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Adsorption Behaviors of 2,4-Dichlorophenol onto Hypercross-linked Resins

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Abstract: Experimental investigations were conducted on the adsorption characteristics of 2,4 -dichlorophenol by two hypercross-linked resins JP-01 and XAD-4. The static adsorption was studied. Within temperature range of 288-313K, the equilibrium adsorption date was fitted to freundlich adsorption isotherm models to evaluate the model parameters. The enthalpies, free energy, entropy were indicative of an exothermic, a spontaneous and disorder decreasing process. The magnitudes for 2,4-dichlorophenol on JP-01 on XAD-4 show a physical adsorption process. The results showed that the JP-01 adsorbent was better than the Amberlite XAD-4 for removing the 2,4-dichlorophenol in aqueous solutions.
Keywords: Hypercrosslinked resin; 2, 4- dichlorophenol; Thermodynamics adsorption.

1. Introduction

Chlorophenolic compounds are very toxic, and many are known or suspected human carcinogens. They have been widely used for many industrial purposes. The removal of chlorophenols are of high industrial and environmental interest [1~2]. The adsorption resin is another adsorbent widely employed for isolation and purification of organic substances, treatment of wastewaters, solid phase extraction, and so on. A variety of materials has been developed and tested, such as Amberlite XAD. Since the adsorption ability is strongly dependent on the nature of the polymers and of the solutes in water, the hypercrosslinked polymers having high surface area and right micropore network were developed and studied [3]. Otherwise, regeneration of the resin can be accomplished by simple, nondestructive means, such as solvent washing, which provide the potential for solute recovery.

The newly hypercrosslinked adsorbent JP-01 was prepared, which was modified by *1-(2-Pyridylazo)-2-naphthol-6-sulphonic Acid* group, and investigation of 2,4-dichlorophenol onto Amberlite XAD-4 and JP-01.

2. Experimental

2.1. Materials and methods

Acetone, methanol, 1-(2-pyridylazo)-2-naphthol-6-sulphonic acid, 2,4-dichlorophenol, zinc chloride were from Shanghai Chemical Reagent Plant (Shanghai, China) and used without further purification. Photographic-grade gelatin was obtained from Yancheng Dafeng Gelatin Plant (Yancheng, China). The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). JP-01 was synthesized as the literature [1].

The concentration of 2,4-dichlorophenol in water was determined by gas chromatography (Agilent HP 6890 series п, USA) and a split /splitless injection port. The column was a 30m×0.25mm I.D. fused-silica capillary column HP-1 and a stationary phase thickness of 0.25um (Agilent USA). The detector was equipped with Flame ionization Detector. The oven temperature was programmed as follows: 80℃ during 1 min, at 10℃ to 150℃, 2min hold at 150℃ The injector and detector temperatures set at 200℃ and 250℃ respectively. nitrogen (99.999%) was used as carrier and make-up gas.

2.2. Experimental Procedure

2.2.1 Selection of adsorbents

Some adsorbents including macroporous Amberlite XAD-4, hypercrosslinked NDa-99 and JP-01 resin were used for adsorbing the 2,4-dichlorophenol from its aqueous solutions of the initial concentration 600mg/L at 293K. The concentration of 2,4-dichlorophenol were measured at 250℃ using GC.

2.2.2. Adsorption isotherm

The adsorption thermodynamics were studied at three different temperatures (288K, 303K and 318K) using JP-01 for the adsorbate 2,4-dichlorophenol. A 100mg of adsorbent was taken in a 250ml glass bottle containing 100ml of the 2,4-dichlorophenol solution of the initial concentration (200mg/L, 400mg/L, 600mg/L, 800mg/L, and 1000mg/L respectively) and the mixture were agitated about 24h to reach the equilibrium using a horizontal shaker operated at 130rpm. Kinetics of sorption were determined by analyzing adsorptive uptake of 2,4-dichlorophenol from aqueous solution whose initial concentration is 800 mg/L at different time intervals of 1min, 5min, 10min, 20min, 30min, 60min, 90min, 120min, 150min and 210min at 293K. In order to get accurate results for each point on the graph, represent independent bottle containing adsorbent and 2,4-dichlorophenol mixture.

3. Results and discussion

3.1. Selection of adsorbents

Amberlite XAD-4, NDa-99, hypercrosslinked JP-01 were used for adsorbing 2,4-dichlorophenol from its aqueous solutions and the results were in Fig. 1, where showed the relatively favorable advantage of the newly hypercrosslinked adsorbents JP-01 for the 2,4-dichlorophenol in water. The typical properties of the above adsorbents were listed in Table 1.

Table 1 Typical properties of the polymeric resins

Property	XAD-4	JP-01	NDa-99
Polarity	Nonpolar	Moderate polar	Moderate polar
Specific surface area (m^2/g)	880	1102.5	726.5
Average diameter (nm)	5.8	1.3	1.3
Micropore area (m^2/g)	3	662	393.8
Average particle size (mm)	0.5	0.5	0.5
Porosity (ml/g)	1.0	0.3	0.59
Residual chlorine content (%)	0	2.62	0.76
Color	White	Brown	Brow

From Table 1, it is obvious that the specific surface area is not only the predominant factor for adsorbing 2,4-dichlorophenol using JP-01 adsorbents because NDa-99 has the least surface area. Besides the difference in the polarity, the microporous structure and the pore distribution of adsorbents are the other important factors affecting adsorption.

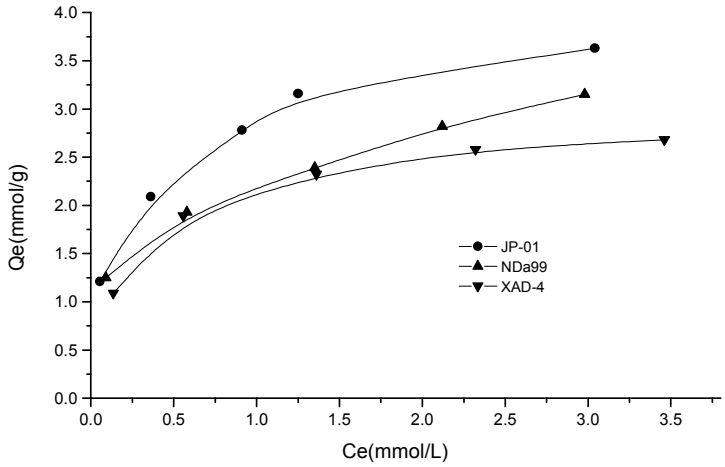

Fig. 1 The Equilibrium Adsorption Isotherms of 2,4-dichlorophenol on three Adsorbents at 303K

3.2. Equilibrium Adsorption of 2,4-dichlorophenol

The equilibrium adsorption isotherms of 2,4-dichlorophenol from water on Amberlite XAD-4 and JP-01 resins at 283K, 288K and 303K were shown in Fig.2a-2b, which indicated the hypercrosslinked adsorbents' satisfactory adsorbing efficiency.

Batch equilibrium adsorption date of 2,-dichlorophenol are fitted to Freundlich adsorption isotherm equations[2], which is expressed respectively as Freundlich equation:

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

where Q_e is the equilibrium adsorption capacity (mmol/g), C_e is the equilibrium concentration (mmol/L), K_F and n are the characteristic constants. Conformation of the date into Freundlich isotherm model indicates the homogenous nature of the adsorbent surface [3] and the formation of the monolayer coverage of the adsorbate molecule over the adsorbent surface at the experimental condition.

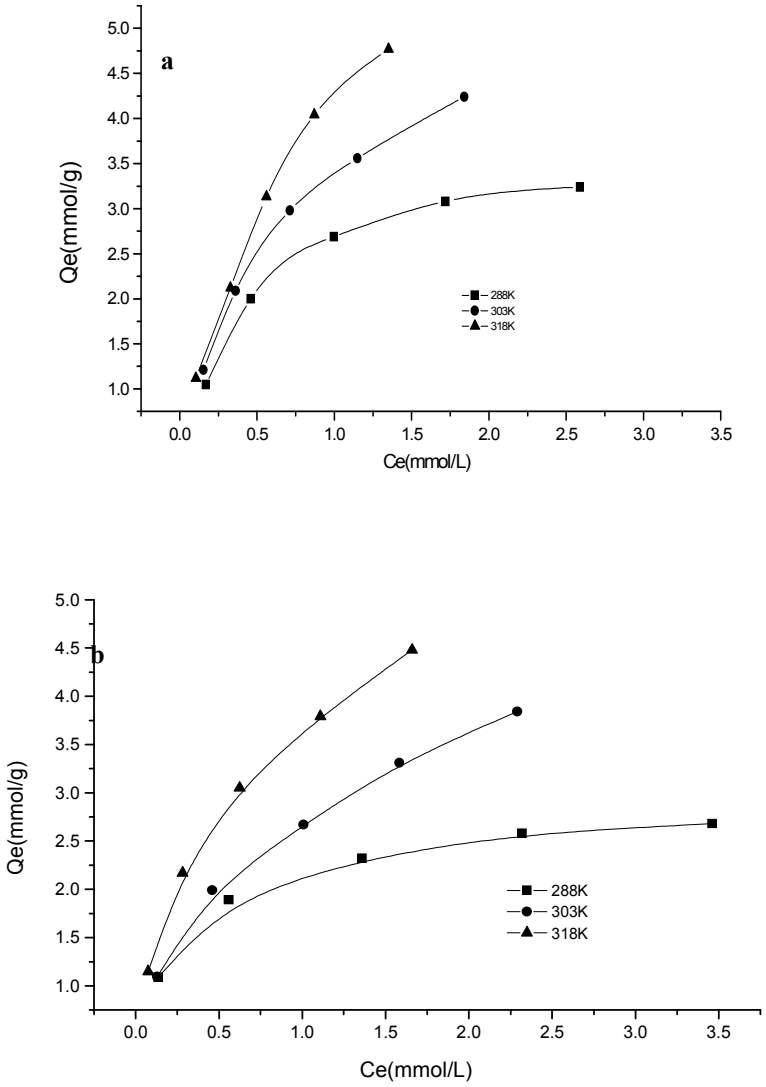

Fig. 2 The Equilibrium Adsorption Isotherms of 2,4-dichlorophenol on JP-01(a) and XAD-4 (b)

From Table 2, it is quite obvious that our set of experimental data corresponds well to the Freundlich adsorption law on JP-01 and Amberlite XAD-4 resins for all the correlative factors R^2 are larger than 0.99. The results indicate that the adsorption capacities on JP-01 is significantly higher than that on Amberlite XAD-4 for the 2,4-dichlorophenol, which can be convinced by the value of K_F, a relative indicator of adsorption capacity according to the Freundlich theory [4].

Table 2 The evaluated constants of 2,4-dichlorophenol from water on JP-01 and Amberlite XAD-4 resins for Freundlich equation isotherms

Adsorbents	T (K)	Freundlich equation	K_F	n	R^2
JP-01	288	logQe =0.3249logCe + 0.4044	2.4728	3.0779	0.9878
	303	logQe = 0.4296logCe + .5938	3.9246	2.3277	0.9975
	318	logQe = 0.3116logCe + 0.6720	4.6989	3.2092	0.9816
XAD-4	288	logQe = 0.2804logCe + 0.3085	2.0354	3.5663	0.9644
	303	logQe = 0.4338logCe + 0.4315	2.7009	2.3052	0.9984
	318	logQe = 0.4399logCe + 0.5637	3.6618	2.2732	0.9975

The value of K_F and low n show that JP-01 will be used for removing the different concentrations 2,4-dichlorophenol in water. It is obvious that surface area of the adsorbents plays an important role in adsorptive process from Table 1 and Fig. 2a and 2b. Due to the right molecular volume of adsorbates, the adsorbates can be adsorbed tightly in the fine pores of the JP-01. In comparison with the 2,4-dichlorophenol owns the structure of double bond, which has the stronger interaction between the 2,4-dichlorophenol molecules and the adsorbents

and results in the higher adsorption capacities. All these data in Table 2 show the consistency using Freundlich isothermal models that JP-01 will exhibit its potential at even higher concentrations for column operations.

3.3. Adsorption thermodynamics of 2,4-dichlorophenol

The isomeric enthalpies of adsorption were calculated with a derivative Van't Hoff equation[5]:

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

where ΔH is the isosteric enthalpy of adsorption when Q_e is a fixed value, R the gas constant, C_e the equilibrium concentration of solute in moles per liter at the absolute temperature T. At different temperatures (283K, 288K, and 298K), the C_e was obtained from the Freundlich isotherms when Q_e equals to 1.5mmol, 2.0mmol and 2.5mmol. ΔH was calculated from the slope of line plotted by $\ln C_e$ verse $1/T$.

The free energies of adsorption were calculated with a derivative Gibbs equation [6]:

$$\Delta G = -n R T \quad (3)$$

where n is a coefficient of Freundlich equation.

The entropies change of adsorption was calculated with Gibbs-HelmhloHz equation.

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

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

A summary of the calculated values for enthalpy, free energy, entropy about JP-01 and XAD-4 adsorbing 2,4-dichlorophenol were listed in Table 3.

Little variety of the enthalpy change at different Q_e shows the homogeneous nature of the adsorbent surface once again. The heat quantities for JP-01 are more than XAD-4's. The adsorption abilities of JP-01 for 2,4-dichlorophenol is stronger than XAD-4's, which indicates their adsorption enthalpies are from the intermolecular hydrogen bond between adsorbent and adsorbate. Duo to the adsorbate molecular after adsorption can orderly cover the surface of adsorption, the disorder and entropy are all decreasing. Values of the enthalpy changes, free energy changes, and entropy changes (always negative) on JP-01 and XAD-4 are indicative of an exothermic, spontaneous and disorder process, which shows a physical adsorption process.

Table 3 Estimated of the Thermodynamic Parameters of the Systems Tested for 2,4-dichlorophenol

Adsorbent	q (mmol/g)	ΔH (kJ/mol)	$-\Delta G$ (kJ/mol)			ΔS (J/mol)		
			288K	303K	318K	288K	303K	318K
JP-01	1.5	-51.57				-153	-151	-135
	2.0	-50.79	-7.4	-5.9	-8.5	-151	-148	-133
	2.5	-50.23				-149	-146	-131
XAD-4	1.5	-26.73	-8.54	-5.81	-6.0	-63.3	-69.0	-65.2
	2.0	-38.80				-105	-107	-103
	2.5	-47.65				-123	-138	-131

4. Conclusion

The hypercrosslinked polymeric adsorbent JP-01 for adsorbing 2,4-dichlorophenol from their aqueous solutions is prepared, and the equilibrium adsorption capacity for 2,4-dichlorophenol compounds on JP-01 is markedly higher than those on XAD-4, which attributes to its high specific surface area, high micropore area.

All the isotherm data for 2,4-dichlorophenol on the XAD-4 and JP-01 can be satisfactorily fitted with the Freundlich equations. The data of the thermodynamics studies for 2,4-dichlorophenol on JP-01 and XAD-4 show the adsorption process of an exothermic, spontaneous and disorder decreasing. The hypercross-linked Resins JP-01 can effectively remove the 2,4-dichlorophenol from aqueous solution. The new feasible measure for resolve 2,4-dichlorophenol is offered in groundwater micropollution.

Acknowledgments

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