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# Treatment of phenol and *p*-cresol in aqueous solution by adsorption using a carbonylated hypercrosslinked polymeric adsorbent

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### ARTICLE INFO

### ABSTRACT

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Keywords: Hypercrosslinked Adsorption Phenol p-Cresol Phenolic compounds are one of the most representative pollutants in industrial wastewater, and efficient removal and destruction of them have attracted significant concerns. In the present study, a carbonylated hypercrosslinked polymeric adsorbent HJ-1 was developed and its ability to remove phenol and *p*-cresol in aqueous solution was tested in comparison with the commercial Amberlite XAD-4 resin. The HJ-1 resin exhibited excellent applicability in the acidic and neutral pH, NaCl posed the positive effect, whereas  $Cd^{2+}$  had the negative effect on the adsorption. The adsorption dynamics obeyed the pseudo-second-order rate equation and the adsorption rate constant of phenol was a little greater than that of *p*-cresol. The adsorption isotherms can be correlated to Langmuir isotherm and the adsorption capacity of phenol and *p*-cresol onto HJ-1 resin was much larger than that onto XAD-4. With regard to the two adsorbates, the adsorption capacity of *p*-cresol was larger than that of phenol at the same temperature and equilibrium concentration. The adsorption thermodynamic parameters were calculated and the adsorption was principally driven by adsorption enthalpy and entropy. Analysis of the different adsorbability of *p*-cresol from phenol suggested that the solubility and polarity of the adsorbate played important roles. © 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Water pollution, especially the industrial wastewater containing aromatic compounds, is one of the most urgent environmental problems. Phenol and its derivatives, widely applied as the common organic intermediates in industry, have attracted particular attentions due to their high toxicity, high oxygen demand, and low biodegradability. Many methods such as catalytic oxidation, membrane separation, and adsorption have been developed to deal with the wastewater containing phenolic compounds, and among which, adsorption by adsorbents is shown effective [1–5].

Activated carbon is frequently used in the adsorption due to its large specific surface area and predominant proportion of micropores. Nevertheless, its application is now limited due to its difficult regeneration and reuse. In contrast, synthetic polymeric adsorbents are more applicable owing to its favorable stability, structural diversity, and high removal efficiency [6–10]. The Amberlite XAD-4 resin is considered to be one of the best synthetic polymeric adsorbents for the removal of phenol from wastewater. However, it possesses much low adsorption capability towards organic compounds exhibiting a strong hydrophilic affinity to water on account of its hydrophobic surface. To attain large adsorption capacity for

\* Fax: +86 731 8879850. E-mail address: xiaomeijiangou@yahoo.com.cn. a specific organic compound, chemical modification of the polymeric adsorbents is often adopted by introducing some special functional groups onto the matrix of the adsorbent [11-14]. These introduced functional groups will modify the chemical composition of the adsorbent surface and hence improve the adsorption [15,16].

In this study, a hypercrosslinked polymeric adsorbent HJ-1 was prepared from chloromethylated poly(styrene-co-divinylbenzene) (PS), its several factors on adsorption, adsorption dynamics and adsorption equilibriums for phenol and *p*-cresol in aqueous solution were thereafter tested in batch experiments, its adsorption thermodynamics were analyzed and the adsorption mechanism was expounded.

### 2. Experimental

### 2.1. Materials

Macroporous low crosslinked chloromethylated PS beads were provided by Langfang Chemical Co. Ltd. (Hebei Province, PR China), its crosslinking degree was 6%, and the chlorine content was 17.3%. The Amberlite XAD-4 resin was purchased from Rohm & Haas Company (USA). Phenol and *p*-cresol used as the adsorbates in this study are of analytical grades and their main properties are shown in Table 1 [17–19], phenol was distilled before use and *p*cresol was used without further purification. Their molecular sizes were obtained from the optimized molecular structures performed

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### Table 1

The main properties of the two adsorbates.

	Phenol	p-Cresol
Formula	C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )(OH)
Structure <sup>a</sup>	مىلىمى بەرمەر	ب وب دری شری د رشری شر
Molecular size (nm) <sup>a</sup>	0.57  imes 0.43	$0.66 \times 0.43$
Molecular weight (g/mol)	94.11	108.14
$pK_{a}$ (at 298 K) <sup>b</sup>	9.89	10.17
Solubility (at 298 K, g/100 mL H <sub>2</sub> O) <sup>b</sup>	8	2.3
$\lambda_{max}$ in aqueous solution	269.9	277.1
Hydrogen bonding acidity $(\alpha)^c$	0.60	0.57
Hydrogen bonding basicity $(\beta)^c$	0.30	0.31
Dipole moment <sup>b</sup>	1.224	1.54

<sup>a</sup> The results were cited from the optimized molecular structures by Gaussian 03 software package [17].

<sup>b</sup> The results were taken from Ref. [18].

<sup>c</sup> The results were cited from Ref. [19].

by Gaussian 03 software package [17]. Becke three-parameter Lee–Yang–Parr (B3LYP) method was proven to be better than ab initio method for the prediction of the optimized molecular structure, and hence the B3LYP/6-311++G method was performed for the calculation, and the optimized molecular structure was achieved if there is no imaginary frequency.

### 2.2. Preparation of the polymeric adsorbent

The polymeric adsorbent HJ-1 was prepared by the following post-crosslinked step. In a 500 mL round-bottomed flask, 40 g of dry chloromethylated PS beads were swollen with 120 mL of nitrobenzene at room temperature overnight. Under mechanical stirring, 5 g of new-cauterized anhydrous zinc chloride was added into the reaction flask as quickly as possible at 323 K. After the zinc chloride was dissolved completely, the reaction mixture was then evenly heated to 388 K within 1 h and was further retained at 388 K for 10 h. Finally, the reaction mixture was poured into an acetone bath containing 1% of hydrochloric acid (w/w), and the filtered polymeric beads were rinsed by deionized water until neutral pH and extracted with ethanol for 8 h.

### 2.3. Characterization of polymeric adsorbent

The porous texture of the resins was determined from N<sub>2</sub> adsorption–desorption curves at 77 K with a Micromeritics ASAP 2010 surface area measurement instrument, and the specific surface area was calculated from the N<sub>2</sub> isotherms by using Brunauer–Emmett–Teller (BET) method. The infrared (IR) spectra before and after the post-crosslinked reaction in the range of  $500-4000 \,\mathrm{cm^{-1}}$  were collected with a pellet of powdered potassium bromide and resin on a Nicolet 510P Fourier transformed infrared instrument. The elemental analysis was obtained with a VarioEL Elemental Analysis System, and the oxygen content was calculated with the following equation:

$$O(\%) = 100 - C(\%) - H(\%) - Cl(\%)$$
(1)

### 2.4. Adsorption assay

Equilibrium adsorption of phenol and *p*-cresol was performed at three different temperatures: 293, 303, and 313 K. About 0.100 g of HJ-1 resin was weighed accurately and introduced into 50 mL of aqueous solution with different initial concentrations,  $C_0$  (mg/L). 0.1 mol/L of HCl and NaOH solution were used to adjust the solution pH throughout the experiment. Solid NaCl was introduced to control the solution salinity and 106.0 mg/L of CdCl<sub>2</sub> solution



Fig. 1. The N<sub>2</sub> adsorption-desorption isotherms of XAD-4 and HJ-1 resins.

was applied to test the effect of the heavy metals on the adsorption. Then the flasks were shaken in a thermostatic oscillator at a desired temperature until the equilibrium was reached. The residual concentration,  $C_e$  (mg/L), was determined and the equilibrium adsorption capacity,  $q_e$  (mg/g), was calculated. Adsorption dynamic curves of phenol and *p*-cresol were performed by analyzing the adsorption capacity with the initial concentration at 600 mg/L at different time intervals with the temperature at 293 K until the adsorption equilibrium was reached.

### 2.5. Analysis concentration of the adsorbates

The concentration of phenol and *p*-cresol in aqueous solution was analyzed by UV analysis carried on a Perkin-Elmer Lambda 17 UV spectrophotometer with the wavelength at 269.9 and 277.1 nm, respectively. The working curve of the UV absorbency of the standard phenol and *p*-cresol solution with different known concentrations was firstly measured, which were A = 0.01495C + 0.01295 and A = 0.0142C + 0.00846 for phenol and *p*-cresol with the correlative factors  $R^2 > 0.999$ . The absorbency of the residual solution was then measured and the equilibrium concentration,  $C_e$  (mg/L), was calculated based on the working curves.

### 3. Results and discussions

### 3.1. The characterization of HJ-1 resin

The N<sub>2</sub> adsorption–desorption isotherms of XAD-4 and HJ-1 resins at 77 K are demonstrated in Fig. 1, it is seen that all of the adsorption isotherms are close to the Type II isotherm of the IUPAC classification, which are typical of mixed micro/mesoporous materials. At the initial part of the adsorption isotherms with a relatively lower pressure ( $P/P_0$ ) below 0.05, the N<sub>2</sub> uptake increases sharply with the increment of the relative pressure, this proves the existence of micropores. Moreover, the visible hysteresis loops for the two resins imply that they contain some mesopores. In addition, Fig. 1 suggests that the two resins may be differentiated with regard to the specific surface area, the chemical composition, and the pore structure, as listed in Table 2.

The IR spectrum of XAD-4 clarifies its representative polystyrene-type structure for the vibrations with frequencies at 1600.7, 1510.1, and 1446.4 cm<sup>-1</sup> (the C=C stretching of the benzene ring) as well as 796.5 cm<sup>-1</sup> (the 1,4-disubstituted =C-H bending). While for HJ-1 resin, after the post-crosslinked reaction, two strong characteristic bands related to the CH<sub>2</sub>Cl groups for the chloromethylated PS at 1265.1 and 669.2 cm<sup>-1</sup> are greatly

### Table 2

The typical properties of XAD-4, chloromethylated PS, and HJ-1 resin.

	XAD-4	Chloromethylated PS	HJ-1 resin
Structure	Polystyrene	Chloromethylated groups modified polystyrene	Formaldehyde carbonyl groups modified polystyrene
Polarity	Non-polar	Weak polar	Moderate polar
Specific surface area (m <sup>2</sup> /g)	750 <sup>a</sup>	28	727
Average pore diameter (nm)	5.8 <sup>a</sup>	25.2	3.25
Particle size (mm)	0.4-0.6	0.4–0.6	0.4-0.6
Porosity (ml/g)	1.0 <sup>a</sup>	-	0.59
Chlorine content (%)	-	17.3	3.66
Oxygen content (%)	0	-	5.65
Characteristic peaks in IR	-	1265.1, 669.2	1704.8
Color	White	White	Brown

<sup>a</sup> These data were provided from Rohm & Haas Company.

weakened, and one moderate vibrational band of formaldehyde carbonyl groups appears with frequencies at 1704.8 cm<sup>-1</sup>, which may be from the oxidation of the CH<sub>2</sub>Cl groups [20]. The IR spectra of XAD-4 and HJ-1 resin are shown in the Supplementary Materials)

# 3.2. Effect of solution pH on the adsorption of phenol onto HJ-1 resin

The effect of the solution pH in equilibrium on the adsorption of phenol onto HJ-1 resin is illustrated in Fig. 2, the temperature is set to be at 298 K and the initial concentration of phenol is 492.7 mg/L. It is seen that the alkaline solution, especially as the pH is higher than 8.0, is not favorable for the adsorption, this may be from the negative ionic form of phenol in the alkaline solution. In addition, the adsorption capacity of phenol onto HJ-1 resin is kept to be approximately steady with the acidic and neutral condition. That is, the HJ-1 resin has its excellent applicability in the acidic and neutral condition.

### 3.3. Effect of NaCl on the phenol uptake onto HJ-1 resin in aqueous solution

Owing to the coexistence of inorganic salts such as NaCl and Na<sub>2</sub>SO<sub>4</sub> with the industrial wastewater containing phenol at a comparatively high level, the effect of NaCl on the ability of the resin to remove phenol in aqueous solution is determined, and the results are depicted in Fig. 3. It is shown that the percentage of NaCl exhibits the positive effect on the adsorption of phenol onto HJ-1 resin at 298 K, the adsorption capacity of phenol onto HJ-1 resin increases with the increasing of the NaCl concentration, which may be from the so called "salting-out" effect [21].



Fig. 2. The effect of the solution pH in equilibrium on phenol uptake onto HJ-1 resin at 298 K.



Fig. 3. The effect of percent of NaCl on the adsorption of phenol onto HJ-1 resin with the temperature at 298 K.

### 3.4. Effect of $Cd^{2+}$ on the adsorption

Taking into account the fact that heavy metals such as  $Hg^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  may coexist with the phenolic compounds in the wastewater,  $Cd^{2+}$  is chosen as the model heavy metal in the current study and its effect on the adsorption capacity of phenol onto the HJ-1 resin is examined. As seen in Fig. 4, increasing  $Cd^{2+}$  inevitably results in the decreasing of the phenol uptake, and presence of  $Cd^{2+}$  poses a negative effect on the adsorption of phenol.



**Fig. 4.** The effect of the concentration of Cd<sup>2+</sup> in the phenol aqueous solution on the adsorption capacity of phenol onto HJ-1 resin at 298 K.



**Fig. 5.** The adsorption dynamic curves of phenol and *p*-cresol adsorbed onto HJ-1 resin with the initial concentration at 600 mg/L and the temperature at 293 K.

### 3.5. Adsorption dynamics

Fig. 5 displays the adsorption dynamic curves of phenol and *p*cresol adsorbed onto HJ-1 resin with the temperature at 293 K. It is evident that the required time from the beginning to the equilibrium of phenol is shorter than that of *p*-cresol, which may be from the different molecular size of the two adsorbates. The molecular size of phenol (0.57 nm  $\times$  0.43 nm) is smaller than *p*-cresol (0.66 nm  $\times$  0.43 nm), and phenol will diffuse more quickly than *p*cresol in the micro/mesopores of HJ-1 resin. Pseudo-first-order and pseudo-second-order rate equations are employed to fit all the data [22,23]:

The pseudo-first-order rate equation:

$$\log\left[1 - \frac{q_t}{q_e}\right] = -\left(\frac{k_1}{2.303}\right) \times t \tag{2}$$

The pseudo-second-order rate equation:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \tag{3}$$

here  $q_t$  is the adsorption capacity at contact time t (mg/g), and  $k_1$  and  $k_2$  is the pseudo-first-order (min<sup>-1</sup>) and pseudo-second-order rate constants [g/(mg min)], respectively.

The correlative parameters are summarized in Table 3. It reveals that the pseudo-second-order rate equation can give a perfect fitting. In addition, the rate constant of phenol is a bit greater than p-cresol, consistent with the shorter required time for phenol than p-cresol. In particular, the calculated  $q_e$  predicted from the pseudo-



**Fig. 6.** The adsorption isotherms of phenol and *p*-cresol adsorbed onto HJ-1 as well as those onto XAD-4 in aqueous solution with the temperature at 293 K.

Table 3

The correlative parameters for the adsorption dynamics of phenol and p-cresol adsorbed onto HJ-1 resin.

	Pseudo-first-order		Pseudo-second-order			
	$k_1$ (min <sup>-1</sup> )	$R^2$	$k_2$ (g/(mg min))	R <sup>2</sup>	<i>q<sub>e</sub></i> (mg/g)	
					Exp.	Cal.
Phenol 9-Cresol	0.00910 0.00813	0.9771 0.9095	$\begin{array}{c} 6.957 \times 10^{-4} \\ 1.850 \times 10^{-4} \end{array}$	0.9994 0.9998	110.2 131.8	111.6 137.4

second-order rate equation is very close to the experimental one, which also implies the pseudo-second-order rate equation is very suitable for characterizing the adsorption.

## 3.6. Comparison of adsorption of phenol and p-cresol onto HJ-1 and XAD-4 in aqueous solution

The XAD-4 resin is usually applied to treat wastewater containing phenol in industry [24,25], and in this study the adsorption behavior of phenol and p-cresol onto HI-1 resin is compared with the XAD-4 resin at 293 K. As can be seen in Fig. 6, the adsorption capacities of phenol and p-cresol onto HJ-1 resin are much larger than XAD-4 at the same equilibrium concentration. The mesopores play predominant roles in the pore structure for XAD-4 resin, whereas the micro/mesopore dominates the pore structure of HJ-1 resin (the pore distribution of XAD-4 and HJ-1 resins are shown in the Supplementary materials which favors the adsorbent-adsorbate interaction via pore filling mechanism [26]. In addition, XAD-4 adsorbs phenol principally through van der Waals force due to its hydrophobic surface, while HJ-1 resin is modified with formaldehyde carbonyl groups on its matrix and its surface polarity is increased, the increased surface polarity will match the polarity of the adsorbates, enhancing the adsorption [27]. With regard to the comparison of phenol uptake as well as the required time from the beginning to the equilibrium onto HJ-1 resin with those of the activated carbon such as the acid treated [28], olive stone-based [29], and eucalyptus wood-based [30], the HI-1 resin shows an excellent kinetic performance for phenol adsorption and the phenol uptake is acceptable. Taken into account the fact that the exhausted HJ-1 beads are amenable to regenerate for repeated used, HJ-1 resin can be taken as an ideal adsorbent for phenol removal from the contaminated water.

To compare the adsorption affinity of HJ-1 with XAD-4, the data in Fig. 6 are further dealt with the distribution ratio  $K_d$  (L/g) by the



Fig. 7. The adsorption isotherms of phenol and *p*-cresol adsorbed onto HJ-1 in aqueous solution at 293, 303, and 313 K.

#### Table 4

The correlated parameters for the adsorption isotherms of phenol and *p*-cresol onto HJ-1 according to Langmuir and Freundlich isotherm.

T(K)	Langmuir	isotherm	Freundlic	Freundlich isotherm		
	$\overline{K_{\rm L}({\rm L/g})}$	$q_m (\mathrm{mg/g})$	R <sup>2</sup>	$K_F ((mg/g) (L/mg)^{1/n})$	n	<i>R</i> <sup>2</sup>
Phenol						
293	9.450	167.8	0.9997	4.522	1.635	0.9785
303	7.817	174.2	0.9992	3.792	1.5710	0.9814
313	7.102	172.7	0.9985	3.427	1.5508	0.9844
p-Creso	ol					
293	17.85	234.2	0.9916	15.27	2.093	0.9771
303	12.80	248.1	0.9960	10.62	1.846	0.9626
313	11.34	241.5	0.9961	9.197	1.7989	0.9551

following equation [31]:

$$K_{\rm d} = \frac{\text{mg of the solutes/1g of dry adsorbent}}{\text{mg of the solutes/1L of the solution}}$$
(4)

The  $K_d$  value provides a measure of the adsorption affinity for the adsorbent [32], and it is seen that  $K_d$  decreases sharply with the increment of the adsorbate uploading fraction ( $\theta$ ), where  $\theta = q_t/q_e$ (plot of  $K_d - \theta$  is not displayed) [33]. Particularly, the  $K_d$  values of phenol and *p*-cresol on HJ-1 resin are much greater than those on XAD-4, especially at low adsorbate fractional loading, which helps the adsorbent to remove phenolic compounds from wastewater completely [34].

### 3.7. Static equilibrium adsorption

Fig. 7 presents the adsorption isotherms of phenol and *p*-cresol onto HI-1 resin in aqueous solution. It is clear that lower temperature is favorable for the adsorption, indicating an exothermic process. In particular, the adsorption capacity of *p*-cresol is larger than phenol at the same temperature and equilibrium concentration, implying the stronger interaction between the adsorbent and *p*-cresol. Langmuir and Freundlich isotherms are adopted to describe the adsorption process [6,35], and the correlative parameters are listed in Table 4, and it is seen that Langmuir isotherm characterizes the experimental results better than Freundlich isotherm due to  $R^2 > 0.99$ , which indicates that the adsorption may be a monolayer adsorption process and the surface energy of the adsorbent may be homogeneous. Additionally, the K<sub>L</sub> values of pcresol are greater than the corresponding ones of phenol, implying the greater adsorption affinity of *p*-cresol with the resin than phenol.

### 3.8. Adsorption thermodynamics

The adsorption thermodynamic parameters such as adsorption enthalpy  $\Delta H$  (kJ/mol), adsorption free energy  $\Delta G$  (kJ/mol), and adsorption entropy  $\Delta S$  (J/(mol K)) can be calculated with the following equations [36–38]:

$$\ln K_{\rm L} = -\frac{\Delta H}{RT} + \ln K_0 \tag{5}$$

(6)

$$\Delta G = -RT \ln K_{\rm L}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

where  $K_L$  is the adsorption equilibrium constant with the unit of L/mol; R is the universal gas constant, 8.314 J/mol K; T is the absolute temperature, K; and  $K_0$  is a constant. By plotting  $\ln K_L$  versus 1/T, a straight line can be gained (plot of  $\ln K_L$  versus 1/T is shown in Fig. 8), and the  $\Delta H$  can be obtained from the slope of the straight line.



**Fig. 8.** Plot of  $\ln K_{\rm L}$  versus 1/T for the adsorption of phenol and *p*-cresol onto HJ-1 in aqueous solution.

The adsorption enthalpies, adsorption free energies, and adsorption entropies of phenol and *p*-cresol adsorbed onto HJ-1 resin are presented in Table 5. The negative adsorption enthalpies indicate that the adsorption is an exothermic process [39]. In particular, the absolute value of the adsorption enthalpy of *p*-cresol is a little greater than phenol, displaying the interaction of the resin with *p*-cresol is a little stronger. The negative adsorption free energies imply the process is favorable and spontaneous. Moreover, the adsorption free energies of *p*-cresol are a little more negative than phenol, displaying the more favorable and spontaneous process for *p*-cresol [39,40].

The adsorption of phenolic compounds onto XAD-4 was proven to be driven mainly by adsorption enthalpy due to the negative adsorption enthalpy and adsorption entropy [34], and it is deduced that the adsorption of phenol or p-cresol onto HJ-1 resin should be driven mainly by both adsorption enthalpy and entropy because of the negative adsorption enthalpy and the positive adsorption entropy. The HJ-1 resin is hydrophilic due to the introduction of the hydrophilic formaldehyde carbonyl groups onto the adsorbent matrix, it can be easily wet by water molecules in aqueous solution and hence its surface is surrounded by water molecules entirely, phenol or p-cresol molecules will also interact with water molecules in aqueous solution due to its hydrophilic hydroxyl groups (which can be seen in the Supplementary Materials). Before phenol or p-cresol molecules can be adsorbed onto the resin surface, they must break the bond between phenol or *p*-cresol molecules and water molecules as well as the bond between HJ-1 resin and water molecules. Then, phenol or *p*-cresol molecules will take the place of the water molecules and form the bond with the HJ-1 resin. This process can be called "Solvent replacement" [41,42], and which should be exothermic [43]. For the much bigger molecular size of phenol or p-cresol than water, the number of water molecules pushed out is much abundant than that of phenol

Adsorption thermodynamic parameters of phenol and <i>p</i> -cresol onto HJ-1 in aqueous
solution.

T(K)	$\Delta H$ (kJ/mol)	$\Delta G (kJ/mol)$	$\Delta S (J/mol K)$
Phenol			
293	-10.92	-16.54	19.18
303		-16.63	18.84
313		-16.93	19.20
p-Cresol			
293	-17.37	-18.43	3.618
303		-18.22	2.805
313		-18.51	3.642

or *p*-cresol molecules adsorbed. So the solvent replacement process will bring on the increase of the adsorption entropy.

### 3.9. Adsorption mechanism

For the polymeric adsorbent with plentiful micropores, pore filling mechanism according to the capillary condensation theory is proven to be very favorable for the adsorption of small molecules onto the macroporous polymeric adsorbent. The better the matching of the pore diameter of the adsorbent with the molecular size of the adsorbate is, the larger the adsorption capacity is. As shown in Table 1, the molecular size of phenol and *p*-cresol is calculated to be 0.57 nm  $\times$  0.43 nm and 0.66 nm  $\times$  0.43 nm, respectively, and the average pore diameter of HJ-1 is measured to be 3.25 nm, which is helpful for the adsorption.

Fig. 7 shows the adsorption capacity of *p*-cresol is larger than that of phenol at the same temperature and equilibrium concentration, and Table 5 lists the adsorption enthalpy of *p*-cresol is more negative than phenol. This different adsorbability may be explained in terms of the solubility, the polarity, and hydrogen bonding acidity/basicity of two adsorbates. The solubility of *p*-cresol in water is less than phenol (2.3 and 8.0 g/100 mL H<sub>2</sub>O at 298 K for *p*-cresol and phenol, respectively), thus it shows less affinity towards water (hydrophobicity). This may be one of the possible reasons for its larger adsorption capacity. In addition, the formaldehyde carbonyl groups of HJ-1 have a large dipole moment (1.60 D), and the dipole moment of *p*-cresol is larger than phenol (1.54 and 1.224 D for *p*-cresol and phenol, respectively), therefore, the more polarity matching between the adsorbent and *p*-cresol is expected to results in the larger adsorption capacity.

The  $pK_a$  of phenol is determined to be 9.4, lower than that of *p*-cresol (10.17). Phenol and *p*-cresol are polar molecules with hydrogen bonding acidity ( $\alpha$ ) as well as hydrogen bonding basicity ( $\beta$ ) (Table 1). *p*-Cresol has a lower value of a hydrogen bonding acidity than phenol, exhibiting a less Lewis acid-base interaction (hydrogen bonding) with the formaldehyde carbonyl groups of HJ-1 resin, contrary to the adsorption capacity results in Fig. 7. This may be explained as follows. Phenol or *p*-cresol is firstly adsorbed onto HJ-1 resin through pore filling mechanism and hydrophobic interaction. After that, the oxygen atoms of the formaldehyde carbonyl groups of HJ-1 resin can interact with the hydrogen atoms of the hydroxyl groups of phenol or p-cresol, and the intermolecular hydrogen bonding will be formed. That is, pore filling and hydrophobic interaction are the precondition for the formation of intermolecular hydrogen bonding between the adsorbent and the adsorbate. Consequently, although the lower  $pK_a$  and higher  $\alpha$  of phenol, the adsorption capacity of phenol onto HJ-1 resin is smaller than *p*-cresol in aqueous solution.

### 4. Conclusions

The HJ-1 resin is prepared by post-crosslinked reaction and it can adsorb phenol and *p*-cresol efficiently in aqueous solution, its adsorption capacity for phenol and *p*-cresol adsorbed is measured to be about 80.52 and 141.5 mg/g, respectively as the equilibrium concentration is 100 mg/L and the temperature was 293 K. Its adsorption for phenol is probably steady in the acidic and neutral pH, the percentage of NaCl shows the positive effect, while  $Cd^{2+}$  poses the negative effect on the adsorption. The adsorption dynamic curves can be well fitted by the pseudo-second-order rate equation and their adsorption isotherms can be corrected to Langmuir isotherm model. The equilibrium adsorption capacities of phenol and *p*-cresol onto HJ-1 resin are much larger than the corresponding ones onto XAD-4. The adsorption enthalpy of *p*-cresol is a little more negative than phenol and the adsorption may be driven by both of adsorption enthalpy and entropy. Pore filling mechanism and hydrophobic interaction may play important roles in the adsorption, and the solubility and the polarity of the two adsorbates can explain their different adsorption capacity.

In conclusion, HJ-1 resin can be synthesized easily and it shows high adsorption capacity and strong adsorption affinity to phenol and *p*-cresol in aqueous solution. Therefore, it is possible that this adsorbent may be applied to treat the wastewater containing phenolic compounds.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.02.141.

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