⁻¹)	34.5 ^a	18.8	17.2	10.2	9.1
PCE-interfacial tension ($\sigma_{PCE-agent}$; dynes cm ⁻¹)	44.4 ^a	22.2	20.6	15.2	9.0
molecular weight (g mol ⁻¹)	18	1365	1365	1303	1303

^a Interfacial tension for PCE and TCE in contact with water; from ref 16.

TABLE 3. Results of the Batch and Column Flushing Experiments

property	water	5% HPCD horizontal	5% HPCD vertical	10% HPCD	5% MCD	10% MCD
TCE						
solubility enhancement (E) from batch experiments	1.0	3.4	3.4	5.5	4.6	6.6
av relative concn at steady state (-)	0.92	3.4		5.5	4.6	9.5
av apparent solubility at steady state (mg L ⁻¹)	997	3686		5962	4553	10298
percent total recovery	93.2	94.4	94.9	91.1	93.0	89.8
percent mobilized of total mass recovered	0	0	0	0	12	6
PCE						
solubility enhancement (E) from batch experiments	1.0	8.1	8.1	15.5	16.1	29.1
av relative concn at steady state (-)	1.0	7.6	7.4	15.1	15.3	36.0
av apparent solubility at steady state (mg L ⁻¹)	195	1479	1458	2962	3025	7138
percent total recovery	88.8	92.8	90.4	93.2	92.0	90.5
percent mobilized of total mass recovered	0	0	0	0	0	1.7

liquid displaced from the column was collected in a glass buret. After the organic liquid was pumped through the column, electrolyte solution was pumped through the top of the column at a flow rate of 0.2 cm³ min⁻¹ for two pore volumes, followed by an additional 10 pore volumes at a flow rate of 1.2 cm³ min⁻¹. The organic liquid displaced from the column was collected in the glass buret. The amount of organic liquid in the soil was determined from the difference of the volume injected, the volume displaced from the column, and the amount of contaminant dissolved in the eluted electrolyte solution. Saturation (organic-liquid volume/pore volume) varied between 10.1% and 18.4% for TCE and between 10.5% and 15.1% for PCE (see Table 1).

For the flushing experiments, the column was placed in a horizontal position to mimic typical groundwater flow conditions. In an additional experiment, the column was placed in a vertical position to evaluate the effect of gravitational forces on the flushing process. For each experiment, the appropriate solution was pumped through the column at an average flow rate of 0.69 cm³ min⁻¹ (\pm 0.06 cm³ min⁻¹), which is equivalent to a darcian velocity of 0.14 cm min⁻¹ (\pm 0.012 cm min⁻¹). Two different concentrations of the flushing agent were used in this study (5% and 10 wt %). Experiments were conducted using electrolyte solution as a control. Column effluent was collected in glass tubes, which were capped and placed in an ice bath to minimize volatilization losses. A specific volume (50 μ L to 1 mL) of the effluent was diluted in 10 mL of deionized water and analyzed

immediately. The concentration of TCE and PCE was determined using a UV-spectrophotometer (Shimadzu UV-1601 or Hitachi U-2000). The lower detection limits were 5 and 2 mg L⁻¹ for TCE and PCE, respectively. During some flushing experiments, small amounts of free phase immiscible liquid were displaced from the column. The recovered free phase was transferred into a glass buret to measure the mobilized fraction of the contaminant. Both the mobilized mass and the solubilized mass were included in the mass removal calculations.

An experiment was terminated when the contaminant concentration in the column effluent reached the detection limit. After selected experiments, the soil was removed from the column and treated with hexane to extract remaining organic compound. The mass remaining was in all cases less than 1% of the initial mass of the contaminant. The overall recovery was generally higher than 90% (see Table 3). Missing mass was attributed to volatilization losses during sample preparation and analysis. Before reusing the column, the sand was flushed with at least 100 pore volumes of electrolyte solution. The experimental conditions for the column experiments are summarized in Table 1.

The apparent solubilities of TCE and PCE in the cyclodextrin solutions were determined by batch experiments (see Table 3). These studies were conducted by adding 20 mL of either TCE or PCE to 250 mL of the flushing agent solution. The resulting two-phase system was then agitated for 24 h, transferred into a separatory funnel, and left to sit for 72 h.

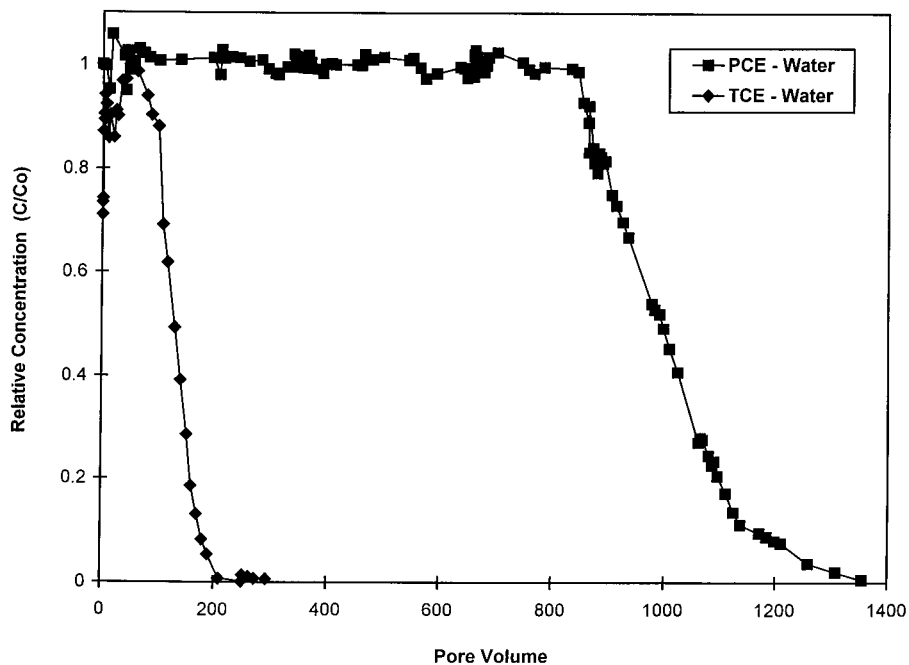


FIGURE 1. Elution curves for flushing residual TCE and PCE with water.

Finally, the organic liquid was drained, and the remaining saturated solution immediately analyzed as described above. The relative apparent solubilities in cyclodextrin solution ranged between 3.4 and 6.6 for TCE and 8.1 to 29.1 for PCE, respectively.

The interfacial tension between TCE and PCE and the cyclodextrin solutions was determined using a ring tensiometer (Fisher Scientific Surface Tensiometer 21). The cyclodextrin solution was equilibrated with the organic liquid prior to the interfacial tension measurement. The reported interfacial tension values (Table 2) are the average of at least five individual measurements.

Data Analysis. Immiscible liquids can be displaced if there is sufficient driving force to overcome the capillary pressure difference between the water and the liquid. The criterion of mobilization can be expressed in terms of the ratio of viscous to capillary forces. This ratio is known as the capillary number N_c , and can be defined as

$$N_c = \frac{k_{\text{intr}} \rho g \Delta H}{\sigma} = \frac{q \mu}{\sigma} \quad (1)$$

where k_{intr} is the intrinsic permeability (cm^2), ρ is the density of water (g cm^{-3}), g is the acceleration due to gravity (cm s^{-2}), ΔH is the hydraulic gradient, μ is the dynamic viscosity of water (N s cm^{-2}), q is the Darcy velocity (cm s^{-1}), and σ is the interfacial tension between the immiscible liquid and water (dynes/cm). Immiscible displacement becomes likely when the viscous forces dominate over the capillary forces.

The effect of buoyancy forces on residual phases can be evaluated using the dimensionless bond number, N_B :

$$N_B = \frac{k_{\text{intr}} \Delta \rho g}{\sigma} \quad (2)$$

where $\Delta \rho$ is the density difference between the aqueous and immiscible liquid phases. The effect of the buoyancy and viscous forces are additive under vertical flow conditions (17). The results of laboratory experiments indicate that immiscible liquids at residual saturation, or less, cannot be displaced from porous media under vertical flow conditions if the $N_c + N_B$ is less than 2×10^{-5} (17). This critical value is a function of the porous medium and may vary with particle

size distribution and packing of the columns. Under horizontal flow conditions, the value of combined effects of buoyancy and viscous forces will be slightly smaller than under vertical flow conditions (17). The potential for the cyclodextrin solutions to cause displacement will be evaluated using eqs 1 and 2, the results of which will be compared to the observed behavior.

Results and Discussion

Water Flushing. Figure 1 shows the change of the relative concentration of TCE and PCE in the column effluent with increasing volume of electrolyte solution flushed through the column. The relative concentration was calculated by dividing the concentration in the column effluent by the solubility of PCE or TCE in water as obtained from the batch experiments. The aqueous solubilities are equal to 198 and 1084 mg L^{-1} for PCE and TCE, respectively, and are comparable to aqueous solubilities reported elsewhere (21, 22).

The TCE concentration began to decline after 60 pore volumes, due to decreasing volume of the immiscible liquid and the associated reduction in interfacial area between immiscible liquid and the flushing solution in the column (19, 20). The rate of decline was essentially constant until about 200 pore volumes, where the concentration began to decline at a much slower rate, causing extensive tailing. Approximately 300 pore volumes of water were necessary to decrease the TCE concentration in solution to 5 mg L^{-1} . The nonequilibrium dissolution behavior resulted in almost twice the number of pore volumes being required for TCE removal as expected based on equilibrium dissolution.

Approximately five times as many pore volumes were required to remove PCE, as compared to TCE, which was expected given PCE's lower solubility. During the steady-state period, which was attained within one pore volume, the effluent concentration was within 2% of the aqueous solubility of PCE. Steady-state equilibrium dissolution (i.e. $C/C_0 = 1$) lasted for the first 850 pore volumes, wherein a total of 76% of the initial mass of PCE was recovered. Afterward, the effluent concentration declined linearly until reaching 1150 pore volumes. At that point, as during the TCE-electrolyte flushing experiment, the concentration began to decline much more slowly.

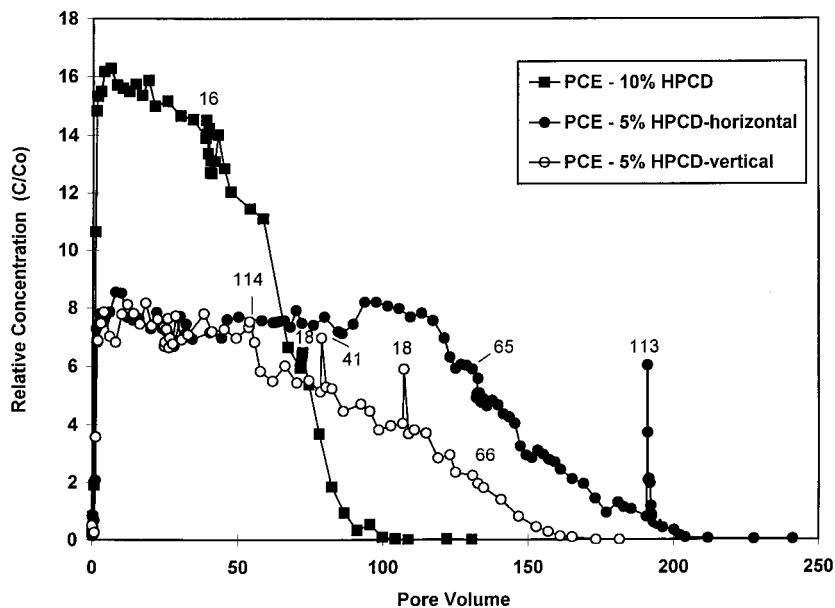


FIGURE 2. Elution curves for flushing residual PCE with 5% and 10% HPCD solutions. The 5% HPCD flushing experiment was performed under both horizontal and vertical flow conditions. Numbers indicate the duration of the flow interruption (in hours).

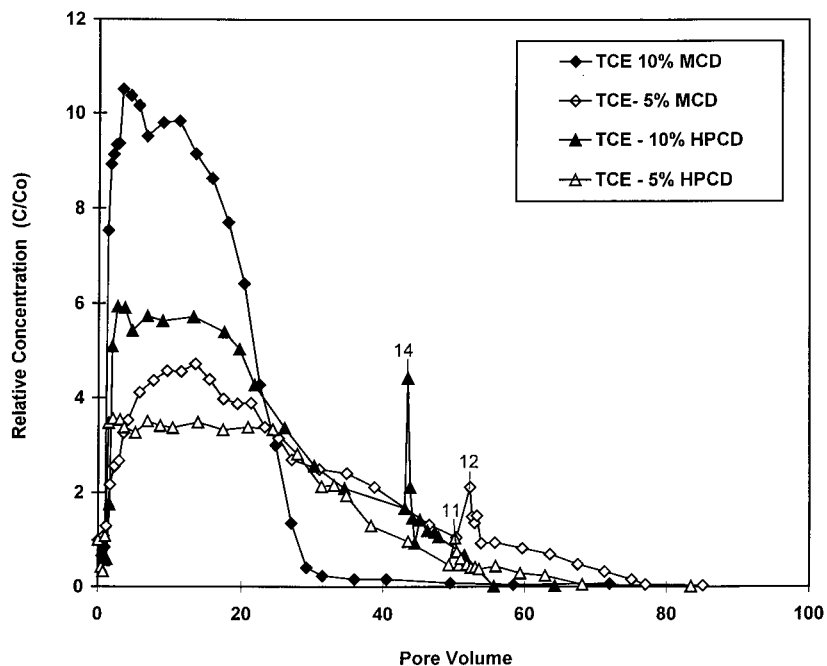


FIGURE 3. Elution curves for flushing residual TCE with 5% and 10% HPCD and MCD solutions. Numbers indicate the duration of the flow interruption (in hours).

HPCD-Flushing. As shown in Figures 2 and 3, the PCE and TCE concentrations in the column effluent increased sharply when flushed with HPCD solution. Following the sharp increase, an approximately constant, steady-state effluent concentration was attained. For both TCE and PCE experiments, the effluent concentrations in the pseudo-steady-state region were within 6% of the equilibrium concentrations determined in the batch experiments (see Table 3). The similarity between the column effluent concentrations and the batch equilibrium concentrations indicates equilibrium dissolution of both compounds during the initial phase of HPCD flushing.

Between 60% and 66% of the initial mass of TCE was solubilized during the steady-state phase of HPCD flushing. These data corresponds to the 66% mass fraction of TCE that was solubilized during the steady-state phase of water

flushing. Similarly, 72% of PCE was recovered with 5% HPCD during steady state versus 76% during the water flushing experiment. The similarity of these data sets indicates that the distribution of mass removal between steady-state and transient phases is equivalent for both water and HPCD systems.

After flushing the column with several tens of pore volumes, the effluent concentration began to decrease in an approximately linear fashion. The linear decline continued until less than 1% of the initial mass of compound remained in the column. At this point tailing was observed for the next 30 pore volumes. A flow interruption technique (23) was used to investigate possible mass-transfer constraints, e.g. rate-limited solubilization. This method involves the interruption of flow during the experiment. If the dissolution of the immiscible liquid is rate-limited, one can expect an increase

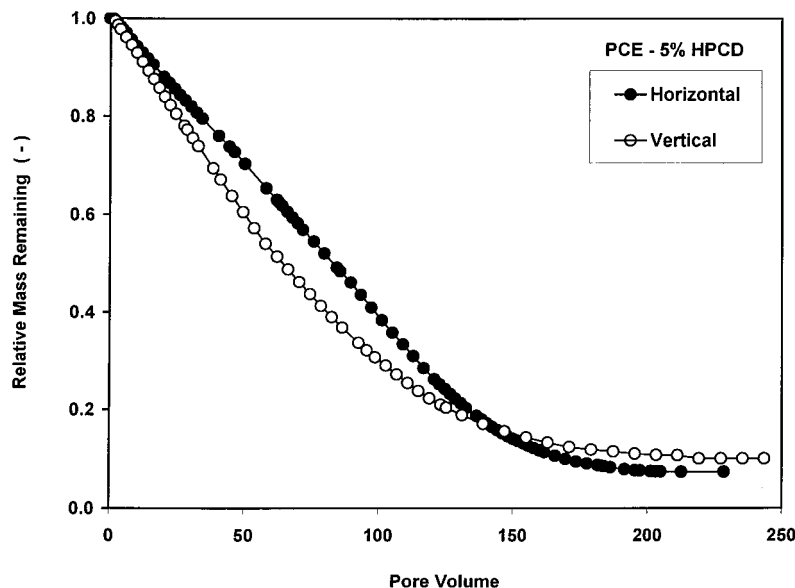


FIGURE 4. Comparison of flushing PCE with 5% HPCD solution under horizontal and vertical flow conditions. The relative mass remaining in the column was normalized to account for different initial saturations.

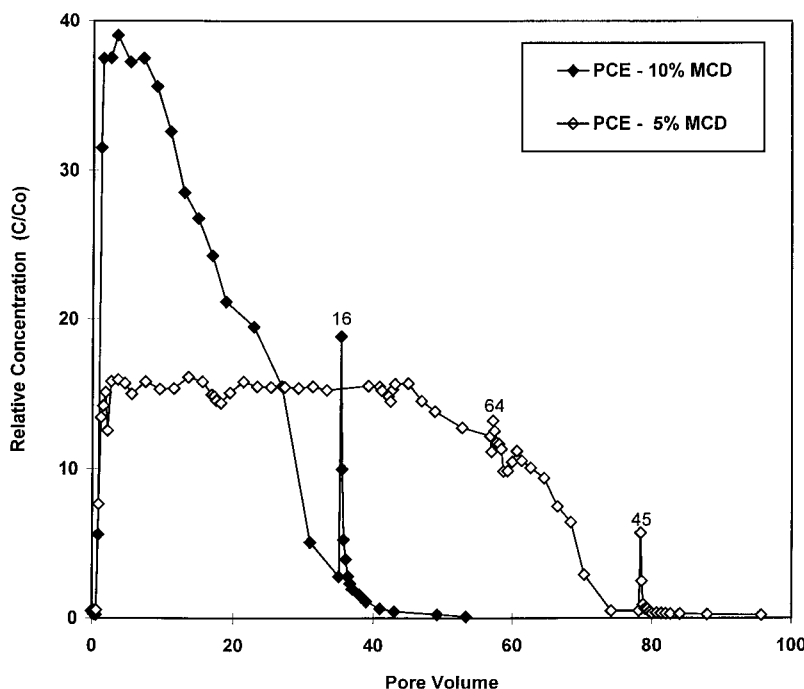


FIGURE 5. Elution curves for flushing residual PCE with 5% and 10% MCD solutions. Numbers indicate the duration of the flow interruption (in hours).

in the effluent concentration after the flow is resumed. Several no-flow periods ranging from 9 to 114 h were implemented during each cyclodextrin flushing experiment.

No significant increase in concentration for either compound was observed after flow interruption during the steady-state period (see Figures 2 and 3). This was expected given that the effluent and batch-equilibrium concentrations were very similar, indicating equilibrium conditions at the applied flow velocities. However, flow interruption during the transient phase of the experiments did result in significant concentration increases, indicating that the dissolution is constrained by rate-limited mass transfer. This rate-limited behavior, as is the case for the water systems, is due primarily to the reduction in immiscible-liquid/water interfacial area as the residual saturation is reduced and its spatial distribution becomes less uniform.

The comparison of the 5% HPCD flushing experiments conducted under vertical (downward) and horizontal flow conditions with PCE as the immiscible liquid reveals that the apparent solubility enhancement was approximately the same for both experiments. However, different rates of concentration decline were observed during the transient phase. For horizontal flow conditions, the effluent concentration decline quasi-linearly for approximately 80 pore volumes, while under vertical flow conditions the concentration decline lasted more than 150 pore volumes. Thus, the dissolution process under vertical flow conditions took about twice as long as under horizontal flow. Some of this difference may be caused by the different degrees of initial saturation, which was higher for the horizontal (15.1%) than for the vertical (10.5%) experiment. To account for this, the mass of PCE remaining in the column was normalized by the

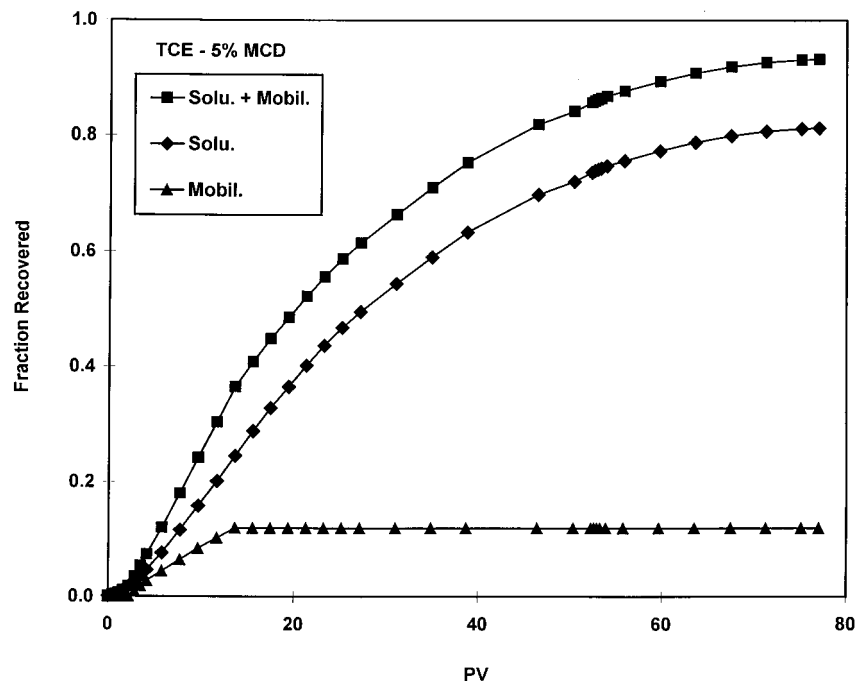


FIGURE 6. Cumulative recovery of residual TCE following the injection of 5% MCD solution.

TABLE 4. Capillary (N_C) and Bond (N_B) Numbers

property	water	5% HPCD horizontal	5% HPCD vertical	10% HPCD	5% MCD	10% MCD
TCE						
N_C	1.7×10^{-6}	3.2×10^{-6}		3.8×10^{-6}	6.9×10^{-6}	7.8×10^{-5}
N_B	9.4×10^{-7}	1.7×10^{-6}		1.9×10^{-6}	3.2×10^{-6}	3.6×10^{-6}
$N_C + N_B$	2.6×10^{-6}	4.9×10^{-6}		5.7×10^{-6}	1.0×10^{-5}	1.2×10^{-5}
PCE						
N_C	5.4×10^{-7}	1.1×10^{-6}	1.2×10^{-6}	1.2×10^{-6}	1.6×10^{-6}	2.7×10^{-6}
N_B	9.9×10^{-7}	2.0×10^{-6}	2.0×10^{-6}	2.1×10^{-6}	2.9×10^{-6}	4.9×10^{-6}
$N_C + N_B$	1.5×10^{-6}	3.1×10^{-6}	3.2×10^{-6}	3.3×10^{-6}	4.6×10^{-6}	7.6×10^{-6}

initial mass of PCE for each experiment. From Figure 4, it is evident that the mass-normalized removal rates of both experiments are similar.

MCD-Flushing. Figures 3 and 5 show the results of the column experiments with MCD as the flushing agent. Similar to the HPCD-data, the column effluent concentrations of both TCE and PCE increased sharply at the beginning of the experiment. The steady-state level occurred after 2–6 pore volumes of flushing, which indicates retardation of the MCD (retardation factor, $R = 2.2 \pm 1.1$). The preliminary batch experiments indicate that MCD is not sorbed by the porous medium. However, MCD was found to partition into TCE/PCE. For example, the measured TCE-MCD partition coefficient, K_{TCE} , is 3.7, which results in expected retardation factors varying from 2.8 to 3.3, depending on the magnitude of initial TCE saturation. These values are consistent with the elution behavior observed in Figures 3 and 5.

The apparent solubilization was greater for PCE than for TCE. This observation is consistent with our previous batch experiments (8), where the magnitude of solubilization enhancement increases as the polarity of the organic compound decreases. It is also consistent with the results obtained for other solubilization enhancing agents, such as surfactants (1).

The steady-state phase for the MCD experiments is again characterized by an approximately constant concentration in the column effluent, as was the case for water and HPCD. The effluent concentrations during the steady-state phase of

the 5% MCD flushing experiments were close to the batch-equilibrium concentrations measured for PCE and TCE. Conversely, the effluent concentrations during the steady-state phase for the 10% MCD experiments were 44% and 24% higher than the batch-equilibrium concentrations for TCE and PCE, respectively. These higher steady-state concentrations were observed prior to the appearance of free-phase compound in the column effluent. It is postulated that microemulsions formed upon arrival of the cyclodextrin solution and that the emulsion dissolved during subsequent dilution of the sample, resulting in a higher apparent solubility than expected based solely on solubilization.

Mobilization was observed for all of the MCD experiments, with the exception of the 5% MCD-PCE experiment. Mobilization was detected visually by inspecting the column effluent where free phase was visible as distinct droplets that sank rapidly to the bottom of the sample container. The onset of mobilization was after 4–8 pore volumes, thus indicating retardation of the free-phase front. Free phase was displaced from the columns during a period of approximately 10 pore volumes of flushing. Figure 6 shows the results of a representative mass recovery calculation for the 5% MCD-TCE flushing experiment.

The concentration decline was sharper for the 10% MCD solutions than for the 5% MCD solutions. Furthermore, the decline in effluent concentration during the transient phase of the MCD experiments was more rapid than that of the HPCD flushing experiments for an equivalent cyclodextrin

concentration. These results are consistent with the larger enhancement factors associated with MCD.

Capillary and Bond Numbers. The addition of cyclodextrin resulted in a reduction in the aqueous immiscible liquid interfacial tension (see Table 2). The decrease was more pronounced for MCD than for HPCD and is greater for higher cyclodextrin concentrations. For example, the interfacial tension of a 5% MCD solution in contact with PCE is 15.2 dynes cm^{-1} , while that of a 10% MCD solution is 9.0 dynes cm^{-1} . For PCE, the reduction in interfacial tension is less than half of that observed for common anionic surfactant systems (1, 24).

The approximate critical value for the onset of mobilization based on literature data ($\sim 10^5$) was not attained for any experiment in which HPCD or water was used as the flushing solution. This is consistent with the results of the HPCD and water flushing experiments, for which no evidence of mobilization was observed. For the MCD flushing experiments, the magnitude of the calculated capillary and bond numbers, which exceeded the values obtained for the HPCD experiments, are in good agreement with the observed mobilization behavior. These observations are attributed to the lower values for $\sigma_{\text{MCD-NAPL}}$ than for $\sigma_{\text{HPCD-NAPL}}$. Based on the calculated values for the capillary and bond numbers and the observed occurrence of mobilization, the critical value for the onset of displacement appears to be close to $\sim 10^5$ for the MCD systems, which is consistent with data reported for other systems (17).

For each PCE experiment, N_c was smaller than N_b (Table 4), indicating that gravitational forces dominated over viscous forces. These findings are similar to the results presented by Pennell et al. (1), who used anionic and nonionic surfactants as flushing agents. Conversely, for the TCE experiments, viscous forces dominated over gravitational forces (i.e. $N_c > N_b$). The difference between the two systems is related to the density difference between the two immiscible fluids, which would favor gravity induced movement of the more dense PCE ($\rho_{\text{PCE}} = 1.623 \text{ g cm}^{-3}$) compared to the less dense TCE ($\rho_{\text{TCE}} = 1.462 \text{ g cm}^{-3}$).

In conclusion, the results from this study indicate that HPCD and MCD significantly increase the apparent solubilities of PCE and TCE. As a result, the total flushing volume necessary to remove residual saturation was reduced substantially compared to water flushing. Due to its less polar character and its impact on interfacial tension, MCD proved to be more effective than HPCD. However, MCD caused mobilization in some experiments, whereas HPCD did not. The results indicate that contaminant concentrations were maintained at the maximum equilibrium level during the initial phase of flushing for both cyclodextrin systems. As a low toxicity sugar derivative, cyclodextrins may have some inherent advantages for use as a remediation agent.

Acknowledgments

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Literature Cited

- (1) Pennell, K. D.; Abriola, L. M.; Weber, W. J. *Environ. Sci. Technol.* **1993**, *27*, 2332–2340.
- (2) Pennell, K. D.; Jin, M.; Abriola, L. M.; Pope, G. A. *J. Contam. Hydrol.* **1994**, *16*, 35–53.
- (3) Brusseau, M. L. *Complex Mixtures and Groundwater Quality*; USEPA Research Brief; EPA/600/S-93/004, 1993.
- (4) Brandes, D.; Farley, K. J. *Water Environ. Res.* **1993**, *65*(7), 869–878.
- (5) Imhoff, P. T.; Gleyzer, S. N.; McBride, J. F.; Vancho, L. A.; Okuda, I.; Miller, C. T. *Environ. Sci. Technol.* **1995**, *29*(8), 1966–1976.
- (6) Rao, P. S. C.; Annable, M. D.; Sillan, R. K.; Dai, D.; Hatfield, K.; Graham, W. D.; Wood, A. L.; Enfield, C. G. *Water Resour. Res.* **1997**, *33*(12), 2673–2686.
- (7) Jawitz, J. W.; Annable, M. D.; Rao, P. S. C.; Rhue, D. *Environ. Sci. Technol.* **1998**, *32*, 523–530.
- (8) Wang, X.; Brusseau, M. L. *Environ. Sci. Technol.* **1993**, *27*, 2821–2825.
- (9) Brusseau, M. L.; Wang, X.; Hu, Q. *Environ. Sci. Technol.* **1994**, *28*, 952–956.
- (10) Wang, X.; Brusseau, M. L. *Environ. Sci. Technol.* **1995**, *29*, 2632–2635.
- (11) Brusseau, M. L.; Wang, X.; Wang, W. *Environ. Sci. Technol.* **1997**, *31*, 1087–1092.
- (12) McCray, J. E.; Brusseau, M. L. *Environ. Sci. Technol.* **1998**, *32*(9), 1285–1293.
- (13) Bizzigotti, G. O.; Reynolds, D. A.; Kueper, B. H. *Environ. Sci. Technol.* **1997**, *31*(2), 472–478.
- (14) Rajaram, H.; Gelhar, L. W. *Water Resour. Res.* **1991**, *27*(6), 1239–1251.
- (15) Bai, G.; Brusseau, M. L.; Miller, R. M. *J. Contam. Hydrol.* **1997**, *24*(2), 157–170.
- (16) Mercer, J. W.; Cohen, R. M. *J. Contam. Hydrol.* **1990**, *17*(6), 106–163.
- (17) Pennell, K. D.; Pope, G. A.; Abriola, L. M. *Environ. Sci. Technol.* **1996**, *30*(4), 1328–1335.
- (18) Ji, W.; Brusseau, M. L. *Water Resour. Res.* **1999**, in press.
- (19) Powers, S. E.; Abriola, L. M.; Weber, W. J. Jr. *Water Resour. Res.* **1994**, *30*(2), 321–332.
- (20) Miller, C. T.; Poirier-McNeill, M. M.; Mayer, A. S. *Water Resour. Res.* **1990**, *26*(11), 2783–2796.
- (21) Pankow, J. E.; Cherry, J. A. *Dense Chlorinated Solvents and other DNAPLs in Groundwater*; Waterloo Press: 1996.
- (22) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley-Interscience, 1993.
- (23) Brusseau, M. L.; Hu, Q.; Srivastava, R. *J. Contam. Hydrol.* **1997**, *24*, 205–219.
- (24) Fountain, J. C.; Klimek, A.; Beirkirch, M. G.; Middleton, T. M. *J. Hazardous Mater.* **1991**, *28*, 295–311.

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