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Adsorption of β -naphthalenesulfonic acid/sulfuric acid from their solution by weakly basic resin: equilibrium

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Abstract: Experiments for single and bisolute competitive adsorption were carried out to investigate the adsorption behavior of β -naphthalenesulfonic acid (NSA) and sulfuric acid (H_2SO_4) from their solution at 25 °C onto weakly basic resin D301R. Adsorption affinity of sulfuric acid on D301R was found to be much higher than that of NSA. The data of single-solute adsorption were fitted to the Langmuir model and the Freundlich adsorption model. The ideal adsorbed solution theory (IAST) coupled with the single-solute adsorption models were used to predict the bisolute competitive adsorption equilibria. The IAST coupled with the Langmuir and the Freundlich model for sulfuric acid and NSA, respectively, yields the favorable representation of the bisolute competitive adsorption behavior.

Keywords: β -naphthalenesulfonic acid; adsorption; weakly basic resin

Introduction

Current production of β -naphthol involves a process which is not environment-friendly under the current environmental regulation, for the process produces a large amount of β -naphthalenesulfonic acid (NSA) wastewater and causes environmental pollution. The removal of NSA from wastewater can be carried out by ion exchange, solvent extraction, reverse osmosis, chemical oxidation, and adsorption. Adsorption is one of the treatment process available, its adoption over other alternative being mainly dependent on economic considerations. Important factors in this sense relative to the adsorbent are cost, adsorption capacity for the particular adsorbate, regeneration, and durability. In a short, adsorption holds promise in the treatment of wastewater, as it is inexpensive, simply designed, easy to handle, and provides sludge-free cleaning operation.

Knowledge of the adsorption equilibrium constitutes the first step in the investigation of the possibility of using an adsorbent for a particular separation task. Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements. Moreover, the isotherm plays a crucial function role in predictive modeling procedures for analysis and design of adsorption systems. An additional potential use of adsorption isotherms is for theoretical evaluation and interpretation of thermodynamic parameters, such as heats adsorption.

Among various adsorbent, activated carbon is the most commonly used. However, there are a number of problems associated with activated carbons such as combustion at high temperature, pore blocking, and hygroscopicity. To overcome these problems, various alternative adsorbent have been developed. Experimental work on the adsorption of strong acids (HCl , HNO_3 , and H_2SO_4) on weakly basic resin have been reported (Bhandari, 1993a; 1992; Li, 2001a). In present study, we consider the possibility of using a weakly basic resin to recover NSA and sulfuric acid from β -salt mother liquor, since weakly basic resin has good selectivity, large capacity and is easy for regeneration (Li, 2001b).

Adsorption equilibrium is studied in detail.

1 Experimental

1.1 Materials

All reagents used were of AR grade. Stock solutions of NSA and sulfuric acid were prepared with double-distilled water. The adsorbents used in this study D301R, D354, and D392, are commercial weakly basic resins (Nankai University Chemical Plant), MCM-41 is pure-silica (Shanghai Zeolite Co.), TDS-10 is a activated carbon (Tsingdao Activated Carbon Plant). Their physical properties are listed in Table 1. The resin were fully swollen by equilibrating with demineralized water and pretreated according to the procedure (Helfferich, 1962).

1.2 Adsorption

First, a sample screening test was made to find appropriate resins for adsorption of NSA and sulfuric acid from solution. Next, we determined the equilibrium isotherms for adsorption of NSA and sulfuric acid on the selected resin.

Single-solute adsorption isotherms on D301R were obtained for each solute dissolved in water. A series of 200 ml test flasks were filled with 50 ml of NSA and sulfuric acid solutions of varying initial concentration at $pH \leq 4$ and 25 °C. 5 g pretreated wet resin was then added into each test flasks and agitated intermittently for 24 h. It was observed that adsorption equilibrium was reached in about 24 h on an orbit shaker revolving at 250 r/min. Single-solute adsorptions for NSA and sulfuric acid were carried out in twice and three times, respectively.

A bisolute system of NSA/sulfuric acid with different initial concentrations was prepared by mixing solutions of the same concentration in a 1:1 volume ratio into a 50 ml solution. We performed bisolute adsorption experiments for the various initial concentrations with the fixed amount D301R resin (5 g) by following the same procedure as the single-solute adsorption experiment.

The concentrations of NSA and sulfuric acid in each solution were determined by a high performance liquid chromatography (HPLC) (Shimadzu). The adsorbed phase concentration was calculated according to

$$q = \frac{(c_0 - c)m}{w} \quad (1)$$

Table 1 Physical properties of adsorbents

Physical parameter	D301R	D354	D392	MCM-41	TDS-10
Polymer matrix	Styrene-DVB	Styrene-DVB	Styrene-DVB	SiO ₂	—
Type	Macroporous	Macroporous	Macroporous	Mesoporous	Micropore
Form as supplied	Free base	Free base	Free base	—	—
Bead size, mm	0.35—0.55	0.477	0.36—1.25	0.25—0.3	0.47—0.63
Pore diameter, nm	10.0—10.5	8.5—9.0	8.0—8.5	2.9	0.1—0.3
Surface area, m ² /g	600—700	500—560	480—520	1120	1100
Moisture content, % w/w	45	50	50—60	—	—
Capacity, meq/ml dry resin	6.8	5	4.5	—	—
Apparent density, g/L	1276	1085	1030	—	—

2 Single and multisolute competitive adsorption models

The sorption isotherms employed frequently for single-solute systems are the 2-parameter Langmuir and Freundlich models. The Langmuir and Freundlich models obey the correct thermodynamic boundary condition of Henry's law over an infinitely dilute concentration range. The Langmuir and Freundlich models for liquid-phase adsorption are written respectively as follows.

$$q = \frac{q_{\max} bc}{1 + bc} = \frac{ac}{1 + bc}, \quad (2)$$

$$q = kc^{1/n}. \quad (3)$$

To analyze multisolute competitive adsorption behavior, the ideal adsorbed solution theory (IAST) (Radke, 1972) is used in this study. The equivalence of spreading pressure (π) in a mixture containing N solutes leads to

$$\frac{\pi A}{RT} = \int_0^{c_1^0} \frac{q_1^0}{c_1^0} dc_1^0 = \int_0^{c_2^0} \frac{q_2^0}{c_2^0} dc_2^0 = \dots = \int_0^{c_N^0} \frac{q_N^0}{c_N^0} dc_N^0, \quad (4)$$

$$c_{m,i} = z_i c_i^0, \quad (5)$$

$$\sum_{i=1}^N z_i = 1, \quad (6)$$

$$q_i^0 = f(c_i^0, T), \quad (7)$$

$$\frac{1}{q_i} = \sum_{i=1}^N \frac{z_i}{q_i^0}, \quad (8)$$

$$q_{m,i} = z_i q_i. \quad (9)$$

The IAST method is formulated on the basis that at equilibrium, the spreading pressures for all species are the same. A Newton-Raphson iteration method was used to solve these equations.

3 Results and discussion

3.1 Screening test of resins

Fig.1 shows that independent equilibrium isotherms for the adsorption of sulfuric and NSA on MCM-41, D301R, TDS-10, D354, and D392. It can be seen that the adsorption capacity of MCM-41, D301R, and TDS-10 is bigger than the other two resins (D354, D392) at the concentration range of $c > 1.0\%$. The experimental results of D301R, TDS-10, and MCM-41 are shown in Table 2.

Where c/c_0 is the ratio of the equilibrium concentration to initial concentration in the liquid phase, and q is the equilibrium concentration in the resin phase. The amount of sulfuric acid adsorbed is larger than that of NSA, which means that the selectivity for sulfuric acid is much higher than that for NSA. The amount of sulfuric acid and NSA

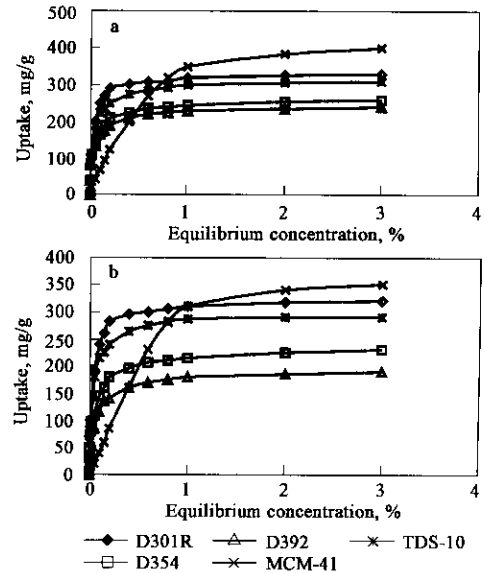


Fig.1 Adsorption isotherm of sulfuric acid and NSA on various adsorbents a. sulfuric acid; b. NSA; adsorbent = 5 g; temperature = 25 °C, pH ≤ 4

adsorbed on MCM-41 is relatively larger than those on the others, however, the MCM-41 has a smaller adsorption amount at a low concentration range of $c < 1\%$. In addition, it can be known from Fig.2 that adsorption rate of D301R is more rapid than that of TDS-10. It indicates that D301R is more appropriate for the removal of sulfuric acid and NSA from solution.

Table 2 Adsorption characteristics of sulfuric acid and NSA in solution

Adsorbent	Sulfuric acid		NSA	
	c/c_0	q_{\max} , mg/g	c/c_0	q_{\max} , mg/g
D301R	0.1500	340	0.200	320
TDS-10	0.2300	310	0.275	290
MCM-41	0.0075	397	0.125	350

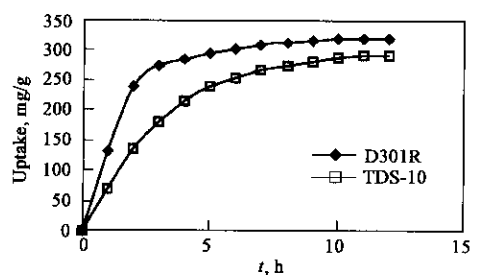


Fig.2 Adsorption kinetics of NSA on D301R and TDS-10 Initial concentration = 4%; adsorbent = 5 g; temperature = 25 °C, pH ≤ 4

3.2 Single-solute adsorption

The experiments of single-solute adsorption of sulfuric acid and NSA were conducted using D301R as an adsorbent. Adsorption isotherms for sulfuric acid and NSA are shown in Fig. 3 and 4, respectively.

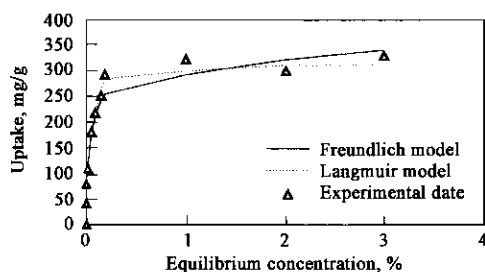


Fig. 3 Single-solute adsorption isotherm of sulfuric acid on D301R resin
Adsorbent = 5 g; temperature = 25 °C; pH ≤ 4

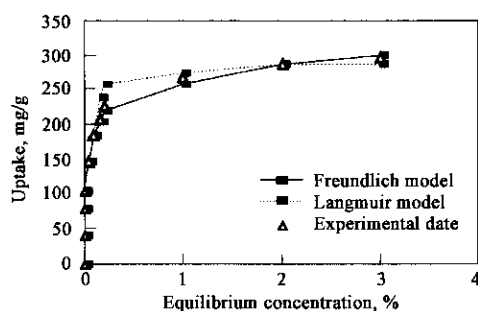


Fig. 4 Single-solute adsorption isotherm of NSA on D301R resin
Adsorbent = 5 g; temperature = 25 °C; pH ≤ 4

Both acids exhibits isotherms of type I (Gregg, 1967). Such isotherms are characteristic of strong adsorbate-adsorbent interactions. The 2-parameter Langmuir and Freundlich models were fitted to the adsorption data of each solute using the regression method. Fitted curves of the Langmuir and Freundlich models are shown in Fig. 3 and 4 for comparison with the adsorption data, and the parameters of both adsorption models are tabulated in Table 3 and 4, respectively. The values of the parameter q_{max} in the Langmuir model, roughly reflect the order of adsorption affinity between the two acids. As a measure of the fitness, the values of R^2 for the single-solute adsorption were computed from the following equation (Kleibaum, 1979).

$$R^2 = \frac{\sum q_i^2 - \frac{(\sum q_i)^2}{n}}{\sum q_i^2} \quad (10)$$

Table 3 Langmuir parameters on D301R resin

Solute	q_{max} , mg/g	b , g/mg	a	R^2
Sulfuric acid	345	9.66	3332.70	0.952
NSA	321	14.83	4760.43	0.974

Table 4 Freundlich parameters on D301R resin

Solute	k , mg/g	$1/n$	R^2
Sulfuric acid	302	0.1922	0.986
NSA	258	0.1695	0.991

Large differences in sorption rates were observed for sulfuric acid (H_2SO_4) and NSA. It can be explained on the

basis of a dual site sorption mechanism for dibasic acids. In this case the adsorbing anion SO_4^{2-} attached to two protonated sites of resin. It is found that the extent of reversibility for dibasic acids was considerably less and there was practically negligible exclusion of H^+ ions from resin pores. This is attributed mainly to the reason that divalent ions are expected to be more strongly anchored on the resin sites than monovalent ions, thereby weakening the electrical potential of the resin surface. As a result, the adsorption affinity of sulfuric acid on D301R is found to be much higher than that of NSA.

In view of values of R^2 listed in Tables 3 and 4, the Freundlich model exhibited a little better fit to the adsorption data than the Langmuir model.

3.3 Bisolute competitive adsorption

Bisolute competitive adsorptions were performed for the sulfuric acid/NSA binary system dissolved in water at 25 °C. The competitive adsorption data are shown in Fig. 5.

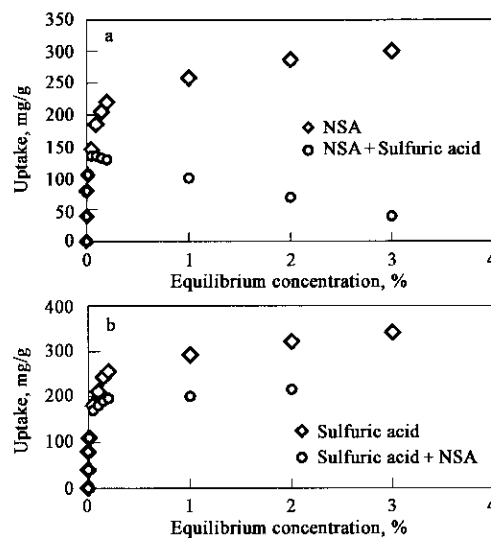


Fig. 5 Single and bisolute competitive adsorption isotherms of (a) NSA and (b) sulfuric acid on D301R resin
Adsorbent = 5 g; temperature = 25 °C; pH ≤ 4

Fig. 5 shows adsorption isotherms for the single and bisolute competitive adsorptions of sulfuric acid and NSA. Adsorption capacities of sulfuric acid (NSA) decrease when NSA (sulfuric acid) is present due to the competition for the available sites between adsorbable components. Sulfuric acid competitively displaces NSA from the limited adsorption sites available on D301R at higher concentrations. One of the main features of adsorption is that adsorption capacity of a solute is reduced when multiple solutes are present due to sharing the finite adsorption sites with other solutes on a competitive basis. The amount of decrease in adsorption capacity was found to be greater for NSA than for sulfuric acid, which can be explained by protonated theory (Takatsuji, 1994; Bhandari, 1993b).

To predict the competitive adsorptions, we applied IAST coupled with single-solute adsorption models (Langmuir, Freundlich models for sulfuric acid, NSA). The parameters of each model are listed in Table 3 and 4.

Fig. 6 shows predictions from IAST coupled with L/F models for sulfuric acid/NSA, respectively. The IAST

coupled with the single solute Langmuir and Freundlich models for sulfuric acid and NSA, respectively, provides the most favorable predictions for the bisolute competitive adsorption of the acids on D301R.

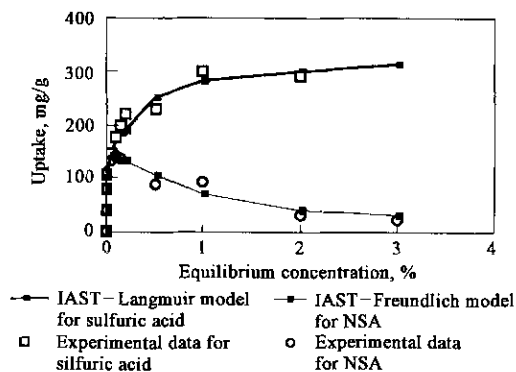


Fig.6 Bisolute adsorption isotherms of NSA/Sulfuric acid system on D301R
Adsorbent = 5 g; temperature = 25°C; pH \leq 4

4 Conclusions

Experiments on single and bisolute competitive adsorption were carried out to investigate the adsorption behavior of sulfuric acid and NSA from solution at 25°C on D301R weakly basic resin. Sorptive affinity of the two acids on D301R is found to be in the order of sulfuric acid > NSA. The single-solute adsorption data were fitted to the Langmuir and the Freundlich adsorption models to obtain the model parameters. The ideal adsorbed solution theory (IAST) coupled with the single-solute adsorption models were used to predict the bisolute competitive adsorption equilibria. The IAST coupled with the Langmuir and Freundlich models for sulfuric acid and NSA, respectively, yields the favorable representations of competitive adsorption behavior.

Nomenclature:

a : q_{max} ; b : equilibrium constant, g/mg; c : final

concentration in liquid phase, %; c_0 : initial concentration in liquid phase, %; c^0 : equilibrium concentration in liquid phase for pure component adsorption, %; c_m : equilibrium concentration in liquid, %; k : empirical Freundlich constant; m : weight of solution, mg; n : empirical Freundlich constant; N : number of components; q_{max} : saturation capacity, mg/g; q : adsorbed phase concentration, mg/g; q^0 : equilibrium concentration in solid phase for pure component adsorption, mg/g; q_m : equilibrium concentration in solid phase, mg/g; q_t : total surface loading, mg/g; \hat{q} : concentration calculated by fitted single-solute adsorption model, mg/g; R : gas constant, J/(mol \cdot K); T : temperature, K; w : weight of wet resin particles, g; z : fraction on surface of the adsorbent; π : spreading pressure, g/(s² \cdot mol); i : solute i .

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