The Solid Phase Extraction of Phenol and Chlorophenols by the Chemically Modified Polymeric Adsorbents with Porphyrins

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The commercially available Amberlite XAD-2 and XAD-4 resins were modified with macrocyclic protoporphyrin IX (PPIX) or tetrakis(*p*-carboxyphenyl) porphyrin (TCPP) to enhance the adsorption capacity for phenol and chlorophenols. The chemically modified polymeric adsorbents (XAD-2+PPIX, XAD-2+TCPP, XAD-4+PPIX, and XAD-4+TCPP) were applied to the solid phase extraction as an adsorbent material for the preconcentration of phenol and chlorophenols in environmental waters. Generally, the synthesized adsorbents showed higher recoveries than underivatized adsorbents, XAD-2 and XAD-4, without matrix interferences. Especially, XAD-4+PPIX showed more than 90% recoveries for all compounds used in this study including hydrophilic phenol. The major factor for the increase of the adsorption capacity was the increase of π-π interaction between adsorbents and samples due to the introduction of the porphyrin molecule. However, the breakthrough volumes and recovery values of the XADs+TCPP columns were slightly decreased for the bulky chlorophenols such as TCP and PCP. Using molecular mechanics methods, the structures of TCPP and PPIX were compared with that of porphine, the parent molecule of porphyrin. Four bulky *p*-carboxyphenyl groups of TCPP were torsional each other, thus the molecular plane of TCPP were not on the same level. In conclusion, the decrease of breakthrough volumes and recovery values of XADs+TCPP columns for bulky phenols can be explained by the steric hindrance of the π-π interaction between porphyrin plane and the phenols.

Key Words : Chemically modified polymeric adsorbents, Solid phase extraction, Phenol, Chlorophenols, XAD-4+PPIX

Introduction

Phenol and chlorophenols has been used as insecticides, fungicides, herbicides, algicides, ovicides, antiseptics and intermediates in the production of dyes, plastics and pharmaceuticals.[1-3] Chlorophenols can be generated as a result of hydrolysis, oxidation and biodegradation of chlorinated pesticides, and can be formed during chlorination of drinking water.[3,4-6] They are carcinogenic compounds and bioaccumulated in the human body. US Environmental Protection Agency (EPA) has regulated eleven phenolic compounds as priority pollutants, and especially, chlorophenols are known to be most toxic among them.[7] European Community (EC) has announced a list of the pollutants including chlorophenols and regulated the maximum permissible concentration as 0.5 ppb.[8]

Considering such a serious toxicity, it is important to develop an adsorbent and a pretreatment method that can remove and recover the chlorophenols. In this study, chemically modified polymeric adsorbents with protoporphyrin IX or tetrakis(*p*-carboxyphenyl) porphyrin synthesized in our group[9,10] were used as substrates in solid phase extraction (SPE) for the preconcentration and determination of phenol and chlorophenols in environmental waters.

Solid phase extraction is the most widely used pretreatment method and has been rapidly developed recently due to the synthesis of new adsorbents, the development of extraction methods and the automation of the adsorption system.[11,12] Many types of adsorbents such as chemically bonded reversed-phase silicas (C_8, C_{18}),[13,14] apolar poly(styrene-divinylbenzene) copolymers (XADs, PRP-1, PLRP-S, LiChrolut EN, Envichrom P),[15-17] carbon-based adsorbents,[18,19] mixed-mode adsorbents (Bond-Elut Certify I, II, Isolute-Confirm HAX/HCX),[20,21] molecularly imprinted polymers (MIPs)[22,23] have been used. A limitation to apply the adsorbents to solid phase extraction is that polar organic compounds are known to be not completely extracted. Thus chemically modified polymeric adsorbents with various functional groups have been developed in recent years.

The objective of this study is to apply the porphyrin modified XAD adsorbents synthesized in our group to solid phase extraction of phenol and chlorophenols in environmental waters in order to improve the recovery of hydrophilic phenol. The structure of the porphyrin groups used as chemical modifiers were compared with porphine, the parent molecule of the porphyrin, using molecular mechanics methods.

Experimental Section

Chemicals and reagents. Phenol and chlorophenols used in this study were phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-chlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP).

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They were purchased from Fluka (Ronkonkoma, NY, USA) and used without further purification. Stock solutions were prepared in methanol and working solutions were prepared by diluting the stock solutions with methanol just before use.

HPLC-grade acetonitrile (J.T. Baker, Phillipsburg, NJ, USA) and Milli-Q water were used to prepare the mobile phase in chromatographic separation. In preparation of the mobile phase, acetonitrile and water were filtered through a 0.2 μm nylon filter (Whatman, Maldstone, England) and 0.45 μm cellulose nitrate filter (Whatman), respectively.

Tap water and river water samples were filtered through a 0.2 μm nylon filter before the solid phase extraction procedure to remove particulates and then adjusted to pH 3 with hydrochloric acid to prevent the dissociation of phenols. All other reagents were of analytical grade.

Apparatus and chromatographic conditions. Chromatographic analysis were performed using a Gilson HPLC system (Gilson SA, Villiers-le-Bel, France) equipped with UV/VIS 151 detector, 321 dual head pump, 231 XL sampling injector with 402 syringe pump and Rheodyne model 7725i injector having a 20 μL loop. System control and data analysis were carried out with a version 2.10 Unipoint system software. Stationary phase was a Mightysil RP-18 GP C_{18} column (250 × 4.6 mm I.D., 5 μm) from Kanto Chemical Co., Inc. (Tokyo, Japan). Chromatographic separations were carried out with a gradient of acetonitrile and 10^{-3} M phosphoric acid mixing from 38 : 62 to 95 : 5 in 20 min. Detection wavelength was set at 280 nm for all phenols and quantitative analysis was executed by an external standard method.

Solid phase extraction. Six adsorbents were used for solid phase extraction : Amberlite XAD-2 and XAD-4 from Rohm and Haas (Philadelphia, PA, USA), XAD-2+PPIX, XAD-4+PPIX, XAD-2+TCPP, and XAD-4+TCPP, which were synthesized in our previous study.[9,10] They were slurry-packed with acetonitrile in a stainless-steel column (20 mm × 2 mm I.D.) and titanium frits were located above and below each adsorbent bed. To make the same condition as real sample solution, residual acetonitrile was removed by flushing the distilled water adjusted to pH 3 with HCl. Adsorbents were not dried. Real sample solutions were flushed at a flow rate of 2.5 mL/min for adsorption and desorbed with acetonitrile in a back-flushing mode at a flow rate of 0.05 mL/min. To determine the desorption volume, elution curves were made by injecting the acetonitrile to the adsorbent columns at intervals of 0.1 mL. After desorption, 1 mL of acetonitrile was flushed to remove the memory effect.

Results and Discussion

Physical properties of the adsorbents. The amount of PPIX or TCPP bonded to XAD resins was determined by atomic absorption spectrometry (AAS) using the same methods described in our previous study.[9,10] The calculated amount of PPIX or TCPP bonded to XAD resins was 1.54%(wt%) and 1.37%(wt%), respectively. The physical properties of the polymeric adsorbents used in this study are listed in Table 1. In general, adsorption capacity of the adsorbent is proportional to the surface area of the adsorbents. The surface area of XAD-4 is well known to be larger than XAD-2. Excepting XAD-2+TCPP, the surface areas of the porphyrin modified XADs were larger than those of the intact XADs. The size of pores is related to that of the molecules adsorbed in diffusion process. The average pore diameter of the XAD-2 was larger than that of the XAD-4, while the total pore volume of the XAD-2 was smaller than that of the XAD-4. These results were correlated with the K_F, Freundlich constant, values which are indicators of adsorption capacity as described in our previous study.[9,10]

Breakthrough volume. The measurement of breakthrough volume is important in solid-phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analytes during elution of the sample. Breakthrough volumes were calculated at which the absorbance reached to 1% of the maximum absorbance. As shown in Table 2, in general, breakthrough volumes were increased for the modified adsorbents and proportional to the number of substituents in phenol molecule. It may be attributed to the additional retention by the increase of the surface area and the π-π interaction due to the introduction of porphyrin molecules. However, breakthrough volumes of

Table 1. Physical Properties of Polymeric Adsorbents

Adsorbents	Specific surface area[a] (m^2/g)	Average pore diameter (nm)	Total pore volume[b] (cm^3/g)
XAD-2	398[a1]	6.08	0.61[b1]
XAD-2+TCPP	357[a2]	8.32	0.74[b2]
XAD-2+PPIX	460[a3]	6.66	0.77[b3]
XAD-4	947[a4]	4.12	0.98[b4]
XAD-4+TCPP	1028[a5]	3.80	0.98[b5]
XAD-4+PPIX	1031[a6]	3.67	0.95[b6]

[a] BET surface area with correlation coefficient of [a1]0.9999, [a2]0.9999, [a3]0.9999, [a4]0.9999, [a5]0.9999, [a6]0.9999. [b] Single point total pore volume of pores less than [b1]65.94832 nm at p/p^o 0.96976823, [b2]70.1256 nm at 0.97161167, [b3]65.97013 nm at 0.96977846, [b4]152.33235 at 0.98713398, [b5]220.36973 nm at 0.99115508, [b6]233.85029 nm at 0.99167151

Table 2. Breakthrough Volumes[a] (mL) of Phenols for Polymeric Adsorbents

Compounds	XAD-2	XAD-2+TCPP	XAD-2+PPIX	XAD-4	XAD-4+TCPP	XAD-4+PPIX
Ph	2.7	3.3	3.7	5.0	6.2	7.1
2-CP	4.3	6.1	9.0	23	21	31
TCP	54	34	63	168	127	379
PCP	209	98	220	> 500	394	> 500

[a] Calculated at 1% of the maximum absorbance. Concentration of samples: 10 mg/L. Flow rate : 2.5 mL/min

XADs+TCPP were decreased for the multi-substituted phenols such as TCP and PCP. The results can be explained by the steric effect of the porphyrin molecules. Our approach to molecular mechenics (MM) modeling of porphyrins is described in 3.3.

The structure of porphyrins. The stable configuration of the porphyrins used in this study, TCPP and PPIX, were compared with the parent molecule of the porphyrin, porphine, using CS Chem 3D Pro program (CambridgeSoft, USA). Molecular properties calculated from MM2 energy minimization are listed in Table 3 and the optimized structures of porphyrins are shown in Figure 1-Figure 4. The E_B, E_T, E_M, and D_P values in Table 3 represent bending energy related to deformation of equilibrium bond angle, torsional energy, summation of the minimized energy, and the deviation from the molecular plane, respectively. The E_B values of porphine and PPIX are similar, while that of TCPP is about 2.5 fold larger than them. The result means that the structure of TCPP deviates from the stable planar formation.

Table 3. Molecular Properties Calculated from MM2[a] Energy Minimization

	Porphine	TCPP	PPIX
E_B[b]	41.68	119.8	45.29
E_T[c]	−12.7	8.96	−6.50
E_M[d]	26.68	156.5	42.02
D_P[e]	0.024	1.157	1.074

[a]Modified version of Allinger's MM2 force field. [b]Angle bending energy, kcal/mole. [c]Torsion energy, kcal/mole. [d]Total energy, kcal/mole. [e]Deviation from plane

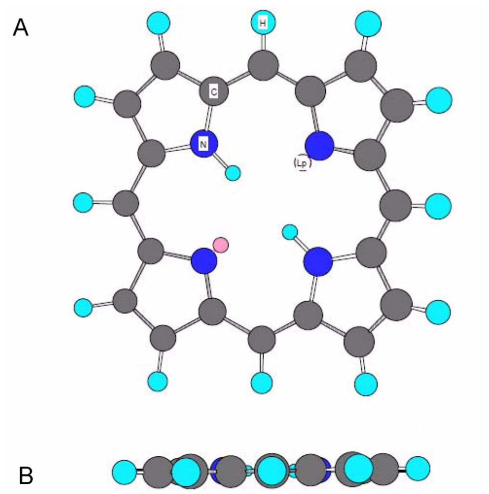

Figure 1. Optimized structure of porphine. (A) plane view (B) side view.

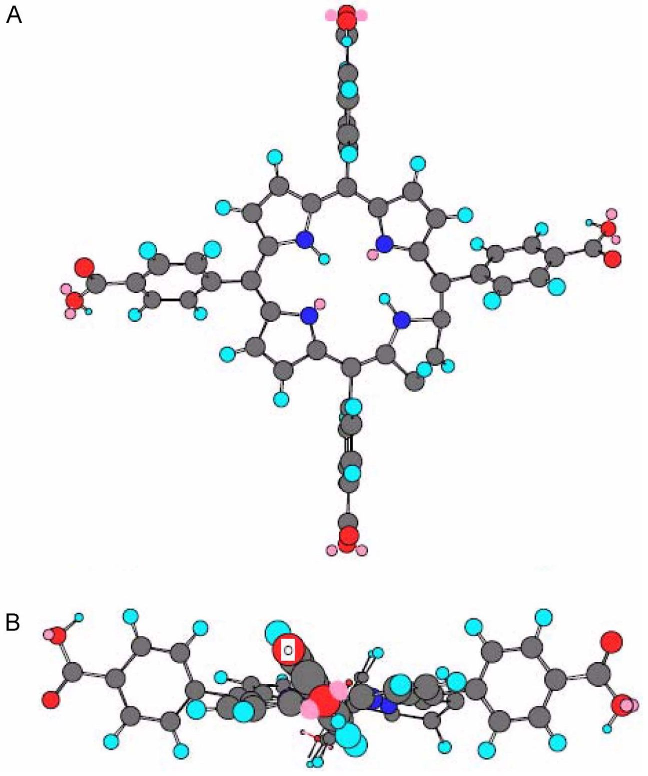

Figure 2. Optimized structure of TCPP. (A) plane view (B) side view.

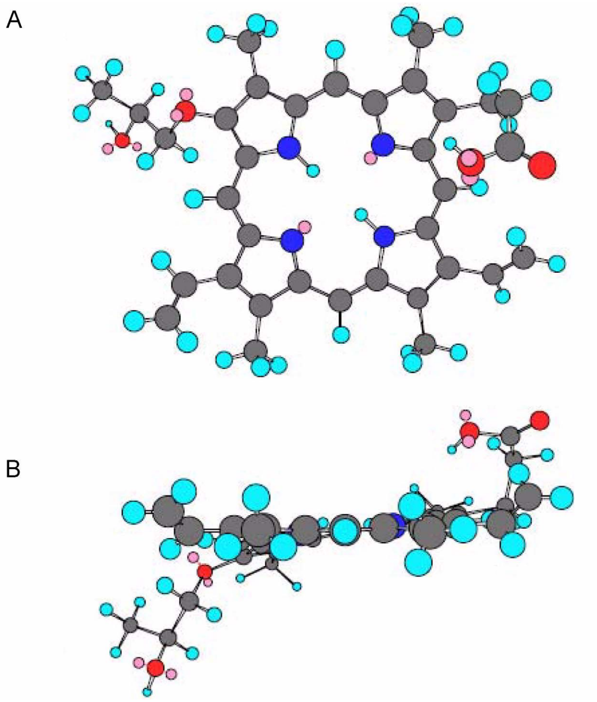

Figure 3. Optimized structure of PPIX. (A) plane view (B) side view.

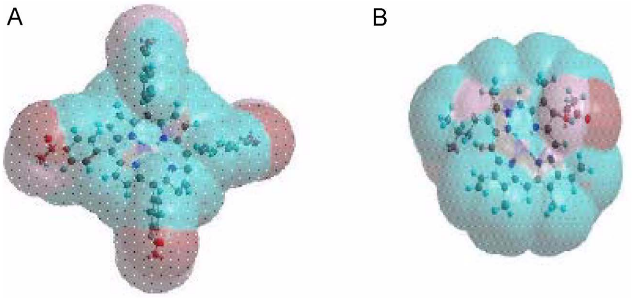

Figure 4. Molecule accessible surface map for PCP. (A) TCPP (B) PPIX

The D_P value of porphine is nearly zero, and that means the molecular plane of porphine is on the same level (Fig. 1). On the contrary, the D_P values of the TCPP and PPIX are about 50-fold larger than that of porphine, thus the structures of TCPP and PPIX are expected to deviate from the molecular plane. As shown in Figure 2 and Figure 3, molecular structures of TCPP and PPIX are not planar because of the functional group attached to porphine ring. Especially, four bulky *p*-carboxyphenyl groups of TCPP are torsional each other, thus the π-π interaction between π electrons in porphyrin plane and the bulky phenols is hindered. The results confirmed by the Figure 4 illustrated the molecular accessible surface map of the TCPP and PPIX for PCP. In conclusion, the decrease of breakthrough volume of XADs +TCPP columns for bulky phenols can be explained by the steric hindrance of the π-π interaction between porphyrin plane and the phenols.

Recovery test. Generally, the porphyrin modified adsorbents showed higher recoveries for the determination of phenols solved in tap water and river water than commercially available adsorbents such as XAD-2 and XAD-4 (Table 4-5). It can be expected that the increase of the recovery values is resulted from the increase of the π-π interaction between the phenol molecules and the adsorbents due to the introduction of macrocyclic porphyrin molecules possessing many π-electrons. However, the recoveries of the XADs+TCPP columns were slightly decreased for the multi-substituted phenols such as TCP and PCP. The results also can be explained by the steric hindrance of the π-π interaction between the porphyrin plane and the phenols in the dynamic adsorption condition.

Recovery values of phenols solved in tap water were higher than those of phenols solved in river water for all SPE adsorbents used in this study as shown in Table 4-5. It can be predicted that the low recovery values for river water arise from the complex matrix of the environmental water. In fact, it is known that fulvic acids and humic acids are existent in river water as a low concentration level and these interfere with substances in adsorption in the column. It has been reported that additional reagents such as sodium sulphite, sodium thiosulphate, potassium permanganate and oxalic acid were added in the environmental samples to remove the matrix effect.[24,25]

The XAD-4+PPIX adsorbent seems to be the most suitable for the solid phase extraction of phenol and chlorophenols. The column showed more than 90% recoveries for both tap water and river water without the addition of the chemical reagents. Especially, the column shows a good result even for hydrophilic phenol, which is easily lost by water during the sample-loading step in solid phase extraction.

Conclusion

The chemically modified polymeric adsorbents, XADs+TCPP and XADs+PPIX, were applied to the solid phase

Table 4. Recoveries of Phenols Extracted with Polymeric Adsorbents from Spiked Samples[a] of Tap Water and River Water[b] (n = 5)

Compounds	XAD-2				XAD-2+TCPP				XAD-2+PPIX			
	tap water		river water		tap water		river water		tap water		river water	
	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)
Ph	9.55	4.69	8.01	0.16	24.5	3.50	24.0	0.87	31.8	0.71	29.9	2.83
2-CP	46.5	0.58	36.2	0.30	53.2	0.18	50.5	0.28	64.2	1.06	62.2	0.28
4-CP	44.8	1.08	34.7	0.41	57.3	0.62	54.2	0.53	69.9	0.19	65.9	1.14
DCP	75.7	0.46	55.0	0.08	76.0	0.36	72.4	0.62	86.6	1.26	84.8	1.99
TCP	76.1	1.60	55.1	0.31	74.3	1.69	72.1	0.77	84.9	1.22	82.5	0.67
PCP	79.9	2.72	57.5	1.87	77.3	3.32	73.1	2.97	89.5	8.14	83.9	9.84
Average	55.4	1.85	41.1	0.52	60.4	1.61	57.7	1.01	71.2	2.10	68.2	2.79

[a]Spiking level : 1 ppm. [b]Han river Water

Table 5. Recoveries of Phenols Extracted with Polymeric Adsorbents from Spiked Samples[a] of Tap Water and River Water[b] (n = 5)

Compounds	XAD-4				XAD-4+TCPP				XAD-4+PPIX			
	tap water		river water		tap water		river water		tap water		river water	
	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)	R(%)	RSD(%)
Ph	40.0	1.52	39.6	0.82	61.5	1.07	49.5	1.11	92.1	0.71	84.2	0.82
2-CP	77.0	0.47	72.8	0.13	77.8	0.25	72.5	0.14	100	0.98	95.4	0.75
4-CP	77.1	1.36	73.0	1.01	79.8	0.46	74.9	0.56	101	0.63	94.8	1.91
DCP	88.6	0.42	83.3	0.54	88.0	0.30	84.9	0.32	104	1.75	101	1.80
TCP	83.7	1.85	79.0	1.72	82.7	1.72	80.1	1.50	98.3	2.49	93.1	2.98
PCP	87.8	3.80	80.6	3.62	84.0	3.38	79.8	3.12	93.1	6.63	84.5	6.13
Average	75.7	1.57	71.4	1.31	79.0	1.20	73.6	1.12	98.1	2.20	92.2	2.40

[a]Spiking level : 1 ppm. [b]Han river Water

extraction of phenol and chlorophenols in environmental waters. The chemically modified adsorbents showed higher recoveries than underivatized adsorbents for phenol and chlorophenols due to the increase of the π-π interaction between the phenol molecules and the adsorbents. Especially, XAD-4+PPIX adsorbent showed more than 90% recoveries for all compounds used in this study including hydrophilic phenol without matrix effect. In conclusion, synthesized adsorbents can sufficiently be applied to the solid phase extraction of phenolic compounds at lower concentration levels and other organic compounds having π-electrons.

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