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Partitioning of Hydrophobic Organic Compounds to Hydroxypropyl-β-cyclodextrin: Experimental Studies and Model Predictions for Surfactant-Enhanced Remediation Applications

SEOK-OH KO,† MARK A. SCHLAUTMAN,* AND ELIZABETH R. CARRAWAY‡

Environmental Engineering Specialty Area, Department of Civil Engineering, Texas A&M University, College Station, Texas 77843-3136

Partitioning studies of hydrophobic organic compounds (HOCs) to hydroxypropyl-β-cyclodextrin (HPCD) and one-dimensional transport simulations were conducted to evaluate the feasibility of using HPCD to remove sorbed HOCs in surfactant-enhanced remediation (SER) applications. HOC partitioning to HPCD was very fast, with over 95% of the complexation occurring within 10 min. Some influence of solution chemistry and HOC concentration on HOC−HPCD complex formation coefficients was observed; in general, the magnitude of the effects was similar to that observed previously for a nonionic surfactant (Tween 80) but much less than that for an anionic surfactant (sodium dodecyl sulfate, SDS). HPCD sorption on kaolinite as quantified by both a fluorescence technique and total organic carbon measurements was negligible, indicating no significant affinity of HPCD for the solid phase. Although the HOC solubilization capability of HPCD was lower than that of conventional surfactants such as SDS and Tween 80, transport simulations showed that HPCD can be effective in removing sorbed HOCs from a model subsurface environment, primarily because of its negligible sorption to the solid phase (i.e., all HPCD added facilitates HOC elution). However, in contrast with SDS and Tween 80, HPCD becomes relatively less effective for HOC partitioning with increasing HOC size and hydrophobicity. Therefore, comparisons between HPCD and conventional surfactants for enhanced remediation applications must consider the specific HOC(s) present and the potential for surfactant material losses to the solid phase as well as other generally recognized considerations such as material costs and potential toxicological effects.

Introduction

The widespread presence of hydrophobic organic compounds (HOCs) in subsurface environments has prompted rigorous development of in-situ remediation technologies for contaminated sites. Because of their low solubilities and slow dissolution/desorption rates, many HOCs typically are associated with the solid phase or exist as nonaqueous phase liquids (NAPLs) and thus are difficult to remove from subsurface environments using traditional technologies such as groundwater pump-and-treat systems. As an alternative to water-based elution techniques, methods in which solubility enhancing materials (e.g., surfactants, cosolvents, organic colloids) are added to subsurface environments contaminated with HOCs have become widely studied. Among the alternative techniques, surfactant-enhanced remediation (SER) has been suggested as a promising technology for the removal of NAPLs (e.g., refs *1* and *2*).

In contrast to NAPLs, fewer studies have been conducted on the removal of HOCs existing in the sorbed state. Results from these studies have shown that surfactant sorption on the solid phase has a significant effect on the distribution of HOCs between the aqueous and solid phases because sorbed surfactants also exhibit HOC partitioning capabilities (*3*−*7*). In general, HOC distribution coefficients initially increase with increasing surfactant addition and only begin to decrease when formation of a sufficient number of surfactant micelles in the aqueous phase allows the micelles to outcompete the sorbed surfactant for HOC partitioning (*5*). As a result, addition of surfactants into contaminated subsurface systems, particularly soils containing low amounts of native organic matter, may not enhance the removal of sorbed HOCs except at the very high surfactant doses necessary to overcome the adverse effects of surfactant sorption to the solid phase (*5*, *6*). Therefore, for a successful SER application it is essential to select a suitable type of HOC solubility enhancing material having a low affinity for the solid phase.

Cyclodextrins (CDs) are naturally occurring, torus-shaped, cyclic oligosaccharides formed from the enzymatic degradation of starch by bacteria (*8*). The capability of CDs to include various guest molecules into their interior cavities in aqueous solution has generated great interest in food, pharmaceutical, and agriculture industries (*8*). Unlike conventional surfactants, CDs have a range of desirable physicochemical properties that may make them attractive for removing sorbed HOCs from contaminated subsurface systems, including the following: (1) CDs are considered to be nontoxic and biodegradable; (2) no minimum or critical CD concentration is necessary to include guest molecules; (3) because of their rigid structure and nonionogenic functional groups, CDs are expected to exhibit relatively stable physicochemical properties over a range of solution chemistry conditions; and (4) CDs can be chemically modified to make them more soluble in water and therefore less susceptible to sorption on solid phases.

A water-soluble modified CD, hydroxypropyl-β-cyclodextrin (HPCD), has been suggested as an alternative HOC solubility enhancing material in SER applications due to its formation of inclusion complexes with HOC molecules (*9*−*11*). Recently, in-situ field-scale tests using HPCD solutions to remove NAPL constituents from a contaminated subsurface environment showed excellent removal rates compared to water-based elution (*12*). Other in-situ HPCD flushing processes have been combined with bioremediation (*13*) and reductive dechlorination (*14*) to treat subsurface organic contaminants. These results show that HPCD elution alone or combined HPCD elution/treatment processes can be promising subsurface remediation technologies. In addition to HPCD, other CDs have been evaluated for potential use in subsurface remediation applications. For example, carboxymethyl-β-cyclodextrin (CMCD) has been studied to

* Corresponding author phone: (409)845-3011; fax: (409)862-1542; e-mail: schlautman@tamu.edu.

† Present address: Environmental Research Team, Daewoo Institute of Construction Technology, Seoul, Korea.

‡ Present address: Department of Environmental Toxicology, Clemson University, Pendleton, SC 29670.

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evaluate its feasibility for simultaneously remediating organic contaminants and heavy metals (*11*, *15*). Although the solubility enhancement of organic contaminants was less for CMCD than for HPCD, the experimental results showed that CMCD has the potential to be effective at contaminated sites containing both organics and heavy metals.

The objectives of the present study were to (1) evaluate the ability of HPCD to complex HOCs under a variety of solution chemistry conditions representative of subsurface environments, (2) determine the relative rate of the complexation reaction, (3) quantify the potential for HPCD sorption to solid phases, and (4) compare the performance of HPCD versus two conventional micelle-forming surfactants, sodium dodecyl sulfate (SDS) and Tween 80, for use in SER applications to remove sorbed HOCs from contaminated subsurface environments. The first three objectives were carried out in batch laboratory experiments, whereas the last objective was accomplished both by comparing the experimental results to those available in the literature and by performing transport simulations with a one-dimensional numerical model previously developed for simulating SER processes in model subsurface systems (*6*).

Methodology

Experimental Materials. A chemically modified (to enhance its water solubility) CD, hydroxypropyl-β-cyclodextrin (HPCD), was purchased from Aldrich (no purity reported) and used as received. Its molecular weight was reported to be 1460. Fresh HPCD stock solutions were prepared monthly in fixed ionic strength solutions and stored in the dark at room temperature; based on total organic carbon (TOC) analyses and replicated experiments over one-month time periods, we saw no evidence of HPCD degradation in the stock solutions. The HOCs used in the experimental portion of this study were phenanthrene (Aldrich, 99.5+%) and naphthalene (Aldrich, 99+%); both were used without further purification. Selected physicochemical properties of phenanthrene and naphthalene and their stock solution preparations have been previously reported (*5*). Solution pH and ionic strength values were adjusted as necessary with 0.5 M HCl and/or 0.5 M NaOH and NaCl, respectively; these and all other reagents were analytical grade or better and used without further treatment.

Analytical Methods. A fluorescence spectrophotometer (Photon Technology International) was used to determine HPCD concentrations in aqueous solutions after first complexing it with 2-*p*-toluidinenaphthalene-6-sulfonate (TNS) (*10*); the excitation/emission wavelengths used for TNS were 366/460 nm with slits set for bandwidths of 4 and 0.5 nm on the excitation and emission sides, respectively. Fluorescence intensities of TNS as a function of HPCD concentration were used to quantify unknown aqueous phase HPCD concentrations in sample systems. HPCD concentrations were also quantified by TOC analysis (Shimadzu Model 5050). Aqueous phenanthrene and naphthalene concentrations were quantified by fluorescence at the excitation/emission wavelengths of 256/364 and 278/322 nm, respectively, using the same slit settings as above. Absorbance measurements (HP 8452A) were also made at the above wavelengths. All analytical determinations utilized standard external calibration curves over their linear response regions and were made well above the instrumental and method detection limits. Relative precisions of 1% and 3% were routinely obtained for spectroscopic and TOC measurements, respectively; only HPCD concentrations greater than 1 mM as determined by TNS fluorescence showed appreciably higher relative standard errors because of the extreme sensitivity of the technique and very large dilutions required before quantification.

HOC Complexation by HPCD. Fluorescence cuvettes with lead foil faced Teflon plugs were used as batch reactors to follow HOC complex formation rates with HPCD. Aqueous HOC solutions were pipetted into cuvettes before filling them to the top with HPCD solutions to minimize the headspace. After tightly capping the cuvettes, the fluorescence of triplicate samples was monitored with time. The fluorescence of control HOC solutions (i.e., no HPCD) was also monitored for background levels and system losses.

Fluorescence techniques previously used for the determination of HOC micellar partition coefficients (*5*, *7*) were adapted to determine HOC complex formation coefficients to HPCD (K_{HPCD}) as a function of solution pH, ionic strength, and HOC concentration. To determine formation coefficients, batch experiments were conducted in triplicate using vials sealed with lead foil faced Teflon-lined caps. HOC stock solutions were spiked into 25 mL aqueous solutions of fixed pH (4, 6, or 10) and ionic strength (0, 0.01, or 0.1 M) to obtain final phenanthrene or naphthalene concentrations ranging from 1.68 to 4.49 or 39 to 195 μM, respectively. HPCD stock solutions were then added to the vials before capping them. The samples were placed on a shaker for 3 days to equilibrate before spectroscopic analyses were conducted. The fluorescence intensity of each sample was measured, and the results were analyzed via nonlinear regression to determine K_{HPCD} values (*5*, *7*). In addition to using fluorescence to determine complex formation coefficients at concentrations below aqueous HOC solubility limits, solubility enhancement experiments were conducted following the procedure described by Wang and Brusseau (*9*) to compare K_{HPCD} values obtained at saturation conditions.

HPCD Sorption on Kaolinite. Batch experiments were conducted in triplicate to determine the rate and extent of HPCD sorption using centrifuge tubes with Teflon-lined screw caps (Corex, 25 mL). Soil-to-solution mass ratios of 1:5 were used. Tubes containing weighed amounts of kaolinite were filled with 25 mL of a 0.1 M NaCl solution of pH 4.6; these solution chemistry conditions were expected to be the most favorable for HPCD sorption based on previous observations for a nonionic surfactant (*7*). HPCD stock solutions were then added such that concentrations ranged from 0 to 10 mM. The samples were placed on an end-over-end tumbler for 48 h to equilibrate. The solids were then separated from the aqueous solution by centrifugation at 7000 rpm for 30 min, and aliquots (4 mL) of the supernatant were mixed with 4 mL of a TNS solution. HPCD concentrations (S_{HPCD}, mM) were determined by spectroscopic analysis after taking into account any dilution factors and system losses. Sorbed HPCD concentrations in the solid phase (q_{HPCD}, μmol/g) were calculated by mass balance. To confirm the HPCD sorption results using the fluorescence method, HPCD concentrations in the centrifuged supernatants were also determined by TOC analysis.

Model Simulations. A one-dimensional numerical model previously developed for evaluating SER applications (*6*) was used to predict the elution of sorbed HOCs from a contaminated model aquifer by flushing with HPCD solutions. The model is based on mass balance equations that incorporate the multiple chemical species (i.e., HOC, HPCD) present in the multiple phases (i.e., aqueous, HPCD, subsurface solids) present. A system of coupled differential equations was used to represent general rate expressions for the removal of adsorbed HOCs from subsurface systems by HPCD flushing and to provide temporal and spatial HOC and HPCD distributions in each phase. In the formulation of the mass balance equations, water was assumed to totally cover all other phases (*6*, *16*). The governing equations including boundary conditions and the numerical solution scheme have been previously described (*6*, *17*). HOC and HPCD mass balances in each phase were computed and monitored over time using the total flux and the mass within the system.

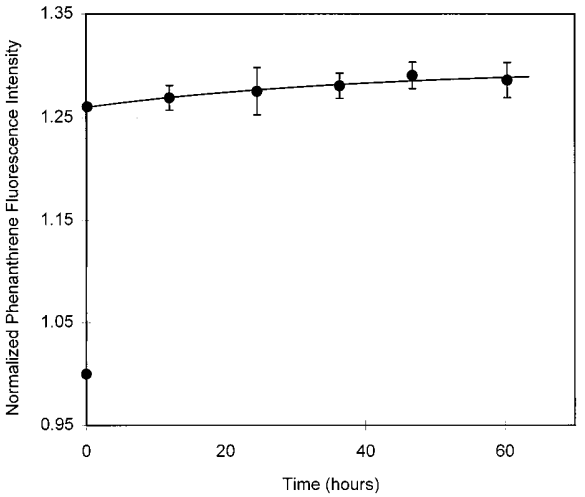

FIGURE 1. Phenanthrene complexation by HPCD at pH 6 and ionic strength 0.1 M NaCl. The solid line shows the fit for a first-order complexation rate constant of 6.64 × 10^{-5} s^{-1}. The phenanthrene and HPCD concentrations were 4.49 μM and 10 mM, respectively. Error bars for some data points are smaller than the symbols.

Numerical Parameters. To demonstrate the importance of HPCD flushing on the enhanced removal of HOCs from subsurface systems, a representative sandy aquifer column system was modeled (*6*). Input parameters used for the numerical simulations were as follows: column length (L) and diameter (d) of 0.1 and 0.025 m, respectively; porosity (θ) of 0.34; bulk solids density (ρ) of 1500 kg/m^3; solids surface area (a) of 3 m^2/g; pore velocity (v) of 2.71 × 10^{-5} m/s; hydrodynamic dispersion coefficient (D) of 1.63 × 10^{-8} m^2/s; time step (Δt) of 1 s; and nodal spacing (Δx) of 1 × 10^{-4} m. Rate and equilibrium parameters for HOC and HPCD sorption to the model aquifer material and for HOC partitioning to dissolved and adsorbed HPCD were based on the experimental data obtained in this study or from the literature. As necessary, parameter values were converted from a mass to surface area basis and normalized for the above solids surface area before their use as has been previously described (*6*, *17*); the appropriateness of such a normalization procedure for reasonably similar mineral surfaces has been discussed (e.g., refs *18* and *19*). First-order model fits to rate data were used to obtain forward rate constants for all sorption/partitioning processes. First-order reverse rate constants were then estimated from the ratios of forward rate constants and the appropriate equilibrium distribution coefficients (*6*, *16*, *20*). This approach is generally valid only if sorption/partitioning isotherms are linear; experimental results for all reactions considered here showed such linearity. Although two-site models are often used to divide the solid phase into fractions representing labile and nonlabile domains (*6*), for this study we chose to focus primarily on HOC sorption/desorption rates for the relatively labile soil fraction to evaluate its importance for HOC remediation. We believe this simpler model is adequate for screening various SER alternatives; however, readers should be aware that such a simple hypothetical model likely will not reflect actual remediation conditions.

Results and Discussion

HOC Complexation by HPCD. Representative rate data and first-order model fit for phenanthrene complexation to HPCD are shown in Figure 1. The initial reaction was very fast with about 98% of the complexation occurring within 10 min. Thereafter, the fluorescence intensity of phenanthrene in the HPCD solution slowly increased and became constant with time after about 48 h, indicating equilibrium had been reached. Similar observations were made for naphthalene complexation by HPCD (data not shown). However, to provide a margin of safety, contact times of 3 days were utilized for the complex formation coefficients reported below.

TABLE 1. Phenanthrene and Naphthalene Complexation Constants for HPCD[a]

HOC	C_t (μM)	NaCl (M)	K_{HPCD} (M^{-1})	R^2	N[b]	K_{oc}[c] (L/g)
phenanthrene	1.68	0	3341 ± 274.3	0.992	21	6.77 ± 0.56
		0.01[d]	3217 ± 122.4	0.994	21	6.52 ± 0.25
		0.01	3186 ± 97.34	0.997	21	6.46 ± 0.19
		0.01[e]	3383 ± 30.54	0.999	21	6.86 ± 0.06
		0.1	3628 ± 129.7	0.997	21	7.36 ± 0.26
	2.81	0.1	3544 ± 104.1	0.998	21	7.19 ± 0.21
	4.49	0.1	3086 ± 224.8	0.994	21	6.26 ± 0.46
	6.73	0.1	2963 ± 94.05[f]	0.993	18	6.01 ± 0.19
naphthalene	39	0.1	823 ± 11	0.997	21	1.67 ± 0.02
	117	0.1	717 ± 23	0.996	21	1.45 ± 0.05
	195	0.1	624 ± 34	0.992	21	1.26 ± 0.07
	241	0.1	508 ± 8[f]	0.998	18	1.03 ± 0.02

[a] K_{HPCD} values (±SD) were obtained by nonlinear regression analysis of fluorescence data using the method of Ko et al. (*5*) unless otherwise noted. The pH was 6 unless otherwise noted. [b] Number of data points used to determine K_{HPCD} values. [c] Calculated from K_{HPCD} values and the average carbon fraction of HPCD as determined by total organic carbon analysis. [d] pH 4. [e] pH 10. [f] K_{HPCD} values determined by linear regression of solubility enhancement data following the procedure of Wang and Brusseau (*9*).

Equilibrium constants for phenanthrene and naphthalene complexation with HPCD cavities are listed in Table 1 as a function of solution chemistry and HOC concentration; the complex formation coefficients measured here are in good agreement with literature values (*9*, *15*). Varying solution chemistry conditions for a total phenanthrene concentration of 1.68 μM exhibited little to no effects on its complex formation with HPCD, presumably because of their respective nonpolar characteristics; similar results have been previously reported for phenanthrene partitioning to micelles formed by the nonionic surfactant Tween 80 (*7*). The apparent increase in phenanthrene-HPCD complexation with increasing ionic strength appears to be within statistical limits of the estimated 6% increase expected due to phenanthrene "salting out" (*7*). In contrast, solution ionic strength played a major role in the partitioning of phenanthrene to SDS micelles, presumably because the micelle structure itself was changing (*7*).

HPCD complex formation coefficients for phenanthrene and naphthalene decreased with increasing HOC concentrations when measured by fluorescence; similar results have been observed for micellar partitioning coefficients (*5*). Additionally, the coefficients obtained from solubility enhancement tests (Table 1) showed slightly lower values than those measured using fluorescence, consistent with the established trend. Direct comparison of the coefficients obtained from the different methods is often difficult, however, and a more detailed study would be necessary to determine conclusively whether changes in the interactions between HOCs and HPCD occur as a function of HOC concentration and, if so, why the changes occur.

A critical parameter for HOC partitioning to CDs is the relative size of the host (i.e., CD cavity) versus guest (i.e., HOC) molecules. For example, using solubility enhancement studies Wang and Brusseau (*9*) found that HOCs having a smaller molecular volume (MV) than the HPCD cavity (0.346 nm^3) fitted completely inside the cavity and thus showed a good log−linear relationship between K_{HPCD} and the octanol−water partition coefficient (K_{ow}); however, the solubility enhancement for *p,p′*-DDT which has a greater MV (0.508

nm^3) than the HPCD cavity did not follow this log−linear relationship because the larger DDT molecule could only partially enter the cavity, thus leaving a portion of its overall volume in the water.

In addition to the relative size of MV versus cavity, other factors can play a role in CD−HOC complexation reactions. For example, α-, β-, and γ-CDs are the three most common homologues produced and consist of 6, 7, and 8 glucopyranose units, respectively, with reported cavity volumes of 0.176, 0.346, and 0.510 nm^3, respectively (*21*). Blyshak et al. (*22*) found that HOC complex formation with these CDs was dependent not only on the MVs and cavity sizes but also on differences between other HOC characteristics such as molecular surface area, HOC orientation in a CD cavity, and overall HOC hydrophobicity. Anthracene, which has a smaller MV than pyrene but a lower solubility in water, had a larger complex formation coefficient with β-CD than did pyrene; conversely, benzo[*a*]anthracene exhibited a larger complexation coefficient with β-CD than did benzo[*a*]pyrene even though both compounds have relatively similar MVs and benzo[*a*]anthracene actually has a higher aqueous solubility (*22*). In general, Blyshak et al. observed variable HOC complex formation coefficients depending on the specific CDs used: anthracene and benzo[*a*]anthracene showed their largest formation coefficients with β-CD, whereas pyrene and benzo[*a*]pyrene had their largest coefficients with γ-CD. Because the exact relationship between complexation coefficients and large HOC MVs is not presently resolved, other factors in addition to the relative sizes of HOCs and CD cavities may need to be considered during the optimization of SER processes that utilize CD flushing solutions. For the two HOCs used in this study, it is important to note that both were smaller (naphthalene and phenanthrene MVs of 0.246 and 0.330 nm^3, respectively (*23*)) than the HPCD cavity although phenanthrene does begin to approach the cavity volume (i.e., 0.346 nm^3).

The average TOC fraction of the HPCD used in this study was determined to be 0.3378 ± 0.0003 based on five replicate measurements, which agrees well with a reported value of about 0.336 (*9*). Organic carbon-normalized partition coefficients (K_{oc}s), calculated from the complex formation coefficients and average organic carbon fraction of HPCD, are also shown in Table 1. These values can be compared with HOC partition coefficients for natural organic carbon as predicted from empirical relationships with K_{ow} values (*24*, *25*); K_{oc} values determined by these procedures show that HPCD is slightly better than natural organic carbon for naphthalene partitioning (K_{oc} of ~1.5 versus ~1 L/g), whereas the values for HPCD are slightly lower than natural organic carbon for phenanthrene partitioning (K_{oc} of ~7.2 versus ~15.5 L/g). These observations agree with the findings of Blyshak et al. (*22*) and show that HPCD complexation constants are not exclusively proportional to HOC hydrophobicities. Finally, it is worth noting that the K_{oc} values reported in Table 1 show that HPCD has a somewhat lower partitioning capability than conventional surfactant micelles such as SDS and Tween 80 (e.g., phenanthrene K_{oc} values of ~15 and ~76 L/g, respectively (*7*) and naphthalene K_{oc} values of ~2 and ~4 L/g, respectively (*5*)).

HPCD Sorption on Kaolinite. Experimental results for HPCD sorption on kaolinite are shown in Figure 2. As discussed above, some data points that used fluorescence to determine HPCD concentrations showed relatively large standard deviations, most likely a result of errors caused by inaccurate dilutions with TNS. In general, however, the fluorescence results were similar to those using a TOC analyzer. In particular, both methods showed negligible sorption of HPCD on kaolinite. Although no specific batch test results for CD sorption on a solid phase have been reported, Brusseau et al. (*10*) showed that HPCD retardation

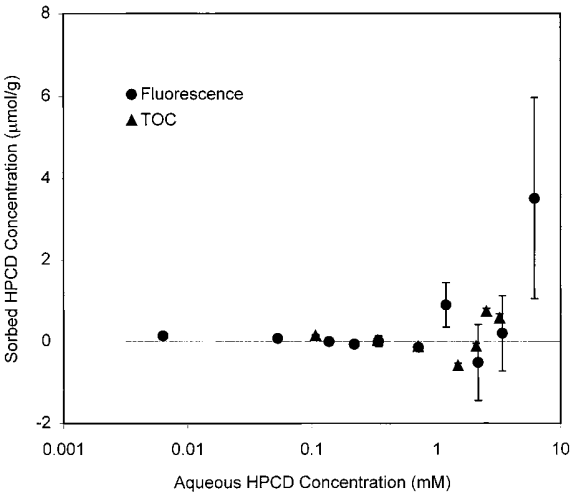

FIGURE 2. HPCD sorption on kaolinite at pH 4.6 and ionic strength 0.1 M NaCl. Kaolinite concentration was 200 g/L. Error bars for some data points are smaller than the symbols.

factors obtained from column studies were 1.0 for both a low (0.29%, Borden sand) and high (12.6%, Mt. Lemmon soil) organic carbon content solid phase, indicating negligible sorption of HPCD; Brusseau et al. also stated that the retardation results agreed with their unpublished batch sorption data. The likelihood of negligible HPCD sorption to solid phases suggests that it should have an advantage versus adsorbing surfactants for decreasing HOC distribution coefficients in subsurface systems. For example, our previous results for SDS and Tween 80 showed that distribution coefficients may initially increase due to surfactant sorption on the solid phase followed by HOC partitioning to the sorbed surfactants; in fact, in some cases the sorbed surfactants had higher affinities for HOCs than did the corresponding micelles (*5*, *7*). Therefore, CDs that do not sorb appreciably to solid phases may be effective in a wide variety of SER applications to remove sorbed HOCs from contaminated subsurface systems.

Model Simulations. The transport of HPCD through and HOC elution from our contaminated model sandy aquifer system was simulated using the input parameters specified above. Additional parameters required for the simulations were taken from the batch experimental results above or from literature results. For example, we observed negligible HPCD sorption on kaolinite; therefore, the equilibrium coefficient and related first-order forward rate constant for HPCD sorption to the subsurface solids were set to zero, resulting in no HPCD retardation in our simulations. Consistent with this action, HOC partitioning to sorbed HPCD also was not considered in the simulations.

Because no HPCD sorption to the solid phase occurs, breakthrough of HPCD shows the traditional curve for a nonsorbing tracer (i.e., one-half the influent concentration occurs at one pore volume; Figure 3). Phenanthrene elution without and with HPCD flushing is also shown in Figure 3 as a function of HPCD concentration; for these simulations, the following phenanthrene parameter values were utilized: complex formation coefficient (K_{HPCD}) of 2.26 L/g (i.e., 3300 M^{-1}; Table 1); first-order complexation rate constant of 6.64×10^{-5} s^{-1} (Figure 1); distribution coefficient between water and the aquifer solids of 4.11×10^{-4} L/g (*6*); and first-order sorption rate constant to the solid phase of 1.39×10^{-3} s^{-1} (*6*). Phenanthrene concentrations in the column effluent (C_t) were normalized by the initial aqueous concentration present within the pores before flushing commences (C_o, at equilibrium with the sorbed phenanthrene concentration, q_{phen}). The retardation factor for phenanthrene in the absence of

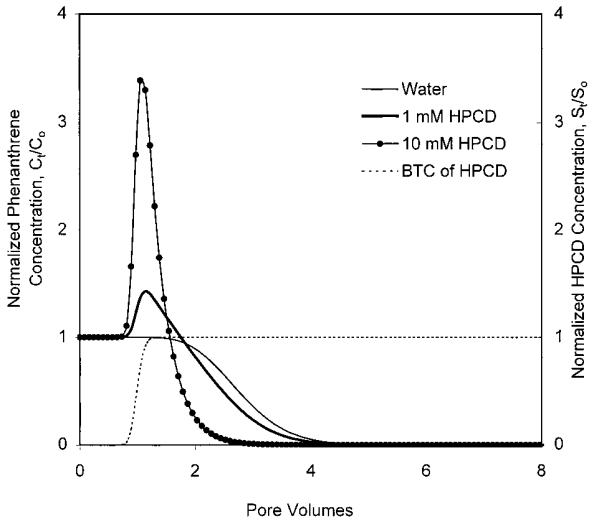

FIGURE 3. Phenanthrene elution curves for various HPCD concentrations. HPCD breakthrough reaches 0.5 at 1 pore volume and is independent of HPCD concentration.

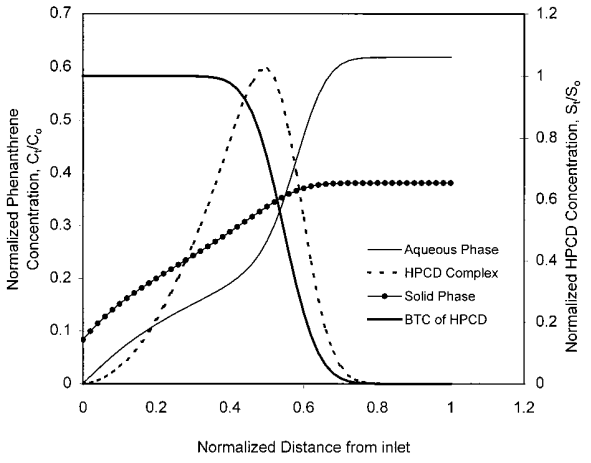

FIGURE 4. Spatial distribution of HPCD and phenanthrene in the aqueous and sorbed phases inside the simulated soil column system. The HPCD concentration used to flush the column was 10 mM, and the amount of HPCD solution added was 0.55 pore volumes, corresponding to a 35-min flushing time.

HPCD is ~2.8 (*6*); correspondingly, phenanthrene elution by water flushing shows a normalized concentration of 0.5 at 2.8 pore volumes (PVs) and also shows that the majority of phenanthrene is removed from the column within 5 PVs (Figure 3). When flushing with HPCD solutions, phenanthrene elution is enhanced relative to using only water (i.e., the effluent concentration ratio, C_t/C_o, goes above 1.0); the enhancement occurs because of the complexation with HPCD. As a result, fewer total PVs are required to remove all of the phenanthrene originally present inside the column, in agreement with the results observed by Brusseau et al. (*10*). In addition, as the influent HPCD concentration increases, an increasing number of HPCD cavities are available for complex formation with phenanthrene which leads to an increase in the elution enhancement and a decrease in the flushing time required to remove all phenanthrene. Similar results were obtained with naphthalene (data not shown), although the relative enhancement by HPCD was less than it was for phenanthrene. These simulation results suggest that HPCD can be very effective in removing sorbed HOCs from contaminated subsurface systems, in contrast with other HOC solubility enhancing materials (e.g., SDS and Tween 80) that may undergo considerable sorption to the solid phase (*5*, *7*) and thereby be less effective in SER applications (*6*).

A snapshot of the spatial distribution of phenanthrene within the one-dimensional column is shown in Figure 4 for the addition of a 10 mM HPCD solution. The front of HPCD extends into the column up to a normalized distance of ~0.75 at a flushing time of 35 min (i.e., 0.55 PVs). The aqueous and solid phase phenanthrene located to the right of this point are largely unaffected by the HPCD solution. To the left of this point, however, phenanthrene originally adsorbed to the solid phase has been redistributed among the aqueous, mobile HPCD, and solid phases; the fraction of phenanthrene in the aqueous phase decreases due to its complex formation with HPCD. If a 1 mM HPCD solution is flushed into the column instead, the fraction of phenanthrene in the aqueous phase generally remains greater than that associated with HPCD (data not shown); therefore, ultimate phenanthrene distributions are dependent on the influent HPCD concentrations selected because that determines the relative number of HPCD cavities that are available and can form inclusion complexes with phenanthrene.

As noted above, HOC complex formation with CDs is dependent on several factors including the relative size between HOCs and CD cavities, HOC hydrophobicity, HOC structure, and CD type. Several examples to demonstrate this complicated behavior are enlightening. The complexation coefficient between pyrene and β-CD has been reported to be ~493 M^{-1} at 25 °C (*22*), a value much less than the ones we measured between phenanthrene and HPCD (Table 1) even though pyrene is a larger and more hydrophobic molecule (MV of 0.355 vs 0.330 nm^3 (*23*) and log K_{ow} of 5.17 vs 4.57 (*6*)). Other batch test results for pyrene complexation (*26*) have reported similar coefficient values as Blyshak et al.; explanations for these low values generally refer to the belief that pyrene is too large to fit completely inside the β-CD cavity. Conversely, a complex formation coefficient between pyrene and HPCD calculated from column tests performed by Brusseau et al. (using eq 4 in ref *10*) would have a value of about 17 000 M^{-1}. Although it is possible that this very large difference in pyrene complexation coefficients is attributable to the slightly different CDs used (i.e., β-CD vs HPCD), batch experiments for naphthalene complexation with β-CD and HPCD showed similar coefficient values (*9*, *26*).

An alternative explanation for the difference in the pyrene complexation coefficients may be that as molecules begin approaching the size of CD cavities, batch experimental systems do not accurately reflect the ability of CDs to facilitate HOC transport in column systems. For example, Wang and Brusseau (*9*) reported a complexation coefficient between anthracene (MV of 0.327 nm^3 (*23*)) and HPCD of ~4425 M^{-1} as determined from batch solubility enhancement measurements; however, an apparent complexation coefficient for the same HOC−CD pair calculated from a column test performed by Brusseau et al. (*10*) shows a much higher value (i.e., ~41 250 M^{-1}). Similarly for 2,4,4′-trichlorobiphenyl (MV of 0.411 nm^3; (*23*)), batch solubility enhancement measurements gave an HPCD complexation coefficient of ~77 400 M^{-1}, whereas the calculated value from a column test is ~206 600 M^{-1} (*10*). Whether the complexation coefficient values obtained from the batch versus column systems above are truly different for these HOCs is not presently known; however, it is difficult to believe that such large differences could result from a propagation of errors when the column coefficients are calculated from breakthrough data.

Elution curves for pyrene flushed with 10 mM HPCD are shown in Figure 5; the only difference between the two simulations is whether the complex formation coefficient from Blyshak et al. (*22*) or Brusseau et al. (*10*) was used.

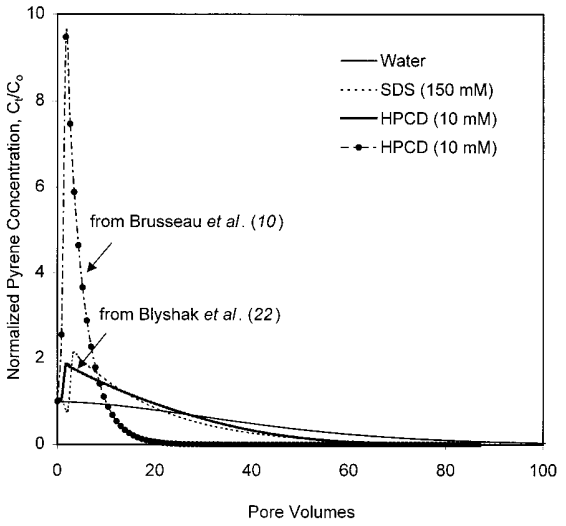

FIGURE 5. Pyrene elution curves with HPCD or SDS flushing. Different complex formation coefficients from Blyshak et al. (*22*) and Brusseau et al. (*10*) were used to simulate pyrene elution by HPCD. SDS elution of pyrene is from Ko and Schlautman (*6*).

Other parameter values utilized in the simulations included a first-order complexation rate constant of 6.64×10^{-5} s^{-1} (i.e., similar to phenanthrene), a distribution coefficient of 9.69×10^{-3} L/g (*6*), and a first-order sorption rate constant to the solid phase of 1.39×10^{-3} s^{-1} (*6*). Using the value by Blyshak et al., it is apparent that the maximum normalized concentration ratio for pyrene is about 1.8 which is less than the value of 3.4 for phenanthrene (Figure 3), implying that HPCD flushing would be less effective for the larger and more hydrophobic molecule. This result is opposite to what is observed when flushing with conventional surfactant solutions (*6*); generally, HOC micellar partition coefficients are proportional to HOC hydrophobicity, and therefore surfactant flushing becomes more effective for subsurface systems containing more hydrophobic contaminants as long as the HOC solubilization overcomes the HOC retardation due to surfactant sorption (*5*, *6*). When the pyrene elution curve for 10 mM HPCD using Blyshak et al.'s complexation coefficient is compared to that obtained with SDS flushing at 150 mM (i.e., 100 × cmc (*6*)), the extent of removal enhancement is similar as can be seen in Figure 5; in fact, flushing with SDS actually shows a slight decrease in overall remediation time. Conversely, use of the pyrene K_{HPCD} value calculated from Brusseau et al. (*10*) shows great elution efficiency and a dramatically smaller number of PVs required to completely remove pyrene from the column. Unfortunately, it is not clear at the present time which remediation scenario is more plausible for pyrene. In addition, it must be remembered that although the results from the simple model used here are adequate for comparing relative differences for the alternative remediation scenarios, they likely will not reflect conditions observed at actual contaminated sites.

If optimization of CD-enhanced subsurface remediation is required at an actual contaminated site, additional studies would be necessary to elucidate important relationships between complexation coefficients and CD types, CD cavity shapes and sizes, and HOC shapes and sizes. Alternatively, use of cosolvents such as cyclopentanol to increase K_{HPCD} values for large HOCs could be examined (*11*, *27*). In all cases, many other factors (e.g., material costs, toxicity) also would have to be considered to truly compare the feasibility of alternative HOC solubility-enhancing remediation technologies.

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