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

Pilot-scale Ultrasonic Assisted Cloud Point Extraction of Polycyclic Aromatic Hydrocarbons from Polluted Water

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(2008) 'Pilot-scale Ultrasonic Assisted Cloud Point Extraction of Polycyclic Aromatic Hydrocarbons from Polluted Water', Separation Science and Technology, 43: 6, 1564 — 1580
To link to this Article: DOI: 10.1080/01496390801955588
URL: http://dx.doi.org/10.1080/01496390801955588

Separation Science and Technology, 43: 1564–1580, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390801955588

Pilot-scale Ultrasonic Assisted Cloud Point Extraction of Polycyclic Aromatic Hydrocarbons from Polluted Water

Bingjia Yao and Li Yang

School of Chemistry and Chemical Technology, Shanghai Jiao Tong
University, Shanghai, China

Abstract: Cloud point extraction (CPE) has been proved to be an efficient and environment-friendly separation technology for polycyclic aromatic hydrocarbons from polluted water in many related researches. However, its traditional phase separation process, based on throughput-limited centrifugation or low-efficient heating, limited the scaling up and continuous operation of CPE process to a large extent. In our previous study, an efficient and easy-scaling up CPE process, namely ultrasonic assisted cloud point extraction (Us-CPE), was developed by performing the CPE process in an ultrasonic environment. The introduction of an ultrasonic environment successfully accelerated the phase separation; and due to that the ultrasonic effect was free from throughput limitation, the process was of a good potential in the scaling up and continuous operation. In this paper, a pilot-scale Us-CPE process of three polycyclic aromatic hydrocarbons (PAHs), anthracene, phenanthrene, and pyrene from polluted water was performed in a pilot-scale extraction column with a volume up to 500 mL, and the treatment was operated continuously with pumps. The steady state time of the continuous system was determined, and the influence of operation parameters including ultrasonic power, temperature, extraction column volume, flow rate, and PAHs initial concentration, were evaluated by determining the PAHs concentrations in the treated water and the corresponding distribution coefficients. Comparing with the batch operation in our previous study, a comparable high performance was able to be obtained by the continuous process in a PAHs initial concentration range lower than 20 mg/L, which means that the continuous process was feasible in the treatment of common PAHs polluted water. And the results that the

Received 3 September 2007, Accepted 27 December 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

extractability of the system increased with the ultrasonic power and system volume indicated that a high performance was expectable in a further scaling up process with a higher column volume, given a suitable ultrasonic power.

Keywords: Polycyclic aromatic hydrocarbons, cloud point extraction, ultrasonic, continuous process, pilot scale

INTRODUCTION

Designated as probable human carcinogens, polycyclic aromatic hydrocarbons (PAHs) were announced to be highly dangerous organic polluted substances by many countries and groups, and strict environment rules limiting the total maximum concentrations of different PAHs species were established (1–4). But many industrial waste waters contained a high concentration of PAHs, especially the one of coke tar industry; so an efficient process was needed to lower the concentration to satisfy the standards. However, even in coal tar waste water, the PAHs concentration was usually mg/L, even μg/L level, the low concentration made conventional liquid-liquid or solid-liquid separation methods uneconomical or behave a low efficiency in the water treatment (5–9).

In comparison, cloud point extraction (CPE), as a promising separation method, has a huge advantage in the separation of trace level substances from polluted water (10–20). Based on the phase separation phenomenon of surfactant aqueous solution above its cloud point, the CPE process does not need organic solvents, environmentally friendly and low cost, and excellent performance of CPE processes have been reported in the concentration of PAHs from polluted water (21–23). However, most current CPE studies were sample preparation or batch experiment and performed in a test tube scale; while a process performed in a rotating disk contactor (RDC) was the only one scaling up the CPE process which was ever reported so far, but a relatively low extractability was obtained, owing to the relatively high surfactant content in the water phase after the inefficient phase separation disturbed by the physical stirring (24, 25).

In our previous research, a higher performance of the CPE process was achieved by selecting suitable surfactants or adjusting the processes, including the introduction of an ultrasonic environment to assist the phase separation process (26–28). In the ultrasonic assisted CPE (Us-CPE) process, ultrasonic was believed to offer sufficient energy to help the break of hydrogen bonding between the water molecules and the surfactant micelles, and accelerate the formation of surfactant aggregates. Based on its flocculation effect, ultrasonic also offered different vibration frequencies for the surfactant aggregates with various volumes, which speeded their combination and the formation of the final surfactant-rich phase, resulting in a quicker phase separation (26, 29). Moreover, the different vibration frequencies between extractable species and micelles also increased their contact chances, leading to an increase of recovery. What is more important is that the technology provided a more feasible potential solution to scale up the CPE process, including a continuous operation. Different from the one based on RDC, scaling up the ultrasonic process does not need any additional operation, thus a large decrease of the phase separation performance was supposed to be avoided, and a high efficient scaling up continuous CPE process was expected.

In this study, a pilot-scale Us-CPE process of three PAHs, anthracene (Anth), phenanthrene (Phen) and pyrene (Pyre) was performed with Tergitol-TMN 6, as the extractant, in a purposely-made extraction column with a volume up to 500 mL. The distribution coefficient and the PAHs concentration remained in the treated water were used to evaluate the performance of the separation process. The effect of the operation parameters including ultrasonic power, temperature, container volume, and the PAHs initial concentration, on the treatment performance were discussed.

EXPERIMENTS

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, and the cloud point of its aqueous solution with different concentrations was shown in Fig. 1. Pyrene

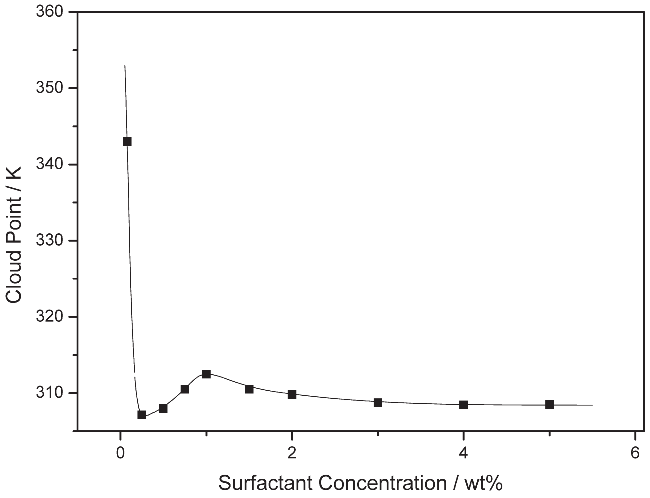

Figure 1. Cloud point of the Tergitol TMN-6 aqueous solution with different concentrations.

(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 $M\Omega \cdot cm$. 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, and the position of the extraction column was fixed in the ultrasonic bath for all the experiments. HL-2D Constant flow pump (Shanghai Huxi Analysis Instrument Factory Co., LTD, China) offering a flow rate in the range of 0.3–600 mL/h was used to transfer the solution during the continuous process. PE-series 200 HPLC system (Perkin Elmer, USA), including the pump, the degasser, the auto injector, the column oven, the ultraviolet detector, and a TOSOH ODS gel column (ODS-100S, 4.6 $*$ 150 mm) were used to determine the amount of PAHs.

Procedure

Pilot-scale Ultrasonic Assisted Cloud Point Extraction Procedure

The diagram of the pilot-scale ultrasonic assisted CPE process was shown in Fig. 2. A desired aqueous solution of PAHs with different initial concentrations, used as polluted water, was obtained by mixing water at an

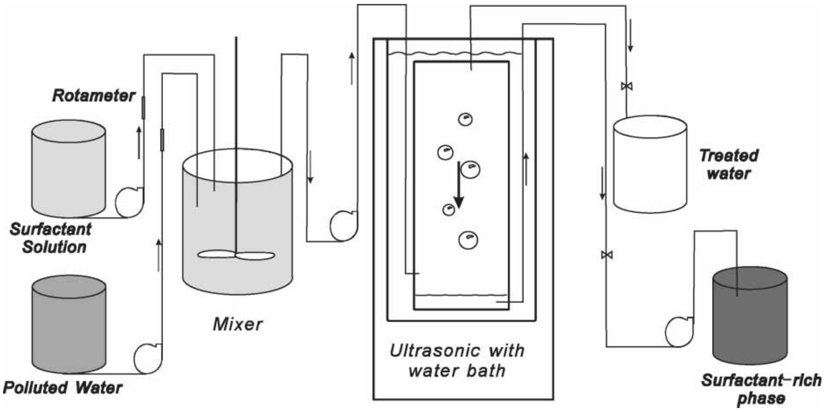

Figure 2. Diagram of the pilot-scale ultrasonic assisted CPE process.

appropriate volume ratio with the stock solution of the three PAHs, which was prepared by dissolving the respective solid specimen (0.1 g) into 50 mL acetonitrile. The polluted water (with a PAHs concentration of 20 mg/L, except indicated) and 10 wt.% Tergitol TMN-6 solution were contained into 2000 mL glass beakers respectively, and pumped into another 2000 mL glass beaker with a fixed flow rates ratios of 10, and then the two solutions were mixed in a 2000 mL beaker with a stirring at 200 rpm. After 30 mins, the mixed solution was pumped at a certain speed (300 mL/hr, except indicated) into a purpose-made glass column (400 mL, except indicated) fixed in the ultrasonic pool with an incubation at a prescribed temperature (318 K, except indicated). After a half of the glass column was filled with the mixed solution, the ultrasonic effect started at a certain power (400 W, except indicated), when the accelerated phase separation of the mixed solution occurred in the glass column. The glass column was designed to be with one inlet in the part close to the bottom end, for the input of the mixed solution of polluted water and surfactant solution, and two outlets in each end respectively, where the surfactant-rich phase obtained from the phase separation was pumped through the bottom outlet slowly, and the aqueous phase in the upper was discharged from the top one. Both of the two phases were collected into the respective container, and then a 1 mL sample of each phase was collected into a sample bottle and sent to the HPLC analysis for the determination of PAHs concentration. Glass columns with different volumes, 200, 300, 400, and 500 mL were prepared for the discussion of the influence of system volume on the performance of the continuous process.

Analytical Procedure

The samples collected from the surfactant-rich phase or aqueous phase (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.

RESULTS AND DISCUSSION

As shown in Fig. 2, the main part of the pilot-scale process was a mixer-settler unit where the surfactant solution and the polluted water were pumped into the mixer, and then the mixture was transferred into the glass column, as the settler, for the phase separation assisted by the ultrasonic environment. Based on the solubilization of the surfactant aqueous solution, most PAHs contained in the feed were captured into the surfactant micelles in the mixer; and then the flocculation effect of the ultrasonic environment in the settler also offered additional contact chances between PAHs and micelles to increase the degree of solubilization, because of their different vibration frequencies in ultrasonic effect (26, 29). So, a enough high degree of PAHs was believed to be solubilized by the surfactant micelles, and the efficiency of the phase separation step was assumed to be more responsible for the variation of the final recovery. Thus, the operation parameters in the phase separation step were paid more attention in the following discussions. Firstly, the steady state time was determined by observing the variation of PAHs concentration remained in the treated water and distribution coefficient with time, and then the corresponding values obtained at the steady state time with different operation parameters, including ultrasonic power, temperature, container volume and PAHs initial concentration were used to evaluate their effects on the performance of the process.

Steady State Time Analysis

The time needed to achieve the steady state (steady state time) of the continuous Us-CPE process with a ultrasonic power of 300 W was obtained by determining the PAHs concentration remained in the treated water ($[PAHs]_a$) and distribution coefficient (K_d, $[PAHs]_s/[PAHs]_a$, where $[PAHs]_s$ is the PAHs concentration in the surfactant-rich phase) every several times during the continuous process. The variation of $[PAHs]_a$ of Anth as a function of time during the processes with two different PAHs initial concentrations in the feed ($[PAHs]_{init}$), 20 mg/L and 40 mg/L, was shown in Fig. 3, while Fig. 4 depicted the K_d of the three PAHs in the same time range with a $[PAHs]_{init}$ of 10 mg/L. Although the steady state of $[PAHs]_a$ and K_d were both achieved in the first 2 hr when the $[PAHs]_{init}$ was 20 mg/L, a longer steady

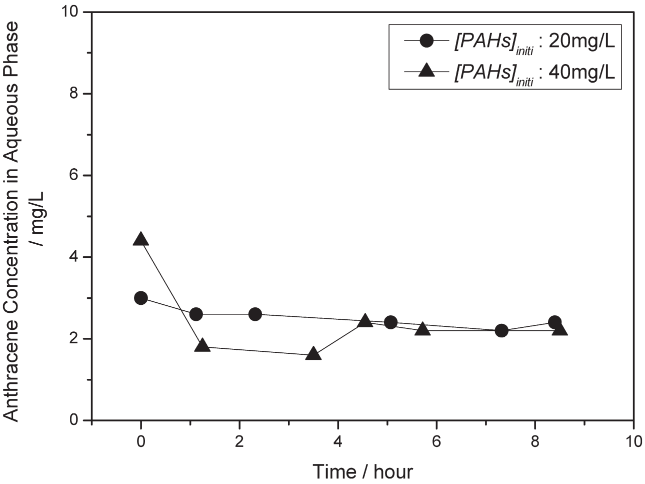

Figure 3. Anthracene concentration in aqueous phase during continuous Us-CPE process with different $[PAHs]_{init}$.

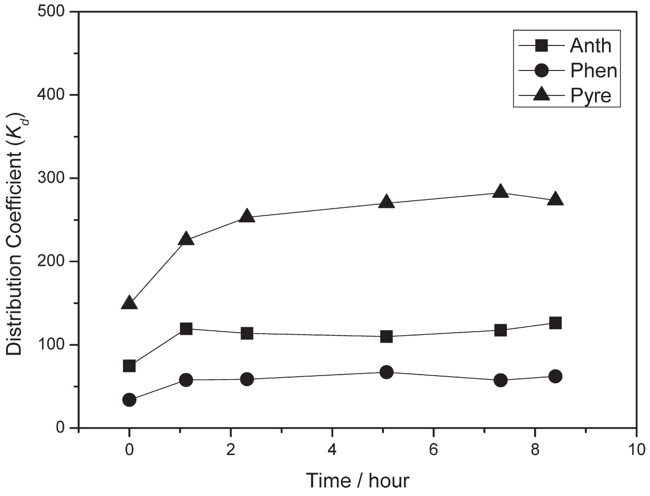

Figure 4. Distribution coefficient (K_d) of the three PAHs during continuous Us-CPE process.

state time (4.5 hr) was required for the process with a higher *[PAHs]*$_{init}$, 40 mg/L, and the time was comparable with that of the process with RDC (24). So, 5 hr was selected as the steady state time for the later discussions of the influences of the different operation parameters on the performance of the continuous process. A similar *[PAHs]*$_a$ was observed after the system achieved steady state in the processes with two different *[PAHs]*$_{init}$, which means that the continuous process offered a sufficient extractability to remove the PAHs to a same relative low concentration in the *[PAHs]*$_{init}$ range discussed.

Effect of Ultrasonic Power

Figures 5 and 6 depicted the influence of ultrasonic power on *[PAHs]*$_a$ and K_d of the three PAHs obtained after the continuous process achieved steady state. When the power was relatively low, below 100 W, ultrasonic effect has little or even negative effect on the decrease of *[PAHs]*$_a$, comparing with that obtained in the process without ultrasonic effect. With a higher ultrasonic power, the extractability of process started to increase, and achieved a maximum of most PAHs at 300 W, where *[PAHs]*$_a$ of 2.2, 1.6, and 0.8 mg/L and resulting high K_d of $10^{2.0}$, $10^{2.0}$, and $10^{2.3}$ for Anth, Phen, and Pyre, respectively, were obtained. No significant effect on K_d, except Pyre, was observed in further increasing ultrasonic power, and a little higher *[PAHs]*$_a$ was even obtained in a 400 W ultrasonic power. Therefore a sufficiently high ultrasonic power was required in a high performance Us-CPE continuous operation,

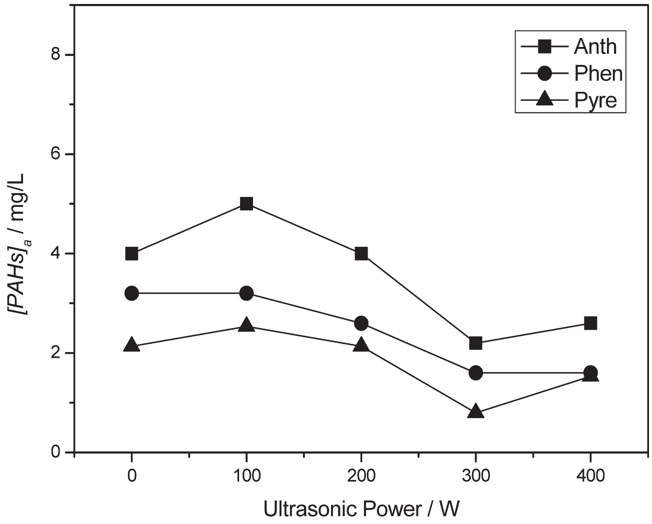

Figure 5. Effect of ultrasonic power on *[PAHs]$_a$* of the three PAHs in pilot-scale Us-CPE process.

although 300 W was preferred under the current condition in the consideration of saving energy. Unlike the current pilot-scale process, in the batch experiment with a test tube scale reported in our previous study, ultrasonic power did not show so obvious an influence on the performance, where a power higher than 100 W was persistently able to offer a close 100% recovery of

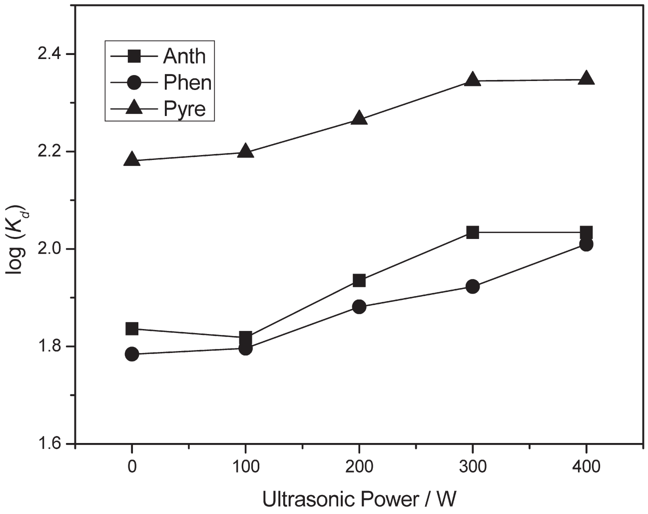

Figure 6. Effect of ultrasonic power on distribution coefficients of the three PAHs in pilot-scale Us-CPE process.

the three PAHs, and 120 W also offered around 90% recoveries in all system volumes from 100 mL to 500 mL. The comparison showed that the continuous process obviously required a higher power, because the continuous operation decreased the effect time for every drop of water treated by the ultrasonic, which would be compensated by a higher power.

Effect of Temperature

The influence of incubation temperature on the *[PAHs]*$_a$ and K_d were discussed and the results were shown in Figs. 7 and 8, respectively. With increasing the temperature, the corresponding *[PAHs]*$_a$ decreased conspicuously, and a same critical temperature of 318 K was observed in *[PAHs]*$_a$ and K_d, where the minimum of *[PAHs]*$_a$ and maximum corresponding K_d were achieved. Compared with the lower temperature, an obviously better extractability was obtained in the temperature range higher than the critical value, although the performances were still slightly lower than the optimum value. In our previous batch experiment, a same critical value and similar effect of temperature on the recovery was also found, but no negative influence of the higher temperature was observed (26). The comparison indicated that the decrease of extractability with temperature was related with the scaling up or continuous operation, and excess heating probably affected the movement and distribution of surfactant aggregates during the phase separation, where an increasing amount of surfactant micelles

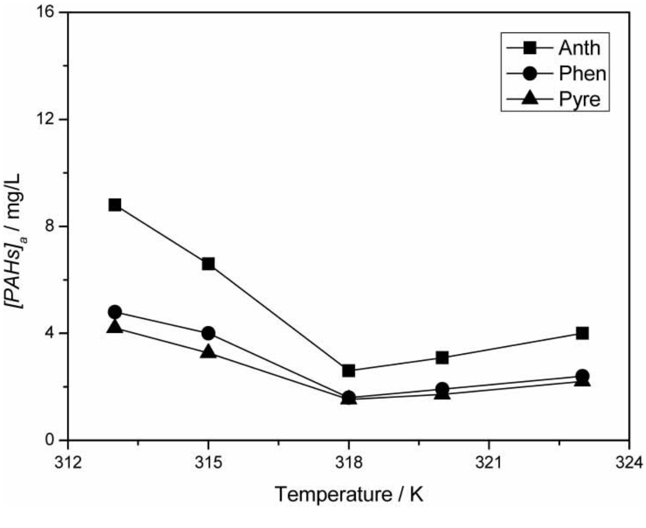

Figure 7. Effect of incubation temperature on *[PAHs]*$_a$ of three PAHs in pilot-scale Us-CPE process.

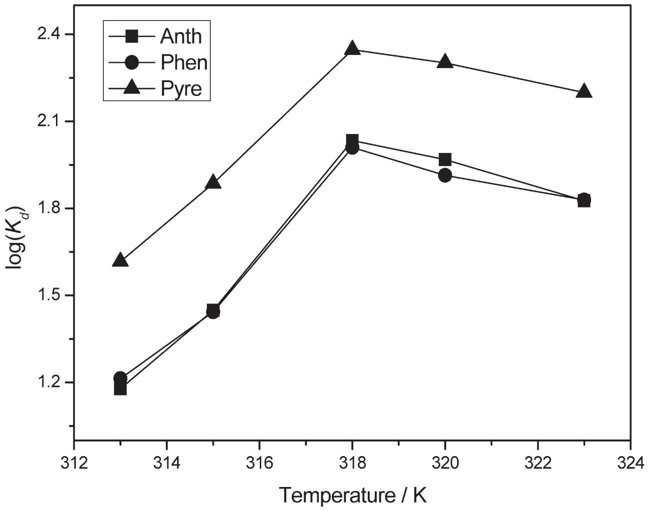

Figure 8. Effect of incubation temperature on distribution coefficients of three PAHs in pilot-scale Us-CPE process.

containing PAHs was remained around the upper end of the extraction column, and was then discharged as the treated aqueous phase, which increased the final $[PAHs]_a$ and affected the resulting K_d.

Effect of System Volume and Total Flow Rate

By continuous operation, the polluted water and surfactant solution were mixed first, and then pumped into the extraction column for the treatment of ultrasonic environment. The volume of the mixed solution passing through the extraction column (referred to system volume in this paper) and the total flow rate codetermined the duration of the ultrasonic effect accepted by every drop of the mixed solution, where a larger system volume and slower flow rate were both able to prolong the duration of the ultrasonic effect for the drops, and a resulting higher extractability was predicable. So, as important parameters, the influences of system volume and total flow rate on the performance of the pilot-scale process were also discussed here. According to Fig. 9, no obvious variation of $[PAHs]_a$ was observed when the system volume increased from 200 mL to 500 mL, although the minimums of $[PAHs]_a$ for all the three PAHs were obtained in the system volume of 500 mL. In contrast, a conspicuous increase of K_d with system volume was obtained in the same volume range, e.g. the K_d of Pyre increased from $10^{2.1}$ of 200 mL to $10^{2.4}$ of 500 mL, which was shown in Fig. 10. And the batch study showed that neither the surfactant-rich phase

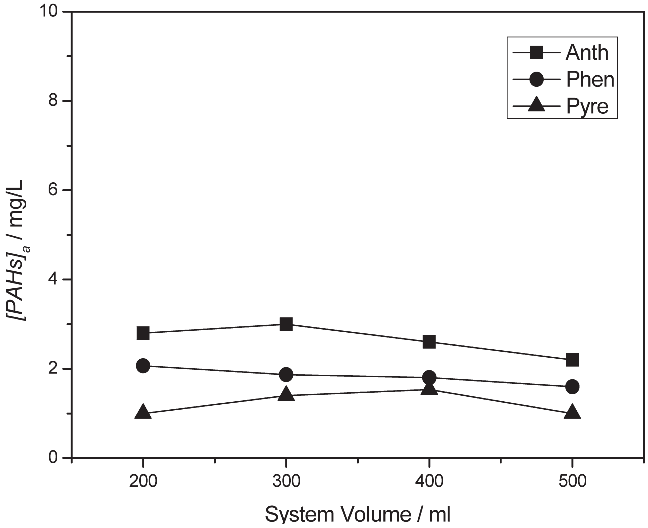

Figure 9. Effect of system volume on *[PAHs]*$_a$ in pilot-scale Us-CPE process.

volume nor the recovery decreased with the increase of the system volume (26). So the different trends of K_d and *[PAHs]*$_a$ meant that the prolonging of ultrasonic effect duration by the increase of system volume effectively improved the PAHs concentration trapped into the micelles, i.e., *[PAHs]*$_s$, resulting in a higher K_d. Although 500 mL was the largest system volume

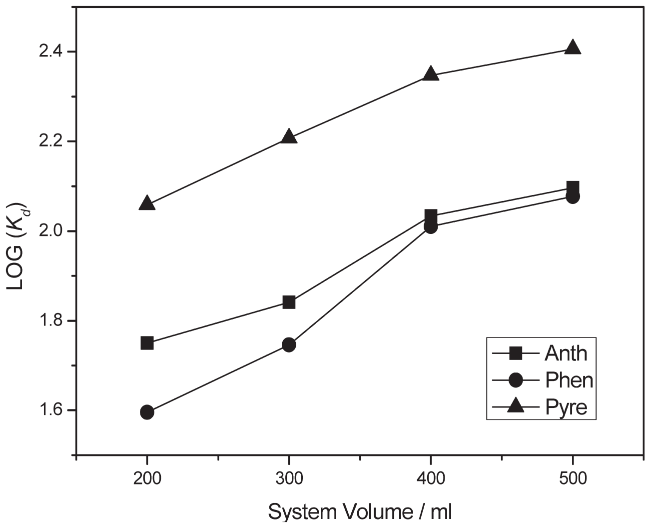

Figure 10. Effect of system volume on K_d in pilot-scale Us-CPE process.

we discussed, due to the volume limitation of the ultrasonic bath used in this study, a higher extractability was able to be presumed in the process with a higher system volume, according to the increase tendency shown in Fig. 10. The total flow rate of the mixed solution pumped into the column had a similar effect as system volume had on the extractability, where a lower flow rate also prolonged the ultrasonic effect duration, resulting in a relatively higher performance, although the data was not shown here. However, different from the system volume, the flow rate not only influenced the ultrasonic effect duration for every drop of the mixed solution, but also decided on the treatment speed and throughput in the whole continuous process. Thus, for achieving a higher performance of the continuous process, increasing the system volume was preferred, compared with slowing down the flow rate.

Effect of PAHs Initial Concentration

The PAHs concentration of common water in environment is lower than μg/L level, however the value will be tremendously increased at the presence of organic solvent or surfactant, especially in the waste water produced from coke plant (5). The performance of the continuous process in the treatment of the solution with different $[PAHs]_{init}$ was shown in Figs. 11 and 12. With the increase of $[PAHs]_{init}$ from 20 mg/L to 80 mg/L, the extractability decreased conspicuously, for example, the $[PAHs]_a$ of Anth increased from 2.6 mg/L to 14 mg/L in the above $[PAHs]_{init}$ range. The corresponding K_d was in an inverse proportion to the $[PAHs]_{init}$, where the K_d of Anth

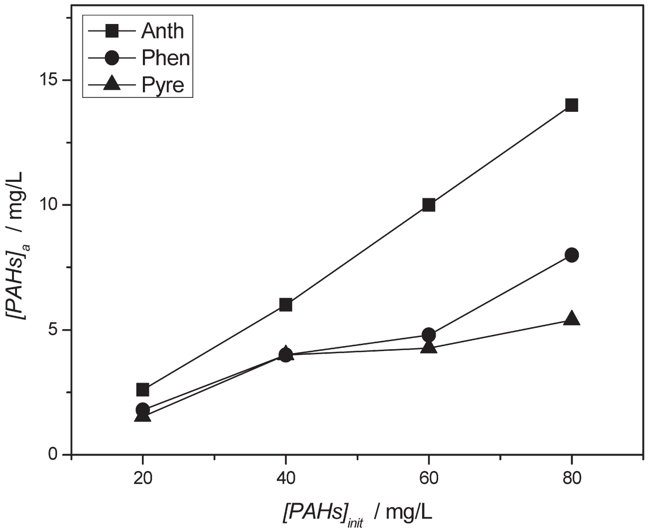

Figure 11. $[PAHs]_a$ obtained in pilot-scale Us-CPE process with different $[PAHs]_{init}$.

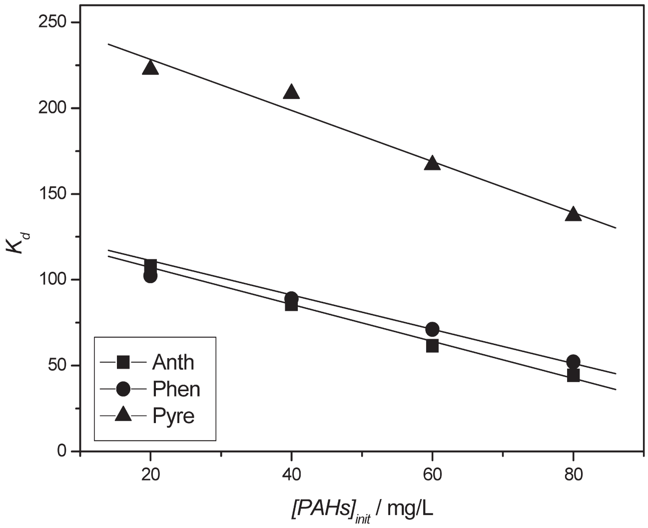

Figure 12. Distribution coefficients of PAHs obtained in pilot-scale Us-CPE process with different $[PAHs]_{init}$.

dropped from 108.10 to 44.34 with the increase of $[PAHs]_{init}$. In comparison, the performance did not decrease that obviously in our previous batch experiment with a test tube scale, and a high performance was also persistent during the scaling up from 100 mL to 500 mL in the treatment of a low PAHs concentration polluted water. The difference between two processes indicted that, with continuous operation, the scaling up of the system volume decreased the treatment capability of the system to the polluted water with a high PAHs concentration. However, 20 mg/L is already a high PAHs concentration even in coke plant waste water, where a good performance, $[PAHs]_a$ of 2.6, 1.6, and 1.5 mg/L and K_d of 108.1, 102.3, and 222.5 for Anth, Phen and Pyre, respectively, was able to be obtained in the continuous process, even with the unoptimized operation parameters. So the continuous Us-CPE process was competent and with a sufficient high performance for the treatment of most PAHs waste waters, although the extractability was relatively lower in the treatment of the water with a very high PAHs concentration.

Comparison of Extraction Performance between Batch and Continuous Operations

A comparison of extraction performance between batch and continuous operations of the pilot-scale Us-CPE was discussed at the same operation parameters, and the results were listed in Table 1. Due to the difference between the two operations, the $[PAHs]_{init\text{-}m}$, (PAHs concentration in the mixed solution of PAHs feed solution and surfactant solution) was used in the

Table 1. Comparison of extractability between batch and continuous operations of Us-CPE

	Batch Us-CPE[a]			Continuous Us-CPE[b]		
$[PAHs]_{init\text{-}m}$[c] (mg/L)	20	40	80	20	40	80
$[PAHs]_a$ (mg/L)						
Anth	4.0	4.2	6.9	2.2	3.0	14.0
Phen	3.6	3.8	1.4	1.6	2.0	8.0
Pyre	3.0	3.6	3.4	1.0	1.8	7.7
$[PAHs]_s$ (mg/L)						
Anth	445.7	807.2	1067.7	281.0	514.2	620.8
Phen	351.2	645.0	255.1	192.4	355.2	417.2
Pyre	520.5	878.0	1351.0	257.0	556.0	741.0
K_d						
Anth	111.2	192.2	154.7	125.9	171.4	44.4
Phen	319.3	169.7	182.2	120.2	177.6	52.2
Pyre	270.0	247.3	196.9	257.0	302.2	48.4
Log (K_d)						
Anth	2.1	2.3	2.2	2.1	2.2	1.7
Phen	2.5	2.2	2.3	2.1	2.3	1.7
Pyre	2.4	2.4	2.3	2.4	2.5	1.7

[a] Batch operation: Ultrasonic power: 400 W; system volume: 500 mL, temperature: 318 K, time: 1 hr.

[b] Continuous operation: Ultrasonic power: 400 W; system volume: 500 mL, temperature: 318 K.

[c] $[PAHs]_{init\text{-}m}$: The PAHs concentration in the mixed solution of PAHs solution and surfactant solution.

comparison, instead of the one in the polluted water ($[PAHs]_{init}$). In both operations, $[PAHs]_a$ increased with $[PAHs]_{init\text{-}m}$, and the amplitude of continuous operation was more conspicuous in the range of $[PAHs]_{init\text{-}m}$ from 20 mg/L to 40 mg/L, which reaffirmed that the continuous operation was not suitable for the treatment of the polluted water with a high PAHs concentration. However, the continuous operation obtained a lower $[PAHs]_a$ than that of the batch operation when the $[PAHs]_{init}$ lower than 20 mg/L, although the presumed advantage was not observed in the corresponding K_d, attributed to the relative lower $[PAHs]_s$. It should be noted that the $[PAHs]_s$ of the continuous process was the instantaneous value collected after 5 hours operation, which was not able to reflect the situation of the entire process, especially the former 2 hrs, although 5 hr was determined as the steady state time in former experiment; whereas the $[PAHs]_s$ of the batch operation was from the whole surfactant-rich phase obtained during 1 hr's batch process, which was an average value. So the comparison depending on the $[PAHs]_s$ and corresponding K_d listed in the table could not exactly reflect the real difference of the two operations; however, a qualitative conclusion could be drawn that the continuous operation was able to offer a comparable extractability when the $[PAHs]_{init\text{-}m}$ below 20 mg/L, which means that the large decrease of performance from the batch to the continuous operation occurred in the RDC process was successfully avoided by substituting the stirring operation with ultrasonic effect. What is more, the mixed solution to be treated was pumped into the extraction column from the bottom end, and meanwhile the surfactant aggregates formed in the ultrasonic effect fell to the bottom gradually, so the countercurrent interaction between surfactant aggregates and the drop of mixed solution also contributed to the higher extraction performance, compared with the batch operation. Therefore it was feasible and with a relative high separation performance for the ultrasonic assisted CPE process to be performed in a continuous and scaling up operation, especially in the treatment of the water with a low $[PAHs]_{init}$.

CONCLUSION

In this study, a pilot-scale continuous ultrasonic assisted cloud point extraction of three PAHs, anthracene, phenanthrene and pyrene, was performed, where $[PAHs]_a$ and K_d were used to evaluate the performance of the continuous process. The results indicated that:

1. The continuous system achieved a steady state within 5 hrs running.
2. A similar positive effect on the performance was observed with the increase of both ultrasonic power and temperature after critical values, where the maximum extractability was achieved, for example $[PAHs]_a$ of 2.2, 1.6, and 0.8 mg/L and the resulting K_d of $10^{2.0}$, $10^{2.0}$, and $10^{2.3}$ for anthracene, phenanthrene and pyrene were obtained respectively at 318 K under the ultrasonic of 300 W, but further increase of the two parameters both led to a negative or negligible effect.
3. Higher K_d of the three PAHs were achieved in a larger extraction column volume or lower total flow rate.
4. An excellent extractability was obtained in a 10 mg/L PAHs solution, where the $[PAHs]_{init}$ was already much higher than that of most practical industrial waste water, although a conspicuous decrease of the extractability was observed when $[PAHs]_{init}$ was increased from 20 mg/L to 80 mg/L.
5. In the comparison of the performance between the continuous process and batch one in the same condition, a similar high K_d and even a lower $[PAHs]_a$ were obtained in the continuous operation, when the $[PAHs]_{init\text{-}m}$ was lower than 20 mg/L.

Therefore, the continuous ultrasonic assisted cloud point extraction was feasible and with a competent high extractability, and a higher performance was expected in a further scaling up process with a higher column volume.

REFERENCES

1. Zakaria, M.P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., and Kumata, H. (2002) Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: A widespread input of petrogenic PAHs. *Environ. Sci. Technol.*, 36 (9): 1907.
2. Stevens, J.L., Northcott, G.L., Stern, G.A., Tomy, G.T., and Jones, K.C. (2003) PAHs, PCBs, PCNs, Organochlorine pesticides, synthetic musks, and polychlorinated n-alkanes in U.K. sewage sludge: survey results and implications. *Environ. Sci. Technol.*, 37 (3): 462.
3. Liu, Y., Zhu, L., and Shen, X. (2001) Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China. *Environ. Sci. Technol.*, 35 (5): 840.
4. Lei, L., Suidan, M.T., Khodadoust, A.P., and Tabak, H.H. (2004) Assessing the Bioavailability of PAHs in field-contaminated sediment using XAD-2 assisted desorption. *Environ. Sci. Technol.*, 38 (6): 1786.
5. Link, A. (2000) Effect of nonionic surfactants on dissolution of polycyclic aromatic hydrocarbons from coal tar. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, 4 (2): 78.
6. Xiao, Y. and Jiang, Z. (1996) Pollution by multiring aromatic hydrocarbon and its preventive treatment strategy. *Environmental Protection of Oil & Gas Field*, 6 (4): 53.
7. Manoli, E. and Samara, C. (1999) Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *TrAC-Trend. Anal. Chem.*, 18 (6): 417.
8. Blanchard, M., Teil, M.J., Ollivon, D., Legenti, L., and Chevreuil, M. (2004) Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France). *Environ. Res.*, 95 (2): 184.
9. Busetti, F., Heitz, A., Cuomo, M., Badoer, S., and Traverso, P. (2006) Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant. *J. Chromatogra. A.*, 1102 (1–2): 104.
10. Tani, H., Kamidate, T., and Watanabe, H. (1997) Micelle-mediated extraction. *J. Chromatogra. A.*, 780 (1–2): 229.
11. 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.
12. Maniasso, N. (2001) Micellar media in analytical chemistry. *Quim. Nova.*, 24 (1): 87.
13. Carabias-Martinez, R., Rodriguez-Gonzalo, E., Moreno-Cordero, B., Perez-Pavon, J.L., Garcia-Pinto, C., and Laespada, E.F. (2000) Surfactant cloud point extraction and preconcentration of organic compounds prior to chromatography and capillary electrophoresis. *J. Chromatogra. A.*, 902 (1): 25.
14. Ferreira, S.L.C., de Andrade, J.B., Korn, M.d.G.A., Pereira, M.d.G., Lemos, V.A., Santos, W.N.L.d., Rodrigues, F.d.M., Souza, A.S., Ferreira, H.S., and da Silva, E.G. P. (2007) Review of procedures involving separation and preconcentration for the determination of cadmium using spectrometric techniques. *J. Hazard. Mater.*, 145 (3): 358.

15. Silva, M.F., Cerutti, E.S., and Martinez, L.D. (2006) Coupling cloud point extraction to instrumental detection systems for metal analysis. *Microchi. Acta.*, 155 (3–4): 349.
16. Korn, M.D.G.A., De Andrade, J.B., De Jesus, D.S., Lemos, V.A., Bandeira, M.L.S.F., Dos Santos, W.N.L., Bezerra, M.A., Amorim, F.A.C., Souza, A.S., and Ferreira, S.L.C. (2006) Separation and preconcentration procedures for the determination of lead using spectrometric techniques: A review. *Talanta*, 69 (1): 16.
17. de Almeida Bezerra, M., Zezzi Arruda, M.A., and Costa Ferreira, S.L. (2005) Cloud point extraction as a procedure of separation and pre-concentration for metal determination using spectroanalytical techniques: A review. *Appl. Spectrosc. Rev.*, 40 (4): 269.
18. Paleologos, E.K., Giokas, D.L., and Karayannis, M.I. (2005) Micelle-mediated separation and cloud-point extraction. *TrAC-Trend. Anal. Chem.*, 24 (5): 426.
19. Burguera, J.L. and Burguera, M. (2004) Analytical applications of organized assemblies for on-line spectrometric determinations: Present and future. *Talanta*, 64 (5SPEC.ISS.): 1099.
20. Carabias-Martinez, R., Rodriguez-Gonzalo, E., Moreno-Cordero, B., Perez-Pavon, J.L., Garcia-Pinto, C., and Fernandez Laespada, E. (2000) Surfactant cloud point extraction and preconcentration of organic compounds prior to chromatography and capillary electrophoresis. *J. Chromatogra. A.*, 902 (1): 251.
21. Merino, F., Rubio, S., and Perez-Bendito, D. (2002) Acid-induced cloud point extraction and preconcentration of polycyclic aromatic hydrocarbons from environmental solid samples. *J. Chromatogra. A.*, 962 (1–2): 1.
22. 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. *Anal. Chim. Acta.*, 330 (2–3): 199.
23. 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.
24. 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. *Sep. Sci. Technol.*, 39 (3): 479.
25. 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. *Sep. Sci. Technol.*, 39 (3): 501.
26. Yao, B. and Yang, L. (2007) Ultrasonic assisted cloud point extraction of polyaromatic hydrocarbons. *Sep. Sci. Technol.*, 42 (8): 1843.
27. Yao, B., Yang, L., Hu, Q., and Akita, S. (2007) Cloud point extraction of polycyclic aromatic hydrocarbons in aqueous solution with silicone surfactants. *Chinese J. Chem. Eng.*, 15 (4): 468.
28. Yao, B. and Yang, L. (2008) Equilibrium partition of polycyclic aromatic hydrocarbons in cloud point extraction with a silicone surfactant. *J. Colloid. Interf. Sci.*, 319 (1): 316–321.
29. Hiigashitani, K., Fukushima, M., and Matsuno, Y. (1981) Migration of suspended particles in plane stationary ultrasonic field. *Chem. Eng. Sci.*, 36 (12): 1877.