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Comparison of amphiphilic polyurethane nanoparticles to nonionic surfactants for flushing phenanthrene from soil

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Abstract

Amphiphilic polyurethane (APU) nanoparticles were synthesized through crosslinking polymerization of nano-aggregates of urethane acrylate nonionomer (UAN). The efficiency of in situ extraction of sorbed phenanthrene from aquifer material was tested using soil columns and compared with that of surfactants such as Triton X-100, Brij 30, and Tween 80. The extraction efficiency of those washing materials strongly depended on their concentration, flow rate, and the degree of sorption within soil column. That is, the extraction efficiency increased with the decrease of flow rate and the degree of sorption and the increase of the concentration. Even though the surfactants are superior to APU nanoparticles at solubilizing phenanthrene, at the same flow rate (0.02 mL/min) and concentration (4000 mg/L), the effectiveness of in situ soil washing of APU nanoparticles was about two times higher than those of surfactants. This is because, at the lower flow rates, the degree of sorption of APU nanoparticles was lower than that of surfactants, owing to the chemically crosslinked nature of APU nanoparticles.
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Keywords: Amphiphilic polymer; Nanoparticles; Desorption; Sorption; Phenanthrene; Surfactant flushing

1. Introduction

Contamination of soil and groundwater by hydrophobic organic carbons (HOCs) is caused by leakage from storage tanks, spillage, or improper disposal of wastes. Once in the soil matrix, HOCs are a source of dissolved contaminants [1–5]. Among HOCs, polyaromatic hydrocarbons (PAHs) are of special interest because they are strongly sorbed to soil or sediment. Consequently, sorbed PAHs may act as a long-term source of groundwater contamination. Many researchers have been using surfactants to enhance desorption of sorbed PAHs from soil through solubilization of sorbed PAHs in surfactant micelles [6–13]. However, surfactant-enhanced remediation techniques have some disadvantages, because of micelle breakage and loss of surfactant through sorption to soil. Therefore, surfactant-enhanced desorption and washing

is effective only when the surfactant dose is much greater than its critical micelle concentration (CMC) [8–11,14–16]. As a result, recent research has been directed towards the design of a surfactant that minimizes such losses and to the development of surfactant recovery and recycling techniques.

Amphiphilic polymers, which have hydrophilic and hydrophobic moieties on the same carbon backbone, have been widely used in various fields. In fact, parallels can be drawn between typical surfactants and amphiphilic polymers, and both materials have been used as emulsifiers, dispersants, foamers, thickeners, rinse aids, and compatibilizers [17–20]. The CMC of amphiphilic polymers is extremely low and their dispersion efficiency is retained even at extremely high dilution, and so amphiphilic polymers can be used as an alternative for the removal of absorbed hydrophobic pollutants from the soil. There are several types of amphiphilic polymers, such as nonionic, anionic, or cationic homopolymers, random copolymers, and diblock-copolymers. It has been generally recognized that amphiphilic block or graft copolymers

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are very effective and versatile but, because these polymers are very expensive and can be obtained only by extremely difficult synthetic processes, their practical applications are limited.

In our preceding paper, we suggested a new process for the enhanced desorption of sorbed phenanthrene, which uses amphiphilic polyurethane (APU) nanoparticles that had been synthesized via soap-free emulsion polymerization of amphiphilic urethane acrylate nonionomer chains (UAN) [21]. We also have used these UAN chains for the synthesis of magnetic nanoparticles and silver nanoparticles dispersed in polymer films [22,23]. Unlike surfactant molecules that completely dissolve in water below its CMC, UAN chains can not be dissolved in water but are just dispersed in water to form nano-aggregates (APU nanoparticles) even at extremely low concentrations, because whole UAN chains are insoluble in water.

As illustrated at Fig. 1, UAN chains have hydrophobic polypropylene oxide (PPO)-based segment and hydrophilic polyethylene oxide (PEO) segment at the same chain. Water is a good solvent for PEO segments in UAN chains but is not a solvent for PPO chains. On contacting water, water-soluble PEO segments in UAN chains are microphase separated from hydrophobic segment and oriented toward water phase to form outer layer. Hydrophobic PPO-based segments are associated with each other to form hydrophobic interior, leading to form micelle-like nano-sized aggregates of UAN chain that is APU nanoparticles as schematically represented at Fig. 1. These nanoparticles are stabilized by PEO chains located on their outer layer like the micelles of nonionic surfactants. Finally, this aggregate structure of APU nanoparticles is permanently locked-in by chemical crosslinking reaction. Even though the solubilizing performance and interfacial activity of APU nanoparticles were inferior to those of the nonionic surfactant, Triton X-100, in the low concentration region, APU nanoparticles could effectively reduce phenanthrene sorption on the aquifer material.
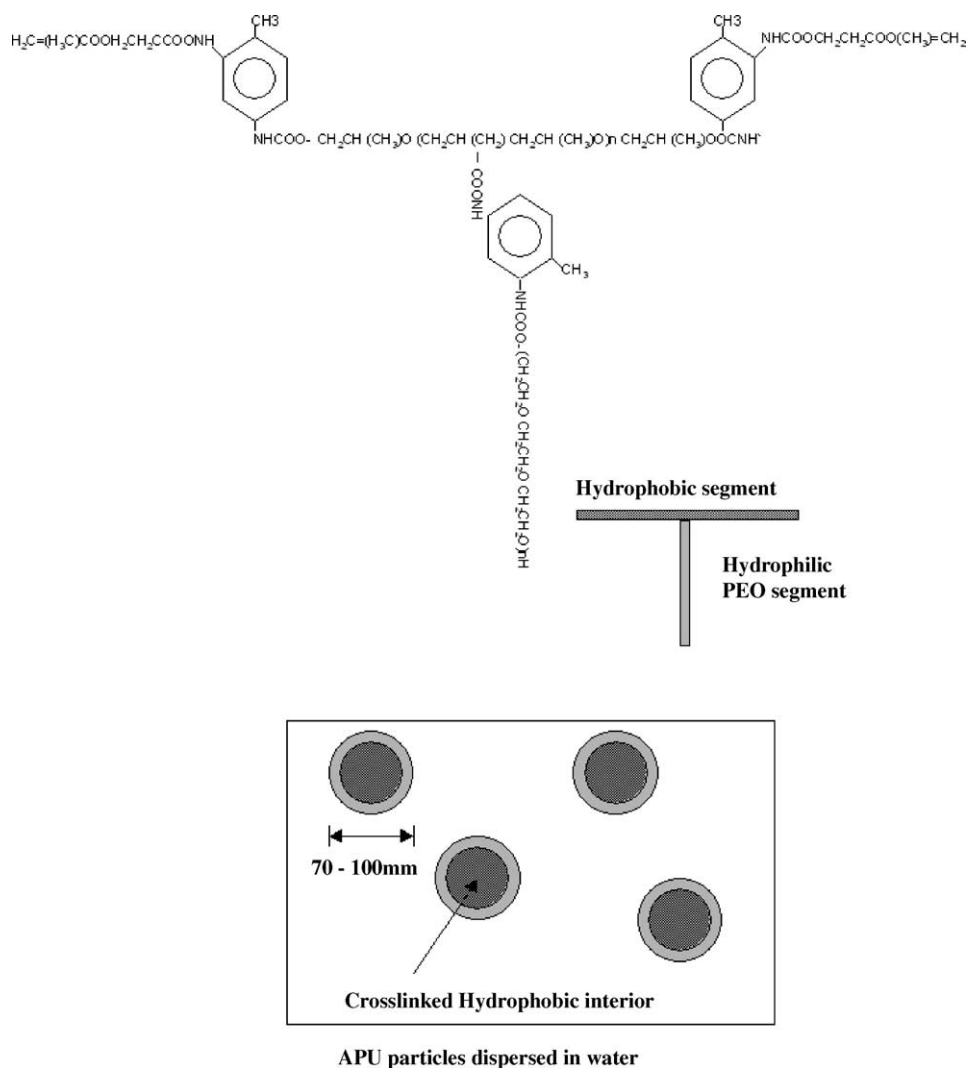

Fig. 1. Schematic presentation of UAN chains and APU nanoparticles.

In this present study, soil column experiments were used to evaluate the extraction efficiency of APU nanoparticles for sorbed phenanthrene and to investigate the potential utility of our system as an in situ extraction process for sorbed PAHs. We first examined the extraction performance of APU nanoparticles relative to the nonionic surfactant, Triton X-100, in a soil column containing aquifer sand contaminated with phenanthrene. The APU nanoparticles were used at various concentrations and flow rates. The soil-washing performance of APU nanoparticles was also compared with those of other nonionic surfactants, such as Brij 30 and Tween 80.

2. Experimental

2.1. Materials

Phenanthrene was used as a model polyaromatic hydrocarbon (PAH). Its aqueous solubility is reported to be 1.29 mg/L and its octanol-water partition coefficient is 3700 [24]. Radiolabeled phenanthrene was purchased from Sigma Chemical Co. (9-^{14}C, 13.1 μCi/μmol). The aquifer sand used in all experiments was obtained from a quarry in Newfield, NY, USA. The organic content of the sand was reported to be $0.049 \pm 0.012\%$ [24]. A size analysis of the sand has been previously reported; 47.2 and 47.6% of the particles were in the fine (0.1–0.25 mm) and medium (0.25–0.5 mm) size ranges, respectively. The remaining constituents included very fine sand (0.05–0.1 mm) at 3.7%, coarse sand (>0.5 mm) at 0.2%, and silt and clay at 1.2%.

In the synthesis of amphiphilic urethane acrylate nonionomer (UAN) precursor chains, poly (propylene oxide) triol) (PPO triol, $M_w = 1000$, Korea Polyol, Korea), 2,4-toluene diisocyanate (TDI, Aldrich Chemical Co., USA), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co., USA), and polyethylene glycol (PEG, $M_w = 600$ and 1500, Aldrich Chemicals Co., USA) were used as received. Potassium persulfate (KPS, Wako Pure Chemicals Co., Japan) was re-crystallized from distilled deionized (DDI, 12.8 MΩ/cm) water.

Three nonionic surfactants, Triton X-100 (polyoxyethylene (10) octylphenol, $M_w = 646$), Tween 80 (polyoxyethylene (20) sorbitan monooleate, $M_w = 1309$), and Brij 30 (polyoxyethylene (4) lauryl ether, $M_w = 363$) were purchased from Aldrich Chemicals Co., USA, and were used as received.

2.2. Synthesis of amphiphilic urethane acrylate nonionomer (UAN) and amphiphilic polyurethane (APU) nanoparticles

The synthesis of a UAN chain, schematically illustrated in Fig. 1, was a three-step process. Each reaction was carried out in a 500 mL four-neck vessel with stirrer, thermometer, and an inlet system for nitrogen gas. The detailed synthetic procedure was described in our previous papers [21–23]. The polystyrene equivalent molecular weight of synthesized UAN chains is a 6700 weight average molecular weight with a polydispersity of 1.93.

To prepare amphiphilic polyurethane (APU) nanoparticles dispersed in water, UAN chains were first mixed with distilled deionized water with vigorous stirring. The UAN emulsions prepared as above were then cross-linked via polymerization in the presence of potassium persulfate (KPS) to form APU nanoparticles dispersed in water. Initiator radicals first formed in the aqueous phase penetrate into the oil phase to initiate the cross-linking reaction between the vinyl end-groups of the precursor UAN chains. The size of the prepared APU nanoparticles was measured by dynamic light scattering The size of the prepared APU nanoparticles was measured by dynamic light scattering and particle sizes were in the range of 32.10 nm.

2.3. Soil column procedures (Protocol I)

The in situ extraction efficiency of washing materials and their flow behavior within a soil matrix have been generally evaluated using soil column experiments. We used an all-glass column (15 mm i.d. and 30 cm long) for the column experiments. Aquifer sand (10 g) was gently mixed with 20 g of DDI water for 2 h in a rotary tumbler. The glass column was then packed with the wet aquifer sand. To investigate the flow behavior of APU nanoparticles and Triton X-100 solutions in the soil column, two concentrations of APU nanoparticles and Triton X-100 solutions were applied to the soil-packed column. The feed solutions were directed downwards at different flow rates using a peristaltic pump (Manostat pump (Simon), Illinois, USA). Flow rates were determined volumetrically and were 0.12 and 0.02 mL/min, resulting in a pore water velocity of 4.45 and 0.73 cm/h, respectively. The column was thermostated as 25 °C using a water jacket connected to a water bath. The initial concentrations of APU nanoparticles and Triton X-100 in the aqueous phase (C_o) were measured prior to feeding onto the soil column. The concentrations, C of APU nanoparticles (219 nm) and Triton X-100 (275.5 nm) in aqueous phase of eluted sample was determined using UV–vis spectrophotometer (Shimadzu 3210).

To prepare contaminated soil, 10 mL of ^{14}C-PAH aqueous solution was mixed with 10 g of aquifer sand for 24 h in a rotary tumbler. The glass column was then packed with the wet contaminated soil. The amount of ^{14}C-PAH in the column was calculated from a material balance on the original phenanthrene used in the sand mixture and the small amount that eluted out of the column during its preparation, which was based on procedure described in previous reports [8,11–13]. The initial concentration of sorbed phenanthrene in the soil column was approximately 756 mg/Kg. All connecting tubes, fittings, and stopcocks were made of Teflon to prevent adsorption of PAH. A peristaltic pump was used to pump three different surfactant aqueous solutions or APU solutions through the column that was thermostated as 25 °C using a water jacket connected to a water bath. A 1 mL sample was transferred into scintillation vials (Poly-Q vial P/N 566740, Beckman Coul-

ter, USA) containing 10 mL of Ecolume cocktail (Ready Safe P/N 141349, Beckman Coulter, USA) and the concentrations of ^{14}C-phenanthrene in the aqueous phase were measured using a liquid scintillation counter (LSC, Beckmann LS6800). At least four replicate experiments were performed for each test.

2.4. Batch experiment: desorption of sorbed phenanthrene in the presence of APU or surfactant solutions (Protocol II)

An aqueous solution of ^{14}C-PAH (1 mL) was added to a scintillation glass vial containing 1 g of aquifer sand and agitated on a rotary tumbler for 2 days. After the completion of mixing, 9 mL of APU or surfactant solutions of various concentrations was added into the vials, which were then re-agitated on a rotary tumbler for a further 2 days. They were then centrifuged ($15,000 \times g$) to separate the soil from the aqueous solution. An aliquot (1 mL) of the supernatant was withdrawn and transferred into scintillation vials containing 10 mL of Ecolume cocktail. The concentration of ^{14}C-PAH in the aqueous phase was measured using a Liquid Scintillation Counter.

3. Results and discussion

3.1. In situ extraction efficiency and flow behavior of Triton X-100 and APU nanoparticles within a soil column

Fig. 2 shows the fraction of phenanthrene remaining in the contaminated soil column versus the number of pore volumes of APU and Triton X-100 solutions eluted from the column. The flow rate of APU and Triton X-100 solution in the column
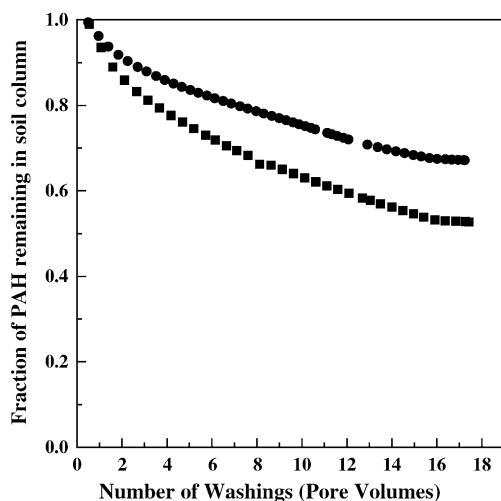

Fig. 2. Extraction of sorbed phenanthrene (PAH) from a soil column using APU nanoparticles and Triton X-100 solutions at the higher flow rate (0.12 mL/min): (■) Triton X-100, (●) APU nanoparticles.
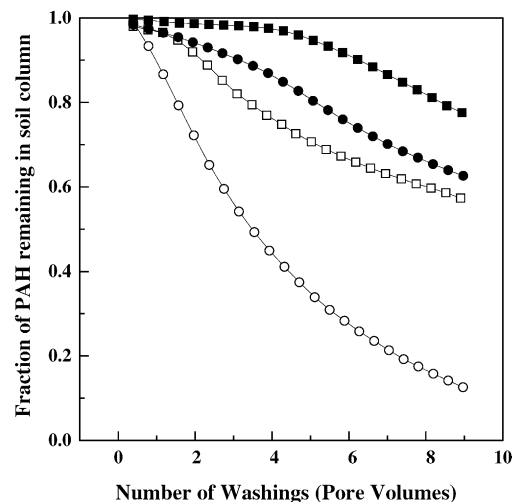

Fig. 3. Extraction of sorbed phenanthrene (PAH) from a soil column using APU nanoparticle and Triton X-100 solutions at a lower flow rate (0.02 mL/min) using two different concentrations: (■) Triton X-100 (100 mg/L), (●) APU nanoparticles (100 mg/L), (□) Triton X-100 (4000 mg/L), and (○) APU nanoparticles (4000 mg/L).

was regulated as 0.12 mL/min (4.45 cm/h pore water velocity) using a peristaltic pump. One pore volume means the total volume of pores in the soil-packed column. In our system, a soil column prepared using 10 g of aquifer sand has 4.27 mL of pore volume. According to the batch experiment results of our previous report [21], Triton X-100 at a concentration less than 2000 mg/L does not extract sorbed phenanthrene from the aquifer soil. Therefore, the concentration of APU and Triton X-100 solutions was fixed at 4000 mg/L. After 18 pore volumes of washing with APU or Triton X-100 solution, 32.6 and 46.9% of the phenanthrene was removed from the soil column, respectively. This result indicates that the in situ extraction efficiency of Triton X-100 is better than that of APU nanoparticles at this concentration and flow rate.

The extraction performances of APU nanoparticles and Triton X-100 solutions were also examined at a lower flow rate (0.02 mL/min), and the results are represented in Fig. 3. More sorbed phenanthrene was washed out by the same number of washings, compared with the experiment at the higher flow rate. This indicates that APU nanoparticles and Triton X-100 solutions can extract sorbed phenanthrene more effectively at a lower flow rate. This result can be explained by the longer contact time of the washing materials (APU nanoparticles and Triton X-100) with the soil.

In contrast to the results in Fig. 2, APU nanoparticles showed better in situ extraction efficiency than did Triton X-100 at the same concentration. At a concentration of 100 mg/L, APU nanoparticles and Triton X-100 extracted 38 and 23%, respectively, of sorbed phenanthrene after nine pore volumes of washing. At 4000 mg/L, APU nanoparticles could wash out 88% of sorbed phenanthrene from soil column, whereas Triton X-100 could extract only 43% of sorbed phenanthrene after nine pore volumes of washing. The superior extraction performance of APU nanoparticles over

Triton X-100 at a low flow rate could be due to the lower degree of sorption of APU nanoparticles onto the aquifer sand.

According to our previous results, the performance of APU in solubilizing phenanthrene is much less than that of Triton X-100 [21]. That is, at the same concentration (2000 mg/L), Triton X-100 and APU nanoparticles can solubilize approximately 50 times and 3.7–4.8 times, respectively, the phenanthrene that an equal amount of pure water could solubilize. However, in batch extraction experiments, the extraction performance of APU nanoparticles was better than that of Triton X-100 at low concentration, which was less or a little greater than the CMC of Triton X-100. This result was due to the lower degree of sorption of APU nanoparticles on the aquifer materials. At lower flow rates, the better in situ extraction performance of APU nanoparticles may be also explained in terms of the lower degree of sorption of APU nanoparticles within the soil column.

The relative concentration of Triton X-100 and APU nanoparticles solutions (with $C_o = 4000$ mg/L) flowing through the soil column is illustrated in Figs. 4 and 5. C_o is the initial concentration of Triton X-100 or APU nanoparticles in the elutant. C is the concentration of Triton X-100 or APU nanoparticles of a sample eluted from the soil column. After adding 2.5 pore volumes (10.67 mL) of APU and Triton X-100 solution to the soil-packed column, rinse water was added to the column to recover APU nanoparticles and Triton X-100 from the soil column. As shown in Fig. 4, at a high flow rate (0.12 mL/min), Triton X-100 and APU nanoparticles exhibited almost identical breakthrough curves. That is, APU and Triton X-100 solution exhibited almost the same relative concentration (C/C_o), indicating that APU and Triton X-100 have almost the same degree of sorption within the soil column under the given conditions. However, as shown in Fig. 5 for a low flow rate (0.02 mL/min), the two solu-

Fig. 5. Elution of Triton X-100 and APU nanoparticles from a soil column at a lower flow rate (0.02 mL/min): (■) Triton X-100 (4000 mg/L), (●) APU nanoparticles (4000 mg/L).

tions exhibited different breakthrough curves. The relative concentration, C/C_o of Triton X-100 is lower than that of APU nanoparticles. This indicates that the degree of sorption of APU nanoparticle onto the soil column is lower that that of Triton X-100.

In Figs. 6 and 7, the mass recovery of the APU particles and Triton X-100 from the soil column is plotted as a function of the volume of the aqueous solution added to the soil column. Here, M_T represents the total mass of APU nanoparticles or Triton X-100 added to the column and M is the accumulated mass of APU nanoparticles or Triton X-100 eluted from the column. At a high flow rate (Fig. 6), over 98% of Triton X-100 and APU nanoparticles was recovered with the almost same amount of rinse water. At a low flow rate (Fig. 7), over 98% of APU nanoparticles was recovered after 12.81 mL of rinse water, but only 96% of Triton X-100 could be recov-
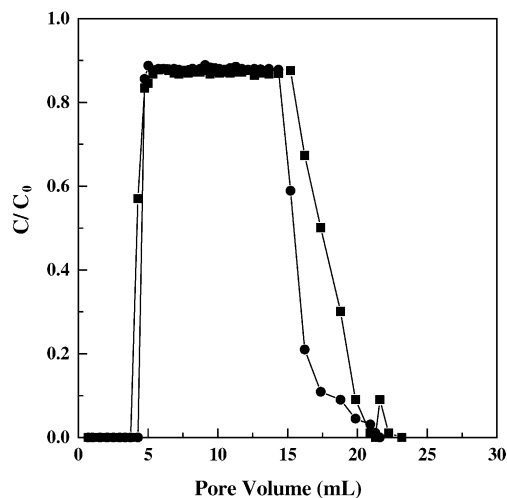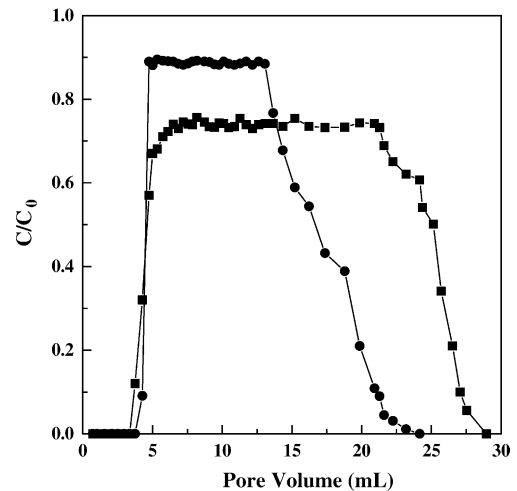
Fig. 4. Elution of Triton X-100 and APU nanoparticles from a soil column at higher flow rate (0.12 mL/min): (□) Triton X-100 (4000 mg/L), (●) APU nanoparticles (4000 mg/L).
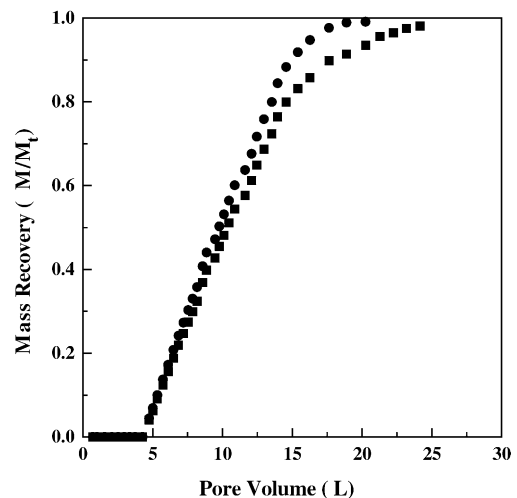
Fig. 6. Mass recovery of Triton X-100 and APU nanoparticles from a soil column at a higher flow rate (0.12 mL/min): (■) Triton X-100 (4000 mg/L), (●) APU nanoparticles (4000 mg/L).
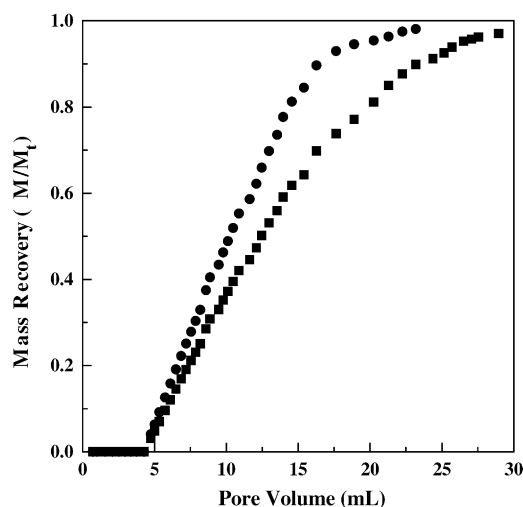
Fig. 7. Mass recovery of Triton X-100 and APU nanoparticles from a soil column at a lower flow rate (0.02 mL/min): (■) Triton X-100 (4000 mg/L), (●) APU nanoparticles (4000 mg/L).

ered with 19.22 mL of rinse water. That is, at a high flow rate, Triton X-100 and APU nanoparticles have the almost same degree of sorption onto the soil, and so Triton X-100 and APU nanoparticles could be recovered with the almost same amounts of rinse water. At a low flow rate, Triton X-100 and APU nanoparticles have the longer contact time with the soil, and so more Triton X-100 and APU nanoparticles were adsorbed onto the soil. Consequently, more rinse water was needed to recover over 98% of Triton X-100 and APU nanoparticles. However, less rinse water was used for the recovery of APU nanoparticles, which can be interpreted as being due to the lower degree of sorption of APU nanoparticles. Hence, it can be thought that the cross-linked structures of APU nanoparticles make it possible for the particles to maintain their structure when in contact with soil for a longer contact time, which causes a lower degree of sorption onto the soil column. It can be tentatively concluded that, as for the batch experiments, the degree of sorption on the soil plays a more important role in the in situ extraction efficiency than the solubilization efficiency of a washing material for hydrophobic pollutants.

3.2. In situ extraction efficiency of APU nanoparticles compared with other nonionic surfactants

We also selected two other nonionic surfactants having different CMC and hydrophilic-lipophilic balance (HLB) to compare their extraction efficiencies with APU nanoparticles. The HLB and CMC of nonionic surfactants used in this study are summarized in Table 1. The HLB value for Brij 30 (9.7) is lower than that for Triton X-100 (13.5); that is, Brij 30 is more hydrophobic than is Triton X-100. In addition, the CMC of Brij 30 (20 mg/L) is lower than that of Triton X-100 (111 mg/L). Tween 80 (15.0) and Triton X-100 have similar HLB values, but the CMC of Tween 80 (15.7 mg/L) is lower than that of Triton X-100. It has been also reported that Brij 30 has a higher solubilization efficiency for phenanthrene than does Trion X-100. We evaluated the soil-washing performance of these surfactants through batch isotherm and soil column experiment as described in Section 2.4 and compared it with APU nanoparticles.

In batch isotherm experiments, the distribution of hydrophobic compounds can be used as an index for evaluating the soil-washing performance of a surfactant and is estimated as:

$$K_d = \frac{[HOC]_s}{([HOC]_w + [HOC]_{mic})}$$

$$= \frac{(\text{mol of HOC sorbed/g of solid})}{(\text{mol of HOC in aqueous and micellar solution/L})}$$

where K_d is the partition coefficient of HOC between solid and aqueous-pseudophase, $[HOC]_s$ is the moles of HOC sorbed per gram of solid (mole/g), $[HOC]_w$ is the moles of HOC in water per liter of solution (mole/L), and $[HOC]_{mic}$ is the moles of HOC in micelles per liter of solution (mole/L) [6–13].

The K_d values of phenanthrene in the presence of the surfactants and APU nanoparticles are plotted as a function of the concentration of surfactant or APU particles in the aqueous phase (Fig. 8). In the absence of APU particles or surfactant in the aqueous phase, the partition coefficient K_d of phenanthrene (log $K_d = -1.7037$ (L/g)) defines the distribution of phenanthrene between pure water and aquifer sand. In the presence of surfactants or APU nanoparticles in the aqueous phase, the value of K_d decreased with an increase in the concentration of surfactant or APU nanoparticles in the aqueous phase, which indicates that the phenanthrene sorbed onto the aquifer soil is extracted by surfactant or APU nanoparticles. The desorption of phenanthrene can be considered in two regions of concentration.

In the low concentration region (10–1000 mg/L), log (K_d) values of surfactant aqueous solutions are larger or little lower than -1.7037 (L/g). This result indicates that none of the surfactants used could extract sorbed phenanthrene and the sorption of phenanthrene onto the aquifer soil is in-

Table 1
Characteristics of nonionic surfactants

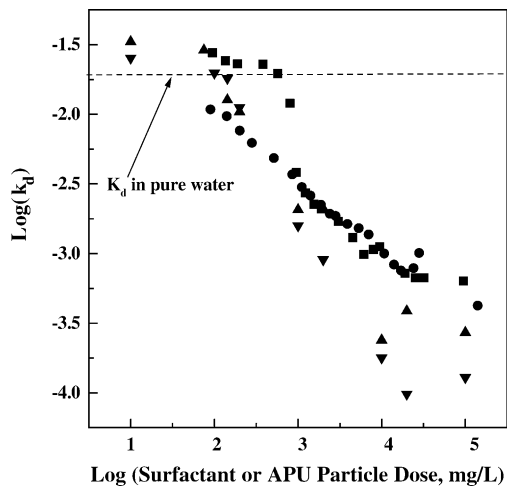| Trade name	Chemical	Molecular weight (g/mol)	HLB	CMC (mg/L)
Brij 30	Polyoxyethylene (4) lauryl ether	363	9.7	20
Tween 80	Polyoxyethylene (20) sorbitan monooleate	1309	15.0	15.7
Triton X-100	Polyoxyethylene (10) isooctylphenyl ether	646	13.5	111

Fig. 8. Distribution of phenanthrene between soil and aqueous pseudophase containing APU nanoparticles and surfactants: (■) Triton X-100, (●) APU nanoparticles, (▲) Tween 80, (▼) Brij 30.

Fig. 9. Extraction of sorbed phenanthrene (PAH) from a soil column using APU nanoparticles and surfactant solutions at the same flow rate (0.02 mL/min) and concentration (100 mg/L): (■) Triton X-100, (●) APU nanoparticles, (▲) Tween 80, (▼) Brij 30.

creased in this concentration region. For APU nanoparticles, however, $\log(K_d)$ values of phenanthrene are smaller than -1.7037 (L/g) and decreased with an increase of the concentration of APU nanoparticles. This result indicates that, in this low concentration region, APU nanoparticles could extract sorbed phenanthrene from aquifer soil. Over a higher concentration region (1000–100,000 mg/L), surfactant solutions and APU solution showed similar values for K_d of phenanthrene, even though Brij 30 solutions exhibited a lower K_d value compared with the other surfactant solutions and APU solution. This indicates that, over this concentration region, all washing materials (surfactants and APU nanoparticles) have similar extraction efficiencies.

According to our previous report, the solubilization efficiency of Triton X-100 for phenanthrene is eight times higher than that of APU nanoparticles [21]. In addition, it was reported by another research group that the solubilization efficiency of Brij 30 is 2.5 times greater than that of Triton X-100 [6]. It can be expected that all surfactants, especially Brij 30, used in this study would exhibit better extraction efficiency for sorbed phenanthrene than APU nanoparticles. However, APU nanoparticles exhibited better extraction efficiency than all surfactants, including Brij 30, in the low concentration region. The results described in previous sections showed that the better extraction efficiency of APU nanoparticles relative to Triton X-100 was due to the lower degree of sorption of APU nanoparticles onto the soil. In the lower concentration region, the better extraction efficiency of APU nanoparticles compared with all other surfactants used can be explained by the lower degree of sorption of APU nanoparticles onto the aquifer sand, which is due to their chemically cross-linked structure.

Fig. 9 shows the fraction of phenanthrene remaining in the contaminated soil column versus the number of pore volumes of APU and surfactant solutions eluted from the column. The flow rate was regulated at 0.02 mL/min and the
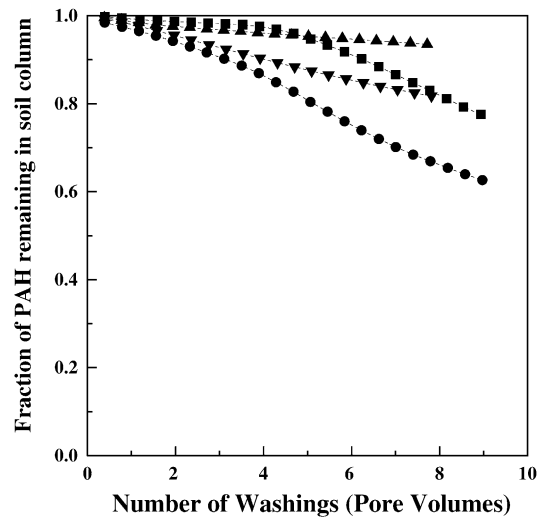
concentration of washing solution was fixed at 100 mg/L. After nine pore volumes of washing, APU washed out a larger amount of phenanthrene (about 40%) from the soil column than did Brij 30 (18%), Triton X-100 (18%), and Tween 80 (4.5%). As illustrated by Fig. 10, at a higher concentration of washing solution (4000 mg/L), APU nanoparticles also showed higher in situ extraction performance compared with the surfactants. As for the batch experimental results, APU nanoparticles exhibited better soil-washing performance than did surfactants and had better solubilization efficiency for phenanthrene. This result shows that the lower degree of
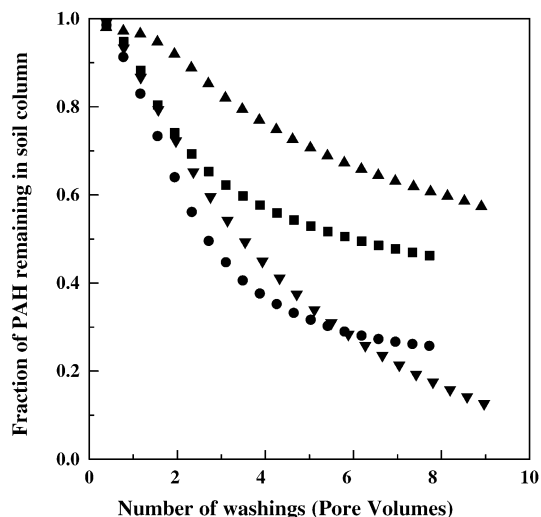

Fig. 10. Extraction of sorbed phenanthrene (PAH) from a soil column using APU nanoparticle and surfactant solutions at the same flow rate (0.02 mL/min) and concentration (4000 mg/L): (■) Triton X-100, (●) APU nanoparticles, (▲) Tween 80, (▼) Brij 30.

sorption of APU nanoparticle causes the better extraction efficiency.

4. Conclusions

Even though surfactants have a better solubilization efficiency for phenanthrene, in the low concentration range, APU nanoparticles dispersed in an aqueous phase exhibited better extraction performance than did the surfactants in both batch and column tests. The soil washing performance of APU nanoparticles was better than those of the surfactants, especially at longer soil contact times. This is because a smaller amount of APU nanoparticles was sorbed on the soil, owing to their chemically cross-linked structure. It can be concluded that the chemically cross-linked structure of APU nanoparticles causes its lower degree of sorption on the soil, even at longer residence times within soil column, which results in better in situ soil-washing performance compared with surfactants that have a higher degree of sorption on the soil. Since the size of APU nanoparticles is much greater than that of surfactant micelles, APU nanoparticles could be recovered 100% through ultrafiltration process at greater pore size of separation membrane. So, we think that low concentration and degree of sorption to the soil would make soil-washing process using APU nanoparticles economical and useful in practical applications. We will investigate in situ extraction of pollutants and recycling and reuse of APU nanoparticles at field scale in future work.

Acknowledgement

References

[1] L.W. Canter, R.C. Knox, Ground Water Pollution Control, Lewis Publishers Inc., Chelsea, Michigan, 1986.
[2] J.L. Haley, B. Hanson, C. Enfield, J. Glass, Ground Water Monit. Rev. 11 (1991) 119.
[3] J.H. Harwell, Transport and remediation of subsurface contaminants, in: D.A. Sabatini, R.C. Know (Eds.), ACS Symposium Series 491, Am Chemical Soc., Washington, DC, 1992. pp. 124–132.
[4] D.M. Mackay, J.A. Cherry, Environ. Sci. Technol. 23 (1989) 630.
[5] J.F. McCarthy, J.M. Zachara, Environ. Sci. Technol. 23 (1989) 496.
[6] I.T. Yeom, M.M. Ghosh, C.D. Cox, Environ. Sci. Technol. 30 (1996) 1589.
[7] W.H. Noordman, J.W. Bruining, P. Wietzes, D.B. Janssen, J. Contam. Hydrol. 44 (2000) 119.
[8] R.R. Kommalapati, R.T. Valsaraj, W.D. Constant, D. Roy, Wat. Res. 31 (1997) 2161.
[9] G.G. Liu, D. Roy, M.J. Rosen, Langmuir 16 (2000) 3595.
[10] J.F. Lee, P.M. Liao, C.C. Kuo, H.T. Yang, C.T. Chiou, J. Colloid Interf. Sci. 229 (2000) 445.
[11] W. Chu, W.S. So, Wat. Res. 35 (2001) 761.
[12] D. Zhao, J.J. Pignatello, J.C. White, W. Braida, F. Ferrandino, Water Resourc. Res. 37 (2001) 2205.
[13] S. Deshpande, L. Wesson, D. Wade, D.A. Sabatini, J.H. Harwell, Wat. Res. 34 (2000) 1030.
[14] K. Urum, T. Pekdemir, M. Copur, J. Colloid Interf. Sci. 276 (2004) 456.
[15] Z. Zheng, J.P. Obbard, Wat. Res. 36 (2002) 2667.
[16] R.A. Doong, W.G. Lei, J. Hazard. Mater. B96 (2003) 15.
[17] S. Förster, M. Antonietti, Adv. Mater. 10 (1988) 195.
[18] A.B.R. Mayer, Polym. Adv. Technol. 12 (2001) 96.
[19] R. Gangopadhyay, D. Amitabha, Chem. Mater. 12 (2000) 608.
[20] W. Caseri, Macromol. Rapid. Commun. 21 (2000) 705.
[21] J.Y. Kim, S.B. Shim, J.K. Shim, J. Hazard. Mater. B98 (2003) 145.
[22] J.Y. Kim, D.H. Shin, K.J. Ihn, C.W. Nam, Macromol. Chem. Phys. 203 (2003) 2454.
[23] J.Y. Kim, D.H. Shin, K.J. Ihn, K.D. Suh, J. Ind. Eng. Chem. 9 (2003) 37.
[24] D.M. Dohse, L.W. Lion, Environ. Sci. Technol. 28 (1994) 541.