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# Thermodynamic study of adsorption of phenolic compounds onto Amberlite XAD-4 polymeric adsorbents and its acetylated derivative MX-4

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**Abstract:** Adsorption equilibrium isotherms of phenolic compounds, phenol, *p*-cresol, *p*-chlorophenol and *p*-nitrophenol, from aqueous solutions by Amberlite XAD-4 polymeric adsorbent and its acetylated derivative MX-4 within temperature range of 283-323K were obtained and fitted to the Freundlich isotherms. The capacities of equilibrium adsorption for all four phenolic compounds from their aqueous solutions increased around 20% on the acetylated resin, which may be contributed to the specific surface area and the partial polarity on the network. Estimations of the isosteric enthalpy, free energy, and entropy for the adsorption process were reported.

**Keywords:** macroporous polymeric adsorbent; phenolic compound; adsorption thermodynamic; temperature effect

## Introduction

In recent years, it has been reported that almost all phenolic compounds are highly toxic at the concentration discharged into the receiving effluents, the removal or destruction of phenolic compounds from such streams has become a significant environmental concern (Juang, 1999). Adsorption is a prominent method for the treatment of effluents containing organic substances from dilute aqueous solutions because of the high concentrating ability of typical adsorbent (Payne, 1988). Activated carbon is the most widely used adsorbent for this purpose. Recently, non-ionic macroreticular polymeric resins have been increasingly viewed as an alternative to activated carbon for the removal of organic pollutants from waste streams because of their wide range of pore structures and excellent physico-chemical characteristics (Gusler, 1993; Xu, 1997; 1999). The commercially available Amberlite XAD-4 polymeric resin is styrene-divinylbenzene copolymer with hydrophobic character and porous structure, which has been shown to be good polymeric adsorbent for a wide variety of organic compounds. Many studies for the adsorption of various organics including phenols, polycyclic aromatic hydrocarbons (PAHs) on Amberlite XAD-4 polymeric resin have been reported (He, 1992). However, the initial extreme hydrophobic chemical structure of these polystyrene-based adsorbents results in their poor contact with aqueous solutions (Philip, 1995; Masque, 1998), some activation solvent (such as methanol, acetone, or acetonitrile) has to be used to enhance surface contact with the aqueous solutions in a pretreatment process, which limits its broad application in the chemical wastewater treatment. In our previous study, Amberlite XAD-4 polymeric resin was chemically modified with an acetyl group, which enables the resin to be used directly without wetting process (Li, 2001). In the present study, we focused on analysis of adsorption isotherms of phenolic compounds on Amberlite XAD-4 and its acetylated derivative MX-4. Values for the enthalpy, free energy, and entropy of adsorption have also been estimated, which is used to develop the thermodynamic framework to explain our adsorption results and determine adsorption mechanism.

## 1 Experimental

### 1.1 Materials

The spherical Amberlite XAD-4 resin was from Rohm-Haas Company (Philadelphia, USA), the

spherical MX-4 resin was manufactured according to reference (Li, 2001). Their physical properties are compiled in Table 1.

**Table 1 Characteristics of the two polymeric resins**

Property	XAD-4	MX-4
Structure	Polystyrene	Acetyl group modified polystyrene
Polarity	Nonpolar	Moderate polar
BET surface area, m <sup>2</sup> /g	880	1114
Average diameter, nm	5.8	5.8
Average particle size, mm	0.5	0.5
Colour	White	Yellow

**Table 2 Physical properties of the adsorbates**

Adsorbate	Phenol	<i>p</i> -cresol	<i>p</i> -chlorophenol	<i>p</i> -nitrophenol
log <i>K</i> <sub>ow</sub> *	2.17	2.83	2.88	1.91
p <i>K</i> <sub>a</sub> **	10.00	10.26	9.38	7.15

\* Calculated according to the reference (Wang, 1990), *K*<sub>ow</sub> is the partition coefficient of *n*-octanol/water; \*\* Taken from reference (Xing, 1984)

conical flask directly, while the unmodified Amberlite XAD-4 resin was firstly "wetted" with 0.5 ml of methanol and then rinsed 3 times with deionized water before use. 100 ml aqueous solution of phenolic compound with concentrations (*C*<sub>0</sub>) of 200, 400, 600, 800, and 1000 mg/L was added into each conical flask. The conical flasks were placed in a G 25 model incubator shaker (New Brunswick Scientific Co. Inc.) at a pre-settled temperature and shaken under 130 r/min. After adsorption reached equilibrium, the concentrations of phenolic compound(*C*<sub>e</sub>) were determined. Adsorbent-phase concentrations of adsorbate, *q*<sub>e</sub>(mmol/g) were calculated according to

$$q_e = V_l(C_0 - C_e)/MW, \quad (1)$$

where *V*<sub>l</sub> is the volume of solution, L; *W* is the weight of dry resin, g; and *M* is the molecular weight of the corresponding phenolic compound.

Concentrations of phenolic compounds were measured at 275 nm using a HPLC with dual λ absorbance detector (Waters Assoc., USA).

## 2 Results and discussion

### 2.1 Adsorption isotherms

Adsorption isotherms of phenol, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol on MX-4 and Amberlite XAD-4 resins at the different temperature are shown in Fig.1 and Fig.2. The experimental data were well fitted to the Freunlich equation (Slejko, 1985):

$$\log q_e = \log K_F + 1/n \log C_e, \quad (2)$$

where *K*<sub>F</sub> is the Freunlich constant and *n* is the empirical constant.

The regression equations at 283K, 303K, 323K along with the constants *K*<sub>F</sub>, *n*, and the correlation coefficient *R* on Amberlite XAD-4 and MX-4 are listed in Table 3 and Table 4 respectively. It is quite obvious that the Freundlich adsorption equation is applicable to adsorption of phenolic compounds on MX-4 and XAD-4 resins. These equations are reliable since all the correlation coefficients (*R*) are larger than 0.98.

### 2.2 Interpretation of the adsorption characteristics

From the results mentioned above, adsorption characteristic of phenolic compounds on the two polymeric resins may be interpreted in terms of physical aspects. Among the four phenolic compounds

Phenol and three of its derivatives, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol, were obtained from Shanghai Third Chemical Reagent Plant (Shanghai, China) and, were dissolved in deionized water in the adsorption test without pH adjustment. Their physical properties are listed in Table 2.

### 1.2 Adsorption assay

Prior to their initial use, all polymeric resins were extracted by acetone for 8h and then dried under vacuum at 333K for 2h.

Equilibrium adsorption of the four phenolic compounds at three different temperatures (283K, 303K and 323K) were performed as follows: 0.100g of resin was introduced into a

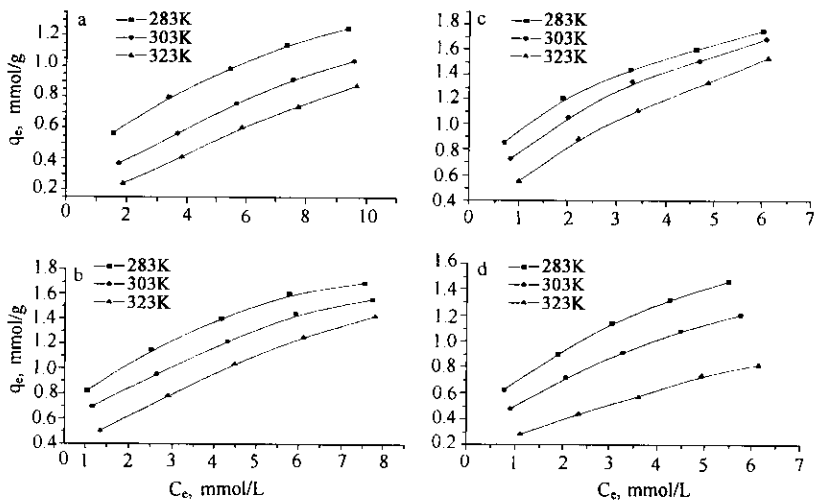


Fig.1 Equilibrium adsorption isotherms at 283K, 303K and 323K for (a) phenol; (b) *p*-cresol; (c) *p*-chlorophenol and (d) *p*-nitrophenol on XAD-4

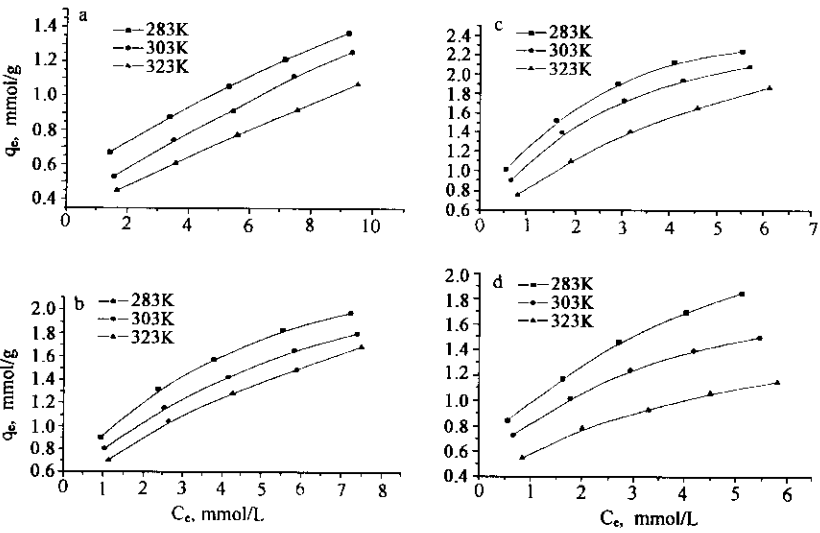


Fig.2 Equilibrium adsorption isotherms at 283K, 303K and 323K for (a) phenol; (b) *p*-cresol; (c) *p*-chlorophenol; (d) *p*-chlorophenol on MX-4

tested, *p*-chlorophenol is the most hydrophobic (Table 2) and had the highest adsorption capacities on both resins (Table 5). This is in agreement with the previous report (Rojas, 1996), namely, high hydrophobicity was found to favor the adsorption of organic compounds onto the non-polar and moderate polar polymeric adsorbents from aqueous solutions. As seen in Table 3 and Table 4, adsorption ability drops with rising temperature for all the systems studied, indicating the exothermic nature of the adsorption process. At the temperature 303K and the same residual concentration ( $C_e$ ) of 4.0 mmol/L, the increase in the adsorption capacities varied within 13% – 30% (Table 5) after acetylation, correlating well to the increase in the specific surface area (27%, Table 1). The results showed that the adsorption tendency between the two adsorbents used in this study is affected by their surface area. On the other hand, the constant  $K_F$ , namely, the adsorption capacity when  $C_e = 1.0$  mmol/L, which is taken as a relative

indicator of adsorption capacity according to the Freundlich theory (Slejko, 1985; Jung, 2001), increased about 60% for phenol and *p*-nitrophenol, suggesting an advantage of MX-4 over Amberlite XAD-4 in the collection of some phenolic compounds from their very dilute solutions.

**Table 3** Regression equation of  $\log q_e$  vs.  $\log C_e$  for Freundlich isotherms on the Amberlite XAD-4

Adsorbate	Adsorbent	<i>T</i> , K	Regression equation	$K_F$	<i>n</i>	$R^2$
Phenol	XAD-4	283	$\log q_e = 0.4802 \log C_e - 0.3194$	0.4793	2.0825	0.9714
		303	$\log q_e = 0.6102 \log C_e - 0.5870$	0.2588	1.6388	0.9909
		323	$\log q_e = 0.7067 \log C_e - 0.8549$	0.1397	1.4150	0.9784
<i>p</i> -cresol	XAD-4	283	$\log q_e = 0.3662 \log C_e - 0.0801$	0.8316	2.7307	0.9910
		303	$\log q_e = 0.4456 \log C_e - 0.1903$	0.6452	2.2442	0.9976
		323	$\log q_e = 0.5266 \log C_e - 0.3784$	0.4184	1.8990	0.9995
<i>p</i> -chlorophenol	XAD-4	283	$\log q_e = 0.3361 \log C_e - 0.0143$	0.9676	2.9751	0.9952
		303	$\log q_e = 0.4157 \log C_e - 0.0956$	0.8024	2.4056	0.9962
		323	$\log q_e = 0.4630 \log C_e - 0.2518$	0.5600	2.1598	0.9887
<i>p</i> -nitrophenol	XAD-4	283	$\log q_e = 0.4631 \log C_e - 0.1557$	0.6987	2.1594	0.9987
		303	$\log q_e = 0.5052 \log C_e - 0.2987$	0.5027	1.9794	0.9996
		323	$\log q_e = 0.5898 \log C_e - 0.5711$	0.2684	1.6955	0.9881

**Table 4** Regression equation of  $\log q_e$  vs.  $\log C_e$  for Freundlich isotherms on MX-4

Adsorbate	Adsorbent	<i>T</i> , K	Regression equation	$K_F$	<i>n</i>	$R^2$
Phenol	MX-4	283	$\log q_e = 0.4108 \log C_e - 0.2546$	0.5564	2.4343	0.9739
		303	$\log q_e = 0.4617 \log C_e - 0.3766$	0.4201	2.1659	0.9963
		323	$\log q_e = 0.4898 \log C_e - 0.4597$	0.3470	2.0416	0.9921
<i>p</i> -cresol	MX-4	283	$\log q_e = 0.3764 \log C_e - 0.0209$	0.9530	2.6567	0.9910
		303	$\log q_e = 0.3951 \log C_e - 0.1011$	0.7923	2.5310	0.9976
		323	$\log q_e = 0.4605 \log C_e - 0.1800$	0.6607	2.1716	0.9982
<i>p</i> -chlorophenol	MX-4	283	$\log q_e = 0.3429 \log C_e + 0.1030$	1.2677	2.9163	0.9903
		303	$\log q_e = 0.3895 \log C_e + 0.0344$	1.0824	2.5674	0.9907
		323	$\log q_e = 0.4247 \log C_e - 0.0525$	0.8861	2.3546	0.9891
<i>p</i> -nitrophenol	MX-4	283	$\log q_e = 0.3386 \log C_e + 0.0090$	1.0209	2.9533	0.9836
		303	$\log q_e = 0.3501 \log C_e - 0.0755$	0.8404	2.8563	0.9986
		323	$\log q_e = 0.4008 \log C_e - 0.2346$	0.5826	2.4950	0.9897

**Table 5** Equilibrium adsorption capacity  $q_e$  (mmol/g) for phenolic compounds on Amberlite XAD-4 and MX-4 polymeric adsorbents

Adsorbent	Adsorbate	$C_e = 4.0$ mmol/L
XAD-4	Phenol	0.6031
XAD-4	<i>p</i> -cresol	1.1764
XAD-4	<i>p</i> -chlorophenol	1.4278
XAD-4	<i>p</i> -nitrophenol	1.1998
MX-4	Phenol	0.7968
MX-4	<i>p</i> -cresol	1.3702
MX-4	<i>p</i> -chlorophenol	1.8574
MX-4	<i>p</i> -nitrophenol	1.3655

It is well known that the matching of polarity between adsorbent and adsorbate should be considered when explaining adsorption process. According to Lewis acid-base theory, the benzene ring of aromatic-based Amberlite XAD-4 and the carbonyl group of MX-4 can be viewed as Lewis bases, while phenolic compounds can be viewed as Lewis acid (Merlin, 1987). Carbonyl oxygen has a large dipole moment, and thus carbonyl group of MX-4 acts as the stronger Lewis base than benzene ring of Amberlite XAD-4 (Russell, 1971). Therefore, the interaction between phenolic compounds and MX-4 is expected to be stronger than that between phenolic compounds and

Amberlite XAD-4. This deduction can be proved by the constant *n* in the Freundlich isotherm, for *n* gives an indication of the favorite of their adsorbent/adsorbate system (Xu, 1999; Jung, 2001). In every case the value of *n* for MX-4 is always larger than that of Amberlite XAD-4, which suggests that MX-4 gives an

easier access of the phenol derivatives in comparison with Amberlite XAD-4.

### 2.3 Thermodynamics of the adsorption

The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff equation (Garcla-Delgado, 1992):

$$\log(1/C_e) = \log(K_0) + \left( \frac{-\Delta H}{2.303RT} \right), \quad (3)$$

where  $\Delta H$  is the isosteric enthalpy of adsorption,  $R$  is the gas constant,  $C_e$  is the equilibrium concentration of solute in moles per liter at the absolute temperature  $T$ . At different temperatures (283 K, 303 K, and 323 K), the  $C_e$  was obtained from the well-fitted isotherms.  $\Delta H$  was calculated from the slope of line plotted by  $\log(1/C_e)$  verse  $1/T$ .

Other thermodynamics parameters, such as the apparent energy ( $\Delta G$ ) and the entropy ( $\Delta S$ ), can be calculated by Eqs. (4) and (5), respectively (Garcla-Delgado, 1992):

$$\Delta G = -RT \int_0^x \frac{qdx}{x}, \quad (4)$$

$$\Delta S = (\Delta H - \Delta G)/T, \quad (5)$$

where  $X$  represents the molar fraction of the adsorbate in solution,  $q$  is then replaced by the adsorption isotherm equation. The use of the Freundlich isotherm would lead to a value for the apparent free energy independent of  $q$  (John, 1987):

$$\Delta G = -nRT. \quad (6)$$

Table 6 shows a summary of the estimated values for these three thermodynamic properties at various adsorbate loadings. Values of the enthalpy (always negative) are indicative of an exothermic process, while the range of their magnitudes ( $< 40$  kJ/mol) manifested a physical sorption process. The higher values of the sorption enthalpy of Amberlite XAD-4 compared with that of MX-4 can be explained by the stronger hydrophobic interaction of the hydrophobic copolymer. In comparison with the XAD-4 resin, the MX-4 did not exhibit any significant change in the adsorption enthalpies, which indicated that the contribution of acetyl group to the total adsorption enthalpy was not important, the similar as that reported previously (Payne, 1989).

Absolute values decreased with increasing loading, meaning that the active sites on the resin surface are not energetically equivalent and those with greater binding energy are occupied first. When the amount of the adsorbed phenolic compounds is low, the adsorption is mainly a mono-molecular layer adsorption, the interaction between adsorbed molecules may be neglected, the direct adsorbate-adsorbent interaction can explain the high adsorption enthalpy of phenolic compounds as discussed above. With the increase of adsorption amount, the multiple-layer adsorption would eventually prevail, the interaction between free solute molecules in solution and adsorbed solute molecules may supplement the isosteric enthalpy, so isosteric enthalpy decreases by degrees.

*p*-nitrophenol showed different enthalpy change trends from its three analogues for Amberlite XAD-4 and MX-4, and owned higher adsorption enthalpy changes at higher loading, which can be explained by the formation of donor-acceptor adducts and hydrogen bond. At low adsorption capacity, the formation of donor-acceptor adducts can explain the high adsorption enthalpy change of *p*-nitrophenol as was discussed. At high adsorption capacity, since *p*-nitrophenol adsorbed on adsorbent can form the stronger hydrogen bonding than its three analogues, it had higher adsorption enthalpy.

Table 6 Estimated of the thermodynamic parameters of the systems tested

Adsorbate	Adsorbent	$q$ , mmol/g	$\Delta H$ , kJ/mol	$\Delta G$ , kJ/mol		$\Delta S$ , J/(mol·K)	
				283K	323K	283K	323K
Phenol	XAD-4	0.50	-28.1	-4.9	-3.8	-81.9	-75.2
		1.00	-13.6	-4.9	-3.8	-30.7	-30.3
	MX-4	0.50	-19.2	-5.9	-5.5	-47.0	-42.4
		1.00	-14.0	-5.9	-5.5	-28.6	-26.3
<i>p</i> -cresol	XAD-4	0.50	-32.2	-6.4	-5.1	-91.2	-83.9
		1.00	-17.7	-6.4	-5.1	-39.9	-39.0
	MX-4	0.50	-19.2	-6.3	-5.8	-45.6	-41.5
		1.00	-13.6	-6.3	-5.8	-25.8	-24.1
<i>p</i> -chlorophenol	XAD-4	0.50	-35.1	-7.0	-5.8	-99.3	-90.7
		1.00	-16.8	-7.0	-5.8	-34.6	-34.1
	MX-4	0.50	-25.9	-6.9	-6.3	-67.1	-60.7
		1.00	-18.9	-6.9	-6.3	-42.4	-39.0
<i>p</i> -nitrophenol	XAD-4	0.50	-34.4	-5.1	-4.6	-102.0	-92.3
		1.00	-26.5	-5.1	-4.6	-75.6	-67.8
	MX-4	0.50	-32.3	-6.9	-6.7	-89.8	-79.3
		1.00	-27.5	-6.9	-6.7	-72.8	-64.4

The adsorption free energy is an indication of the adsorption driving force. Table 6 indicates the negative free energy change values were as expected because the solute is expected to be more concentrated on the adsorbent than in the bulk solution. At the 323K, the adsorption free energy on MX-4 was always lower than on Amberlite XAD-4, which manifests that phenolic compound give priority to select MX-4 adsorbent.

The negative values of the adsorption entropy change are in agreement with restricted mobilities of the adsorbed molecules of phenolic compounds as compared with those in solution. Absolute entropy values increased slightly with the increase of temperature. The adsorption entropy change of phenolic compounds on MX-4 was higher than that on Amberlite XAD-4 at lower loading  $q \approx 0.5$  mmol/g, which can be explained by different interaction mechanisms between adsorbent and adsorbate (Table 6). The interaction between phenolic compound and Amberlite XAD-4 resin displays the interaction of  $\pi - \pi$ , while the interaction between phenolic compound and MX-4 resin mainly displays the interaction of hydrogen bond, the former proved to require more ordered arrangement (plane interaction), so Amberlite XAD-4 owns lower adsorption entropy than MX-4 for phenolic compound.

### 3 Conclusions

The adsorption isotherm data for the four phenolic compounds on Amberlite XAD-4 and MX-4 polymeric resins can be satisfactorily fitted with the conventional Freundlich equation in this study. The interaction between the two adsorbents and phenolic compound is viewed as the interaction between Lewis acid and Lewis base. The higher adsorption capacity of phenolic compounds on MX-4 than Amberlite XAD-4 is mainly attributed to the increase of surface area of MX-4 and the strong interaction between adsorbent and adsorbate.

The values of the enthalpy change (always negative) are indicative of an exothermic process, and their magnitudes ( $< 40$  kJ/mol) manifest a physical sorption process. The negative free energy values show that the solute is to be more concentrated on the adsorbent than in the bulk solution. The adsorption free energy on MX-4 is always lower than on Amberlite XAD-4, manifesting that phenolic compound give priority to select MX-4 adsorbent. The negative values of the adsorption entropy change are consistent with restricted mobilities of the adsorbed molecules of phenolic compounds as compared with those in solution. The

adsorption entropy change of phenolic compounds on MX-4 is higher than that on Amberlite XAD-4 at lower loading, meaning that the phenolic compounds on the surface of Amberlite XAD-4 require more ordered arrangement.

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