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Preparation of micro- and nano-emulsions of soybean oil and removal of sorbed phenanthrene from sandy soil

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ABSTRACT

Soybean oil was used as a biodegradable extracting agent for the removal of sorbed phenanthrene (PHE) in sandy soil. In this study, several methods of forming emulsions using soybean oil and their extraction properties were investigated. The stable and homogeneous oil emulsions were formed more effectively by ultrasonication (U1) than by homogenization (H1). Moreover, homogenization before ultrasonication (HU1) established more stable emulsions than U1 alone. The mean diameter of oil droplets in U1 or HU1 was reduced to the nanometer range (approximately 70 nm) by U1 with 750 W using a high-power sonic tip operated at 33% amplitude and 20 kHz frequency for 5 min. The extraction efficiency of sorbed PHE from soil by oil emulsions increased with decreasing size of droplets of oil emulsions; the maximum extraction of PHE was achieved with HU1. Thus, nano-emulsions of vegetable oil made by U1 could be an environmentally benign alternative for effectively washing soil.

Keywords: Emulsion; Phenanthrene; Soil washing; Soybean oil; Ultrasonication

1. Introduction

Remediation of soil contaminated with hazardous hydrophobic organic compounds (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), is a major environmental concern because of the toxic and carcinogenic properties of these compounds [1–3]. Due to their hydrophobicity, PAHs have low water solubility and are strongly adsorbed to soils and sediments. Therefore, biodegradation of PAHs is very slow, resulting in their persistence in environments over long periods of time. In this way, soil and sediments progressively become rich sources of PAHs like benz(a)pyrene [4]. A potential technology for rapid removal of sorbed PAHs from soils involves washing with a surfactant solution [5,6]. The use of a surfactant enhances the solubility of HOCs significantly by partitioning them into the hydrophobic cores of surfactant micelles [7–9]. While the use of surfactants significantly enhances the performance of soil washing, operation costs increase as surfactant dosages increase; additionally, surfactant recovery can be required [10,11].

Edible oils are relatively inexpensive, innocuous, and biodegradable materials that have been used for soil and groundwater remediations. The oils can be

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used to stimulate biodegradation as a carbon substrate [12] and to extract hazardous organic contaminants as an effective solvent [13–15]. Recently, sunflower oils have been used for the extraction of soil contaminated with PAHs [14]. Emulsions, colloidal dispersions of at least two immiscible liquids, made with edible oils can be an alternative to enhance extraction of sorbed PAH in soil due to their high solubilization capacities and large surface areas [13]. The extraction properties of oil emulsions depend on the thermodynamic conditions of oil emulsions and their preparation methods [16]. Thus, the extraction efficiency of oil emulsions can be enhanced by forming oil droplets with smaller sizes. Oil emulsions with nano-sized oil droplets (typically in the range of 20–200 nm) are often referred to in the literature as nano-emulsions; these oil emulsions are of tremendous interest in food technology, cosmetics, lubrication, coatings, environmental science, and pharmaceutical field applications because of their high interfacial area, low viscosity, visibility to unaided eyes, prolonged shelf life, and stability against sedimentation or creaming (thermodynamically stable). Moreover, in this study, they are valuable because of their ability to solubilize HOCs due to the hydrophobicity of oil droplets [13,17]. Nano-emulsions are nonequilibrium systems, and the spontaneous formation of nano-emulsions cannot be achieved. Nano-emulsion formation is guided by high-energy emulsification methods involving high-speed stirring, high-pressure homogenization, and ultrasonication [18]. However, the treatment of toxic materials like PAHs from oil is required after soil washing process and it is very important from the environmental point of view as it is very toxic. There are different methods like countercurrent supercritical CO_2 extraction and activated carbon treatment to remove contaminants from oil [19]. The recycling of edible oil after soil washing process by removing the contaminants from the oil could reduce the operation cost of the method. The cross-flow microfiltration method could also be used to separate oil from the oil in water emulsions [20].

The objectives of this study are to establish methods for the formation of effective and stable emulsions using soybean oil and to investigate their efficiency in extracting sorbed phenanthrene (PHE), a three-ring PAH, from soil. The PHE is used as a model PAH in this study because of its low aqueous solubility, poor biodegradation rate, and potentially carcinogenic and toxic nature. The PHE is composed of three fused benzene rings and is derived from coal tar. Three different methods—homogenization (H1), ultrasonication (U1), and combined homogenization and ultrasonication (HU1)—were applied to develop the most stable and homogeneous nano-emulsions of soybean oil. The effectiveness of these emulsions in the extraction of PHE from contaminated soil was compared.

2. Materials and methods

2.1. Materials

The PHE (greater than 98% pure) and soybean oil were purchased from Aldrich (USA). The PHE is a three-ring polycyclic aromatic hydrocarbon with a molecular formula of $C_{14}H_{10}$. Soil with sand texture was purchased from Fluka (USA). Other analytical grade solvents were purchased from Sigma (USA).

2.2. Preparation of emulsions

Soybean oil was added to 50 mL deionized water at a final concentration of 10 g/L. Three types (H1, U1, and HU1) of emulsion were prepared with this solution. The first emulsion was homogenized (HHZ-200 N, Global Lab., Korea) at 5,000 rpm for 5 min (H1). The second sample was prepared using an ultrasonicator (Vibra Cell VCX 750, Sonics Materials Inc., USA) with high-power sonic tip operated at 750 W with 33% amplitude and 20 kHz frequency for 5 min (U1). The final emulsion involved both instruments (homogenization and subsequent ultrasonication) with the same conditions as described above (HU1). The mean diameters and size distributions of the three emulsions were measured at 0 and 30 days after storage at room temperature. The mean diameter was measured for emulsions prepared by ultrasonication at various operation times (0.5–10 min) and amplitudes varying from 7 to 67%.

2.3. Extraction of PHE

The effect of various emulsions on the extraction of sorbed PHE from soil was investigated. Sandy soil (200 mg) and 0.5 mL of methylene chloride containing 1 mg of PHE was added into a 20-mL glass vial. After evaporation of the methylene chloride, 10 mL of an emulsion was poured into the vial. The U1 emulsion diluted with deionized water was also investigated at various concentrations (10, 20, 50, and 100%). The vials were shaken at 180 rpm at 25.1°C for 6 h to reach equilibrium. The emulsion was sampled periodically to measure PHE extracted. All of the extraction experiments were conducted in triplicate, and the concentration of PHE in the solution was determined using high-performance liquid chromatography (HPLC, Dionex, USA).

2.4. Analysis

The mean diameter and size distribution of the particles in the emulsions were measured using a particle size analyzer (Beckman Coulter LS230, Brea, USA). Optical microscopic photographs of emulsions were taken using a Nikon Microscope Eclipse 80i (Japan). The oil content that was dispersed in the emulsion was determined from the dry weight difference after drying a 5 mL emulsion sample on an aluminum dish in an oven at 95˚C for 24 h. For PHE measurements, the emulsion sample (0.1 mL) was added into 0.9 mL of n-butanol/acetonitrile (4:1) solution to make a single phase. The solution was properly diluted and injected into the HPLC. The PHE was analyzed using an ultraviolet detector at 250 nm. The analytical column was a reversed phase Acclaim 120 column (250 mm × 4.6 mm). The mobile phase (85% acetonitrile and 15% deionized water) was eluted at a flow rate of 1.5 mL/min.

3. Results and discussion

3.1. Effect of emulsification method

Optical microscopic photographs of H1, U1, and HU1 emulsions were presented in Fig. 1.

In the case of H1, the size of the oil droplets was larger than U1 or HU1 and sparsely distributed in water. The contents of oil dispersed in emulsions were 0.19 ± 0.075, 0.70 ± 0.036, 0.60 ± 0.017 wt.% for H1, U1, and HU1, respectively. This data indicated that not all the added oil (1 wt.%) was dispersed in the emulsion; some portion of the oil (approximately 80% in H1, 30% in U1, and 40% in HU1) was present on the surface of the solution in the form of large droplets. The photograph of the H1 oil emulsion in a glass vial was bright white compared to U1 and HU1, which indicated that its amount of oil was less than in the others. The low content of dispersed oil when prepared by homogenization not only reduced the effectiveness of the emulsion as a washing solution, but also caused a handling problem due to the large amount of phase separation.

The size distributions of particles based of the various methods of preparation are presented in Fig. 2a. Table 1 shows that the mean diameters of the droplets of H1, U1, and HU1 were 2.61, 0.074, and 0.069 µm, respectively. The results showed that the ultrasonic methods (U1 and HU1) caused the formation of much smaller oil droplets than did the H1 method. The particle size distributions in volume percentage of emul-

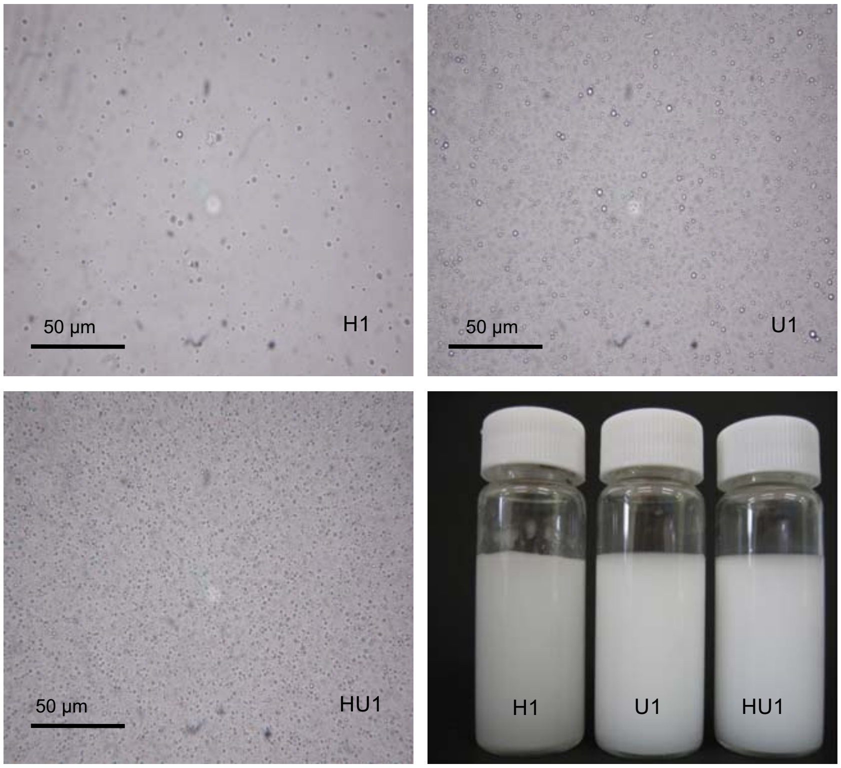

Fig. 1. Optical micrographs of various emulsions made by homogenization (H1), ultrasonication (U1), and mixed method (HU1) with 1% soybean oil.

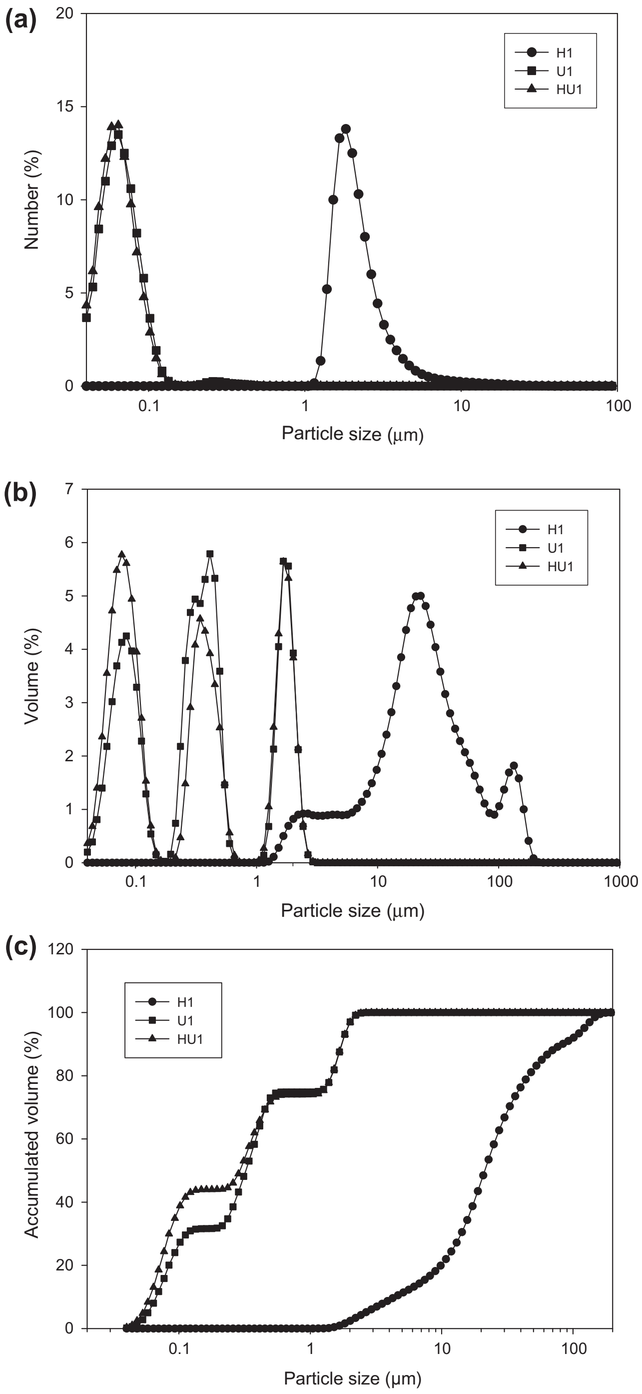

Fig. 2. Size distribution of emulsion particles made by various mixing methods: (a) number distribution, (b) volume distribution, and (c) accumulated volume distribution.

sions based on the preparation method are presented in Fig. 2b. The volume percentage of droplets for H1 was concentrated in the range of 1–200 μm diameters with a mean of 35 μm diameter. However, oil droplets of U1 and HU1 indicated that they contained a higher volume of small oil droplets relative to H1. The particle size distributions in volume percentage of both U1 and HU1 showed that the diameter varied from 0.04 to 2.9 μm. Fig. 2c shows particle size distributions in accumulated volume percentage. Less than 20% of droplets in H1 had diameters that were less than 10 μm. More than 75% droplets of U1 and HU1 had diameter less than 1 μm. Therefore, the particle size distribution results indicate that the droplets of U1 and HU1 were on the nanoscale and that the droplets of U1 and HU1 were much smaller than those of H1.

The dispersed degree of emulsion polydispersity, (P_a), is defined as:

$$P_a = \frac{\delta a}{\bar{a}} \tag{1}$$

where $\bar{a}$ is the average droplet radius and δa is the standard deviation. Alternatively, dispersion can be described by the uniformity factor, U, that is defined as:

$$U = \frac{1}{\bar{d}} \frac{\sum_i N_i d_i^3 \left|\bar{d} - d_i\right|}{\sum_i N_i d_i^3} \tag{2}$$

where $\bar{d}$ is the median size of distribution (the diameter for which the cumulative undersized volume fraction is 50%) and N_i is the total number of droplets with diameter d_i [18,19]. An emulsion with $P_a \approx 0.1$ or $U < 0.2$ is termed "monodisperse" [21,22].

The values of $\bar{d}$ that were obtained for H1, U1, and HU1 were 2.108, 0.0678, and 0.0653 μm, respectively. Using the values of these parameters in Equation 2, the U values were determined to be 15.4, 8.22, and 8.30 for H1, U1, and HU1, respectively; these results indicate that the oil emulsion samples were very polydisperse. The U values for H1, U1, and HU1 decreased to 11.7, 1.54, and 4.01, respectively, indicating that uniformity of the oil emulsions increased over the 30 days of storage.

As shown in Table 1, the polydispersity values of H1, U1, and HU1 were 0.89, 0.53, and 0.43, respectively. The values of polydispersity for H1, U1, and HU1 after 30 days of storage were 0.14, 0.42, and 0.40, respectively, indicating that polydispersity of the emulsions decreased over time. The mean diameter of particles in the H1 emulsion decreased to 1.84 μm after 30 days probably due to the aggregation of large droplets and the reduction of the amount of dispersed oils. The mean diameter of U1 and HU1 emulsion after 30 days increased moderately to 0.19 and 0.11 μm, respectively. The results indicate that ultrasonic methods can provide stable and uniform nano-emulsions compared to homogenization meth-

Table 1
Summarized size property of emulsions made by different mixing methods

Emulsion	Mean diameter (μm)		Polydispersity factor		Uniformity factor	
	0 d	30 d	0 d	30 d	0 d	30 d
H1	2.61	1.84	0.89	0.14	15.4	11.7
U1	0.074	0.19	0.53	0.42	8.22	1.54
HU1	0.069	0.11	0.43	0.40	8.30	4.01

ods. Homogenization before ultrasonication did not further reduce the droplet size, although it increased the stability during storage.

3.2. Optimization of ultrasonic method

In generating stable nano-emulsions, the ultrasonication method (U1) and the combined process of ultrasonication and homogenization (HU1) were found to be more effective than emulsions generated by homogenization alone. The optimization of conditions for the ultrasonic method was done by varying the duration of ultrasonication. As shown in Fig. 3, the mean diameter of droplets in the emulsion produced by 30 s or 1 min ultrasonication was approximately 2.6 μm.

Mean diameter size was dramatically reduced to 0.18 μm by employing ultrasonication for 2 min; no significant reduction in the mean diameter was noticed by prolonging the ultrasonication time beyond 2 min. The polydispersity factor was not significantly reduced by increasing ultrasonication time up to 10 min, indicating that the duration of ultrasonication had little effect on the polydispersity of U1 and HU1.

The droplet size in the emulsion produced by ultrasonication was found to decrease as the ultrasonication power increased. As shown in Fig. 4, the mean diameters of droplets were reduced from approximately 2.5 to 0.1 μm by enhancing the ultrasonication amplitude from 7% (53 W) to 33% (250 W) of 750 W. However, the size of the droplets did not decrease further by enhancing the amplitude of ultrasonication (750 W) up to 67% (500 W).

The polydispersity was also significantly reduced by increasing the amplitude of the ultrasonication power (750 W) up to 40% (300 W); further increasing the amplitude of ultrasonication up to 67% did not produce any further decrease in polydispersity. Thus, ultrasonication should be operated at 750 W with 33 to 40% amplitude for no longer than 2 min in order to obtain effective size distribution of droplets.

3.3. Extraction of PHE

Extraction efficiency of sorbed PHE from soil with various emulsions is presented in Fig. 5.

The removal efficiency of PHE increased in order of H1 < U1 < HU1, which inversely coincided with the pattern of droplet sizes (H1 > U1 > HU1). This trend

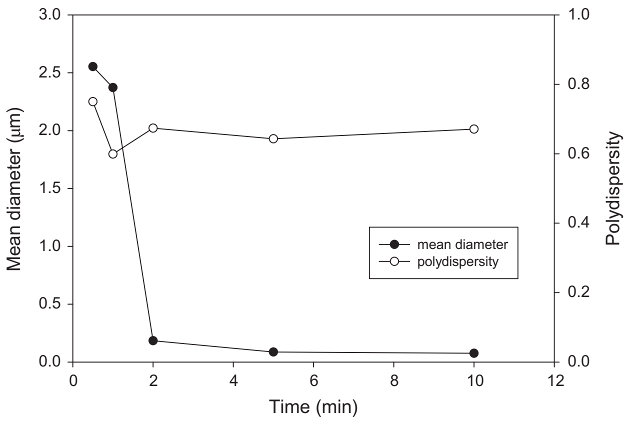

Fig. 3. Effect of operation time of 750 W ultrasonication operated at 33% amplitude and 20 kHz frequency on mean diameter and polydispersity of emulsion particles made with 1% soybean oil.

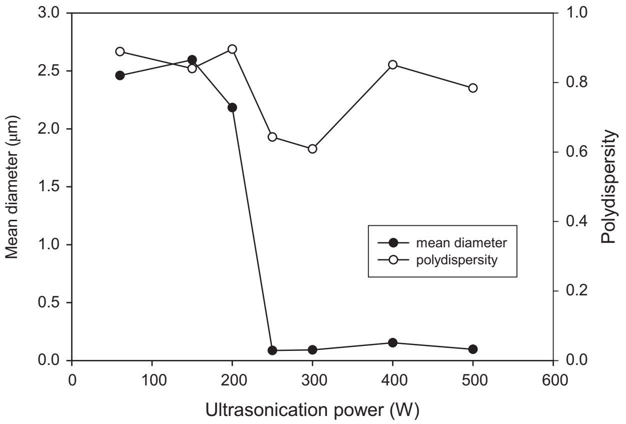

Fig. 4. Effect of ultrasonication power on mean diameter and polydispersity of emulsion particles made with 1% soybean oil and 10 min of ultrasonication.

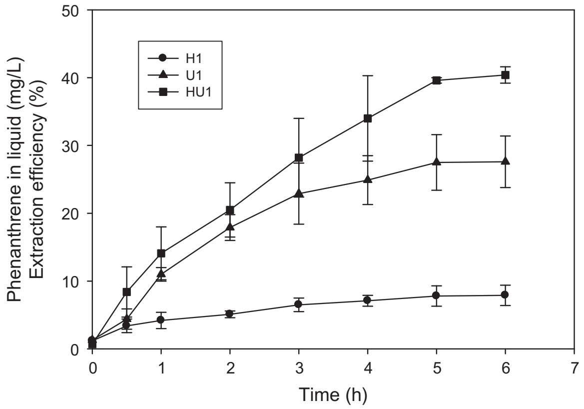

Fig. 5. Extraction of sorbed phenanthrene from sand by oil emulsions.

indicated that smaller size droplets in an emulsion were more effective for the extraction of PHE-contaminated soil. The average diameter of particles in U1 and HU1 was 74 and 69 nm, respectively, indicating that nano-emulsions formed by ultrasonication methods were more effective than micro-emulsions, with an average diameter of 2.61 μm, formed by homogenization method. The maximum extraction efficiency of PHE from soil was approximately 40.4%, which was obtained with HU1 after 6 h of extraction. The maximum removal of PHE from soil using H1 and U1 was 7.9 and 27.6% after 6 h of extraction, respectively. These results indicate that the emulsion prepared by HU1 was more effective in the extraction of sorbed PHE from soil than the emulsions formed by H1 or U1. Therefore, the combination of homogenization and ultrasonication could be used to develop stable oil nano-emulsions for maximum efficiency in the extraction of sorbed PHE from soil.

3.4. Effect of dilution

In examples of the washing process similar to slurry of soil mixed with water, the dilution of an injected emulsion is inevitable. The U1 was diluted to 10% (U1-10), 20% (U1-20), and 50% (U1-50) with deionized water; of the nondiluted U1(U1-100) was a control in this study. The size (mean diameter) of droplets and the ability to extract sorbed PHE from soil of the diluted emulsions (10, 20, 50, and 100% emulsion of U1) were studied. Fig 6a shows the particle size distribution in number percentage for dilutions of U1. The mean diameters of the droplets of U1 with 10, 20, 50, and 100% dilutions were 0.24, 0.23, 0.12, and 0.074 μm, respectively; this trend indicated that the mean diameter of the diluted emulsions significantly increased with successive dilutions.

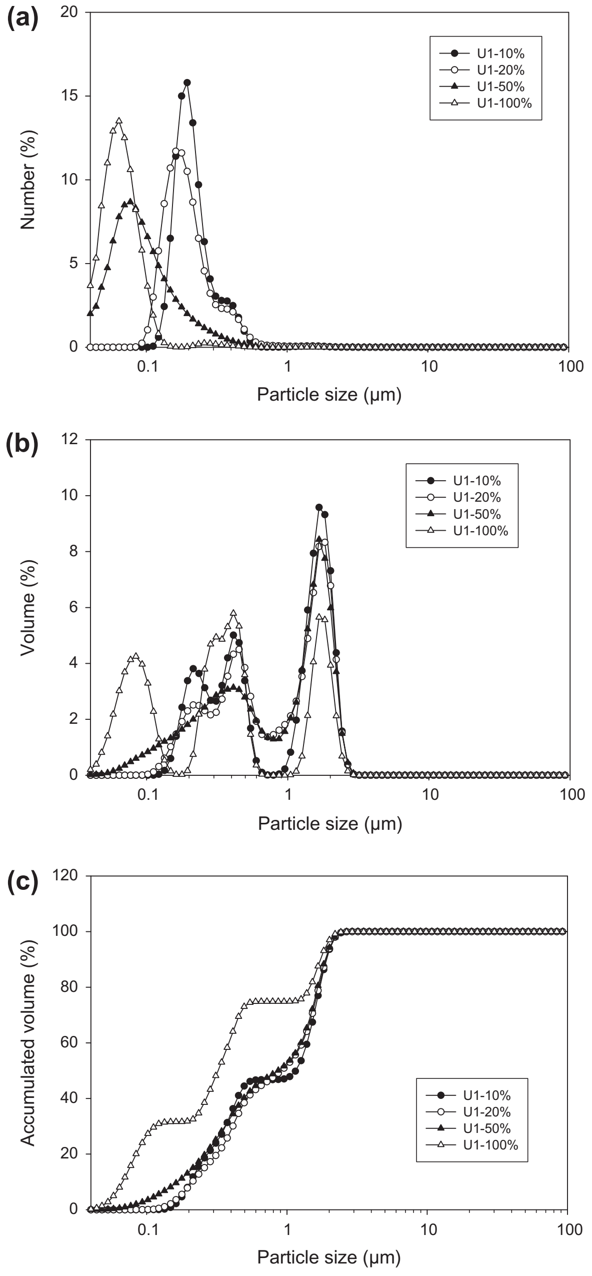

Fig. 6. Size distribution of emulsion particles with different dilutions: (a) number distribution, (b) volume distribution, and (c) accumulated volume distribution.

As shown in Fig. 6b, particle size distributions in volume percentage of the diluted emulsions indicated that the diameter range of droplets over all the dilutions of U1 was 0.04 to 3 μm. The samples of U1-10, U1-20, and U1-50 indicate that large oil droplets were found in higher volume than in the U1-100. Fig. 6c displayed the particle size distributions of U1-10, U1-20, U1-50, and U1-100 in accumulated volume percentage. More than 75% of droplets in U1-100 exhib-

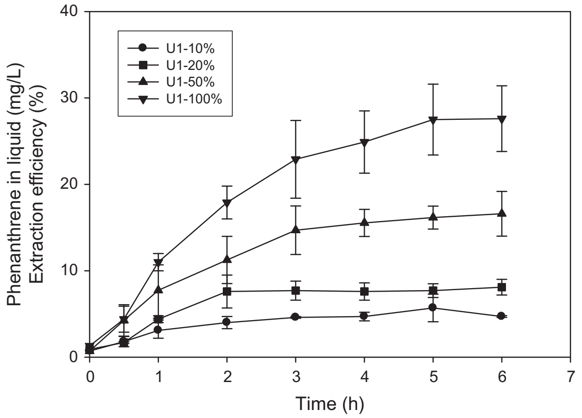

Fig. 7. Effect of dilution ratio of emulsions on extraction of sorbed phenanthrene from sand.

ited diameters less than 1 μm, whereas less than 50% of droplets from diluted samples of U1 had diameters less than 1 μm. Therefore, the particle size distribution results indicate that the mean diameters of U1 droplets were significantly increased by the dilution.

The PHE removal efficiency of U1-10, U1-20, U1-50, and U1-100 for sorbed PHE from soil is presented in Fig. 7.

The removal efficiency of PHE increased in order of U1-10 < U1-20 < U1-50 < U1-100, which inversely coincided with the pattern of the droplet sizes in the diluted nano-emulsions of U1. The maximum extraction efficiencies of PHE from soil using U1-10, U1-20, U1-50, and U1-100 were 4.7, 8.1, 16.6, and 27.6% after 6 h, respectively. These data indicate that the ability to extract PHE from contaminated soil was partially reduced by the dilutions. The maximum extraction efficiency with pure water was 1.1% at a PHE concentration of 1.1 mg/L in liquid, which is almost the same as PHE solubility. It is noticeable that even 10%-diluted U1 solution has 4.3 times higher extraction efficiency than water extract. Thus, the results suggest that the U1 nano-emulsion can be highly effective in extracting PHE from soil contaminated with PAH. However, for field applications, dilutions of injected oil emulsions should be considered in order to properly assess the effectiveness of emulsion-mediated soil washing to extract PAHs from contaminated soil. Additionally, the effect of residual of soybean oil in soil after extraction should be further considered. It might have positive effects on the biodegradation of PAHs residual tightly bound on soil by supplying additional carbon substrates or negative effects by some unknown secondary factors even though edible oils are not to be toxic in themselves.

4. Conclusions

Emulsions made from soybean oil were used to extract sorbed PHE from soil. Nano-emulsions were made by U1 of this edible oil in deionized water (74 nm particles), whereas homogenization produced micro-emulsions (H1) with larger sized droplets (2.61 μm). The combined method of H1 and U1 resulted in more stable nano-emulsions (HU1) with similar sized droplets (69 nm) as U1. The ability of these emulsions to extract PHE increased with decreasing size of oil droplets in emulsions. Diluting U1 reduced the extraction efficiency of sorbed PHE from soil. The reduction in the removal efficiency was inversely related to the increase in droplet size in the dilutions.

Acknowledgments

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