

ADSORPTION OF 1,2,4-ACID BY WEAKLY BASIC RESIN: ISOTHERMS, THERMODYNAMICS AND KINETICS*

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Abstract The adsorption properties, including the adsorption isotherms, thermodynamics and kinetics, of 1-amino-2-naphthol-4-sulfonic acid (1,2,4-acid) onto weakly basic resin ND900 are investigated. Both the Langmuir and Freundlich equations can give a good fit to the adsorption isotherms, which indicates an endothermic and a favorable adsorption in our study range. A high yield in elimination of about 45.21%–97.28% is obtained for the tested adsorption systems. The capacity and affinity of the adsorption increase with temperature, due to the phenomena of “solvent-motivated” effects. The value of ΔH is 51.59 kJ/mol, which indicates a chemical adsorption and then expects the poor desorption property of ND900. The negative value of ΔG indicates the spontaneous nature of the adsorption process, and the positive value of ΔS shows the increased randomness at the solid/solution interface during the adsorption process. The value of the adsorption rate constant lower than 0.013 min^{-1} is indicative of a slow adsorption rate. The intra-particle diffusion must be one of the rate limiting steps.

Keywords Weakly basic resin, 1,2,4-Acid, Isotherms, Thermodynamics, Kinetics, Intra-particle diffusion

INTRODUCTION

In recent years polymeric adsorbents have been increasingly viewed as an alternative to activated carbons for purification and separation by selectively removing and recovering organics from contaminated water with an efficiency high enough to meet chemical-scientific standards due to their wide variations in functionality, surface area, size of pores and porosity^[1–5]. Many researchers have studied the adsorption isotherms, thermodynamic and kinetic properties for various adsorption systems^[6–8]. These studies are helpful in developing new adsorption materials with high adsorption capacities and high selectivities and extending their wider practical applications.

The macroporous weakly basic resins have been proved to be effective in removing those anionic pollutants from aqueous media^[9]. However, there is no report on the adsorption of 1-amino-2-naphthol-4-sulfonic acid (1,2,4-acid) with $-\text{SO}_3^-$ anion, which is an important intermediate in the dyestuff industry with some toxicity. The paper focuses on the adsorption isotherms, thermodynamics and kinetics of 1,2,4-acid onto weakly basic resin ND900.

EXPERIMENTAL

Materials and Methods

Chemicals

1,2,4-acid was of A.R. grade, obtained from Tingxin Chemical Reagent Plant (Shanghai, China). The weakly basic resin ND900, whose network was macroporous styrene-divinylbenzene and furnished with some amino

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basic groups, was purchased from Langfang Chemical Co. (China). The key physicochemical characteristics of ND900 can be found in Table 1.

Characterization of the weakly basic resin ND900

The specific surface area and the pore distribution of ND900 were measured using a Micromeritics ASAP-2010 instrument (Micromeritics Instrument Corp., Norcross, USA) following the BET method. Infrared spectra of the polymeric adsorbent were obtained from a Nicolet 170 SX IR spectrometer (USA). The chlorine content was measured according to the method of Volhard. The basic exchange capacity was measured by titration with 0.1 mol/L HCl and 0.1 mol/L NaOH solution. Elemental analysis of the adsorbent was performed on a Perkin-Elmer 240 C Elemental Analytical Instrument (USA).

Analysis

The solute concentrations were determined using high performance liquid chromatography (HPLC) equipped with a Waters 600 controller, a Waters 600 pump (Waters Assoc., USA) and a Waters 2487 Dual Absorbance UV detector at 230 nm. The mobile phase was 70% methanol: 30% 0.017 M H_3PO_4 (pH = 2.27).

Adsorption Procedure

Adsorption isotherms were performed using the common bottle-point technique at three different temperatures (288 ± 0.5 K, 303 ± 0.5 K and 318 ± 0.5 K). Fixed amounts of resin (0.1 g) were contacted, in 250 mL stoppered bottles, with 100 mL 1,2,4-acid solution of known initial concentration (c_0 , mg/L): 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), and shaken at the rate of 130 r/min until equilibrium.

For batch kinetic studies, at the initial solute concentrations of 200 mg/L and 500 mg/L, the changes of adsorption amounts were measured at definite time intervals (2, 5, 10, 15, 20, 25, 30, 40, 60, 120, 180, 240, 300 min.....) until equilibrium was reached at determined temperatures (*i.e.* 293 K and 313 K).

The adsorption amounts, q (mmol/g), were calculated according to Eq. (1)

$$q = \frac{(c_0 - c)V}{M_w} \quad (1)$$

where c_0 is the initial concentration of 1,2,4-acid (mg/L), c is the concentration tested of 1,2,4-acid (mg/L), V is the volume of solution (L), W is the weight of dry resin ND900 (g), and M is the molecule weight of 1,2,4-acid (239.2 g/mol).

Adsorption Isotherms

The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase (c_e) and that in the adsorbent particles (q_e) at a given temperature, and can provide information on the adsorption strength and capacity^[10]. Equilibrium data concerning the adsorption of 1,2,4-acid from aqueous solutions on ND900 are presented in Fig. 1. The L-type isotherms with convex curves upward in all cases involve favourable type isotherms according to the classification reported earlier^[11, 12].

A high yield in elimination is obtained for all the cases studied from both Fig. 1 and Fig. 2, in the range of 45.21%–97.28%. This can be attributed to the relatively stronger interaction between the acid groups (*i.e.* sulfonic acid groups) of the solute and the basic groups on the adsorbent at the beginning of the adsorption process. But with the adsorption amount increasing there are some shields for the limited amount of adsorption sites or basic functional groups^[13]. And the curves corresponding to lower temperatures lay below the ones corresponding to higher temperatures, which indicates that adsorbents have higher adsorption capacities at higher temperatures. The evident increasing tendency of adsorption capacity with temperature is indicative of an endothermic process. The higher reaction energy obtained at higher temperature may account for this, and it is mainly due to the interaction between the sulfonic acid group of 1,2,4-acid and the basic groups on the adsorbent including $-\text{N}^+\text{A}_3$ and $-\text{NA}_2$, where A is an alkyl hydrocarbon. But based on the overall exchange capacity (about 5.25 mmol/g) calculated from the information given in Table 1, the above interaction is considered to be

the dominant contributor to the much lower adsorption capacity on ND900 which varies from 0.28 mmol/g to 1.94 mmol/g in our tested range.

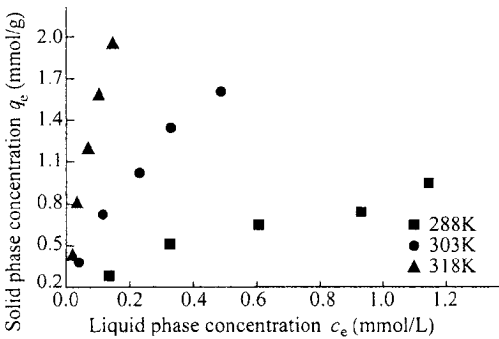


Fig. 1 Adsorption isotherms of 1,2,4-acid by ND900

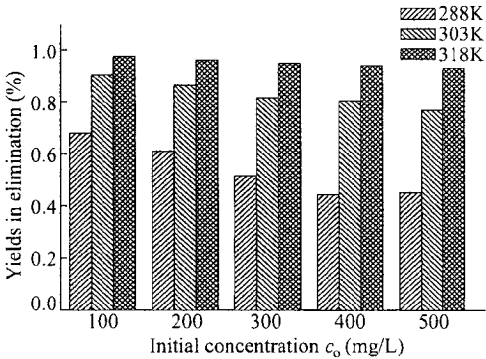


Fig. 2 Yields in elimination of 1,2,4-acid by ND900 at different temperatures and initial solute concentrations

Table 1. Typical properties of the weakly basic resin ND900*

Properties	ND900 resin
Structure	Weakly basic, macroporous
Polarity	Strongly polar
BET specific surface area (m ² /g)	38.2
Average pore diameter (nm)	4.5
Desorption average pore diameter (nm)	8.4
Particle size (mm)	0.4–0.6
Micropore area (m ² /g)	8.1
Micropore volume (mL/g)	0.003
Chloride content before aminize (%)	19.5
Residual chloride content (%)	1.2
Oxygen content (%)	0.1
Weakly basic exchange capacity (mmol/g)	4.90
Strongly basic exchange capacity (mmol/g)	0.35

*Analyzed by Ai-min Li and considered the standard of product quality

Many theories, used to model the adsorption process with varying degrees of complexity and success, have been proposed to explain the adsorption phenomenon and to describe the adsorption isotherm relationships^[14]. Among them the Langmuir and Freundlich models have been widely used, and their linear forms are given below respectively:

Langmuir model: $c_e/q_e = c_e/M + 1/(MK_L)$ (2)

Freundlich model: $\lg q_e = \lg K_f + n \lg c_e$ (3)

where M , K_L , K_f and n are characteristic constants. The Langmuir constant M (mmol/g) is the maximum amount per weight of adsorbent to form a complete monolayer on the surface bound, and K_L (L/g) is a constant related to the affinity of the binding sites^[15]. The Freundlich coefficient K_f (L/mmol) is an index of the sorption capacity of the resins and the Freundlich exponent n (dimensionless) denotes the heterogeneity of the surface and the intensity of adsorption^[16, 17].

By a nonlinear least squares routine, the regression equations corresponding to the above isotherms can be obtained, and their constants along with the correlation coefficients r are all summarized in Table 2. The results clearly show that the adsorption data for the studied adsorption systems fit well to both the Langmuir and the Freundlich models for the correlative factors larger than 0.995.

Table 2. Fitted results for Langmuir and Freundlich isotherms

Regression equations		288 K	303 K	318 K
Langmuir	M	1.136	1.865	2.270
	K_L	2.456	6.278	18.83
	r	0.996	0.995	0.995
Freundlich	K_f	0.842	2.480	6.390
	n	0.524	0.581	0.615
	r	0.999	0.996	0.999

As can be seen from the values of M and K_f in Table 2, the capacity of the adsorption increases with temperature, indicating the predominant phenomena of “sorbent-motivated” effects caused mainly by the electrostatic interaction and ion change which are endothermic interactions^[18]. And the constant n is always less than 1 and K_L is always more than 1 in our study range, both indicating a favorable type adsorption^[19, 20].

Thermodynamics

Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the adsorption of 1,2,4-acid onto the weakly basic resin ND900 are given in Table 3.

Table 3. Thermodynamic parameters for the adsorption of 1,2,4-acid onto the weakly basic resin ND900 at different solid loadings

Temperatures	ΔH (kJ/mol)	ΔS (kJ/mol · K)	ΔG (kJ/mol)
288 K	51.59	0.186	-1.98
303 K	51.59	0.186	-4.77
318 K	51.59	0.186	-7.56

ΔG is calculated according to Eq. (4)^[8].

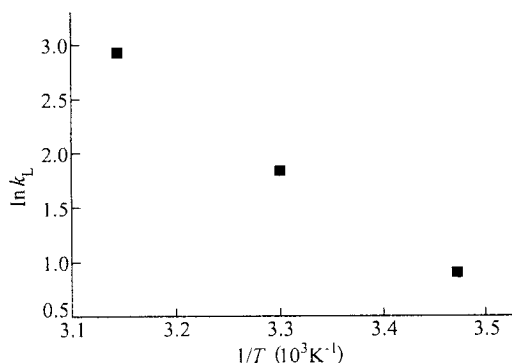
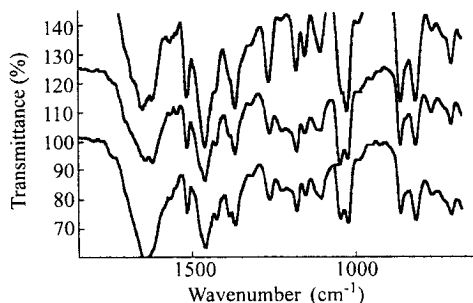
$$\Delta G = -RT \ln K_L \quad (4)$$

where K_L is the Langmuir characteristic constants, R is the gas constant (kJ/mol · K), and T is the absolute temperature (K).

The following Van't Hoff equation can be obtained to describe the relation between the K_L and the other two thermodynamic parameters.

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

Then, ΔH and ΔS can be calculated respectively from the slope and intercept of the Van't Hoff plot (Fig. 3).

**Fig. 3** Van't Hoff plot**Fig. 4** The IR spectra of the weak basic resin ND900 at different stages (1-the original, 2-after adsorbed, 3-after desorbed)

A positive value of ΔH confirms the endothermic adsorption nature of 1,2,4-acid onto ND900. In addition, the value of ΔH is 51.59 kJ/mol, much larger than in the range (10–30 kJ/mol) where physical adsorption is expected to be the dominant mechanism^[21]. So a chemical adsorption process does take place. The larger value of ΔH indicates the weak desorption property of weakly basic resin ND900. Furthermore, from Fig. 4, the IR spectra of the adsorbent after desorption by 8% NaOH solution cannot match that of the unused ND900 resin.

The negative value and the increment in the negative direction of ΔG indicate the spontaneous nature of the adsorption process and the increasing affinity between the solute and adsorbent with temperature owing to the higher reaction energy at higher temperature. And the positive value of ΔS shows the increased randomness at the solid/solution interface during the adsorption process, which exhibits the same tendency reported earlier^[8].

Kinetics

The plots of q_t versus all the tested cases can be found in Fig. 5.

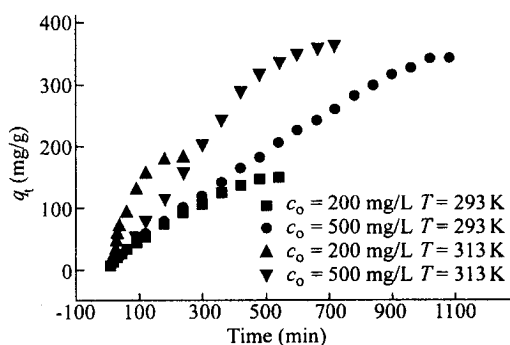


Fig. 5 First order kinetic plots for the adsorption of 1,2,4-acid by ND900

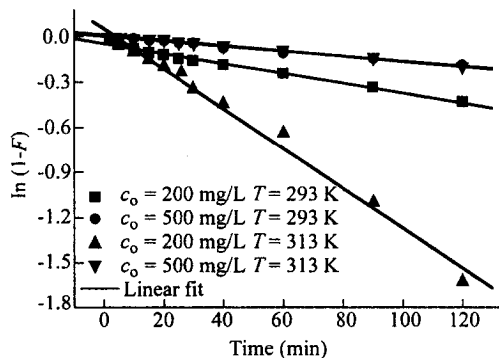


Fig. 6 Adsorption rate determination curves at different conditions

An obviously higher kinetic rate can be observed at a higher temperature, corresponding to a shorter time required to achieve the equilibrium, but this phenomenon becomes more obvious at a lower initial solute concentration. This is probably due to the presence of relatively more adsorption sites on the adsorbent. A higher initial solute concentration gives a lower kinetic rate and results in a longer time required to reach equilibrium at the same temperature, but this phenomenon becomes more obvious at a higher temperature. The higher energy of the reaction site at higher temperature may account for this divergence.

To evaluate the kinetic rate for various cases, the so-call Lagergren pseudo-first-order equation (Eq. 6) was used^[22, 23].

$$\ln(q_e - q_t) = \ln q_e - K_{ad} t \quad \text{or} \quad \ln(1 - F) = -K_{ad} t \quad (6)$$

where q_e and q_t are the amount of 1,2,4-acid adsorbed per unit mass of the adsorbent (mg/g) at equilibrium time and contact time t , respectively, k_{ad} is the adsorption rate constant (min^{-1}), and F ($F = q_t/q_e$) represents the fractional attainment of the equilibrium.

The lines on Fig. 6 show reasonably good linearity in the plot of $\ln(1 - F)$ versus t (120 min as the initial fast adsorption time section for all cases), and Table 4 illustrates the values of first order rate constants and correlation coefficient (r -value). All the linear correlations indicate the applicability of the kinetic equation and confirm the first order nature of the tested adsorption process. The adsorption rate constant of 0.013 min^{-1} implies a slow adsorption rate. And the intercepts of the lines in Fig. 6 indicate that the intra-particle diffusion process must be one of the rate limiting steps.

CONCLUSIONS

Weakly basic resin ND900 was used to adsorb 1,2,4-acid at different conditions. The Langmuir and Freundlich equations can both give fairly good fits to the batch adsorption data, which indicates an endothermic and a favorable adsorption process in the range studied. A very high yield in elimination is obtained in the range of

45.21%–97.28%. The adsorption capacity and affinity both increase with temperature, due to the dominant ‘sorbent-motivated’ effects caused by the basic functional groups on ND900.

Table 4. Kinetic rate constants and correlation coefficient

Kinetic model	Parameters	Initial concentrations (mg/L)			
		200		500	
		Temperatures (K)		Temperatures (K)	
		293	313	293	313
Lagergren equation	k_{ad} (min ⁻¹)	0.00327	0.00159	0.01321	0.00167
	Intercept	-0.04718	-0.00383	0.05025	-0.00008
	<i>r</i> -Value	0.994	0.993	0.995	0.993

The value of ΔH is 51.59 kJ/mol, which indicates that the adsorption is a chemical rather than a physical one and a poor desorption property of ND900 is expected. The negative values of ΔG indicate the spontaneous nature of the adsorption process and the increasing affinity between the solute and adsorbent with the change of temperature. The positive value of ΔS implies the increase of randomness at the solid/solution interface during the adsorption process.

The adsorption rate constant lower than 0.013 min⁻¹ is indicative of a slow adsorption rate and the intra-particle diffusion is considered as one of the rate limiting steps.

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