Journal of Korean Society on Water Quality, Vol. 24, No. 6, pp.801-805 (2008)

Applicability of Fibrous Solid Phase Extraction to Alkyl Phthalates Analysis

Yong-Jun Jung†

Department of Environmental Engineering, Catholic University of Pusan

알킬프탈레이트 분석을 위한 섬유상 고상 추출법의 적용 가능성

정용준†

부산가톨릭대학교 환경공학과

(Received 2 September 2008, Revised 7 October 2008, Accepted 14 October 2008)

Abstract

A fibrous material (*p*-phenylene-2,5-benzobisoxazole, PBO) was used as an adsorbent for solid phase extraction in order to simplify the extraction procedure. The extraction performance for di-(2-ethylhexyl) phthalate (DEHP) was examined with two types of PBO fibers (HM (High modulus) and AS (Regular type) types) by batch type sorption/desorption experiments. When 100 mg of the HM fibers were applied to 20 mL of the aqueous DEHP solution (less than 50 μg/L), more than 95% of DEHP was adsorbed on the fibers, however, the AS type fibers adsorbed alkyl phthalate up to 80%. In the case of 50 μg/L of the initial concentration of DEHP, the adsorbed DEHP was extracted effectively with methanol and the maximum overall recovery ratio was 92.3%. The results indicated that the PBO fibers could be used as an adsorbent for alkyl phthalate analysis, and that the extraction procedure was not affected by suspended solids in a water sample.

keywords : Adsorbent, Alkyl phthalate, *p*-phenylene-2,5-benzobisoxazole (PBO) fiber, Solid phase extraction

1. Introduction

Water pollution caused by organic micropollutants such as endocrine disrupting compounds (EDCs), pesticides, and pharmaceutically active compounds is attracting much attention from the viewpoint of its effect on people's health and the aquatic ecosystem. Alkyl phthalates, used widely as a plasticizer, are also assumed to be useful as a typical EDC, and their toxicities have been reported even on the reproductive organisms of rats, including environmental incidents (Caldwell, 1999; Willoughby et al., 2000). With the rapid development of analytical methods, the trace elements in the environment can be detected even at very low concentrations, and thus the pollution example of aquatic environment by them has been continuously reported (Boyd et al., 2003; Ying et al., 2002).

Aqueous organic micro-pollutants have been commonly determined by gas chromatography (GC) equipped with mass spectrometry (MS) or by high performance liquid chromatography (HPLC) coupled with sensitive detection systems. The instrumental analytical processes have been automated and their sensitivity capabilities have been improved as a result. The processes that influence the accuracy of analysis, however, are the sample preparation steps including extraction, enrichment, and cleanup. These processes are complicated and are affected by the co-existing pollutants in a sample. Suspended solids (SS) in an aqueous sample interfere with the efficiency of the solvent extraction and the solid phase extraction (SPE) with a cartridge adsorbent. These are commonly used extraction methods. Solid phase micro-extraction (SPME) and stir-bar extraction (SBE) do not interfere with SS, however these methods can be applied to the GC analytical system. The rapid and simple extraction methods coupled with HPLC analysis have also been developed by using the in-tube solid-phase microextraction (Eisert and Pawliszyn, 1997; Saito and Jinno, 2003: Saito et al., 2004). In the case of samples containing a high concentration of SS and common organic pollutants measured by COD or TOC, it is important to extract the target analytes selectively. When a fibrous material was used as a stationary phase for the in-tube solid-phase microextraction, the alkylphthalates in domestic wastewater were analyzed successfully (Saito et al., 2003), although SS removal was required before the analysis. The results suggest that fibrous materials are of use as an adsorbent for the solid phase extraction of hazardous micro-pollutants.

In this work, the fibrous solid phase extraction method was examined in order to simplify the experimental analysis procedure.

† To whom correspondence should be addressed.
yjjung@cup.ac.kr

2. Materials and Methods

2.1. Materials and Reagents

Fibrous material (PBO: *p*-phenylene-2,5-benzobisoxazole) was employed as an adsorbent for solid phase extraction. The fibers are known to be strongly hydrophobic and too rigid to be woven due to the chemical structure of rigid-rod chain molecules, as illustrated in Fig. 1.

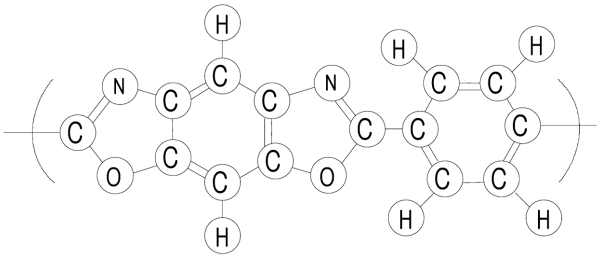

Fig. 1. Chemical structure of the PBO fibers.

Two types of PBO fibers such as the regular type (AS) and the high modulus type (HM) were used in this work. Fig. 2 shows the photographs of two different types of PBO fibers for the sorption/desorption experiments. The detailed physicochemical properties of the PBO fibers are presented in Table 1, and they have some differences in terms of the modulus and moisture etc. The fibers were washed with distilled water and organic solvents prior to the sorption experiments.

Di-(2-ethylhexyl) phthalate (DEHP), used as an analyte, was purchased from the Tokyo Chemicals Industry Co. Ltd (Tokyo, Japan) and employed without further purification. The aqueous solution for the adsorption experiment was prepared by the following procedure: The solute was dissolved in methanol at concentration of ca. 1000 mg/L. An appropriate amount of the methanol solution was dropped on to a glass plate. The methanol was evaporated, and then the glass plate was put into ultra pure water in order to dissolve the solutes. The final concentrations were adjusted to be within the range of 10 and 100 μg/L.

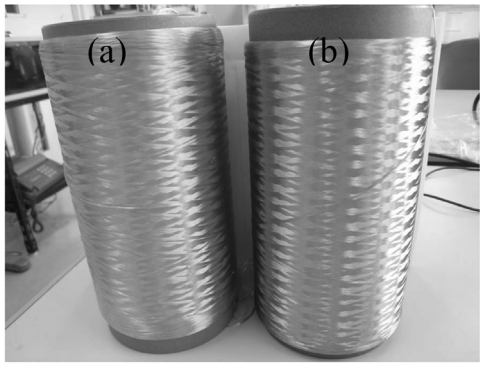

Fig. 2. Photographs of PBO fibers used in this work. (a) AS type, (b) HM type.

Table 1. Typical properties of PBO fibers

Item	AS	HM
Filament decitex (dtex)	1.7	1.7
Density (g/cm^3)	1.54	1.56
Tensile strength (kg/mm^2)	590	590
Elongation at break (%)	3.5	2.5
Moisture regain (65% RH)	2.0	0.6
Decomposition temp. (°C)	650	650
Limiting Oxygen Index (ppm/°C)	68	68
Thermal expansion coefficient	-	-6×10^{-6}
Melting temperature	none	none
Dissipation factor	-	0.001

2.2. Sorption procedure

The extraction performance of the PBO fibers for the DEHP solution was examined by batch type sorption experiments under the following conditions: An appropriate weight of the fiber was placed in contact with 20 mL of the aqueous DEHP solution by shaking at 25°C. Detailed experimental conditions are summarized in Table 2, where the effects of the amount of solution, fibers and the pre-cleaning method of the fibers were mainly examined.

2.3. Desorption procedure

The fibers that adsorbed DEHP were picked up with a pair of tweezers and rinsed with ca. 50 mL of distilled

Table 2. The sorption experiments

	Mode-1	Mode-2	Mode-3
Initial conc. (μg/L)	50	50	10, 50, 100
Pre-cleaning	Methanol + Distilled water	Methanol + Distilled water	1. Distilled water 2. Acetone 3. Chloroform + Acetone
Fiber	AS & HM	HM	HM
Fiber weight (mg)	10 ~ 100	10 ~ 150	50, 100
Sample volume (mL)	20	20	20
Method	Mixing	mixing	stirring
Contact time (hr)	1 or 48	1 or 24	24

water, followed by extraction with 2 mL of methanol under ultrasonic radiation. The concentrations of DEHP in the aqueous solution, including the initial and the equilibrium solutions, were analyzed by the HPLC-direct injection method (Kiso et al., 1996). Kiso et al. (2001) reported that alkyl phthalates have been determined to be at a level lower than 1 μg/L with this method. The methanol solutions after desorption were also analyzed by HPLC. The HPLC analysis was conducted under the following conditions: Stationary phase VX-ODS (monomeric ODS, 5 μm, 4.6 mm i.d. × 250 mm long, Shinwa Chemicals Co. Ltd., Japan); mobile phase CH_3CN/H_2O (CH_3CN = 95%), flow rate 1.5 mL/min and detector UV detector (λ = 220 nm). Methanol, CH_3CN and H_2O were used for the HPLC grade. In the case of the aqueous samples, 2 mL of the sample were injected into the HPLC.

3. Results and Discussion

3.1. Sorption Property

The effects of the solution amounts on DEHP removal were examined by the batch type sorption experiments. According to the value of log P which is employed as one of the parameter of hydrophobicity for solutes (Kiso et al., 2001), DEHP (log P = 7.45) (Hansh and Leo, 1995) can be expected to be effectively adsorbed on the hydrophobic materials.

DEHP removal, in Mode-1, was plotted against the phase ratio (fiber weight/solution volume: mg/mL) as shown in Fig. 3, where the initial concentration of DEHP was 50 μg/L. The removal rates increased with the increase of the phase ratio, although the removal rates fluctuated in the range of the lower phase ratio. HM type of the PBO fiber could generally sorb DEHP more effectively than the AS type. Thus, HY type of PBO fiber was employed for further experiments.

Since the fibrous material has a low specific surface area, a longer contact time was applied. In the case of the AS type fiber, DEHP was removed effectively for 2 days as shown in Fig. 4. In the case of the HM type fiber, however, the removal rates after 24 hours were more than 95% for the entire range of the phase ratio (0.54~8.37 mg/mL) as shown in Fig. 5. Although reducing contact time is a separate subject, the HM type fiber was a useful adsorbent from the viewpoint that it could be applied at a low phase ratio.

The effects of the fiber pre-cleaning are shown in Fig. 6, where distilled water, acetone, and chloroform+acetone were used as cleaning solvents in Mode-3-1, Mode-3-2, and Mode-3-3, respectively. Among the three kinds of solvents, acetone was the most effective because it obtained the highest removal rates.

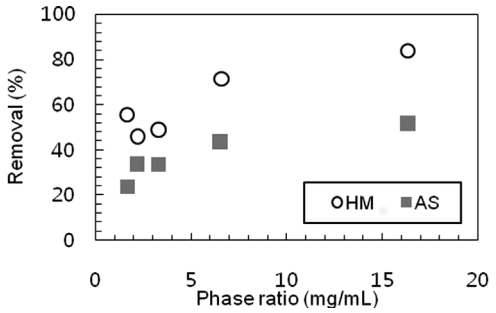

Fig. 3. Effects of the phase ratio on DEHP removal (Mode-1).

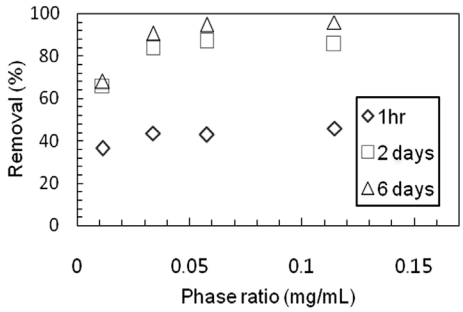

Fig. 4. Effects of contact time on DEHP removal in Mode-1.

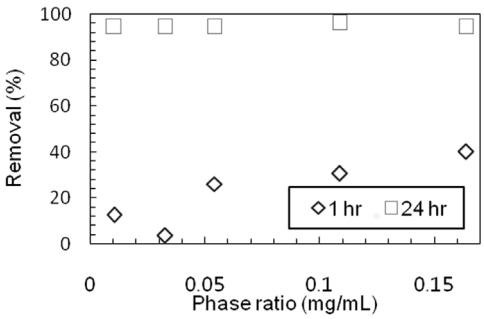

Fig. 5. DEHP removals for 24 h.

The removals were also influenced by the initial concentrations of DEHP as shown in Fig. 6. In the case of a 10 μg/L initial concentration, more than 97% of the removal rate was obtained at 2.5 mg/mL of the phase ratio. In the cases of other initial concentrations, the maximum removal rates decreased with a decrease of the phase ratio. The results indicated that the phase ratio of 5 mg/mL can be applied to the solution containing less than 50 μg/L of DEHP. A phase ration of more than 5 mg/mL may be preferable for the solutions containing more than 50 μg/L of DEHP.

3.2. Desorption

The PBO fibers were able to be picked up and rinsed easily with distilled water. The attached water on the fibers was also removed easily by filter paper because of

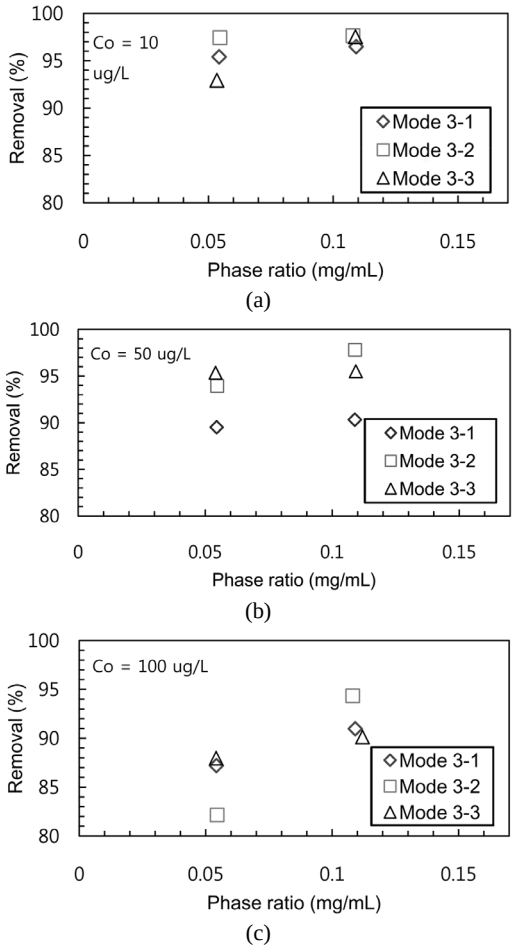

Fig. 6. Effects of the pre-cleaning solvent and the initial concentration on DEHP removal. (a) C_o=10 μg/L, (b) C_o=50 μg/L, (c) C_o=100 μg/L.

the very hydrophobic properties of the fibers. When the fibers were in contact with domestic wastewater in the preliminary experiments, the suspended solids did not attach to the fibers and could be removed easily by the rinsing process. The results suggest that the PBO fibers can be applied as an adsorbent to the samples containing a high concentration of SS, where the filtration of the sample does not need to be similar to the SPME method.

The PBO fibers that adsorbed DEHP were in contact with 2 mL of methanol under ultrasonic radiation. The average desorption ratios and the average overall recovery of 3 times experiments are summarized in Table 3. The average desorption ratio increased with an increase of the phase ratio and with a decrease of the initial concentration. In the case of an initial concentration of 50 μg/L, the highest desorption ratio of 97.9% was obtained and the relative standard deviation (RSTD) was also low. In the case of an initial concentration of 10 μg/L, the desorption ratios were more than 100%. This may be caused mainly by the contamination of the operation process due to the environment of the laboratory.

The overall recovery rates are also listed in Table 3. In the case of an initial concentration of 50 μg/L, high and stable recovery rates were obtained. The following subjects remain for further research: The performance of other micro-pollutants including alkyl phthalates, pesticides, and EDCs, and the development of extraction conditions for higher concentration of pollutants.

4. Conclusions

The extraction performance of the PBO fibers for di-(2-ethylhexyl) phthalate was examined by batch type sorption and desorption experiments, and the results obtained in this work are summarized as follows:

1) When HM type fibers were applied at 5 mg/mL of the phase ratio, DEHP of less than 50 μg/L was removed at more than 95% and it was desorbed effectively with 2 mL of methanol.
2) The removal of DEHP was influenced by the phase ratio and the PBO fibers were of use as an adsorbent for the analysis of DEHP.
3) DEHP removal was affected by the phase ratio and the pre-treatment method, and the phase ratios used in this work were not sufficient for DEHP solution of 100 mg/L.

국문요약

본 연구에서는 섬유상 재료(PBO)가 고상 추출을 위한 흡착제로 사용되어 분석 과정을 간소화하였다. 두 종류의

Table 3. Desorption and overall recovery ratios

Initial conc. (μg/L)	Phase ratio (mg/mL)	Desorption ratio (%)		Overall recovery (%)	
		Average	RSTD	Average	RSTD
100	2.5	75.4	0.14	64.8	0.16
	5.0	83.0	0.08	76.1	0.06
50	2.5	89.8	0.03	83.4	0.01
	5.0	97.9	0.10	92.3	0.06
10	2.5	134.1	0.41	127.8	0.41
	5.0	148.6	0.23	144.3	0.22

PBO섬유(HM, AS)를 이용한 회분식 흡/탈착 실험으로 DEHP 물질의 추출 특성을 평가하였다. 100 mg의 HM 섬유를 20 mL의 수용성 DEHP 용액(50 ug/L이하)에 주입한 결과, 95%의 DEHP가 흡착되었다. 초기 50 ug/L의 DEHP 수용액의 경우, 흡착된 DEHP는 메탄올로 탈착되어 전체 회수율은 92.3%로 나타났다. 따라서 PBO섬유는 알킬프탈레이트 분석을 위한 흡착제로 유용한 것으로 나타났고, 이런 추출 과정은 수중의 SS에 영향을 받지 않았다.

References

Boyd, G. R., Reemtsma, H., Grimm, D. A., and Mitra, S. (2003). Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. *The Science of the Total Environment*, **311**, pp. 135-149.

Caldwell, D. J. (1999). Review of mononuclear cell leukemia in F-344 rat bioassays and its significance to hyman cancer risk: a case study using alkyl phthalates. *Regulatory Toxicology and Pharmacology*, **30**, pp. 45-53.

Eisert, R. and Pawliszyn, J. (1997). Automated in-tube solid-phase microextraction coupled to high-performance liquid chromatography. *Anal. Chem.*, **69**, pp. 3140-3147.

Hansh, C. and Leo, A. (1995). Exploring QSAR Fundamentals and Applications in Chemistry and Biology. ACS, Washington DC, USA.

Kiso, Y., Kon, T., Kitao, T., and Nishimura, K. (2001). Rejection properties of alkyl phthalates with nanofiltration membranes. *Journal of Membrane Science*, **182**, pp. 205-214.

Kiso, Y., Li, H., Shigetoh, K., Kitao, T., and Jinno, K. (1996). Pesticide analysis by high-performance liquid chromatography using the direct injection method. *Journal of Chromatography A.*, **733**, pp. 259-265.

Saito, Y., Imaizumi, M., Ban, K., Tahara, A., Wada, H., and Jinno, K. (2004). Development of miniaturized sample preparation with fibrous extraction media. *Journal of Chromatography A.*, **1025**, pp. 27-32.

Saito, Y. and Jinno, K. (2003). Miniaturized sample preparation combined with liquid phase separations. *Journal of Chromatography A.*, **1000**, pp. 53-67.

Saito, Y., Nakao, Y., Imaizumi, M., Morishita, Y., Kiso, Y., and Jinno, K. (2003). Miniaturized solid-phase extraction as a sample preparation technique for the determination of phthalate in water. *Anal. Bioanaly. Chem.*, **373**, pp. 81-86.

Willoughby, C. R., Fulcher, S. M., Creasy, D. M., Heath, J. A., Priston, R. A. J., and Moore, N. P. (2000). Two-generation reproduction toxicity studies of di-(C_7-C_9 alkyl) phthalate and di-(C_9-C_{11} alkyl) phthalate in the rat. *Reproductive Toxicology*, **14**, pp. 427-450.

Ying, G. G., Kookana, R. S., and Ru, Y. J. (2002). Occurrence and fate of hormone steroids in the environment. *Environment International*, **28**, pp. 545-551.