

Feasibility of Fibrous Solid Phase Extraction to Alkylphenols Analysis

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섬유상 고상 추출물질을 이용한 알킬페놀 화합물 분석 가능성

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Abstract

p-phenylene-2,5-benzobisoxazole (PBO; Zylon[®]) fibers as an adsorbent were employed for solid phase extraction of aqueous alkylphenols. The removal ratios for 10 kinds of alkylphenols at initial concentration of 100 μgL^{-1} were in the range of 16.8-96.3% and the removals increased with the increase of the phase ratio (fiber weight/solution volume). The plots of the logarithm of partition coefficient (log K) were correlated with the logarithm of the *n*-octanol/water partition coefficient (log P). The adsorbed alkylphenols were completely desorbed with the mixture of acetonitrile and dichloromethane.

keywords : Alkylphenols, log P, Partition coefficient, PBO fibers, Solid phase extraction

1. Introduction

With the proliferation of the chemicals and the expansion of industry, wide ranges of micro-organic pollutants are being steadily discharged into the aquatic environment. Among these substances, alkylphenols (APs) classified as the endocrine disrupting compounds (EDCs) have drawn particular attention because of their endocrine disrupting properties and high concentrations detected in the environment (Cespedes et al., 2008). These findings have been reported in the surface water, effluent from sewage treatment plants and even in the drinking water sources (Ying et al., 2002). The discharged APs from sewage treatment plants in Europe was observed with levels at the ppm range (Andreu et al., 2007), and this may be due to that APs are intermediates by biological degradation of nonionic surfactants. The removal techniques for them are urgently required, and some effective techniques such as membrane (Jung et al., 2007a), sorption processes (Iwasaki et al., 2002) have been developed to the purpose.

Although APs are being reported on the wide occurrence in the environment, it is not easy to detect them. In general, APs can be analyzed by chromatographic separation, such as GC and LC coupled with a variety of detection methods (Jonsson et al., 2008). In the analytical procedure, however,

the sample preparation steps including extraction, purification and enrichment are the most difficult and the time consuming processes. Especially for the waters containing high concentration of organic and particulate pollutants, such as wastewaters, the sample preparation is difficult and influence accuracy of the analysis. Meanwhile, frequent monitoring is also required. For this reasons, development of a simple and effective sample preparation method is a useful approach for this subject.

In this study, we focused on PBO (*p*-phenylene-2,5-benzobisoxazole) fibers as an adsorbent, because the fibers does not entrap suspended solids and strongly hydrophobic. PBO fibers have been reported as a useful adsorbent for solid phase extraction for micro-organic pollutants (Saito et al., 2002; Shamsul et al., 2001), where gas chromatography or liquid chromatography were used as an analytical instrument. In our previous work (Jung et al., 2007b), it was found that PBO fibers effectively removed polycyclic aromatic hydrocarbons (PAHs), and indicated the probability of an alternative adsorbent for SPE. The adsorption and desorption properties of the PBO fibers were examined with 10 kinds of APs. In addition, the effects of physicochemical properties of APs on the adsorption performance were discussed.

2. Experimentals

2.1. Materials and Reagents

The high modulus type (HM) of PBO (*p*-phenylene-2,5-

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benzobisoxazole; Zylon ®: Toyobo Co. Ltd., Osaka, Japan) fibers were used as an adsorbent. Due to the chemical structure, PBO fibers are known to be strongly hydrophobic and too rigid to be woven. Ten kinds of APs used in this work are listed in Table 1, where the values of *n*-octanol/water partition coefficient (log P) are also described. The chemical structures of APs are shown in Fig. 1. The purchased alkylphenols (Tokyo chemicals Industry Co. Ltd, Tokyo, Japan or GL Sciences Inc. Tokyo, Japan) were used without further purification. The aqueous solutions applied to the sorption/desorption experiments were prepared by the following procedure: each alkylphenol was dissolved in methanol at 5000 mg/L, an appropriate amount of the methanol solution was dropped onto a glass plate, methanol was evaporated, then the glass plate was put into a vial

containing ultra-pure water (distilled ionized water) to dissolve the alkylphenol. The final concentrations were in the range of 10~200 µg/L.

2.2. Sorption experiment

A bundle of PBO fibers (90 cm long; ca. 0.01 g) were washed with ultra-pure water, CH₂Cl₂, CH₃CN and again with ultra-pure water before the sorption tests. The adsorption properties of PBO fibers were examined by batch type sorption experiments. The appropriate weight of cut fibers was put into 20 mL of an aqueous alkylphenol solution, and the solution was shaken for 24 hours at 25°C. Then, the PBO fibers were taken out by a pair of tweezers and served for the desorption process, and the APs concentration in the residual solution was analyzed by HPLC-direct injection method (Kiso et al., 1996) under the following conditions: VX-ODS column (monomeric ODS, 5 µm, 4.6 mm i.d. X 250 mm long, Shinwa Chemicals Co. Ltd., Kyoto, Japan); mobile phase: CH₃CN/H₂O (CH₃CN = 60~90%); flow rate of the mobile phase: 1.0 mL.min⁻¹; detector UV detector (λ = 220 nm); the sample size: 1 mL of the aqueous solution.

The adsorption amount of the solutes per unit mass of the fibers was calculated and was plotted against the equilibrium bulk concentration of the solute. In most cases, the adsorption amount was correlated linearly with the equilibrium bulk concentration, and the partition coefficient, *K*, was evaluated on the basis of the slope.

Table 1. Properties of alkylphenols used in this work

No.	Alkylphenol	Formula	Molecular weight	log P
1	4- <i>n</i> -Buthylphenol	C ₁₀ H ₁₄ O	150.2	3.64
2	2- <i>tert</i> -Buthylphenol	C ₁₄ H ₁₀ O	150.2	3.31
3	4- <i>tert</i> -Buthylphenol	C ₁₄ H ₁₀ O	150.2	3.31
4	2-Phenylphenol	C ₁₂ H ₁₀ O	170.2	3.09
5	4-Phenylphenol	C ₁₂ H ₁₀ O	170.2	3.20
6	4- <i>n</i> -Pentylphenol	C ₁₁ H ₁₆ O	164.2	4.06
7	4- <i>n</i> -Heptylphenol	C ₁₃ H ₂₀ O	192.3	4.15
8	4- <i>tert</i> -Octylphenol	C ₁₄ H ₂₂ O	206.3	5.14
9	4- <i>n</i> -Octylphenol	C ₁₄ H ₂₂ O	206.3	5.16
10	4- <i>n</i> -Nonylphenol	C ₁₅ H ₂₄ O	220.4	5.76

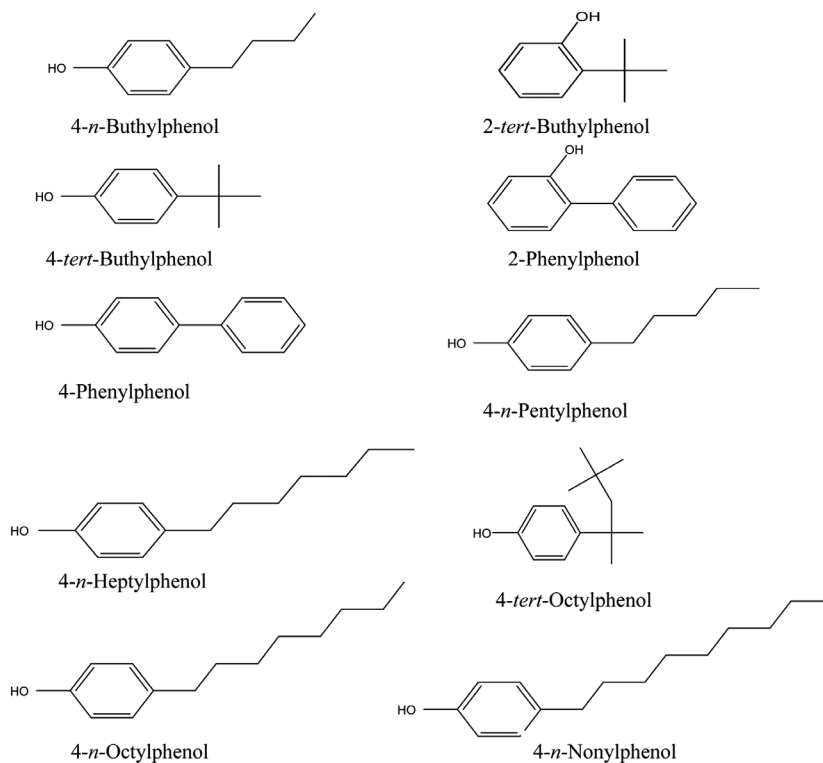


Fig. 1. Chemical structure of the APs used in this work.

$$K = \frac{q_e}{C_e} \quad (1)$$

where q_e is the adsorption amount per unit mass of the fiber [$\mu\text{g/g}$], C_e is the concentration in bulk solution [$\mu\text{g/L}$], and the unit of K is [$\mu\text{g/g}$] / [$\mu\text{g/L}$].

2.3. Desorption experiment

The desorption properties of the PBO fibers were examined with the following organic solvents: methanol, acetonitril and dichloromethane. The PBO fibers adsorbed the APs were picked up and rinsed with ca. 50 mL of ultra-pure water, where APs were not detected in the exhausted rinse water. The water remained on the rinsed fibers was easily removed by shaking the fibers with a pair of tweezers. Then, the fibers were extracted with the organic solvents under ultrasonic radiation. The desorption conditions are described in Table 2. The APs concentrations were analyzed by a HPLC.

3. Results and Discussion

3.1. Removal properties of APs

Fig. 2 shows the percent removals of the APs under the following conditions, the initial concentration: 100 $\mu\text{g/L}$; fiber weight: 0.3 g (sample No. 1-8) or 0.1 g (sample No. 9 and 10 only). The removals of APs increased with the increase of the phase ratio (fiber weight/ solution volume).

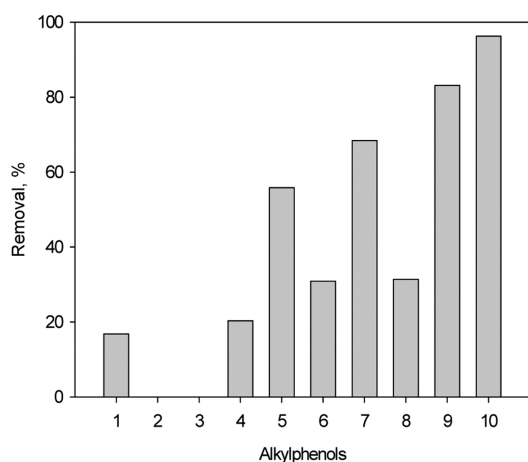


Fig. 2. Alkylphenol removals. The numbers (1 to 10 in x-axis) mean the solutes described in Table 1.

Table 2. Desorption conditions

	Mode-1	Mode-2	Mode-3
Solvent	CH ₃ OH	CH ₃ CN	CH ₃ CN (50%) + CH ₂ Cl ₂ (50%)
Volume	5 mL	5 mL	5 mL
Ultrasonic radiation	5 min	5 min	5 min

The removals varied in the range from 20% (4-*n*-butylphenol) to more than 96% (4-*n*-nonylphenol). In the case of 4-*n*-nonylphenol and 4-*n*-octylphenol, the removals more than 95% were obtained at the initial concentration of lower than 50 $\mu\text{g/L}$, and the removals were influenced by the initial concentration. The fact that a large proportion of the octylphenol was sorbed to the bed sediments of rivers (Johnson et al., 1998) corresponded to the results appeared in Fig. 2. However, 2-*tert*-butylphenol and 4-*tert*-butylphenol were not adsorbed, and it can be pointed out that *tert*-butyl group is significant bulky than *n*-alkyl group.

3.2. Adsorption properties on PBO fiber

The adsorption isotherm was examined, where the adsorbed amounts per unit mass of the fibers were plotted against the equilibrium concentrations of the solute. The adsorption isotherms for APs such as 4-*n*-Nonylphenol and 4-*n*-Octylphenol were approximated by Freundlich type as seen in Fig. 3, where q_e is the equilibrium adsorption amount at equilibrium concentration (C_e). The logarithm of partition coefficient K was plotted against $\log P$ (*n*-octanol/water partition coefficient) as seen in Fig. 4. However, the data of 2-*tert*-butylphenol and 4-*tert*-butylphenol were not plotted because of $K \approx 0$.

For most APs except 2-phenylphenol, 4-phenylphenol and 4-*tert*-octylphenol, $\log K$ was linearly correlated with $\log P$, and the results indicated that adsorption was mainly controlled by hydrophobic interaction and phenyl-phenyl interaction between APs and PBO. Comparing 4-*tert*-octylphenyl with 4-*n*-octylphenol, $\log K$ value of 4-*tert*-octylphenol was significantly lower than that of 4-*n*-octylphenol. Considering these results and the results of *tert*-butyl phenols (Fig. 1), *tert*-butyl group may inhibit the adsorption by steric effect. Similar effect was reported by Kiso et al. (2001) as follows: the hydrophobic interaction between NF membrane and aromatic pesticides was influenced by steric effect due to a bulky substituent. On the other hand, $\log K$ value of 4-phenylphenol was significantly larger than the line described in Fig. 4. The structure of 4-phenylphenol is planar, and phenyl-phenyl interaction may be enhanced.

3.3. Desorption of alkylphenols

Four kinds of alkylphenols adsorbed on PBO fibers were extracted with three different kinds of organic solvents. The desorption efficiency was strongly influenced by the solvent

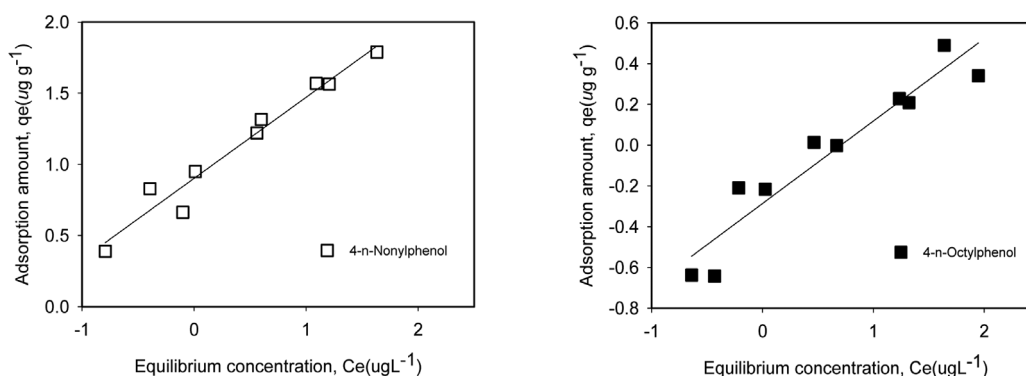


Fig. 3. Adsorption isotherm of alkylphenols (4-*n*-Nonylphenol and 4-*n*-Octylphenol).

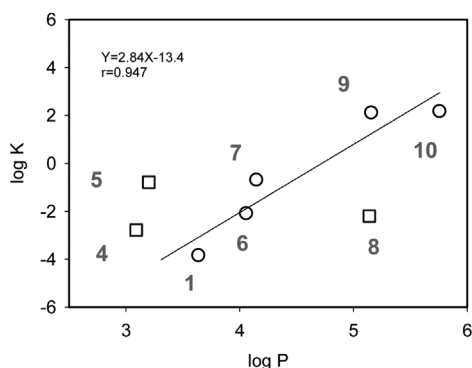


Fig. 4. Relationship between $\log K$ and $\log P$.

as shown in Table 2.

In the cases of pure CH_3OH and CH_3CN , the desorption degrees were low, and these solvents are not suitable for the extraction. Relatively less adsorbed APs showed less extraction efficiency, and this seems to be contradictory.

The mixture of CH_3CN and CH_2Cl_2 (50/50) could efficiently extract these alkylphenols. Polyaromatic hydrocarbons (PAHs) and diethylphtalate (DEHP) adsorbed on PBO fibers were not desorbed even by several organic solvents in our previous work (Jung et al., 2007b). From desorption efficiency shown in Table 2, we can conclude that the PBO fibers is a useful adsorbent for alkylphenols analysis. When the PBO fibers are submerged in a water sample, suspended solids does not be entrapped and easily washed out by rinse. These points may be desirable for environmental and wastewater samples.

4. Conclusions

Table 2. Desorption degrees of alkylphenols

No.	Alkylphenol	Desorption degree (%)		
		CH_3OH	CH_3CN	$\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (50/50)
1	4- <i>n</i> -Buthylphenol	46.0	55.3	Not tested
8	4- <i>tert</i> -Buthylphenol	40.6	41.2	97.0
9	4- <i>n</i> -Octylphenol	65.5	77.6	105.8
10	4- <i>n</i> -Nonylphenol	74.4	80.9	112.5

PBO fibers were employed solid phase extraction of APs as an adsorbent, and the adsorption and desorption performances were examined by batch type experiments. In addition, these APs could effectively desorbed with $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (50/50). Considering that suspended solids does not influence the extraction efficiency, the PBO fibers is a useful adsorbent as an alternative for solid phase extraction of APs.

PBO fibers were employed as an adsorbent for the removal of APs, and the adsorption and desorption performances were conducted with batch type experiments. The results can be summarized as follows,

- 1) The maximum removal ratios of APs ranged from 20% (4-*n*-buthylphenol) to more than 96% (4-*n*-nonylphenol)
- 2) The adsorption performance was high especially for APs having long alkylchain such as 4-*n*-octylphenol and 4-*n*-nonylphenol.
- 3) The logarithm of partition coefficient ($\log K$) for APs was linearly correlated with $\log P$, and the adsorption property was influenced by molecular structure such as branching and the position of substituent.
- 4) The mixture of CH_3CN and CH_2Cl_2 could completely extract most APs.

국문요약

흡착제로서의 PBO 섬유가 수용성 알킬페놀 화합물의 고상 추출용으로 사용되었다. 초기농도 $100 \mu\text{gL}^{-1}$ 에서 10 종류의 알킬페놀에 대한 제거율은 16.8~96.3%였고, 제거율은 섬유무게/액체부피비의 증가에 따라 증가하였다. $\log K$ 는 $\log P$ 와 일치하였다. 흡착된 알킬페놀은 아세트니트릴과 디클로로메탄의 혼합액으로 충분히 탈착되었다.

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