

Binary competitive adsorption of naphthalene compounds onto an aminated hypercrosslinked macroporous polymeric adsorbent

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Abstract: An aminated hypercrosslinked macroporous polymeric adsorbent was synthesized and characterized. Adsorption isotherms for 1-amino-2-naphthol-4-sulfonic acid (1, 2, 4-acid) and 2-naphthol obtained from various binary adsorption environments can be well fitted by Freundlich equation, which indicated a favorable adsorption process in the studied range. Adsorption for 1, 2, 4-acid was an endothermic process in comparison with that for 2-naphthol of an exothermic process. 2-naphthol molecules put a little influence on the adsorption capacity for 1, 2, 4-acid. However, the adsorption to 1, 2, 4-acid depressed that to 2-naphthol in a large extent for the stronger electrostatic interaction between 1, 2, 4-acid and adsorbent. The predominant mechanism can be contributed to the competition for adsorption sites. And the simultaneous environment was confirmed to be helpful to the selective adsorption towards 1,2,4-acid based on the larger selectivity index.

Keywords: aminated hypercrosslinked macroporous polymeric adsorbent; 1, 2, 4-acid; 2-naphthol; competitive adsorption

Introduction

Adsorption on solid matrix without the addition of any chemicals or UV radiation is proved attractive for their extremely large adsorption capacities towards various organic pollutants from aqueous media (Nirmalakhandan, 1989; Speth, 1990; Humphrey, 1995; Knaebel, 1995). Although adsorption reagents, especially activated carbons, have been found effective in removing organics from waters still present some shortcomings during the water and wastewater treatment process, such as the difficult regeneration and high disposal cost (Hassler, 1963; Cairo, 1982; Leitao, 1995; Furuya, 1997; Matatov, 2000; Kannan, 2001; Walker, 2001). In recent years, polymeric adsorbents, due to their wide variations in functionality, surface area, pores size and porosity, have been increasingly viewed as an alternative to activated carbons for removing and recovering organics from contaminated water with excellent efficiency (Tsyurupa, 1995; Azanova, 1999; Juang, 1999; Gokmen, 2002; Li, 2002a; 2002b). Most studies concentrate on single solute adsorption. Although with high adsorption capacity to 2-naphthol, these hypercrosslinked poly (styrene-divinylbenzene) copolymers appear much lower adsorption capability towards those extremely hydrophilic aromatic organic compounds such as 1-amino-2-naphthol-4-sulfonic acid (1, 2, 4-acid) (Xu, 1997; 1999). In fact, nowadays, chemical modification is widely applied to improve the surface chemistry of polymeric adsorbent for the aim of strengthening the adsorption affinity, as described earlier (Martel, 1994; Andrzej, 2001).

Competitive adsorption systems of micro-pollutants and the natural organic matter (NOM) or dyes onto activated carbons have ever deeply discussed in many publications

(Newcombe, 1997; Frimmel, 1999; Pelekani, 1999; Ebie, 2001; Li, 2001; Matsui, 2002a; 2002b). The competitive mechanism is mainly attributed to the pore size and/or the pore size distribution (PSD). In this paper, an aminated hypercrosslinked macroporous polymeric adsorbent (LA-8) is synthesized and selected as the solid reagent, for its effective adsorption ability towards both 1, 2, 4-acid and 2-naphthol that are important intermediates in dyestuff industry and are somewhat toxicity, poorly-biodegradability and colour causing (Greim, 1994). The focus of this paper is the competitive adsorption behaviors and mechanism for 1, 2, 4-acid and 2-naphthol onto LA-8.

1 Materials and methods

1.1 Chemicals

1, 2, 4-acid and 2-naphthol were of A. R. grade, purchased from Tingxin Chemical Reagent Plant and Shanghai Chemical Reagent Plant respectively (Shanghai, China). Hypercrosslinked polymeric adsorbent and dimethylamine solution were both obtained from Langfang Chemical Co. (Hebei Province, China).

1.2 Synthesis and characterization of the new bi-functional resin LA-8

The modified adsorbent LA-8 was synthesized through the following steps: in a 2000 ml round-bottomed flask, 300.0 g of hypercrosslinked polymeric adsorbent with certain chlorine content was swollen in 600 g of dimethylamine solution (40%). The mixture was mechanically stirred continuously at 318 K for 10 h. The polymer beads were extracted by successive washings with acetone and deionized water for more than 8 h, then dried in an oven at 333 K for about 8 h, finally stored in a desiccator overnight till no loss of weight before experimentation.

1.3 Characterization of polymer beads

The specific surface area and the pore size distribution of LA-8 (Fig. 1) were measured using a Micromeritics ASAP-2010 measurement instrument (Micromeritics Instrument Corp., Norcross, USA) following the Brunauer-Emmett-Teller (BET) method. Infrared spectra of LA-8 (Fig. 2) were obtained from a Nicolet 170 SX IR spectrometer (USA). The chlorine content was measured according to the method of Volhard. The elemental analysis of the adsorbent was obtained from a Perkin-Elmer 240 C Elemental Analytical Instrument (USA). The basic exchange capacity was measured by titration with 0.1 mol/L HCl and 0.1 mol/L NaOH solution. And the key characteristics of LA-8 are tabulated in Table 1.

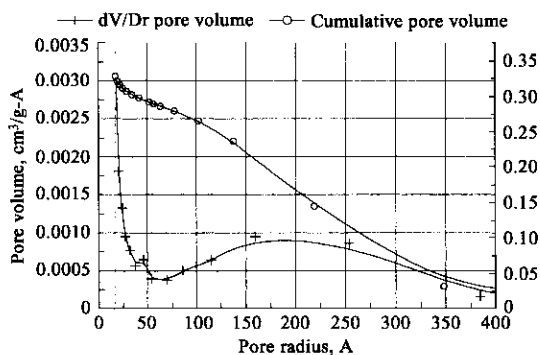


Fig. 1 Pore size distribution curve of LA-8

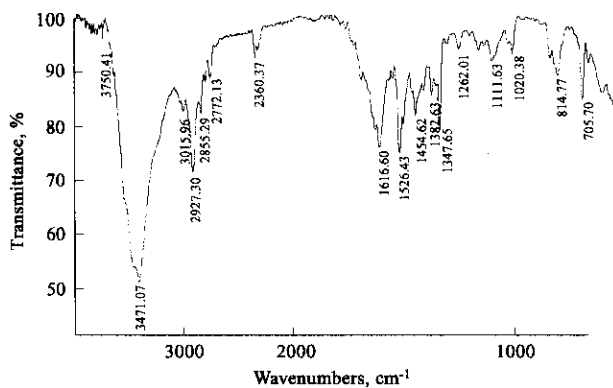


Fig. 2 Infrared spectra of LA-8

Table 1 Typical properties of LA-8

Properties	LA-8
Structure	Amine modified hypercrosslinked polymeric adsorbent
Polarity	Moderate polar
BET specific surface area, m ² /g	765.4
Average pore diameter, nm	1.3
Desorption average pore diameter, nm	10.6
Particle size, mm	0.4-0.6
Micropore area, m ² /g	430.8
Micropore volume, ml/g	0.195
Chloride content before aminize, %	6.02
Residual chloride content, %	0.85
Oxygen content, %	2.6
Weakly basic exchange capacity, mmol/g	1.51
Strong basic exchange capacity, mmol/g	0.05

1.4 Analysis

The solute concentrations were determined using High Performance Liquid Chromatography (HPLC) assembled by Waters 600 controller, Waters 600 pump (Waters Assoc., USA) and Waters 2487 Dual Absorbance UV detector at 230 nm. Mobile phase was 70% methanol: 30% 0.017 mol/L H₃PO₄ (pH = 2.27).

1.5 Experiments of adsorption

Single solute adsorption isotherms were performed using the conventional bottle-point technique at three different temperatures (288 ± 0.5 K, 303 ± 0.5 K and 318 ± 0.5 K). Fixed resin dosages of 0.1 g were contacted, in 250 ml stoppered bottles, with 100 ml of aqueous solutions of different concentrations of 1, 2, 4-acid or 2-naphthol. Followings are the determined initial concentrations (C₀, mg/L): 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L.

Simultaneous competition isotherms for binary mixtures were performed following the above procedure. The main differences lay here: (1) the initial concentrations of 2-naphthol were constant at 500 mg/L as the assumed background compound, while the concentrations of 1, 2, 4-acid varied in the range of 100–500 mg/L; (2) on the other hand, the initial concentrations of 1, 2, 4-acid were constant at 500 mg/L as the assumed background compound, while the concentrations of 2-naphthol varied in the range of 100–500 mg/L.

The preloading adsorption experiments were carried out according to the following steps. First, achieve the adsorption equilibrium for 2-naphthol and 1, 2, 4-acid (initial concentration controlled at 500 mg/L, temperature at 288 ± 0.5 K) respectively follow the method described in the next paragraph. Then, throw out the solutions, convert and centrifugalise every bottle until no solution on the adsorbent's surface. Finally, exactly add 100 ml of 1, 2, 4-acid solution of the same determined initial concentration into flasks furnished with 2-naphthol-preloaded adsorbents. In the same way, exactly add 100 ml of 2-naphthol solution of the same concentration into flasks furnished with 1, 2, 4-acid-preloaded adsorbents.

All flasks were completely sealed and then placed in a G25 model incubator shaker (New Brunswick Scientific), under the shaken rate of 130 r/min for 24 h.

The equilibrium adsorption capacity, q_e (mmol/g), was calculated with Eq. (2).

$$q_e = \frac{(C_0 - C_e)V}{MW} \quad (1)$$

Where, C₀ is the initial concentration (mg/L); C_e is the residual concentration at equilibrium (mg/L); V is the volume of solution (L); W is the weight of dry resin (g); and M is the molecule weight of 1, 2, 4-acid (239.2 g/mol) or 2-naphthol (144.2 g/mol).

2 Results and discussion

2.1 Single solute adsorption

Equilibrium adsorption isotherms of the single solute of

1, 2, 4-acid and 2-naphthol onto LA-8 are presented in Fig. 3. The L-type isotherms with convex upward in all cases involve favourable type isotherms according to the classification reported earlier (Giles, 1974; Weber, 1991). With the increasing adsorption amount, the affinity decreases expectably because of the reduction in the adsorption sites (Belmouden, 2001). There is an obvious difference in the isotherms for two adsorbates. The isotherm corresponding to higher temperature for 1, 2, 4-acid lies above, while for 2-naphthol below. Although the two kinds of solute molecules can both form hydrogen-bonding with the adsorbent as well as with solvent, the larger adsorption affinity involving electrostatic interaction between the sulfonic group of 1, 2, 4-acid and the basic group of $-N(CH_3)_2$ on the adsorbent increases with temperature, which maybe account for the above phenomena. The presence of amino group on LA-8 is further supported by the absorbance peaks at 2855 and 2772 cm^{-1} .

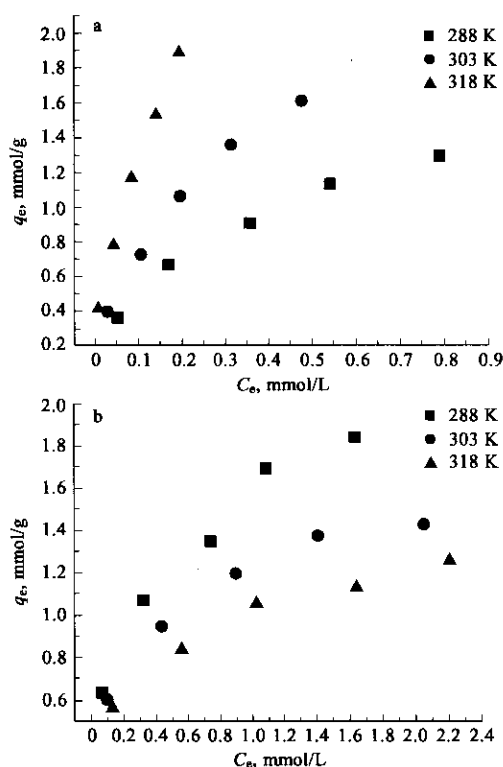


Fig.3 Adsorption isotherms for single solute of (a) 1, 2, 4-acid and (b) 2-naphthol

The experimental equilibrium isotherms were described by the experienced Freundlich equation in the following logarithmic form:

$$\log(q_e) = \log(K_f) + 1/n \log(C_e) \quad (2)$$

Where K_f and n are characteristic constants. And the Freundlich coefficient K_f is an indicator of the sorption capacity and the Freundlich exponent n denotes the adsorption site energy distribution of adsorbent (Carmo, 2000).

The regression equations established along with the constants K_f , n and the correlative coefficients R are summered in Table 2. It is quite obvious that the Freundlich

adsorption law is applicable to the studied adsorption systems since the values of R are larger than 0.996 in all cases. According to the value of K_f in Table 2, the capacity of the single adsorption for 1, 2, 4-acid increases with temperature, the reverse for 2-naphthol. Consequently, adsorption towards 1, 2, 4-acid is considered an endothermic rather than an exothermic process of that towards 2-naphthol. The value of constant n is always more than 1, indicating a favorable adsorption.

Table 2 Regression parameters of Freundlich isotherms

Adsorbate	Adsorption environment	Temperature, K	K_f	n	R
1, 2, 4-acid	Singly	288	1.471	2.208	0.999
		303	2.358	1.992	0.998
		318	4.495	1.845	0.999
	Simultaneously	288	1.590	2.381	0.992
		303	2.759	1.938	0.999
		318	2.251	1.976	0.989
	Preloading	288	1.307	2.987	0.994
		303	2.586	2.294	0.997
		318	2.588	2.793	0.999
2-naphthol	Singly	288	1.571	2.916	0.997
		303	1.208	3.333	0.996
		318	1.005	3.484	0.998
	Simultaneously	288	0.578	4.504	0.993
		303	0.718	5.102	0.994
		318	0.527	8.403	0.998
	Preloading	288	0.175	1.324	0.994
		303	1.048	3.058	0.996
		318	0.502	4.902	0.999

2.2 Simultaneous adsorption

The simultaneous adsorption isotherms of the tested compounds from binary solute solutions can also be given a good fit with Freundlich model, the results added in Table 2. At lower temperature, the adsorption capacity to 1, 2, 4-acid increases a little when 500 mg/L of 2-naphthol as the background, compared with single adsorption environment. So the adsorbed molecules of 2-naphthol enhance the adsorption of 1, 2, 4-acid. Some naphthalene ring interacts with the benzene ring of the adsorbent through van der Waals force, and the outward hydroxyl of both kinds of molecules at the meantime can form hydrogen bonding. On the other hand, the electrostatic interaction between the hydroxyl and amino groups should as well respond to the phenomena. However, at higher temperature, the net adsorption affinity to 1, 2, 4-acid becomes weaken, by reason of the increasing desorption amounts of 2-naphthol molecules shown in Fig. 4a.

As to much lower adsorption capacity of 2-naphthol from the tested simultaneous systems than that from the sole solute solution, considered the pore size is large enough for the studied molecules to pass through, the main reason is that the faster adsorption process for 1, 2, 4-acid appears because of the presence of larger electrostatic interaction, then molecules of 1, 2, 4-acid further shield the adsorption sites. Thus, the competition for the adsorption sites is considered the predominant mechanism. The increase of temperature to 303 K causes the larger adsorption capacity to 2-naphthol, which

can be explained by the stronger interaction of solute-solute. However, if keeping temperature further increasing up to 318 K, the change of the adsorption capacity to 2-naphthol is in the reverse direction, which is obviously influenced by the increasing desorption effect of water molecules, i. e., the larger affinity between solute-solvent. As expected, more molecules of 1, 2, 4-acid are brought to the liquor seen from Fig.4b.

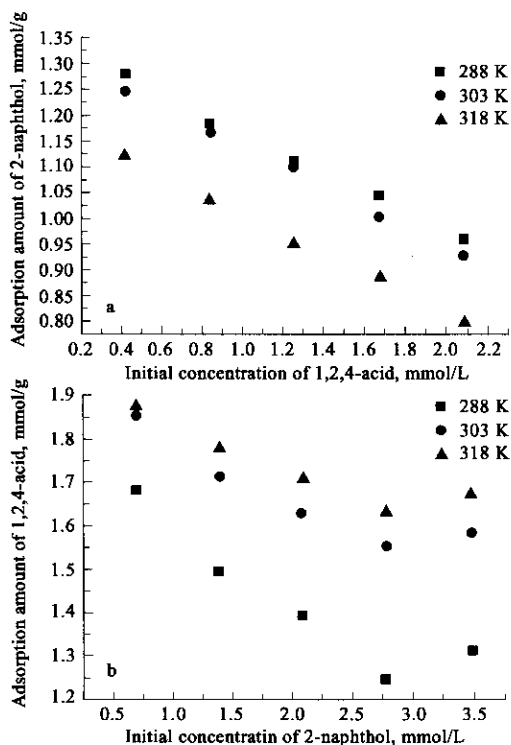


Fig.4 Influence of initial concentration of target solute on the adsorption amount of the background compound at simultaneous situation (a) 500 mg/L of 2-naphthol as surrounding and (b) 500 mg/L of 1, 2, 4-acid as surrounding

2.3 Preloading adsorption

Freundlich model is expectably appropriate to describe the preloading adsorption processes for different cases since *R* in Table 2 is over 0.994. The preloaded molecules of 2-naphthol pay a little influence on the adsorption of 1, 2, 4-acid. But from Fig.5a the initial concentrations of 1, 2, 4-acid mainly affect the amounts of 2-naphthol on the solid phase in a linear way at the same temperature, and the increasingly steeper slopes of the curves in Fig. 5a imply certain impact of temperature. The similar trend is visible in Fig. 5b. As expected, there is an apparent effect of preloaded molecules of 1, 2, 4-acid on the adsorption of 2-naphthol. In another word, the surface furnished with 1, 2, 4-acid results in relatively lower adsorption potential energy for the presence of the larger interaction between solute-sorbent in comparison with that between solute-solvent.

2.4 Selectivity index

Selectivity index is often used to evaluate an adsorbent. Define the separation factor as:

$$D = q_a / C_e \tag{3}$$

Then the selectivity index of the first component has the

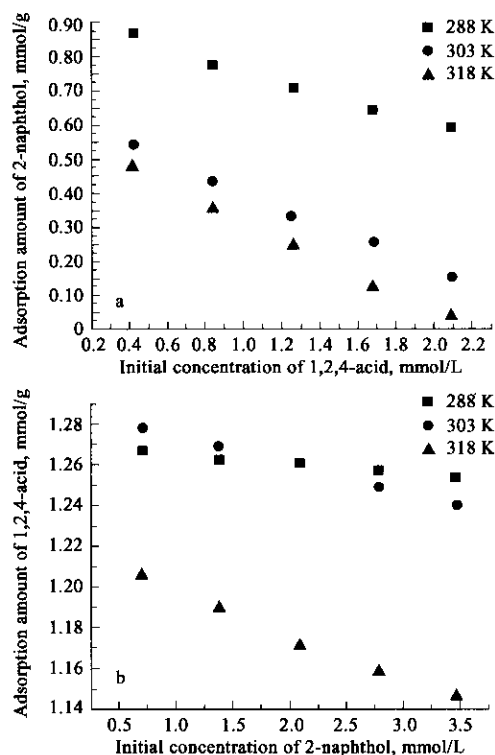


Fig.5 Influence of initial concentration of target solute on the adsorption amount of the background compound at preloading situation (a) 500 mg/L of 2-naphthol as surrounding and (b) 500 mg/L of 1, 2, 4-acid as surrounding

following form:

$$S_{1/2} = D_1 / D_2 \tag{4}$$

Where *D*₁ and *D*₂ represent the separation factor of two solutes respectively.

It certainly be irrational the selectivity indexes of 1, 2, 4-acid on the preloaded surface of LA-8 with 2-naphthol be calculated with Eq.(4), for the unequal matter of 2-naphthol in the studied adsorptive systems. The selectivity indexes of 1, 2, 4-acid for simultaneous adsorption systems are given in Table 3, those for single solution as the reference. The original concentration of 2-naphthol controlled to be the constant value of 500 mg/L. It can be clearly seen that the adsorption selectivity of 1, 2, 4-acid increases with temperature while decreases with initial concentrations as expected. Generally speaking, the simultaneous environment helps to the selective adsorption of 1, 2, 4-acid. We can then conclude that the molecule of 1, 2, 4-acid other than 2-naphthol is ready to leave bulk to the solid phase since the much stronger affinity occurs. The exception happens at the

Table 3 Selectivity index of 1, 2, 4-acid

Adsorption environment	Temperature, K	The original concentration of 1, 2, 4-acid, mg/L				
		100	200	300	400	500
Singly	288	6.71	3.48	2.26	1.86	1.44
	303	20.84	9.71	7.69	6.19	4.8
	318	61.73	31.83	24.72	18.98	17.04
Simultaneously	288	16.98	11.24	7.58	5.25	4.76
	303	31.64	16.89	13.95	13.29	12.06
	318	45.66	31.99	29.79	21.61	16.33

highest temperature as well lowest initial concentration, i. e., the minimum ratio of initial concentration. This reason is probably in the integrated reverse influences of solute-solute and solute-solvent interaction.

3 Conclusions

Freundlich equation can give an excellent fit to both single and binary adsorption isotherms, which indicates a favorable adsorption process for the studied cases. An endothermic adsorption process for 1, 2, 4-acid takes place, while for 2-naphthol an exothermic process.

Different degrees of competitive adsorption phenomena take place for various tested binary solute environments. 2-naphthol molecules put a little influence on the adsorption capacity for 1, 2, 4-acid, however, just opposite effect of 1, 2, 4-acid is put on 2-naphthol adsorption. The stronger electrostatic interaction between 1, 2, 4-acid and adsorbent is considered the main reason and it causes the prior adsorption for 1, 2, 4-acid.

Generally speaking, the simultaneous environment helps to the selective adsorption of 1, 2, 4-acid according to the larger selectivity index, also because the competition of adsorption sites happens.

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