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EFFECT OF HYPERCROSSLINKED RESINS SURFACE CHEMISTRY ON THE ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION*

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Abstract Two hypercrosslinked resins with similar physical characters but different surface chemistry were synthesized and used to remove phenol from aqueous solutions. The FTIR spectra, elemental analysis and the Boehm titration were used to characterize the chemical properties of the resins. The adsorption experiments were carried out using the bottle-point technique, and the effects of the surface chemistry on the adsorption were discussed. The adsorption data fit well with the Freundlich model, indicating the heterogeneity of the resins surface. It could be seen from the experimental results that the adsorption capacity increased with the increase in the total surface concentration of oxygen-containing groups. The pH dependence and the effects of ionic strength were also discussed. The kinetic adsorption data fit well with the pseudo-second order model, and the results showed that the surface oxygen-containing groups have little effect on the adsorption rate.

Keywords: Hypercrosslinked resin; Phenol; Surface chemistry; Adsorption isotherm; Kinetic study.

INTRODUCTION

Phenols are commonly found in contaminated water. These pollutants appear in the water as a result of degradation of the phenolic compounds that are used in the synthesis of dyes, pesticides, insecticides, *etc.* Phenol is also an important raw material in petrochemical, pharmaceutical, plastic and pesticide chemical industries[1–3]. Due to their poor degradability, developing an efficient method for the phenol removal is more and more urgent.

Adsorption is a major pollution treatment method used for the elimination of organic compounds from water. Activated carbons have been applied as adsorbents for removal of phenolic pollutants from wastewater in view of their high surface area and pore volume[4]. Commercial activated carbons, however, have some disadvantages such as the difficulty for regeneration and poor mechanical properties of the particles.

Over the last two decades, hypercrosslinked polymeric adsorbents are used as alternatives for activated carbon to remove and recover various organic pollutants from the wastewater[5–9]. The synthesis method of hypercrosslinked polystyrene proposed by Davankov and Tsyurupa in 1969 consists of post-crosslinking the linear polystyrene chains by means of Friedel-Crafts reaction in high swollen state producing methylene bridges between neighboring phenyl groups[10–13]. When adsorption occurs between the polar adsorbent and adsorbate, the surface chemistry of the adsorbents as well as their porous property and the solution property (solution pH and ionic strength of solution) are of great importance.

In the present work, the effects of surface chemistry of hypercrosslinked resins on adsorptive properties toward phenol was experimentally investigated. The effects of aqueous solution pH and ionic strength on

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adsorption were also studied. The ASAP-2010C Micromeritics Instrument was used to characterize the physical properties of the resins. The FTIR spectra, the elemental analysis and the Boehm titration were used to characterize the chemical properties of the resins. The adsorption experiment was carried out using the bottle-point techniques and the effects of surface chemistry on the equilibrium and kinetic adsorption were discussed. The pH dependence and the effects of ionic strength were also discussed.

EXPERIMENTAL

Synthesis of Resins

Two hypercrosslinked resins NG-1 and NG-2 were synthesized as follows[7]. In a 100 mL flask, 10 g of chloromethylated polystyrene-divinylbenzene (chlorine content: 19.5%) was swollen in 40 mL nitrobenzene. Under mechanical stirring, 1 g zinc chloride was added and the temperature was raised to 388 K. The reaction was processed at this temperature in oxygen and nitrogen, respectively, for 12 h, and NG-1 and NG-2 were obtained. Prior to use, they were extracted by ethanol in Soxhlet apparatus for 8 h to remove the impurities in the resins and then dried at 343 K under vacuum for 5 h.

Reagents and Methods

Phenol, sodium chloride, sodium hydroxide and hydrochloric acid of analytical pure grade were purchased from Nanjing First Chemical Reagent Plant (Nanjing, China).

An ASAP-2010C Micromeritics Instrument (USA) was used to measure the specific surface area and pore structure of the two adsorbents using nitrogen as sorbate according to the BET method. The infrared spectra were recorded on a Vector 22 FTIR spectrometer (Bruker, USA) using KBr pellets. An HPLC (Waters, USA) was used to determine the concentrations of phenol (λ = 270 nm; eluent:H_2O:CH_3OH = 70:30; flow rate: 1 mL/min).

Boehm Titration

The Boehm titration was conducted as follows: dried resins (0.5 g) were accurately weighed and placed into 100 mL conical flasks prior to the addition of 25 mL of different bases. The flasks were sealed and stirred in an orbital shaker for 7 days. Each mixture was prepared in duplicate. Blank solution of each base was also stirred in the same conditions. After shaking, 10 mL of the bases were put into a flask with 25 mL 0.05 mol/L hydrochloric acid, then the mixture was titrated by 0.05 mol/L standard solution of sodium hydroxide after 30 min using phenolphthalein as indicator.

The Effect of pH and Ionic Strength on Adsorption

The pH of the phenol solutions was adjusted with sodium hydroxide and hydrochloric acid. The effect of pH on adsorption test was conducted as follows: 0.100 g dry resin was put into a 250 mL airtight flask prior to the addition of 100 mL phenol solution with an initial concentration (c_0) of 5.3 mmol/L and different pH values. The flasks were put into a constant temperature shaker and operated at 120 rpm at 303 K for 24 h. Finally, the concentrations (c_e) of phenol were determined. The adsorption capacity Q_e (mmol/g) was calculated according to

$$Q_e = V_1(c_0 - c_e)/WM \qquad (1)$$

where V_1 is the volume of solution (L), W is the mass of dry resin (g) and M is the molecular weight (g/mol).

The ionic strength of phenol solutions was adjusted with sodium chloride. The effect of ionic strength on adsorption test was conducted as follows: 0.100 g dry resin was put into a 250 mL airtight flask prior to the addition of 100 mL phenol solution with the initial concentration of 5.3 mmol/L and different ionic strengths. The flasks were put in a constant temperature shaker and operated at 120 r/min at 303 K for 24 h. Finally, the concentrations of phenol were determined.

Equilibrium Adsorption Tests

Equilibrium adsorptions of phenol on NG-1 and NG-2 at three different temperatures (288, 303, 318 K) were conducted as follows: 0.100 g dry resin was put into a 250 mL airtight flask. To each flask, the 100 mL aqueous solution of phenol with initial concentrations of 0.21, 0.42, 0.64, 0.85, 1.06, 2.13, 4.26 and 6.38 mmol/L were added. The flasks were put in a constant temperature shaker and operated at 120 r/min for 24 h. Finally, the concentrations of phenol were determined.

Kinetic Adsorption Tests

The kinetic adsorptions of phenol on NG-1 and NG-2 at 303 K were conducted as follows: 0.100 g dry resin was put into a 250 mL airtight flask. To each flask, the 100 mL aqueous solution of phenol with an initial concentration of 6.38 mmol/L was added. The flasks were put in a constant temperature shaker and operated at 120 r/min. The instantaneous phenol uptakes onto the resins were calculated by measuring the concentrations of phenol in solution at different contact times.

RESULTS AND DISSCUSSION

Physical Properties and FTIR Spectra Analysis

The physical characteristics of the two resins employed in this study are listed in Table 1. The BET surface area of NG-1 is a little lower than that of NG-2. The difference in surface area may be induced by the formation of more oxygen containing groups on the surface of NG-1 during synthesis.

Table 1. Physical characterization of the two resins

Adsorbent	Structure	BET surface area (m^2/g)	Average pore diameter (nm)
NG-1	St-DVB	876.2	2.29
NG-2	St-DVB	1083.0	2.40

The IR spectra of the two resins are depicted in Fig. 1. The strong band at about 1700 cm^{-1} can be assigned to the stretching vibration of C=O and the presence of carbonyl groups verified. The bands at about 1212 and 1110 cm^{-1} can be assigned to C—O stretching vibrations of ether structures and hydroxyl groups, respectively[14].

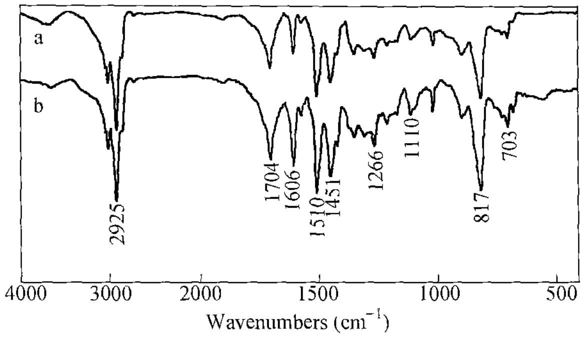

Fig. 1 IR spectra of (a) NG-1 and (b) NG-2

Boehm Titration and Elemental Analysis

The Boehm titration[15] uses bases of different strengths to differentiate between surface functionalities of various acid strengths. It is generally accepted that sodium hydrogen carbonate neutralizes only carboxyl groups on the resin surfaces, sodium carbonate neutralizes carboxyls and lactones, sodium hydroxide neutralizes carboxyls, lactones and phenolic groups, sodium ethoxide neutralizes carboxyls, lactones, phenolic groups and carbonyls.

The Boehm titration results of NG-1 and NG-2 are listed in Table 2. Both resins have different amounts of oxygen containing groups, which are the results of oxidation of chloromethyl groups by nitrobenzene. NG-1 contains more carboxylic acid groups than NG-2, possibly because of the oxidation of a part of phenolic or carbonyl groups in NG-1 by oxygen during the synthesis.

The elemental analysis results of NG-1 and NG-2 are listed in Table 3. The oxygen content of NG-1 is higher than that of NG-2. This is consistent with the Boehm titration result. From the chlorine content, we can see that the post-crosslinking degree of NG-1 is lower than that of NG-2 and this is consistent with the surface area measurements.

Table 2. The Boehm titration results of NG-1 and NG-2

Adsorbent	Carbonyls (mmol/g)	Phenols (mmol/g)	Lactones (mmol/g)	Carboxyls (mmol/g)	Total acidic groups (mmol/g)	Acidic groups per square meter of resin (μmol/m^2)
NG-1	2.13	3.51	0.01	0.93	6.58	7.5
NG-2	2.24	2.59	0.74	0	5.57	5.1

Table 3. The elemental analysis results of NG-1 and NG-2

Adsorbent	C (%)	H (%)	Cl (%)	O (%)
NG-1	76.87	6.40	2.96	13.77
NG-2	83.32	6.73	2.44	7.51

The Effect of pH and Ionic Strength on Adsorption

The effect of pH on adsorption is depicted in Fig. 2. The adsorption capacity changes a little in the range of pH < 9, because most of the phenol exists in the molecular form, and there is no electrostatic interaction between phenol and adsorbents. When the solution pH > 9, most of the phenol exists in the anion form, and there is negative electrostatic interaction between the anion and the negative charge on the surface of the resins caused by dissociation of surface acidic groups. So the adsorption capacity decreases significantly as the pH increases when pH > 9.

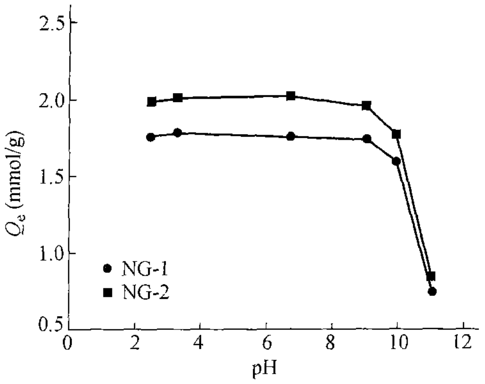

Fig. 2 The pH dependence of phenol adsorption at 303 K (c_0 = 5.3 mmol/L)

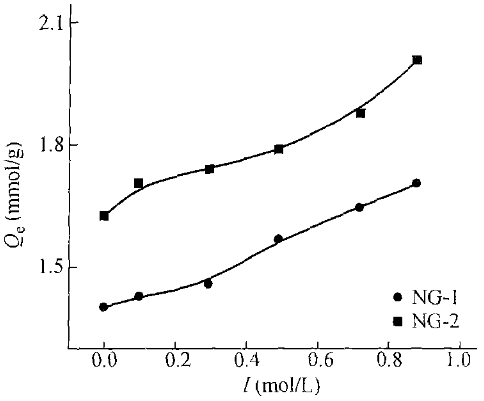

Fig. 3 Ionic strength dependence of phenol adsorption at 303 K (c_0 = 5.3 mmol/L)

The effect of ionic strength on adsorption is depicted in Fig. 3. The adsorption capacity increases with the increase of the ionic strength in solution. This is probably due to the existence of sodium chloride and therefore it decreases the solubility of phenol in aqueous solution. As a result, phenol is more likely to be adsorbed on the surfaces of the solid adsorbents.

Adsorption Isotherms of Phenol

The equilibrium adsorption isotherms of phenol on NG-1and NG-2 are depicted in Figs. 4(a) and 4(b). The adsorption capacities of the two resins decrease with an increase of temperature, indicating the prevailing physical adsorption. The equilibrium adsorption data obtained are correlated with the classic adsorption isotherm equation of Freundlich model:

$$Q_e = K_f c_e^{1/n} \qquad (2)$$

where K_f and n are the thermodynamic characteristic constants, which can be determined by plotting lnQ_e against lnc_e based on the above equation. The correlative Freundlich isotherm equations along with the relative parameters are listed in Table 4. The Freundlich isotherm is well applicable to the adsorption data of the two resins because of the square of almost all the correlative factors $R^2 > 0.98$. K_f/A increases in the order: NG-1 > NG-2 and represents the relative adsorption capacity toward phenol. The adsorption capacity per square meter of phenol on adsorbents is NG-1 > NG-2 because NG-1 has more oxygen-containing groups, which increase the polarity of the resin. The polar adsorbent more easily adsorbs polar adsorbates from water. So NG-1 has higher phenol adsorption capacity than NG-2. In all cases, $n > 1$ indicates a favorable adsorption.

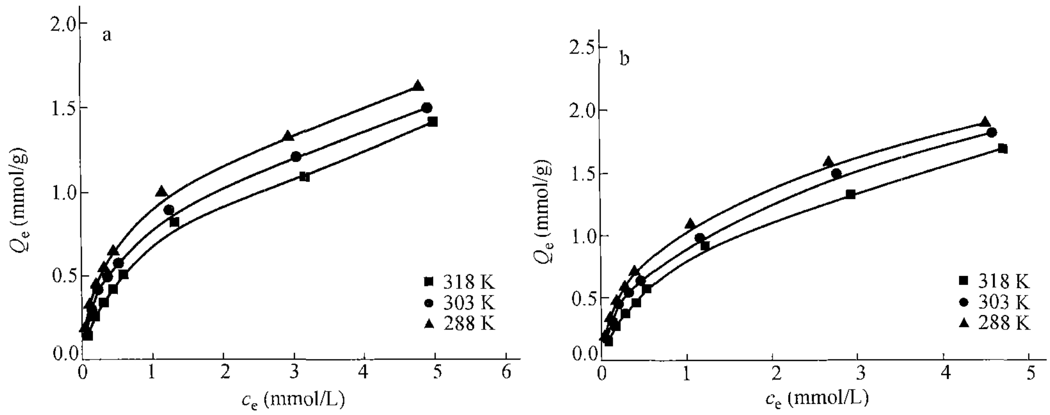

Fig. 4 (a) Equilibrium adsorption isotherm of phenol on NG-1 and (b) equilibrium adsorption isotherm of phenol on NG-2

Table 4. Correlative isotherm equations of the Freundlich model for phenol adsorption on the two resins

Adsorbent	T (K)	Freundlich isotherm	K_f	K_f/A^* ($\times 10^{-4}$)	n	R^2
NG-1	288	$\ln Q_e = 0.4059 \ln c_e - 0.2299$	0.795	9.07	2.46	0.9868
	303	$\ln Q_e = 0.4891 \ln c_e - 0.2886$	0.749	8.55	2.04	0.9878
	318	$\ln Q_e = 0.5539 \ln c_e - 0.471$	0.624	7.13	1.81	0.9871
NG-2	288	$\ln Q_e = 0.4386 \ln c_e - 0.0621$	0.940	8.68	2.28	0.9863
	303	$\ln Q_e = 0.4963 \ln c_e - 0.1485$	0.862	7.96	2.01	0.9822
	318	$\ln Q_e = 0.5866 \ln c_e - 0.292$	0.747	6.9	1.70	0.9881

* The specific surface area of the adsorbent

Thermodynamics of the Adsorption

The adsorption enthalpy change, free energy change and entropy change were estimated using the Freundlich equation. The adsorption enthalpy change can be calculated by the Van't Hoff equation.

$$\ln\left(\frac{1}{c_e}\right) = \ln K_0 + \left(-\frac{\Delta H}{RT}\right) \tag{3}$$

where c_e (mol/L) is the equilibrium concentration of solute at temperature T, ΔH (kJ/mol) is the enthalpy change of the adsorption when Q_e is the fixed value, T (K) is the absolute temperature, R and K_0 are constants. c_e was obtained from the Freundlich equation at fixed Q_e values at different adsorption temperatures. ΔH was calculated from the slope of the line plotted by $\ln c_e$ against $1/T$ when ΔH is assumed to be independent of temperature.

The free energy change can be obtained from the Gibbs adsorption isotherm

$$\Delta G = -RT \int_0^x q \frac{dx}{x} \tag{4}$$

where ΔG (kJ/mol) is the free energy change of the adsorption, q (mol/g) is the number of solute absorbed per unit mass of adsorbent, x is the mole fraction of absorbed solute in solution. Applying the Freundlich isotherm, ΔG can be expressed as

$$\Delta G = -nRT \tag{5}$$

where n is the Freundlich exponent.

Entropy change of adsorption can be calculated with the Gibbs-Helmholtz equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{6}$$

The thermodynamic values of phenol adsorption on the two adsorbents are listed in Table 5. The adsorption enthalpy changes are all negative and in the range of 10–35 kJ/mol, indicating a physical adsorption process. The negative ΔG values indicate that the adsorption processes of phenol on the two resins are spontaneous. The absolute ΔG values of the phenol adsorption decrease with the increase of temperature, which indicates the decreasing adsorption spontaneity and further confirms the physical character of adsorption. As to the two adsorbents, the absolute ΔG values of phenol adsorption on NG-1 at different temperatures are higher than that of NG-2, indicating that the former has higher adsorption spontaneity than that of the latter.

Table 5. Thermodynamic values of phenol adsorption on the two resins

Adsorbent	Q_e (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/(mol • K))		
			318 K	303 K	288 K	318 K	303 K	288 K
NG-1	0.2	−34.15	−4.79	−5.14	−5.89	−92.34	−95.74	−98.12
	0.4	−22.50				−55.71	−57.31	−57.68
	0.6	−15.69				−34.29	−34.83	−34.03
	0.8	−10.86				−19.09	−18.87	−17.28
NG-2	0.2	−32.51	−4.49	−5.06	−5.46	−88.11	−90.59	−93.94
	0.4	−22.40				−56.31	−57.22	−58.82
	0.6	−16.48				−37.70	−37.69	−38.28
	0.8	−12.29				−24.50	−23.81	−23.65

Kinetic Sorption Study

The influences of contact time on the adsorption of phenol on NG-1 and NG-2 are shown in Fig. 5. The adsorption is rather fast in the first 2 h. At the beginning, phenol is very easy to be adsorbed on the solids. As the time goes on, the adsorption reaches its equilibrium state and the adsorption rate slows down. The sorption equilibrium of both resins completed within 5 h with the initial phenol concentration of 6.38 mmol/L at 303 K and there are little differences between the adsorption processes, implying the little effect on the adsorption process of surface groups. The kinetic adsorption data were processed to understand the dynamics of adsorption process in terms of the order and the rate constant. The pseudo-second order model was applied to fit the data.

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{7}$$

where Q_e is the equilibrium adsorption capacity (mmol/g), Q_t is adsorption capacity at the contact time t (mmol/g), and K_2 is the pseudo-second order rate constant (min^{-1}).

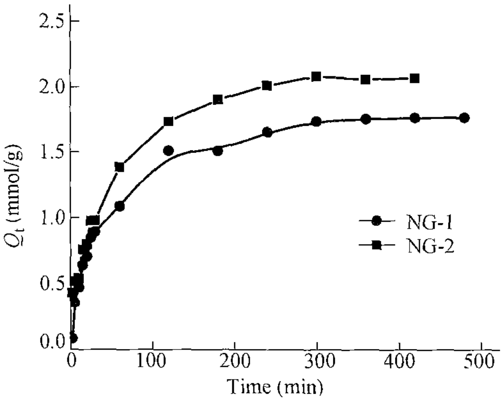

Fig. 5 Effect of contact time on the uptakes of phenol by NG-1 and NG-2 at 303 K

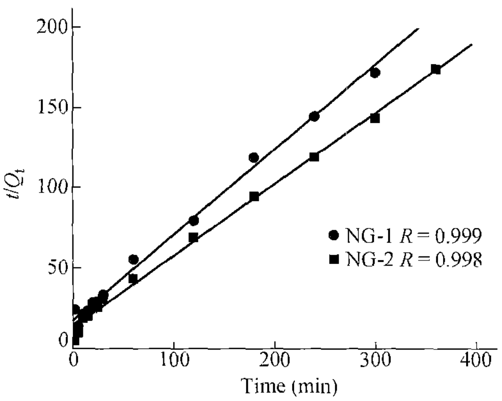

Fig. 6 The straight lines of t/Q_t versus t of phenol uptakes by NG-1 and NG-2

Figure 6 shows that the pseudo-second order model fits both the kinetic adsorption data very well with the correlative parameter $R^2 > 0.99$. The values of K_2 can be obtained from the intercept of the plot of t/Q_t versus t. The K_2 values of phenol adsorption on NG-1 and NG-2 are 0.0162 and 0.0158 g mmol^{-1} min^{-1}, respectively. It means that the surface oxygen-containing groups have little effect on the adsorption rate of phenol on the two resins.

CONCLUSIONS

The adsorption capacity decreases with the increase of solution pH and increases with the increase of solution ionic strength. The adsorption data fit well with the Freundlich model, indicating the heterogeneity of the resin surface. According to the adsorption isotherm, the adsorption decreases with the increase of temperature, indicating a physical adsorption process. As shown in the adsorption isotherm, the sorption capacity order is NG-1 > NG-2, which is consistent with the total oxygen containing groups on resin surfaces. The relative adsorption capacity shows that the polar groups on the adsorbents favor the sorption of polar sorbate from the solution. The kinetic adsorption shows that the surface polar groups on the resins have little effect on the adsorption rate of phenol.

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