Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Ultrasonic Assisted Cloud Point Extraction of Polyaromatic Hydrocarbons

Bingjia Yao[a]; Li Yang[a]
[a] School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai, China

To cite this Article Yao, Bingjia and Yang, Li(2007) 'Ultrasonic Assisted Cloud Point Extraction of Polyaromatic Hydrocarbons', Separation Science and Technology, 42: 8, 1843 — 1858
To link to this Article: DOI: 10.1080/15363830701313438
URL: http://dx.doi.org/10.1080/15363830701313438

Separation Science and Technology, 42: 1843–1858, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/15363830701313438

Ultrasonic Assisted Cloud Point Extraction of Polyaromatic Hydrocarbons

Bingjia Yao and Li Yang
School of Chemistry and Chemical Technology, Shanghai Jiao Tong
University, Shanghai, China

Abstract: Cloud point extraction (CPE) of three PAHs, anthracene, phenanthrene, and pyrene was performed in an ultrasonic environment with Tergitol TMN-6 as extractant. During the process, surfactant micelle aggregates came out gradually and deposited to form a surfactant-rich phase. Under the ultrasonic condition, an obvious higher phase separation speed was obtained than the process with heating alone. In the comparison with the conventional cloud point extraction process accelerated by centrifugation, the ultrasonic assisted process offered higher recoveries of the three PAHs with a similar or quicker speed, and relative high recoveries were still preserved even in a high initial PAHs concentration of 60 mg/L. Moreover, the water content in the surfactant-rich phase obtained by the ultrasonic process was lower than that by the centrifugation process when the surfactant concentration was lower than 2 wt%, leading to a higher preconcentration factor and treatment efficiency in a continuous water treatment process with CPE. Scaling up experiments of the new developed ultrasonic process were performed in the polluted water with different volumes, and recoveries of 80.4%, 92.6%, or 79.3% for anthracene, phenanthrene or pyrene respectively were obtained in 500 mL polluted water, which indicated the process had a great potential to be used in the water treatment in a large scale.

Keywords: Ultrasonic, cloud point extraction, Tergitol TMN-6, polyaromatic hydrocarbons

Received 18 October 2006, Accepted 28 January 2007
Address correspondence to Li Yang, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China. Tel.: 862154748917; Fax: 862154741297; E-mail: liyangce@sjtu.edu.cn

INTRODUCTION

Due to its high performance and no organic solvent used in the whole process, cloud point extraction (CPE) was thought to be an efficient and environmentally-friendly process with a wide future application (1–6). For example, CPE has been reported as a potential separation and preconcentration method for many hydrophobic substances with trace level, such as polyaromatic hydrocarbons (PAHs), alkylbenzene, and chlorobenzene, which widely existed in the water (7–12). However, most studies so far were concentrated in the analysis field. Contrast to a lab operation, a large scale and continuous CPE process is much desired, which should be qualified with:

1. high speed of phase separation between surfactant-rich phase and water phase;
2. low water content left in the surfactant-rich phase; and
3. available for the treated water in a large volume.

Till up to now, centrifugation or addition of salt was the main method to accelerate the phase separation of the CPE process, however, the former was high energy cost and unavailable for a large scale and continuous operation for its limited treatment capacity (3, 13, 14), moreover, the latter required a further desalting treatment to the water obtained by the CPE process, which resulted in decreasing the efficiency and increasing the cost of the process (10, 15, 16).

In fact, water is the main part of the surfactant-rich phase, commonly around 80 wt% (17), and the water content was not only associated with the volume of surfactant-rich phase (Vs), but also with $Vs/(Vs + Vw)$ (Vw: the volume of aqueous phase after phase separation), which is usually in inverse proportion to the preconcentration factor, when the recovery of extractable species was high enough (18). In a continuous water treatment process, it is uneasy to remove the surfactant-rich phase in a timely fashion, so reducing the water content plays an important role in improving the efficiency and enlarging the treatment capacity of every unit cycle. Because the efficiency of every unit cycle of the process was determined by the treatment volume directly, a process suitable to a large-scale treatment volume is aspired. Although a rotating disk contactor process was reported to offer a large scale operation for CPE, the physical stirring decreased the phase separation performance and resulted in a relatively high surfactant content in the water phase (19, 20).

Most reports so far concerning the application of ultrasonic in the traditional extraction were focused on ultrasonic assisted extraction, which offered a higher recovery and large saving of extraction time, compared with normal extraction methods (21–26). In the CPE process, ultrasonic was also reported to speed the transfer of the extractable species from surfactant-rich phase into the stripped solution in back-extraction (27). In this research, the ultrasonic environment was introduced into the phase separation process of CPE. Ultrasonic energy was able to help weaken the hydrogen bondings between water molecules and surfactant micelles, and the generation of surfactant aggregates would probably be accelerated in the ultrasonic environment (28, 29). What is more, based on its flocculation effect, ultrasonic was also expected to offer different vibration frequencies for surfactant aggregates with various volumes, which was supposed to speed their combination and the formation of the surfactant-rich phase, offering a quick phase separation; moreover, the different vibration frequencies between extractable species and micelles was also thought to be beneficial for increasing their contact chances, leading to an increase of the recovery (30).

An obvious positive influence of ultrasonic was observed in our study when Tergitol TMN-6 was employed as the extractant in the CPE process. Tergitol TMN-6 has little absorption in ultraviolet (UV) detection, thus its surfactant-rich phase was able to be injected into HPLC with UV detector directly, which largely facilitated the determination process of species. In this paper, the advantages of ultrasonic assisted CPE (Us-CPE) instead of CPE processes with heating alone (H-CPE) or with centrifugation (C-CPE) were compared. Phase separation process, recoveries of three PAHs, anthracene (Anth), phenanthrene (Phen), and pyrene (Pyre), surfactant-rich phase volume and its water content were used to evaluate their performances in detail.

EXPERIMENTAL

Reagents

Tergitol TMN-6 obtained from Fluka (USA) is a mixture containing 90% active ingredients, whose structure is trimethylnonylpolyethylene glycol with an average ethylene oxide number of 6. Pyrene (98%), anthracene (99%), and phenanthrene (98%) were purchased from Acros Organics. HPLC-grade acetonitrile was from Calendon Laboratories Ltd., and the deionized water used in the mobile phase of HPLC was with a resistivity of 18.2 MΩ · cm. All the other reagents were of analytical grade and used without further treatment.

Apparatus

SCQ-300A ultrasonic bath system (Shanghai Shengpu Ultrasonic Instrument Factory, China) was used to provide an ultrasonic environment, having an adjustable ultrasonic power at 50 kHz and an incubation unit. The bath size is 46.5 cm $*$ 27 cm $*$ 26 cm. For the reproducibility, the position of sample tube was fixed in the ultrasonic bath for all the experiments. PE-series 200 HPLC system (Perkin Elmer, USA), including pump, degasser, auto injector, column oven, ultraviolet detector, and a TOSOH ODS gel column (4.6 $*$ 150 mm) were used to determine the amount of PAHs.

Procedure

Ultrasonic Assisted Cloud Point Extraction Procedure

A desired aqueous solution was obtained by mixing the surfactant aqueous solution and the stock solution of three PAHs, which was prepared by dissolving the respective solid specimen (around 0.1 g) into 50 mL acetonitrile at an appropriate volume ratio. The solution was contained in 10 mL graduated glass test tubes, and the ultrasonic pool with an incubation at a prescribed temperature (318 K, except indicated) was used to provide an ultrasonic environment at a certain power for some time (30 mins, except indicated). In the study of the effect of polluted water volume on the recovery, a glass beaker with a suitable volume was used. After the ultrasonic process, an incubation was followed to complete the deposition of the micelle aggregates produced during the ultrasonic, when the ultrasonic power was higher than 100 W. The volume of the surfactant-rich phase was determined by reading the graduation of the test tube. The aqueous top phase was removed by using a disposal pipette, and then 1 mL surfactant-rich phase was transferred into a sample bottle and sent to the HPLC analysis.

Other Cloud Point Extraction Procedures

In the cloud point extraction with heating alone (H-CPE), the surfactant solution containing PAHs, which was the same as the one used in the Us-CPE process, was put into an incubator set at a prescribed temperature (318 K, except indicated), then the phenomena of the phase separation in each H-CPE process in the following 2 hrs was observed. In the cloud point extraction accelerated by centrifugation (C-CPE), after an incubation at the prescribed temperature (318 K, except where indicated) over a 15 min period, the surfactant solution containing PAHs was taken into a 10 mL graduated centrifuge tube and treated by a centrifugation at 300 g for 30 min, except indicated. The volume and the composition of surfactant-rich phase in two CPE processes were determined in the same methods described above.

Analytical Procedure

The samples obtained from cloud-point extraction (5 μL aliquots) were injected into the HPLC system, which was equilibrated with 75 wt%

acetonitrile/water at a flow rate of 1.0 mL/min at 308 K. UV absorbance at 255 nm was monitored by using UV detector.

RESULT AND DISCUSSION

Phase Separation Process

Tergitol TMN-6 has a relative low cloud point (around 310 K), shown in Fig. 1, and like most nonionic surfactants, the addition of sodium chloride decreased its cloud point efficiently, and the effect increased with the concentration of the additive. Figure 2 depicts the process of the phase separation in Us-CPE. At a temperature higher than the cloud point, surfactant aggregates (SA) with different volumes gradually appeared in the surfactant micelle solution in the ultrasonic environment with a power higher than 66 W. The volume of SA increased with time, due to their combination between each other, and slowly fell to the tube bottom, on the basis of the difference of density. However, in the existence of ultrasonic with a power higher than 100 W, some SA kept floating in the solution or staying beside the tube wall, and did not fall down to the tube bottom until the ultrasonic stopped and underwent an incubation for a period of time at the ultrasonic temperature. Although the glass wall weakened the energy of ultrasonic transmitted into the surfactant micelle solution, the remainder was still sufficient to cause ultrasonic cavitation, and was believed to be strong enough to help to weaken

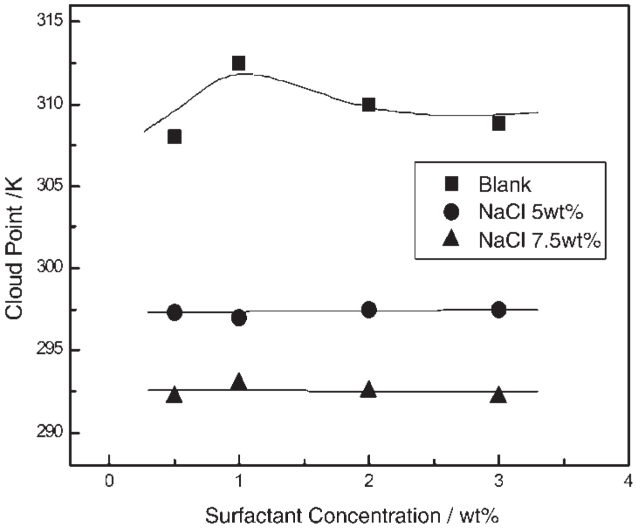

Figure 1. Cloud point of Tergitol TMN-6 in different concentrations.

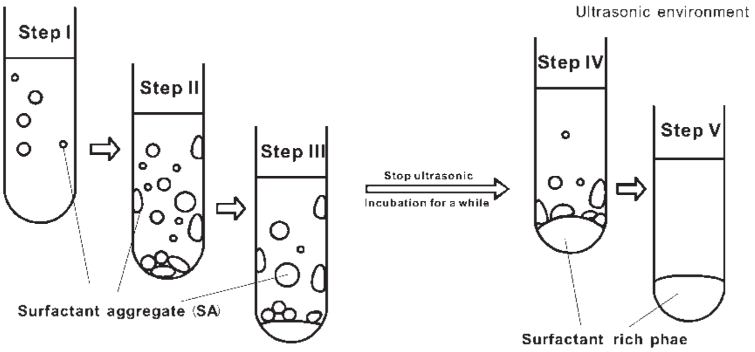

Figure 2. Pictorial steps involved in the Us-CPE process: Step I: surfactant aggregate (SA) came out with ultrasonic; Step II: SA increased and combined into larger ones with time; Step III: SA slowly fell to the tube bottom to form a surfactant-rich phase; Step IV: After ultrasonic stopped and underwent a period of incubation, the SA floating in the solution or staying beside the tube wall fell and formed the surfactant-rich phase; Step V: After about 5 min's incubation, the phase separation was finished (When ultrasonic power was blow 100 W, little SA floating or staying beside the tube wall, so no Step IV and V was needed).

the hydrogen bondings (28, 29) and responsible for the quick coming out of SA from the solution and its combination. In addition, another main effect of ultrasonic, steady-state cavitation effect, endowed with different vibration speeds to SA with different volumes, which was also thought to be beneficial for the formation of the larger SA and the final surfactant-rich phase.

Figure 3 compares the phase separation processes between Us-CPE and the CPE process with heating alone (H-CPE). Surfactant-rich phase volume increased with time in both two CPE processes; however, with heating alone, Vs increased very slowly and much more time was needed than Us-CPE for achieving the complete phase separation. In the case of low surfactant concentration solution (1 wt%), phase separation occurred relatively more difficultly, it was till 40 min's incubation that the surfactant-rich phase began to come out in H-CPE. In contrast, the introduction of ultrasonic accelerated the phase separation obviously; a visible surfactant-rich phase was able to be obtained in the first 20 min, and a complete phase separation was achieved within 1 hr. In the case of the conventional CPE process with centrifugation, the phase separation usually finished within 15 min, while another 15 min's incubation at the temperature higher than cloud point was necessary prior to the centrifugation process for a high recovery (31). Different time was required for Us-CPE to achieve the phase separation in different surfactant concentration solutions, and a higher ultrasonic power helped to increase the process speed. Therefore, it is foreseeable that Us-CPE with an enough high ultrasonic power was able to offer a quicker phase separation speed than H-CPE or C-CPE.

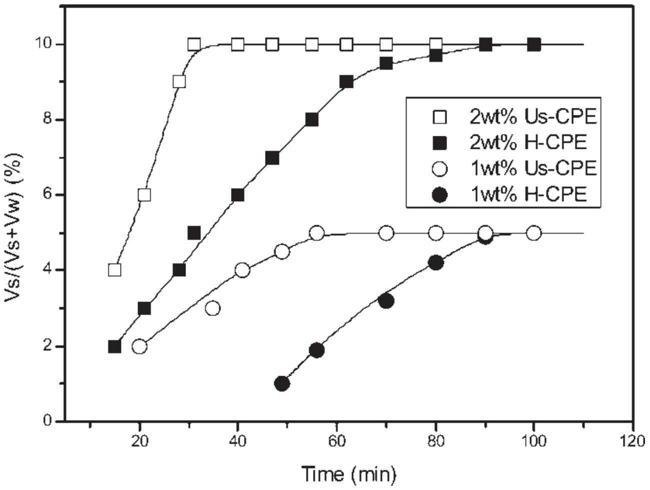

Figure 3. Comparison of the phase separation processes between Us-CPE[1] and the CPE process with heating alone (H-CPE)[2].

[1] Us-CPE: with 120 W ultrasonic power at 318 K.

[2] H-CPE: with an incubation at 318 K.

Water Content in Surfactant-rich Phase

In this research, the volume contributed by every specific mass surfactant in the surfactant-rich phase (Vs/Ms, Ms: Mass of surfactant in the surfactant-rich

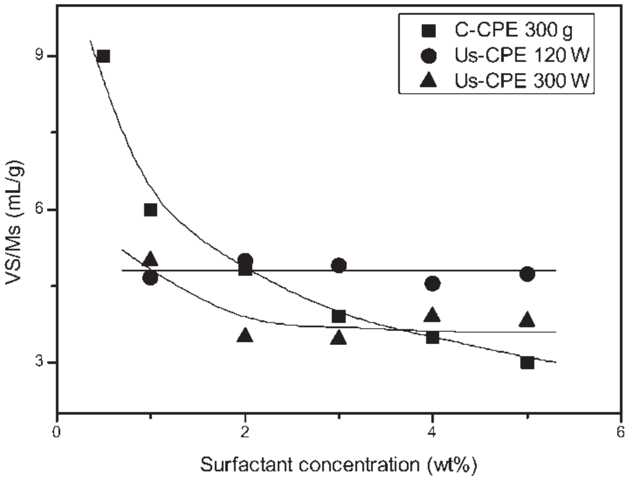

Figure 4. Vs/Ms obtained by Us-CPE or C-CPE in different surfactant concentration solutions.

phase) was used to compare the water content in the surfactant-rich phase. Lower Vs/Ms denoted lower water content. Since it was difficult to obtain the exact value of Ms, the mass of the surfactant in the whole solution was used as Ms for the evaluation when phase separation was finished. Figure 4 shows the values of Vs/Ms obtained by two CPE processes, Us-CPE and C-CPE, in different surfactant concentrations respectively. In C-CPE, Vs/Ms decreased sharply with the increase of surfactant concentration, the results with a centrifugation of 300 g were reported here. However, in Us-CPE, the surfactant concentration has a less effect on the Vs/Ms; and an almost constant Vs/Ms in different surfactant concentrations was obtained with a power of 120 W at 318 K. With a higher power of 300 W, the corresponding Vs/Ms became even lower in most cases. No matter with the power of 120 W or 300 W in Us-CPE, it was easy to obtain a lower Vs/Ms than C-CPE, when the surfactant concentration was lower than 2 wt%. The detailed report about the effect of ultrasonic power on the Vs/Ms is shown in Fig. 5. The Vs/Ms decreased with the increase of ultrasonic power at a same surfactant concentration (2 wt%). On the contrary, centrifugation speed had a lesser effect on Vs/Ms, and most values were higher than that obtained by Us-CPE. Due to the same surfactant concentration was used, Vs/(Vs + Vw) had a similar change tendency as that of Vs/Ms, and the Vs/(Vs + Vw) obtained by Us-CPE was also lower than that by C-CPE in most conditions. The results indicated that Us-CPE efficiently lowered the water content left in the surfactant-rich phase compared with C-CPE, when the surfactant concentration was lower than 2 wt%, a concentration range commonly used in CPE process, and

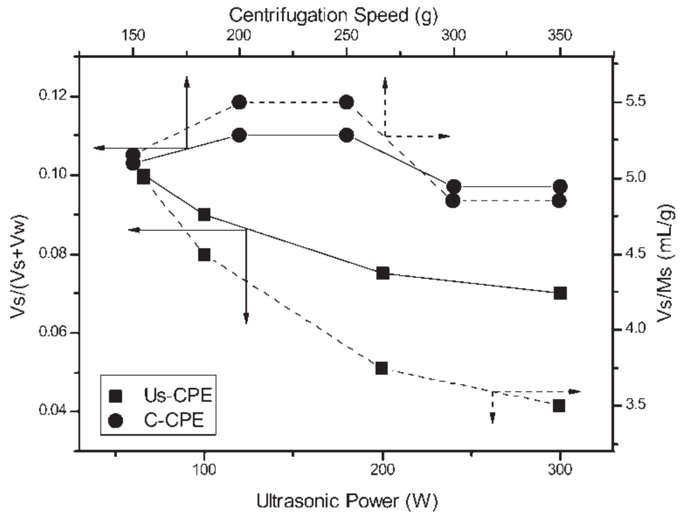

Figure 5. Vs/(Vs + Vw) and Vs/Ms obtained by Us-CPE or C-CPE process in different conditions with 2 wt% surfactant concentration.

a higher preconcentration factor was obtained. This great performance is important to large-scale applications, especially in the continuous water treatment system.

Recoveries of PAHs

The recovery of PAHs in Us-CPE system was investigated on the basis of the effects of various factors, i.e. the ultrasonic power, the experimental temperature, the surfactant concentration, the initial concentration of the PAHs, and the polluted water volume.

The chromatograms of the surfactant-rich phase containing three PAHs obtained from the Us-CPE process with 1 wt% Tergitol TMN-6 are shown in Fig. 6, where the initial PAHs concentration was 2 mg/L. The retention times of anthracene, phenanthrene and pyrene are 9.48, 10.26, and 13.41 min respectively. The surfactant had no interference with PAHs in the chromatogram obviously, and the surfactant-rich phase was able to be examined by HPLC directly, not needing any further clean-up treatment.

Effect of Ultrasonic Power

Figure 7 presented the recovery dependence as a function of ultrasonic power in Us-CPE system, in which the surfactant concentration was 2 wt%. A high recovery of Pyre over 96% was obtained in the entire whole ultrasonic power

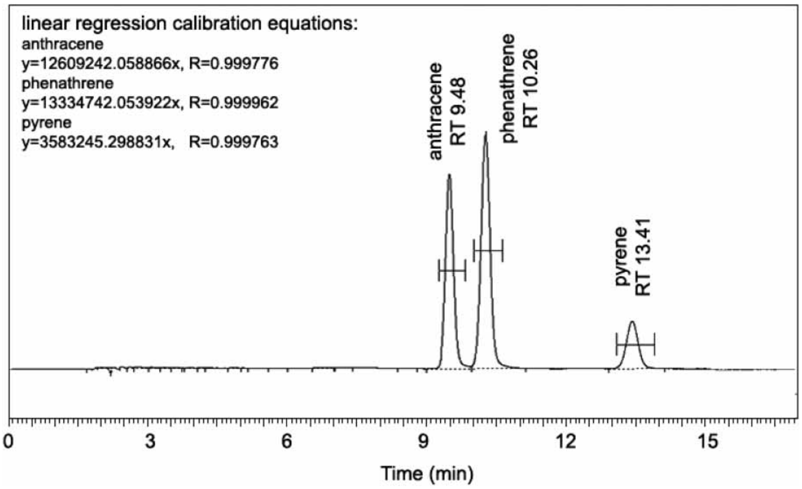

Figure 6. Chromatogram of the surfactant-rich phase obtained by CPE process with Tergitol TMN-6 (surfactant concentration: 1 wt%, initial PAHs concentration: 2 mg/L).

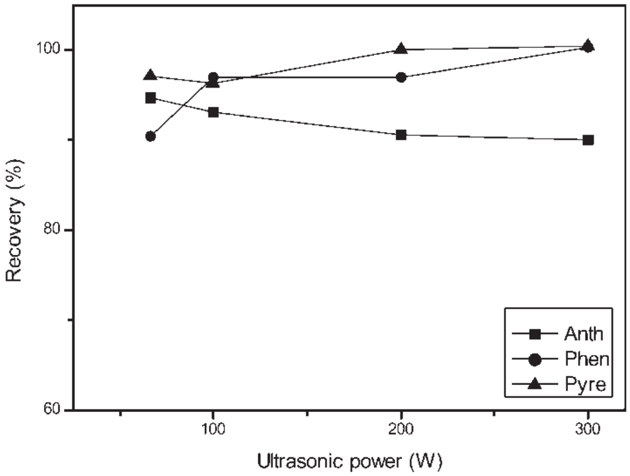

Figure 7. Recoveries of three PAHs obtained in Us-CPE with different ultrasonic powers in 2 wt% surfactant solution at 318 K.

range which was observed. For Anth, although a tiny decrease of recovery was observed with the increase of ultrasonic power, its recovery was still above 90% at a high ultrasonic power of 300 W. And a high and constant recovery of Phen was obtained when ultrasonic power was higher than 100 W. Thus for a high recovery above 90% of all the three PAHs, Us-CPE process should be performed with an ultrasonic power higher than 100 W.

Effect of Temperature

Us-CPE at different temperatures was performed in 2 wt% surfactant solution at an ultrasonic power of 120 W, and the corresponding recoveries were shown in Fig. 8. Recovery increased with temperature, and at a temperature above 318 K, the recoveries of the three PAHs stopped increasing and the maximum was obtained at a higher PAHs concentration. This means that a temperature of 318 K was sufficient to offer a high recovery.

Effect of Surfactant Concentration

Figure 9 illustrated the recoveries of PAHs obtained by Us-CPE and C-CPE as a function of surfactant concentration. A plateau of recoveries of the three PAHs was obtained in Us-CPE with a surfactant concentration higher than 2 wt%, where the recoveries were 99.6%, 91.1%, 80.5% for Anth, Phen, and Pyre respectively. In contrast, for C-CPE, recovery increased as the surfactant concentration rose up to 1 wt%, but above which it

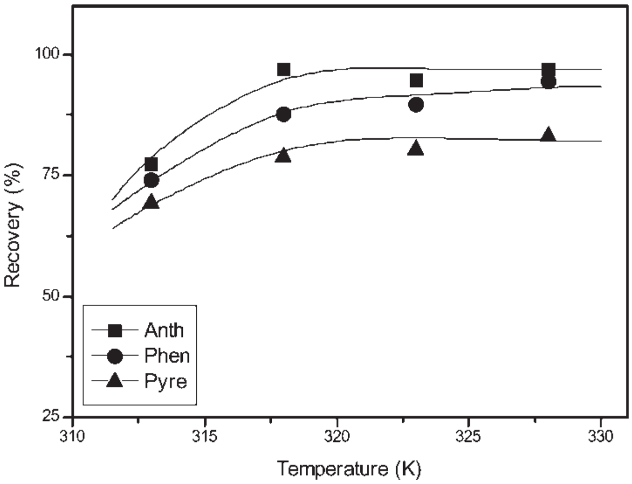

Figure 8. Recoveries of thee PAHs obtained by Us-CPE underwent at different temperatures with 120 W in 2 wt% surfactant solution.

decreased rapidly. We did not find the explicit reason for the phenomenon, in our assumption, which is probably due to the fact that C-CPE was not able to offer a complete phase separation in the high surfactant concentration solution.

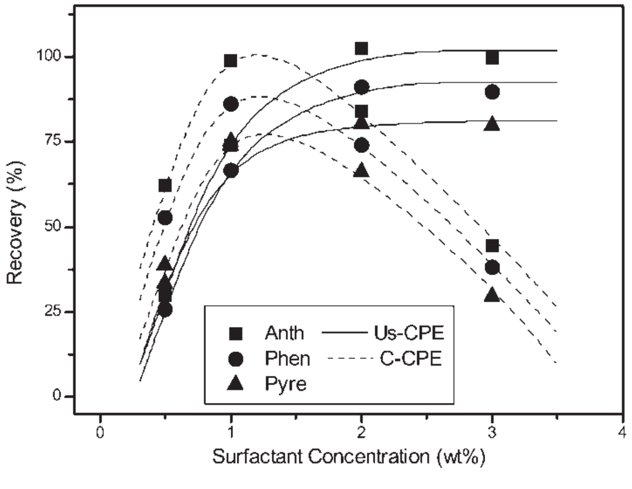

Figure 9. Comparison of the recoveries of three PAHs obtained by Us-CPE[1] and C-CPE[2] with different surfactant concentration solutions.

[1]Us-CPE condition: 300 W, 318 K, 30 min ultrasonic.

[2]C-CPE condition: 300 g, 30 min centrifugation.

Effect of Initial Concentration of PAHs

The variation in recoveries of the three PAHs with different initial concentrations was examined. Figure 10 showed the difference observed in the two CPE processes. In the case of C-CPE, the recoveries of all the three PAHs decreased rapidly with an increase of initial PAHs concentration and attained about 50% at 6 mg/L of PAHs concentration. In contrast, a significant effect of initial PAHs concentration on the recovery was not found in Us-CPE. For instance, a recovery of 99.6%, 92.9%, or 80.5% for Anth, Phen, or Pyre respectively was obtained at an initial PAHs concentration of 4 mg/L, and only a little decrease was observed at 60 mg/L, where their recoveries were 96.9%, 98.0%, and 77.2% respectively. In our knowledge, the highest PAHs initial concentration reported in the CPE process till now was 20 mg/L with Tergitol 15-S-5 as the surfactant (32). Therefore, this finding is useful in the treatment of polluted water with a high PAHs concentration.

Effect of Volume of Polluted Water

The cloud point extraction process was usually operated in a 10 mL centrifugation tube in most literatures, and only one group reported the scaling up process, where the CPE process was performed in a continuous rotating disk contactor with a column smaller than 500 mL (19, 20). Generally,

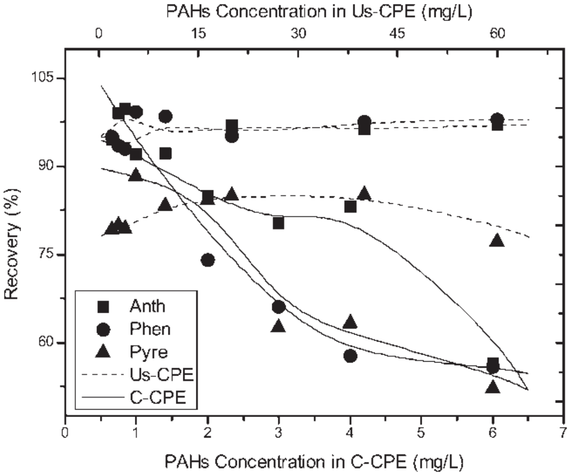

Figure 10. Recoveries of PAHs with different initial concentrations in by Us-CPE[1] and C-CPE[2] with 2 wt% surfactant concentration.

[1]Us-CPE condition: 120 W, 318 K, 30 min ultrasonic.

[2]C-CPE condition: 300 g, 30 min centrifugation.

Table 1. Recovery of PAHs in Us-CPE for the treatment of polluted water with different volumes

Pollued water	Recovery (%)		
Volume (mL)	Anth	Phen	Pyre
100	83.5	96.4	81.9
250	82.0	95.9	80.6
500	80.4	92.6	79.3

Us-CPE condition: 120 W, 323 K, 2 wt% surfactant solution, 30 min ultrasonic.

since the feasibility of ultrasonic is independent to the volume of container, Us-CPE is thought to be available in a common large scale water treatment container, when the ultrasonic generator supplies sufficient power. To investigate the capability of Us-CPE for the large scale treatment of the polluted water, the recoveries of the three PAHs were determined with different water volumes and summarized in Table 1. High recoveries were obtained for all volumes of the polluted water studied, although the extraction system was not optimized. These results indicated the Us-CPE process has a great potential for the large scale application. Another advantage of ultrasonic is that it is able to be supplied continuously and the whole CPE process is performed in one container, which suggests the possibility of applying Us-CPE system to a continuous water treatment process. In contrast, the extraction and phase separation step of C-CPE has to be performed in different containers, a temperature decrease was inevitable when the micelle solution is transmitted to a centrifuge machine, which leads to a decrease of final recovery, and also limits its application in a continuous operation (2). Moreover, its treatment capability was also limited by the volume of the centrifuge machine.

CONCLUSION

In this research, the ultrasonic environment was introduced into the cloud point extraction process, and the performance of the developed process, the phase separation, and the recoveries of three PAHs, anthracene, phenanthrene, and pyrene, were discussed.

In the ultrasonic assisted cloud point extraction (Us-CPE) process, the surfactant-rich phase was formed by the combination of surfactant micelle aggregates, which came out gradually during the process. Depending on the powerful ultrasonic effect, Us-CPE offered a quicker phase separation speed than the process with heating alone (H-CPE). Comparing with the conventional CPE process with centrifugation (C-CPE), the Us-CPE process also offered several advantages as follows:

1. Lower water content in the surfactant-rich phase was obtained in a common used surfactant concentration range (lower than 2 wt%), which leading to a lower $Vs/(Vs + Vw)$, i.e. a higher preconcentration factor;
2. high recoveries of the three PAHs were reached even with a high PAHs initial concentration of 60 mg/L;
3. feasible for a scaling up process, and a high recovery was also achieved even in the 500 mL polluted water;
4. the whole process was performed in one container, which is significant in the continuous water treatment with CPE process especially.

Based on the above characteristics, Us-CPE was expected to be a candidate process in large-scale treatment of polluted water with a high PAHs concentration.

REFERENCES

1. Tani, H., Kamidate, T., and Watanabe, H. (1997) Micelle-mediated extraction. *Journal of Chromatography A*, 780 (1–2): 229–241.
2. Frank, H., Quina, H.F., and Willie, L.H. (1999) Surfactant-mediated cloud point extractions: An environmentally benign alternative separation approach. *Ind. Eng. Chem. Res.*, 38 (11): 4150–4168.
3. Rubio, S. and Perez-Bendito, D. (2003) Supra-molecular assemblies for extracting organic compounds. *Trac-Trends in Analytical Chemistry.*, 22 (7): 470–485.
4. Maniasso, N. (2001) Micellar media in analytical chemistry. *Quimica Nova*, 24 (1): 87–93.
5. Carabias-Martinez, R. et al. (2000) Surfactant cloud point extraction and preconcentration of organic compounds prior to chromatography and capillary electrophoresis. *Journal of Chromatography A*, 902 (1): 251–265.
6. Halko, R. and Hutta, M. (2000) Review on utilization of non-ionic tensides for sample pretreatment in environmental analysis of organic pollutants. *Chemicke Listy.*, 94 (11): 990–993.
7. Saitoh, T., Matsudo, T., and Matsubara, C. (2000) Micelle-mediated extraction for concentrating hydrophobic organic compounds. *Journal of Chromatography A*, 879 (2): 121–128.
8. Delgado, B. et al. (2004) Nonionic surfactant mixtures: a new cloud-point extraction approach for the determination of PAHs in seawater using HPLC with fluorimetric detection. *Analytica Chimica Acta*, 518 (1–2): 165–172.
9. Ferrer, R., Beltran, J.L., and Guiteras, J. (1996) Use of cloud point extraction methodology for the determination of PAHs priority pollutants in water samples by high-performance liquid chromatography with fluorescence detection and wavelength programming. *Analytica Chimica Acta*, 330 (2–3): 199–206.
10. Casero, I. et al. (1999) An acid-induced phase cloud point separation approach using anionic surfactants for the extraction and preconcentration of organic compounds. *Anal. Chem.*, 71 (20): 4519–4526.

11. Fuoco, R. et al. (2005) Optimized cleanup methods of organic extracts for the determination of organic pollutants in biological samples. *Microchemical Journal*, 79 (1–2): 69–76.
12. Ferrera, Z.S. et al. (2004) The use of micellar systems in the extraction and preconcentration of organic pollutants in environmental samples. *Trac-Trends in Analytical Chemistry.*, 23 (7): 469–479.
13. Sirimanne, S.R. et al. (1998) Application of cloud-point extraction-reversed-phase high-performance liquid chromatography: A preliminary study of the extraction and quantification of vitamins A and E in human serum and whole blood. *Journal of Chromatography B: Biomedical Sciences and Applications*, 716 (1–2): 129–137.
14. Schwarz, A., Terstappen, G.C., and Futerman, A.H. (1997) Isolation of gangliosides by cloud-point extraction with a nonionic detergent. *Analytical Biochemistry*, 254 (2): 221–225.
15. Merino, F., Rubio, S., and Perez-Bendito, D. (2002) Acid-induced cloud point extraction and preconcentration of polycyclic aromatic hydrocarbons from environmental solid samples. *Journal of Chromatography A*, 962 (1–2): 1–8.
16. Sicilia, D. et al. (1999) Anionic surfactants in acid media: a new cloud point extraction approach for the determination of polycyclic aromatic hydrocarbons in environmental samples. *Analytica Chimica Acta*, 392 (1): 29–38.
17. Li, J.-L. and Chen, B.-H. (2003) Equilibrium partition of polycyclic aromatic hydrocarbons in a cloud-point extraction process. *Journal of Colloid and Interface Science*, 263 (2): 625–632.
18. Akita, S. and Takeuchi, H. (1995) Cloud-point extraction of organic compounds from aqueous solutions with nonionic surfactant. *Separation Science and Technology*, 30 (5): 833–846.
19. Trakultamupatam, P., Scamehorn, J.F., and Osuwan, S. (2004) Scaling up cloud point extraction of aromatic contaminants from wastewater in a continuous rotating disk contactor. I. Effect of disk rotation speed and wastewater to surfactant ratio. *Separation Science and Technology*, 39 (3): 479–499.
20. Trakultamupatam, P., Scamehorn, J.F., and Osuwan, S. (2004) Scaling up cloud point extraction of. aromatic contaminants from wastewater in a continuous rotating disk contactor. II. Effect of operating temperature and added electrolyte. *Separation Science and Technology*, 39 (3): 501–516.
21. Hemwimol, S., Pavasant, P., and Shotipruk, A. (2007) Ultrasound-assisted extraction of anthraquinones from roots of Morinda citrifolia. *Ultrasonics Sonochemistry.* 13 (6), 543–548.
22. Li, H., Chen, B., and Yao, S. (2005) Application of ultrasonic technique for extracting chlorogenic acid from Eucommia ulmodies Oliv. (E. ulmodies). *Ultrasonics Sonochemistry*, 12 (4): 295–300.
23. Banjoo, D.R. and Nelson, P.K. (2005) Improved ultrasonic extraction procedure for the determination of polycyclic aromatic hydrocarbons in sediments. *Journal of Chromatography A*, 1066 (1–2): 9–18.
24. Shibata, E. et al. (2004) Synthesis of amorphous carbon particles by an electric arc in the ultrasonic cavitation field of liquid benzene. *Carbon*, 42 (4): 885–888.
25. Niemczewski, B. (1999) Chemical activation of ultrasonic cavitation. *Ultrasonics Sonochemistry*, 6 (4): 211–216.
26. Prokhorenko, P.P., Kuvshinov, G.I., and Dezhkunov, N.V. (1986) The effect of temperature on mass transfer of a fluid in capillaries under the action of ultrasonic cavitation. Experiment and application. *International Communications in Heat and Mass Transfer*, 13 (1): 43–53.

27. Theodosios, I., Sikalos, T.I., and Paleologos, E.K. (2005) Cloud point extraction coupled with microwave or ultrasonic assisted back extraction as a preconcentration step prior to gas chromatography. *Anal. Chem.*, 77 (8): 2544–2549.
28. Li, S.Y. et al. (2003) Ultrasonic treatment of cotton pulp cellulose. *Chinese Journal of Applied Chemistry*, 20 (11): 1030–1034.
29. Laland, S.G. et al. (1954) The ultraviolet absorption of some degraded desoxyribonucleic acids. *Biochimica et Biophysica Acta*, 14: 356–365.
30. Hiigashitani, K., Fukushima, M., and Matsuno, Y. (1981) Migration of suspended particles in plane stationary ultrasonic field. *Chemical Engineering Science*, 36 (12): 1877–1882.
31. Calvo Seronero, L. et al. (2000) Cloud point preconcentration of rather polar compounds: application to the high-performance liquid chromatographic determination of priority pollutant chlorophenols. *Journal of Chromatography A*, 897 (1–2): 171–176.
32. Li, J.L., Bai, R.B., and Chen, B.H. (2004) Preconcentration of phenanthrene from aqueous solution by a slightly hydrophobic nonionic surfactant. *Langmuir*, 20 (14): 6068–6070.