ADSORPTION BEHAVIOR OF PHENOLIC COMPOUNDS ONTO POLYMERIC ADSORBENTS MODIFIED WITH 2-CARBOXYBENZOYL GROUPS[*]

Jing-ping Wang[**], Shu-he Tang, Zheng-hao Fei, Jian Chen and Yu-feng Sun
Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources and Environmental Protection,
Yancheng 224002, China
Institute of Applied Chemistry & Environmental Engineering, Department of Chemistry,
Yancheng Teachers College, Yancheng 224002, China

Abstract Two hypercrosslinked polymeric adsorbents (ZH-01 and Amberlite XAD-4 resin) were employed to remove three kinds of phenolic compounds including phenol, 4-nitrophenol and 2,4-dinitrophenol from aqueous solutions. The study was focused on the static equilibrium adsorption behavior, the column dynamic adsorption and desorption profiles. The Freundlich model gave a perfect fitting to the isotherm data. The adsorbing capacities for these three compounds on ZH-01 were higher than those on Amberlite XAD-4 within the temperature range 288−318 K, which was attributed to the large micropore area and 2-carboxybenzoyl functional groups on the network of ZH-01 resin. The adsorption for phenol and 4-nitrophenol on ZH-01 was a physical adsorption process, while for 2,4-dinitrophenol it was a coexistence process of physical adsorption and chemisorption's transitions. The column test showed the advantages of ZH-01 in the dynamic adsorption processes of phenolic compounds. Being used as the desorption reagent, sodium hydroxide solution showed an excellent performance.

Keywords: Hypercrosslinked polymeric adsorbent; Phenolic compounds; Adsorption; Chemisorption's transition.

INTRODUCTION

Phenol and its derivatives, as one of the most important organic intermediates, were widely used for the manufacture of pesticides, rubber, drugs and dyestuffs. As a result, more and more phenol-containing wastewater had been introduced into water bodies. Because of the high toxicity of phenolic compounds, the treatment of these organic waste water had draw significant concern[1–3].

Presently, various methods of wastewater treatment had been developed such as catalytic oxidation, liquid membrane separation, biological degradation and adsorption[4, 5]. Due to the high concentration ability of typical adsorbents, adsorption was proved to be one of the most attractive and effective techniques for purification and separation in wastewater treatment[6–12].

In the present work, the adsorption behavior of phenolic compounds onto ZH-01 resin was investigated, including the static equilibrium adsorption behavior, the column dynamic adsorption and desorption. In comparison with Amberlite XAD-4, ZH-01 had higher adsorption capacity for phenolic compounds such as phenol, 4-nitrophenol and 2,4-dinitrophenol, because of large micropore area and the presence of 2-carboxybenzoyl functional groups.

EXPERIMENTAL

Materials

Acetone, ethanol, zinc chloride, dichloromethane, hydrochloric acid, nitrobenzene, phthalic anhydride, phenol, 4-nitrophenol and 2,4-dinitrophenol were used in this study. All these chemicals were of analytical grade and were purchased from Shanghai Chemical Reagent Plant (Shanghai, China). Styrene and divinylbenzene were purchased from Dongda Chemical Co. Ltd, (Shandong province, China). Chloromethyl methylether was obtained from Langfang Chemical Co. Ltd. (Hebei province, China). The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). Phenol, 4-nitrophenol and 2,4-dinitrophenol used in this study were analytical grade reagents of 99.5% purity (Shanghai Chemical Reagent Plant, China). These reagents were used to prepare the stock solutions with a concentration of 2000 mg/L, which were kept in sealed ground-glass-stoppered brown bottles and stored in a refrigerator at 4°C.

Synthesis and Characterization of ZH-01 Adsorbent

ZH-01 was synthesized according to literature[13]. In a 500 mL round-bottomed flask, 50 g of chloromethylated poly(styrene-divinylbenzene) beads (chlorine content 19.5%) were swollen in 600 mL nitrobenzene. Under mechanical stirring, 5 g of zinc chloride was added slowly at room temperature. The mixture was further stirred for 8 h at 408 K. After cooling, 10 g phthalic anhydride was added to the above mixture at 383 K and stirred for another 15 h. Finally, the mixture was poured into an acetone bath, which contained 1% hydrochloric acid. The filtered polymers were extracted with ethanol for 8 h in a Soxhlet apparatus and dried under vacuum at 333 K for 8 h. The specific surface area and the pore distribution of resins were determined in dry state with a Micromeritics ASAP 2010 M surface area measurement instrument (Micromeritics Instrument, Norcros, USA) by the three-point BET method. Infrared spectra of the polymeric adsorbent before and after the post-crosslinking reaction were obtained from a Nicolet 170 SX IR spectrometer (USA) with a pellet of powdered potassium bromide and resin (Fig. 1). Compared with the chloromethylated polymer beads, the band of C−Cl at about 677.01 cm^{-1} of ZH-01 decreased obviously and the band at 1645.30 cm^{-1} in ZH-01 suggested that the 2-carboxylbenzeoyl groups were successfully bonded onto ZH-01 resin. The chlorine content was measured according to the method of Volhard. The properties of ZH-01 and XAD-4 resins are given in Table 1. The structure of ZH-01 is given in Scheme 1.
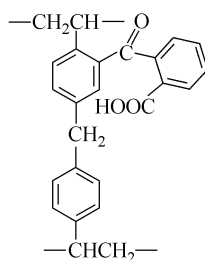
Scheme 1 The chemical formulation of ZH-01

Table 1. Typical properties of the polymeric adsorbents

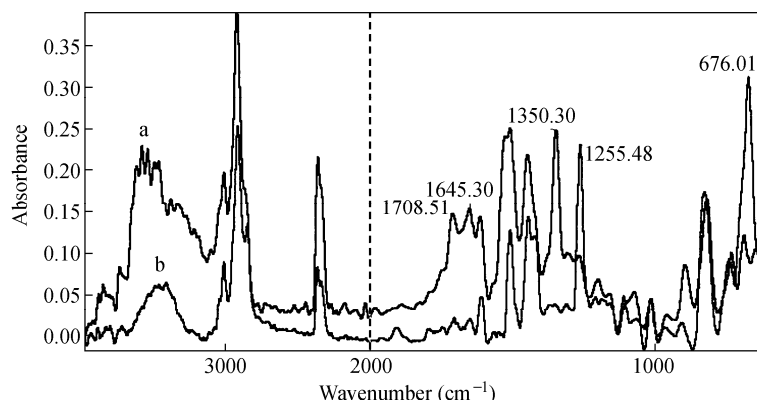| Property	XAD-4	ZH-01
Polarity	Nonpolar	Moderate polar
Specific surface area (m^2/g)	880	1118
Average diameter (nm)	5.8	1.2
Micropore area (m^2/g)	3	686
Average particle size (mm)	0.5	0.5
Porosity (mL/g)	1.0	0.69
Residual chlorine content (%)	0	2.8
Color	White	Brown

Fig. 1 IR spectra of the chloromethylated polymer beads before and after the post-crosslinking reaction: (a) ZH-01 resin and (b) chloromethylated polymer beads

Equipments

The equipments used in the present study included an orbital shaker, with a temperature controlling of 288 K or 303 K or 318 K and rotation speed of 130 r/min. An Agilent gas chromatograph equipped with a detector (FID) and a HP-5 column (30 m × 0.35 mm × 0.25 μm) was used to separate and determine the concentration of phenol, 4-nitrophenol and 2,4-dinitrophenol in aqueous solutions. Of course, all samples were filtered with a 0.45 μm membrane, and phenolic compounds were extracted with dichloromethane for analysis. The oven temperature was programmed as follows: 80°C for 1 min, increasing to 150°C at 15 K/min and hold for 1 min, then increasing to 250°C at 10 K/min and hold for 1 min. The injector and detector temperatures were kept at 250°C and 280°C, respectively. Nitrogen (99.999%) was used as gas carrier and make-up gas.

Static Equilibrium Adsorption

Static equilibrium adsorption of the three phenolic compounds was performed at three different temperatures: 288, 303 and 318 K. Dry ZH-01 resin (0.1 g) was weighed accurately and introduced into a 250 mL conical flask directly, while the XAD-4 resin should be wetted in 0.5 mL methanol and rinsed with deionized water for more than three times before use. Then, 100 mL aqueous solution of certain concentration (c_0, mg/L) ranging from 100 mg/L to 500 mg/L was added to each flask. The flask was completely sealed and shaken in a ZD-880D model incubator shaker (Taichang, bolate Scientific Co. Inc.) at different temperatures under 130 r/min until it reached equilibrium. The concentration (c_e, mg/L) of the residual aqueous phase was determined using GC. Thus, the equilibrium adsorption quantity, Q_e (mmol/g), is calculated by Eq. (1).

$$Q_e = V_1 (c_0 - c_e)/MW \tag{1}$$

Where V_1 is the volumn of solution (L), W is the weight of dry resin (g) and M is the molecular weight of corresponding adsorbate.

Column Tests

Column adsorption was conducted using a 10 cm × 4.6 mm I.D. glass column with a 1 cm glass-wool connected with a 6672 reciprocating pump (Beijing Analytical Instrument Plant) at room temperature. The phenolic compounds solutions with initial concentration of 800 mg/L for phenol, 800 mg/L for 4-nitrophenol and 500 mg/L for 2,4-dinitrophenol were used to carry out column adsorption tests under the identical operation at a flow rate of 4 BV/h (1 BV = the volume of resin bed), and sodium hydroxide was used for desorbing phenolic compounds from ZH-01 at 333 K.

RESULTS AND DISCUSSION

Static Adsorption Isotherm

Equilibrium data concerning the adsorption of the adsorbates from aqueous solutions onto the two adsorbents are shown in Figs. 2a–2c and Figs. 3a–3c. It was well known that increasing temperature was disadvantageous for a physical adsorption process and the process had the reversible character. The equilibrium adsorption capacities of phenol, 4-nitrophenol and 2,4-dinitrophenol on Amberlite XAD-4 decreased with the increase of temperature, which was the characteristics of physical adsorption process. As for ZH-01, the equilibrium adsorption capacities for 2,4-dinitrophenol increased with the rise of temperature, which might be ascribed to the coexistence of the irreversible chemical process and the reversible physical process. The adsorbing capacities for phenol, 4-nitrophenol and 2,4-dinitrophenol on ZH-01 were significantly higher than those on Amberlite XAD-4, which might be attributed to its high micropore area and 2-carboxybenzoyl functional groups on the networks.
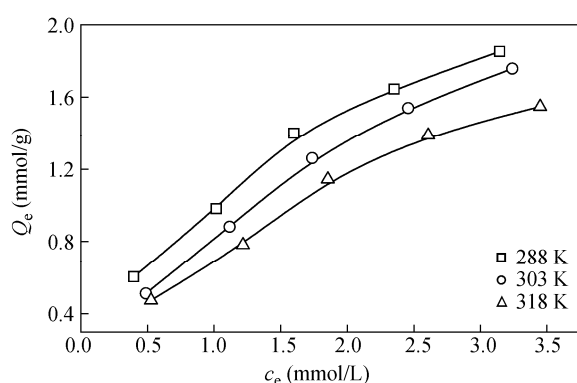

Fig. 2a Equilibrium adsorption isotherms for phenol on ZH-01 at different temperatures
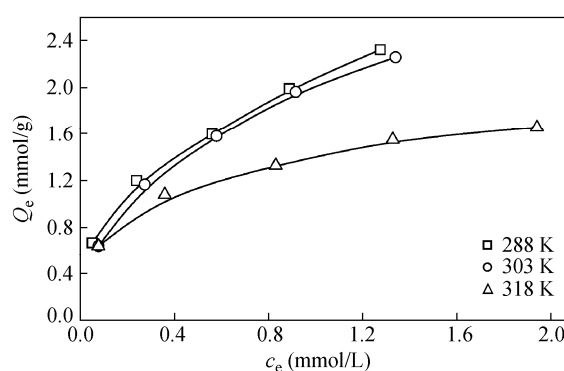
Fig. 2b Equilibrium adsorption isotherms for 4-nitrophenol on ZH-01 at different temperatures
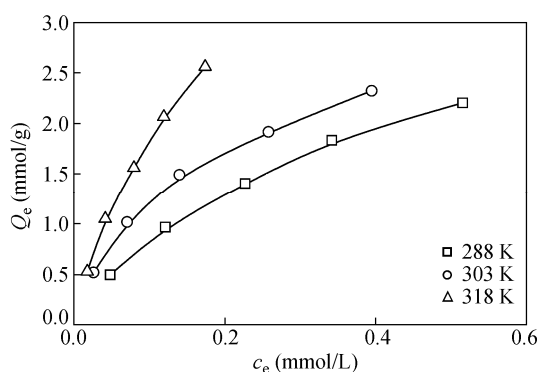

Fig. 2c Equilibrium adsorption isotherms for 2,4-dinitrophenol on ZH-01 at different temperatures

The Freundlich model[14, 15] was used to fit the equilibrium adsorption data. The model was rearranged and expressed as Eq. (2).

Freundlich equation: $$\lg Q_e = \lg K_f + 1/n \lg c_e \qquad (2)$$

Where Q_e was the equilibrium adsorption capacity (mmol/g), c_e the equilibrium concentration (mmol/L), K_f and n the characteristic constants. The correlative parameters of Freundlich adsorption isotherm equations for phenol, 4-nitrophenol and 2,4-dinitrophenol at different temperatures are listed in Table 2 and Table 3.
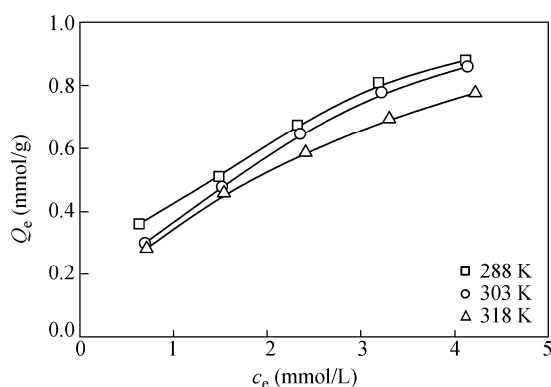
Fig. 3a Equilibrium adsorption isotherms for phenol on XAD-4 at different temperatures
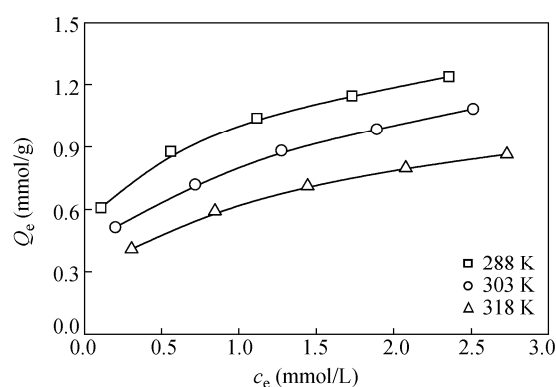

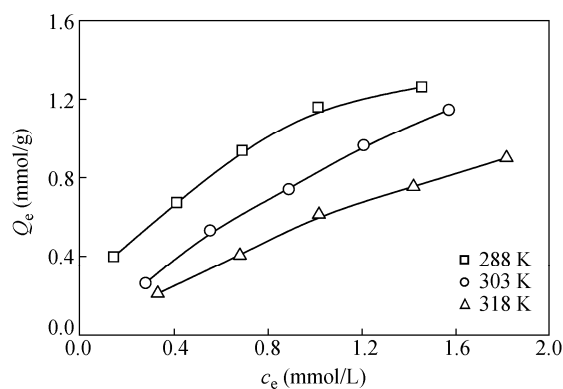**Fig. 3b** Equilibrium adsorption isotherms for 4-nitrophenol on XAD-4 at different temperatures

Fig. 3c Equilibrium adsorption isotherms for 2,4-dinitrophenol on XAD-4 at different temperature**s**

Table 2. Regression equation of $\lg Q_e$ versus $\lg c_e$ for Freundlich isotherms on ZH-01

Adsorbate	T (K)	Regression equation	K_f	n	R^2
Phenol	288	$\lg Q_e = 0.5581 \lg c_e + 0.0047$	1.0108	1.7918	0.9919
	303	$\lg Q_e = 0.6681 \lg c_e - 0.0798$	0.8322	1.4968	0.9958
	318	$\lg Q_e = 0.6556 \lg c_e - 0.1431$	0.7193	1.5253	0.9908
4-Nitrophenol	288	$\lg Q_e = 0.3841 \lg c_e + 0.3158$	2.0692	2.6035	0.9981
	303	$\lg Q_e = 0.4441 \lg c_e + 0.3047$	2.0170	2.2517	0.9988
	318	$\lg Q_e = 0.2979 \lg c_e + 0.1470$	1.4028	3.3568	0.9938
2,4-Dinitrophenol	288	$\lg Q_e = 0.6321 \lg c_e + 0.5464$	3.5188	1.5820	0.9952
	303	$\lg Q_e = 0.5446 \lg c_e + 0.6091$	4.0653	1.8362	0.9890
	318	$\lg Q_e = 0.6824 \lg c_e + 0.9413$	8.7357	1.4654	0.9960

Table 3. Regression equation of $\lg Q_e$ versus $\lg c_e$ for Freundlich isotherms on Amberlite XAD-4

Adsorbate	T (K)	Regression equation	K_f	n	R^2
Phenol	288	$\lg Q_e = 0.4932 \lg c_e - 0.3543$	0.4423	2.0276	0.9921
	303	$\lg Q_e = 0.6054 \lg c_e - 0.4252$	0.3757	1.6518	0.9970
	318	$\lg Q_e = 0.5726 \lg c_e - 0.4567$	0.3494	1.7464	0.9971
4-Nitrophenol	288	$\lg Q_e = 0.2316 \lg c_e + 0.0049$	1.0113	4.3178	0.9997
	303	$\lg Q_e = 0.2962 \lg c_e - 0.0881$	0.8164	3.3761	0.9967
	318	$\lg Q_e = 0.3427 \lg c_e - 0.2070$	0.6209	2.9180	0.9986
2,4-Dinitrophenol	288	$\lg Q_e = 0.5185 \lg c_e + 0.0407$	1.0982	1.9286	0.9916
	303	$\lg Q_e = 0.8465 \lg c_e - 0.0880$	0.8166	1.1813	0.9930
	318	$\lg Q_e = 0.8615 \lg c_e - 0.2496$	0.5629	1.1608	0.9943

The Freundlich adsorption model was a perfect fitting to the isotherm data with all the correlative factors $R^2 > 0.98$. Based on the Freundlich theory, coefficient K_f is an indication of the adsorbing capacity, and R^2 denotes the degrees of deviation from isotherm linearity. According to K_f in Table 2 and Table 3, the obviously higher adsorbing capacities toward phenol, 4-nitrophenol and 2,4-dinitrophenol on ZH-01 could be expected. The micropore area of ZH-01 was larger than that of Amberlite XAD-4, so the adsorbing capacities for these three adsorbates on ZH-01 were higher than those on Amberlite XAD-4 within the temperature range 288–318 K, which further proved that besides micropore area, the adsorption capacity would be affected by several other factors, including adsorbent polarity, active groups, and so on. Table 2 and Table 3 show the consistency using the above isothermal model that ZH-01 would exhibit its potential at even higher concentrations for column operations.

Isosteric Enthalpies for Phenolic Compounds Adsorption
The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff equation[15]:

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

where ΔH was the isosteric enthalpy change of adsorption reaction (kJ/mol) when Q_e was a fixed value, R was the ideal gas constant, and c_e was equilibrium concentration of solute in moles per liter at the absolute temperature T. At different temperatures (288, 303 and 318 K), c_e was obtained from the Freundlich isotherms when Q_e equaled to 0.6, 0.9 and 1.2 mmol. ΔH was calculated from the slope of lines plotted by $\ln c_e$ verse $1/T$. A summary of the calculated enthalpy values for ZH-01 adsorbing three phenolic compounds is listed in Table 4. The ΔH values implied that the adsorption of phenol and 4-nitrophenol by ZH-01 was an exothermic process, and however for 2,4-dinitrophenol it was an endothermic process, which indicated the adsorption enthalpies of 2,4-ditrphenol was not only from the intermolecular hydrogen bond between adsorbent and adsorbate. It was possible that the 2-carboxybenzoyl groups of the ZH-01 surface will interact with the 2,4-dinitrphenol molecules at high concentrations because it had much higher pKa value allowing a chemisorption's transition. However, it showed a physical adsorption process for phenol, 4-nitrophenol and 2,4-nitrophenol on XAD-4.

Table 4. Estimated thermodynamic parameters of the systems tested

Adsorbate	Adsorbent	Q_e (mmol/g)	ΔH (kJ/mol)	$-\Delta G$ (kJ/mol)			$-\Delta S$ (J/(mol·K))		
				288 K	303 K	318 K	288 K	303 K	318 K
Phenol	ZH-01	0.6	−27.69				81.08	84.24	84.27
		0.9	−22.19	4.34	3.43	3.42	58.91	61.91	61.95
		1.2	−18.29				43.87	46.73	46.76
	XAD-4	0.6	−13.05				29.03	31.39	29.83
		0.9	−10.22	4.69	4.01	4.46	18.25	20.50	19.01
		1.2	−8.214				11.08	13.22	11.81
4-Nitrophenol	ZH-01	0.6	−34.25				310.0	303.4	301.0
		0.9	−28.02	10.34	8.51	7.72	247.0	241.1	238.0
		1.2	−23.59				203.0	197.6	195.0
	XAD-4	0.6	−18.50				37.12	36.11	30.9
		0.9	−4.92	7.81	8.10	9.60	23.47	22.51	17.56
		1.2	−12.20				13.81	12.89	8.18
2,4-Dinitrophenol	ZH-01	0.6	28.69				−112.78	−109.97	−108.43
		0.9	29.78	3.79	4.63	3.87	−129.72	−113.56	−105.81
		1.2	30.61				−119.44	−116.30	−108.43
	XAD-4	0.6	−31.33				92.74	93.56	88.87
		0.9	−23.41	4.62	2.98	3.07	65.24	67.43	63.96
		1.2	−17.80				45.76	48.91	46.32

The Free Energies and Entropies of Adsorption for Phenolic Compounds

The free energies of adsorption were calculated with a derivative Gibbs equation:

$$\Delta G = -nRT \tag{4}$$

where *n* was a coefficient of Freundlich equation. The entropies change of adsorption was calculated with Gibbs-Helmholtz equation.

$$\Delta G = \Delta H - T\,\Delta S \tag{5}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{6}$$

A summary of the calculated values for enthalpy, free energy, entropy of ZH-01 and XAD-4 adsorbing phenic compounds is listed in Table 4.

Little change in enthalpy at different Q_e showed the homogeneous nature of the adsorbent surface once again. The absolute heat quantities for ZH-01 were larger than XAD-4's. So, the adsorption abilities of ZH-01 for phenolic compounds were stronger than XAD-4's. As the adsorbate molecules after adsorption could orderly cover the surface of adsorbent, the disorder and entropy were almost decreasing. Changes in enthalpy, free energy and entropy (always negative) were indicative of an exothermic, spontaneous and disorder process for phenol and 4-nitrophenol. All the data of ZH-01 and XAD-4 showed that they belonged to a physical adsorption process. While the values of the enthalpy changes, free energy changes and entropy changes for 2,4-dinitrophenol showed an endothermic process, and its magnitudes on ZH-01 for 2,4-dinitrophenol indicated a chemisorption's transition process.

Column Adsorption and Desorption

Based on the equilibrium adsorption capacities for the phenolic compounds on ZH-01, it was hopeful for ZH-01 to act as a polymeric adsorbent for removal of organic pollutants from drinking water and the recovery of organics from wastewater. So it was necessary to test the dynamic adsorption and desorption. The adsorption curves of phenolic compounds from the wastewater by the continuous flow column are shown in Fig. 4, where *c* was the concentration at different bed volumes of the effluent. The breakthrough point appeared at 25 BV, 100 BV and 120 BV, respectively. Desorption experiments were performed with sodium hydroxide solution (40 g/L) as the desorption agent and the volume of sodium hydroxide at the rate of desorption 1.0 BV/h is about 6 bed volume. More than 94.1% of the adsorbed phenolic compounds were desorbed in all cases, indicating that ZH-01 possesses excellent desorption performance. The desorption curves are shown in Fig. 5.
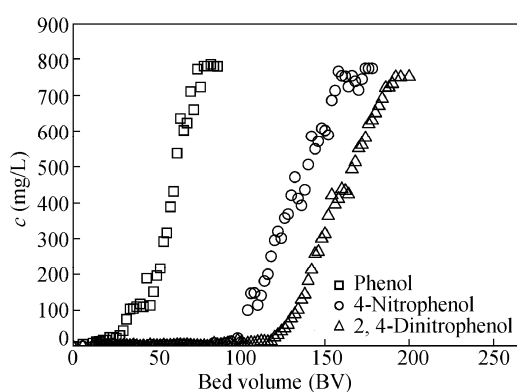

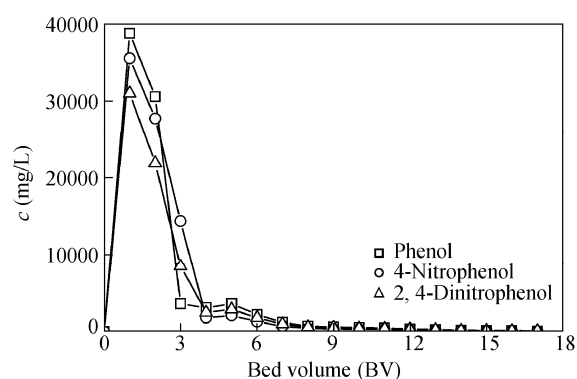**Fig. 4** Dynamic adsorption for nitrophenols on ZH-01

Fig. 5 Dynamic desorption for nitrophenols on ZH-01

CONCLUSIONS

A hypercrosslinked polymeric adsorbent (ZH-01) for adsorbing and removing phenolic compounds from their aqueous solutions had been studied, and the equilibrium adsorption capacity for phenolic compounds on ZH-01 was markedly higher than that on XAD-4, which could be attributed to its high micropore area and the 2-carboxybenzoyl functional groups. The Freundlich isotherm model could perfectly fit the experimental data in the temperature range of 288−318 K.

The thermodynamics study drew a conclusion for adsorbing phenolic compounds on ZH-01 that there was a coexistence process of physical adsorption and chemical transitions for 2,4-dinitrophenol but for phenol and 4-nitrophenol on ZH-01 were physical adsorption processes.

Column adsorption studies for phenolic compounds of wastewater on ZH-01 showed the higher adsorption capacity. Sodium hydroxide was used for desorpting phenolic compounds from ZH-01 with excellent performance.

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