

ADSORPTION CHARACTERISTICS OF CHLOROPHENOLS FROM AQUATIC SYSTEMS BY HYPERCROSSLINKED RESINS MODIFIED WITH BENZOYL GROUP*

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Abstract A hypercrosslinked polymeric adsorbent (ZH-03) for adsorbing and removing chlorophenolic compounds from their aqueous solutions was studied, including the static adsorption. The equilibrium adsorption data were fit to Freundlich adsorption isothermic models to evaluate the model parameters. Thermodynamic studies on the adsorption of chlorophenolic compounds on ZH-03 indicated that there were chemisorption transitions for 2,4,6-trichlorophenol and physical adsorption processes for 2-chlorophenol and 2,6-chlorophenol, and ZH-03 showed the homogeneous nature of the adsorbent surface. Column adsorption for chlorophenols wastewater shows the advantages of the ZH-03 adsorbent for adsorbing the following chlorophenolic compounds as 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol. Sodium hydroxide was used for desorbing chlorophenols from ZH-03 and showed excellent performance.

Keywords: Hypercrosslinked polymeric adsorbent; Chlorophenolic compounds; Adsorption; Adsorption enthalpy; Thermodynamics; Chemisorption's transition.

INTRODUCTION

The aquatic environment is increasingly affected by organic chemicals, which are inevitably introduced into the environment in large quantities according to their specific application. Chlorophenols have been widely used as preservatives, pesticides, antiseptics and disinfectants^[1]. These substances are carcinogenic and quite persistent. The US Environmental Protection Agency (EPA) has compiled a list of 11 phenol compounds considered to be priority pollutants in the aquatic medium. Among them, chlorophenols are especially toxic and potentially carcinogenic. In 1982, the Environmental European Community (EEC) issued another pollutant list^[2] that included many polychlorophenols and established their maximum allowable concentration in drinking water (0.5 mg/L). Development of efficient methods to remove these compounds from wastewater becomes more and more urgent.

Current methods for removing phenols from wastewater include microbial degradation, physical absorption, chemical oxidation, incineration, solvent extraction, reverse osmosis and irradiation. A variety of adsorbents used for removal of phenols from aqueous solutions include activated carbon^[3], bentonite and perlite^[4], rubber seed coat^[5], hydrotalcite and its calcined product^[6], acid-activated bituminous shale^[7], zirconium (IV) arsenate-vanadate ion-exchanger^[8], cross-linked polyvinylpyrrolidone^[9], and polymeric XAD-16 resins^[10]. Amberlite XAD-4 resin is one of polystyrene adsorbents and has high surface area^[11] as widely reported, which is considered as the best polymeric adsorbent for removing phenolic compounds from aqueous

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streams. However, Amberlite XAD-4 resin has hydrophobic surface^[12] and a lower adsorption capacity for most organic substances than activated carbon^[13, 14], which limits its wide applications in the chemical treatment for wastewater.

Hypercrosslinked polymers developed by Davankov and Tsyurupa are remarkable materials exhibiting extremely high apparent surface area and exceptional sorption properties. Hypercrosslinking prevents collapse of the expanded network after removal of the solvent and the result is the creation of an extensive micropore network^[15].

It was reported that some hypercrosslinked polymers modified by different functional groups such as acetyl (MX-4)^[16], phenolic hydroxyl (AM-1)^[14], oxygen (NJ-8)^[13] and 2-carboxyl benzoyl (ZH-01)^[17] have shown better performances and have overcome the difficulties of Amberlite XAD-4 because of the polarity matching between the modified adsorbents and polar adsorbate and the microporous structure of adsorbents^[13, 16].

In the present research, a hypercrosslinked polymeric adsorbent containing benzoyl groups (ZH-03) for the removal of chlorophenolic compounds from their aqueous solutions was investigated. In comparison with Amberlite XAD-4, ZH-03 has higher adsorption capacity for chlorophenolic compounds such as 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol, because of its high micropore area and the presence of benzoyl functional groups.

EXPERIMENTAL

Materials

Styrene and divinylbenzene (purity: 50.4%) were purchased from Dongda Chemical Co. (Shandong province, China). Chloromethyl methylether was obtained from Langfang Chemical Co. (Hebei province, China). Acetone, methanol, zinc chloride, toluene and benzoyl chloride were supplied by Shanghai Chemical Reagent Plant (Shanghai, China) and used without further purification. The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). 2-Chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol 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 solution with a concentration of 4000 mg/L, which was kept in sealed ground-glass-stoppered brown bottles and stored in a refrigerator at 4°C.

Wastewater samples were collected from the mixing pond of Huang Long Chemical Plant in Yancheng, China. The major pollutants in these samples are 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol with chemical oxygen demand (COD) of about 47050 mg/L. To maintain the stability of the samples, the wastewater was filtered through a 0.45 µm membrane to remove suspended particles, and the filtered wastewater was subsequently kept at 4°C.

Synthesis of ZH-03 Adsorbent

ZH-03 were synthesized according to literature^[18]. 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 were added slowly at room temperature. The mixture was further stirred for 8 h at 408 K. After being cooled, 6 g benzoyl chloride were added to the above mixture at 338 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 properties of ZH-03 and XAD-4 resins are given in Table 1.

Table 1. Typical properties of the polymeric resins

Property	XAD-4	ZH-03
Polarity	Nonpolar	Moderate polar
Specific surface area (m ² /g)	880	883.4
Average diameter (nm)	5.8	1.33
Micropore area (m ² /g)	3	492.6
Average particle size (mm)	0.5	0.5
Porosity (mL/g)	1.0	0.224
Residual chlorine content (%)	0	4.4
Color	White	Brown

Equipment

Equipment used in the present study included an orbital shaker, with a temperature controlling of 288 or 303 or 318 K and a rotation speed of 130 r/min.

An Agilent gas chromatograph equipped with an HP-5 column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$) was used to separate and determine the level of 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol in water samples. Of course, all samples were filtered with a $0.45\text{ }\mu\text{m}$ membrane and chlorophenols were extracted with toluene for analysis. The oven temperature was programmed as follows: 80°C for 1 min, increasing to 150°C at $10^\circ\text{C}/\text{min}$ and hold for 2 min, then increasing to 250°C at $15^\circ\text{C}/\text{min}$, hold for 1 min. The injector and detector temperatures were kept at 250°C and 280°C , respectively. Nitrogen (99.999%) was used as carrier gas and make-up gas.

Experimentation

Adsorption isotherm

The adsorption thermodynamics was studied at three different temperatures (288, 303 and 318 K) using ZH-03 for the following adsorbate of 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol. 100 mg of adsorbent was placed in a 250 mL glass bottle containing 100 mL of 2-chlorophenol and 2,6-dichlorophenol solutions of initial concentrations of 200, 400, 600, 800, and 1000 mg/L, respectively, and 2,4,6-chlorophenol compound solutions of initial concentrations of 100, 200, 300, 400, and 500 mg/L, respectively, and the mixture was equilibrated by agitatin using a horizontal shaker operated at 130 r/min.

Column tests

Column adsorption was conducted using a $10\text{ cm} \times 4.6\text{ mm}$ I.D. glass column with a 1 cm glass-wool connected with a 6672 reciprocating pump (Beijing Analytical Instrument Plant) at room temperature. The chlorophenols solution with initial concentration of 8970 mg/L for 2-chlorophenol, 1869 mg/L for 2,6-dichlorophenol and 975 mg/L for 2,4,6-trichlorophenol in the wastewater (Chemical Plant of Yancheng, Jiangsu) were used to carry out column sorption tests under the identical operation at flow rate 4 BV/h (1 BV = the volume of resin bed), and sodium hydroxide was used for desorpting chlorophenol from ZH-03 at 318 K.

RESULTS AND DISCUSSION

Equilibrium Adsorption

The results of a series of isothermal adsorption experiments performed at 288, 303 and 318 K are shown in Figs. 1a–1c and Figs. 2a–2c.

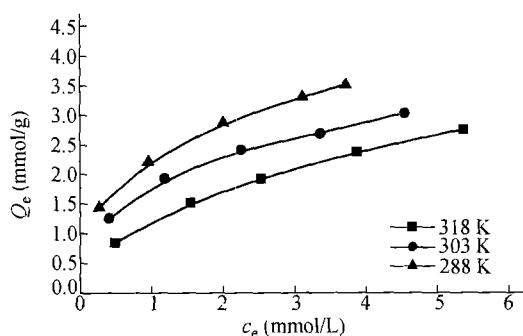


Fig. 1a Equilibrium adsorption isotherms for 2-chlorophenol on ZH-03 at different temperatures

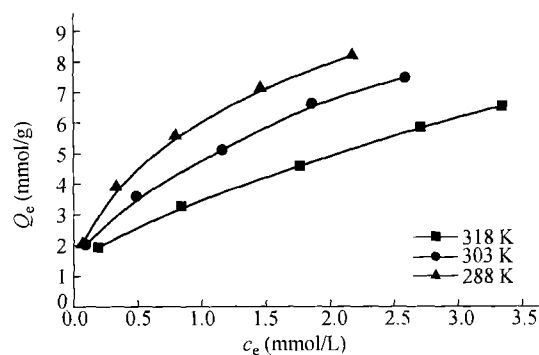


Fig. 1b Equilibrium adsorption isotherms for 2,6-dichlorophenol on ZH-03 at different temperatures

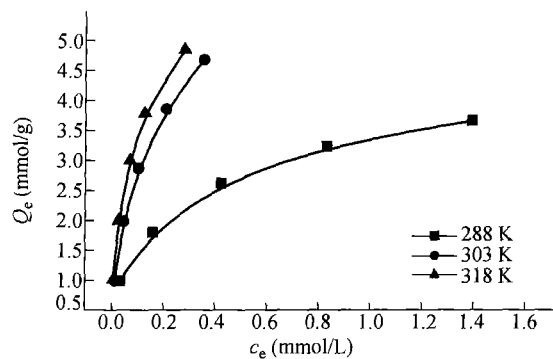


Fig. 1c Equilibrium adsorption isotherms for 2,4,6-trichlorophenol on ZH-03 at different temperatures

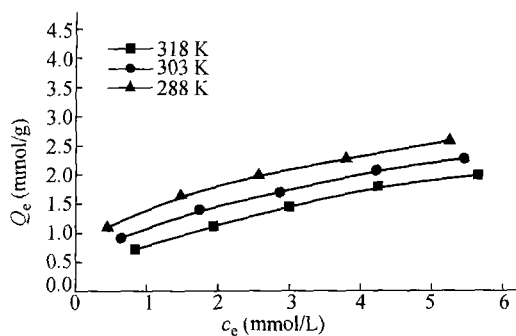


Fig. 2a Equilibrium adsorption isotherms for 2-chlorophenol on XAD-4 at different temperatures

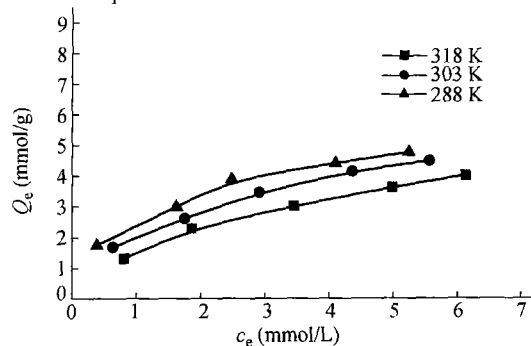


Fig. 2b Equilibrium adsorption isotherms for 2,6-dichlorophenol on XAD-4 at different temperatures

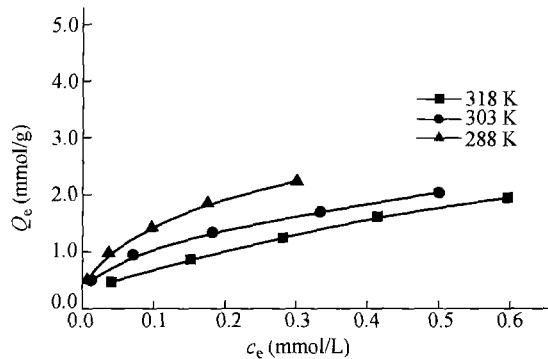


Fig. 2c Equilibrium adsorption isotherms for 2,4,6-trichlorophenol on XAD-4 at different temperatures

On ZH-03 adsorbent greater adsorption for 2-chlorophenol and 2,6-dichlorophenol is apparent at a lower temperature. In contrast, 2,4,6-trichlorophenol shows higher adsorption at higher temperatures. The data were also evaluated in accordance with the Freundlich adsorption equation.

$$\ln Q_e = \ln K_F + 1/n \ln c_e \quad (1)$$

where Q_e is the equilibrium adsorption capacity (mmol/g), c_e the equilibrium concentration (mmol/L), and K_F and n the characteristic constants. The evaluated constants for the isotherms are shown in Table 2.

Table 2. Regression equation of $\lg Q_e$ versus $\lg c_e$ for Freundlich isotherms of ZH-03

Adsorbate	T (K)	Regression equation	K_f	n	R^2
2-Chlorophenol	288	$\lg Q_e = 0.3420 \lg c_e + 0.3531$	2.2548	2.9239	0.9998
	303	$\lg Q_e = 0.3633 \lg c_e + 0.2479$	1.7697	2.7525	0.9985
	318	$\lg Q_e = 0.4950 \lg c_e + 0.0847$	1.2153	2.0202	0.9996
2,6-Dichlorophenol	288	$\lg Q_e = 0.4001 \lg c_e + 0.7850$	6.0954	2.4994	0.9998
	303	$\lg Q_e = 0.3964 \lg c_e + 0.7015$	5.0292	2.5227	0.9944
	318	$\lg Q_e = 0.4240 \lg c_e + 0.5771$	3.7766	2.3585	0.9902
2,4,6-Trichlorophenol	288	$\lg Q_e = 0.3560 \lg c_e + 0.5334$	3.4151	2.8074	0.9956
	303	$\lg Q_e = 0.4633 \lg c_e + 0.8997$	7.9378	2.1584	0.9946
	318	$\lg Q_e = 0.4174 \lg c_e + 0.9449$	8.8085	2.3958	0.9915

From Tables 2 and 3, it is quite obvious that our experimental data of ZH-03 and Amberlite XAD-4 resins correspond to the Freundlich adsorption law for all the correlative factors R^2 are larger than 0.99, and the results indicate that the adsorption capacities on ZH-03 are significantly higher than that on Amberlite XAD-4 for the three chlorophenolic compounds, which can be convinced by the value of K_f , a relative indicator of adsorption capacity according to the Freundlich theory^[19]. All these data in Table 2 show the consistency using the above isothermal model that ZH-03 will exhibit its potential at even higher concentrations for column operations.

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

Adsorbate	T (K)	Regression equation	K_f	n	R^2
2-Chlorophenol	288	$\lg Q_e = 0.3441 \lg c_e + 0.1614$	1.4501	2.9061	0.9996
	303	$\lg Q_e = 0.4248 \lg c_e + 0.0459$	1.1115	2.3540	0.9987
	318	$\lg Q_e = 0.5468 \lg c_e - 0.0957$	0.8022	1.8288	0.9973
2,6-Dichlorophenol	288	$\lg Q_e = 0.3895 \lg c_e + 0.4085$	2.5615	2.5674	0.9926
	303	$\lg Q_e = 0.4585 \lg c_e + 0.3181$	2.0802	2.1810	0.9978
	318	$\lg Q_e = 0.5421 \lg c_e + 0.1864$	1.5360	1.8447	0.9915
2,4,6-Trichlorophenol	288	$\lg Q_e = 0.3946 \lg c_e + 0.5574$	3.6091	2.5674	0.9915
	303	$\lg Q_e = 0.3827 \lg c_e + 0.4148$	2.5990	2.6130	0.9978
	318	$\lg Q_e = 0.5390 \lg c_e + 0.4004$	2.5142	1.8553	0.9926

Isosteric Enthalpies for Chlorophenolic Compounds Adsorption

The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff equation^[20]:

$$\ln(1/c_e) = \ln(K_0) + (-\Delta H/RT) \quad (2)$$

where ΔH is the isosteric enthalpy change of adsorption reaction (kJ/mol) when Q_e is a fixed value, R is the ideal gas constant, and c_e is equilibrium concentration of solute in moles per liter at the absolute temperature T . At different temperatures (288, 303 and 318 K), c_e is obtained from the Freundlich isotherms when Q_e equals to 1.5, 2.0 and 2.5 mmol. ΔH was calculated from the slope of line plotted by $\ln c_e$ versus $1/T$. A summary of the calculated enthalpy values for ZH-03 adsorbing the three chlorophenolic compounds is listed in Table 4. The ΔH values imply that the adsorption of 2-chlorophenol and 2,6-dichlorophenol by ZH-03 is an exothermic process, however, for 2,4,6-trichlorophenol it is an endothermic process because almost all the values are less than 42 kJ/mol except for the adsorption of 2,4,6-trichlorophenol on ZH-03, which indicates that the adsorption enthalpies of 2,4,6-trichlorophenol are not only from the intermolecular hydrogen bond between the adsorbent and adsorbate. It is possible that the benzoyl group of the ZH-03 surface will interact with the 2,4,6-trichlorophenol molecule at high concentrations because it has much higher pK_a value allowing a chemisorption's transition to come into being. However, it shows a physical adsorption process for 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol on XAD-4.

The Free Energies and Entropies of Adsorption for Chlorophenolic Compounds

The free energies of adsorption were calculated with a derivative Gibbs equation^[21]:

$$\Delta G = -nRT \quad (3)$$

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

$$\Delta G = \Delta H - T \Delta S \quad (4)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (5)$$

A summary of the calculated values of enthalpy, free energy and entropy for ZH-03 and XAD-4 adsorbing chlorophenolic compounds is listed in Table 4.

Little change in enthalpy at different Q_e shows homogeneous nature of the adsorbent surface once again. The absolute heat quantities for ZH-03 are larger than those for XAD-4. So, the adsorption abilities of ZH-03 for chlorophenols are stronger than those of XAD-4. Because the adsorbate molecules can orderly cover the surface of adsorbent, the disorder and entropy are almost decreasing. Changes in enthalpy, free energy, and entropy (always negative) are indicative of an exothermic, spontaneous and disorder process for 2-chlorophenol and 2,6-dichlorophenol. All the data on ZH-03 and XAD-4 show that they belong to physical adsorption process. While the values of the enthalpy changes, free energy changes and entropy changes for 2,4,6-trichlorophenol show an endothermic process and its magnitudes on ZH-03 for 2,4,6-trichlorophenol indicate a chemisorption's transition process.

Table 4. Estimated thermodynamic parameters of the systems tested

Adsorbate	Adsorbent	Q_e (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/(mol • K))		
				288 K	303 K	318 K	288 K	303 K	318 K
2-Chlorophenol	ZH-03	1.5	-40.95	-7.00	-6.93	-5.34	-117.9	-112.3	-111.9
		2.0	-34.43				-95.24	-90.76	-91.48
		2.5	-29.36				-77.64	-74.03	-75.53
	XAD-4	1.5	-26.46	-6.96	-5.93	-4.84	-67.71	-67.76	-67.99
		2.0	-18.59				-40.38	-41.78	-43.24
		2.5	-12.52				-19.31	-21.75	-24.15
2,6-Dichlorophenol	ZH-03	1.5	-33.83	-5.99	-6.36	-6.24	-96.67	-90.66	-86.76
		2.0	-32.77				-92.97	-87.16	-83.43
		2.5	-31.96				-90.17	-84.49	-80.88
	XAD-4	1.5	-33.74	-6.15	-5.49	-4.88	-95.80	-93.23	-90.75
		2.0	-28.48				-77.54	-75.88	-74.21
		2.5	-24.39				-63.33	-62.38	-61.35
2,4,6-Trichlorophenol	ZH-03	1.5	49.23	-6.72	-5.44	-6.33	194.3	180.4	174.7
		2.0	52.35				205.1	190.7	184.5
		2.5	54.77				213.5	198.7	192.1
	XAD-4	1.5	-32.26	-6.15	-6.58	-4.91	-90.66	-84.75	-86.01
		2.0	-27.42				-73.85	-68.78	-70.79
		2.5	-23.64				-60.73	-56.30	-58.90

Adsorption of Chlorophenols in Wastewater by ZH-03

Because of the advantages of high adsorption capacity for chlorophenolic compounds in our research and high specific surface area and microporous area of ZH-03, it will be hopeful for ZH-03 to be developed as a polymeric adsorbent for removal of organic pollutants from drinking water or recovery of organics from wastewater. Therefore, it is necessary to test the column adsorption and desorption. The removal curve of chlorophenolic compounds from the wastewater by the continuous flow column is shown in Fig. 4. When bed volume is 18 BV, the adsorption ratio of the ZH-03 is 91% for 2-chlorophenol, 94% for 2,6-dichlorophenol and 99% for 2,4,6-trichlorophenol.

Desorption experiments were performed with sodium hydroxide solution (4%, W/V) as the desorption agent, and the volume of sodium hydroxide at the rate of desorption 1.0 BV/h was about 6 bed volume. More than 95.8% of the adsorbed chlorophenols was desorbed in all cases, indicating that ZH-03 possessed excellent desorption performance. The adsorption and desorption curves are shown in Fig. 5.

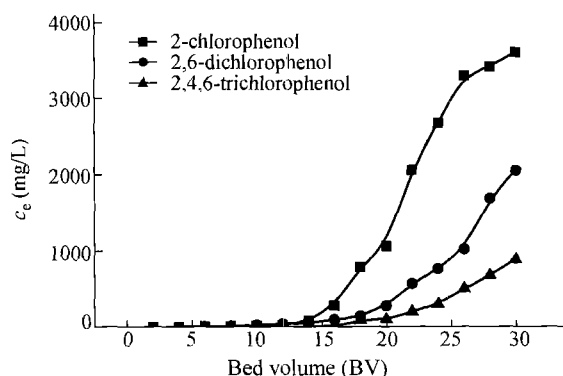


Fig. 4 Dynamic adsorption for chlorophenols on ZH-03

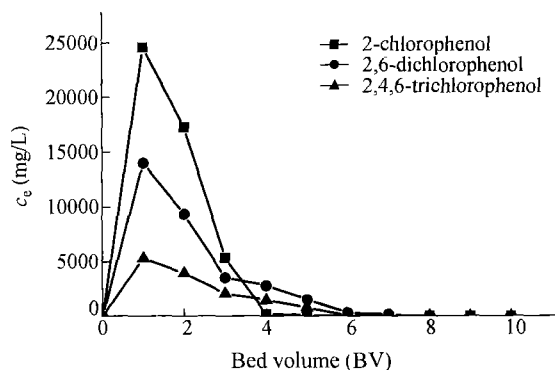


Fig. 5 Dynamic desorption for chlorophenols on ZH-03

CONCLUSIONS

A hypercrosslinked polymeric adsorbent (ZH-03) for adsorbing and removing chlorophenolic compounds from their aqueous solutions has been studied, and the equilibrium adsorption capacity for chlorophenolic compounds on ZH-03 are markedly higher than that on XAD-4, which can be attributed to its high micropore area and the benzoyl functional group.

The thermodynamics study draws a conclusion for adsorbing chlorophenolic compounds on ZH-03 that there is chemisorption's transitions for 2,4,6-trichlorophenol but for 2-chlorophenol and 2,6-phenol on ZH-03 are physical adsorption processes.

All the isotherm data for the chlorophenolic compounds on the XAD-4 and ZH-03 can be satisfactorily fit for the Freundlich equation.

Column adsorption studies for chlorophenols of wastewater on ZH-03 show a higher adsorption capacity. Sodium hydroxide was used for desorpting chlorophenol from ZH-03 with the excellent performance.

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