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Effects of the surface chemistry of macroreticular adsorbents on the adsorption of 1-naphthol/1-naphthylamine mixtures from water

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Abstract: The adsorption behaviors of 1-naphthol, 1-naphthylamine and 1-naphthol/1-naphthylamine mixtures in water over two macroreticular adsorbents were investigated in single or binary batch systems at 293 K, 303 K and 313 K respectively. All the adsorption isotherms in the studied systems can be adequately fitted by Langmuir model. In the case of aminated macroreticular adsorbent NDA103, 1-naphthol is adsorbed to a larger extent than 1-naphthylamine; while, the opposite trend is found for nonpolar macroreticular adsorbent NDA100. It is noteworthy that at higher temperature(303 K and 313 K), the total uptake amounts of 1-naphthol and 1-naphthylamine in all binary-component systems are obvious larger than the pure uptake amounts in single-component systems, which is presumably due to the cooperative effect primarily arisen from the hydrogen-bonding interaction between the loaded 1-naphthol and 1-naphthylamine molecules. The simultaneous adsorption systems were confirmed to be helpful to the selective adsorption towards 1-naphthol according to the larger selective index.

Keywords: macroreticular adsorbent; adsorption; 1-naphthol; 1-naphthylamine; cooperative effect

Introduction

Different organic compounds are commonly found in contaminated water. Among these, aromatic compounds are relatively frequent as contaminants. Owing to their acute toxicity and poor biodegradation, 1-naphthol and 1-naphthylamine, representatives of naphthalene compounds, are of top priority contaminants and also the most important substructures of potentially carcinogenic pollutants discharged from pharmaceutical, dyestuff, photographic, and agrochemical industries (Li, 2001; Zhu, 2000). Therefore, the efficient removal of 1-naphthol and 1-naphthylamine from waste streams has increasingly become a significant environmental concern (Lee, 1996; Liu, 2003). Adsorption is still a major pollution treatment method used for the elimination of organic compounds from water (Suzuki, 1997). In the past two decades, polymeric adsorbents have been used as an alternative to activated carbon in industrial applications to remove and recover the valuable aromatic compounds from wastewater. In order to increase the efficiency of polymeric adsorbents, a better knowledge of the interactions between adsorbent and adsorbate as well as between the loaded adsorbates in single or multi-component system is required. In this sense, various aspects such as: the effect of polymer matrix and/or chemical surface characteristics, the contribution of dispersive-electrostatic forces on the adsorbate-adsorbent interaction, etc., are still under discussion (Pan, 2002; Gusler, 1993; Juang, 1999; Xu, 1999; Karan, 1999a).

Generally, contaminated water contains more than one organic compounds. It is thus of industrial interest and significance to study the adsorption behaviors of multiple organic compounds on polymeric adsorbents. Owing to the repulsive or attractive interactions between the loaded adsorbates, the adsorption process of the binary components is expected to be competitive or cooperative. The competitive adsorption of organic pollutants onto polymeric adsorbents has been reported in literature (Liu, 2004; Damien, 2000; Jia, 2003; Daniela, 2004), but the cooperative adsorption (Faisal, 1996; Kazuhiko, 2000) can be hardly found.

In the current study batch adsorption runs of 1-naphthol and 1-naphthylamine were carried out on the two commercial macroreticular adsorbents NDA103 and NDA100 (with and without amino groups respectively) in single or binary systems. The purpose of the study is to achieve a better understanding on the interactions between adsorbate and adsorbent as well as between the loaded 1-naphthol and 1-naphthylamine molecules.

1 Materials and methods

1.1 Adsorbates and adsorbents

The aqueous solutions of adsorbates were prepared by dissolving 1-naphthol and 1-naphthylamine (Shanghai Chemical Reagent Station, China) into deionized water without further pH adjustment. Because the values of pH at adsorption equilibrium in the tested single or binary systems are kept from 5 to 8, it is assumed that the varied values of pH would not significantly influence the adsorption behaviours of adsorbates. The pK_a values of 1-naphthol and 1-naphthylamine were 9.30 and 10.08 respectively.

The nonpolar macroreticular adsorbent NDA100 was prepared by controlling the post-crosslinking reaction, while the aminated macroreticular adsorbent NDA103 was obtained by amination of NDA100 with dimethylamine in the postcrosslinking process (Pan, 2002), both of which were supplied by Jiangsu N&G Environmental Technology Co. Ltd. (Jiangsu, China). The specific surface area and the pore distribution of both resins were determined with a surface area measurement instrument (ASAP 2010 M, Micromeritics Instrument, Norcros, USA). The basic exchange capacity was measured by acidimetric method.

1.2 Adsorption isotherms

Single component adsorption isotherms were performed using the conventional bottle-point technique at three temperatures (293 K, 303 K and 313 K). Batch adsorption runs were carried out in 100 ml glass flasks. Prior to use, NDA100 and NDA103 adsorbents were extracted with ethanol for 8 h in a Soxhlet apparatus and vacuum desiccated at 325 K for 24 h. A definite amount of 0.050 g adsorbents were directly introduced into a 100 ml glass flask. Subsequently,

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50 ml of an aqueous solution of 1-naphthol or 1-naphthylamine with an initial concentration ranging from 0.6 to 8.0 mmol/L was added into each flask.

Adsorption of binary components system were conducted by following the above procedures except that the initial total concentrations of aqueous solutions were varied from 0.6 to 8.0 mmol/L with 50/50 molar ratio of 1-naphthol/1-naphthylamine.

The flasks were then transferred into a G 25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 150 r/min for 24 h. Note that the adsorption equilibrium is readily attained according to preliminary kinetics studies at the given temperature. The amount adsorbed of 1-naphthol and 1-naphthylamine can be calculated by the following equation:

$$Q_e = V_l(C_o - C_e)/1000W, \quad (1)$$

where C_o and C_e denote the initial concentration (mmol/L) and the residual concentration at equilibrium (mmol/L) respectively, Q_e refers to the amount adsorbed of 1-naphthol or 1-naphthylamine on the adsorbents (mmol/g), V_l is the volume of the aqueous solution (ml), and W is the mass of dry adsorbents (g).

The solution concentrations were determined using HPLC, which was connected to a Waters 600 controller, Waters 600 pump and Waters 2487 dual absorbance UV detector at 274 nm (Waters, USA). The mobile phase used was 0.1% $KH_2PO_4 \cdot H_2O$: methanol = 70 : 30 (V/V) and corresponding flow rate was determined as 1 ml/min.

2 Results and discussion

2.1 Characterization of polymeric beads

Characteristic properties of NDA100 and NDA103 are listed in Table 1. It can be seen that the polymer matrix of both adsorbents are nonpolar polystyrene which is believed to favour the adsorption of aromatic compounds due to π-π dispersion interaction between the aromatic ring of adsorbates and the phenyl ring of the polymer matrix (Coughlin, 1968; Juang, 1999). In addition, the amino groups on surface of NDA103 provide the greater adsorption affinity to 1-naphthol according to hydrogen-bonding interaction between adsorbate and adsorbent (Xu, 1999).

Table 1 Characteristics of NDA100 and NDA103 adsorbents

Property	NDA100	NDA103
Structure	Polystyrene	Polystyrene
Polarity	Nonpolar	Weakpolar
BET surface area, m^2/g	1225	611
Micropore area, m^2/g	740	376
Micropore volume, ml/g	0.336	0.171
Average pore diameter, nm	3.0	3.4
Desorption average pore diameter, nm	16.7	17.6
Particle size, mm	0.4—0.6	0.4—0.6
Tertiary amino group, mmol/g	0	1.57
Colour	Deep brown	Deep brown

2.2 Single-component adsorption

Adsorption of aromatic compounds on polymeric adsorbents in single-component system has been successfully described by Langmuir model (Dabrowski, 2001):

$$\text{Langmuir equation} \quad Q_e = \frac{K_l Q_m C_e}{1 + K_l C_e}, \quad (2)$$

where Q_m is the maximum adsorption capacity (mmol/g), namely complete coverage of available adsorption sites, K_l is the affinity constant (Xu, 1999; Slejko, 1985).

The adsorption isotherms of 1-naphthol or 1-naphthylamine in single-component system are shown in Fig.1. All the parameters in Langmuir model obtained by nonlinear regression of the experimental data are listed in Table 2. As shown in Fig.1 and Table 2, Langmuir model gives a good correlation of the single-component adsorption. It can also be seen that the larger adsorption capacity and affinity of 1-naphthylamine onto nonpolar adsorbent NDA100 is probably due to the greater electronic density of aromatic ring of 1-naphthylamine molecule, which gives the greater π-π dispersion interaction between adsorbate and adsorbent (Katrin, 2001). While, the more excellent adsorption property of 1-naphthol onto aminated adsorbent NDA103 may be attributed to the partial amino groups on the surface of NDA103, which causes hydrogen-bonding interaction between the amino group of adsorbent and the hydroxyl group of 1-naphthol molecule.

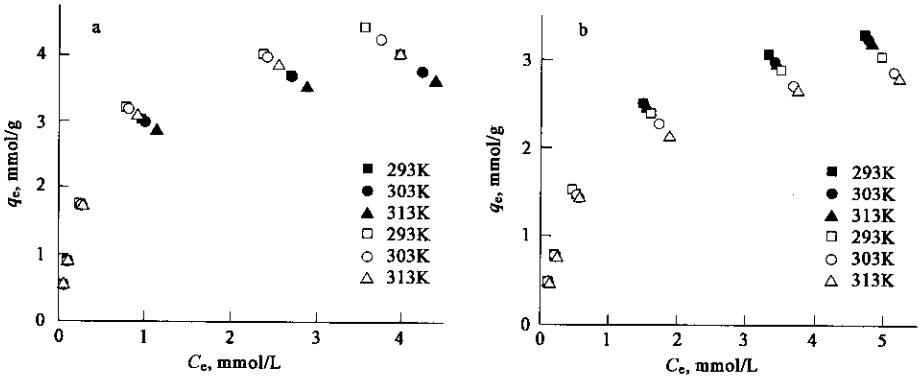

Fig.1 Equilibrium adsorption isotherms of 1-naphthol (solid symbols) and 1-naphthylamine (blank symbols) on NDA100 (a) and NDA103 (b) in single-component system

2.3 Binary components adsorption

Net attractive hydrogen-bonding interaction between the loaded 1-naphthol and 1-naphthylamine molecules may cause the extra uptake on adsorbents. Cooperative adsorption at the solid/liquid interface in binary-component system is defined when the total uptake of adsorbates ($B_t = B_1 + B_2$) in binary-component system is larger than the individual uptake of pure component (S_a or S_b) in single-component system at the same total equilibrium concentration ($C_t = C_1 + C_2$ in binary-component system; $C_t = C_1$ or C_2 in single-component system) (Faisal, 1996).

Fig.2 depicts the adsorption isotherms of 1-naphthol/1-naphthylamine on NDA100 and NDA103 in aqueous binary-component system. Their adsorption isotherms also show a

good fit with Langmuir model with a correlative factor $R^2 > 0.99$, and the results are summarized in Table 3. As shown in Fig.2 and Table 3, the total uptakes (B_t) of 1-naphthol and 1-naphthylamine in binary-component systems on both adsorbents are obviously higher than the individual uptakes (S_a or S_b) in single-component system at 303 K and 313 K, indicating the cooperative adsorption. It is probably attributed to the hydrogen-bonding interaction between the loaded 1-naphthol and 1-naphthylamine molecules, which can decrease the free energy of adsorption. Additionally, the electrostatic repulsion of 1-naphthol or 1-naphthylamine could be partly shielded and neutralized by each other, allowing a closer packing on the hydrophobic surface(Kazuhiko, 2000).

Table 2 Langmuir isotherms parameters in single-component system

Adsorbent	Adsorbate	Temp., K	K_l	Q_m, mmol/g	R^2
NDA103	1-naphthol	293	1.190	3.880	1.000
		303	1.140	3.826	0.997
		313	1.130	3.757	0.999
	1-naphthylamine	293	1.608	3.404	0.998
		303	1.576	3.186	0.999
		313	1.287	3.164	0.996
NDA100	1-naphthol	293	2.549	4.330	0.999
		303	2.611	4.153	0.999
		313	2.612	3.926	0.999
	1-naphthylamine	293	2.360	4.876	0.998
		303	2.314	4.738	0.999
		313	2.241	4.505	0.999

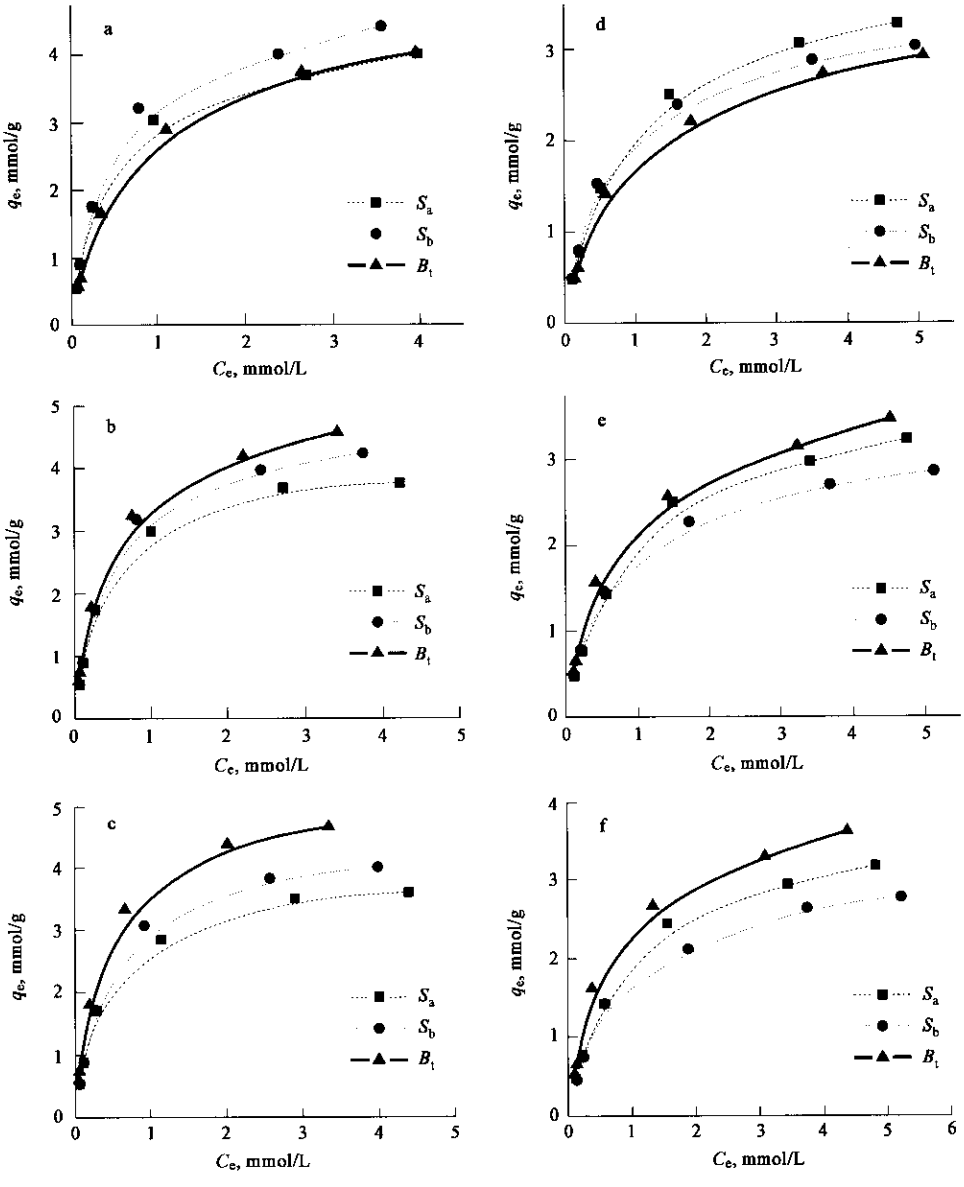

Fig.2 Equilibrium adsorption isotherms of 1-naphthol and 1-naphthylamine on NDA100 (a: 293 K; b: 303 K; c: 313 K), NDA103(d: 293 K, e: 303 K, f: 313 K) in binary-components system.
S_a or S_b means 1-naphthol or 1-naphthylamine absorbed in single-component system, B_t means both 1-naphthol and 1-naphthylamine adsorbed in binary-components system, respectively

With respect to the effect of temperature, it is shown from Fig.2 and Table 3 that the larger cooperative adsorption effect of 1-naphthol/1-naphthylamine mixtures with higher temperature may be contributed to the stronger hydrogen-bonding interaction between the loaded 1-naphthol and 1-naphthylamine molecules at higher temperature.

2.4 Selectivity index

Selectivity index is often used to evaluate the adsorption affinity of different adsorbates to adsorbent. The selectivity index of the first component is defined as:

$$S_{1/2} = K_{d1}/K_{d2} = \frac{(C_{o1} - C_{e1})C_{e2}}{C_{e1}(C_{o2} - C_{e2})}, \quad (3)$$

where K_{d1} and K_{d2} represent the distribution coefficient(L/g) of two adsorbates respectively. The selectivity indexes of 1-naphthol to 1-naphthylamine on NDA100 and NDA103 in binary components system at 293 K, 303 K and 313 K are

given in Table 4, those in single system as the reference. As shown in Table 4, the adsorption selectivity of 1-naphthol in binary system is much higher than that in single system as a reference, indicating that the loaded 1-naphthylamine molecules help 1-naphthol molecules to leave bulk to the solid phase by hydrogen-bonding interaction. It can also be seen that the adsorption selectivity of 1-naphthol on NDA103 is much more than that on NDA100 in both single and binary systems. This is probably due to the greater adsorption affinity of 1-naphthol to NDA103 by the additional hydrogen-bonding interaction between adsorbent and adsorbate.

Table 3 Langmuir isotherms parameters in binary-component system

Adsorbent	Adsorbate	Temp., K	K_1	Q_m, mmol/g	R^2
NDA103	1-naphthol	293	0.882	2.181	0.998
		303	1.227	2.366	0.996
		313	1.286	2.438	0.996
	1-naphthylamine	293	1.599	1.263	0.998
		303	1.852	1.557	0.997
		313	1.946	1.654	0.996
	1-naphthol +	293	1.138	3.402	0.998
	1-naphthylamine	303	1.469	3.902	0.997
		313	1.550	4.067	0.996
NDA100	1-naphthol	293	1.946	2.152	0.999
		303	2.877	2.365	0.999
		313	3.304	2.371	0.999
	1-naphthylamine	293	1.246	2.547	0.998
		303	2.174	2.684	0.998
		313	2.465	2.794	0.999
	1-naphthol +	293	1.566	4.662	0.999
	1-naphthylamine	303	2.503	5.036	0.999
		313	2.845	5.152	0.999

Table 4 Selectivity index of 1-naphthol to 1-naphthylamine in single and binary components system

Adsorbent	Adsorption system	Temp., K	The original concentration of adsorbate, mmol/L					
			0.6	1.0	2.0	4.0	6.4	8.0
NDA103	Single	293	0.904	0.888	0.872	1.128	1.122	1.138
		303	0.910	0.898	0.916	1.271	1.186	1.221
		313	1.182	1.106	1.005	1.395	1.212	1.239
NDA100		293	0.974	0.948	0.931	0.772	0.812	0.813
		303	0.945	0.976	0.968	0.759	0.829	0.786
		313	1.003	1.007	0.993	0.743	0.810	0.816
NDA103	Binary	293	1.747	1.786	1.973	2.072	2.125	2.111
		303	2.101	2.067	2.181	2.252	1.886	1.979
		313	2.008	2.102	2.033	2.007	1.871	1.922
NDA100		293	2.011	2.025	1.707	1.156	0.840	0.775
		303	1.352	1.368	1.295	0.993	0.826	0.757
		313	1.139	1.118	1.076	0.800	0.699	0.695

3 Conclusions

Nonpolar adsorbent NDA100 and aminated adsorbent NDA103 were used for removal of 1-naphthol and 1-naphthylamine from aqueous solutions. The adsorption behaviors of 1-naphthol, 1-naphthylamine and 1-naphthol/1-naphthylamine mixtures were compared in single or binary batch systems at 293 K, 303 K and 313 K. All the adsorption isotherms can be described by Langmuir model. The results show that the polymer matrix and surface chemistry of adsorbents play a significant role on the adsorption of 1-naphthol and 1-naphthylamine both in single and binary systems.

The larger uptake of 1-naphthylamine on NDA100 may be attributed to its greater electron density in the aromatic ring, which provides stronger π-π dispersion interaction between adsorbate and adsorbent. On the contrary, the greater affinity of 1-naphthol to NDA103 is probably due to the additional hydrogen-bonding interaction between adsorbate and adsorbent. At the higher temperatures, the extra uptake of 1-naphthol and 1-naphthylamine can be notably observed in binary adsorption system, which is attributed to the cooperative effect arisen from the hydrogen-bonding interaction between the loaded adsorbates. The binary simultaneous adsorption system helps to the selective adsorption of 1-naphthol according to the larger selective index.

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