

## Interaction of $\beta$ -Cyclodextrin with Lipophilic Ring Compounds Deposited in a Sandy Soil Matrix during Flushing

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**Abstract**—Chemical soil flushing in a packed sandy soil matrix using a natural surfactant,  $\beta$ -cyclodextrin (CD) was investigated via a fluorescence spectroscopy and a dye labeling. The contaminants are lipophilic ring compounds - phenanthrene and naphthalene. Sand type and flushing intensity (rate and concentration) are critical investigation variables. The removal efficiencies were proportional to flow rate, concentration, temperature of the flushing solution and voidity of the sand column. Initial sorption of the surfactant onto the soil matrix was found to be a key step while flow shear was more crucial in the later steps. From time delay experiments before flushing, we speculate that the complexation reaction appears to be rate-limiting in non-equilibrium washing schemes.

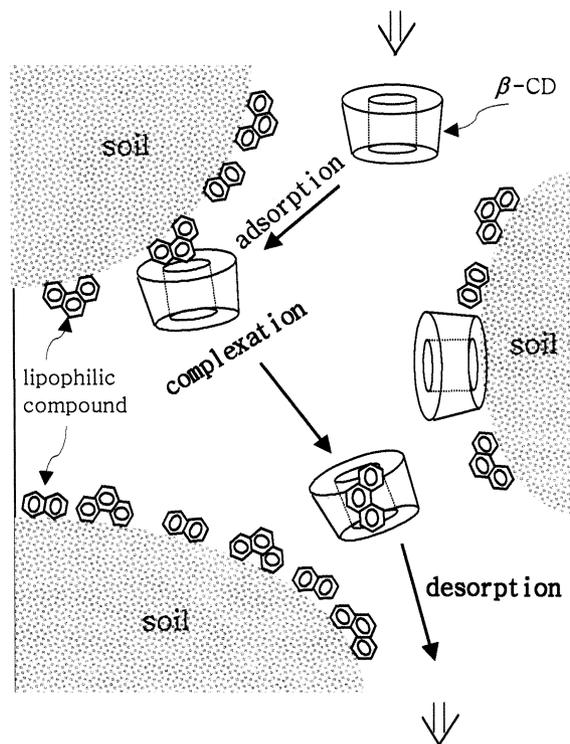
**Key words:** Surfactant Flushing,  $\beta$ -Cyclodextrin, Lipophilic Compounds, Sandy Soil, Complexation

### INTRODUCTION

Lipophilic organic contaminants beneath the subsurface soil have been a long term problem against land use and protection of groundwater. In countries like Korea where land is heavily populated and more space is deadly needed for quality living and business, quick clean-up technologies are favored urgently. To date, chemical washing technology using surfactants and cosolvents is known to be one of the fastest, the most economical and the most built-in for treating the soil contaminants provided with some proper techniques for recovery of surfactants or solvents [Fountain et al., 1996; Rao et al., 1997; Lee et al., 1999]. For almost two decades, much practical surfactant flushing - whether executed *in situ* or *ex situ* - has been attempted for removal of hazardous lipophilic compounds and for replacement of nonaqueous phase liquid (NAPL) within reasonable time frames [Pennell et al., 1994; Imhoff et al., 1995; West and Harwell, 1992]. Surfactant flushing, which originates from enhanced oil recovery, is a technique or mechanism that exploits “solubilization” and/or “mobilization (migration)” phenomena. Solubilization is simply a thermodynamic partitioning of hydrophobic (or low polarity) molecules between surfactant-rich phase and surfactant-deficient one [Ko et al., 1999; Friberg and Mortensen, 1985; Park et al., 2001]. Mobilization of lipophilic compounds trapped within porous media like soil is facilitated by a reduction in the interfacial tension between the two different phases near the solid interface [Imhoff et al., 1995; Abdul et al., 1992].

Most flushing practices are based on cost-effective flushing agents and elaborate recovery system of the agents from the treating sites. Years ago a few researches on use of contamination free chemicals as flushing agents were reported [Shiau et al., 1996; Wang and Brusseau, 1993]. Cyclodextrins are one example. They have been used for a long time as food additives, pharmaceutical agents, cosmetics, dyes and other agricultural applications like pesticide neutralizer

[Szejtli, 1988]. Brusseau group [Ko et al., 1999; Wang and Brusseau, 1993, 1995; McCray and Brusseau, 1999; Brusseau et al., 1994] published a series of works on soil flushing with cyclodextrin or its hydrophilic derivatives. They reported cyclodextrin’s performance on diverse pollutants in various soil media - sand, hayhook soil, real surface soil with organic impurities under invariant experimental conditions - fixed flushing rate and flushing concentration. However, their work was also limited in that only pollutants, not surfactant



**Fig. 1.** A plausible mechanism in  $\beta$ -CD flushing within lipophilic compound deposited in soil bed.

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behavior, were measured to determine their removal efficiency. For enhanced solubilization (complexation) and mobility, more hydrophilic  $\beta$ -cyclodextrins - HPCD (hydroxypropyl  $\beta$ -CD), CMCD (carboxymethyl  $\beta$ -CD), etc. - were used in their another work [Ko et al., 1999; Wang and Brusseau, 1995]. In spite of cyclodextrin's favorable properties - non-toxicity, biodegradability, free CMC, stability, etc. - few successful field applications were made. That means that there was no strategic application based on solid lab-scale operation data including mechanistic analysis of the flushing action, parameter optimization, and surfactant behavior during flushing. A simple schematic of CD flushing is shown in Fig. 1. With the idea of the figure, the objective of this work was to obtain a basic rule of thumb for efficient and economical soil flushing with CD by investigating behavior of CD and lipophilic pollutants during entire flushing.

## MATERIALS AND METHOD

### 1. Raw Materials

Phenanthrene and naphthalene (Aldrich Chemical Co., 99.5+% purity) were dissolved in methyl alcohol (Hayman Ltd., 99.8%) and stored at 4 °C under darkness for avoiding photochemical degradation and evaporation. Reagent grade  $\beta$ -CD from Aldrich Chemical was used as flushing agent in aqueous solution. Two forms of soil columns were introduced: local sea sand and Ottawa sand. The locally prepared sand (mined at several sea shore areas in Incheon) has 0.29 mm of average diameter and 0.35 of porosity after sieving. Ottawa sand was purchased from Fisher Scientific (assay unknown). All sands were washed with distilled water several times, and heated at 550 °C for 0.5 hours and dried at 105 °C for additional 3 hours before use in order to remove organics that might be included in the sand. Table 1 shows the characteristics and properties of the materials used in the experiments [Szejtli, 1988].

### 2. Analysis

Concentration of the two lipophilic compounds in solution was measured with a fluorescence spectroscopy (HITACHI Model F-4500). The wavelengths for analysis were 250/360 nm (excitation/emission) for phenanthrene and 278/322 nm (excitation/emission) for naphthalene with 400 volts at 23 °C [Ko, 1999]. The  $\beta$ -CD concentration was determined with dye labeling; an inclusion complex formed from methyl red and  $\beta$ -CD develops coloring for UV absorbance. Methyl red was added to effluent solutions containing  $\beta$ -CD with ratio 1 to 50 and absorbance of the mixture was measured at 200 nm in a UV/Visible spectroscopy (Analytikjena, SPECORD 40) [Hong and Youm, 1998; Lejeune et al., 1989]. For surface pres-

sure-surface area isotherm ( $\pi$ -A), dynamic surface tension ( $\pi=\gamma_0-\gamma$ ) was measured with a Wilhelmy plate method in a Langmuir Blodgett trough (LB trough; KSV minitrough, Finland). The details are found elsewhere [Cho et al., 1997].

### 3. Spreading Experiment in LB Trough

For  $\beta$ -CD spreading, 50  $\mu$ l of 0.75 mM of CD was placed on the aqueous surface (distilled and millipored pure water) by using a glass rod which was positioned upright at the bottom of the trough. In 30 minutes of the equilibration of the spread layer, a  $\pi$ -A isotherm was obtained with one stroke of compression (10 mm/min of barrier speed). For mixed layer formation, which might represent a type of interaction between a lipophilic compound and  $\beta$ -CD, 50  $\mu$ l of 11.2 mM phenanthrene or naphthalene was spread onto the  $\beta$ -CD layer before the compression for isotherm.

### 4. Equilibrium Experiment

Five milliliters of 0.75 mM phenanthrene in methanol was added to 10 g of sand with 10 ml of  $\beta$ -CD solution (0.75 mM) and mixed thoroughly in a vial. For naphthalene, the same concentration and volume were applied. The vial was then stood still and was sampled at intervals of 6 or 8 hours for determining its fluorescence intensity. In another vial, the three components were gently placed under static condition and then their equilibrium state was checked in the same interval as noted above. To see the ionic effect, the same procedure as above for equilibrium was repeated with added NaCl whose concentration ranged 0.01 to 1.0 M.

### 5. Continuous Flushing in Columns

Sand and oil were premixed in a beaker (0.076 mg/g-sand for phenanthrene or 0.057 mg/g-sand for naphthalene). A pyrex-glass column packed with the contaminated sand (5.25 g), whose dimension 10 mm of diameter and 70 mm long, was flushed downwards with  $\beta$ -CD solution by using a peristaltic pump (Model Perimax 12, SPETEC, Germany). Its feeding rates were 0.41, 0.54, 0.8, 1.3, 1.8, 2.3 and 2.7 cm/min in superficial velocity ( $V_s$ ). The effluents were collected for 5 min for each analysis. Concentrations of the surfactant solution ( $C_s$ ) ranged from 0.75 mM to 7.5 mM. Also, temperature (25-90 °C) and concentration of NaCl solution were tested as experimental variables.

## RESULTS AND DISCUSSION

### 1. Mutual Interaction in Three Phase System - Soil, Lipophilic Compound and $\beta$ -CD

In absence of soil particles, phenanthrene as a lipophilic compound was mixed with  $\beta$ -CD on the aqueous surface in the LB trough. Fig. 2 shows the  $\pi$ -A isotherm of the mixed layer. As  $\beta$ -CD itself

**Table 1. General properties of the materials used in the experiments**

	Sea sand	Ottawa sand	
Particle diameter (average, mm)	0.29	0.55-0.85	
Porosity when packed	0.35	0.55	
Total organic content (%)	0.45	0.14	
Compounds	Formula	MW	Solubility in distilled water
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178.23	7.2 ( $\mu$ M)
Naphthalene	C <sub>10</sub> H <sub>8</sub>	128.17	240 ( $\mu$ M)
$\beta$ -CD	C <sub>42</sub> H <sub>70</sub> O <sub>35</sub>	1135	complete

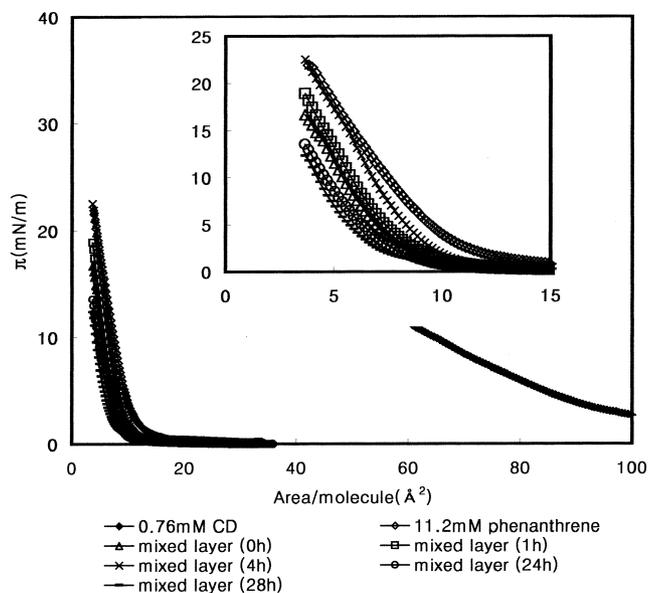


Fig. 2. Surface pressure-area per molecule isotherms of  $\beta$ -CD, phenanthrene and their mixed layers at 25 °C. The inset shows the detailed curves with time.

dissolves well in water, forming a stable layer of  $\beta$ -CD on the aqueous surface is very difficult. Using a traditional monolayer spreading method - the so called Trumit's Method - a metastable CD layer was formed first (shown as an isolated curve in the figure). And phenanthrene molecules were gently spread on the  $\beta$ -CD layer, resulting in a mixed layer. The phenanthrene replaced the  $\beta$ -CD fast enough for  $\pi$ -A to shift to the left compared to isotherm of pure phenanthrene. The instantly mixed phases were likely to become unstable because two types of molecules were present on the surface in random. Slow rearrangement of the molecular layer caused right shift with time (see 1 h and 4 h curves). However, the mixed layer in order deformed slowly in longer times such as 24 and 48 h (shown as left shift) with loss of CD [Kobayashi et al., 1999] and phenanthrene molecules most possibly due to phenanthrene's inclusion into the hydrophobic holes of inherently hydrophilic  $\beta$ -CD. Fig. 3 shows the behavior of phenanthrene in the presence or absence of  $\beta$ -CD at the interface of solid phase. Within a few minutes, sorption strongly occurred to the sand and the sorbate (phenanthrene) released back to the bulk phase in hours as found in Carroll's and Chan et al.'s work [Carroll, 1981; Chan et al., 1976]. The sorption is not believed to be an actual adsorption because slow diffusion-out of the lipophilic compound from the solid phase shortly followed the early sorption that also might include temporary entrapment by the sand matrix. Presence of  $\beta$ -CD did not appear to affect the sorption whether  $\beta$ -CD was adsorbed onto the solid particles or not (Fig. 3B). Addition of salts caused stronger initial sorption and higher reduction of phenanthrene in bulk phase as expected because decrease of the solubility of phenanthrene in the  $\beta$ -CD phase facilitated its attraction to the sand particles and retarded its desorption (a kind of "salting out" due to lowering of cloud point) [Evans and Wennerstrom, 1994].

## 2. $\beta$ -CD Sorption vs Phenanthrene or Naphthalene Elution

Like sorption of phenanthrene to the sand in very early times (Fig.

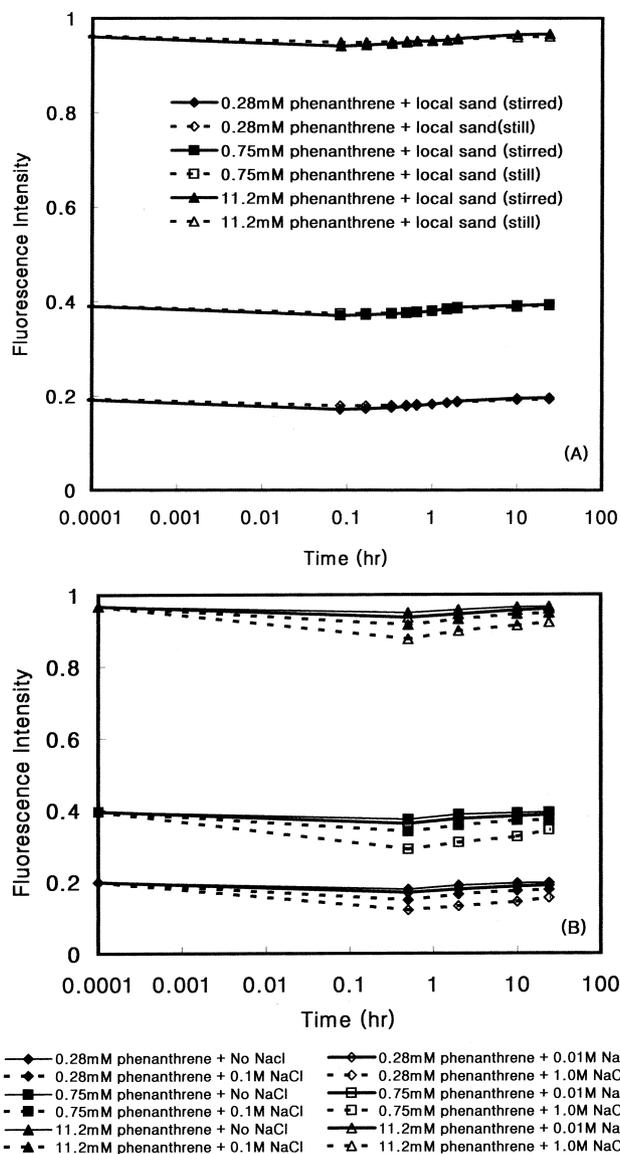


Fig. 3. Fluorescence intensity measured during phenanthrene-sand interaction after vigorous mixing or being remained still. Top figure (A) denotes change of fluorescence in the absence of  $\beta$ -CD while bottom (B) with salt (NaCl) ranging 0.01 M to 1.0 M in the presence of standard concentration of  $\beta$ -CD (0.75 mM).

3),  $\beta$ -CD was also found to be sorbed at the very early washing as shown in Fig. 4 (see the initial deep valleys). It is very interesting that phenanthrene or naphthalene started to elute out of the sand column right after the  $\beta$ -CD sorption. In other words, we can speculate that immediate  $\beta$ -CD sorption on the vicinity of the solid interface was followed by the molecular collisions between CD and phenanthrene (or naphthalene) so as to form inclusion complexes which are released easily with aid of solution shear. Another interesting fact is that the initial reduction rate of  $\beta$ -CD diminished with higher flow rate and higher CD concentrations as listed in Table 2. For example, at 2.7 cm/min with local sand, the  $\beta$ -CD reduction in concentration was no more than 10% (compare this number to 31% at 0.4 cm/min). Significant reduction did not show up until the 5th

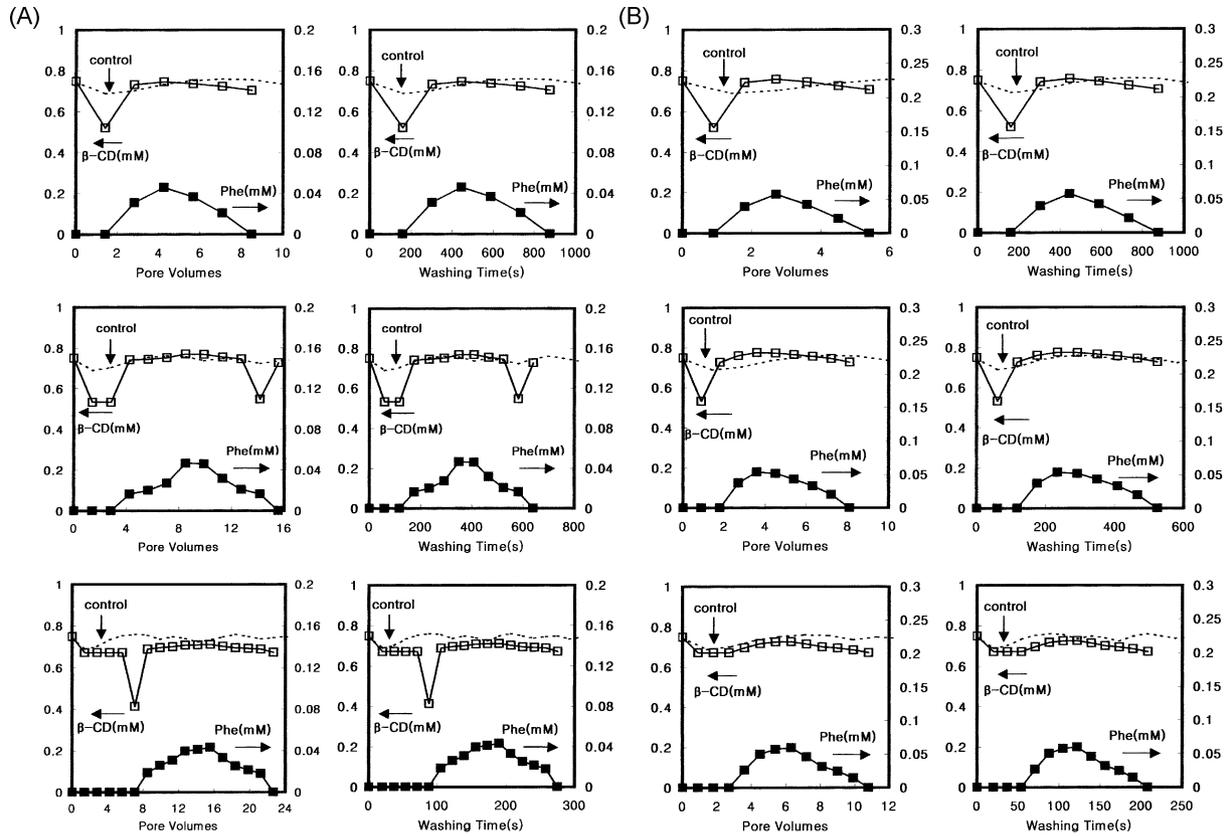


Fig. 4. Variation of  $\beta$ -CD and phenanthrene in the effluents during flushing: left six figures (A) for sea sand and right six figures (B) for Ottawa sand. The concentration of  $\beta$ -CD feed was fixed at 0.75 mM and feeding rates were 0.41, 1.3 and 2.7 cm/min downwards, respectively. Y-axes represent concentrations of related chemicals.

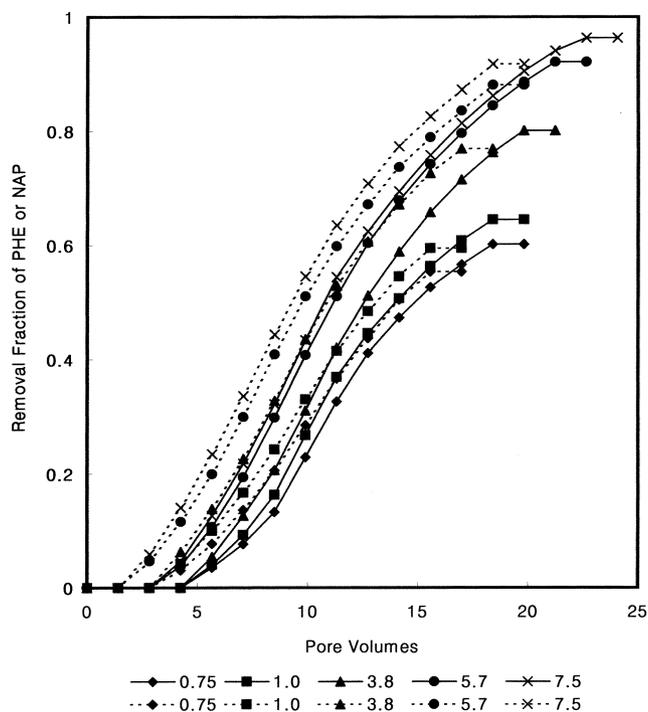
Table 2.  $\beta$ -CD concentration [mM]\* in effluent at maximum adsorption to the soil matrix (reduction percentage [%] in parenthesis)

		Local sand		Ottawa sand	
		Phenanthrene	Naphthalene	Phenanthrene	Naphthalene
$V_s$ (cm/min)	0.41	0.52 (31)	0.53 (29)	0.52 (31)	0.54 (28)
	0.54	0.53 (29)	0.53 (29)	0.53 (29)	0.54 (28)
	0.8	0.72 (3)	0.53 (29)	0.53 (30)	0.54 (28)
	1.3	0.53 (29)	0.53 (29)	0.53 (29)	0.54 (28)
	1.8	0.53 (29)	0.53 (29)	0.53 (29)	0.54 (28)
	2.3	0.67 (10)	0.68 (9)	0.67 (10)	0.54 (28)
	2.7	0.67 (10)	0.67 (10)	0.67 (10)	0.67 (10)
$C_s$ (mM)	0.75	0.53 (29)	0.53 (29)	0.53 (29)	0.54 (28)
	1.0	0.79 (21)	0.81 (19)	0.88 (12)	0.90 (11)
	3.8	3.60 (5)	3.58 (6)	3.52 (7)	3.42 (10)
	5.7	5.16 (9)	5.24 (8)	5.16 (9)	5.16 (9)
	7.5	6.72 (10)	6.94 (7)	6.90 (8)	6.75 (10)

\* feed  $\beta$ -CD concentration : 0.75 mM.

washing in this case. This trend was also found in Ottawa sand experiments. Since each sample was collected in 5 cm<sup>3</sup>-volume for analysis, there might be not enough time for complexation with high flow rate like 2.7 cm/min (contact time given as less than a minute). However, high flow rates would benefit from their strong shear generation rather than complexation as reported by Pennell et al. [1993]. That is, the early reduction in  $\beta$ -CD concentration was shortly fol-

lowed by recovery of the feed concentration or higher meanwhile phenanthrene was drawn out at its maximum. The extra surplus of  $\beta$ -CD including phenanthrene was found in the effluent in some cases. After that, a gradual decrease in CD concentration was found until initial CD concentration was recovered or there was no further elution of phenanthrene. Around this time zone, only a trivial amount of  $\beta$ -CD is most likely to be adsorbed onto the locally phenanthrene-



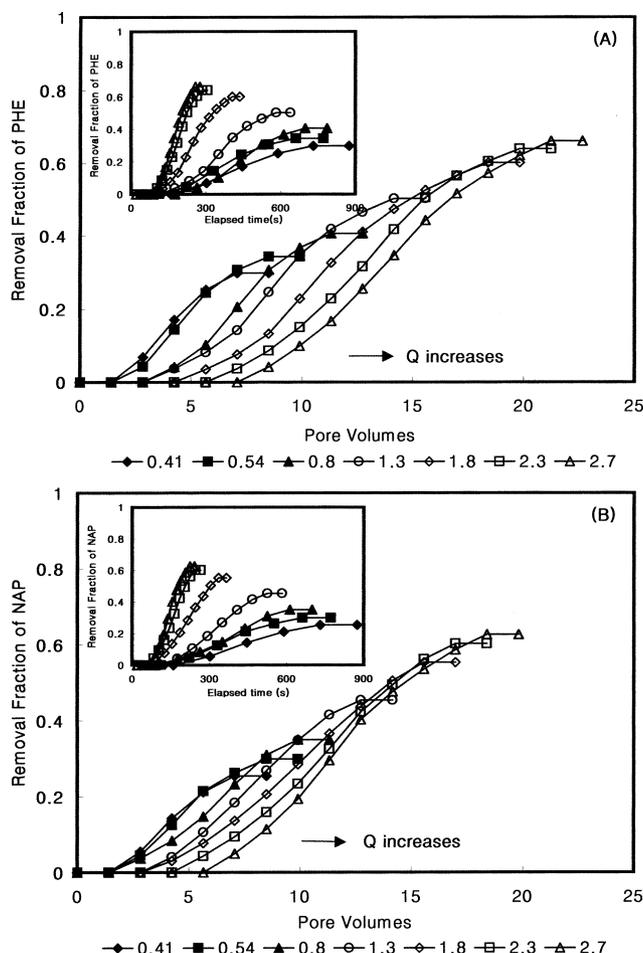
**Fig. 5.** Removal efficiencies with pore volumes of the surfactant fed at its different concentrations under fixed flow rate,  $V_s = 1.8$  cm/min for phenanthrene (solid lines) and naphthalene (dotted lines). The unit for the legends is mM.

poor part of solid phase or to be trapped in ganglia-like void space in the soil matrix. Another decreasing reduction rate of CD concentration with its higher feed concentrations reminded us of its growing saturation within the matrix. In the absence of the contaminant (control), the eluted  $\beta$ -CD concentration pattern was the same as the case with the contaminants except for more damped amplitude of the curve (refer to the dotted lines in Fig. 4).

### 3. Effect of CD Concentration, Superficial Velocity, Salt Concentration, and Temperature

CD concentration increased by 10 times almost caused double withdrawal of the contaminants (see Fig. 5). The number of CD molecules equivalent to 7.5 mM concentration was about 10 times the number of molecules of residual phenanthrene or naphthalene. Assuming all phenanthrene-including  $\beta$ -CD comes out, 3.3 molecules of  $\beta$ -CD should collect 1 molecule of phenanthrene in each washing (the theoretical complexation ratio of phenanthrene with  $\beta$ -CD is 1 : 2 [Brusseau et al., 1994]). The efficiency dropped drastically with lower CD concentrations. For naphthalene, the highest efficiency was also obtained when  $\beta$ -CD to naphthalene ratioed 3.3 to 1.

On the other hand, Fig. 6 indicates that the lower the feed flow rate is, the earlier in washes the removal develops. Reversely, a higher flow rate guarantees a higher removal efficiency finally at a cost of more pore volumes. This observation tells us that a complexation time scale of a few to tens of minutes favors slow feeding of  $\beta$ -CD at early times, but it ends up with quick termination of continuous withdrawal of the contaminants due to insufficient shear action. Hence, it is quite obvious for efficient washing to be accompanied by strong shear that high flow rate generates.



**Fig. 6.** Removal efficiencies with pore volumes of the surfactant fed at its different feeding rates under the standard concentration of 0.75 mM for phenanthrene (A) and for naphthalene (B). Insets also show the removal efficiencies with elapsed flushing time. The unit for the legends is cm/min.

Figs. 7 and 8 show the effects of salt and temperature, respectively. As salt concentration increases, the cumulative phenanthrene concentration at the bottom reaches a maximum and then decreases because higher ion concentration reduces solubility of  $\beta$ -CD in liquid phase to lower the activity of the surfactant. Similarly, CD solution becomes more activated for washing at higher temperature because of lowering of the activation energy for hydrophobic interaction between apolar hole of CD and lipophilic compound, and probable increase of molecular collisions.

### 4. Kind of Soil

The comparison between the local sand and Ottawa sand for their performance is summarized in Table 3. The flushing through Ottawa sand with the higher voidity and larger particle size resulted much higher removal rate as shown in Fig. 9. For example, with Ottawa sand, less than 10 pore volumes were sufficient to attain 98% removal while 20-24 pore volumes were used for maximum removal with the local sand. All the removal rates with Ottawa sand were also larger than those with the local sand at varied flow rates. This result was exactly opposite to the reported fact in elsewhere [Cho and Kim, 2002]; i.e., contaminant removal rate in soil columns (po-

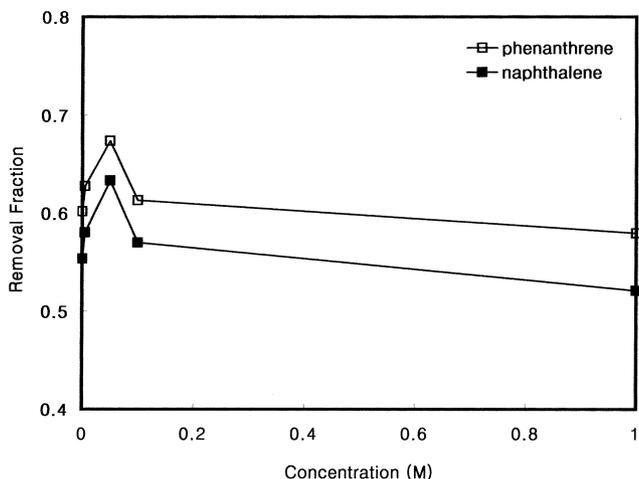


Fig. 7. Comparison of removal efficiencies of the two compounds at different NaCl concentrations under the standard feed concentration and 1.8 cm/min of  $V_s$ .

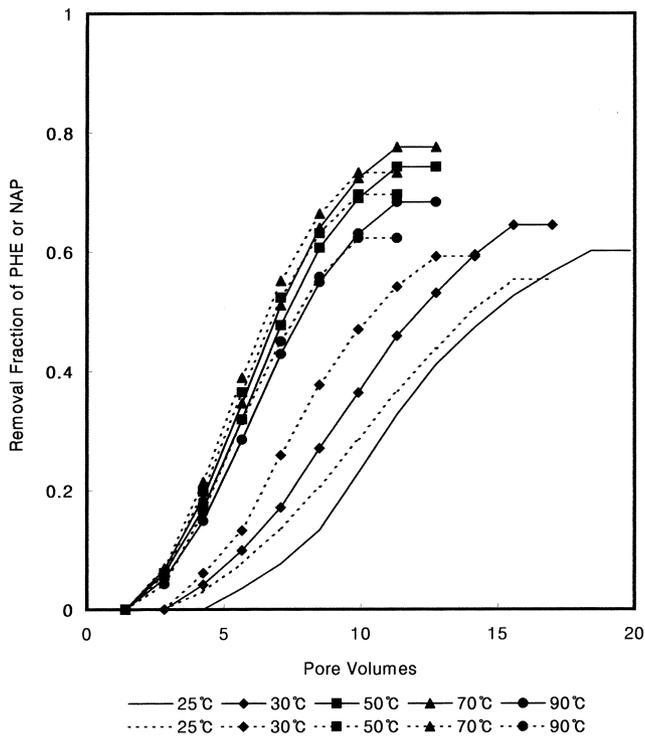


Fig. 8. Removal efficiencies with pore volumes of the surfactant fed at feed temperatures of 25°C to 90°C under the standard feed concentration and 1.8 cm/min of  $V_s$  for phenanthrene (solid lines) and for naphthalene (dotted lines).

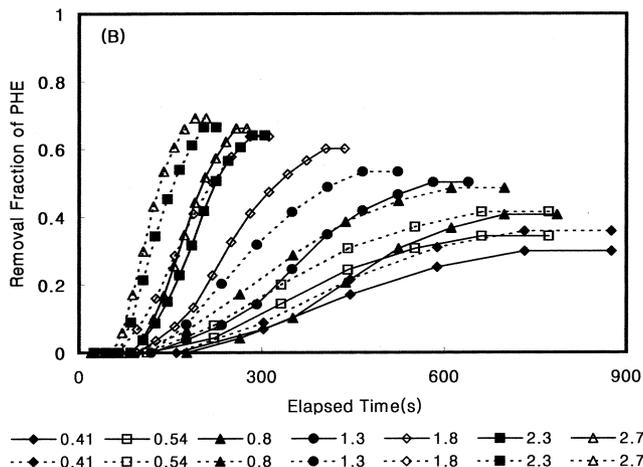
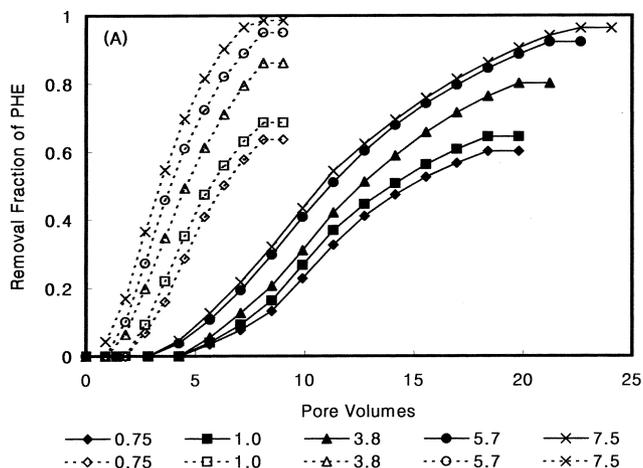


Fig. 9. Comparison of removal efficiencies of the two sands with varied  $\beta$ -CD concentrations (A) and with varied feeding rates (B). Solid lines stand for sea sand while dotted lines do for Ottawa sand. The unit for legend in the top figure is mM and that in the bottom is cm/min.

rosities were 0.29, 0.20 and 0.16) with higher porosity was reported to be decreased due to shorter contact time during flushing with surfactant SDS and Tween-80. It may be explained as follows: for sufficiently large void volume, the  $\beta$ -CD molecules with size of about 1.5 nm, migrate freely to contact the phenanthrene or naphthalene clumps and to form inclusion complexes. As shown in Fig. 4,  $\beta$ -CD, whether it is a free form or an inclusion complex, would not adsorb to the solid phase in a significant amount. Then it comes out under shear action. In summary, randomly embedded lipophilic compounds can be drawn out in a form of inclusion complex through relatively large vacant space provided by Ottawa sand's larger par-

Table 3. Performance comparison between local sea sand and Ottawa sand

	Local sand		Ottawa sand	
	Phenanthrene	Naphthalene	Phenanthrene	Naphthalene
Max. removal efficiency in final (%)	96.3	91.8	98.6	94.0
Total washing time (min)	8.8	7.1	5.2	4.7
Total pore volumes	24.1	20.0	9.0	8.1

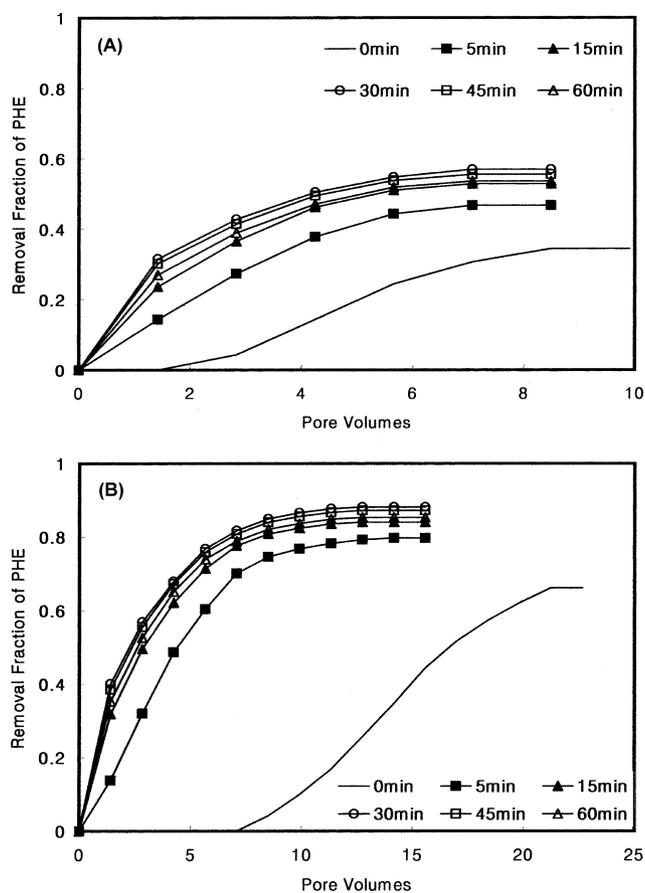


Fig. 10. Removal efficiencies with pore volumes of the surfactant fed at different delayed times before feeding with fresh CD solution at 0.54 cm/min of  $V_s$  (A) and at 2.7 cm/min of  $V_s$  (B) for phenanthrene and sea sand under standard experimental conditions.

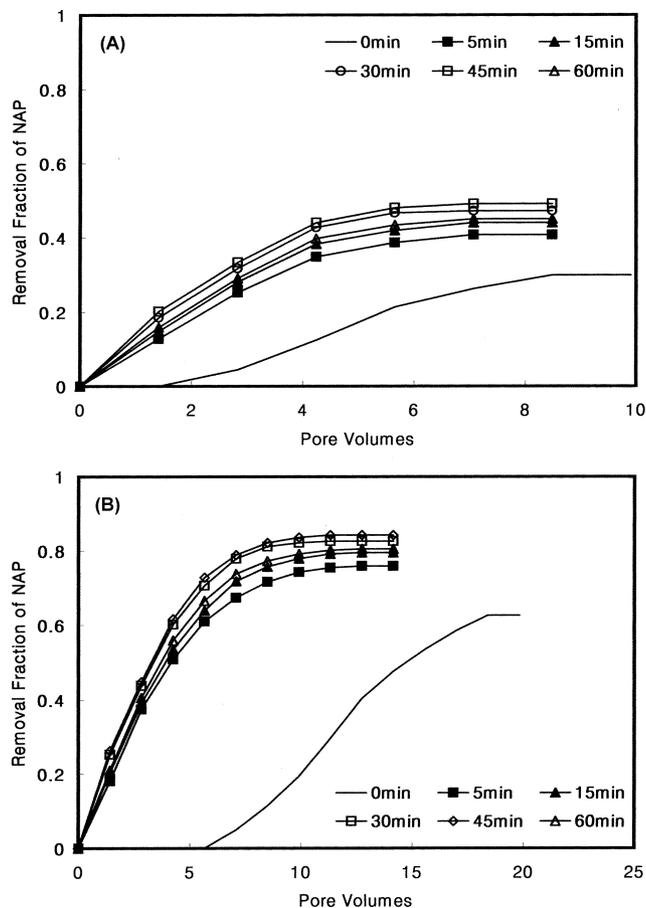


Fig. 11. Removal efficiencies with pore volumes of the surfactant fed at different delayed times before feeding with fresh CD solution at 0.54 cm/min of  $V_s$  (A) and at 2.7 cm/min of  $V_s$  (B) for naphthalene and sea sand under standard experimental conditions.

ticle packing without any obstacles - heavier contaminant load, finer sand packing, possible bypass phenomena, etc. - which could be found in the previous paper.

### 5. Effect of Reaction Time for Hydrophobic Complexation

During continuous flushing, a reaction for hydrophobic complexation should take time to form "washable complex." Complexation rate which was low initially compared to the surfactant feeding rate was predicted to produce relatively lower removal rate of the contaminant in a simple flushing model (not published yet). Tests were given to obtain the effect of reaction time (delay) for hydrophobic complexation (Fig. 10). The results showed that about thirty minutes of delay caused the highest removal fraction for phenanthrene regardless of the CD flow. The fact is that longer delay might cause re-adsorption of the complex to the soil surface under the dynamic conditions; meanwhile, shorter delay would not allow enough time for complexation. For naphthalene, that optimal time was found to be about 45 minutes (Fig. 11). Also, the removal rates (slope of the curves) with delays were greatly increased compared to that under normal washing conditions. Fig. 12 shows similar results for Ottawa sand, which implies that the hydrophobic complexation strongly depends on the reaction time, not either on porosity or sand type. Fig. 13 shows an example of economic washings which reuse the

initial CD solution. As expected, the already eluted contaminants were likely to be partially captured in the soil matrix with recycling. That gives much lower removal amount than that with fresh CD feeding. Nonetheless, the removal was greatly enhanced with some delayed reaction times as much as in the washings with fresh feeding. As a result, all these findings point out that the rate-limiting step for continuous CD washing could be complexation reaction, which is not observed in the equilibrium experiments such as Chan et al.'s [1976].

### CONCLUSION

Chemical soil flushing in a packed sandy soil matrix using a natural surfactant,  $\beta$ -cyclodextrin was investigated via a fluorescence spectroscopy and a dye labeling method. We found that initial sorption, which was speculated as a short term adsorption, onto the solid phase or sand void surfaces was the most crucial step at first and flow shear dominated in the later removal steps. It was also found that the removal efficiencies were proportional to flow rate, concentration, temperature of the flushing solution and voidity of the sand column. In addition, sorption of  $\beta$ -CD molecules onto the sand phase did not apparently affect the entire removal process under

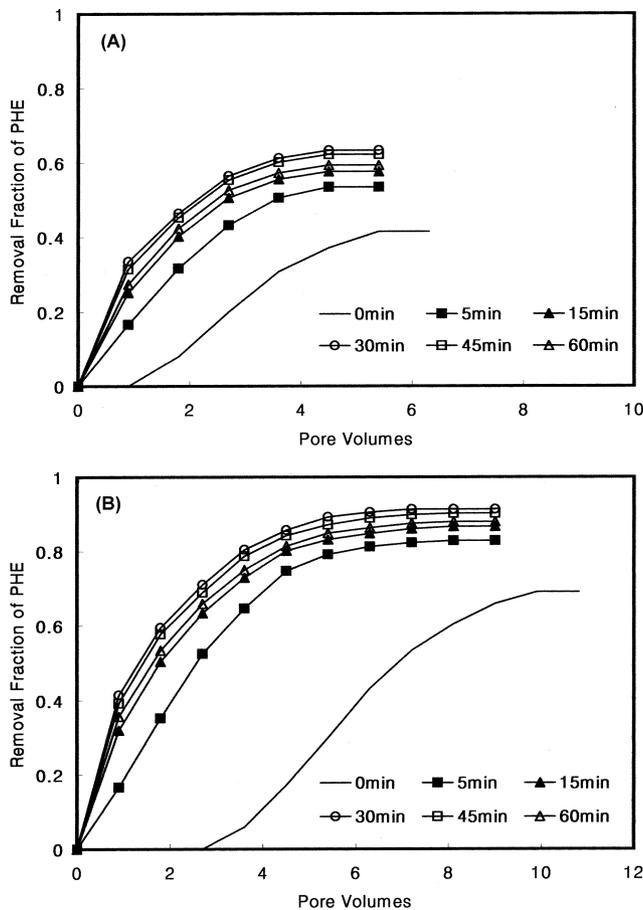


Fig. 12. Removal efficiencies with pore volumes of the surfactant fed at different delayed times before feeding with fresh CD solution at 0.54 cm/min of  $V_s$  (A) and at 2.7 cm/min of  $V_s$  (B) for phenanthrene and Ottawa sand under standard experimental conditions.

our experimental conditions. Time delay experiments indicated that the complexation reaction should be rate-limiting in the non-equilibrium washing scheme. These results could be used as a useful flushing strategy with cyclodextrins or some other biodegradable

surfactants if further optimization of operation parameters such as soil type and feeding schedule is achieved.

## ACKNOWLEDGMENT

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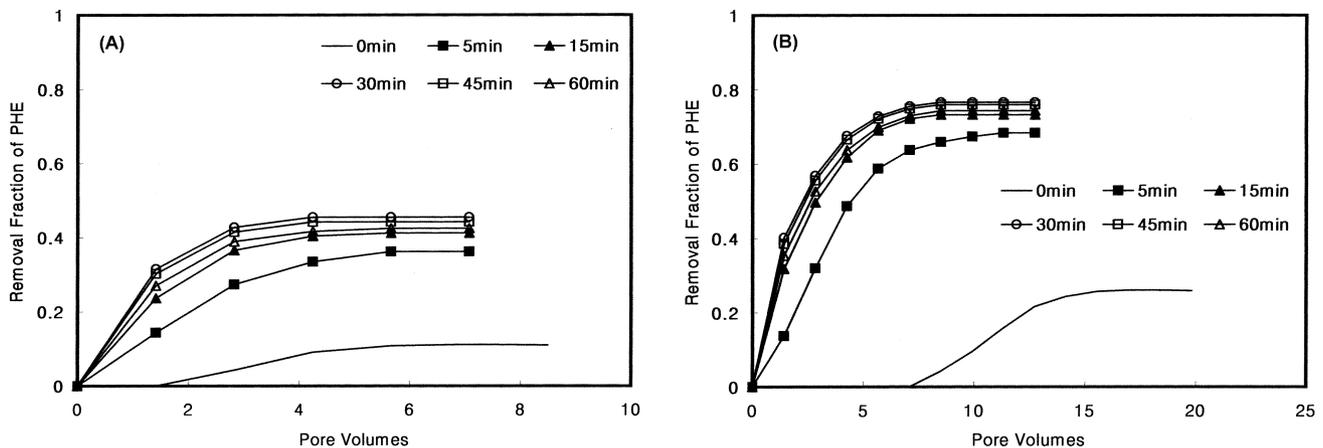


Fig. 13. Removal efficiencies with pore volumes of the surfactant fed at different delayed times before feeding with reused CD solution at 0.54 cm/min of  $V_s$  (A) and at 2.7 cm/min of  $V_s$  (B) for phenanthrene and sea sand under standard experimental conditions.

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