Application of surfactants and microemulsions to the extraction of pyrene and phenanthrene from soil with three different extraction methods

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Received 31 March 2007; received in revised form 3 June 2007; accepted 6 June 2007

Available online 8 June 2007

Abstract

In the present work, the use of surfactants and oil-in-water (O/W) microemulsions as alternative extractants in accelerated solvent extraction (ASE) for the extraction of polycyclic aromatic hydrocarbons (pyrene and phenanthrene) from soils was investigated. In particular, the effect of each individual component within the microemulsions, i.e., oil phase, surfactant and co-surfactant, and extraction conditions on the percentage recovery was systematically studied. When compared to the water and organic solvent, the important findings were that the common surfactant solutions at the concentrations above their critical micelle concentrations (CMC) were shown to enhance the percentage recovery at the lower extraction temperature. Moreover, the highest percentage recovery can be obtained using microemulsion as the extractant. The chemical component within the microemulsions and relative amounts of the oil phase appeared to play a much more significant role in ensuring high percentage recovery. Finally, an overall comparison between the percentage recoveries obtained with ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE) and ASE using organic solvents, surfactants and microemulsions as extractants was exhibited.

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Keywords: Surfactant; Microemulsion; Polycyclic aromatic hydrocarbons; Accelerated solvent extraction; Ultrasound-assisted extraction; Microwave-assisted extraction

1. Introduction

In recent years, there has been a growing research interest in the extraction of polycyclic aromatic hydrocarbons (PAHs) from environmental soil samples due to risks of them causing adverse effects to human health [1,2]. The conventional sample extraction methods (e.g., Soxhlet extraction and shake flask) have some drawbacks, such as long extraction time, large amount of organic solvents, labor intensive procedures and/or poor reproducibility [3]. Therefore, some new extraction techniques including ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE) and accelerated solvent extraction (ASE) have been developed.

The use of UAE has been shown to be a simpler and more effective alternative to the classical Soxhlet extraction method for the extraction of a variety of organic compounds from differ-

ent matrices, including the extraction of PCBs from soil [4] and PAHs from sediments [5], soil [6] and atmospheric aerosols [7]. ASE and MAE mainly take the advantage of the ability of solvents at elevated temperature and pressure in the enhancement of percentage recovery or the rate of extraction process [8]. Since the first commercial ASE instrument was introduced, it has been widely applied in the extraction of environmental organic pollutants in soil [9–11], aerosol [12], airborne particles [13] and smoked food samples [14]. MAE utilizes the microwave energy to cause molecular movement and liquids rotation with a permanent dipole, leading to a very fast heating of the solvent and sample. During the last few years, several applications utilizing MAE for the extraction of PAHs and PCBs from environmental solid samples have been published [15–18]. However, irrespective of the sophistication of these techniques, each approach has a common feature, i.e., choice of solvent.

The selection of suitable solvent systems is a key factor in the optimization of the extraction process, due to its significant effect on percentage recovery, kinetics and selectivity [19]. The predominant extractants in the applications for PAHs from soil are organic solvents such as hexane, cyclohexane,

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dichloromethane, and 1:1 (v/v) mixtures of acetone with one of the others [20]. However, organic solvents are toxic, expensive and difficult to be degraded. Recently, studies have demonstrated the use of micellar media as an alternative to organic solvent for extracting organic pollutants from solid environmental samples [21–24]. Moreover, Huie [25,26] and Ong [27,28] proved that the surfactant solutions in ASE can effectively extract the active ingredients in medicinal plants, and avoid the degradation of thermally unstable ingredients at high temperature. To the best of our knowledge, the reports on the use of environmental friendly surfactant solutions in ASE of PAHs from soil are rather limited.

Different from surfactant solution, microemulsions are solutions containing dispersed nanometer-sized droplets. It consists of a surfactant, a water-immiscible oil and a cosurfactant in a proper ratio so that a single, optically transparent and thermodynamically stable phase is formed [29]. Due to the special structure, microemulsion exhibits good wetting ability, moderate viscosity, low interfacial tensions and high solubilization for both hydrophilic and hydrophobic compounds [29], resulting in its wide application in separation science [30], polymerization [31], oil recovery [32], removal of organic pollutants from water [33] and *ex situ* soil washing [34]. However, the use of O/W microemulsion as alternative solvent system in ASE has not been reported.

In the present work, the effectiveness of employing different surfactant solutions (Triton X-100 and SDS) and microemulsions as the extracting medium in ASE was evaluated by comparing with conventional extractants (organic solvents and water) as a function of various experimental parameters, such as temperature and concentration of surfactant, for the extraction of PAHs (phenanthrene and pyrene) from soil. The influence of each individual component within the microemulsions, i.e., oil phase, surfactant and co-surfactant, and extraction conditions on the percentage recovery was systematically studied. Furthermore, an overall comparison between the percentage recoveries obtained with UAE, MAE and ASE using organic solvent, surfactant and microemulsion as extractants was exhibited. In addition, the percentage recovery screening analysis of phenanthrene and pyrene in soil using spectrofluorimetry was developed, which obviated costly and time-consuming chromatographic procedures and provided a rapid yes/no answer [35].

2. Experimental

2.1. Chemicals

Ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). All solvents used in the study were of analytical reagents (purity). Triton X-100, dodecyl sulfate sodium salt (SDS) and PAH standards pyrene and phenanthrene were obtained from Sigma–Aldrich (St. Louis, MO, USA) and their purities are greater than 99%. HPLC-grade ethyl acetate, diethyl ether, acetone, and hexane were purchased from LAB-SCAN (Patumwan, Bangkok, Thailand). *n*-Heptane (HPLC-grade) was purchased from Ajax (Auburn, Australia). 1-Propanol, 1-pentanol, 1-butanol and 1-octane were of spectro-

scopic grade and purchased from Acros (Pittsburgh, PA, USA). Stock standard solutions of each PAH at a concentration of 0.5 mg mL^{-1} were prepared in diethyl ether and stored at -4°C in the dark.

2.2. Sample preparation

Surface soil was collected from a sampling depth of 0–5 cm at a relatively uncontaminated grassland spot and was air-dried in a vacuum dryer at room temperature for 72 h. Then the soil samples were passed through a 10-mm sieve to remove large particles, e.g., stone, plant stalks, followed by grounding and passing through 1-mm sieve to produce samples with homogeneous particle size. The fine powdered soil samples were sealed and stored in a moisture-controlled cabinet.

The spiking procedures were as follows: first, 10 g of soil was weighed accurately and 50 mL of diethyl ether containing 20 or 40 μL of stock solution of phenanthrene or pyrene was added in order to obtain a total concentration of $1.0 \mu\text{g g}^{-1}$ phenanthrene or $2.0 \mu\text{g g}^{-1}$ pyrene (related to dry soil mass) that was within the linear range of phenanthrene or pyrene in extracts of blank soil. Then, the slurry was shaken for 4 h and the soil was completely dried by an N_2 stream. Finally, the soil samples were stored at -4°C for 12 h until use in order to establish sorption equilibrium. Unspiked blank soil was prepared with the same spiking procedure and an equivalent volume of diethyl ether without phenanthrene or pyrene stock solution.

2.3. Ultrasound-assisted extraction

1.0 g of accurately weighed soil was mixed with 10 mL of extractant in a 40-mL reagent bottle, and then placed in an ultrasonic cleaning bath (model 2510E-DTH, Branson, Danbury, CT, USA) for 1 h. Afterwards, the solution was centrifuged for 5 min at 2500 rpm. The two last steps were repeated two times. Finally, the soil extracts were collected, followed by filtering through nylon filters ($0.45 \mu\text{m}$) prior to fluorescence analysis.

2.4. Accelerated solvent extraction

ASE extractions were carried out using a Dionex ASE 200 system (Sunnyvale, CA, USA). To begin with, 1.0 g of soil sample was accurately weighed into the stainless steel cells (volume 11 mL) that had been prefitted with a cellulose filter at the bottom and the headspace was filled with diatomaceous earth (Dionex). The cells were placed in the carousel and the extraction was carried out with the particular solvent system. The automatic extraction sequence started with a dynamic extraction, during which the cell was heated to the preset extraction temperature in the oven and then solvent was continuously pumped through the sample. When the cell was full of extractant, the cell was heated and pressurized for a fixed time 10 min to ensure that the sample reached thermal equilibrium. Subsequently, the extraction continued under static conditions, i.e., with the preset extraction temperature and pressure for 5 min. After the static step, the extracts were purged from the sample cell with fresh solvent (50% of the empty extraction cell volume) under low pressure

for 60 s, and finally collected in the extract reservoir. All extracts obtained were filtered through a 0.45 μm nylon filter prior to fluorescence analysis.

2.5. Microwave-assisted extraction

A CEM MARS-1000 Microwave-assisted Reaction System (CEM Corporation, Matthews, NC, USA) was used. 1.0 g of accurately weighed soil was loaded into hermetically sealed PTFE vessels and 10 mL of particular solvent was added. The extraction vessels were closed and introduced into the microwave cavity. At the preset extraction temperature, the program was as follows: microwave power 600 W (100%), ramp to temperature for 10 min, hold at temperature for 10 min and pressure at 571.107 kPa. After fixed program was completed, the vessels were cooled to 25 °C, then opened and centrifuged at 1500 rpm for 5 min. Finally, the extracts were transferred into a bottle. All extracts obtained were filtered through a 0.45 μm nylon filter prior to fluorescence analysis.

2.6. Fluorescence measurements

All experiment results were recorded by an F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) and the peak height was used as analytical signal. The maximal excitation and emission wavelengths were fixed at 370 nm/466 nm for pyrene and 350 nm/400 nm for phenanthrene. All the spectra were obtained for excitation and emission slit widths of 5.0 nm and scanned at a rate of 240 nm min⁻¹.

3. Results and discussion

3.1. Percentage recovery screening analysis

Experiments on percentage recovery were carried out by spiking known concentration standards in the extracts of blank soil which was previously found containing very low amounts of PAHs. The percentage recovery was defined as the ratio of the peak height of the extracts of spiked soil to the peak height of the spiked extracts of blank soil (the amount of the added PAHs was equal in spiked soil and the extracts of blank soil). The validation study showed that the linear ranges were from 0.01 to 2.5 $\mu\text{g mL}^{-1}$ ($r=0.9968$) for phenanthrene and from 0.05 to 1.0 $\mu\text{g mL}^{-1}$ ($r=0.9953$) for pyrene. The detection limits (the ratio of signal-to-noise is 3) for phenanthrene and pyrene were 5.0 and 10.0 ng mL⁻¹, respectively. In this work, the evaluation of the extraction results was reflected by spectrofluorimetric method for the screening and determination of percentage recovery of phenanthrene and pyrene from soil.

3.2. Different solvent systems for the extraction of phenanthrene and pyrene

The percentage recovery of the different solvent systems in the ASE of two representative PAHs in soil, phenanthrene and pyrene, which possess a relatively large difference in polarity (e.g., the log K_{ow} is 4.46 for phenanthrene and 5.30 for pyrene),

Fig. 1. Comparison of different solvent systems (water, SDS solutions, Triton X-100 solutions, microemulsions and organic solvent) for the ASE of phenanthrene (A) and pyrene (B) at extraction temperatures of 50 and 120 °C. The average value of each bar was determined from the extraction of five samples. The extraction time and pressure for each solvent system were set at 10 min and 10342.14 kPa, respectively.

is illustrated in Fig. 1A and B. By comparing water and various concentrations of the aqueous non-ionic surfactant (Triton X-100) and anionic surfactant (SDS), it can be seen that at either of the extraction temperatures, the percentage recovery was almost the same among these three solvent systems when the concentrations of the surfactants Triton X-100 and SDS were 0.001% and 0.3 mM, respectively, which is far below CMC of Triton X-100 (ca. 0.03%) and SDS (ca. 8.2 mM), except that the percentage recovery of 0.3 mM SDS in the extraction of phenanthrene was a little higher, as shown in Fig. 1A.

However, it can be seen in Fig. 1A and B that when the surfactant concentrations were above CMC, the percentage recoveries appeared to increase as a function of surfactant concentration. It is interesting to note that the percentage recoveries of the two surfactant systems in the extraction of phenanthrene were higher than that in the extraction of pyrene. Furthermore, when the extraction temperature was increased from 50 °C to 120 °C, the percentage recoveries in the extraction of pyrene increased dramatically and the enhancement was much larger than that in

the extraction of phenanthrene. These results were likely in large part due to the weak polarity and the lower solubility of pyrene in water and aqueous surfactant solutions (compared to that of phenanthrene). These phenomena also indicated that the higher percentage recoveries of surfactant solutions for the ASE of the more hydrophobic PAH (Fig. 1B) were obtained at the higher extraction temperature (e.g., 120 °C). However, for the ASE of the less hydrophobic PAH (Fig. 1A) at lower extraction temperature (e.g., 50 °C), the percentage recovery of the surfactant solutions was satisfactory.

n-Hexane/acetone is one of the most commonly applied organic solvents in the research of PAHs extraction from soil, and 50%(v/v) acetone in *n*-hexane is the most proper constitution [20]. The data in Fig. 1 show that at higher extraction temperature of 120 °C, the use of *n*-hexane/acetone for the ASE of phenanthrene or pyrene from soil exhibited much higher percentage recoveries (e.g., higher than those obtained with 0.5 M SDS or 5% Triton X-100 and slightly lower than those obtained with microemulsions). However, at lower extraction temperature (e.g., 50 °C), the percentage recovery with *n*-hexane/acetone was found to be significantly lower. Importantly, Fig. 1A and B show that the percentage recovery of *n*-hexane/acetone at 50 °C was lower than that of the surfactants at concentrations above CMC. The ability of surfactant solutions in providing higher percentage recovery at a lower extraction temperature may be related to the solubility-enhancement effect of micelles.

In particular, Fig. 1 shows that compared to water, surfactant systems and organic solvents, the use of microemulsion systems for the ASE of phenanthrene or pyrene from soil presented almost the highest percentage recovery. When using microemulsions composed of 0.5 M SDS/1-butanol/1:1 (v/v) hexane:acetone at a volume ratio of 90:7:3, the percentage recovery obtained for the ASE of phenanthrene from soil reached ca. 97%. The higher percentage recovery was in large owing to the particular characteristics of the microemulsion (e.g., the wetting properties, moderate viscosity, low interfacial tensions and high solubilization capacity). It also can be seen that the percentage recoveries of non-ionic surfactant (Triton X-100) microemulsion systems were a little lower than those of anionic surfactant (SDS) microemulsion systems, which is likely due to the formation of highly viscous liquid crystals in the non-ionic surfactant microemulsion [36].

3.3. Types of cosurfactant and oil phase in the microemulsion

A microemulsion is a spherical aggregate comprised of a small amount of organic solvent (oil phase) dispersed in an aqueous surfactant solution in the presence of a cosurfactant. Usually, the highly hydrophobic and water-insoluble organic compounds are used to form the oil phase whereas an alcohol or ether with somewhat lower hydrophobicity (compared to the oil) is employed as a cosurfactant. In the present research, 1-propanol, 1-butanol and 1-pentanol were used as the cosurfactants in 0.5 M SDS solution in the presence of hexane:acetone 1:1 (v/v) as the oil phase to study the influence of the short-chain alcohols on the extraction. From the results it can be noted that

Fig. 2. The effect of different oil phases in the microemulsions for the ASE of phenanthrene and pyrene on the percentage recovery. The volume ratio of the surfactant, cosurfactant and oil phase in the microemulsions was 90:7:3. The extraction temperature was set at 120 °C. The extraction time and pressure for each solvent system were set at 10 min and 10342.14 kPa, respectively. The average value of each bar was determined from the extraction of five samples.

1-propanol and 1-butanol showed little effect on the percentage recovery, whereas the percentage recovery was dramatically decreased when 1-pentanol was used due to the increased viscosity of the solution. In this research, 1-butanol was selected as the cosurfactant because it is the most commonly used organic solvent in the microemulsion [37].

Fig. 2 shows the effect of different oil phases in the microemulsions for the ASE of phenanthrene and pyrene at an extraction temperature of 120 °C. It can be seen that the microemulsion composed of 0.5 M SDS/1-butanol/octane (90:7:3, v/v) was a better solvent for the ASE of the more hydrophobic pyrene, whereas for the ASE of the less hydrophobic phenanthrene, the microemulsion composed of 0.5 M SDS/1-butanol/1:1 (v/v) hexane:acetone (90:7:3, v/v) was better. Furthermore, the percentage recoveries of microemulsions with the much more hydrophobic oil core for the extraction of the more hydrophobic pyrene were higher than those for the extraction of the less hydrophobic phenanthrene, which indicated that the nature of the internal oil phase in the microemulsion had a pronounced influence on the percentage recovery.

3.4. Effects of different proportions of microemulsions

The effects of different proportions of cosurfactant and oil phase in the different microemulsions for the ASE of phenanthrene at an extraction temperature of 120 °C are shown in Fig. 3. It was noted that the percentage recovery was enhanced with the increase in the amount of oil. However, in the absence of the oil phase (e.g., the proportions of 0.5 M SDS/1-butanol at 95%:5% and 90%:10%, v/v), the percentage recoveries almost have no difference compared to that using 0.5 M SDS as extractant. Interestingly, at a constant amount of SDS, adding different oils to form the microemulsions at the volume ratio of 90:9:1,

Fig. 3. The effects of different proportions of cosurfactant and oil phase in the different microemulsions for the ASE of phenanthrene. The proportions are the volume ratios. The extraction conditions were the same as in Fig. 2.

the percentage recoveries were sharply enhanced. Moreover, for the extraction of the relatively less hydrophobic phenanthrene, the enhancement in the percentage recovery was little with the addition of more polar oil (e.g., octane). These results probably indicated that the enhancement of the percentage recovery of microemulsion in the ASE of phenanthrene may be mostly governed by the interaction of PAH, surfactant and oil phase. Furthermore, according to the nature of the oil (e.g., the polarity of oil phase), PAH can strongly favor inclusion into the oil. However, for the cosurfactant, as a component of microemulsion in the extraction process, it may only reduce the surface tension to further stabilize the extraction system. The explanations of the exact mechanism are ongoing.

3.5. Effects of pressure and temperature using microemulsion

The ability of using high pressure and high temperature to enhance or accelerate the extraction of phenanthrene from soil was investigated. Fig. 4A shows that when microemulsion containing 0.5 M SDS/1-butanol/1:1 (v/v) hexane:acetone at a volume ratio of 90:7:3 was used as extractant, the increase in pressure from 3447.38 to 10342.14 kPa led to an increase of percentage recovery, but it remained relatively constant from 10342.14 to 17236.9 kPa. On the other hand, the percentage recoveries were increased as a function of temperature from 50 to 150 °C (200 °C being the upper temperature limit of the ASE used), but when the extraction temperature was above 120 °C, the enhancement of the percentage recovery became unobvious. These results were largely because higher temperatures decrease the viscosity of the extractant, allowing better penetration of matrix particles, and higher pressures force extractant to be in complete contact with the matrix, resulting in an enhancement of the extraction process.

In contrast, Fig. 4B shows that when using hexane:acetone 1:1 (v/v) as the extractant, the pressure had little influence on the

Fig. 4. Comparison of microemulsion (A) composed of 0.5 M SDS/1-butanol/1:1 (v/v) hexane:acetone at a volume ratio of 90:7:3 and hexane:acetone 1:1 (v/v) (B) for the ASE of phenanthrene as a function of pressure and temperature. The extraction time for each solvent system was set at 10 min.

percentage recovery because the pressure was only used to maintain the organic solvent as liquids at or above its atmospheric boiling point. However, with the increasing extraction temperatures, percentage recovery was enhanced due to the faster mass transfer rates.

3.6. Comparison of UAE, MAE and ASE methods for extraction of phenanthrene and pyrene

An overall comparison between the percentage recoveries obtained with the different extraction techniques UAE, MAE and ASE for the extraction of phenanthrene and pyrene as a function of time, pressure and temperature using 0.5 M SDS, hexane:acetone (1:1, v/v) and microemulsion composed of 0.5 M SDS/1-butanol/1:1 (v/v) hexane:acetone (90:7:3, v/v) as the extractants is shown in Tables 1–3. When viewed as a whole, it was indicative that ASE led to slightly better percentage recovery than the other methods. Moreover, MAE provided the overall lowest SD-values.

Table 1

Comparison of UAE, MAE and ASE methods for the extraction of phenanthrene and pyrene using 0.5 M SDS as the extractant

Method	Time	Temperature (°C)	Pressure (kPa)	Recovery (%) ^a	
				Pyrene	Phenanthrene
UAE	1 h + 1 h	4	101.325	68.7 ± 0.86	77.4 ± 0.82
UAE	1 h + 1 h	50	101.325	66.3 ± 0.95	75.8 ± 0.91
UAE	10 min	4	101.325	41.4 ± 0.76	67.7 ± 0.84
MAE	10 min	50	517.107	51.8 ± 0.68	67.1 ± 0.75
MAE	10 min	90	517.107	67.4 ± 0.73	72.8 ± 0.81
MAE	10 min	120	517.107	73.5 ± 0.78	79.3 ± 0.85
ASE	10 min	50	10342.14	65.6 ± 2.02	73.6 ± 2.08
ASE	10 min	90	10342.14	72.8 ± 1.92	76.3 ± 2.01
ASE	10 min	120	10342.14	78.3 ± 1.96	80.7 ± 1.91

^a The average value was determined from the extraction of five samples.

Table 2

Comparison of UAE, MAE and ASE methods for the extraction of phenanthrene and pyrene using hexane:acetone 1:1 as the extractant

Method	Time	Temperature (°C)	Pressure (kPa)	Recovery (%) ^a	
				Pyrene	Phenanthrene
UAE	1 h + 1 h	4	101.325	78.2 ± 0.54	86.6 ± 0.52
UAE	1 h + 1 h	50	101.325	70.5 ± 0.63	82.3 ± 0.59
UAE	10 min	4	101.325	61.3 ± 0.51	69.7 ± 0.53
MAE	10 min	50	517.107	62.7 ± 0.45	78.1 ± 0.49
MAE	10 min	90	517.107	69.3 ± 0.49	84.2 ± 0.53
MAE	10 min	120	517.107	78.6 ± 0.52	89.5 ± 0.55
ASE	10 min	50	10342.14	50.2 ± 1.13	70.5 ± 1.15
ASE	10 min	90	10342.14	68.4 ± 1.08	80.8 ± 1.12
ASE	10 min	120	10342.14	82.1 ± 1.07	94.2 ± 1.16

^a The average value was determined from the extraction of five samples.

Compared to the data in Tables 1 and 3, it was noted that using hexane:acetone (1:1, v/v) as solvent for UAE of phenanthrene and pyrene, the percentage recoveries were much better than those obtained with using the surfactant and microemulsion as solvents as shown in Table 2, which is possibly due to the lower viscosity of organic solvent than that of surfactant and microemulsion at lower temperature, resulting in the faster transfer rate. Interestingly, in Tables 1 and 3, the percentage recoveries of UAE decreased markedly for the more hydrophobic pyrene when the extraction time was reduced from 2 h to 10 min. It was clear that longer extraction time was required for complete UAE of the water-insoluble pyrene when

surfactant and microemulsion were used as solvents. Moreover, at 50 °C, it is important to note that the percentage recoveries of UAE with extraction time of 2 h were almost near to those of ASE with the extraction time of 10 min, which indicated that the mass transfer rate in UAE was much lower than that in ASE.

On the other hand, the data in Tables 1–3 indicate that using MAE as the extraction method, the percentage recoveries decreased with the decrease in the extraction temperature. Especially for the extraction of the more hydrophobic pyrene with surfactant as solvent (in Table 1), the percentage recoveries decreased sharply (e.g., from 73.5% to 51.8%) when the temperature dropped from 120 to 50 °C. Compared to the data in

Table 3

Comparison of UAE, MAE and ASE methods for the extraction of phenanthrene and pyrene using 0.5 M SDS/1-butanol/1:1 (v/v) hexane:acetone as the extractant

Method	Time	Temperature (°C)	Pressure (kPa)	Recovery (%) ^a	
				Pyrene	Phenanthrene
UAE	1 h + 1 h	4	101.325	72.4 ± 0.82	82.6 ± 1.03
UAE	1 h + 1 h	50	101.325	69.6 ± 0.96	79.3 ± 1.08
UAE	10 min	4	101.325	52.1 ± 0.87	64.4 ± 0.92
MAE	10 min	50	517.107	66.5 ± 0.71	81.5 ± 0.73
MAE	10 min	90	517.107	73.6 ± 0.74	88.3 ± 0.75
MAE	10 min	120	517.107	79.1 ± 0.76	95.4 ± 0.81
ASE	10 min	50	10342.14	71.2 ± 1.93	85.2 ± 2.05
ASE	10 min	90	10342.14	78.4 ± 1.87	93.6 ± 1.94
ASE	10 min	120	10342.14	83.2 ± 1.83	97.1 ± 1.92

^a The average value was determined from the extraction of five samples.

Tables 1 and 2, Table 3 shows that the highest percentage recovery of MAE can be obtained using microemulsion as solvent in the extraction of pheanthrene, which was still slightly lower than that in ASE at the higher temperature 120 °C (e.g., 95.4% for MAE and 97.1% for ASE).

4. Conclusions

In the present work, the use of surfactants and O/W microemulsions, instead of toxic and expensive organic solvents, as the extractants in ASE for the extraction of PAHs (pyrene and phenanthrene) from soils was investigated. Compared to the organic solvents as the extractants, the addition of common surfactants (SDS and Triton X-100) in water at concentrations above CMC was found to enhance the percentage recovery at low extraction temperature. In other words, for avoiding the degradation of thermally unstable PAHs in soil, surfactant solutions can be used as extractants in ASE at low extraction temperature. On the other hand, this current research proved that the percentage recoveries of microemulsion as extractant were much higher than those using surfactants and organic solvents as extractants. Moreover, compared to the surfactants and cosurfactants, the chemical composition and relative amounts of the oil phase within the microemulsions appeared to play a much more significant role in ensuring high percentage recovery. For the extraction of the more hydrophobic PAH, the higher percentage recovery can be obtained by using microemulsion composed of strong polar oil phase and cosurfactant. By comparing the three extraction techniques (UAE, MAE and ASE) with different extractants as shown in Tables 1–3, as a whole, the highest percentage recovery can be obtained by using microemulsion as solvent in ASE. These results demonstrate that the microemulsion technique of ASE is very efficient in the extraction of PAH from soil and can be easily implemented with existing laboratory equipment.

Sample preparation is a critical step in chemical analysis. The present research demonstrated the feasibility of utilizing aqueous surfactant solutions and microemulsion as novel solvent systems for the extraction of PAHs from soil, thus avoiding the use of volatile, toxic and flammable organic solvents. Especially, the microemulsion system proved to be more effective than surfactant and organic solvent systems. Such analytical capabilities should be important for the rapid screening of chemical pollutants present in environmental solid matrices.

Acknowledgements

This work was supported by the Natural Science Foundation of China (Nos. 20437020, 20621703) and Major Research Program of Chinese Academy of Sciences (KZCX3-SW-432).

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