

ADSORPTION OF 2,4-DICHLOROBENZOXYACETIC ACID ONTO HYPERCROSSLINKED RESIN MODIFIED BY PHENOLIC HYDROXYL GROUP (AM-1)

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Abstract An experimental comparison of the adsorption properties of hypercrosslinked resin AM-1 modified by phenolic hydroxyl group with Amberlite XAD-4 toward 2,4-dichlorobenzoxyacetic acid was performed. This paper focuses on the static equilibrium adsorption behaviors and the adsorption thermodynamics. Two isotherm models were used to explain the results. It is seen that the Langmuir equation can give a perfect fit. The adsorption capacities from the different ranges of temperature, the adsorption enthalpy change value and the comparison of desorption conditions lead to the same conclusion that the adsorption of 2,4-dichlorobenzoxyacetic acid from water onto AM-1 is a type of physical and chemical transition.

Keywords Hypercrosslinked polymeric adsorbent, 2,4-Dichlorobenzoxyacetic acid, Thermodynamic properties, Chemical adsorption transition

INTRODUCTION

Adsorption has been considered to be the best available technology for removing organics from water in the US Safe Drinking Water Act^[1]. Due to many drawbacks of activated carbon^[2–7], the most widely used adsorbent, hypercrosslinked polymeric adsorbents developed by Tsyurupa and Davankov^[8] have been increasingly viewed as an alternative to activated carbon for selective removal of specific organic substances from contaminated water^[9–12], and series of researches have been done^[13–16]. The AM-1 resin, one of the hypercrosslinked adsorbents modified by phenolic hydroxyl group, has often been investigated for the adsorption for organic compounds such as phenol, aniline and their derivatives^[17–19]. However, there is little work on the chemical adsorption of adsorption resin^[18–20]. In our work on the chemical adsorption of adsorbent, we choose 2,4-dichlorobenzoxyacetic acid for its acidity and because there are no insights into the adsorption of 2,4-dichlorobenzoxyacetic acid on macroporous polymers or activated carbons from aqueous solutions.

EXPERIMENTAL

Materials and Methods

Adsorbents

Spherical Amberlite XAD-4 adsorbent was available from Rohm-Haas. Hypercrosslinked polymeric adsorbent AM-1 was prepared by using the method described in the literature^[17]. Typical properties of XAD-4 and AM-1 resins are listed in Table 1.

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Received July 29, 2003; Revised December 2, 2003; Accepted December 22, 2003

Table 1. Typical properties of the studied adsorbents

Polymeric resins	Amberlite XAD-4 ^a	AM-1
Polarity	Nonpolar	Weak polar
BET specific surface area (m ² /g)	880	590
Average diameter (nm)	5.8	8.60
Particle size (mm)	0.4–0.6	0.4–0.6
Pore volume (mL/g)	1.05	0.52
Micropore area (m ² /g)	3.1	340
Residual chloride content (%)	–	3.46
Phenol hydroxyl content (%)	–	1.33
Colour	White	Deep brown

^a Measured by ourselves

Adsorbate

The solubility of 2,4-dichlorobenzoxyacetic acid in water is 2.8 mmol/L and its pK_a value is 2.64. Its aqueous solutions were prepared by dissolving 2,4-dichlorobenzoxyacetic acid (A.R) in deionized water without pH adjustment.

Static adsorption experiment

Equilibrium adsorption of 2,4-dichlorobenzoxyacetic acid was performed at four different temperatures, 288 K, 303 K, 318 K and another at 288 K dropped from 318 K. Briefly, 0.100 g of resin was introduced directly into a 250 mL conical flask, 100 mL aqueous solution of 2,4-dichlorobenzoxyacetic acid was added into each flask. The initial concentrations (*c*₀) of the solutions were 100, 200, 300, 400 and 500 mg/L, respectively. The flasks were tightly sealed and placed in a G25 model incubator shaker (New Brunswick Scientific Co. Inc.) kept at a pre-set temperature and were shaken at a rate of 130 r/min. The batch equilibrium test was run continuously for over 24 h to attain adsorption equilibrium. The concentrations of adsorbate (*c*_e) were determined by HPLC (Nov-Parker C₁₈ column, flow phase: methanol/0.25% H₃PO₄ = 70/30, wavelength: 230 nm, flow rate: 1 (mL/min). Thus *Q*_e (mmol/g), the adsorption capacity, was calculated according to the following equation

$$Q_e = V_1(c_0 - c_e) / M \cdot W \quad (1)$$

where *V*₁ is the volume of solution (L), *W* is the weight of dry resin (g), and *M* is the molecular weight of 2,4-dichlorobenzoxyacetic acid.

Selection of desorption condition

To each 250 mL conical flask containing 0.100 g of dry resins, 100 mL aqueous solution of 2,4-dichlorobenzoxyacetic acid was added. All the initial concentrations of the solutions were 2.0 mmol/L. The flasks were tightly sealed and placed in a G25 model incubator shaker at 318 K and shaken at a rate of 130 r/min. After adsorption equilibrium was attained, all the resins were filtered and centrifugally separated and again introduced respectively into the flasks. 10 mL of the different desorption solvent was added respectively at 323 K and shaken continually. Later, 1 mL of the desorption solution was diluted to 100 mL and its concentration was determined by using HPLC. The removal efficiency was evaluated.

RESULTS AND DISCUSSION

Equilibrium Adsorption of 2,4-Dichlorobenzoxyacetic Acid

The equilibrium adsorption isotherms of 2,4-dichlorobenzoxyacetic acid from water on Amberlite XAD-4 and AM-1 resins at different temperature are shown in Fig. 1(a) and 1(b), respectively. It is obvious that the equilibrium adsorption capacities of 2,4-dichlorobenzoxyacetic acid from water on Amberlite XAD-4 decrease with increasing temperature and show no differences at the same temperature from different temperature range, which indicates a physical exothermal process. However, the equilibrium adsorption capacities of 2,4-dichlorobenzoxyacetic acid from water on AM-1 increase with rising temperature and further increase as the temperature was dropped, which indicates a chemical endothermic transition.

It is well known that increasing of temperature is disadvantageous for the adsorption capacities in a physical

process. Thus the equilibrium adsorption capacities of 2,4-dichlorobenzoxyacetic acid on Amberlite XAD-4 decrease with increasing temperature, and show no differences at the same temperature of 288 K as the result of the reversible character of a physical process even if the adsorption equilibrium had reached 318 K at first. However, when the physical and chemical transition of adsorption existed, the adsorption would be selective for some groups, which resulted in increased chemical adsorption with increasing temperature because of activation energy and also being irreversible as a rule. Therefore, the active phenolic hydroxyl group in AM-1 would easily interact with the carboxyl group of 2,4-dichlorobenzoxyacetic acid, which caused the increase in adsorption amounts of 2,4-dichlorobenzoxyacetic acid when the temperature increased. In addition, due to the irreversible chemical process and the reverse physical process, there were the highest adsorption capacities in AM-1 at 288 K fallen from 318 K. The difference was about 0.696 mmol/g resin for different ways of reaching 288 K, about 88.95 percent of the theoretical amount, which demonstrates the catalytic performance of the AM-1 resin.

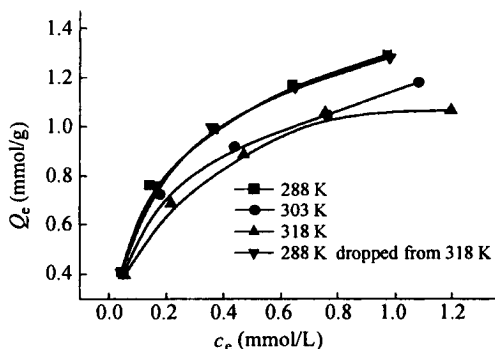


Fig. 1a The equilibrium adsorption isotherms of 2,4-dichlorobenzoxyacetic acid from water on Amberlite XAD-4 resin at different temperatures

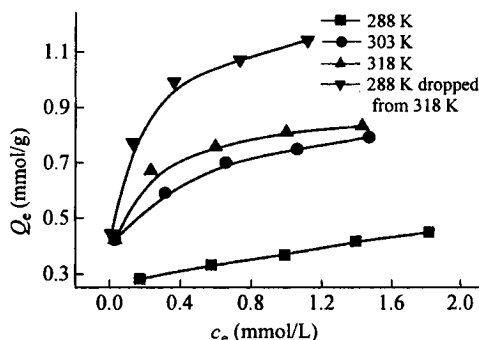


Fig. 1b The equilibrium adsorption isotherms of 2,4-dichlorobenzoxyacetic acid from water on AM-1 resin at different temperatures

Adsorption Thermodynamics

The isothermal equilibrium adsorption data for AM-1 was processed and compared with those for Amberlite XAD-4 employing the rearranged Langmuir and Freundlich^[21] adsorption models, which may be expressed respectively as

$$\text{Langmuir equation} \quad c_e/Q_e = c_e/Q_m + 1/(K_L Q_m) \quad (2)$$

$$\text{Freundlich equation} \quad \ln Q_e = \ln K_F + 1/n \ln c_e \quad (3)$$

where Q_e is the equilibrium adsorption capacity (mmol/g), c_e is the equilibrium concentration (mmol/L), Q_m is the maximum surface coverage (formation of the monolayer) of the adsorbent (mmol/g), K_L is the adsorption constant, and K_F and n are the characteristic constants. The evaluated constants for both isotherms are shown in Table 2, which suggests that the Langmuir equation can give a perfect fit. The conformation of experimental data with the Langmuir isotherm model shows the homogeneous nature of the adsorbent surface^[22].

Estimations of the change of adsorption enthalpy ΔH , free energy ΔG , and entropy ΔS are calculated from the data using the better fitting Langmuir equations, and the results are given in Table 3. The related equations are listed as follows:

$$\Delta G = -RT \ln K_L \quad (4)$$

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

From Eq. (4) and (5), the relation between K_L and thermodynamic parameters ΔH and ΔS can be described by Van't Hoff's equation:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

Then, ΔH and ΔS are calculated from the slope and intercept of the straight line of $\ln K_L \sim 1/T$ from the above equation.

Table 2. The evaluated constants of 2,4-dichlorobenzoxyacetic acid from water on AM-1 and Amberlite XAD-4 resins for both isotherms

Adsorbent	Temperature (K)	Langmuir			Freundlich		
		Q_m	K_L	R_2	K_F	n	R_2
XAD-4	288	1.437	7.614	0.996	1.077	2.910	0.972
	303	1.296	6.910	0.993	1.051	2.938	0.977
	318	1.230	6.664	0.996	1.042	2.943	0.975
	288 (dropped from 318 K)	1.440	7.636	0.995	1.079	2.907	0.968
AM-1	288	0.483	4.637	0.985	0.385	5.149	0.954
	303	0.819	12.276	0.995	0.739	6.135	0.994
	318	0.857	18.346	0.999	0.816	5.590	0.975
	288 (dropped from 318 K)	1.174	19.848	0.997	1.157	4.897	0.993

Table 3. Thermodynamic parameters for the adsorption process of 2,4-dichlorobenzoxyacetic acid on AM-1 and Amberlite XAD-4 resins

Adsorbent	Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	R^2
XAD-4	288 K	-4.861			
	303 K	-4.870	-3.405	4.984	0.949
	318 K	-5.015			
AM-1	288 K	-3.673			
	303 K	-6.317	35.12	135.36	0.951
	318 K	-7.692			

The negative ΔG values indicate that all these adsorption processes are spontaneous. Little change of spontaneous tendency happens with the increase of temperature on XAD-4 for the slight change of ΔG while the spontaneous tendency on AM-1 is remarkable. The ΔH value for AM-1 is in agreement with the other reports^[18, 19] and shows a chemical transition process. The positive value of ΔS indicates that there is an increase of randomness at the solid/solution interface during the adsorption of 2,4-dichlorobenzoxyacetic acid onto adsorbents. The extraneous water formed from the reaction of phenolic hydroxyl of AM-1 and carboxyl of 2,4-dichlorobenzoxyacetic acid might be an important factor resulting in a higher value of ΔS for AM-1^[18, 19].

Comparison of Desorption Conditions

Different solvents were used to desorb the static equilibrium adsorbents, and the experimental results are given in Table 4.

Table 4. The results of desorption with different solvents

Adsorbent	Desorption solvent	Desorption efficiency (%)
XAD-4	Methanol	98.3
	Methanol: 2% NaOH = 1:1	98.1
	2% NaOH	98.6
AM-1	Methanol	37.9
	Methanol: 2%NaOH = 1:1	86.6
	2% NaOH	88.5

Obviously, 2,4-dichlorobenzoxyacetic acid adsorbed on XAD-4 can be desorbed easily, and the desorption efficiency reaches about 98%. However, methanol could desorb a small amount of 2,4-dichlorobenzoxyacetic

acid from AM-1. Once, the solvents are alkalized, the desorption efficiency could be improved greatly, providing additional proof of chemical transition when 2,4-dichlorobenzoxyacetic acid is adsorbed on AM-1.

CONCLUSIONS

The isotherms for liquid-phase adsorption of 2,4-dichlorobenzoxyacetic acid from water on Amberlite XAD-4 and AM-1 resins have been analyzed. The following results are obtained.

The adsorption capacities of 2,4-dichlorobenzoxyacetic acid on AM-1 increased with rising temperature while further increasing when the temperature had fallen. But the opposite effect occurs in XAD-4.

All the data fit the Langmuir model and the Freundlich equation and Langmuir equation can give a better fitting.

The change of adsorption capacities according to the different ways of reaching 288 K, the adsorption enthalpy changes and the comparison of desorption conditions prove that the adsorption of 2,4-dichlorobenzoxyacetic acid from water on AM-1 is a type of physical and chemical transition.

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