Synthesis of Amphiphilic Polyurethane Nanonetwork Particles and Their Application for the Soil-Washing Process

Ju-Young Kim,[1] Sun-Bo Shim,[1] Jin-Kie Shim[2]

[1]*Department of Advanced Materials Engineering, Samcheok National University, Samcheok, Kangwon 245-711, South Korea*
[2]*Cleaner Production Technology Center, Korea Institute of Industrial Technology, Chonan 330-825, South Korea*

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ABSTRACT: Nanosized amphiphilic polyurethane (APU) particles synthesized on the basis of amphiphilic urethane acrylate nonionomers could solubilize phenanthrene within their hydrophobic interiors in the same way that surfactant micelles do in the aqueous phase. At low concentrations of APU or Triton X-100 in the aqueous phase, APU particles exhibited a greater extraction efficiency of sorbed phenanthrene than did the Triton X-100 aqueous pseudophase. At higher APU particle and Triton X-100 doses in aqueous solution, the extraction efficiency of the APU aqueous solution was almost same as that of the Triton X-100 aqueous solution, even though APU particles exhibited a lower solubilizing efficiency than Triton X-100 micelles in the absence of aquifer soil. This was because APU particles have a relatively low degree of sorption on aquifer sand because of their chemically crosslinked structure. APU particles could be also recovered at a rate of 100% through an ultrafiltration process at a greater pore size of the separation membrane, which would make soil washing with APU particles more economical and useful in practical applications. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1666–1677, 2003

Key words: amphilic polyurethane; phenanthrene; sorption; desorption; soil washing

INTRODUCTION

The 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 can act as a source of dissolved contaminants.[1–5] For example, polycyclic aromatic hydrocarbons (PAHs) are commonly found in ground water at coal–tar waste sites.[3,4] A common remediation process of soil and ground water at contaminated sites is based on the extraction of groundwater by wells or drains, followed by the treatment of the extracted water, a method called *pump-and-treat remediation*.[2,4,5]

Unfortunately, many hydrophobic organic liquids that are common groundwater pollutants cannot be efficiently extracted by the pump-and-treat method because of their low solubilities in water and high interfacial tensions. So, surfactant-enhanced remediation techniques have been proposed for the potential use in *in situ* soil remediation and as improvements to the pump-and-treat technology.[6–10] Surfactants, one of typical amphiphilic molecule, can increase the extraction of hydrophobic materials through micellar solubilization and the mobilization of such materials through a reduction in their interfacial tension. Such approaches for the extraction of HOCs have been pursued extensively during last decade.[6–16]

Among HOCs, PAHs are of special interest because they are strongly sorbed to soil or sediment. As a consequence, sorbed PAHs may act as long-term sources of groundwater contamination, even when groundwater contaminated by HOCs, such as nonaqueous phase liquids, are completely extracted and treated by surfactant-enhanced remediation process.[17–19] So, many researchers have used various surfactants to enhance the desorption of sorbed PAHs from soil through the solubilization of sorbed PAHs in surfactant micelles.[20–27] Surfactant-enhanced desorption and the washing process are only effective when the surfactant dose is greater than its critical micelle concentration (CMC) because most surfactant molecules below their CMC are sorbed onto soil below its CMC, resulting in the enhanced sorption of PAHs from the aqueous phase to the soil surface.[13,16,19,22–25]

In a previous article, we reported the extraction of sorbed phenanthrene from aquifer materials with anionic crosslinked polyurethane nanoparticles dispersed in the aqueous phase.[28] These particles were shown to adsorb weakly to a sandy aquifer in batch experiments, which was attributed to the chemically crosslinked nature of their microstructure. Most of the

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Correspondence to: J.-Y. Kim (juyoungk@samcheok.ac.kr).

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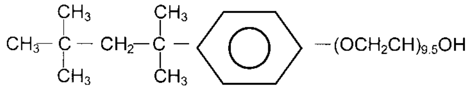
extraction conditions tested with the anionic crosslinked polyurethane nanonetwork emulsions, extracted a very high level (95%) of the hydrophobic tested pollutant (phenanthrene) from the aquifer sand with extremely low loss of the applied particles. Relatively smaller numbers of washings were needed to achieve a high level of remediation. The concentration of anionic crosslinked polyurethane particles in the washing solution was greater than that typically used for surfactant solution. This was, however, compensated by the high level of phenanthrene removal achieved, the smaller number of pore volumes required for the application of the anionic crosslinked polyurethane emulsions, and the ability to recover applied the anionic crosslinked polyurethane particles.

The purpose of this work was to evaluate the potential of novel amphiphilic polyurethane (APU) nanonetwork particles for the *in situ* extraction of sorbed HOCs from contaminated soil. The APU particles used in this study had hydrophilic polyethylene oxide groups on their surface and a hydrophobic backbone in their core. The APU particles represented a microphase-separated structure similar to that of surfactant micelles. When APU network particles are dispersed in water, the outer hydrophilic groups stabilize the particles by extending into the aqueous phase. Hydrophobic backbones make up the interior of the particles and have a high affinity for hydrophobic organic pollutants (Fig. 1). This research focused on the application of APU particles to remove sorbed PAHs, so we present the extraction of sorbed PAHs from aquifer materials and the distribution of phenanthrene between the aqueous phase and aquifer materials in the presence of APU particles. These results are compared with those of a batch system containing nonionic surfactant, Triton X-100, aquifer materials, and phenanthrene aqueous solution.

EXPERIMENTAL

Materials

We used phenanthrene as a model PAH. The aqueous solubility of phenanthrene was reported to be 1.29 mg/L, and its octanol–water partition coefficient was 3700. Radio-labeled phenanthrene was purchased from Sigma Chemical Co. (9-^{14}C, 13.1 μCi/μmol). The aquifer sand used in all of the experiments was obtained from a quarry in Newfield, NY. The organic content of the sand was reported to be 0.049 ± 0.012%.[29] A size analysis of the sand was previously reported, and it was revealed that 47.2 and 47.6% of the sand were in the fine (0.1–0.25 mm) and medium (0.25–0.5 mm) size ranges, respectively.[29] The remaining constituents included very find sand (0.05–0.1 mm, 3.7%), coarse sand ($>$0.5 mm, 0.2%), and slit and clay (1.2%). Triton X-100 (Sigma Chemical Co.) used in this study was a nonionic heterogeneous octylphenol ethoxylate surfactant with the following molecular structure:



In the synthesis of amphiphilic urethane acrylate nonionomer (UAN) precursor chains, poly(propylene oxide triol) [PPO triol; weight-average molecular weight (M_w) = 700 and 1000; Korea Polyol Co.], 2,4-toluene diisocyanate (TDI; Aldrich Chemical Co., South Korea), 2-hydroxyethyl methacrylate (2-HEMA; Aldrich Chemical Co.), and polyethylene glycol (PEG; M_w's = 600, 1000, and 1500; Aldrich Chemicals Co.) were used. PPO triol and PEG were dried and degassed at 80°C and 3–5 mmHg for 2 days. Potassium persulfate (KPS; Wako Pure Chemicals Co., Japan) was recrystallized from distilled deionized (DDI) water before use.

Synthesis of amphiphilic UAN

The synthesis of UAN chains, schematically illustrated in Figure 1, was carried out through a three-step process. Each reaction was performed in a 500-mL four-necked vessel with a stirrer, a thermometer, and an inlet system for nitrogen gas. In the first step, hydroxyl groups of PPO triol were reacted with NCO groups of TDI to form NCO-capped intermediate precursor chains (Chain A). In the second step, two NCO groups of Chain A were reacted with the hydroxyl groups of 2-HEMA to introduce reactive vinyl groups to precursor chains (Chain B). Finally, PEG was added and reacted with residual NCO groups of Chain B. The molar ratio of TDI/PPO triol/2-HEMA/PEG was 3/1/2/1. The recipe for the synthesis of UAN chains is illustrated in Table I. The polystyrene-equivalent M_w of synthesized UAN chains was 3750–6,700 with a polydispersity of 1.93–2.01.Characterization of the synthesis of UAN chains based on ^{1}H-NMR spectra was reported in our previous article.[30]

Synthesis of crosslinked polyurethane nanoparticles

To be used in the *in situ* removal of hydrophobic pollutants from soil, UAN chains should be prepared at a nanoscale size to allow them to flow through a soil bed. To prepare the dispersion of APU nanoparticles in water, UAN precursor chains were first emulsified without an external surfactant through the mixture of UAN (10 g) with DDI water (100 g). The crosslinking polymerization of the obtained UAN emulsion containing dissolved KPS (0.5 wt % total weight of emulsion) was carried out in a four-necked glass kettle equipped with a stirrer, a thermometer, a reflux con-

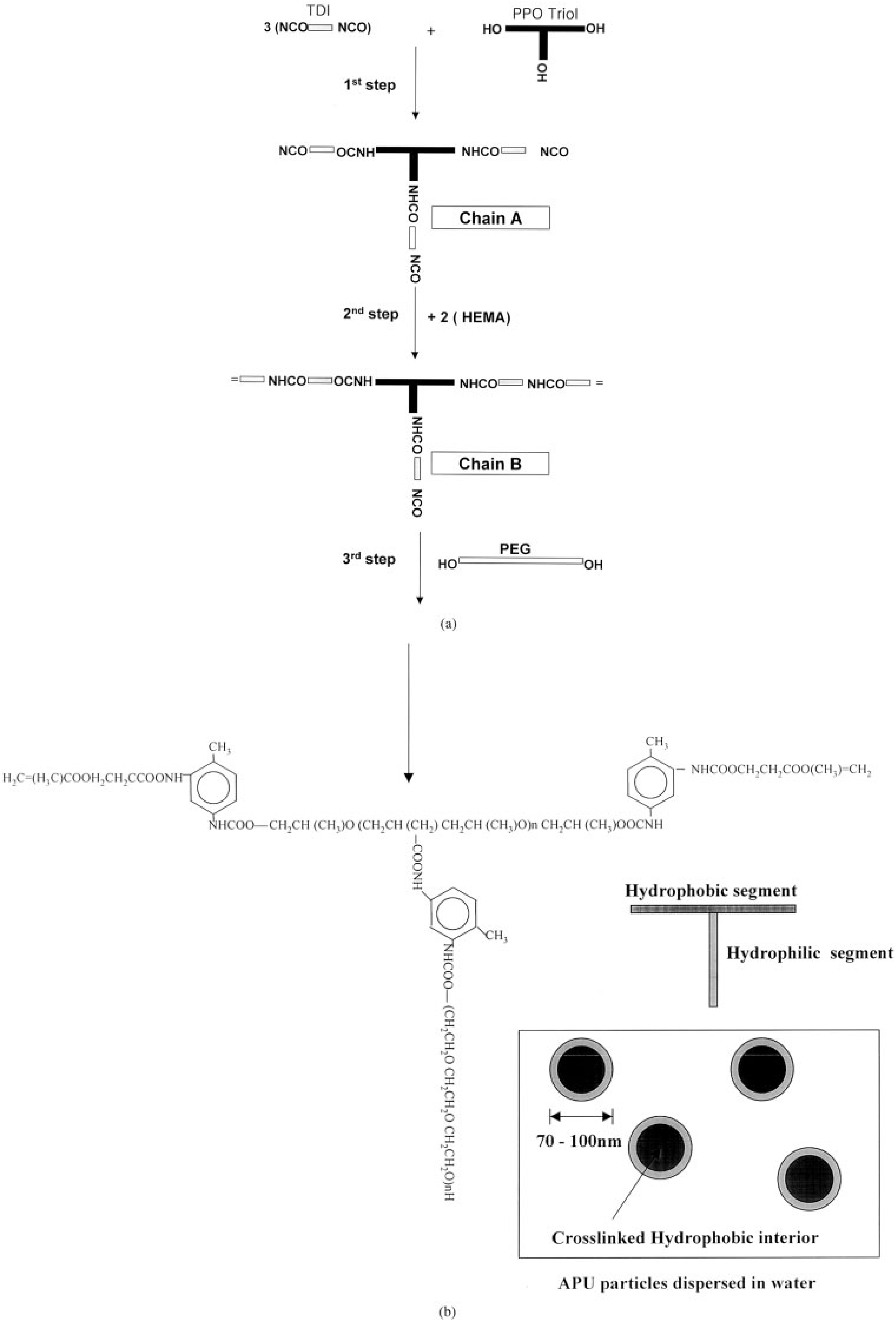


Figure 1 Schematic presentation of UAN chains and APU particles.

TABLE I
Recipe for the Synthesis of UAN Chains and Their M_w's

Molar ratio of TDI/PPO triol/ 2-HEMA/PEG	M_w of PPO triol	M_w of PEG	Symbol	M_w of UAN
3/1/2/1	700	600	UAN700-1	3750
3/1/2/1	700	1000	UAN700-2	4350
3/1/2/1	700	1500	UAN700-3	4120
3/1/2/1	1000	1500	UAN1000	6700

denser, and an inlet system for N_2 gas. The kettle was placed in a thermoset-controlled oil bath, in which the polymerization temperature was kept at 65 ± 0.5°C.

After the completion of polymerization, the APU emulsion was poured into a 100-mL beaker containing methanol and the polymerization inhibitor hydroquinone and was dried for 24 h in a vacuum oven. The conversion of UAN chains was determined with following equation:

$$\text{Conversion (wt \%)} = (W_d/W_t \times \text{TSC}) \times 100\%$$

where W_d and W_t are the collected sample weight (g) and the sample weight after washing and drying (g), respectively, and TSC is the theoretical solid content value per gram of collected sample at 100% conversion. The size of the prepared APU particles was measured by dynamic light scattering and was in the range of 60–100 nm. The particles synthesized with UAN700-1, UAN700-2, UAN700-3, and UAN1000 chains were named APU700-1, APU700-2, APU700-3, and APU1000, respectively.

Surface tension tests

The surface tensions of Triton X-100 solution and APU emulsions were determined with a model 20 surface tensiometer (Fisher Scientific). This instrument operates on the duNouy principle, in which a platinum ring is suspended from a torsion balance. Each aqueous sample was tested with the tensiometer at controlled temperature (25°C) until at least three consistent surface tension readings were obtained. Between each reading, the ring was cleaned with acetone and heated to redness in a gas flame.

Solubilization of crystalline phenanthrene with surfactant or APU solutions

The solubility of phenanthrene in surfactant or APU solutions was determined with the mixture of radiolabeled phenanthrene and nonlabeled phenanthrene. Concentrated phenanthrene solutions (35 g/L) were prepared in methylene chloride. Phenanthrene solution (2 mL) was added into a 25-mL glass scintillation vial equipped with open-top screw caps and a Teflon-backed septa. After the evaporation of methylene chloride, Triton X-100 or APU aqueous solutions (10 mL) of various concentrations were added into the vials. Because the amount of phenanthrene remaining in the vials was much greater than the solubility of phenanthrene in water, the loss of phenanthrene due to evaporation was inconsequential. The vials were sealed and gently agitated with a rotary tumbler for 7 days. After mixing was complete, 5 mL of supernatant was withdrawn and centrifuged at an acceleration 15,000 × g. The sample (1 mL) was transferred into a scintillation vial containing 10 mL of Ecolume cocktail, and the concentration of ^{14}C–phenanthrene in the aqueous phase was measured with a liquid scintillation counter (LSC).

Extraction of sorbed phenanthrene by Triton X-100 or APU solutions

A ^{14}C–phenanthrene aqueous solution (activity = 0.056–0.068 μCi/mL) was prepared by a method described previously.[29,31] To prepare contaminated soil samples, 1 mL of ^{14}C–phenanthrene from prepared aqueous solution was added into a scintillation glass vial containing 1 g of aquifer sand and was agitated with a rotary tumbler for 2 days. After mixing was complete, 9 mL of Triton X-100 solution or APU emulsion at varying concentrations was added into the vial and reagitated with a rotary tumbler for 2 days, at which point it was then centrifuged (15,000 × g) to separate the soil from the aqueous solution. The supernatant (1 mL) was withdrawn and was transferred into a scintillation vial containing 10 mL of Ecolume cocktail, and the concentration of ^{14}C–phenanthrene in the aqueous phase was measured with an LSC.

Sorption of phenanthrene on aquifer sand in the absence of interfacial agents

For the sorption of phenanthrene onto the aquifer, 1 mL of the ^{14}C–phenanthrene from the prepared solution was added into a glass vial with a screw cap filled with varying amounts of sand. Samples were agitated with a rotary tumbler for 1 day. Supernatant (5 mL) was withdrawn and centrifuged at an acceleration 15000 × g to separate the soil from the aqueous solution. The sample (1 mL) was transferred into a scintil-

TABLE II
Conversion and Size of APU Particles

	Size of APU particles (nm)		
	Before polymerization	After polymerization	Conversion (%)
APU700-1	100	Aggregated	—
APU700-2	89	93	92.20
APU700-3	73	81	89.78
APU1000	82	85	88.72

lation vial containing 10 mL of Ecolume cocktail, and the concentration of ^{14}C–phenanthrene in the aqueous phase was measured with an LSC.

Sorption of phenanthrene on aquifer sand in the presence of interfacial agents

Case 1: mixing phenanthrene, aquifer sand, and interfacial agents simultaneously

Triton X-100 solution or APU emulsion (9 mL) at varying concentrations and 1 mL of ^{14}C–phenanthrene aqueous solution were simultaneously added into a scintillation vial containing 1 g of aquifer, and then the vial was agitated with a rotary tumbler for 2 days. After mixing was complete, the vial was then centrifuged (15000 × g) to separate the soil from the aqueous solution. Supernatant (1 mL) was withdrawn and transferred into a scintillation vial containing 10 mL of Ecolume cocktail, and the concentration of ^{14}C–phenanthrene in the aqueous phase was measured with an LSC.

Case 2: premixing interfacial agents with aquifer sand

Triton X-100 solution or APU emulsion (9 mL) at varying concentrations was added into a glass vial containing 1 g of aquifer sand, and the vial was agitated with a rotary tumbler for 2 days. After mixing was complete, 1 mL of ^{14}C–phenanthrene aqueous solution was added to the vial, and the sample was reagitated for 1 day, at which point it was centrifuged (15000 × g) to separate the soil from the aqueous solution. Supernatant (1 mL) was withdrawn and transferred into a scintillation vial containing 10 mL of Ecolume cocktail, and the concentration of ^{14}C–phenanthrene in the aqueous phase was measured with an LSC.

Ultrafiltration process for the recovery of APU particles and Triton X-100

For the recovery of APU particles and Triton X-100 from the aqueous phase, APU emulsion and Triton X-100 aqueous solutions of varying concentrations were added to ultrafiltering centrifuge tubes [Centriplus YM-100; molecular-weight cutoff (MWCO) = 100,000; Millipore]. Membranes were made of regenerated cellulose and had an effective filtration area of 2.34 cm^2. The aqueous solutions was weighted and centrifuged at 2500 rpm until the desired volume of the permeate (V) was reached. The permeate or retentate was weighed and diluted before analysis. The concentration of APU particles (219 nm) and Triton X-100 (275.5 nm) in the aqueous phase was determined with an ultraviolet–visible (UV–vis) spectrophotometer (Shimadzu 3210, Japan) in the range of 20–200 mg/L.

RESULTS AND DISCUSSION

Soap-free emulsion polymerization of UAN chains

Because UAN chains has a polypropylene oxide-based hydrophobic segment and a polyethylene oxide hydrophilic segment in the same chains like nonionic surfactants, the UAN chain can be soap-free emulsified to form nanosized particles (APU particles). On contact with water, water-insoluble hydrophobic segments were phase-separated from the hydrophobic segment and aggregated with each other to form a hydrophobic interior, whereas polyethylene oxide chains dissolved in water and oriented toward the water phase to form hydrophilic outer layers. As a consequence, nanosized APU particles with micelle-like structures were dispersed in water and stabilized by outer polyethylene oxide chains [see Fig. 1(b)]. As the chain length of PEG increased, the size of APU particles decreased, as illustrated in Table II. APU700-1 particles synthesized with UAN700-1 chains lost their emulsion stability and were aggregated in the course of emulsion polymerization. This was because the hydrophilicity of polyethylene oxide chains in UAN700-1 significantly decreased with increasing temperature. At elevated temperatures, the aggregation of APU700-1 particles and crosslinking polymerization occurred simultaneously because a dramatic decrease in the hydrophilicity of the polyoxyethylene chains and polymerization occurred at the same time. So, in the course of polymerization, a low-viscosity liquid, APU700-1 emulsions, was changed to a cheese-like solid. We reported this rapid aggregation and polymerization mechanism and the thermal stability of UAN chain in previous articles.[32,33]

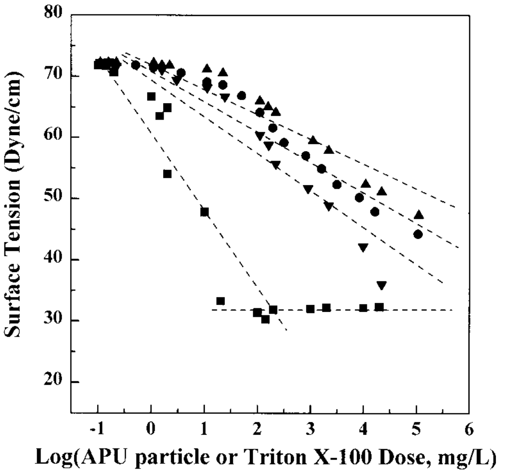


Figure 2 Surface tension for Triton X-100 and APU particle solutions: (■) Triton X-100, (▲) APU700-2, (●) APU700-3, and (▼) APU1000.

For APU700-2, APU700-3, and APU1000 particles having longer polyethylene oxide chains, however, crosslinking polymerization of these APU emulsions could be carried out without any coagulation during polymerization. This was because the hydrophilicity of longer polyethylene oxide chains did not largely change with increasing temperature. The maximum conversion of APU700-2, APU700-3, and APU1000 particles was in the range 88–92% in 4–5 h of polymerization (see Table II).

Surface tension of aqueous solutions containing APU particles and Triton X-100

Figure 2 shows the surface tension versus concentration of APU particles and Triton X-100 in the aqueous phase. Like that of the Triton X-100 solution, the surface tension of APU emulsions decreased with increasing concentration of APU particles in the emulsions, indicating that crosslinked APU particles had an interfacial activity. As the concentration increased in the aqueous solution, the surface tension of the Triton X-100 solution abruptly changed and remained constant, whereas the surface tension of the APU emulsion gradually decreased. This result also indicates that Triton X-100 had a critical concentration for the aggregation of molecules but that APU particles did not have this critical concentration. This may be because of the difference in water solubility between UAN chains and Triton X-100.

Unlike Triton X-100, which completely dissolves in water below its CMC, UAN chains do not dissolve in water but are just dispersed in water to form APU particles, even at extremely low concentrations in aqueous solutions because of the insolubility of whole UAN chains in water. To confirm the lack of water solubility of UAN chains in water, UAN aqueous solutions of various concentrations (100–20,000 mg/L) were added into centrifugal ultrafiltration tubes and centrifuged to separate the water phase. After ultrafiltration, the concentration of UAN chains in permeate aqueous solution was examined with UV–vis spectroscopy. UV–vis spectra of permeated aqueous solution exhibited that there were no dissolved UAN chains in the aqueous solutions, indicating that 100% of UAN chains existed not as dissolved molecules but as aggregated particles (APU particles). So, the aqueous pseudophase of APU emulsions may consist of micelle-like nanoparticles only. In other words, UAN chains have no critical concentration to form aggregates (APU particles) in aqueous solutions.

Enhanced solubility of phenanthrene by APU particles

Amphiphilic molecules, surfactant, can increase the solubility of HOC molecules in the water phase because the hydrophobic core of surfactant micelles can accommodate a certain amount of lipophilic organic compound as a solubilizate. This solubilization capability makes surfactants useful for the soil-washing process. So, the enhanced solubility of a certain HOC by a surfactant can be used as an index for the evaluation of a surfactant for the soil-washing process and for wastewater treatment process of sorbed and solubilized HOCs.

We describe the increase of phenanthrene solubility in water as an enhanced solubility, that is, the ratio of C/C_0, where C is the concentration of phenanthrene in aqueous solution containing APU particles or Triton X-100 and C_0 is the concentration of phenanthrene in the pure water phase. The saturation equilibrium concentration of phenanthrene in Triton X-100 or APU particle aqueous solution is given in Figure 3. The solubility of phenanthrene in the aqueous phase increased with increasing APU particles dose in aqueous solution, indicating micelle-like APU particles can solubilize phenanthrene within their hydrophobic interiors just like the solubilization of HOCs in surfactant micelles. At a higher concentration of Triton X-100 or APU particles in the aqueous phase, Triton X-100 micelles and APU particles could solubilize about 50 times and 2–8 times the phenanthrene that an equal amount of pure water would solubilize. So, this result indicates that APU particles can solubilize phenanthrene within their hydrophobic interior but that the effectiveness of APU particles in solubilizing phenanthrene is lower compared with that of Triton X-100 solutions.

Extraction of phenanthrene from aquifer sand

To examine the extraction efficiency of sorbed phenanthrene by Triton X-100 or APU particles, we mixed

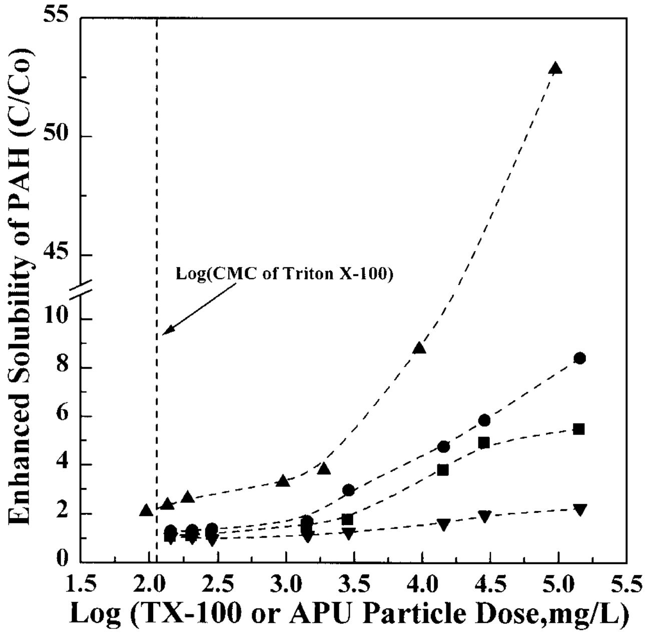


Figure 3 Enhanced solubility of phenanthrene in the aqueous phase in the presence of Triton X-100 or APU particles: (▲) Triton X-100, (▼) APU700-2, (■) APU700-3, and (●) APU1000

Triton X-100 and APU aqueous solutions of varying concentrations with aquifer sand contaminated with phenanthrene. Desorption of sorbed phenanthrene as a function of surfactant or APU particle dose was replotted as extraction efficiency (%) and is illustrated in Figure 4. Extraction efficiency was calculated as (Desorbed amount of phenanthrene)/(Sorbed amount of phenanthrene on aquifer sand) × 100 (%).

When the concentration of Triton X-100 was smaller or a little greater than its CMC, Triton X-100 and APU700-2 solution did not extract sorbed phenanthrene, whereas APU700-3 and APU1000 emulsions extracted 20–35% of sorbed phenanthrene. At a concentration of Triton X-100 much greater than its CMC, Triton X-100 (94–98%) and APU700-3 or APU1000 solution (92–93%) showed almost the same degree of extraction efficiency.

As shown earlier, Triton X-100 aqueous solution exhibited a much greater enhanced solubility of phenanthrene and interfacial activity than did APU particle solutions (see Figs. 2 and 3), indicating that Triton X-100 micelles had a stronger affinity with phenanthrene than APU particles. However, APU particles and Triton X-100 exhibited almost same extraction efficiency at a concentration greater than the CMC of Triton X-100. In addition, APU particles had a greater extraction performance than Triton X-100 at a concentration less or a little greater than the CMC of Triton X-100. This result may also be interpreted as due to the greater degree of sorption of Triton X-100 onto the aquifer.

It is known that the surfactant can exist in a soil/aqueous phase as dissolved monomers or aggregates of monomers called *micelles*.[16,21,23–25] That is, the aqueous pseudophase of surfactants consists of the micelles and dissolved monomers of surfactants in water. When the concentration of surfactant is equal to or

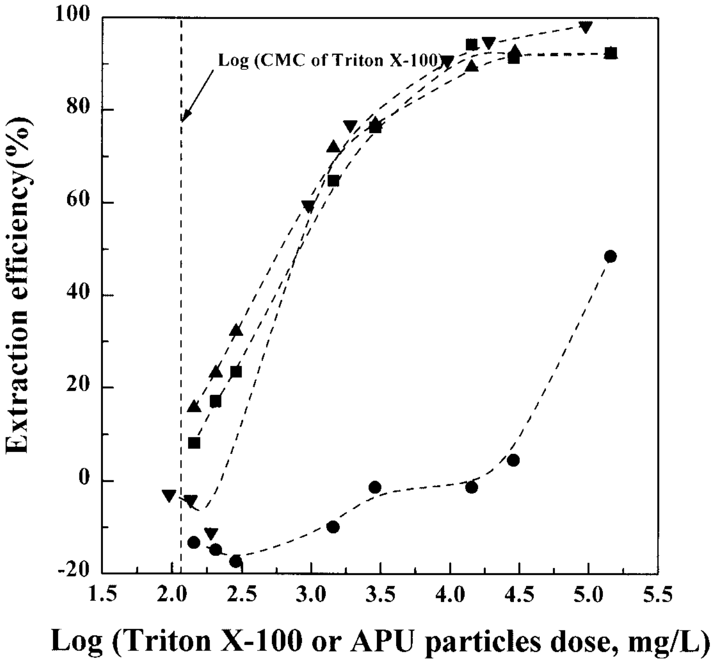


Figure 4 Extraction efficiency of APU particles and Triton X-100 solution: (▼) Triton X-100, (●) APU700-2, (■) APU700-3, and (▲) APU1000.

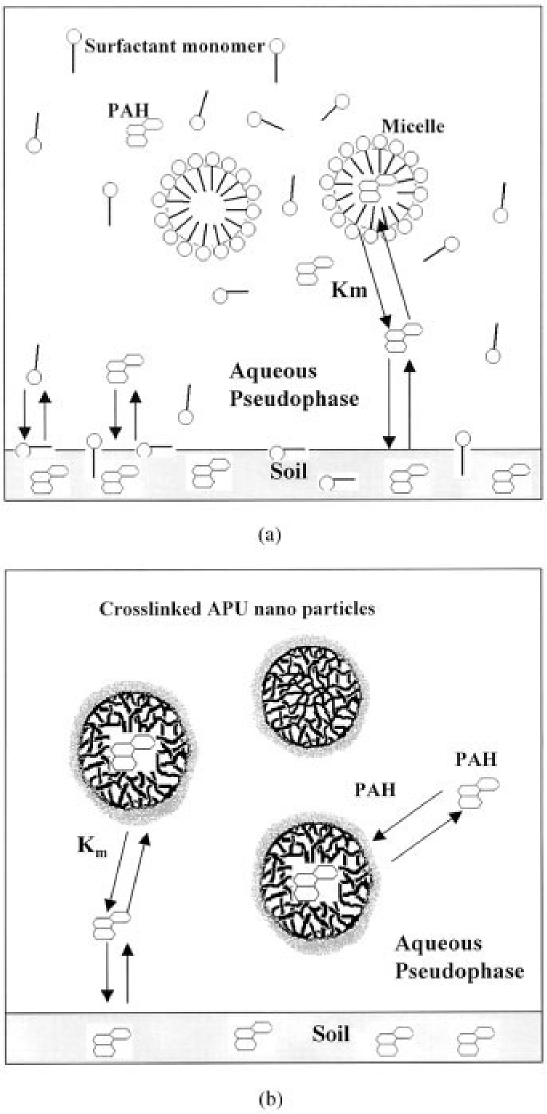


Figure 5 Schematic presentation of (a) Triton X-100 and (b) APU aqueous pseudophases.

greater than its CMC, surfactant molecules make up micelles via the aggregation of surfactant monomers. At surfactant concentrations less than the CMC, surfactant monomers do not make up micelles in the aqueous phase and completely dissolve in the aqueous phase [see Fig. 5(a)]. Many researchers also reported earlier that below the CMC of the surfactants, surfactant monomers can extract sorbed HOCs, but most of the surfactant monomers are easily sorbed onto the soil. These sorbed surfactants on soil increase the soil's organic carbon content and solubilize HOCs as well, resulting in the enhanced sorption of HOCs onto the soil.[14,23,25,30] So, at a concentration of Triton X-100 lower or a little greater than its CMC, most Triton X-100 molecules were sorbed on the aquifer sand; as a consequence, Triton X-100 did not extract sorbed phenanthrene, regardless of its greater affinity with phenanthrene.

Unlike Triton X-100, which completely dissolved in water below its CMC, UAN chains did not dissolve in water but were just dispersed in water to form APU particles, even at extremely low concentrations in aqueous solutions [see Fig. 5(b)]. This was because of the insolubility of whole UAN chains in water. So, the APU particles had a relatively low degree of sorption of APU particles at low concentrations because of their crosslinked aggregated structures. As a consequence, on comparison with Triton X-100, APU particles exhibited similar extraction efficiency at higher concentrations and greater extraction efficiency at low concentrations.

At concentrations greater than the CMC, surfactant micelles are formed by the physical association of monomeric molecules in aqueous phase. These micelles are not permanent structures, so their structures can be break down on contact with hydrophobic materials such as HOCs and hydrophobic matter of soil, causing the sorption of surfactant on the soil. Adsorbed surfactant molecules onto the soil act as a sorbing agent for the dissolved HOCs in the aqueous phase. So, the extraction of phenanthrene by Triton X-100 was largely offset by the sorption of Triton X-100, even at concentrations of Triton X-100 greater than the CMC. For APU particles, however, their micelle-like structures are permanently locked in by chemical reaction, allowing APU particles to remain intact on contact with HOCs or soil. So, a relatively low degree of sorption of APU particle effectively extracted sorbed phenanthrene, regardless of the weaker affinity between APU particles and phenanthrene.

Even though APU700-2 particles were crosslinked micelle-like particles like APU700-3 and APU1000 particles, APU700-2 particles showed much lower extraction efficiencies than the other APU particles and Triton X-100. This can be explained by two reasons: (1) a weaker affinity with phenanthrene and (2) a larger degree of sorption onto aquifer sand.

Sorption of phenanthrene on aquifer sand in the presence of APU particles

Many researchers have represented the sorption of HOCs on the soil or sediment in terms of the distribution of compounds between the soil and aqueous solutions. Distribution of HOCs between the aqueous phase and soil is largely changed by the addition of surfactant because surfactant molecules enhance the apparent solubility of HOCs in the aqueous phase through the micellar solubilization of HOCs.[17–27] So, this distribution of compounds can be used as an index for evaluating the soil-washing performance of a surfactant.[23–25] So, we examined the sorption of phenanthrene in the presence and absence of Triton X-100 and APU particles with different experimental

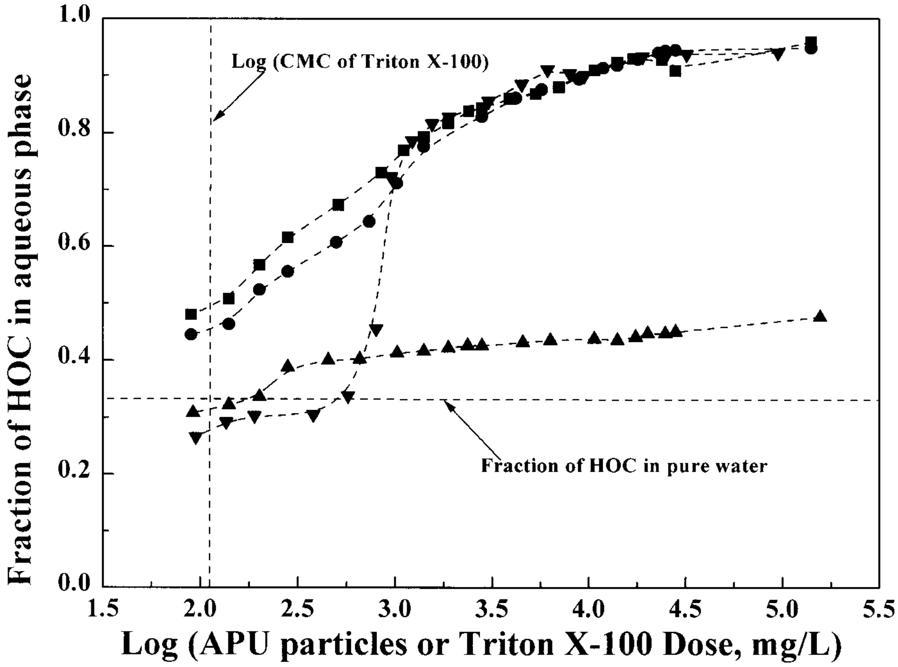


Figure 6 Distribution of phenanthrene between soil and the aqueous pseudophase containing Triton X-100 or APU particles. We performed the experiments by mixing phenanthrene, water, soil, and APU or Triton X-100 simultaneously: (▼) Triton X-100, (▲) APU700-2, (●) APU700-3, and (■) APU1000.

conditions to investigate how the sorption of Triton X-100 or APU particles influenced the sorption of phenanthrene on the aquifer soil. That is, two kinds of batch isotherm tests were conducted based on case 1 and case 2, as presented in the Experimental section, to determine the distribution of phenanthrene between the aqueous phase and aquifer sand in the presence and absence of Triton X-100 or APU particles.

We present distribution of HOCs between soil and the aqueous phase as a fraction of HOCs in the aqueous phase, which is estimated as

$$\text{Fraction of HOCs in the aqueous phase} = [\text{HOC}]_w/([\text{HOC}]_{\text{soil}} + [\text{HOC}]_w)$$

where $[\text{HOC}]_w$ is the amount of HOCs in the aqueous phase and $[\text{HOC}]_{\text{soil}}$ is the total amount of HOCs in the soil.

Figure 6 represents the fraction of phenanthrene in the aqueous phase when aquifer sand, water, and Triton X-100 or APU particles were mixed at the same time (see case 1 in the Experimental section). The fraction of phenanthrene in the aqueous phase increased with increasing Triton X-100 or APU particle dose in the aqueous phase. This result indicates that sorption of phenanthrene on the soil was reduced by APU particles or Triton X-100. This may be due to the solubilization of phenanthrene in Triton X-100 micelles and APU particles, which resulted in an increase of the partitioning of phenanthrene in the aqueous phase through the reduced sorption of phenanthrene onto aquifer sand.

In the absence of APU particles or Triton X-100 in the aqueous phase, the fraction of phenanthrene in the aqueous phase was 0.3318, which presented a distribution of phenanthrene between pure water and aquifer sand. When the concentration of Triton X-100 was smaller or a little greater than its CMC, the fraction of phenanthrene in the aqueous phase was smaller than the fraction of phenanthrene in the absence of Triton X-100. This indicates that the sorption of phenanthrene onto the aquifer soil was rather increased by the addition of Triton X-100 into the aqueous phase. This may have been due to the sorption of monomeric Triton X-100 molecules on the aquifer sand at Triton X-100 concentrations less than or a little greater than the CMC. However, APU particles showed a greater value of fraction than 0.3318 in all ranges of APU particle doses in aqueous solutions, indicating that the sorption of phenanthrene on aquifer sand can be reduced by APU particles even at very low concentrations. This result can be also interpreted in terms of the relatively low degree of APU particle sorption on the aquifer sand. So, this result also shows that APU particles had a greater extraction performance than Triton X-100 because of a low degree of sorption on the soil.

For APU700-2 particles showing lowest solubilizing effect, the fraction of phenanthrene in the aqueous phase slightly increased with the concentration of APU700-2 particles in the aqueous phase. This may

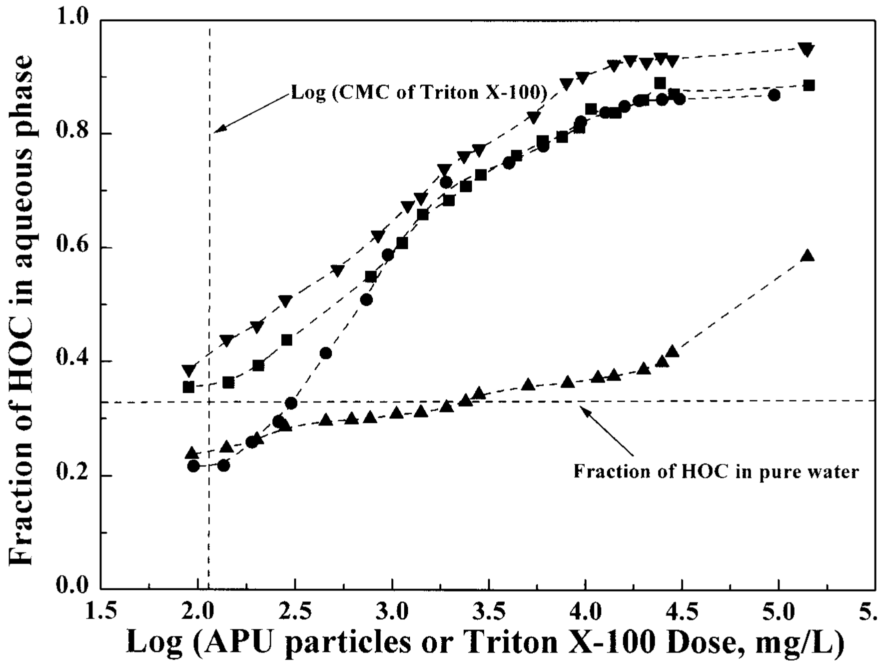


Figure 7 Distribution of phenanthrene between soil and the aqueous pseudophase containing Triton X-100 or APU particles. We performed the experiments by mixing phenanthrene aqueous solution after mixing soil with APU or Triton X-100 solution for 48 h: (●) Triton X-100, (▲) APU700-2, (■) APU700-3, and (▼) APU1000.

have been due to the weakest affinity of APU700-2 particles with phenanthrene. Because APU700-2 particles have smaller poly(ethylene oxide) chains compared with APU700-3 and APU1000 particles, the stability of APU700-2 particles on contact with aquifer sand was lower than that of APU700-3 and APU1000 particles, which led to a larger degree of sorption onto the aquifer sand. As consequence, at lower concentrations, the fraction of phenanthrene in the aqueous phase containing those particles was smaller compared with pure water.

We also examined the sorption of phenanthrene onto the aquifer sand that was premixed with Triton X-100 or APU particles for 48 h. At the same concentration of APU particles or Triton X-100, the fraction of phenanthrene in the aqueous phase, as represented in Figure 7, was smaller than those of phenanthrene, as plotted in Figure 6. This may have been because of the enhanced sorption of Triton X-100 and APU particles on the aquifer sand. So, the premixing of Triton X-100 with aquifer sand may have largely increased the sorption of Triton X-100 on aquifer sand, resulting in an increase of the partitioning of phenanthrene in aquifer sand. Although APU particles also showed the decrease in the fraction of phenanthrene in aqueous phase, the fraction of phenanthrene in the aqueous phase in the range of low concentration was still greater compared with the pure water phase. This result also showed the low degree of sorption of APU particles on aquifer sand compared with Triton X-100.

Recovery of Triton X-100 and APU particles through ultrafiltration

After the completion of the surfactant-enhanced soil-washing process, the aqueous pseudophase containing entrapped HOCs and surfactant should be treated before reinjection into the soil. Use of an ultrafiltration process has been suggested for the separation of HOCs and surfactant from the aqueous phase.[11,35,36] If the size of surfactant micelles is larger than the pore size of the ultrafiltration membrane, most of the surfactant micelles solubilizing HOCs can be rejected by the ultrafiltration process, whereas surfactant monomers, smaller than membrane pores, cannot be filtered and collected. As a consequence, 100% recovery and separation of the surfactant from the aqueous phase cannot be achieved. However, the size of APU particles (<100 nm) is much larger than that of surfactant micelles (a few nanometers), and there is no dissolved UAN chain in the APU aqueous pseudophase. So, it can be expected that 100% of APU particles could be separated with a separation membrane with a relatively larger pore size.

Figure 8 shows the retention recovery of APU articles and Triton X-100 as function of V/V_0, where V_0 is the volume of the starting aqueous solution. Retention recovery was calculated based on the following equation:

$$\text{Retention recovery} = (W_r \times C_r)/(W_0 \times C_0)$$

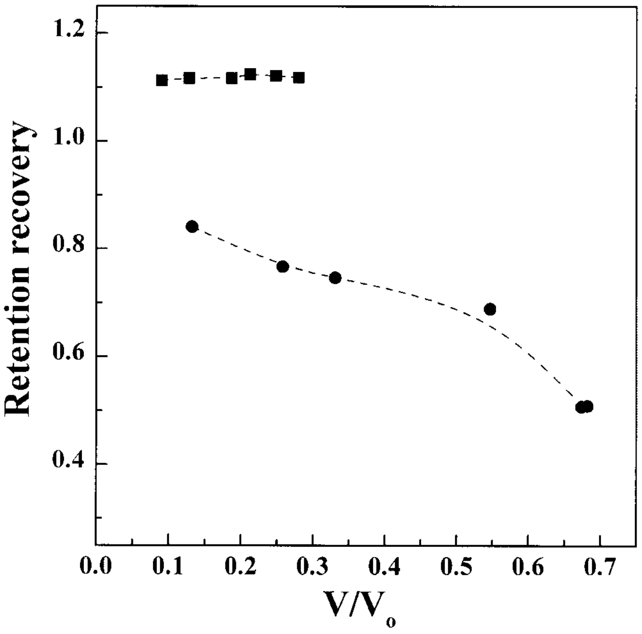


Figure 8 Retention and filtration of APU1000 and TritonX-100 solution through ultrafiltration process: (●) Triton X-100 (1180 mg/L) and (■) APU1000 (1180 mg/L).

where W_r is the total weight of the retentate, W_0 is the weight of the starting materials, C_r is the retentate concentration, and C_0 is the starting material concentration.

Retention recovery of Triton X-100 largely decreased (from 0.84 to 0.495) with increasing V/V_0, indicating that most of Triton X-100 permeated through the separation membrane. So, the ultrafiltration process could not separate Triton X-100 micelles containing phenanthrene from the aqueous phase. For APU particles, however, the value of retention recovery was always greater than 1.0 at various V/V_0. This result indicates that almost 100% of APU particles were rejected and collected by the separation process at the same pore size of membrane. That is, APU particles and entrapped phenanthrene could be recovered from the aqueous phase through the filtration process. From the industrial application viewpoint, the flow rate through the membrane is one of the important factors. As the pore size, or MWCO, of the separation membrane increases, the flow rate increases, but retention recovery or separation efficiency decreases. Even though surfactant molecules can be effectively separated with a very small pore size of the membrane, the flow rate may be too small, causing an increase in the time and cost of the separation process. At the same pore size (MWCO) of the membrane, although Triton X-100 molecules cannot be separated, almost 100% recovery of APU particles was effectively achieved, which would reduce the time and cost of the separation process at a greater flow rate.

CONCLUSIONS

APU particles synthesized based on amphiphilic UANs could solubilize phenanthrene within their hydrophobic interiors in the same way that surfactant micelles do in the aqueous phase. Although APU particles have weaker interactions with phenanthrene compared with Triton X-100, APU particles and Triton X-100 showed almost the same extraction efficiency. When the concentration of APU or Triton X-100 was smaller than or a little greater than the CMC of Triton X-100, APU700-3 and APU1000 emulsions exhibited a greater extraction efficiency than Triton X-100 solutions. This was due to the relatively larger degree of sorption of Triton X-100 molecules on the aquifer sand, causing a reduction in the extraction efficiency of Triton X-100. For APU particles, however, sorption on the aquifer sand was smaller compared with that of Triton X-100 because of the chemically crosslinked structure; as a consequence, APU particles could effectively extract sorbed phenanthrene, regardless of the weaker affinity with phenanthrene. APU particles could also be 100% recovered through an ultrafiltration process at a greater separation membrane pore size, which will make soil-washing processes with APU particles more economical and useful in practical applications.

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