

Methylamino-Group-Modified Hypercrosslinked Polystyrene Resin for the Removal of Phenol from Aqueous Solution

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ABSTRACT: Chemical modification was performed for macroporous crosslinked chloromethylated polystyrene. The obtained HJ-K01 resin was used to remove phenol from aqueous solution, and its adsorption behaviors for phenol were compared with commercial Amberlite XAD-4. The results indicate that methylamino groups were successfully uploaded onto the surface of the HJ-K01 resin and the adsorption capacity of phenol onto the HJ-K01 resin was much larger than that onto XAD-4. Furthermore, the original phenol solution was suitable for the

adsorption, the adsorption isotherms could be fitted by the Freundlich model, and its kinetic curves could be characterized by a pseudo-second-order rate equation. The fixed-bed column adsorption demonstrated that the HJ-K01 resin was an excellent resin for the removal of phenol. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1435–1442, 2011

Key words: adsorption; macroporous polymers; polystyrene

INTRODUCTION

Phenol and its derivatives are important organic intermediates, and they are used to produce pesticide, paper, textiles, and synthetic rubber.¹ They are prevalent in the effluent of their manufacture and are, consequentially, introduced into water. However, they are toxic and difficult to degrade biologically; the permissible concentration limit of phenol is 0.002 mg/L in potable water and 0.02 mg/L according to general emission regulations in China. As a result, the efficient removal of phenol from wastewater is an urgent environmental problem.

Many techniques, including solvent extraction, catalytic oxidation, membrane separation, and ion exchange, have been developed to treat phenol, and adsorption by adsorbents has been proven to be one of the most effective techniques.^{2–5} Activated carbon has good adsorption behavior for phenol because of its predominant micropores and high specific surface area. Nevertheless, its infirm mechanical

strength and inefficient regeneration limit its field application.⁶ In recent years, synthetic polymeric adsorbents have been gradually developed as alternatives for the removal of organic contaminants because of their excellent mechanical strengths and feasible regeneration under mild conditions.^{7–10}

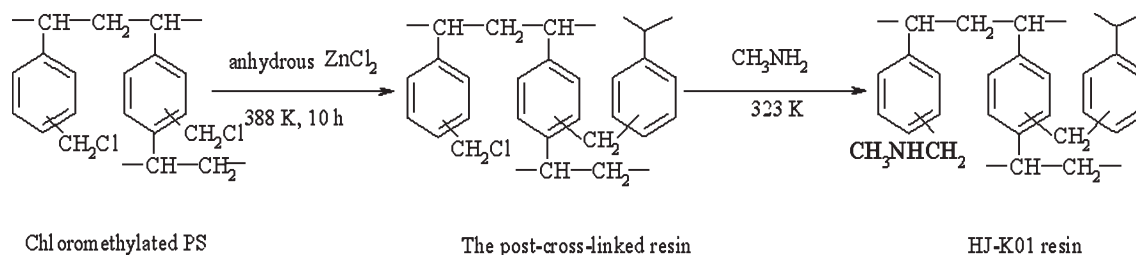
Amberlite XAD-4 is considered to be one of the best polymeric adsorbents for the removal of phenol from wastewater.¹¹ Nevertheless, its extreme hydrophobic skeleton results in its poor interaction with polar compounds, and hence, its adsorption capacity for polar compounds is comparatively small. Certainly, these drawbacks can be improved upon by some methods. One is the chemical modification of the skeleton by polar functional groups.^{12,13} Actually, amino, hydroxyl, acetyl, and amide groups have been reported to be successfully uploaded onto the adsorbent skeleton,^{14–17} and the adsorption behaviors of the gained adsorbents for some specific polar organic compounds were improved. Another is the copolymerization of monomers containing polar functional groups, and some of these adsorbents, such as Amberlite XAD-7, are commercially available. When they were tested for the solid-phase extraction of polar organic compounds, the polar functional groups of the obtained adsorbents led to their greater retention.^{18,19}

In the 1970s, Davankov and coworkers^{20,21} synthesized a kind of superexcellent hypercrosslinked polystyrene (PS) resin using bifunctional crosslinking

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Scheme 1 Synthetic procedure of the HJ-K01 resin.

agents and Friedel–Crafts catalysts from linear PS or low-crosslinked PS. By this method, many rigid methylene bridges are formed between the polymeric chains, and hence, the polymeric skeleton is reinforced. If macroporous, low-crosslinked chloromethylated PS is used as the reactant, the achieved postcrosslinked resin will have more or fewer residual chloromethyl groups on its skeleton, and chemical modification can be implemented by a nucleophilic substitution reaction.^{22,23}

In this study, the chemical modification of hypercrosslinked PS by methylamino groups was performed, and the HJ-K01 resin was prepared. Then, the HJ-K01 resin was used as a resin to remove phenolic compounds from an aqueous solution, and phenol was selected as a model adsorbate in the adsorption. Batch adsorption runs, including adsorption isotherms, kinetics, and column experiments, were investigated and compared with Amberlite XAD-4.

EXPERIMENTAL

Materials

Chloromethylated PS was purchased from Langfang Chemical Co., Ltd. (Langfang, Hubei province, People's Republic of China); its crosslinking degree was 6%, and the chlorine content was 17.3%. Amberlite XAD-4 was purchased from Rohm & Haas Co. (The United States) 1,2-Dichloroethane and methylamine aqueous solution (methylamine content = 25–30%) were analytical reagents and were used without further purification. Phenol was distilled before use, and zinc chloride was dealt so that it was free from water.

Chemical modification of the macroporous chloromethylated PS

As illustrated in Scheme 1, the chemical modification of the macroporous chloromethylated PS was carried out by a Friedel–Crafts reaction (the postcrosslinked resin was obtained in this step), and this was followed by a methylaminated reaction. The Friedel–Crafts reaction was performed according to the method in ref. 8, and its residual chlorine content was measured to be 5.2%. As for the methylaminated reaction, 40 g of the postcrosslinked resin was swollen by

100 mL of 1,2-dichloroethane for 12 h, superfluous 1,2-dichloroethane was poured out, and 60 mL of methylamine aqueous solution was added to the reaction mixture. The reaction mixture was filtered after it was kept at 323 K for about 20 h, and the solid-particle HJ-K01 resin was achieved. Its weak basic exchange capacity was determined to be 0.82 mmol/g.

Pretreatment of the HJ-K01 resin

Before use, the HJ-K01 resin was first rinsed by 0.1 mol/L hydrochloric acid and then deionized water until a neutral pH was reached. Then, it was subjected to 0.1 mol/L sodium hydroxide and washed with deionized water until a neutral pH was reached. Finally, the resin was extracted with ethanol for 8 h and dried *in vacuo* at 323 K for 8 h.

Adsorption isotherms and adsorption kinetics

The batch adsorption was performed in aqueous solution at 298 K. About 0.100 g of the resin was weighed accurately, and 50 mL of a phenol aqueous solution with a known initial concentration [C_0 (mg/L)] was added to a cone-shaped flask. C_0 of phenol was set to be 100–500 mg/L with 100 mg/L intervals. Hydrochloric acid and sodium hydroxide were applied to adjust the solution pH. The flasks were then shaken in a thermostatic oscillator at a stirring rate of 150 rpm for about 24 h until the adsorption equilibrium was reached. The residual concentration [C_e (mg/L)] of phenol was determined, and the equilibrium adsorption capacity [q_e (mg/g)] of phenol onto the resin was calculated. The adsorption kinetic curves of phenol onto the resin were performed by analysis of the adsorption capacity until the adsorption equilibrium was reached.

Dynamic adsorption and desorption

The dynamic adsorption was conducted with a glass column (10 mm in diameter) at room temperature, and 10 mL of wet HJ-K01 resin was packed in the glass column. An HL-2 pump (Shanghai Huxi Analysis Instrument Factory Co., Ltd., Shanghai, China) was used to ensure a constant flow rate. Phenol

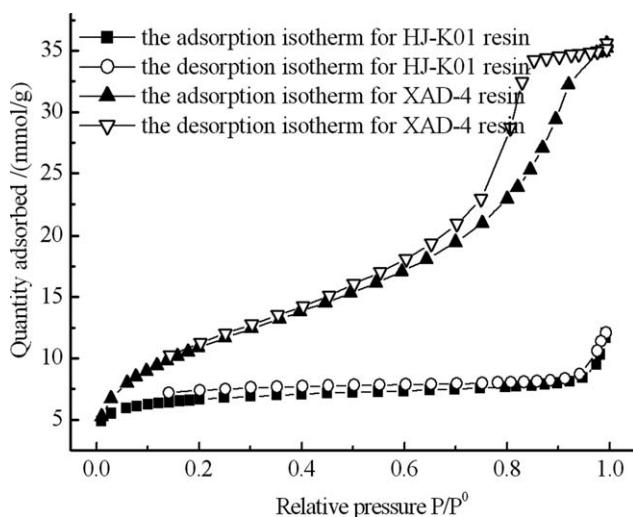


Figure 1 N_2 adsorption-desorption isotherms onto the XAD-4 and HJ-K01 resins. P/P_0 is the relative pressure.

aqueous solution (200 mg/L; sodium chloride content = 0, and the solution pH was not adjusted) was passed through the column at a flow rate of 8 BV/h (1 BV = 10 mL), and the solvent (2% sodium hydroxide) was used for desorption at a flow rate of 3 BV/h.

Analysis

The specific surface area was determined via N_2 adsorption-desorption curves at 77 K by a Tristar 3000 surface area measurement instrument (Micromeritics Instrument Corp., the United States). The pore diameter distribution of the resin was achieved by the application of the Barrett, Joyner, and Halenda method to the N_2 adsorption-desorption isotherms. The IR spectra were collected by KBr disks on a 370 Fourier transform infrared instrument (Thermo Nicolet Corp., USA). The chlorine content of the postcrosslinked resin was measured by the Volhard method,²⁴ and the weak basic exchange capacity of the HJ-K01 resin was determined by the method in ref. 25. The concentration of phenol in the aqueous solution was analyzed by UV analysis via a UV-2450 spectrophotometer (Shimadzu Corp., Japan) at a wavelength of 269.9 nm.

RESULTS AND DISCUSSION

Characterization of the HJ-K01 resin

The specific surface area and pore volume of the HJ-K01 resin were measured to be 462.8 m^2/g and 0.330 cm^3/g , respectively; these values were much lower than those of XAD-4 (873.1 m^2/g and 1.21 cm^3/g , respectively). Figure 1 describes the N_2 adsorption-desorption isotherms of the XAD-4 and HJ-K01 resins; it seemed that the adsorption isotherm of XAD-4

was close to a type IV isotherm, whereas that of the HJ-K01 resin was close to a type II one. At a relative pressure below 0.05, the N_2 adsorption capacity increased sharply with increasing relative pressure; this implied that micropores were existent for the two resins. In addition, the visible hysteresis loops of the desorption isotherms indicated that some mesopores were also existent. Moreover, the N_2 adsorption capacity onto XAD-4 was much larger than that onto the HJ-K01 resin at the same relative pressure, which may have been due to the fact that XAD-4 was a nonpolar resin, whereas the HJ-K01 resin was a medium polar one.

Figure 2 displays the pore diameter distribution of the XAD-4, chloromethylated PS, and HJ-K01 resins. A great transformation occurred for the pore diameter distribution from the chloromethylated PS to the HJ-K01 resin. Mesopores and macropores were the main pores for the chloromethylated PS, and the average pore diameter was 25.2 nm. However, mesopores in the range of 2–5 nm dominated the pores for the HJ-K01 resin, and the average pore diameter was determined to be 2.84 nm. As for XAD-4, mesopores ranging from 2 to 18 nm played a predominant role, and the average pore diameter was 5.55 nm.

As presented in Figure 3, after the Friedel-Crafts reaction, two strong characteristic vibrations at 1265.1 and 669.2 cm^{-1} , related to CH_2Cl groups, were greatly weakened,²⁶ and another moderate absorption peak at 1704.9 cm^{-1} appeared.²⁷ After the methylaminated reaction, an absorption peak appeared at 3442.4 cm^{-1} , and it was assigned to the N–H stretching of CH_3NH- groups. Additionally, the vibration at 1100.6 cm^{-1} broadened, which may have been from C–N stretching. These results imply that the chemical modification of hypercrosslinked PS by CH_3NH groups was successful. As

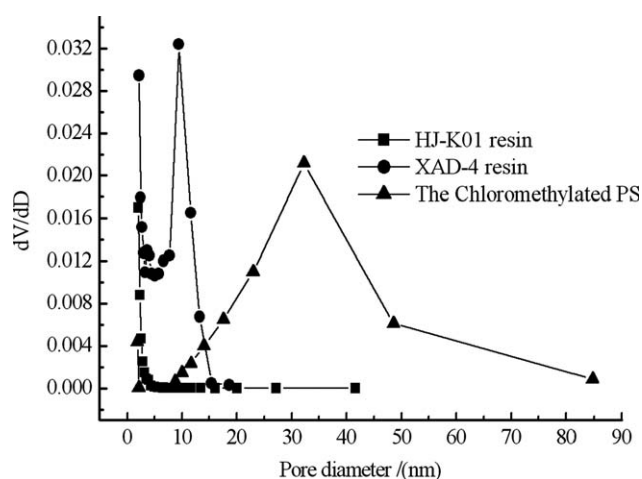


Figure 2 Pore diameter distribution of the XAD-4, chloromethylated PS, and HJ-K01 resins.

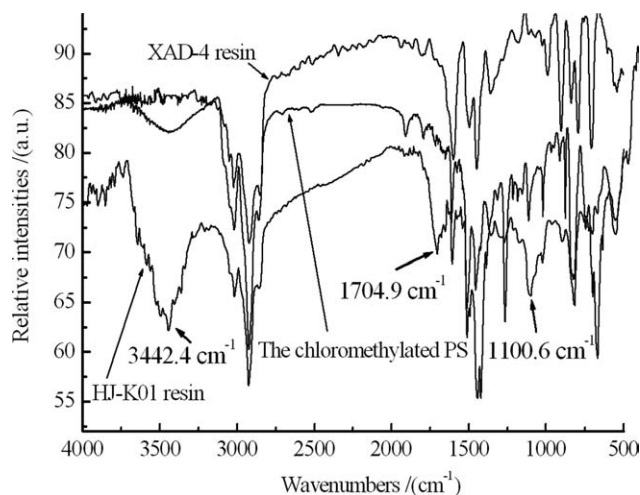


Figure 3 IR spectra of the XAD-4, chloromethylated PS, and HJ-K01 resins.

for XAD-4, the IR spectrum characterized its PS-type structure.

Effect of the solution pH on the adsorption

Figure 4 illuminates the effect of the solution pH on the adsorption of phenol onto the XAD-4, postcrosslinked, and HJ-K01 resins, along with the dissociation curve of phenol with the dependency of the solution pH (the pK_a of phenol applied in this study was 9.89²⁶). The pH dependency trend of the HJ-K01 resin was greatly different from those of the XAD-4 and postcrosslinked resins. The pH dependency trend of XAD-4 was consistent with the dissociation curve of phenol; this revealed that the molecular form of phenol was suitable for the adsorption. Hydrophobic interaction and π - π interaction are known to be the main driving forces for the adsorption of phenol onto XAD-4 from an aqueous solution.^{28,29} When the solution pH is higher than 8.9, phenol will be gradually ionized as a hydrophilic phenoxy negative ion, negative for the adsorption.

The adsorption capacity of phenol onto the HJ-K01 resin was hypersensitive to the solution pH, and the original phenol solution, unadjusted by hydrochloric acid or sodium hydroxide, was optimum (the original phenol solution pH was about 6.0); this proved that the molecular forms of phenol and the uploaded methylamino groups onto the HJ-K01 resin were appropriate for the adsorption. When the solution pH was higher than 6.0, the excursion of the ionization equilibrium of phenol took place, and phenol was presented as a phenoxy negative ion, which was not favorable for the adsorption.³⁰ On the other hand, when the solution pH was lower than 6.0, the methylamino groups on the HJ-K01 resin accepted protons and were formed as ammonium

positive ions,³¹ which also reduced the adsorption. With the introduction of the methylamino groups onto the HJ-K01 resin, the formation of hydrogen bonds was possible between the methylamino groups on the HJ-K01 resin and the phenolic hydroxyl groups of phenol.³² In conclusion, the pH dependency trend of the HJ-K01 resin in contrast with XAD-4 indicated that the uploaded methylamino groups had a positive effect on the adsorption.

Comparison of the adsorption of phenol onto the HJ-K01 resin with those of the XAD-4 and postcrosslinked resins

The adsorption capability of the adsorbent is one of the most important aspects to be concerned in field applications, and hence, the adsorption isotherm of phenol onto the HJ-K01 resin was compared with those of the XAD-4 and postcrosslinked resins, which is shown in Figure 5. The adsorption capacity of phenol onto the three resins followed the following order: HJ-K01 > Postcrosslinked resin > XAD-4. As compared with other adsorbents, such as activated carbons, chitin, and bentonite, the adsorption of phenol onto the HJ-K01 resin was comparable with that of activated carbon and better than those of chitin and bentonite.^{33–36} Mesopores ranging from 2 to 5 nm dominated the pores for the postcrosslinked and HJ-K01 resins, and the molecular size of phenol was predicted to be 0.58 nm. Thus, the size matching between the pore diameter of the postcrosslinked and HJ-K01 resins and the molecular size of phenol induced the enhanced adsorption.²⁵ After the

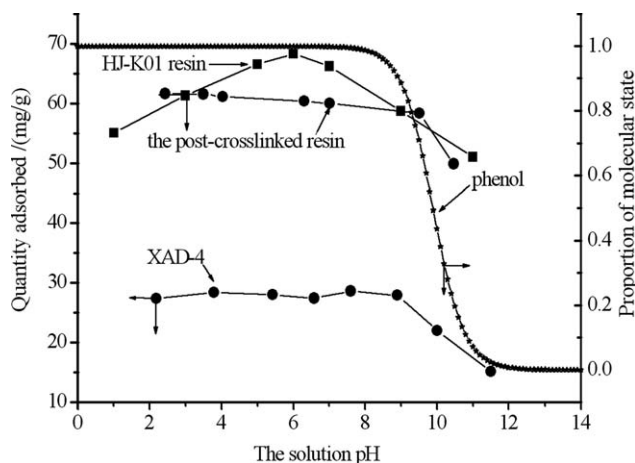


Figure 4 Effect of the solution pH on the adsorption capacity of phenol adsorbed onto the XAD-4, postcrosslinked, and HJ-K01 resins, along with the dissociation curves of phenol on the dependency of the solution pH at a temperature of 298 K (about 0.100 g of resin, 50 mL of phenol aqueous solution, 0.1 mol/L of hydrochloric acid, and sodium hydroxide were used to adjust the solution pH).

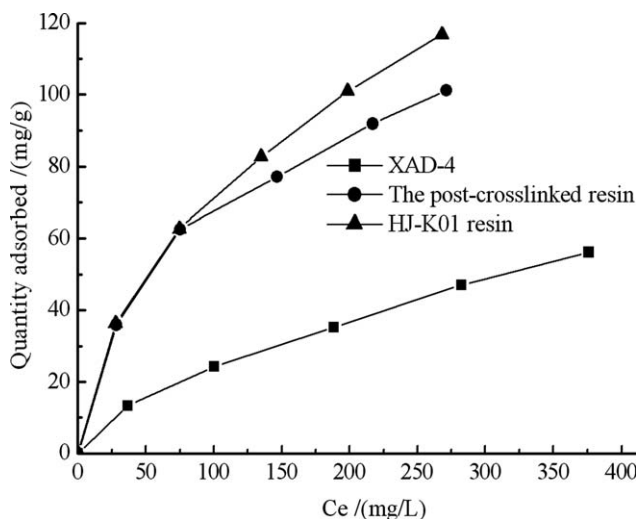


Figure 5 Adsorption isotherms of phenol onto the XAD-4, postcrosslinked, and HJ-K01 resins at 298 K.

methylaminated reaction, methylamino groups were uploaded onto the HJ-K01 resin; the polarity matching between the methylamino groups on the HJ-K01 resin (dipole moment = 1.31 D) and the phenolic hydroxyl groups of phenol (dipole moment = 1.60 D) strengthened the adsorption.³⁷ In addition, after the introduction of the methylamino groups onto the HJ-K01 resin, the formation of the intermolecular hydrogen bonding was possible,^{31,32} which would have enhanced the surface adsorption.

The uploaded amino groups on a polymeric adsorbent are frequently regarded as a solid-phase extraction reagent, and a solid-phase extraction mechanism is often adopted to elucidate the effect of the amino groups on the adsorption.³¹ Here, we define the margin of the adsorption capacity [q_a (mg/g)] for the HJ-K01 resin and contrasted it with that for the postcrosslinked resin as the ideal adsorption capacity caused by the methylamino groups on the HJ-K01 resin. From the q_a - C_e curve presented in Figure 6 (q_e for the postcrosslinked resin subtracted from that for HJ-K01 gave q_a at a given C_e), a linear relationship between q_a and C_e was observed with a correlation coefficient (R^2) of 0.9750. An intercept existed instead of zero in Figure 6, which may have been caused partly by the

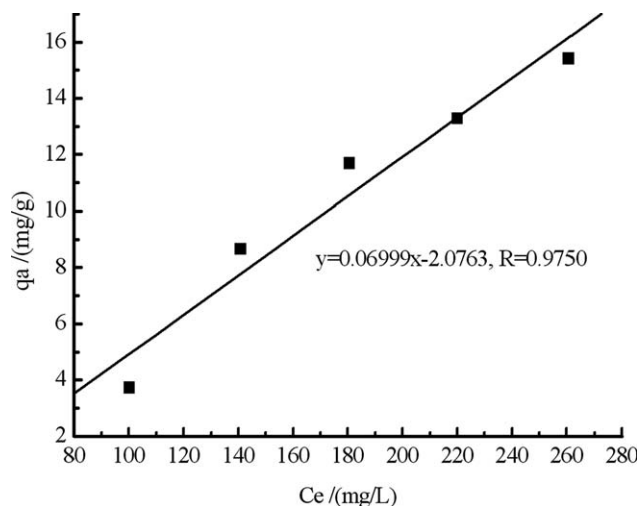


Figure 6 Correlation of q_a and the equilibrium concentration for the adsorption of phenol from aqueous solution.

variation of the micropore region due to the methylaminated reaction.

The Langmuir and Freundlich isotherm models were used to describe the adsorption isotherm data.^{23,29}

Langmuir isotherm:

$$C_e/q_e = C_e/q_m + 1/(q_m K_L) \quad (1)$$

Freundlich isotherm:

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

where q_m is the maximum adsorption capacity, K_L is a binding constant in the Langmuir isotherm,²² and K_F and n are the Freundlich constants, where K_F is taken as a relative indicator of the adsorption capacity and n is related to the magnitude of the adsorption driving force.³¹ The parameters predicted by the Langmuir and Freundlich isotherm models are summarized in Table I. The Langmuir model was not suitable for the adsorption of phenol onto the XAD-4 resin, whereas the Freundlich model was appropriate. As for the postcrosslinked and HJ-K01 resins, the R^2 values from

TABLE I
Correlated Parameters for the Adsorption Isotherm Data of Phenol Adsorbed onto the XAD-4, Postcrosslinked, and HJ-K01 Resins According to the Langmuir and Freundlich Isotherm Equations

	Langmuir isotherm equation			Freundlich isotherm equation		
	q_m (mg/g)	K_L (L/g)	R^2	K_F [(mg/g)(L/mg) ^{1/n}]	n	R^2
XAD-4 resin	90.09	0.3578	0.9444	1.419	1.617	0.9990
Postcrosslinked resin	126.6	0.0127	0.9892	8.414	2.240	0.9882
HJ-K01 resin	158.7	0.0092	0.9817	6.742	1.955	0.9991

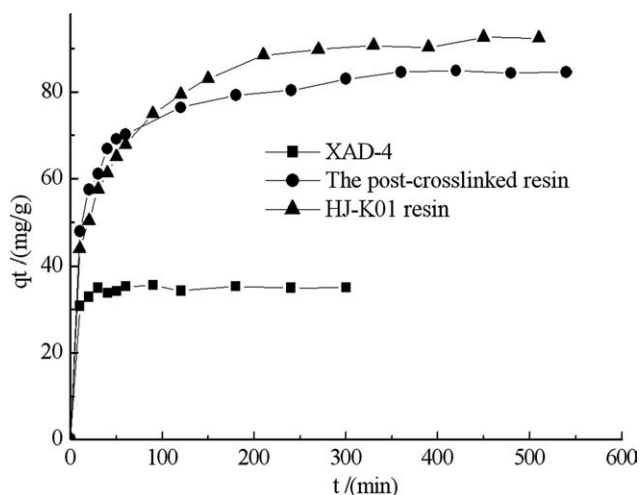


Figure 7 Adsorption kinetic curves of phenol adsorbed onto the XAD-4, postcrosslinked, and HJ-K01 resins at 298 K (ca. 1.000 g of resin, 250 mL of phenol aqueous solution, 150 rpm of stirring rate, 0.4–0.6 mm sample size, and 0.5 mL of phenol aqueous solution was taken for analysis at different intervals).

the Langmuir and Freundlich models were both higher than 0.98; that is, these two models were both suitable for the adsorption. The chemical modification of the postcrosslinked resin should not have affected the heterogeneity of the resin, according to the adsorption parameters obtained. In particular, K_F and n onto the HJ-K01 resin were greater than those onto XAD-4; this implied the larger adsorption capacity and the greater driving force for the adsorption of phenol onto HJ-K01 resin.

Adsorption kinetics

Figure 7 shows the adsorption kinetic curves of phenol onto the XAD-4, postcrosslinked, and HJ-K01 resins at 298 K. The required adsorption time from the beginning to the equilibrium for XAD-4 was less than 100 min; this was much shorter than those for the postcrosslinked and HJ-K01 resins. This implied that the rate constant (k_2) of XAD-4 was much greater than those of the postcrosslinked and HJ-K01 resins.

In general, a pseudo-first-order rate equation is suitable for characterizing the beginning adsorption process but is not feasible for the whole,^{38,39} whereas a pseudo-second-order rate equation is suitable for

describing the whole adsorption process.⁴⁰ Its linear form is

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e \quad (3)$$

where q_t is the adsorption capacity at contact time t (mg/g) and k_2 is the rate constant ($\text{g mg}^{-1} \cdot \text{min}^{-1}$). The fitted results listed in Table II reveal that the pseudo-second-order rate equation gave a perfect fit for the adsorption due to $R^2 > 0.999$. The calculated k_2 values for the three resins showed an order of $k_{2(\text{XAD-4})} > k_{2(\text{postcrosslinked resin})} > k_{2(\text{HJ-K01 resin})}$. In addition, the calculated q_e values predicted from the pseudo-second-order rate equation were very close to the experimental ones; this implied excellent fitting by the pseudo-second-order rate equation.

The pseudo-second-order rate equation could not elucidate the diffusion mechanism and rate-controlling step affecting the adsorption kinetics, so the intraparticle diffusion model, in which the rate of intraparticle diffusion is a function of $t^{1/2}$, proposed by Weber and Morris^{41,42} was applied to fit the kinetic experimental results, as follows:

$$q_t = k_p \times t^{1/2} \quad (4)$$

where k_p is the diffusion rate parameter [$(\text{mg/g})/(\text{min})^{1/2}$] and t is the adsorption time (min) and k_p can be figured out by the plot of q_t versus $t^{1/2}$. If intraparticle diffusion is involved in the adsorption process, the plot of q_t versus $t^{1/2}$ will result in a linear relationship, and if this line passes through the origin, the intraparticle diffusion will be the sole controlling step.⁴³

Figure 8 shows the intraparticle diffusion plots for the adsorption of phenol onto the XAD-4, postcrosslinked, and HJ-K01 resins. The plots showed similar features in that they had two linear segments followed by a plateau. In the first stage, the linear portion passed through the origin; this implied that intraparticle diffusion played a dominant role and controlled the adsorption rate. The k_p values evaluated from the first linear portions of these curves were 9.756, 15.15, and 13.90, respectively. In the following stage, the regression was nearly linear but did not pass through the origin; this suggested that the intraparticle diffusion was not the

TABLE II
Correlated Parameters for the Adsorption Kinetic Data of Phenol Adsorbed onto the XAD-4, Postcrosslinked, and HJ-K01 Resins According to the Pseudo-Second-Order Rate Equation

	k_2 ($\text{g mg}^{-1} \cdot \text{min}^{-1}$)	q_e (mg/g)		R^2
		Experimental	Calculated	
XAD-4 resin	3.3873×10^{-2}	35.05	35.19	0.9998
Postcrosslinked resin	9.0892×10^{-4}	84.54	86.66	0.9997
HJ-K01 resin	4.8623×10^{-4}	92.58	96.25	0.9995

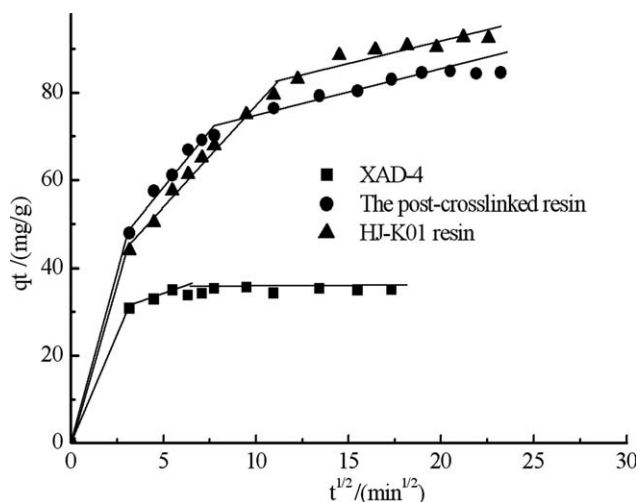


Figure 8 Intraparticle diffusion plot for the adsorption of phenol onto the XAD-4, postcrosslinked, and HJ-K01 resins at 298 K.

sole rate-limiting step in this stage.⁴⁴ After that, the adsorption reached equilibrium.

Dynamic adsorption and desorption

The result of minicolumn dynamic adsorption for phenol removal on the HJ-K01 resin from the synthetic aqueous solution is shown in Figure 9, where C_v is the concentration at different bed volumes of the effluent (mg/L). Phenol did not leak out until 82 BV, and its total adsorption volume was up to 275 BV. As 2% of sodium hydroxide was applied to desorb phenol from the HJ-K01 resin column, a nearly 100% regeneration efficiency was achieved. A continuous adsorption–regeneration run of the used HJ-K01 resin bed was performed, and the fifth cycle was almost identical to the first cycle; this implied

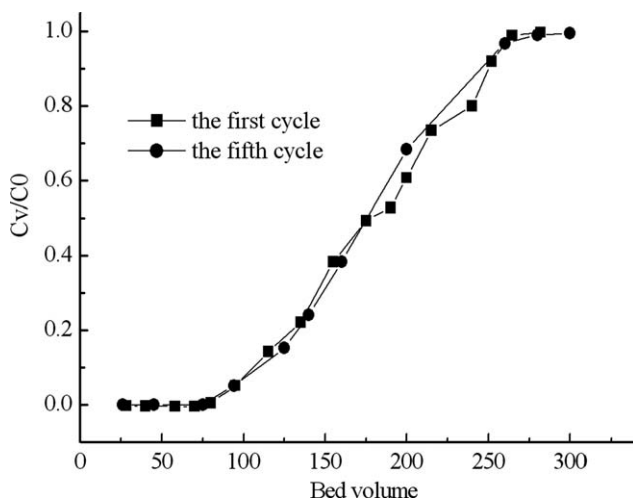


Figure 9 Dynamic adsorption of phenol onto the HJ-K01 resin.

that the HJ-K01 resin could be completely regenerated and that its adsorption efficiency was excellent.

CONCLUSIONS

The chemical modification of macroporous cross-linked PS was successful, and the gained HJ-K01 resin exhibited excellent adsorption behaviors for phenol. After the Friedel–Crafts and methylaminated reactions, the HJ-K01 resin possessed a high specific surface area and predominant mesopores in the range of 2–5 nm. The HJ-K01 resin had a much larger adsorption capacity for phenol than XAD-4, which have been because of the polarity matching and size matching between the HJ-K01 resin and phenol. The adsorption isotherms could be fitted by the Freundlich isotherm, and the adsorption kinetic curves obeyed the pseudo-second-order rate equation. The dynamic adsorption revealed that phenol did not leak out until 82 BV.

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