Evaluation on the adsorption capabilities of new chemically modified polymeric adsorbents with protoporphyrin IX

Min-Woo Jung[a], Kyu-Hong Ahn[a], Yonghun Lee[a], Ki-Pal Kim[b], InSook Rhee Paeng[c], Jae-Seong Rhee[d], Jung Tae Park[e], Ki-Jung Paeng[b],*

[a]*Environment and Process Technology Division, Korea Institute of Sciene and Technology (KIST), P.O. Box 131, Cheongryang, Seoul 130-650, South Korea*
[b]*Department of Chemistry, Yonsei University, Wonju 220-710, South Korea*
[c]*Department of Chemistry, Seoul Women's University, Seoul 139-774, South Korea*
[d]*Water Environment Research Center, Korea Institute of Science and Technology (KIST), P.O. Box 131, Cheongryang, Seoul 130-650, South Korea*
[e]*Department of Environmental Engineering, Yonsei University, Wonju 220-710, South Korea*

Abstract

A chemically modified polymeric adsorbent was synthesized to evaluate the availability as an adsorbent for solid-phase extraction (SPE) of phenol and chlorophenols. Commercially available Amberlite XAD-2 and XAD-4 resins were modified with macrocyclic protoporphyrin IX (PPIX) through the ketone linkage. Adsorption isotherms were obtained by batch experiments and the data were fitted to the Freundlich equation to calculate the adsorption parameters. Breakthrough volumes were measured by column experiments. Physical properties such as surface area, average pore diameter and micropore volume of resins were measured to correlate with the adsorption characteristics. As a result, adsorption capacity was increased for the chemically modified resins and it can be concluded that the increase of π–π interaction due to the introduction of the porphyrin molecule is the major factor for the increase of the adsorption capacity. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The commercially available Amberlite XAD-2 and XAD-4 resins are styrene–divinylbenzene copolymer with hydrophobic character and porous structure, which have been shown to be good adsorbents for a wide variety of organic compounds. Many publications for the adsorption of various organics includ-ing phenols, polycyclic aromatic hydrocarbons (PAHs), pesticides, fulvic acids, amino acids and surfactants onto these polymeric resins have been reported [1–7]. However, polar organic compounds are known to be not completely extracted. In recent years, chemically modified polymeric resins with functional groups such as acetyl [8–11], hydroxy-methyl [10,11], benzoyl [12] and *o*-carboxybenzoyl [9,13] and highly cross-linked polymers [9,12,14–16] have been synthesized to overcome the limitation to the polar ones.

*Corresponding author. Fax: +82-33-760-2239.
E-mail address: paengk@dragon.yonsei.ac.kr (K.-J. Paeng).

In this study, a macrocyclic porphyrin molecule was introduced as a chemical modifier to enhance the adsorption capacity for phenol and chlorophenols. Porphyrins are a class of naturally occurring macrocyclic compounds, which contain four pyrrole rings linked via sp^2-hybrid carbons and π-electrons are delocalized over the molecule by conjugation. The porphyrin ring system is very stable and exhibits aromatic character [17]. Phenol and chlorophenols used in this study contain the aromatic ring bearing the π-electrons. It is expected that the adsorption capacity can be enhanced by increase of π–π interaction due to the introduction of π-conjugated porphyrin molecule. Meyerhoff and co-workers described the applications of synthesized porphyrin stationary phases based on porphyrins immobilized onto silica gel through a peptide bond for the separation of aromatic carboxylate, sulfonate, polycyclic aromatic hydrocarbons and amino acids [18–21]. The mechanism of retention has been observed including the coordinative interaction via metallic center of porphyrin and π–π interaction between π-electrons in macrocycles of porphyrin and π-electrons in solutes.

The objective of this study is to evaluate the effect of the introduction of porphyrin molecules to the polymeric resins on the adsorption capacity for phenol and chlorophenols. The adsorption experiment was performed followed by fitting the data to the Freundlich equation and breakthrough volumes were measured in order to calculate the adsorption capacity of the synthesized polymeric adsorbents.

2. Experimental

2.1. Chemicals and reagents

Phenol and chlorophenols used in this study were phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenols (4-CP), 2,4-chlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP). They were purchased from Fluka (Ronkonkoma, NY, USA) and used as obtained 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 as a 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, UK) and 0.45 μm cellulose nitrate filter (Whatman) respectively. Protoporphyrin IX was purchased from Aldrich (Milwaukee, WI, USA). Standard solutions for the determination of porphyrin contents were prepared with manganese standard solution from Aldrich (Milwaukee, WI, USA). All other reagents were of analytical grade.

2.2. Apparatus and analytical conditions

Chromatographic experiments were performed using a Hewlett-Packard (Waldbronn, Germany) 1050 series ternary gradient liquid chromatograph with a diode-array detector (DAD). System control and data analysis were carried out with a HPLC^{3D} Chemstation (DOS series). 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). A Rheodyne Model 7125 injector having a 20 μl loop was used. 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. The mobile phase was degassed by helium (99.99%) purging during the separation. Detection wavelength was set at 225 nm for all phenols and quantitations were executed using an external standard method for calibration.

2.3. Preparation of the chemically modified polymeric adsorbents

Amberlite XAD-2 and XAD-4 resins purchased from Rohm and Haas (Philadelphia, PA, USA) were ground and sieved to 100–150 mesh and purified in a Soxhlet extractor with methanol, acetonitrile and diethyl ether for 8 h per each solvent. PPIX was metallated with Mn(II) by refluxing with $MnCl_2$ (three times in excess of the porphyrin) in DMF for 5 h. Chemically modified adsorbents were prepared from XAD resins and Mn(II)PPIX through the ketone linkage (Friedel-Crafts acylation). Thionyl chloride ($SOCl_2$, 0.134 *M*) was added to Mn(II)P-PIX (0.0019 *M*) and heated after adding a portion of XAD resins and 30 ml of 1,1,2,2-tetrachloroethane

(1,1,2,2-TCE). After cooled to room temperature, aluminum chloride (AlCl$_3$) was added and the solution was kept at 10°C for 16 h. The slurry was filtered and washed with 1,1,2,2-TCE, methanol and basic aqueous solution. The resulting chemically modified polymeric adsorbents were stored in a vacuum desiccator. Synthetic scheme for the preparation was shown in Fig. 1.

Physical properties of all adsorbents were measured using a Micromeritics ASAP 2010 system according to the BET method.

2.4. Adsorption experiments

Adsorption experiments were carried out in a batch mode with following procedure. A fixed amount of the adsorbents (10 mg) and a known concentration of adsorbate solutions with acidified water (pH 3 with HCl) were placed in a glass vial and shaken at 200 rpm at 25°C for 1 h using a Fisher Vortex-Genie 2 Mixer (Fisher Scientific, Pittsburgh, PA, USA). After mixing, solutions were filtered through a 0.2 μm PTFE syringe filter (Whatmann, Maldstone, UK) and injected into the HPLC to determine the adsorption amount of analytes on the adsorbents.
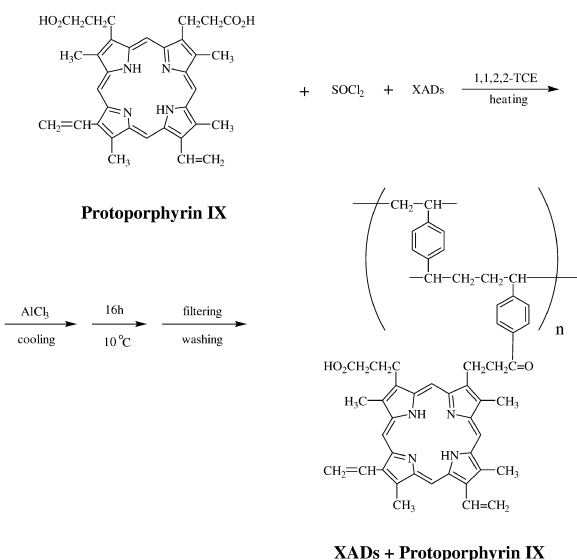

Fig. 1. Synthetic scheme for the preparation of chemically modified polymeric adsorbents.

2.5. Breakthrough volumes

Measurements of the breakthrough volume were carried out using a stainless steel column (20 mm×2 mm I.D.) dry-packed with each adsorbent. Titanium frits (10 μm pore size) were located above and below each adsorbent bed. Before measurements, adsorbents were conditioned by flushing with methanol at a flow rate of 1 ml/min and subsequently with acidified water (pH 3 with HCl) at a flow rate of 2.5 ml/min until the detector response reached stability. Breakthrough curves were obtained by flushing the 10 ppm aqueous solutions of phenols into the adsorbent columns directly connected to the detector at a flow rate of 2.5 ml/min. Solutions were acidified with HCl to pH 3. Breakthrough volumes were calculated at 1% of the maximum absorbance of the adsorbates.

3. Results and discussion

3.1. Characterization of the adsorbents

The amount of PPIX bonded to XAD resins was determined by atomic absorption spectrometry (AAS). Mn(II) was extracted from synthesized Mn(II)PPIX+XADs with 5 ml of concentrated H$_2$SO$_4$, and then the solution was filtered and diluted for the measurement of AAS. The calculated amount of PPIX bonded to XAD resins was 1.54% (wt%). Mn(II) is chelated by PPIX in a ratio of 1:1, so the amount of Mn(II) extracted from the resulting adsorbents should be equal to that of PPIX bonded to XAD resins.

Physical properties such as surface area, average pore diameter and pore volume of adsorbents are mostly considered in mentioning to the adsorption process. In general, adsorption capacity of the adsorbent is proportional to the surface area of the adsorbent. The size of pores is related to that of the molecules adsorbed in diffusion process. The surface area of XAD-4 is well known to be larger than XAD-2. Physical properties measured to correlate with the adsorption capacity of the adsorbents were listed in Table 1.

Table 1
Physical properties of the adsorbents used in this study

Adsorbents	BET surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
XAD-2	398	6.08	0.61
XAD-2 + PPIX	460	6.65	0.76
XAD-4	946	4.12	0.97
XAD-4 + PPIX	1030	3.67	0.95

3.2. Adsorption isotherms

Adsorption isotherms of phenol and chlorophenols for the adsorbents are shown in Figs. 2–5. Small

Fig. 4. Adsorption isotherms of phenols for XAD-4.

windows indicate the isotherms of each compound plotted in their own scale. The amount of adsorbates adsorbed on each adsorbent was calculated according to the following equation:

$$Q_e = V(C_o - C_e)/W \tag{1}$$

where C_o and C_e are initial and equilibrium liquid-phase concentration (mg/l) respectively, V is volume of solution (l), and W is weight of adsorbents (g). All isotherms showed the shape of type L according to the classification of Giles et al. [22]. The L-shape of the isotherms means that there is no strong competition between the solvent and the adsorbate to
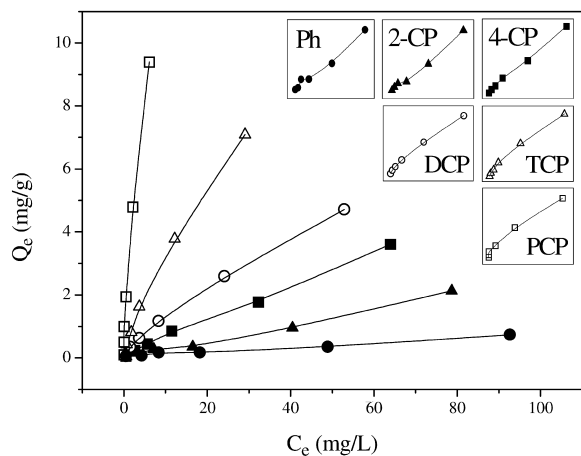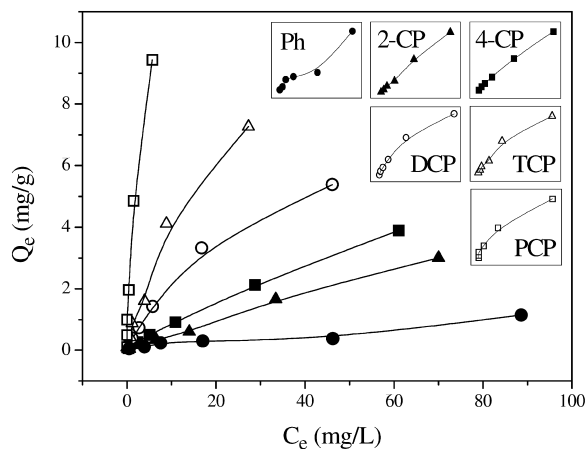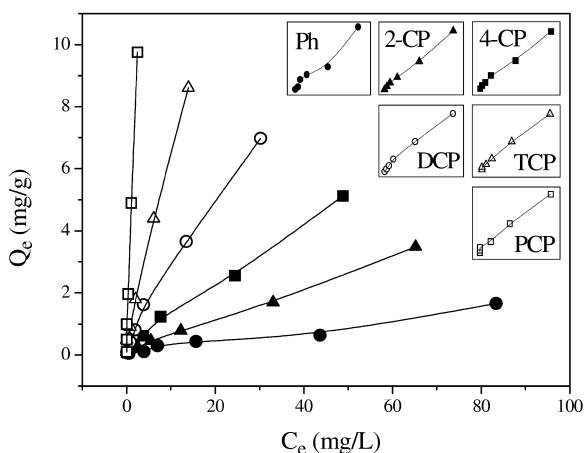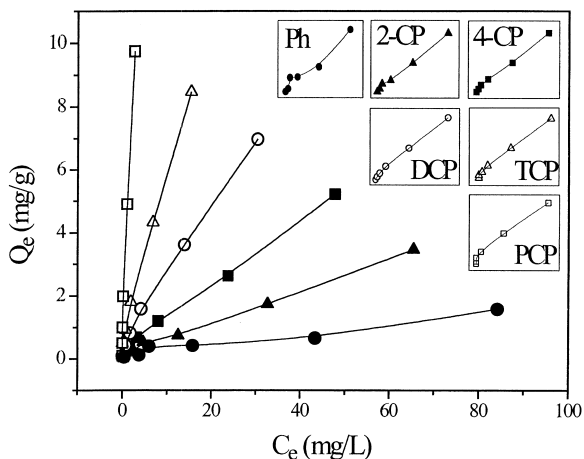
Fig. 2. Adsorption isotherms of phenols for XAD-2.

Fig. 3. Adsorption isotherms of phenols for XAD-2 + PPIX.

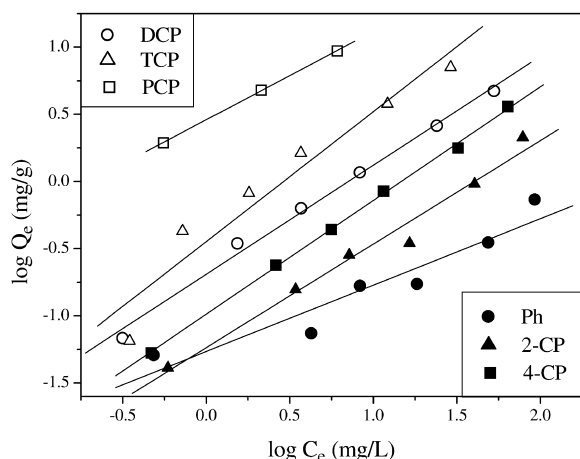Fig. 5. Adsorption isotherms of phenols for XAD-4 + PPIX.

Fig. 6. Freudlich fitting curves of phenols for XAD-2.

occupy the adsorbent surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface [23]. The experimental data were fitted to the Freundlich equation:

$$Q_e = K_F C_e^{1/n} \tag{2}$$

where K_F is a Freundlich constant that is taken as an indicator of adsorption capacity and $1/n$ is an empirical constant related to the magnitude of the adsorption driving force [24]. A linearized form of the equation is as follows:

$$\log Q_e = \log K_F + (1/n) \log C_e \tag{3}$$

Freundlich isotherms can be plotted by Eq. (3), K_F and $1/n$ values are obtained from the intercept and slope in linear regression result. The example of the

Freundlich fitting curves is shown in Fig. 6 and Freundlich parameters are summarized in Table 2. Other fitting curves showed a similar straight-line shape. The correlation coefficient (r) showed a relatively good linearity for most of the adsorbents used. Similar slopes indicate that the affinity of phenol and chlorophenols to all adsorbents used is nearly the same.

3.3. Interpretation of the adsorption characteristics

From the results mentioned above, adsorption characteristic of phenol and chlorophenols on the adsorbents may be interpreted in terms of physical and chemical aspects. As seen in Table 2, the overall order of K_F value is XAD-4+PPIX>XAD-4> XAD-2+PPIX>XAD-2, which means that the adsorption capacity is the highest for XAD-4+PPIX and the lowest for XAD-2. The result shows that the adsorption tendency among the adsorbents used in this study is affected by their surface area. It is well known that matching of the pore size of adsorbent and the size of adsorbate molecule should be considered when explaining adsorption process. Molecular diameter can be estimated from the bond lengths and the van der Waals radii for atoms. The bond lengths required for the calculation are measured using CS Chem3D Pro program (CambridgeSoft, USA) and the radii for chlorine, hydrogen and oxygen atoms are obtained from reference data [25]. The calculated diameters of phenol and chlorophenols were in the range of about 0.8–1.0 nm. As seen in Table 1, the values of average pore diameter of the adsorbents are about 3–6 times of those calculated, which means that it is easy for phenols to diffuse into the inner

Table 2
Freudlich parameters and correlation coefficients for phenol and chlorophenols calculated from the adsorption isotherm data

Compound	XAD-2			XAD-2+PPIX			XAD-4			XAD-4+PPIX		
	K_F	$1/n$	r	K_F	$1/n$	r	K_F	$1/n$	r	K_F	$1/n$	r
Ph	0.054	0.494	0.949	0.067	0.546	0.962	0.069	0.658	0.973	0.090	0.596	0.964
2-CP	0.058	0.771	0.989	0.071	0.861	0.996	0.132	0.745	0.997	0.158	0.698	0.993
4-CP	0.103	0.846	0.999	0.141	0.801	0.999	0.225	0.793	0.999	0.230	0.805	0.998
2,4-DCP	0.204	0.811	0.997	0.233	0.911	0.976	0.508	0.774	0.998	0.564	0.725	0.999
2,4,6-TCP	0.357	0.967	0.967	0.650	0.759	0.988	1.040	0.799	0.999	1.172	0.709	0.999
PCP	2.877	0.657	0.999	3.573	0.580	0.997	4.624	0.861	0.999	5.358	0.572	0.996

Table 3
Breakthrough volumes (ml) of phenol and chlorophenols for the adsorbents

Compound	XAD-2	XAD-2+PPIX	XAD-4	XAD-4+PPIX
Ph	2.7	3.7	5.0	7.1
2-CP	4.3	9.0	23	31
2,4,6-TCP	54	63	168	379
PCP	209	220	>500	>500

pores of the adsorbents and adsorb on the internal surfaces. In other words, the range of pores is sufficient for phenols to adsorb and it is not an important factor in adsorption process. Furthermore, it can be concluded that the dispersion forces related to the π–π interactions between the phenol molecules and the adsorbents control the adsorption of phenol and chlorophenols on the adsorbents. In other words, the increase of the adsorption capacity among the adsorbents is resulted from the increase of the π–π interaction due to the introduction of porphyrin molecules possessing π-electrons. Since the macrocycles of protoporphyrin IX and phenols have planar structures, it can be predicted that the adsorption capacity is considerably affected by π–π interactions, based on the result of the L-shape of the isotherms as mentioned above. This conclusion can also be applied to the interpretation for the series of phenol molecules. The adsorption capacity (K_F) increases as the degree of chlorination is higher (Table 2). The chlorine atom has an electron-withdrawing character, and therefore, the electron density in aromatic ring decreases as the number of chlorine atom increases. As a result, pentachlorophenol shows the highest affinity to the π-electrons in the adsorbents.

3.4. Breakthrough volumes

To evaluate the applicability of the synthesized adsorbents to solid-phase extraction, breakthrough volumes were measured using the small columns. Breakthrough volume is important in SPE because it represents the sample volume that can be preconcentrated without loss of analytes during the loading of sample. Breakthrough volumes were calculated at which the absorbance reached to 1% of the maximum absorbance. The results are shown in Table 3.

As seen from Table 3, breakthrough volumes were increased for the synthesized adsorbents and proportional to the number of substituents in phenol molecules likewise the results of adsorption isotherms. It may be attributed to the additional retention by increase of the surface area and the π–π interaction due to the introduction of porphyrin molecules.

4. Conclusion

In this paper, new polymeric adsorbents chemically modified by introducing the protoporphyrin IX molecules were synthesized and investigated to evaluate the applicability to solid-phase extraction as an adsorbent material. From the results of the Freundlich parameters fitted by adsorption isotherm data and the breakthrough volumes, it was concluded that the π–π interactions between the phenol molecules and the adsorbents were the main forces controlling the adsorption characteristics. As a result of the introduction of protoporphyrin IX, adsorption capacity for hydrophilic phenol, which is easily lost during the sample-loading step in solid-phase extraction, could be increased.

In conclusion, it can be predicted that the synthesized adsorbents (XAD-2+PPIX and XAD-4+PPIX) having higher adsorption capacity can sufficiently be applied to the solid-phase extraction as an adsorbent material.

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