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A NEW PHENOLIC HYDROXYL MODIFIED POLYSTYRENE ADSORBENT FOR THE REMOVAL OF PHENOLIC COMPOUNDS FROM THEIR AQUEOUS SOLUTIONS

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ABSTRACT

A new phenolic hydroxyl modified polystyrene adsorbent (AM-1) was synthesized for the removal of phenolic compounds from their aqueous solutions. This new adsorbent can be used directly without the wetting pretreatment. A comparison of the sorption properties of the AM-1 and the commercial Amberlite XAD-4 toward four phenolic compounds, phenol, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol, was made. The capacities of equilibrium adsorption of AM-1 for all four phenolic compounds were around two times higher than that of Amberlite XAD-4, which may be contributed to the presence of phenol hydroxyl

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group on the surface and the unique pore structure of AM-1. Freundlich isotherm equations and the values of isosteric adsorption enthalpies for the four phenolic compounds indicated a physical adsorption mechanism on both adsorbents. Column studies showed that both the breakthrough adsorption capacity and the total adsorption capacity of phenol on AM-1 were higher than on Amberlite XAD-4 while less acetone was needed for desorbing phenol from AM-1 than from Amberlite XAD-4.

Key Words: Polymeric adsorbent; Phenolic compound; Adsorption; Synthesis; Adsorption enthalpy

INTRODUCTION

Increasing concerns on public health and environmental quality have led to the establishment of limits on the acceptable environmental levels of specific pollutants. Consequently, various methods including aeration, biological degradation, oxidation, and adsorption, have been developed and implemented for the removal of specific organics from water. Among them, adsorption is an attractive technique because of the high concentrating ability of typical adsorbents.[1–4] Advances in polymer science have provided an opportunity to produce adsorbents with well-controlled chemical structures and high specific surface areas. In recent years, polymeric resins have been used increasingly as an alternative to activated carbon for the removal of specific organics from contaminated water.[5,6]

Phenol and its derivatives are versatile raw materials in chemical industry. Since most phenolic compounds are extremely toxic at the concentrations discharged into receiving effluents,[2] the removal or destruction of phenolic compounds from such streams has become a significant environmental task.[1] Amberlite XAD-4, an organic porous adsorbent manufactured by copolymerization of styrene and divinylbenzene, is generally considered as the best polymeric adsorbent for removing phenolic compounds from aqueous streams.[1,5] Series researches have been done on the removal of phenolic compounds using Amberlite XAD-4 polymeric resin.[7] However, the initial extreme hydrophobic chemical structure of this polystyrene-based adsorbents results in their poor contact with aqueous solutions.[8,9] Some activation solvents (e.g., methanol, acetone, or acetonitrile) have to be used to enhance surface contact with the aqueous solutions in a pretreatment process,[7] which limits its broad application in the wastewater treatment. Therefore, various chemical modifications have been carried out to enhance the hydrophilicity of the polystyrene-based polymeric adsorbents without affecting their adsorption capacities.[8–11] For example, the acetylized Amberlite XAD-4 exhibited higher adsorption capacities toward four different phenolic derivatives while the "wetting" pretreatment became unnecessary.[11] In the current research, water compatibility of polystyrene adsorbent was improved by covalent bonding of phenolic hydroxyl groups to the surface of porous polystyrene–divinylbenzene beads during the process of post-crosslinking of the porous chloromethyl polystyrene by itself, but without introducing ionic functional groups.

EXPERIMENTAL

Chemicals

Styrene and divinylbenzene were obtained from Dongda Chemical Co. (Shandong Province, China). Chloromethyl methylether was purchased from Langfang Chemical Co. (Hebei Province, China). The spherical Amberlite XAD-4 adsorbent was obtained from Rohm & Haas Company (Philadelphia, PA). Phenol and three of its derivatives, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol, as well as some other chemicals were all from Shanghai Chemical Reagent Plant (Shanghai, China). The physical properties of these phenolic compounds are listed in Table 1. In the adsorption assay, they were dissolved in deionized water without pH adjustment.

Adsorbent Synthesis

1. Synthesis of poly(styrene-*co*-divinylbenzene) macroporous beads was carried out following the process reported previously.[12] Briefly, 176 g of styrene, 24 g of divinylbenzene, 2 g of dibenzoyl peroxide, and 100 g of liquid paraffin were mixed at room temperature in a 2000 mL round-bottomed flask. A

Table 1. Physical Properties of the Adsorbates

	Phenol	*p*-Cresol	*p*-Chlorophenol	*p*-Nitrophenol
$\log(K_{ow})^a$	2.17	2.83	2.88	1.91
$pK_a{}^b$	10.00	10.26	9.38	7.15

[a] Calculated according to Ref. [14], where K_{ow} is the partition coefficient of *n*-octanol/water.
[b] From Ref. [15].

quantity of 1200 g of 1 wt% gelatin aqueous solution was then added to the flask. Suitable stirring rate was adjusted and the polymerization was performed at 353K for 12 hr. The polymer beads were filtered, rinsed three times with hot water, extracted with acetone for 8 hr, and finally dried under vacuum at 333K.

2. Chloromethylation of the macroporous copolymer: In a 2000 mL round-bottomed flask, 100 g of the macroporous poly(styrene-*co*-divinylbenzene) beads was swollen in 600 mL of monochloromethylether. Under mechanical stirring, 40 g of zinc chloride was added slowly. The mixture was stirred continuously at 312K for 12 hr. The chloromethylated copolymer (CCSD-6) were filtered, extracted with ethanol for 8 hr in a Soxhlet apparatus, and then dried under vacuum at 333K for 8 hr.

3. In a 2000-mL round-bottomed flask, 100.0 g of chloromethylated copolymer (CCSD-6) beads and 10.0 g of phenol were mixed and suspended in 600 mL of nitrobenzene. Under mechanical stirring, 10.0 g of zinc chloride was added slowly to the flask. The mixture was then stirred for 4 hr at 343K, and 8 hr at 388K. Finally, the mixture was poured into an acetone bath containing 1% of hydrochloric acid. The polymer beads were filtered and extracted with ethanol in a Soxhlet apparatus for 8 hr and dried under vacuum at 333K for 8 hr.

Polymer Characterization

The specific surface area and the pore diameter of the porous adsorbents were measured using a Micromeritics ASAP-2010C apparatus, (Micromeritics Instrument Corporation, (North Gosford, NSW, Australia)) following the BET (Bruaaures S-Emmett H-Teller) method. Infrared spectra of the polymeric adsorbents before and after the Friedel-Crafts reaction were obtained with a Nicolet 170 SX IR Spectrometer (Madison, WI, USA). The chlorine content was measured following a method proposed by Volhard.[13] The elemental analysis of the AM-1 polymeric adsorbent was performed using a Perkin-Elmer 240 C Elemental Analytical Instrument (Wellesley, MA, USA). The oxygen content was calculated from

$$O\% = [100 - (C + H) - Cl]\% \tag{1}$$

Adsorption Assay

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

Equilibrium adsorption of the phenolic compounds at three different temperatures (283, 303, and 333K) 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 three times with deionized water before use. An aqueous solution of phenolic compounds (100 mL) with known concentration was added into each flask. The flasks were placed in a G 25 model incubator shaker (New Brunswick Scientific Co. Inc., Edison, New Jersey, USA) at a pre-settled temperature and shaken under 130 rpm. After adsorption reached equilibrium, the concentrations of phenolic compounds (C_e) were determined. The initial concentrations (C_0) of the solutions were 200, 400, 600, 800, and 1000 mg L^{-1}, respectively. The adsorbent-phase concentration of adsorbates, q_e (mmol g^{-1}) was calculated according to

$$q_e = V_1(C_0 - C_e)/MW \tag{2}$$

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

Column adsorption was conducted using a 10 cm × 4.6 mm stainless-steel column with a 2-μm stainless-steel frit connected with a 6672 reciprocating pump (Beijing Analytical Instrument Plant, Beijing, China) at room temperature. Phenol solution with initial concentration of 70.9 mmol L^{-1} was applied to the column at a flow rate of 6 BV hr^{-1} (BV = the volume of resin bed). Adsorption capacities of the resins were evaluated by (1) the breakthrough capacity, the total amount of the adsorbed phenol until the effluent concentration reached 0.05 mmol L^{-1}, and (2) the total capacity, the total amount of the adsorbed phenol until the effluent concentration reached the initial concentration. The adsorbent-phase concentration of the adsorbate in column, q_c was calculated according to

$$q_c = V_2(C_{\mathrm{I}} - C_e)/V_3 \tag{3}$$

where V_2 is the volume of solution passed through the column, C_{I} is the initial concentration of the solution, V_3 is the volume of polymeric adsorbent in column, and C_e is the average concentration of the effluent.

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

RESULTS AND DISCUSSION

Characterizations of Polymeric Adsorbents

Figure 1 shows the IR spectra of the chloromethylated poly(styrene-*co*-divinylbenzene) beads before and after the Friedel-Crafts reaction with phenol. The characteristic peak of phenolic hydroxyl group at 3512 cm^{-1} was observed in the IR spectrum of AM-1 while the strong band of chloromethyl of

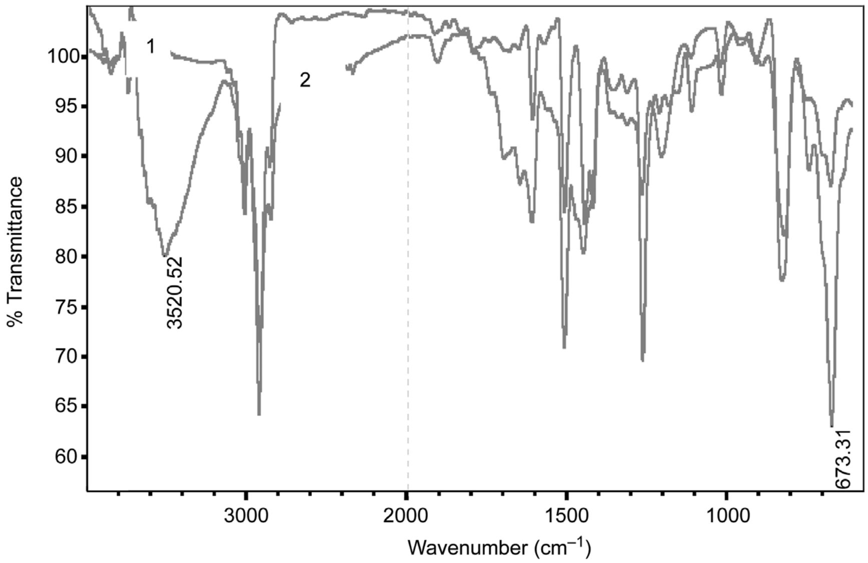

Figure 1. IR spectra of the chloromethylated poly(styrene-*co*-divinylbenzene) beads before and after the Friedel-Crafts reaction with phenol. 1 Chloromethylated copolymer of styrene-*co*-divinylbenzene(CCSD-6); 2 Phenolic hydroxyl modified polystyrene.

chloromethylated copolymer of styrene–divinylbenzene at 671 cm^{-1} decreased greatly after the reaction.

This is in agreement with the result of the elemental analysis (Table 2). The chlorine content of the chloromethylated poly(styrene-*co*-divinylbenzene) beads decreased from 19.5% to 3.5%, whereas the oxygen content of resin increased from 0 to 1.25%.

The specific surface area and pore structures of polymeric adsorbents were examined using the BET method. As shown in Fig. 2 and Table 2, AM-1 exhibits a higher content of micropores ($<$2.0 nm) while the pore distribution of Amberlite XAD-4 concentrates mainly in the mesopore range (2.0–18.0 nm).

Equilibrium Adsorption

The equilibrium adsorption isotherms of phenol, *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol on AM-1 and Amberlite XAD-4 at 303K are shown in Fig. 3a–d, respectively. For all the four phenolic compounds, the adsorption capacities on AM-1 are around two times higher than that on Amberlite XAD-4 at low loading.

Table 2. Characteristics of the Polymeric Resins

Property	XAD-4	CCSD-6	AM-1
Structure	Polystyrene	Chloromethylated copolymer of styrene-divinylbenzene	Phenol hydroxyl modified polystyrene
Polarity	Nonpolar		Moderate polar
BET surface area ($m^2 g^{-1}$)	880[a]	6.3	590
Average diameter (nm)	5.8		8.6
Micropore area ($m^2 g^{-1}$)	3		340
Mesopore area ($m^2 g^{-1}$)	645		138
Particle size (mm)	0.4–0.6		0.4–0.6
Porosity ($mL\,g^{-1}$)	1.0		0.52
Residual chlorine content (%)		19.5	3.5
Oxygen content (%)		0	1.25
Color	White	White	Brown

[a] Value measured in our study, and the reference value is 750.[1]

The adsorption isotherms were further correlated to the well-known Freunlich equation:[14]

$$\log q_{\mathrm{e}} = \log K_{\mathrm{F}} + 1/n \log C_{\mathrm{e}} \tag{4}$$

where K_{F} and n are characteristic constants.

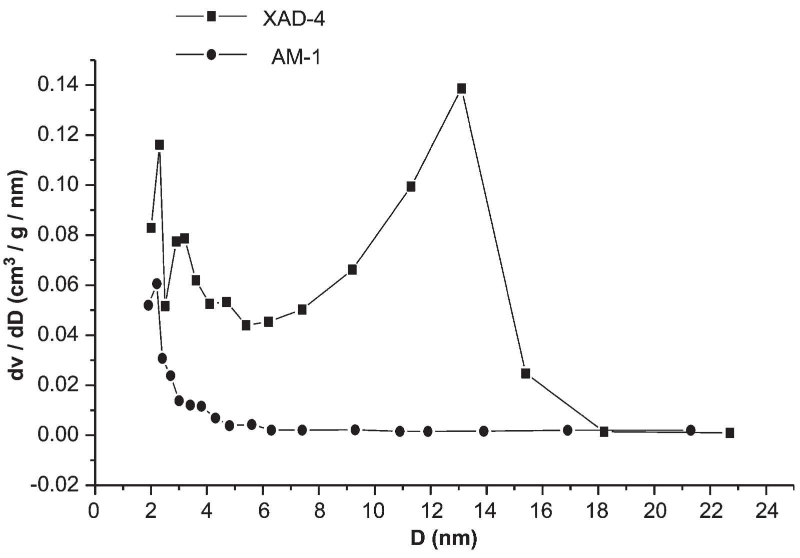

Figure 2. Pore size distributions of AmberliteXAD-4 and AM-1, ● AM-1; ■ XAD-4.

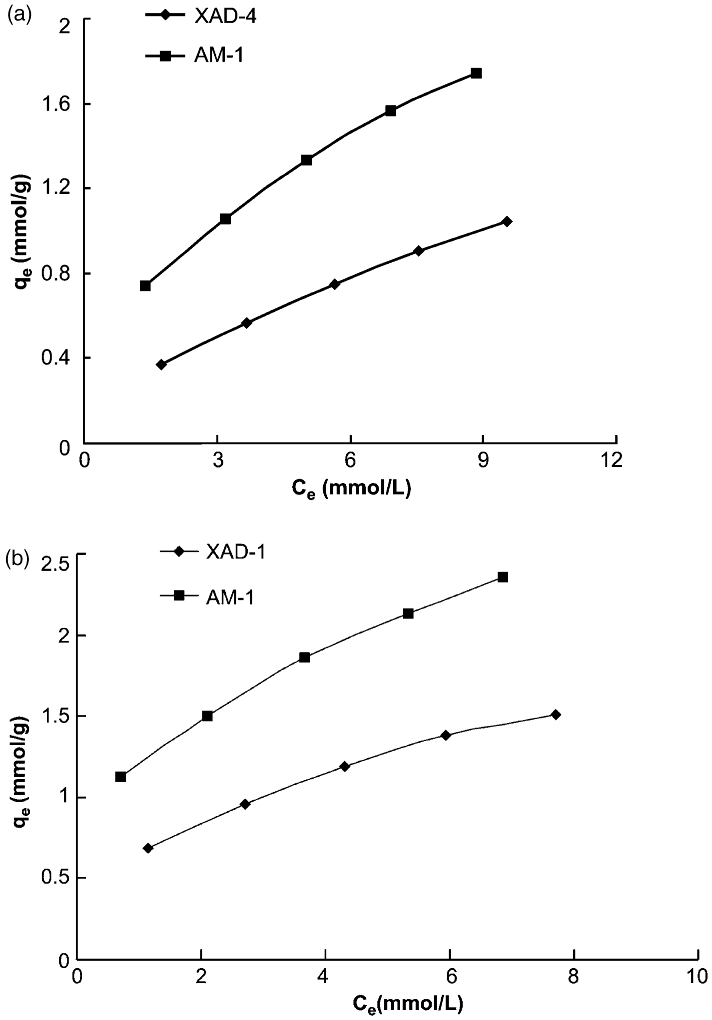

Figure 3. Equilibrium adsorption isotherms at 303K for (a) phenol, (b) *p*-cresol, (c) *p*-chlorophenol, and (d) *p*-nitrophenol on Amberlite XAD-4 and AM-1. ◆ XAD-4; ■ AM-1.

The regression equations at 303K along with the constants K_F, n, and the correlative coefficient R are given in Table 3. It is obvious that the Freundlich adsorption law is applicable to the adsorption of phenolic compounds on AM-1 and Amberlite XAD-4 resin. Since the constant K_F is taken as a relative indicator of adsorption capacity in the Freudlich theory,[16]

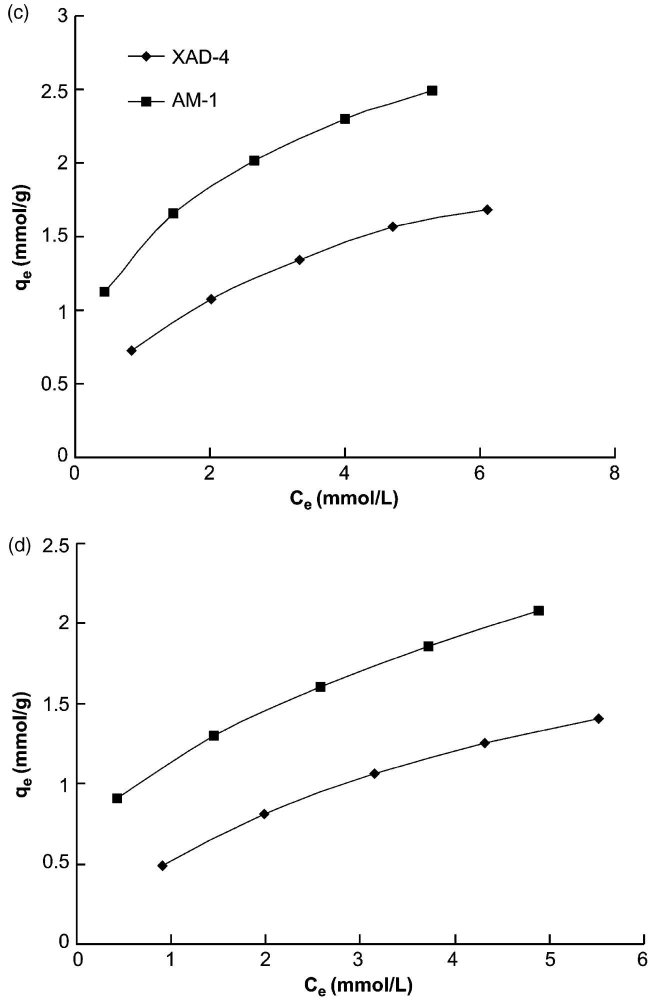

Figure 3. Continued.

the comparison of the calculated K_F (Table 3) further confirmed that the adsorption capacities of the AM-1 are higher than that of Amberlite XAD-4 for the four phenolic compounds. These equations are reliable because all the correlative factors R are larger than 0.99. The exponents are $n > 1$ in all cases, indicating that the adsorption is favorable. In the same way, Freundlich adsorption law is also applicable to equilibrium adsorption at 283 and 333K as above.

Table 3. Regression Equation of $\log q_e$ vs. $\log C_e$ for Freudlich Isotherms

Adsorbate	Adsorbent	Regression Equation	K_F	n	R
Phenol	XAD-4	$\log q_e = 0.6102 \log C_e - 0.587$	0.2588	1.6388	0.995
p-Cresol	XAD-4	$\log q_e = 0.4208 \log C_e - 0.1828$	0.6564	2.3764	0.997
p-Chlorophenol	XAD-4	$\log q_e = 0.4157 \log C_e - 0.0956$	0.8024	2.4055	0.998
p-Nitrophenol	XAD-4	$\log q_e = 0.5935 \log C_e - 0.2782$	0.5260	1.6849	0.999
Phenol	AM-1	$\log q_e = 0.4582 \log C_e - 0.1965$	0.6361	2.1825	0.998
p-Cresol	AM-1	$\log q_e = 0.3191 \log C_e + 0.0948$	1.2439	3.1338	0.997
p-Chlorophenol	AM-1	$\log q_e = 0.3162 \log C_e + 0.1656$	1.4642	3.1626	0.998
p-Nitrophenol	AM-1	$\log q_e = 0.3522 \log C_e + 0.0678$	1.1690	2.8393	0.999

Table 4 lists adsorption capacities of the four compounds on Amberlite XAD-4 and AM-1 at the same residual concentrations (C_e), 1.0 and 4.0 mmol L^{-1}. When $C_e = 4.0\,\text{mmol}\,L^{-1}$, for all the four phenolic compounds, the adsorption capacities on AM-1 were 60% more than that on Amberlite XAD-4. When C_e was lowered to 1 mmol L^{-1}, the adsorption capacities on AM-1 were around two times higher than that on Amberlite XAD-4, suggesting an advantage of AM-1 in the removal of phenol at low concentrations.

It is well known that the surface area of adsorbent plays an important role in adsorption process. However, the surface area of AM-1 (590 $m^2\,g^{-1}$) is greatly smaller than that of Amberlite XAD-4 (880 $m^2\,g^{-1}$) (Table 2). The higher adsorption capacities of AM-1 towards phenolic compounds are thus contributed by some other factors other than the difference in the surface areas.

The first factor that should be considered is the matching of polarity between adsorbent and adsorbate. Generally, polar adsorbent is more selective towards polar

Table 4. Equilibrium Adsorption Capacity q_e (mmol g^{-1}) for Phenolic Compounds on Amberlite XAD-4 and AM-1 Polymeric Adsorbents

Adsorbent	Adsorbate	$C_e = 1.0\,\text{mmol}\,L^{-1}$	$C_e = 4.0\,\text{mmol}\,L^{-1}$
XAD-4	Phenol	0.2588	0.6031
XAD-4	*p*-Cresol	0.6564	1.1764
XAD-4	*p*-Chlorophenol	0.8024	1.4278
XAD-4	*p*-Nitrophenol	0.5270	1.1998
AM-1	Phenol	0.6360	1.2005
AM-1	*p*-Cresol	1.2439	1.9361
AM-1	*p*-Chlorophenol	1.4642	2.2697
AM-1	*p*-Nitrophenol	1.1690	1.9048

compounds. Contrary to the Amberlite XAD-4, the AM-1 resin, which its surface is covered by the phenol hydroxyl group, which is polar and similar to phenolic compounds in chemical structure, according to the Similarity Theory, the crosslinked network will be favorable to the adsorption of compounds with similar structures. The increase in the adsorption capacity of phenol on AM-1 resin is therefore larger than that of its three derivatives.

Besides the difference in the polarity, the porous structure and the pore distribution of the adsorbent are also important factors affecting the adsorption. In comparison with the mesoporous structure of Amberlite XAD-4, AM-1 is mainly microporous (Fig. 2 and Table 2). According to the Capillary Condensation Theory,[17] the fine pore structure of adsorbent can enhance the solute–solute interaction and capillary condensation, the "unique" multiple-layer adsorption.[17,18] Presence of macropore and mesopore in the AM-1 adsorbent may facilitate adsorption processes inside polymer particles. This assumption was supported by the constant *n*, an indication of the favorite of the adsorbent/adsorbate system,[6] in the Freundlich isotherm. In every case, the value of *n* for AM-1 is always larger than that of Amberlite XAD-4, which suggests that it is easier for phenol derivatives to access the AM-1 pores than Amberlite XAD-4 pores.

Another factor that may affect adsorption is the property of adsorbates. In general, high hydrophobicity may help the adsorption of solutes on the nonpolar and moderate polar polymeric adsorbent in aqueous solution.[19] *p*-Chlorophenol, the most hydrophobic one in the test, exhibited the highest adsorption capacity towards both adsorbents.

Isosteric Enthalpies for Phenolic Compound Adsorption

The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff equation:[20]

$$\log(1/C_e) = \log(K_0) + \left(\frac{-\Delta H}{2.303\,RT}\right) \tag{5}$$

where ΔH is the isosteric enthalpy of adsorption, R the gas constant, and C_e the equilibrium concentration of solute in moles per liter at the absolute temperature T. At different temperatures (283, 303, and 333K), the C_e was obtained from the well-fitted isotherms. ΔH was calculated from the slope of line plotted by $\log C_e$ vs. $1/T$.

Table 5 shows a summary of the estimated values for the adsorption enthalpy of phenolic compounds on the two adsorbents. Values of the enthalpy changes (always negative) are indicative of an exothermic process, and their magnitudes ($< 40\,\mathrm{kJ\,mol^{-1}}$) manifest a physical sorption process. The adsorption

Table 5. Isosteric Enthalpy of Adsorption ΔH ($\mathrm{kJ\,mol^{-1}}$) Evaluated at Different Adsorption Capacities in the Temperature Range 283–323K

Adsorbate	Adsorbent	$q = 0.5\,\mathrm{mmol\,g^{-1}}$	$q = 1.0\,\mathrm{mmol\,g^{-1}}$
Phenol	XAD-4	−28.1	−13.6
	AM-1	−18.3	−12.3
p-Cresol	XAD-4	−32.2	−17.7
	AM-1	−31.7	−21.5
p-Chlorophenol	XAD-4	−35.1	−16.8
	AM-1	−35.4	−22.6
p-Nitrophenol	XAD-4	−34.4	−26.5
	AM-1	−32.5	−19.8

enthalpy of the phenolic compounds on AM-1 resin decreases with the increase in adsorption capacity, which further confirms that the adsorption of phenolic compounds on AM-1 resin follows the capillary condensation theory or fine pore volume filling adsorption mechanism. At low adsorption capacity, the interaction between adsorbate and adsorbent display mainly the direct interaction between the solute and adsorbent, with the increase in the adsorption capacity, the fine pore is filled with adsorbate gradually, the interaction between the adsorbate and the adsorbent gradually display the interaction between the solute in solution and solute adsorbed on adsorbent, namely, solute aggregation on the surface of adsorbent, the isosteric enthalpy decreases by degrees. Since *p*-nitrophenol adsorbed on the adsorbent can form the stronger hydrogen bonding than its three analogues, it has higher adsorption enthalpy.

Column Adsorption and Desorption of Phenol on Two Adsorbents

Since the AM-1 resin is developed as a polymeric adsorbent for removal and recovery of organic pollutants from wastewater, the column adsorption and desorption studies are thus practically very important. In the current study, breakthrough capacities and total capacities of adsorbents for the adsorption of phenol were determined by the continuous flow column methods.

The adsorption capacity obtained in column studies depends upon the diameter of the column, the flow rate, and other experimental factors. In the present study, all those factors are settled constant for the two polymeric adsorbents. The adsorption curves of phenol on the two polymeric adsorbents were shown in Fig. 4a, and the acetone desorption curves of the two resins saturated with phenol are shown in Fig. 4b. It is obvious that the adsorption capacity for phenol on AM-1 is higher than on Amberlite XAD-4, in spite of the

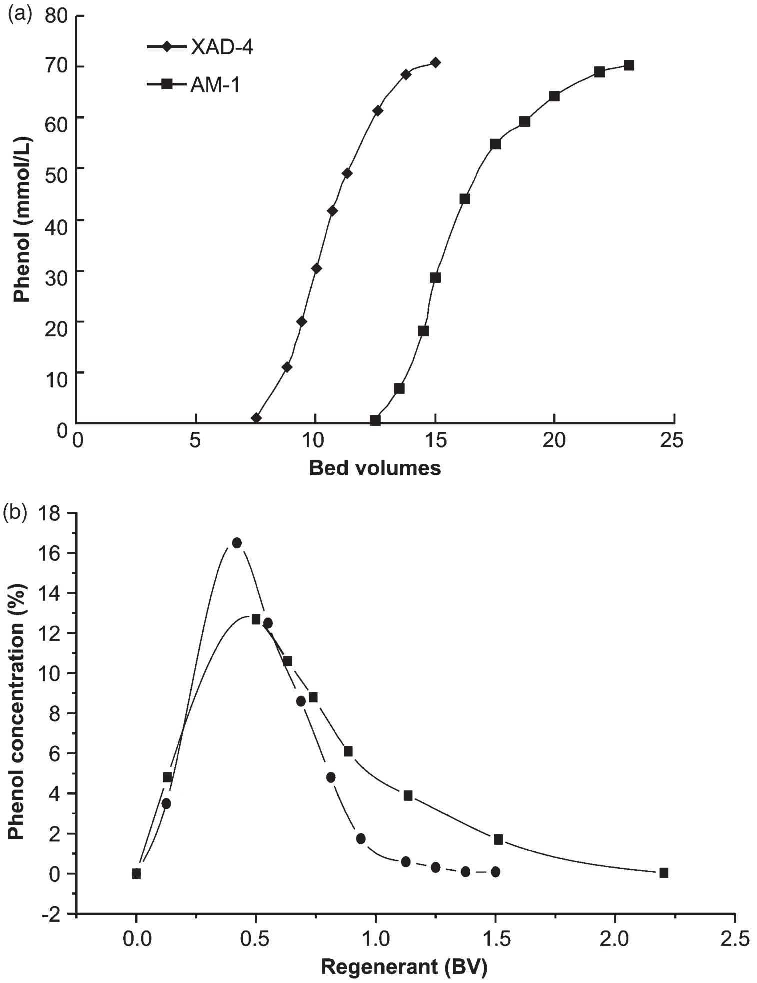

Figure 4. (a) Column adsorption for phenol on Amberlite XAD-4 (◆) and AM-1 (■) at the rate of 6 BV/hr from aqueous solutions. (b) Phenol desorption from AM-1 (●) and Amberlite XAD-4 (■) at a rate of 1 BV/hr with acetone.

quite similar adsorption and desorption curves. At the flow rate of 6 BV/hr and the initial concentration of 70.9 mmol L^{-1}, the breakthrough adsorption capacities for phenol on Amberlite XAD-4 and AM-1 were calculated as 0.54 and 0.89 mmol mL^{-1}, respectively. The total adsorption capacities were 0.62 mmol mL^{-1} for Amberlite XAD-4 and 1.09 mmol mL^{-1} for AM-1.

One unique property of polymeric adsorbents over classical carbonaceous adsorbents is that the adsorbed organic compounds can be recovered in a usable form. The solvents found to be most effective in phenol regeneration from the two resins are methanol, acetone, and dilute caustic. As shown in Fig. 4b, at a desorption rate of $1\,\mathrm{BV\,hr^{-1}}$, the volume of acetone needed for removing all the adsorbed phenol on AM-1 and Amberlite XAD-4 are 1.5 and 2.0 times of bed volume, respectively, indicating that the volume of acetone needed for removing all the phenol adsorbed on AM-1 resin is only 75% of that on Amberlite XAD-4.

CONCLUSIONS

A new phenolic hydroxyl modified polystyrene adsorbent (AM-1) was synthesized for adsorbing and removing phenolic compounds from their aqueous solutions. This product can be used directly without wetting process.

The isotherm data for the four phenolic compounds on AM-1 resin can be satisfactorily fitted to the conventional Freundlich equation. The hydrophobicity of adsorbate determines the adsorption capacities of phenolic compounds from their aqueous solutions onto Amberlite XAD-4 and AM-1 resins. The higher adsorption capacity of phenolic compounds on AM-1 than that on Amberlite XAD-4 is mainly contributed to its micropore structure, the unique pore distribution, and the presence of the phenol hydroxyl group on the network of AM-1 resin.

The adsorption enthalpy of the phenolic compounds on AM-1 resin decreases with the increase in adsorption capacity, which confirms that the adsorption of the phenolic compounds on AM-1 resin follows the capillary condensation theory or fine pore volume filling adsorption mechanism. The values and the magnitudes of the enthalpy indicate an exothermic and physical adsorption process.

In the column adsorption, the breakthrough adsorption capacities for phenol on Amberlite XAD-4 and AM-1 are 0.54 and $0.89\,\mathrm{mmol\,mL^{-1}}$, and the total capacities are 0.62 and $1.09\,\mathrm{mmol\,mL^{-1}}$. On the other hand, the volume of acetone needed for removing all the phenol adsorbed on AM-1 resin is only 75% of that on Amberlite XAD-4.

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