

## 사이클로덱스트린을 이용한 PAH오염토양의 화학적 세정

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### Chemical Washing of PAH-Contaminated Soil with Cyclodextrins as a Main Surfactant: A Labscale Study

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**요약** 본 연구는 천연계 계면활성제의 하나인 사이클로덱스트린을 이용한 화학적 토양세정을 다룬다. 두가지 polycyclic aromatic hydrocarbon인 phenanthrene과 naphthalene을 오염물질로 선정하고 토양종류 및 세정강도를 주변수로 하여 수직칼럼 상에서의 오염물질 제거효과를 분석, 고찰하였다. 실험실 규모의 연구결과, 오염원 제거효율은 세정액의 유량, 농도, 온도 및 토양칼럼의 공극률에 비례하는 것으로 나타났으며, 형광광도 분석과 methylene blue와 같은 염료 라벨링 분석을 통하여 초기 세정은 토양과 계면활성제의 흡착에 의존하고 세정이 거듭될수록 유체흐름에 의한 전단력이 주요변수임을 확인할 수 있었다. 본 데이터는 향후 pilot 규모의 현장세정시 기초자료로 활용가능하며, 세정전략(회분식, 연속식) 수립에 유용할 것으로 사료된다.

**Abstract** PAHs (polycyclic aromatic hydrocarbons) deposited in soil are one of serious problems against sustainable land use. In this paper, chemical soil flushing in a packed sandy soil matrix using a natural surfactant,  $\beta$ -cyclodextrin (CD) was studied via a fluorescence spectroscopy and a dye labelling. The contaminants are lipophilic ring compounds - phenanthrene and naphthalene. Sand type and flushing intensity (rate and concentration) are chosen as important 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 latter steps. The residual portion of the surfactant, which was most likely to be due to the initial sorption, would not be so influential on this type of soil washing for long times. These results will be useful in future for pilot scale *in situ* washing and for establishing better soil washing strategy.

**Key Words** : surfactant flushing, cyclodextrin, PAH, sandy soil

## 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), beneath the subsurface of the 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. Up 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 contami-

nants provided with some proper techniques for recovery of surfactants or solvents [1, 2]. For almost two decades, many of practical surfactant flushing - whether it is executed *in situ* or *ex situ* - have been attempted for removal of hazardous lipophilic compounds and for replacement of nonaqueous phase liquid (NAPL) within reasonable time frames [3-5]. Surfactant flushing, which is originated 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 [6, 7]. Mobilization of lipophilic compounds trapped within porous media

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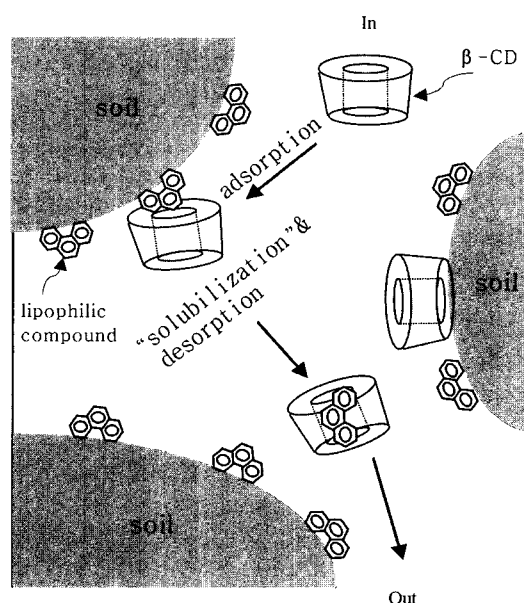
like soil is facilitated by a reduction in the interfacial tension between the two different phases near the solid interface [4, 8].

Most of flushing practices are based on cost-effective flushing agents and elaborate recovery system of the agents from the treating sites. Years ago, few researches on use of contamination free chemicals as flushing agents were reported [9, 10]. Cyclodextrins are some of those examples. They have been used for a long time as food additives, pharmaceutical agents, cosmetics, dyes and other agricultural applications like pesticide neutralizer [11]. Brusseau group [6, 10, 12, 13, 14] published a series of work 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. The work was limited only on pollutants, not surfactant behavior, and were measured to determine their removal efficiency. For enhanced solubilization and mobility, more hydrophilic  $\beta$ -cyclodextrins - HPCD (hydroxypropyl  $\beta$ -CD), CMCD (carboxymethyl  $\beta$ -CD), etc. - were used in their another work [6, 15]. In spite of cyclodextrin's favorable properties - non-toxicity, biodegradability, free CMC, stability, etc. - few successful field applications were made to date. It means that there was no strategic application based on solid lab-scale operation data including mechanistic analysis of the flushing action, parameter optimization, surfactant behavior during flushing. A simple schematic diagram of CD flushing is shown in Figure 1. With the idea of the figure, the objective of this work - 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- can be easily expressed.

## 2. MATERIALS AND METHOD

### 2.1 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



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

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 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). In order to remove organics that might be included in the sand, all sand was washed several times 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.

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

|                                 |   | local sand | Ottawa sand                   |
|---------------------------------|---|------------|-------------------------------|
| particle diameter (average, mm) |   | 0.29       | 0.55-0.85                     |
| voidity when packed             |   | 0.35       | 0.55                          |
| organic content (%)             |   | 0.45       | 0.14                          |
| compound                        | 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                      |

Table 1 shows the characteristics and properties of the materials used in the experiments [11].

Concentration of the two lipophilic compounds in solution was measured with a fluorescence spectroscopy (HITACHI Model F-4500). The wavelengths were measured as 250/360 nm (excitation/emission) for phenanthrene and 278/322 nm (excitation/emission) for naphthalene at 400 volts and 23°C [16]. The  $\beta$ -CD concentration was determined with a dye labeling; an inclusion complex formed by methyl red and  $\beta$ -CD, which develops coloring in UV absorbance. Methyl red was added to effluent solutions containing  $\beta$ -CD with ratio of 1 to 50 and absorbance of the mixture was measured at 200 nm in a UV/Visible spectroscopy (Analytikjena, SPECORD 40) [17, 18].

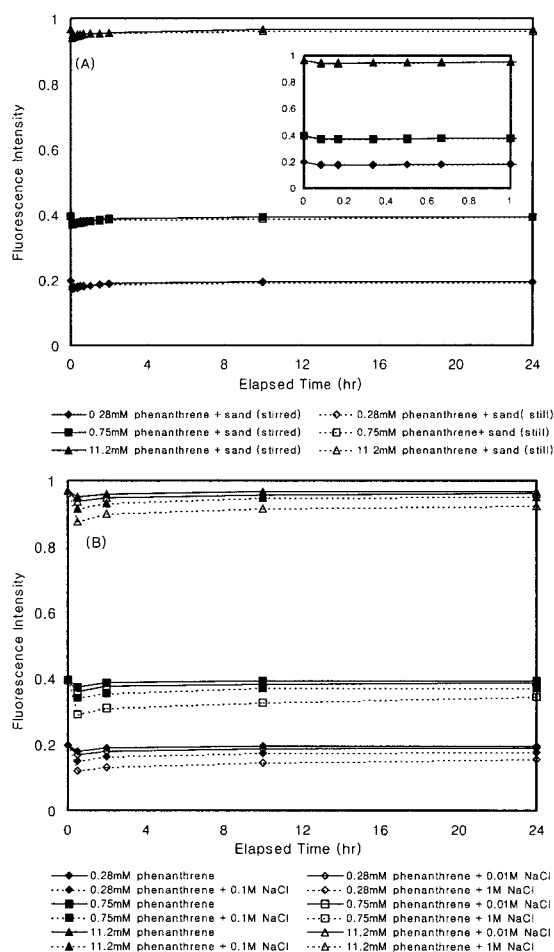
## 2.2 Method

### 2.2.1 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. The same concentration and volume was applied to naphthalene, too. The vial was then kept still and was sampled at every 6 or 8 hour to determine its fluorescence intensity. In another vial, three components were gently placed under static condition and then the equilibrium state of them was checked in the same interval as noted above. To see the ionic effect, the same procedure as above was repeated in equilibrium with added NaCl whose concentration ranged 0.01 to 1.0 M.

### 2.2.2 Continuous washing

A pyrex-glass column packed with sand (5.25 g) consisting of a lipophilic compound (0.076 mg/g-sand for phenanthrene or 0.057 mg/g-sand for naphthalene), 10 mm of diameter and 70 mm long, was flushed with  $\beta$ -CD solution 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 ( $V_s$ ). Concentrations of the surfactant solution ( $C_s$ ) ranged from 0.75 mM to 7.5 mM. Temperature (25-90°C) and concentration of NaCl were also tested as experimental variables.



**Figure 2.** Fluorescence intensity measured during phenanthrene-local 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. RESULTS AND DISCUSSION

### 3.1 Interaction among soil, lipophilic compound and $\beta$ -CD

Figure 2 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) was released back to the bulk phase in hours as found in Carroll's and Chan et al's work [19, 20]. 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 (Figure 2B). Addition of salts caused stronger initial sorption and higher reduction of phenanthrene in bulk phase as expected. This may be due to the decrease of the solubility of phenanthrene in the  $\beta$ -CD phase that facilitates its attraction to the sand particles and retards its desorption (a kind of "salting out" due to lowering of cloud point) [21].

### 3.2 $\beta$ -CD sorption vs phenanthrene or naphthalene elution

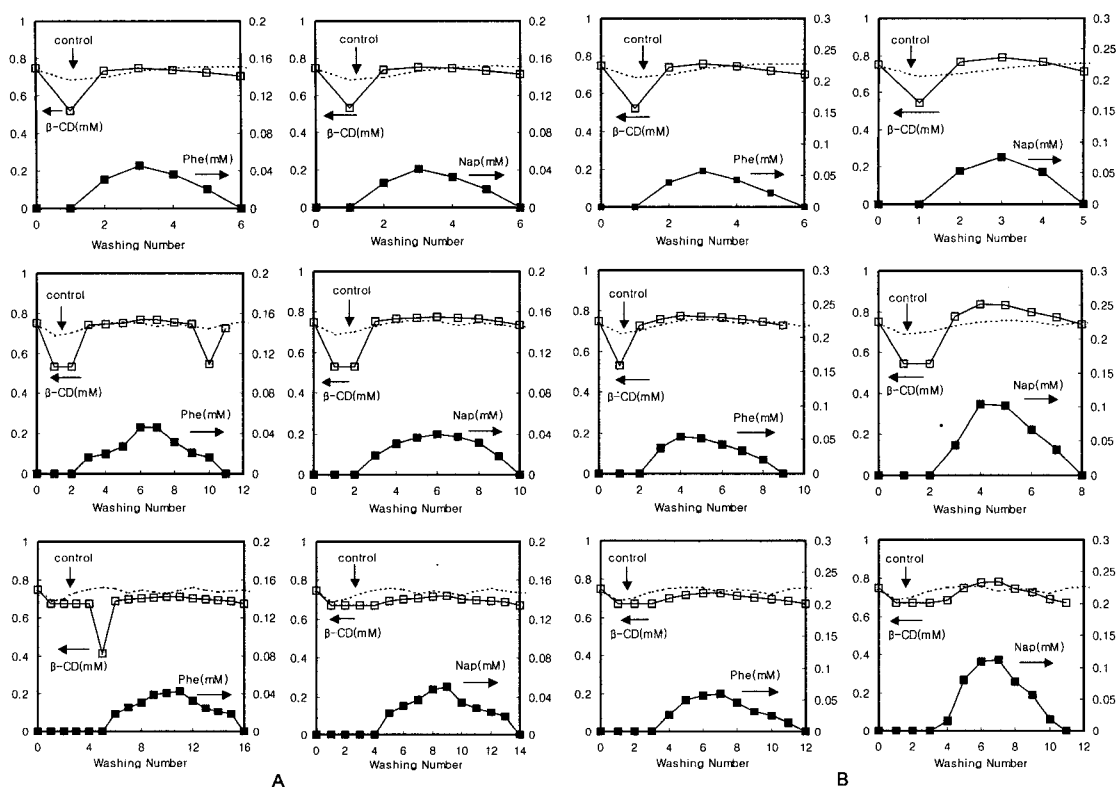
Like sorption of phenanthrene to the sand in very early times (Figure 2),  $\beta$ -CD was also found to be sorbed at the very early washing as shown in Figure 4 (see the initial deep valleys). It is very interesting that phenanthrene or naphthalene starts to elute out of the sand column right after the  $\beta$ -CD sorption. In other words, we can speculate that immediate 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 the 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 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 solubilization 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 solubilization as reported by Pennell et al. [22]. That is, the early reduction in  $\beta$ -CD concentration was shortly followed 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. Also, 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 trivial amount of  $\beta$ -CD is most likely to be adsorbed onto the locally phenanthrene-poor part of solid phase or to be trapped in ganglia-like void space in the soil matrix.

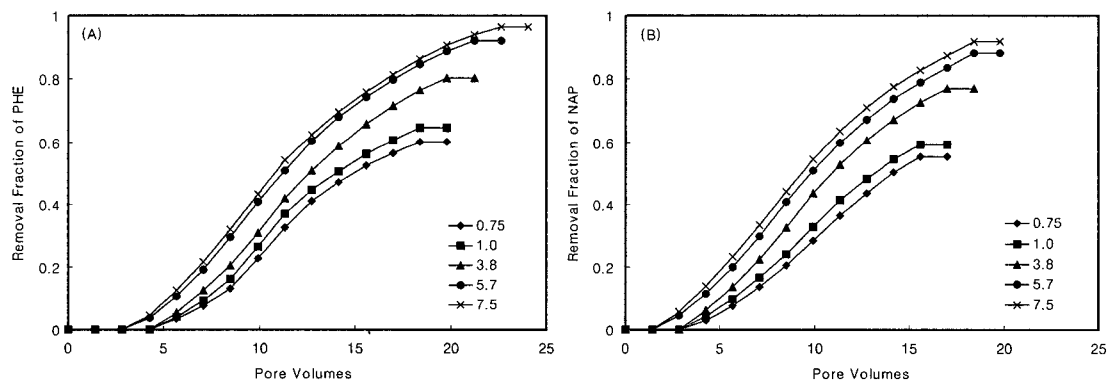
**Table 2.**  $\beta$ -CD concentration [mM]\* in effluent at maximum adsorption to the soil matrix (reduction percentage [%] in parenthesis)

|                   |      | local sand   |             | Ottawa sand  |             |
|-------------------|------|--------------|-------------|--------------|-------------|
|                   |      | phenanthrene | naphthalene | phenanthrene | naphthalene |
| $V_s$<br>(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)   |
| $C_s$<br>(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 -CD concentration : 0.75 mM



**Figure 3.** Variation of  $\beta$ -CD and phenanthrene or naphthalene in the effluents during flushing : top six figures (A) for local sand and bottom 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.



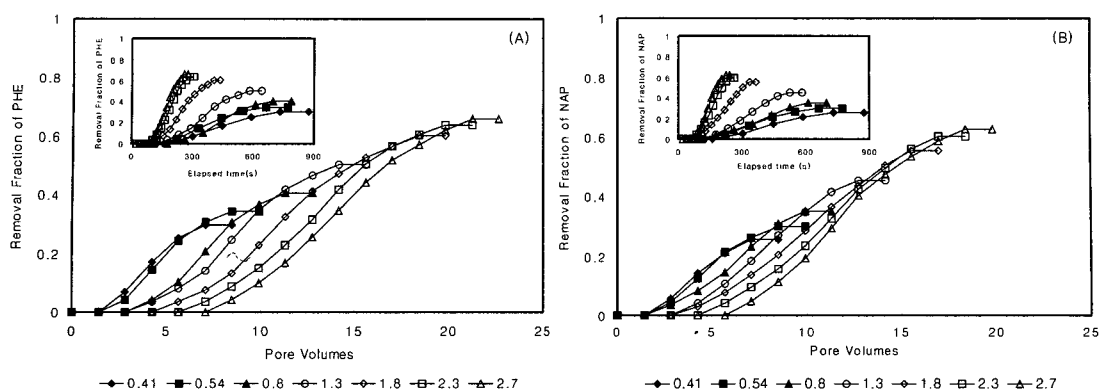
**Figure 4.** Removal efficiencies with pore volumes of the surfactant fed at its different concentrations under fixed flow rate,  $V_s=1.8$  cm/min for phenanthrene (A) and for naphthalene (B). The unit for the legends is mM.

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 as same as the case with the contaminants except for more damped amplitude of the curve

(refer the to dotted lines in Figure 3).

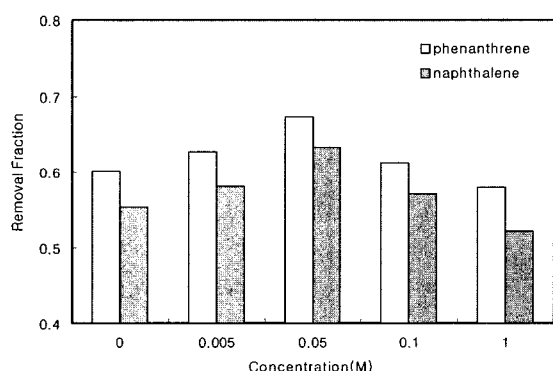
### 3.3 Effect of CD concentration, superficial velocity, salt concentration, and temperature

The CD concentration increased by 10 times almost doubled withdrawal of the contaminants (see



**Figure 5.** 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.

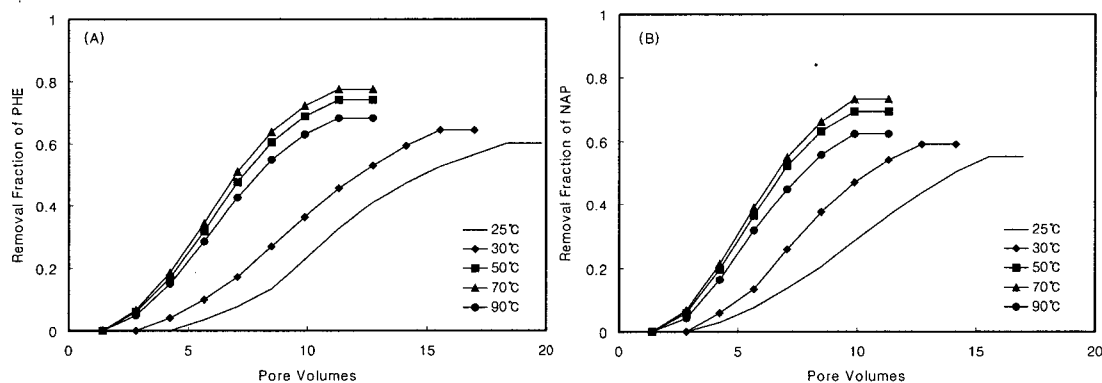
Figure 4). The number of CD molecules equivalent to 7.5 mM concentration is about 10 times of the number of molecules of residual phenanthrene or



**Figure 6.** Comparison of removal efficiencies of the two compounds at different NaCl concentrations under the standard feed concentration and 1.8 cm/min of  $V_s$ .

naphthalene. Based on thorough outcome of phenanthrene-including  $\beta$ -CD, 3.3 molecules of  $\beta$ -CD should collect 1 molecule of phenanthrene in each washing. 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.

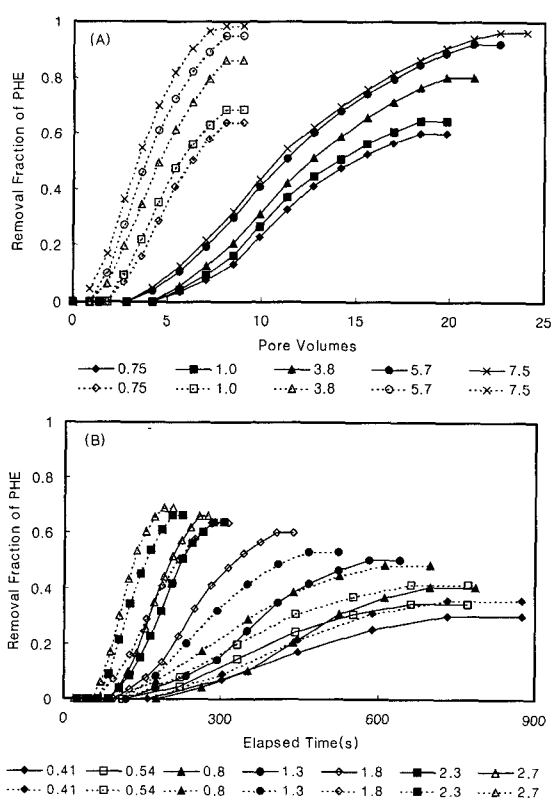
On the other hand, Figure 5 indicates that the lower is the feed flow rate during the earlier stages of washes, the faster the removal develops. Reversely, the higher flow rate guarantees the higher removal efficiency in final at cost of more pore volumes. This observation tells us that solubilization 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,



**Figure 7.** 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 (A) and for naphthalene (B).

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

|                                 |       | local sand   |             | Ottawa sand  |             |
|---------------------------------|-------|--------------|-------------|--------------|-------------|
|                                 |       | phenanthrene | naphthalene | phenanthrene | naphthalene |
| removal efficiency in final (%) | $V_s$ | 66.1         | 62.7        | 69.1         | 65.1        |
|                                 | $C_s$ | 96.3         | 91.8        | 98.6         | 94.0        |
| total washing time (min)        | $V_s$ | 14.6         | 14.6        | 14.6         | 12.2        |
|                                 | $C_s$ | 8.8          | 7.1         | 5.2          | 4.7         |
| total pore volumes              | $V_s$ | 22.6         | 19.8        | 10.8         | 9.9         |
|                                 | $C_s$ | 24.1         | 20.0        | 9.0          | 8.1         |



**Figure 8.** Comparison of removal efficiencies of the two sands with varied  $\beta$ -CD concentrations (A) and with varied feeding rates (B). Solid lines stand for local 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.

it is quite obvious for efficient washing to be accompanied by strong shear that high flow rate generates.

Figures 6 and 7 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. This

is because too strong ion concentration reduces the solubility of  $\beta$ -CD in liquid phase to lower the activity of the surfactant. Similarly, CD solution becomes more activated for washing with 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.

### 3.4 Type of soil

Comparison between the local sand and Ottawa sand was summarized in Table 3. Flushing through Ottawa sand with the higher voidity and larger particle size resulted much higher removal rate as shown in Figure 8. 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 [23]; i.e. contaminant removal rate in soil columns (porosities 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. We now reason it in this way: for sufficiently large void volume, the beta - CD molecules (size of about 1.5 nm) migrate freely to contact the phenanthrene or naphthalene clumps and can form inclusion complexes. As shown in Figure 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, scarcely embedded lipophilic compounds can be drawn out in a form of inclusion

complex through relatively large vacant space provided by Ottawa sand's larger particle packing without any obstacles - heavier contaminant load, finer sand packing, possible bypass phenomena, etc. - which could be found in the previous paper.

#### 4. CONCLUSION

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 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. Also, sorption of  $\beta$ -CD molecules onto the sand phase did not apparently affect the entire removal process under our experimental conditions. The 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, feeding schedule, etc. is achieved.

#### REFERENCES

- [1] J. C. Fountain, R. C. Starr, T. Middleton, M. Beikirch, C. Taylor, and D. Hodge, *Ground Water*, 34(5), 910 (1996).
- [2] P. S. C. Rao, M. D. Annable, R. K. Sillan, D. Dai, K. H. Hatfield, W. D. Graham, A. L. Wood, and C. G. Enfield, *Water Resour. Res.*, 33(12), 2673 (1997).
- [3] K. D. Pennell, M. Jin, L. M. Abriola, and G. A. Pope, *J. Contam. Hydrol.*, 16(1), 35 (1994).
- [4] P. T. Imhoff, S. N. Gleyzer, J. F. McBride, L. A. Vancho, I. Okuda, and C. T. Miller, *Environ. Sci. Technol.*, 29(8), 1966 (1995).
- [5] C. C. West and J. F. Harwell, *Environ. Sci. Technol.*, 26(12), 2324 (1992).
- [6] S. -O. Ko, M. A. Schlautman, and E. R. Carraway, *Environ. Sci. Technol.*, 33(16), 2765 (1999).
- [7] S. E. Friberg and M. Mortensen, *Sep. Sci. Technol.*, 20(4), 285 (1985).
- [8] A. S. Abdul, T. L. Gibson, C. C. Ang, J. C. Smith, and R. E. Sobczynski, *Ground Water*, 30(2), 219 (1992).
- [9] B. J. Ahiau, D. A. Sabatini, J. H. Harwell, and D. Q. Vu, *Environ. Sci. Technol.*, 30(1), 91 (1996).
- [10] X. Wang and M. L. Brusseau, *Environ. Sci. Technol.*, 27, 2821 (1993).
- [11] J. Szejtli, *Cyclodextrin Technology*, Kluwer Academic Publishers, Netherland (1988).
- [12] J. E. McCray and M. L. Brusseau, *Environ. Sci. Technol.*, 33(1), 89 (1999).
- [13] X. Wang and M. L. Brusseau, *Environ. Sci. Technol.*, 29, 2346 (1995).
- [14] M. L. Brusseau, X. Wang, and Q. Hu, *Environ. Sci. Technol.*, 28, 952 (1994).
- [15] X. Wang and M. L. Brusseau, *Environ. Sci. Technol.*, 29, 2632 (1995).
- [16] S. -O. Ko, *J. Korean Soc. Env. Eng.*, 21(8), 1537 (1999).
- [17] J. K. Hong and K. H. Youm, *Membrane Journal*, 8(3), 170 (1998).
- [18] A. Lejeune, K. Sakaguchi and T. Imanaka, *Anal. Biochem.*, 181, 6 (1989).
- [19] B. J. Carroll, *J. Colloid Interface Sci.*, 79(1), 126 (1981).
- [20] A. F. Chan, D. F. Evans, and E. L. Cussler, *AIChE J.*, 22, 1006 (1976).
- [21] D. F. Evans and H. Wennerstrom, *The Colloidal Domain*, VCH publishers, Inc. NY 1994.
- [22] K. D. Pennell, L. M. Abriola, and W. J. Jr. Weber, *Environ. Sci. Technol.*, 27(12), 2332 (1993).
- [23] D. Cho and H.-S. Kim, *Korean J. Chem. Eng.*, 19(5), 783-790 (2002).