Adsorption of phenolic compounds from aqueous solutions by aminated hypercrosslinked polymers

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Abstract

Two novel polymers (NJ-1 and NJ-2) were synthesized by chemically modified a hypercrosslinked polymer NJ-0 with dimethylamine and trimethylamine, respectively. The comparison of the adsorption properties of the three polymers toward phenol, resorcin and phloroglucin was made. The study focused on the static equilibrium adsorption behaviors and the adsorption thermodynamics. Freundlich equation was found to fit the adsorption results well. The effect of amino groups introduced onto the surface of the resin and the structure of phenolic compounds on the adsorption were also studied. The hydrogen-bonding interaction and electrostatic interaction could happen between the amino groups and the adsorbates. The adsorption impetus increased as quantity of hydroxyl groups increased, but the adsorption capacity decreased due to the drop of the matching degree of the aperture of resins and the diameter of adsorbate molecules.

Key words: hypercrosslinked polymer; phenolic compounds; amino groups modified; static adsorption

Introduction

Phenolic compounds that are widely used as industrial intermediates for the manufacture of drugs, pesticides, dyestuffs and so on, are of particular interest due to its negative environmental and human healthy impacts once discharged into the receiving water system with industrial waste streames.

Presently, extraction, adsorption, biodegradation, catalytic oxidation and some other methods (Jiang *et al.*, 2003; Shen, 2002; Atwater *et al.*, 1997; Quan *et al.*, 2002) have been applied well in the treatment of wastewater containing phenol compounds. Due to the high concentrating ability and possibility of resource reuse, adsorption is proved to be one of the most attractive and effective techniques for purification and separation of wastewater.

Compared with traditional adsorbents such as the activated carbons, silica gels and aluminas, polymers are viewed as more attractive adsorbents for the controllable pore structures and surface characteristics. In the development of polymeric adsorbents, hypercrosslinked polymers have aroused more attention for its higher surface area and adsorption capacity than usual macropolymers (Davankov and Tsyurupa, 1990). Whereas, the adsorption results of aromatic organics compounds with high water-solubility are dissatisfactory. Recently, the enhancement of adsorption capacity has been achieved by introducing functional groups such as amino groups, pyridine groups, carboxyl, phenolic hydroxyl, acetyl and so on, onto the surface of the hpercrosslinked polymers (Li, 2002; Yu *et al.*, 1997; Li *et al.*, 2001, 2002; Zhang and Fei, 2002).

The objectives of the current study were to synthesize two novel adsorbents by chemically modified a hypercrosslinked polymer by dimethylamine and trimethylamine, respectively, and compare the adsorption properties of phenolic compounds including phenol, resorcin and phloroglucin on the three polymers. We focused on the thermodynamic analysis of adsorption of phenolic compounds on the hypercrosslinked polymeric adsorbents (NJ-0, NJ-1 and NJ-2). Values of enthalpy, free energy and entropy, have been estimated.

1 Experiments materials and method

1.1 Materials

Phenol, resorcin and phloroglucin were used in this study without further purification. All chemicals are of analytical grade and were purchased from Nanjing First Reagent Station (China). NJ-0, a hypercrosslinked polymeric adsorbent, was provided kindly by Jiangsu N&G Environmental Technology Co. Ltd. (China). The phenolic

compounds were dissolved in deionized water without pH adjustment. Physiochemical properties of the adsorbates used in this study are listed in Table 1.

1.2 Resin synthesis

Adsorbent NJ-0 is a hypercrosslinked polystyrene-divinylbenzene resin with 5.49% residual chloromethyl groupes which can be replaced by other functional groups such as amino group during the synthetic process. At first, the resin particles were soaked in benzene solution at 298 K for 12 h. Then, the benzene solution was removed from the container and dimethylamine or trimethylamine was gradually introduced into the synthesis system. After 10 h amination at 318 K or 303 K, residual dimethylamine or trimethylamine was removed by filtering the reaction mixture. Finally, the resins were extracted with ethanol for 8 h in a Soxlet apparatus and were vacuum dried at 333 K for 2 h before use. Surface area and pore size distribution of the adsorbents were determined by a Micromertics ASAP-2010C automatic analyzer (Micromeritics Co. Inc., Australia). Infrared spectra of NJ-0 and its modified polymers were collected with a Nexus 870 FT-IR spectrometer (Madison Co. Inc., USA). The exchange capacity of all three resins was obtained by titration.

1.3 Static adsorption experiments

Equilibrium adsorptions of the three phenolic compounds at three different temperature (288 K, 303 K and 318 K for phenol and resorcin, and 283 K, 293 K and 303 K for phloroglucin) were performed as follows: 0.1000 g of resin was introduced into a flask directly, 100 ml of aqueous solution of each phenolic compound with known concentration was added into each flask. The flasks were placed in a G 25 model incubator shaker (New Brunswick Scientific Co. Inc., Germany) 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 by a 752-UV spectrophotometer (Shanghai Jinghua Technology Apparatus Co. Inc., China). Thus the adsorbent-phase concentrations of adsorbates, q_e (mmol/g) were calculated according to

$$q_e = V_1(C_0 - C_e)/MW \tag{1}$$

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

2 Results and discussion

2.1 Characterization of the polymeric adsorbent

Several important properties of adsorbents NJ-0 and its aminated derivative NJ-1 and NJ-2 are presented in Table 2. After amination, the average particle size of resin NJ-1 and NJ-2 was found to be identical to the original polymer NJ-0. However, the BET surface area, average pore diameter and pore volume decreased respectively. The difficulty of chemical modifying increase as the more complicated structure of amino groups, so the total anion exchange capacity of resin NJ-2 was lower than NJ-1.

After amination, the strong band of 816 cm^{-1} (chloromethyl group) in NJ-0 was weakened (Fig.1). The presence of amino group on NJ-1 and NJ-2 was further supported by the absorbance bands at 2773 cm^{-1} (tertiary amido group), 2768 cm^{-1} (quaternary amido) and 3422 cm^{-1} (N–H bond) in the IR spectra (Ke and Dong, 1998).

2.2 Static equilibrium adsorption

Equilibrium data concerning the adsorption of the adsorbates from aqueous solution onto the adsorbent NJ-1 at three different temperatures were presented in Figs.2a, 2b and 2c. Experimentally collected equilibrium adsorption

Table 1 Properties of phenolic compounds

Phenolic compounds	Molecular formula	Molecular weight	λ_{max} (nm)	pKa	Solubility (%)
Phenol	C_6H_6O	94	270	9.99	8.2
Resorcin	$C_6H_6O_2$	110	274	9.34	63.7
Phloroglucin	$C_6H_6O_3$	126	268	7.0*	1.12

Data are from literature (Yao *et al.*, 1985); *Data is from literature (Wang and Yang, 1997).

Table 2 Typical properties of the studied polymers

|	NJ-0	NJ-1	NJ-2
Framework	Hypercrosslinked polystyrene-diethylene		
Functional group	Chlorine	Tertiary amido	Quaternary amido
Polarity	Moderate polar	Moderate polar	Polar
BET specific surface area (m^2/g)	820.6	796.7	696.4
Mean pore diameter (nm)	2.35	2.33	2.32
Mean pore volume (cm^3/g)	0.48	0.46	0.40
Micropore area (m^2/g)	461.8	446.2	408.1
Total exchange capacity (mmol/g)	0	1.54	1.23
Strongly basic exchange capacity (mmol/g)	0	0	0.99
Weekly basic exchange capacity (mmol/g)	0	1.54	0.24
Color	Maple	Maple	Light yellow
Mean particle diameter (mm)	0.4–0.6	0.4–0.6	0.4–0.6
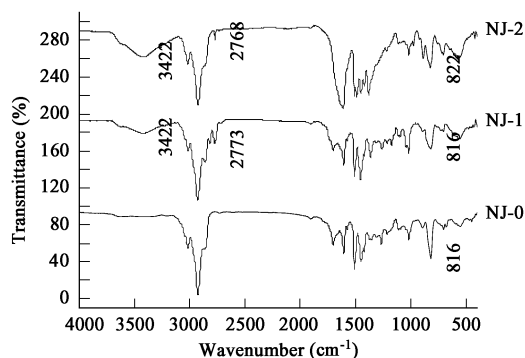
Fig. 1 IR spectra of the polymers before and after amination.

data were fit into the Freundlich equation (Slejko, 1985) as

$$\lg Q_e = \lg K_F + 1/n \lg C_e \qquad (2)$$

where n and K_F are characteristic constants. The regression equations at three different temperatures along with the constants K_F, n and the correlative coefficient R on NJ-1 are listed in Table 3. The tendency of the equilibrium adsorption isotherms and regression equations of resins NJ-0 and NJ-2 is similar to that of NJ-1 (not show).

It is quite obvious that the Freundlich adsorption law is applicable to the adsorption of phenolic compounds on NJ-0, NJ-1 and NJ-2 adsorbents within the concentration in our study. These equations are reliable since all the correlative factors R are larger than 0.98. In all cases, the exponents are $n>1$, indicating favorable adsorptions. Based on the Freundlich theory, coefficient K_F and n are indication of the adsorbing capacity and impetus repectively (Jung et al., 2001), and R denotes the degrees of deviation from isotherm linearity. The decline of adsorption capacity of phenolic compounds on the three resins within temperature from 288 K to 318 K was visible, which suggests some

properties of physical adsorption. According to Louis acid-alkali theory, the phenolic hydroxyls are acid, and the amino groups are alkali (Merlin et al., 1987), therefore, the hydrogen-bonding interaction and electrostatic interaction between the adsorbents and adsorbates became stronger for more phenolic hydroxyls in the phenolic compounds molecules, which also enhanced the adsorption impetus.

The equilibrium adsorption capacity q_e (mmol/g) for phenolic compounds on NJ-0, NJ-1 and NJ-2 adsorbents at 303 K, C_e=4.0 mmol/L are listed in Table 4. The adsorption behaviors of organic compounds on polymeric adsorbent in aqueous solution are related to the surface area, pore volume, pore structure, polarity of adsorbents and the structure and physical chemistry properties of the adsorbates. Because of the π-π interaction between the framework of adsorbents and the benzene rings of adsorbates, the highest adsorption capacity was obtained by the solute with the smallest polar. The sequence of adsorption capacity of phenolic compounds on a certain polymer was phenol>resorcin>phloroglucin, which was contrary to acidity of the phenolic compounds. Otherwise, more phenolic hydroxyls in the adsorbate molecules increase the three-dimensional size of molecules, which lead to the drop of the matching degree of the aperture of resins and the diameter of adsorbate molecules. Further, more phenolic hydroxyls make the possibility for that hydrogen-bonding interaction activities among adsorbate molecules become higher. In that case, adsorbate molecules would like to form clusters to increase the size. Thus, the adsorption capacity decreased due to the effect of "space block", especially for the micropore polymers.

Generally, the adsorption capacity of organic compounds on non-polar and moderate polar polymeric adsorbent mainly depend on surface area of resins, but for bifunctional polymers, the functional groups intro-
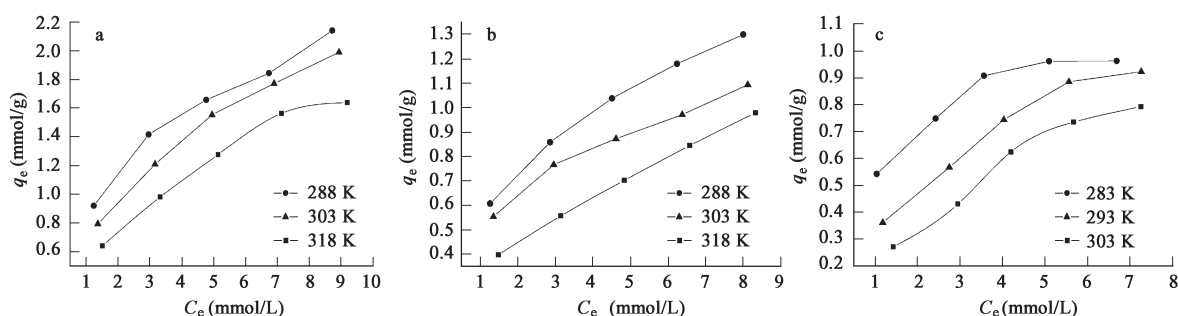

Fig. 2 Equilibrium adsorption isotherms for phenol (a), resorcin (b) and phloroglucin (c) on NJ-1.
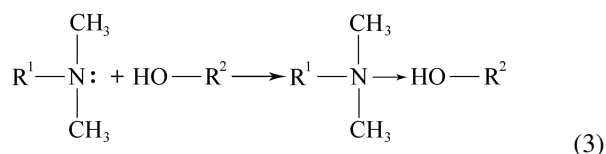
Table 3 Correlative parameters of Freundlich model for phenolic compounds on NJ-1 resin at different temperatures

| Adsorbate	Temp. (K)	Regration	K_F	n	R^2
Phenol	288	$\lg q_e = 0.4189\ \lg C_e - 0.0665$	0.8580	2.3872	0.9908
	303	$\lg q_e = 0.4946\ \lg C_e - 0.1649$	0.6841	2.0218	0.9979
	318	$\lg q_e = 0.5429\ \lg C_e - 0.2882$	0.5150	1.8420	0.9923
Resorcin	288	$\lg q_e = 0.4131\ \lg C_e - 0.2570$	0.5534	2.4207	0.9997
	303	$\lg q_e = 0.3687\ \lg C_e - 0.3011$	0.4999	2.7122	0.9951
	318	$\lg q_e = 0.5207\ \lg C_e - 0.5008$	0.3156	1.9205	0.9946
Phloroglucin	283	$\lg q_e = 0.3277\ \lg C_e - 0.2566$	0.5539	3.0516	0.9979
	293	$\lg q_e = 0.5503\ \lg C_e - 0.4903$	0.3234	1.8172	0.9987
	303	$\lg q_e = 0.6935\ \lg C_e - 0.6712$	0.2132	1.4420	0.9828

Table 4 Equilibrium adsorption capacity q_e (mmol/g) for phenolic compounds on adsorbents at 303 K (C_e=4.0 mmol/L)

Adsorbent	Phenol	Resorcin	Phloroglucin
NJ-0	1.1532	0.7817	0.3286
NJ-1	1.3579	0.8334	0.5576
NJ-2	1.0128	0.8175	0.6789

duced into the polymers also play an important role (Pan *et al.*, 2003). The tertiary amido groups in adsorbents and phenolic hydroxyls of adsorbates could form weak hydrogen-bonding interaction (Garcla-Delgado *et al.*, 1992):

$$R^1\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}\!: + HO\!-\!R^2 \longrightarrow R^1\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}\!\rightarrow HO\!-\!R^2 \tag{3}$$

The quaternary amido groups in adsorbents and anion ionized from phenolic hydroxyls of adsorbates could form electrostatic interaction:

$$(CH_3)_3\!-\!\overset{\displaystyle +}{\underset{\displaystyle R^1}{N}} + {}^-OR^2 \longrightarrow (CH_3)_3\!-\!\underset{\displaystyle R^1}{N}\!-\!OR^2 \tag{4}$$
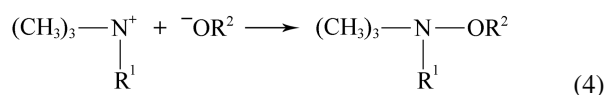
Where R^1 represents polymeric matrix of resin, R^2 represents benzene rings.

During the adsorption of phenol with highest hydrophobicity onto these resins, the π–π interaction played a more important role than hydrogen-bonding interaction and electrostatic interaction, consequently, the adsorption capacity of phenol on resin NJ-1, which has the most total exchange capacity and high surface area, was most among these three resins; resin NJ-0 has the most surface area, but no exchange capacity, so the adsorption capacity of phenol on NJ-0 was lower than NJ-1; the lowest surface area of resin NJ-2 leaded to the lowest adsorption capacity of phenol. As the increase of quantity of phenolic hydroxyls in adsorbates molecules and polarity of phenolic compounds, the hydrogen-bonding interaction and electrostatic interaction gradually become stronger to be the main factor affecting adsorptions. For the adsorption of resorcin with moderate polarity on these three resins, the sequence of adsorption capacity depends on the total exchange capacity of each resin. For the adsorption of phloroglucin with the highest polarity, the surface area and total exchange capacity of resin NJ-2 was lower than that of NJ-1, but the adsorption capacity of phloroglucin on resin NJ-2 was higher than NJ-1, which was contributed to its higher strongly basic exchange capacity to form stronger electrostatic interaction. Under that situation, the adsorption was mainly affected by the functional groups rather than surface area. Although NJ-1 resin has higher surface area, its functional groups are only some weakly basic tertiary amido groups to form weak hydrogen-bonding interaction, thus, the adsorption capacity of phloroglucin on resin NJ-1 was lower than NJ-2; resin NJ-0 has not functional groups to form effective hydrogen-bonding interaction and electrostatic interaction, therefore, the adsorption capacity

of phloroglucin on NJ-0 was the lowest among these adsorbents.

2.3 Thermodynamics of the adsorption

Estimations of the isosteric adsorption enthalpy change, free energy change, and entropy change were calculated using the well fitting Freundlich equation. The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff equation (Bell and Tsezos, 1987):

$$\lg C_e = -\lg K_0 + \frac{\Delta H}{2.303RT} \tag{5}$$

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 (288, 303, and 318 K, or 283, 293, and 303 K), C_e was obtained from the well-fitted isotherms. ΔH was calculated from the slope of line plotted by $\lg C_e$ versus $1/T$.

Free energy of adsorption can be obtained using an expression derived from the Gibbs adsorption isotherm by a procedure shown elsewhere (Bell and Tsezos, 1987). Finally, we get

$$\Delta G = -RT \int_0^x q \frac{dx}{x} \tag{6}$$

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 (Juang and Shiau, 1999).

$$\Delta G = -nRT \tag{7}$$

The entropy change associated with adsorption can be calculated from the Gibbs-Helmholtz equation (Juang and Shiau, 1999).

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

Table 5 shows a summary of the estimated values for the three thermodynamic properties at various adsorbate loadings. The isosteric adsorption enthalpy change of phenolic compounds on the three adsorbents are negative and in the range of 10–40 kJ/mol except three data, which indicates a physical adsorption process. This is in good agreement with the above conclusion, that is, the equilibrium adsotption capacities of phenolic compounds on the three resins decrease with the increasing temperature.

The negative values of ΔG show that all these adsorptions are spontaneous. The absolute ΔG values of adsorption decrease with the increase of temperature, which elucidates the decreasing tendency of adsorption spontaneity and further confirms the physical character of the adsorption. The absolute free energy values of adsorption on NJ-2 are higher than those on NJ-0 and NJ-1 for resorcin and phloroglucin, which indicates these phenolic compounds are in priority to be adsorbed on NJ-2.

Table 5 Estimated thermodynamic parameters of the systems tested

Adsorbate	Adsorbent	q (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)		ΔS (J/(mol·K))	
				288 K	318 K	288 K	318 K
Phenol	NJ-0	0.50	−28.9	−5.5	−4.6	−81.3	−76.4
		1.00	−19.2	−5.5	−4.6	−47.6	−45.9
	NJ-1	0.50	−31.4	−5.7	−4.9	−89.2	−83.3
		1.00	−21.7	−5.7	−4.9	−55.6	−52.8
	NJ-2	0.50	−25.9	−5.0	−4.2	−72.6	−68.2
		1.00	−17.0	−5.0	−4.2	−41.7	−40.3
Resorcin	NJ-0	0.50	−27.1	−5.6	−4.8	−74.7	−70.1
		1.00	−17.9	−5.6	−4.8	−42.7	−41.2
	NJ-1	0.50	−28.4	−5.8	−5.1	−78.5	−73.3
		1.00	−19.9	−5.8	−5.1	−49.0	−46.5
	NJ-2	0.50	−29.7	−6.7	−6.7	−79.9	−72.3
		1.00	−25.7	−6.7	−6.7	−66.0	−60.0
Phloroglucin	NJ-0	0.50	−51.8	−6.3	−3.2	−158.0	−152.8
		1.00	−14.7	−6.3	−3.2	−29.2	−36.2
	NJ-1	0.50	−55.2	−7.2	−3.6	−169.0	−170.3
		1.00	−15.2	−7.2	−3.6	−28.3	−38.3
	NJ-2	0.50	−53.0	−8.8	−6.5	−156.2	−153.5
		1.00	−24.4	−8.8	−6.5	−55.1	−59.1

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 of phenolic compounds onto NJ-0, NJ-1 and NJ-2 resins were drove by the isosteric adsorption enthalpy.

3 Conclusions

Two novel polymers (NJ-1 and NJ-2) for adsorbing phonol, resorcin and phloroglucin were synthesized by chemically modified a hypercrosslinked polymer NJ-0 with dimethylamine and trimethylamine, respectively. After amination, the average particle size of resin NJ-1 and NJ-2 was found to be identical to the original polymer NJ-0. However, the BET surface area, average pore diameter and pore volume decreased respectively.

Freundlich equation was found to fit the experimental data perfectly in the temperature range of 288–318 K. The results of static equilibrium adsorption manifest that the adsorption of the three phenolic compounds on adsorbents NJ-0, NJ-1 and NJ-2 are all physical process. With the increase of phenolic hydroxyls in adsorbate molecules and polar of phenolic compounds, the adsorption was mainly affected by the functional groups rather than surface area.

The isosteric adsorption enthalpy change of all adsorptions further confirmed that these were physical adsorptions. The higher absolute free energy values of adsorption on NJ-2 than those on NJ-0 and NJ-1 for resorcin and phloroglucin indicate that these phenolic compounds are in priority to be adsorbed on NJ-2. The thermodynamics parameters show that the adsorption of phenolic compounds onto the three resins were drove by the isosteric adsorption enthalpy.

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