

THERMODYNAMIC STUDY OF ADSORPTION OF PHENOLIC COMPOUNDS FROM AQUEOUS SOLUTION BY A WATER-COMPATIBLE HYPERCROSSLINKED POLYMERIC ADSORBENT*

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Abstract Equilibrium data for the adsorption of phenolic compounds, *i.e.*, phenol, *p*-cresol, *p*-chlorophenol and *p*-nitrophenol from aqueous solutions by a water-compatible hypercrosslinked polymeric adsorbent (NJ-8) within temperature range of 283–323 K were obtained and correlated with a Freundlich-type of isotherm equation, so that equilibrium constants K_F and n were obtained. The capacities of equilibrium adsorption for all the four phenolic compounds on the NJ-8 from aqueous solutions are around 2 times as high as those of Amberlite XAD-4, which may be attributed to the unusual micropore structure and the partial polarity on the network. The values of the enthalpy (always negative) are indicative of an exothermic process, which manifests the adsorption of all the four phenolic compounds on the two polymeric adsorbents to be a process of physical adsorption. The negative values of free energy change show that the solute is more concentrated on the adsorbent than in the bulk solution. The absolute free energy values of adsorption for NJ-8 are always higher than those for Amberlite XAD-4, which indicates that phenolic compounds are preferentially adsorbed on NJ-8. The negative values of the adsorption entropy are consistent with the restricted mobilities of adsorbed molecules of phenolic compounds as compared with the molecules in solution. The adsorption entropy values of phenolic compounds for NJ-8 are lower than those for Amberlite XAD-4, which means the micropores of NJ-8 require more orderly arranged adsorbate.

Keywords Macroporous polymeric adsorbent, Hypercrosslinked resin, Phenolic compound, Adsorption thermodynamic, Temperature effect

INTRODUCTION

Wastewater containing phenols presents a serious disposal problem. This is particularly true for very low or very high concentrations of phenols in water when biological degradation cleaning works too slowly or does not work at all^[1]. Increasing concern for public health and environmental quality has led to the establishment of limits on the acceptable environmental levels of specific pollutants^[2]. Consequently there has been a growing interest in developing and implementing various methods of removing specific organics from water. In recent years polymeric adsorbents have been increasingly viewed as an alternative to activated carbon for selective removal of specific organics from contaminated water because of their wide variations in functionality, surface area, and porosity available^[3–12].

Amberlite XAD-4 resin is one of the polystyrene adsorbents and has a large surface area^[1], as widely reported. It was considered as the best polymeric adsorbent for removing phenolic compounds from aqueous

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streams. Much work has been done on the removal of phenolic compounds using Amberlite XAD-4 resin^[13]. However, Amberlite XAD-4 resin has two apparent shortcomings, which limit its broad application in chemical wastewater treatment. First, its extremely hydrophobic surface results in poor contact with aqueous solutions^[14–16]. Some activation solvents (such as methanol, acetone or acetonitrile) have to be used to enhance the surface contact with aqueous solutions during the pretreatment process. Secondly, it has a lower adsorbing capacity for most organics than activated carbon.

Of the many studies showing excellent performance of polymeric adsorbents, mention can be made of an important contribution to the “hypercrosslinked” resin developed by Tsyurupa and Davankov^[17]. The resin consisted of post-crosslinking linear or low-crosslinked macroporous polystyrene chains in solution or in highly swollen state by means of large amounts of bifunctional cross-linking agents which form conformationally restricted crosslinking bridges. This technique yielded polystyrene adsorbents of unusual “hypercrosslinked” structure and exceptionally high adsorbing capacity^[18]. In fact, “hypercrosslinked” polystyrene represents a third generation of polystyrene material, in addition to traditional gel-type and macroreticular copolymers^[19–25].

In a previous study, a new water-compatible hypercrosslinked polymeric adsorbent (NJ-8) for adsorbing and removing phenolic compounds from aqueous solutions was prepared by “oxygen modified hypercrosslinked polystyrene” during the post-crosslinking process. This resin enables its direct use without a wetting process^[26]. In the present study, we focus on the thermodynamic analysis of adsorption of phenolic compounds on Amberlite XAD-4 and on the hypercrosslinked polymeric adsorbent (NJ-8). Values of enthalpy, free energy and entropy have been estimated.

EXPERIMENTAL

Materials and Methods

Chemicals

The spherical Amberlite XAD-4 adsorbent was available from the Rohm-Haas Company (Philadelphia, USA). The spherical hypercrosslinked polymeric adsorbent (NJ-8) was prepared according to reference^[26]. Their physical properties are compiled in Table 1.

Table 1. Typical properties of the polymeric adsorbants

Property	XAD-4	NJ-8
Structure	Aromatic, polystyrene	Oxygen modified polystyrene
Polarity	Nonpolar	Moderate polar
BET surface area (m ² /g)	880*	906
Average pore diameter (nm)	5.8	2.5
Desorption average pore diameter (nm)	7.0	6.8
Particle size (mm)	0.4–0.6	0.4–0.6
Micropore area (m ² /g)	3.1	529.0
Desorption cumulative pore surface area of pores between 1.8–10 nm	644	211.7
Porosity (mL/g)	1.0	0.52
Residual chloride content (%)		3.5
Oxygen content (%)		5.95
Color	White	Deep brown

* BET surface area = 750^[1]

Phenol and three of its derivatives, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol, were obtained from Shanghai 3rd 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.

Adsorption Assay

Prior to the initial use, the adsorbent was extracted with acetone for 8 h and then dried for 2 h under vacuum at 333 K.

Table 2. Physical properties of the adsorbates

Adsorbate	Phenol	<i>p</i> -Cresol	<i>p</i> -Chlorophenol	<i>p</i> -Nitrophenol
$\lg K_{ow}^*$	2.17	2.83	2.88	1.91
pK_a^*	10.00	10.26	9.38	7.15

* Calculated according to Ref. [27]; K_{ow} is the partition coefficient of *n*-octanol/water; ** Taken from Ref. [28]

Equilibrium adsorptions of the four phenolic compounds at three different temperature (283 K, 303 K and 323 K) were performed as follows: 0.100 g of resin was introduced into a flask directly, while Amberlite XAD-4 resin was first "wetted" with 0.5 mL of methanol and then rinsed 3 times with deionized water before use. 100 mL of an aqueous solution of each phenolic compound of known concentration was added into each flask. The flasks were placed in a G25 model incubator shaker (New Brunswick Scientific Co. Inc.) at a preset temperature and shaken at 130 r/min. The initial concentrations (c_0) of the solutions were 200, 400, 600, 800 and 1000 mg/L, respectively. After adsorption reached equilibrium, the equilibrium concentrations of phenolic compounds (c_e) were determined. Thus the adsorbent-phase concentrations of adsorbates, q_e (mmol/g) were calculated according to

$$q_e = V_1 (c_0 - c_e)/MW \quad (1)$$

where V_1 is the volume of solution (L), and W is the weight of dry resin (g), and M is the molecular weight of the corresponding phenolic compound.

The concentrations of phenolic compounds were measured at 275 nm using a HPLC assembled with a Waters 600 controller, a Waters 600 pump (Waters Assoc., USA) and a Waters Dual λ Absorbance Detector.

RESULTS AND DISCUSSION

Equilibrium Adsorption

Adsorption data are often quantified via a theoretical or empirical isotherm equation because it describes how the solutes interact with adsorbents and is critical in optimizing the use of adsorbents. The equilibrium adsorption isotherms of phenol, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol on Amberlite XAD-4 and NJ-8 resins at different temperatures are shown in Figs. 1(a)–(d) and Figs. 2(a)–(d), respectively. It is well known that the Freundlich equation has the general form^[29]:

$$\lg q_e = \lg K_F + 1/n \lg c_e \quad (2)$$

where K_F and n are characteristic constants.

The regression equations at 283 K, 303 K and 323 K along with the constants K_F , n , and the correlative coefficient R on Amberlite XAD-4 and NJ-8 are listed in Table 3 and Table 4, respectively. It is quite obvious that the Freundlich adsorption law is applicable to the adsorption of phenolic compounds on NJ-8 and XAD-4 adsorbents within the concentration range in our study. These equations are reliable since all the correlative factors R are larger than 0.98. The exponents are $n > 1$ in all cases, indicating favorable adsorptions.

As shown in Figs. 1(a)–(d) and Figs. 2(a)–(d), adsorbability drops with rising temperature for all the systems studied, indicating the exothermic nature of the physical adsorption process.

At temperature of 303 K and at the same equilibrium concentration (c_e) of 1 mmol/L and 4.0 mmol/L respectively, the adsorbing capacities (q_e) for both Amberlite XAD-4 and NJ-8 were calculated and listed in Table 5. The adsorbing capacity ratio of NJ-8 over XAD-8 was about 1.97–2.41 and 2.25–3.12 for $c_e = 4.0$ mmol/L and $c_e = 1.0$ mmol/L, respectively.

Generally speaking, surface areas of adsorbents play an important role in the adsorption process. But from Table 2, the surface area of NJ-8 (906 m²/g) is slightly higher than that of Amberlite XAD-4 (880 m²/g), while the adsorption capacity of the former is about 2 times larger than that of the latter, so the difference may by no means be caused by the surface area.

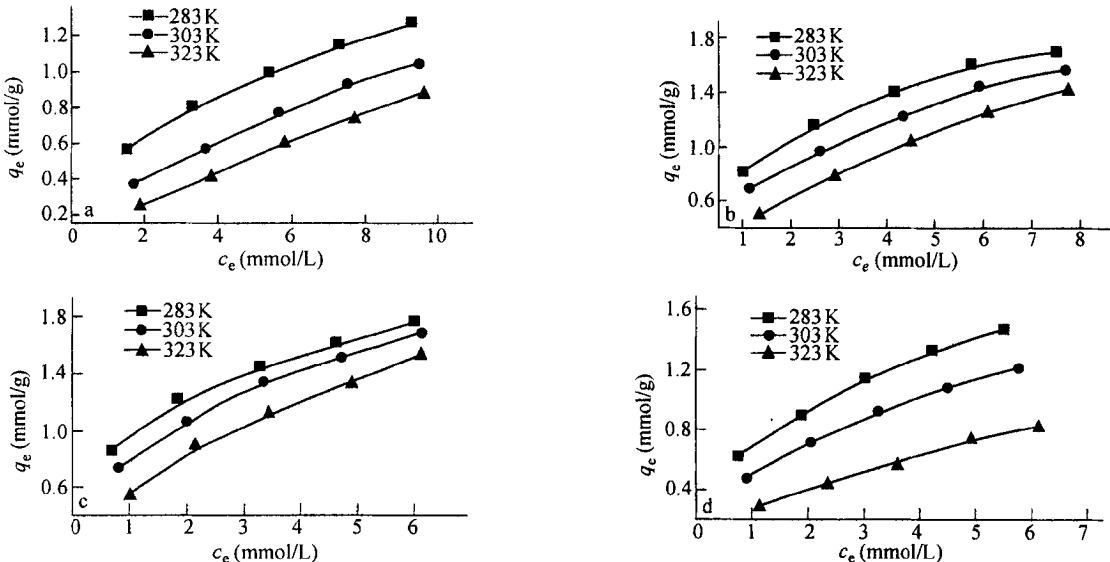


Fig. 1 Equilibrium adsorption isotherms at 283K, 303 K and 323 K for phenol (a), *p*-cresol (b), *p*-chlorophenol (c) and *p*-nitrophenol (d) on XAD-4

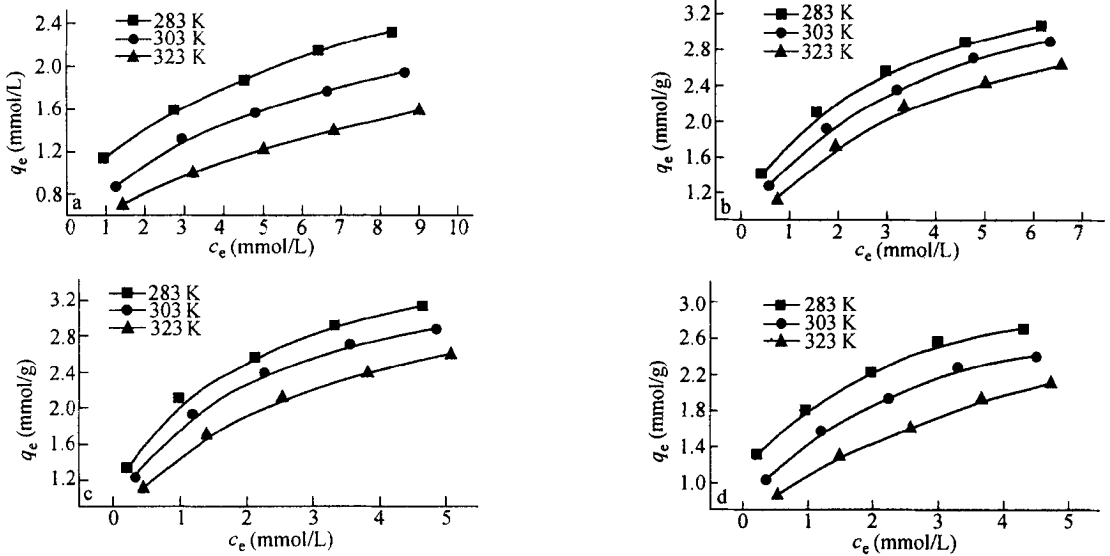


Fig. 2 Equilibrium adsorption isotherms at 283K, 303 K and 323 K for phenol (a), *p*-cresol (b), *p*-chlorophenol (c) and *p*-nitrophenol (d) on NJ-8

It is well understood that the matching of polarity between adsorbent and adsorbate should be taken into consideration when conducting adsorption processes. Generally, adsorbent possessing polarity is more susceptible to polar compounds, such as phenolic compounds. Compared with Amberlite XAD-4, the surface of NJ-8 resin is covered with polar groups, *i.e.*, carbonyl, hydroxyl and residual chloromethyl groups *etc.*, which are responsible for its high adsorbing capacity.

In spite of the difference in polarity, the microporous structure and the pore distribution of adsorbent are also important factors affecting adsorption. Strictly speaking, it is not quite correct to apply the concept of surface area evaluation based on monolayer adsorption to interpret the adsorption capacity of the hypercrosslinked adsorption resin. In comparison with Amberlite XAD-4, the pore volume of NJ-8 resin is

distributed predominantly in the micropore range (< 2 nm, Table 1). As the molecular diameters of phenolic compounds are estimated to be within the range of 0.43–0.70 nm roughly in terms of bond lengths^[30], this means that the adsorbates can be adsorbed into the pores of NJ-8, because the fine pore structure of the adsorbent is favorable for the solute-adsorbent interaction with respect to the capillary condensation theory^[31]. This expression agrees with those reported earlier^[32]. Beside micropores, NJ-8 resin also contains macropores and mesopores which may facilitate the diffusion processes of adsorbate inside polymer particles. This deduction can be proved by the constant *n* in the Freundlich isotherm, because *n* gives an indication of the favorableness of their adsorbent/adsorbate system^[20]. In every case the value of *n* for NJ-8 is always larger than that of Amberlite XAD-4, suggesting that NJ-8 gives an easier access of the phenolic compounds into the pores in comparison with Amberlite XAD-4.

Table 3. Regression equation of $\lg q_e$ vs. $\lg c_e$ for Freundlich isotherms on the Amberlite XAD-4

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

Table 4. Regression equation of $\lg q_e$ vs. $\lg c_e$ for Freundlich isotherms on NJ-8

Adsorbate	Adsorbent	<i>T</i> (K)	Regression equation	<i>K_F</i>	<i>n</i>	<i>R</i> ²
Phenol	NJ-8	283	$\lg q_e = 0.3290 \lg c_e + 0.0485$	1.1181	3.0395	0.9865
		303	$\lg q_e = 0.4245 \lg c_e - 0.0927$	0.8078	2.3557	0.9916
		323	$\lg q_e = 0.4404 \lg c_e - 0.2202$	0.6023	2.2707	0.9999
<i>p</i> -Cresol	NJ-8	283	$\lg q_e = 0.2957 \lg c_e + 0.2550$	1.7989	3.3818	0.9972
		303	$\lg q_e = 0.3405 \lg c_e + 0.1910$	1.5524	2.9369	0.9983
		323	$\lg q_e = 0.3836 \lg c_e + 0.1111$	1.2915	2.6069	0.9928
<i>p</i> -Chlorophenol	NJ-8	283	$\lg q_e = 0.2836 \lg c_e + 0.3135$	2.0583	3.5261	0.9985
		303	$\lg q_e = 0.3375 \lg c_e + 0.2579$	1.8109	2.9630	0.9966
		323	$\lg q_e = 0.3649 \lg c_e + 0.1717$	1.4849	2.7405	0.9993
<i>p</i> -Nitrophenol	NJ-8	283	$\lg q_e = 0.3078 \lg c_e + 0.2576$	1.8097	3.2489	0.9996
		303	$\lg q_e = 0.3432 \lg c_e + 0.1671$	1.4693	2.9138	0.9973
		323	$\lg q_e = 0.4135 \lg c_e + 0.0424$	1.1026	2.4184	0.9986

Generally, the adsorption behaviors of organic compounds on non-polar and moderately polar polymeric adsorbent in aqueous solution are related to the hydrophobic properties of solutes^[33], namely, the more hydrophobic the solute is, the more readily it can be adsorbed. *p*-Chlorophenol shows the highest hydrophobicity among the four phenolic compounds; therefore, it has the highest adsorbability as expected. However, in Table 5, *p*-nitrophenol is an exception. There is considerable evidence in the literature for the formation of donor-acceptor complexes between nitro-aromatic compound and several kinds of electron donors^[31], which suggests that *p*-nitrophenol is adsorbed on polystyrene by a donor-acceptor adduct mechanism involving benzene group and carbonyl of polystyrene surface acting as the electron donor and *p*-nitrophenol compounds acting as the acceptor^[34]. Consequently *p*-nitrophenol shows different adsorption behavior from the hydrophobicity sequence for phenolic compounds on NJ-8 and Amberlite XAD-4.

Table 5. Equilibrium adsorbing capacity q_e (mmol/g) for phenolic compounds on Amberlite XAD-4 and NJ-8 polymeric adsorbents at 303 K

Adsorbent	Adsorbate	$c_e = 1.0$ mmol/L	$c_e = 4.0$ mmol/L
XAD-4	Phenol	0.2588	0.6031
XAD-4	<i>p</i> -Cresol	0.6564	1.1764
XAD-4	<i>p</i> -Chlorophenol	0.8024	1.4278
XAD-4	<i>p</i> -Nitrophenol	0.5270	1.1998
NJ-8	Phenol	0.8078	1.4550
NJ-8	<i>p</i> -Cresol	1.5524	2.4889
NJ-8	<i>p</i> -Chlorophenol	1.8109	2.8913
NJ-8	<i>p</i> -Nitrophenol	1.4693	2.3644

Thermodynamics of the Adsorption of Single Solutes

Estimations of the isosteric enthalpy of adsorption, free energy, and entropy were calculated from interpolated data using the best fitting isotherm. The values obtained were dependent upon the amount of adsorbate adsorbed by the adsorbent. While the estimated values of the enthalpy of adsorption are probably not accurate because of the assumptions involved in their calculation, but they are considered to be the correct order of magnitude.

The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff equation^[35]:

$$\lg c_e = -\lg K_0 + \frac{\Delta H}{2.303RT}$$

(3)

where ΔH is the isosteric enthalpy of adsorption, R is the gas constant, c_e (mol/L) is the equilibrium concentration at the absolute temperature T , K_0 is a constant. At different temperatures (283 K, 303 K, and 323 K), c_e was obtained from the well-fitted isotherms. ΔH was calculated from the slope of a plot of $\lg c_e$ versus $1/T$. Figures 3(a)–(d) show some of these curves for the NJ-8 system.

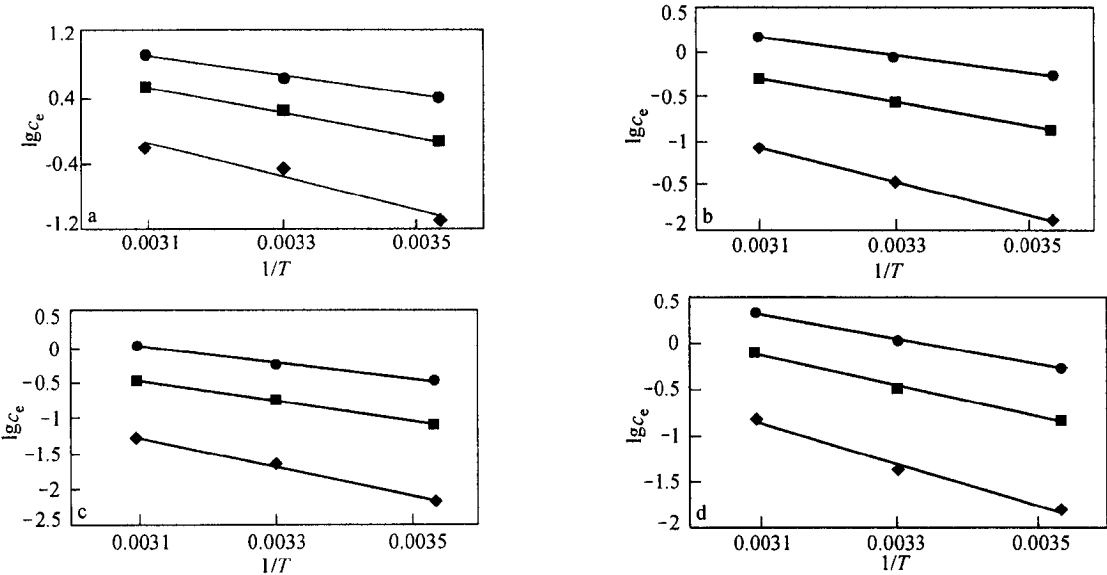


Fig. 3 Determination of isosteric enthalpy changes of adsorption of phenol (a), *p*-cresol (b), *p*-chlorophenol (c) and *p*-nitrophenol (d) on NJ-8

The free energy of adsorption can be obtained using an expression derived from the Gibbs adsorption isotherm by a procedure shown elsewhere^[35]. Finally, we get

$$\Delta G = -RT \int_0^X \frac{q dX}{X}$$

(4)

where X represents the molar fraction of the adsorbate in solution. q is then replaced by the isotherm equation. The use of the Freundlich isotherm would yield a free energy value not relevant to $q^{[36]}$.

$$\Delta G = -nRT \quad (5)$$

The entropy change associated with adsorption can be calculated from the Gibbs-Helmholtz equation^[35].

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (6)$$

Table 6 shows a summary of the estimated values for the three thermodynamic properties at various adsorbate loadings.

The negative values of the enthalpy changes are indicative of an exothermic process. From Table 6, NJ-8 resin shows a higher isosteric adsorption enthalpy changes for all four phenolic compounds than Amberlite XAD-4, which implies that NJ-8 has a stronger affinity for phenolic compounds in aqueous solution than Amberlite XAD-4. This is in agreement with the result of adsorbing capacity. On the other hand, *p*-nitrophenol shows a different enthalpy change trend among its three analogues on XAD-4 and NJ-8 resins, which can be explained by the formation of donor-acceptor adducts and the pore-filling mechanism. At low c_e , the interaction between adsorbate and adsorbent displays mainly their direct interaction. The formation of donor-acceptor adducts can interpret the high adsorption enthalpy change of *p*-nitrophenol as was discussed previously. With the increase of adsorbing capacity, the micropores can be filled by adsorbate, and the interaction between adsorbate and adsorbent can be displays of the interaction between the solute in solution and the solute adsorbed on adsorbent, gradually, the isosteric enthalpy decreases to some extent. Since *p*-nitrophenol adsorbed on adsorbent can form stronger hydrogen bonds than its three analogues, it has the highest adsorption enthalpy.

Table 6. Estimated thermodynamic parameters of the systems tested

Adsorbate	Adsorbent	q_e (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)		ΔS (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
	NJ-8	0.50	-38.6	-7.2	-6.1	-111.1	-100.6
		1.00	-28.3	-7.2	-6.1	-74.6	-68.7
<i>p</i> -Cresol	XAD-4	1.50	-22.3	-7.2	-6.1	-53.4	-50.2
		0.50	-32.2	-6.4	-5.1	-91.2	-83.9
	NJ-8	1.00	-17.7	-6.4	-5.1	-39.9	-39.0
		0.50	-35.3	-8.0	-7.0	-96.5	-87.6
<i>p</i> -Chlorophenol	XAD-4	1.00	-25.0	-8.0	-7.0	-60.1	-55.7
		1.50	-19.1	-8.0	-7.0	-39.2	-37.5
	NJ-8	0.50	-35.1	-7.0	-5.8	-99.3	-90.7
		1.00	-16.8	-7.0	-5.8	-34.6	-34.1
<i>p</i> -Nitrophenol	XAD-4	0.50	-38.2	-8.3	-7.4	-105.6	-95.4
		1.00	-27.8	-8.3	-7.4	-68.9	-63.2
	NJ-8	1.50	-21.7	-8.3	-7.4	-47.3	-44.3
		0.50	-34.4	-5.1	-4.6	-102.0	-92.3
<i>p</i> -Nitrophenol	XAD-4	1.00	-26.5	-5.1	-4.6	-75.6	-67.8
		0.50	-42.9	-7.6	-6.5	-124.7	-112.7
	NJ-8	1.00	-32.2	-7.6	-6.5	-86.9	-79.6
		1.50	-25.7	-7.6	-6.5	-64.0	-59.4

The free energy of adsorption indicates a favorable adsorption process for the adsorbent/adsorbate system. As can be seen from Table 6, variations of the adsorption free energy with temperature as well as with superficial coverage are always small. This confirms the physical character of the adsorption process and also verifies a compensation effect of the entropic contribution at low adsorption levels. The negative free energy change values

are as expected because the solute tends to be more concentrated on the adsorbent than in the bulk solution. At all temperatures, the adsorption free energy for NJ-8 is always lower than that for Amberlite XAD-4, which manifests that phenolic compounds undergo preferential adsorption on NJ-8.

Finally, the negative values of the adsorption entropy are consistent with restricted mobilities of the adsorbed molecules of phenolic compounds as compared with those molecules in solution. Absolute entropy values increase slightly with increasing temperature. From Table 6, the adsorption entropy of phenolic compounds on NJ-8 is lower than that on Amberlite XAD-4; this is because the micropores of NJ-8 require more orderly arranged adsorbate molecules.

CONCLUSIONS

The isotherm data of the four phenolic compounds for Amberlite XAD-4 and NJ-8 polymeric adsorbents can be satisfactorily correlated with the conventional Freundlich equation within the concentration range in the present study. The higher adsorbing capacity of phenolic compounds on NJ-8 than on XAD-4 is mainly attributed to its micropore structure and partial polarity of the network.

Polar NJ-8 resin shows that isosteric adsorption enthalpy changes for all four phenolic compounds are higher than over nonpolar Amberlite XAD-4 at low c_e , which means that polar NJ-8 has a stronger affinity for phenolic compounds in aqueous solution than nonpolar Amberlite XAD-4. All the negative values of the enthalpy are indicative of an exothermic adsorption process.

The negative values of free energy change show that the solute is more concentrated on the adsorbent than in the bulk solution. The adsorption free energy of NJ-8 is always lower than that on Amberlite XAD-4, which manifests that phenolic compounds are preferentially adsorbed on NJ-8 adsorbent.

The negative values of the adsorption entropy are consistent with restricted mobilities of the adsorbed molecules of phenolic compounds as compared with those molecules in solution. The adsorption entropy of phenolic compounds on NJ-8 is lower than on Amberlite XAD-4, which implies that the micropores of NJ-8 require more orderly arranged adsorbate molecules.

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REFERENCES

- 1 Kunin, R., *Pure Appl. Chem.*, 1976, 46: 205
- 2 Juang, R.S. and Shiau, J.Y., *J. Hazardous Materials*, 1999, B70: 171
- 3 Juang, R.S., Shiau, J.Y. and Shao, H.J., *Sep. Sci. Technol.*, 1999, 34: 1819
- 4 Payne, G.F., Payne, N.N., Ninomiya, Y. and Shuler, M.L., *Sep. Sci. Technol.*, 1989, 24: 453
- 5 Gusler, G.M., Browne, T.E. and Yoran, C., *Ind. Eng. Chem. Res.*, 1993, 32: 2727
- 6 Xu, Z.Y., Zhang, Q.X. and Wu, C.L., *Chemosphere*, 1997, 35: 2269
- 7 Kawabata, N., Higuchi, I. and Yoshida, J.I., *Bull. Chem. Soc. Jpn.*, 1981, 54: 3253
- 8 Payne, G.F. and Shuler, M.L., *Biotechnol. Bioeng.*, 1988, 31: 922
- 9 Li, A.M., Zhang, Q.X., Chen, J.L., Fei, Z.H., Long, C. and Li, W.X., *React. Funct. Polym.*, 2001, 49: 225
- 10 Li, A.M., Zhang, Q.X., Chen, J.L., Fei, Z.H., Long, C. and Li, W.X., *J. Environ. Sci.*, 2002, 14: 457
- 11 Li, A.M., Long, C., Suen, Y., Zhang, Q.X., Liu, F.Q. and Chen, J.L., *Sep. Sci. Technol.*, 2002, 37: 3211
- 12 Li, A.M., Zhang, Q.X., Liu, F.Q., Fei, Z.H., Wang, X.J. and Chen, J.L., *Ion Exchange and Adsorption* (in Chinese), 2001, 17: 515
- 13 He, B.L. and Huang, W.Q., "Ion Exchange and Adsorption Resins" (in Chinese), The Science and Education Press of Shanghai, Shanghai, 1992, p.353; p.439
- 14 Masque, N., Galia, M., Marce, R.M. and Borrul, F., *J. Chromatogr. A.*, 1998, 803: 147

- 15 Dumont, P.J. and Fritz, J.S., *J. Chromatogr. A.*, 1995, 691: 123
- 16 Masque, N. and Galia, M., *J. Chromatogr. A.*, 1997, 771: 55
- 17 Davankov, V.A. and Tsyurupa, M.P., *React. Polym.*, 1990, 13: 27
- 18 Davankov, V.A. and Tsyurupa, M.P., *Pure Appl. Chem.*, 1989, 61: 1881
- 19 Tayurupa, M.P., Maslova, L.A. Andreeva, A.I., Mrachkovskaya, T.A. and Davankov, V.A., *React. Polym.*, 1995, 25: 69
- 20 Xu, Z.Y., Zhang, Q.X., Chen, J.L. and Wang, L.S., *Chemosphere*, 1999, 38: 2003
- 21 Veverka, P. and Jerabek, K., *React. Funct. Polym.*, 1999, 41: 21
- 22 Azanova, V.V. and Hradil, J., *React. Funct. Polym.*, 1999, 41: 163
- 23 Podlesnyuk, V.V., Hradil, J. and Kralova, E., *React. Funct. Polym.*, 1999, 42: 181
- 24 Streat, M. and Sweetland, L.A., *Trans. I ChemE.*, part B, 1998, 76: 115
- 25 Tai, M.H., Saha, B. and Streat, M., *React. Funct. Polym.*, 1999, 41: 149
- 26 Li, A.M., Zhang, Q.X., Zhang, G.C., Chen, J.L., Fei, Z.H. and Liu, F.Q., *Chemosphere*, 2002, 47: 981
- 27 Wang, L.S., "Organic Pollutant Chemistry", China Science Press, Beijing, 1990, p.9
- 28 Xing, Q.Y., Xu, R.Q. and Zhou, Z., "Fundamental Organic Chemistry (2nd Ed.)", China Higher Education Press, Beijing, 1984, p.737
- 29 Slejko, F.L., "Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application", Marcel Dekker, New York, 1985, p.13
- 30 Lide, D.R., "CRC Handbook of Chemistry and Physics, 76th Ed", CRC Press Inc., Boca Raton, 1995, 9-5-9-37
- 31 Mattson, James S. and Mark, Harry B., *J. Colloid Interface Sci.*, 1969, 31: 16
- 32 Pavel, V. and Karel, J., *React. Funct. Polym.*, 1999, 41: 21
- 33 Rojas, J.A. and Voilley, A., *Sep. Sci. Technol.*, 1996, 31: 2473
- 34 Drago, R.S., Vogel, G.C. and Needham, T.E., *J. Am. Chem. Soc.*, 1971, 17: 6014
- 35 Garcla-Delgado, R.A., Cotouelo-Minguez, L.M. and Rodfiguez, J.J., *Sep. Sci. Technol.*, 1992, 27 : 975
- 36 John P.B. and Marios T., *J. Water Pollut. Control Fed.*, 1887, 59: 191