

Removal enhancement of 1-naphthol and 1-naphthylamine in single and binary aqueous phase by acid–basic interactions with polymer adsorbents

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Abstract

In the present study removal performance of 1-naphthol and 1-naphthylamine from wastewater by single and binary adsorption was compared. Synergistic effects were investigated in single-solute, binary-solute, and the preloading adsorption systems at 293 K. Two commercial polystyrene adsorbents Amberlite XAD-4, a macroporous adsorbent, and NDA-100, a hyper-cross-linked adsorbent, were employed here for their frequent use in organic pollutants removal from contaminated waters. All the adsorption isotherms of 1-naphthol and 1-naphthylamine on both adsorbents were found to be well represented by the Langmuir equation. Adsorption capacity of the primary solute was enhanced in the presence of the co-solute, arising presumably from the synergistic effect caused by the laterally acid–base interaction between the adsorbed 1-naphthol and 1-naphthylamine molecules. Due to the stronger adsorption affinity of 1-naphthylamine to nonpolar adsorbents, adsorption enhancement of 1-naphthylamine in the presence of 1-naphthol is greater than that of 1-naphthol in the presence of 1-naphthylamine. The greater synergistic effect of 1-naphthol/1-naphthylamine equimolar mixtures on XAD-4 than that on NDA-100 partly results from the larger average pore size of the former adsorbent. A modified extended Langmuir model is proved to well describe the synergistic adsorption of 1-naphthol/1-naphthylamine equimolar mixtures in the binary-solute system. The synergistic coefficient of one adsorbate is linearly correlated with the amount of the other adsorbed on the adsorbent. © 2008 Elsevier B.V. All rights reserved.

Keywords: Synergistic adsorptions; 1-Naphthol; 1-Naphthylamine; Polymer adsorbent

1. Introduction

Water pollution by organic chemicals has been of great concern over decades. One of the major sources of organic pollutants is the chemical wastewater discharged from chemical plants, particularly in developing countries such as China [1]. Recently there is a growing interest on how to effectively and economically treat the chemical wastewater [2–4]. In the past decades, adsorption of chemical wastewater by polymeric adsorbents has been regarded as a potential technology, partly due to the

recovery of the chemical waste after regeneration of the spent adsorbent in field application, which subsequently results in a low operation cost and makes the chemical waste reuse [5,6].

As we know, most of them focus on adsorption of a single-solute from water. Little is known about bi-solutes or multi-solutes systems. In fact, adsorption behavior of bi-solutes or multi-solutes from water is more significant for chemical wastewater treatment by polymeric adsorbents, because organic contaminants are almost always released to the environment as solute mixtures. For example, ammonolysis of phenols, a basic and universal chemical reaction, usually produces a mass of waste steams containing both phenols and amines simultaneously. Multi-solute experiments may provide additional information on the removal technology by adsorption, such as the fraction of adsorption sites being shared with each solute tested, their relative affinities toward these sites, and the

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lateral interaction between the adsorbed solutes. Therefore, it is critically important to understand the altered adsorption properties caused by competitive or synergistic effects and the underlying mechanisms of the processes to accurately predict the adsorption behaviors of contaminants in phenols/amines co-solute systems. These two mechanisms, direct competition for sites and pore blockage, have been published as the two major mechanisms of competitive adsorption [7–9] in small studies, but less work focusing on the synergistic adsorption processes and mechanisms was reported [10–13]. Our understanding of factors controlling the competitive or synergistic adsorption of multiple organic compounds on resins is still limited. Specially, the multi-solute adsorption process is not well understood at the quantitative level. Good predictive tools are not currently available due to an insufficient understanding of the lateral interactions between the adsorbed adsorbates in multi-solute adsorption systems [14].

In the present study 1-naphthol and 1-naphthylamine were selected as typical adsorbates because: (1) they are listed among top priority contaminants and (2) they are widely used as industrial intermediates and frequently they are both in present wastewater [15]. Two commercial polystyrene adsorbents Amberlite XAD-4, a macroporous adsorbent, and NDA-100, a hyper-cross-linked adsorbent, were employed here for their wide use in removal of organic pollutants from wastewater [13,16]. A model [12,16], based on both the confirmed competitive adsorption mechanism due to direct competition for adsorption sites and the proposed synergistic adsorption mechanism drawn from the lateral acid–base interaction of the adsorbed adsorbates, was adopted to describe the multiple organic compound adsorption processes. The objective of the current study is to test for the removal enhancement mechanisms by synergistic adsorption and to model the synergistic effects of 1-naphthol/1-naphthylamine co-solute adsorption onto polymer adsorbents.

2. Experimental

2.1. Adsorbents and adsorbates

Two commercial nonpolar polymer adsorbents, Amberlite XAD-4 and NDA-100, were purchased from Rohm & Haas Co. Ltd. (USA) and Jiangsu N&G Environmental Technology Co. Ltd. (PR China), respectively. They were chosen because they were characterized systematically in a number of prior studies of single organic contaminant adsorption [4] and were widely used in industrial applications for efficient removal and recovery of the valuable organic compounds from waste streams [1,13]. Both adsorbents were extracted with ethanol for 8 h in a Soxhlet apparatus and desiccated in vacuum at 325 K for 24 h prior to use. Their specific surface area and the pore size distribution were measured by using nitrogen adsorption on ASAP-2010C Micromeritics Instrument (USA), and then calculated by BJH and HK models [4,13]. Physio-chemical properties of both adsorbents are presented in Table 1. 1-Naphthol and 1-naphthylamine used in this study are of analytical grade and were purchased from Shanghai reagent station.

Table 1
Properties of polymer adsorbents

Sorbent	NDA-100	XAD-4
Matrix	Polystyrene	Polystyrene
Polarity	Nonpolar	Nonpolar
BET surface area (m ² /g)	1109	814
Micropore volume (cm ³ /g)	0.336	0.012
Average pore diameter (nm)	3.0	5.8
Particle size (mm)	0.4–0.6	0.4–0.6

2.2. Solutions and analytical techniques

The background solution used in the adsorption experiments contained 10^{−3} M KH₂PO₄ for buffering the aqueous solutions at neutral pH, where more than 99% of 1-naphthol and 1-naphthylamine were nonionic. The primary stock solution of each solute was prepared by dissolving a predetermined mass of solute in methanol. Specified amounts of stock solution were delivered into the aqueous phase of each reactor. Methanol volume was controlled below 0.1% (v/v) of the total aqueous phase to minimize cosolvent effects. The solute concentrations in the initial and equilibrated aqueous solutions were measured with a reverse-phase HPLC (Waters 600) equipped with dual absorbance UV detector (Waters 2487). Both 1-naphthol and 1-naphthylamine were analyzed using the UV detector set at wavelength of 274 nm. The mobile phase was a mixture of HPLC-grade methanol and MilliQ water at volumetric ratios of 7:3 and the corresponding flow rate was 1 mL/min.

2.3. Adsorption experiments

Equilibrium adsorption experiments of single-solute system were carried out at 293 ± 0.5 K in 100 mL glass flasks. Owing to their non-polarity, XAD-4 and NDA-100 were necessarily wetted with methanol and then rinsed three times with deionized water prior to use. Subsequently, all flasks contained a fixed mass of the adsorbent and a known volume of initial aqueous solutions with the desired single-solute concentration. The flasks were then transferred to a G 25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 150 rpm for 24 h to ensure that the adsorption process reached equilibrium.

The adsorption isotherms for binary-solute system were conducted by above-mentioned procedures, except that the initial 1-naphthol and 1-naphthylamine concentration in aqueous solution were identical (equimolar solutes experiments), or that of one solute was determined at two different constant levels of 0.6 and 4 mmol/L and the other varies at different levels (primary-co-solutes experiments).

The preloading adsorption experiments were conducted by one solute (1-naphthol or 1-naphthylamine) adsorption on adsorbents preloaded with the other. The details of the experimental procedure were very similar to those described above for single-solute adsorption experiments.

For all above systems, control experiments were conducted using flasks prepared similarly but containing no adsorbent for

assessing loss of solutes to the flask components during sorption tests. Results of triplicate flasks showed that the average solution phase concentrations of each solute were within 96–102% of the respective initial concentration of the same solution analyzed similarly. Hence, compound loss was negligible.

The equilibrium solid-phase concentrations of the adsorbates, Q_e , were quantified based on a mass balance of each solute between the two phases with the following equation:

$$Q_e = \frac{V_1(C_0 - C_e)}{W} \quad (1)$$

where W and V_1 are the mass (g) of dry adsorbent and the volume (L) of aqueous solution in a given flask; C_0 and C_e are the initial and final residual aqueous-phase solute concentrations expressed in mmol/L; and Q_e is in (mmol/g). The volume of aqueous solution was calculated from its weight assuming a density of 0.998 g/mL at 293K.

2.4. Isotherm model

The isotherm data measured for single-solute system and for the primary solute of the preloaded systems were fit to the Langmuir model (LM)

$$Q_e = \frac{K_1 Q_m C_e}{1 + K_1 C_e} \quad (2)$$

where Q_m is the maximum adsorption capacity (mmol/g) of the adsorbent, K_1 is the affinity constant (L/mmol).

For binary-solute cases, the extended Langmuir model (ELM) [17–19], based on the mechanism of direct competition for adsorption sites, is the simplest and most widely used model

$$Q_{ei} = \frac{K_{li} Q_{mi} C_{ei}}{1 + K_{11} C_{e1} + K_{12} C_{e2}} \quad (i = 1 \text{ or } 2) \quad (3)$$

where Q_{mi} and K_{li} are the model parameters (the subscript 1 or 2 represents the corresponding adsorbate) obtained expediently from Eq. (2) in the single-solute system. The ELM model usually could not give a satisfactory description partly due to ignoring the competitive or synergistic effect by the specific interaction between the adsorbed adsorbate molecules [20].

Therefore, a modified extended Langmuir model (MLM) [12,16] was developed to describe the 1-naphthol/1-naphthylamine co-solute adsorption system. By introducing synergistic efficiencies (θ) of adsorbates into Eq. (3) we got

$$Q_{ei} = \frac{K_{li} Q_{mi} C_{ei}}{1 + K_{11} C_{e1} + K_{12} C_{e2}} (1 + \theta) \quad (i = 1 \text{ or } 2) \quad (4)$$

Assume that synergistic efficiency (θ) arises from the adsorbate–adsorbate lateral interaction which is linearly related with the amount adsorbed (Q_e) at equilibrium of the other adsorbate

$$\begin{aligned} \theta_1(Q_{e2}) &= a_1 Q_{e2} + b_1 \\ \theta_2(Q_{e1}) &= a_2 Q_{e1} + b_2 \end{aligned} \quad (5)$$

where a and b are the constant parameters of synergistic efficiency (the subscript 1 and 2 represent different adsorbates). By combining Eqs. (1), (4) and (5), the calculated amount of

1-naphthol (Q_{ea}^{cal}) and 1-naphthylamine (Q_{eb}^{cal}) adsorbed at equilibrium can be obtained as

$$\begin{aligned} Q_{ea}^{cal} &= \frac{K_{1a} Q_{ma} C_{ea}}{1 + K_{1a} C_{ea} + K_{1b} C_{eb}} \left(\frac{1 + a_a(C_{0b} - C_{eb})V_1}{1000W + b_a} \right) \\ Q_{eb}^{cal} &= \frac{K_{1b} Q_{mb} C_{eb}}{1 + K_{1a} C_{ea} + K_{1b} C_{eb}} \left(\frac{1 + a_b(C_{0a} - C_{ea})V_1}{1000W + b_b} \right) \end{aligned} \quad (6)$$

where the subscript a and b represents 1-naphthol and 1-naphthylamine, respectively; the superscripts cal and exp indicate calculated and experimental amounts adsorbed, respectively. The Chi-square (χ^2) was adopted to evaluate the validity of the MLM model and n is the total number of experimental data point

$$\chi^2 = \frac{\sum_{i=1}^n (Q_{ei}^{exp} - Q_{ei}^{cal})^2 / Q_{ei}^{exp}}{n - 1} \quad (7)$$

3. Results and discussion

3.1. Characterization of polymeric adsorbents

Characteristic properties of XAD-4 and NDA-100 adsorbents employed in this study are listed in Table 1. The matrix structures 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 the compounds and the phenyl ring of the polymer matrix. In addition, the specific surface area and micropore volume of NDA-100 are higher than XAD-4, which may result in a larger adsorption capacity of NDA-100 to 1-naphthol and 1-naphthylamine. It is noteworthy that more than 60% of the specific surface area of NDA-100 is distributed in the micropore region (pore diameter < 2 nm), while only about 8% for XAD-4 is distributed there. Contrarily, the average pore diameter of XAD-4 is almost twice as large as for NDA-100.

3.2. Adsorption equilibria of single-solute systems

LM model parameters of 1-naphthol/1-naphthylamine in single-solute adsorption systems are listed in Table 2, obtained by nonlinear regression of the experimental data with Levenberg–Marquardt algorithm. The experimental data and the correlating curves based on the LM model are plotted in Fig. 1. LM yields a good correlation for all the three adsorption systems.

AS presented in Table 2, the affinity of 1-naphthylamine for both XAD-4 and NDA-100 is higher than for 1-naphthol, presumably due to the thicker electron density phenyl ring of 1-naphthylamine [21]. In addition, higher adsorption capacity of NDA-100 than XAD-4 may be attributed to its higher micropore structure.

3.3. Adsorption equilibria on preloaded adsorbents

A preloaded adsorption experiment was conducted wherein 1-naphthol (2.7 mmol/g) was first adsorbed on XAD-4 and the preloaded XAD-4 was then used as adsorbent for 1-naphthylamine adsorption isotherm in Fig. 1. LM also yields

Table 2
Langmuir isotherms parameters at 293 K

		Adsorbent	K_1 (L/mmol)	Q_m (mmol/g)	R^2	
Single-solute adsorption system						
1-Naphthol	XAD-4		2.057	2.941	0.998	
	NDA-100		2.549	4.330	0.999	
1-Naphthylamine	XAD-4		1.922	3.391	0.998	
	NDA-100		2.360	4.876	0.998	
Primary solute	Preloaded adsorbate	Adsorbent	K_1 (L/mmol)	Q_m (mmol/g)	R^2	
Preloaded adsorption system						
1-Naphthol	1-Naphthylamine	XAD-4	0.534	3.708	0.995	
		NDA-100	0.937	3.310	0.993	
1-Naphthylamine	1-Naphthol	XAD-4	0.281	9.155	0.984	
		NDA-100	0.573	5.329	0.985	
Primary solute	Co-solute	Concentration (mmol/L)	Adsorbent	K_1 (L/mmol)	Q_m (mmol/g)	R^2
Primary-coexist binary-solute adsorption system						
1-Naphthol	1-Naphthylamine	0.6	XAD-4	0.389	7.958	0.998
		4		0.065	12.860	0.998
		0.6	NDA-100	3.170	4.835	0.999
		4		0.431	5.732	0.994
1-Naphthylamine	1-Naphthol	0.6	XAD-4	0.209	18.968	0.998
		4		0.069	38.440	0.995
		0.6	NDA-100	1.063	9.118	0.999
		4		0.402	9.871	0.997
Primary solute	Adsorbent	K_1 (L/mmol)	Q_m (mmol/g)	R^2		
Equimolar binary-solute adsorption system						
1-Naphthol	XAD-4	1.534	2.031	0.996		
	NDA-100	1.946	2.152	0.999		
1-Naphthylamine	XAD-4	0.935	2.815	0.995		
	NDA-100	1.246	2.547	0.998		
1-Naphthol + 1-naphthylamine	XAD-4	1.186	4.793	0.996		
	NDA-100	1.566	4.662	0.999		

a good correlation for this system and the correlated parameters are added in Table 2. In general, the presence of a preloaded adsorbate on the surface of an adsorbent will diminish the capacity of the adsorbent for other solutes [22]. However, there are some unique systems in which adsorbate interactions can lead to enhanced adsorption. This phenomenon has been observed for graphitized carbon blacks [11,23]. The generally accepted explanation for this “synergistic” type of adsorption is that on homogeneous surfaces lateral attractive interactions between adsorbate molecules can cause enhanced adsorption of some adsorbates. In this study, Table 2 and Fig. 1 show that the adsorption capacity of 1-naphthylamine on XAD-4 preloaded with 1-naphthol is apparently greater than single-solute adsorption systems. For example, at the equilibrium concentration of 3 mmol/L, 2.9 mmol/g of 1-naphthylamine was adsorbed on XAD-4 firstly and an additional 1.3 mmol/g of 1-naphthylamine was adsorbed on the 1-naphthol-modified XAD-4. This clearly demonstrates that preloaded 1-naphthol on XAD-4 changes the chemistry and adsorption properties of the adsorbent and that 1-naphthylamine can be adsorbed synergistically by the additional acid–base interaction and the natural π – π dispersion interaction.

The similar reason could also explain the synergistic adsorption of 1-naphthol on XAD-4 preloaded with 1-naphthylamine (2.5 mmol/g).

However, the synergistic effect of the latter is much greater than the former. This is because that adsorption and desorption are dynamic processes, and the direct competition adsorption of 1-naphthol and 1-naphthylamine for similar π – π dispersion interaction sites on XAD-4 could not be ruled out. Due to the stronger affinity of 1-naphthylamine for the nonpolar adsorbent XAD-4 discussed in previous sections, the displacement of 1-naphthylamine molecules in solution to 1-naphthol molecules preloaded on adsorbent is greater than the one of 1-naphthol molecules in solution to 1-naphthylamine molecules preloaded on adsorbent. Hence, considering both competitive and synergistic effect, the greater affinity enhancement of 1-naphthol to XAD-4 preloaded with 1-naphthylamine is obviously observed.

On the other hand, Table 2 and Fig. 1 show that the adsorption capacity of preloaded NDA-100 (3.9 mmol/g 1-naphthol or 3.2 mmol/g 1-naphthylamine) is apparently less than single-solute adsorption systems. The negative effect on the adsorption

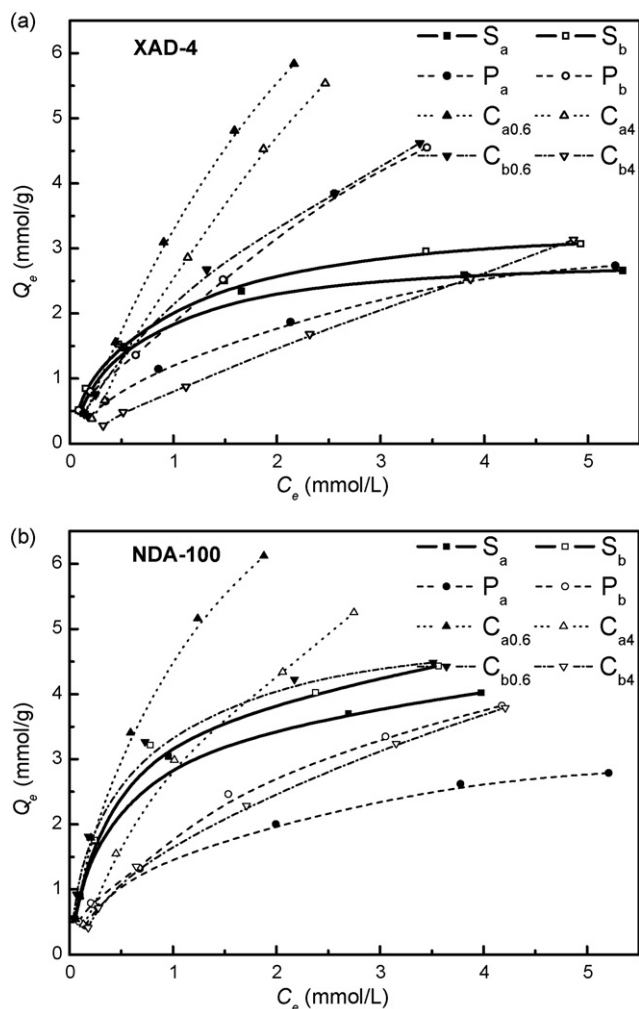


Fig. 1. Equilibrium adsorption isotherms of 1-naphthol and 1-naphthylamine on (a) XAD-4 and (b) NDA-100 in single-solute, preload, and binary-solute systems at 293 K. S_a , 1-naphthol in single-solute adsorption system; S_b , 1-naphthylamine in single-solute adsorption system; P_a , primary solute 1-naphthol on adsorbent preloaded with 1-naphthylamine; P_b , primary solute 1-naphthylamine on adsorbent preloaded with 1-naphthol; $C_{a0.6}$, primary solute 1-naphthol with 0.6 mmol/L co-solute 1-naphthylamine; C_{a4} , primary solute 1-naphthol with 4 mmol/L co-solute 1-naphthylamine; $C_{b0.6}$, primary solute 1-naphthylamine with 0.6 mmol/L co-solute 1-naphthol; C_{b4} , primary solute 1-naphthylamine with 4 mmol/L co-solute 1-naphthol.

of preloaded NDA-100 is probably attributed to its much smaller pore size. Macroporous adsorbents with small pore size are preferably jammed by the preloaded adsorbate molecules. Then, the pore distribution structure of adsorbents plays a very important role on synergistic adsorption of 1-naphthol/1-naphthylamine on preloaded adsorbents.

3.4. Adsorption equilibria of binary-solute systems with primary-co-solutes

Fig. 1 and Table 2 present that the adsorption capacity of XAD-4 displays significantly higher values for the primary solute compared to the single-solute experiment. The plots show that the adsorption performance of XAD-4 for 1-naphthol is

apparently enhanced by the presence of 1-naphthylamine in the mixture. Although the competitive adsorption of 1-naphthol and 1-naphthylamine on XAD-4 could not be ruled out due to their same adsorption driving force of π - π dispersion interaction between the aromatic ring of the compounds and the phenyl ring of the polymer matrix, the adsorption data suggest that it is more likely that we have a greater affinity driven by the additional acid-base interaction [10]. The adsorbed 1-naphthylamine molecules will change the chemical characteristics of the adsorbent and being basic and cationic in nature, they could further interact with the acidic and anionic 1-naphthol in the solution leading to some closer adsorption and to the observed enhancement in the adsorption of 1-naphthol on adsorbent. By the same reason, the great synergistic effect on adsorption capacity of XAD-4 for 1-naphthylamine is also observed in the presence of 1-naphthol. Additionally, the measured primary solute isotherm of 1-naphthol or 1-naphthylamine becomes more linear and the adsorption capacity of primary solute notably increases as the concentration of co-solute increases.

Fig. 1 and Table 2 also indicate that the synergistic adsorption phenomenon of NDA-100 is also observed in the co-solute of 1-naphthol and 1-naphthylamine. However, the degree of synergistic effect is much less than that of XAD-4 under the same experiment conditions. Sequentially, the calculated adsorption capacity of XAD-4 (in Table 2) is much larger than NDA-100 in co-solute adsorption system, in revise with single-solute adsorption. In addition, the augment of the adsorption capacity of primary solute on NDA-100 as the concentration of co-solute increases is not as much as XAD-4. These strongly suggest that the movement of acid-base molecules in solution are restricted to greater extent by the smaller pore size of NDA-100.

3.5. Adsorption equilibria of binary-solute systems with equimolar solutes

Fig. 2 shows 1-naphthol/1-naphthylamine equimolar binary-solute adsorption isotherms predicted with MLM and ELM model onto XAD-4 and NDA-100, respectively, and the validity of the above-mentioned models was indicated by the χ^2 values. The optimum a and b values for ELM and MLM are listed for each equimolar binary-solute system in Table 3. The much lower values of χ^2 for MLM than ELM proved more valid of the MLM when describing the equimolar 1-naphthol/1-naphthylamine binary-solute adsorption system on nonpolar polymer adsorbents.

Though competitive adsorption between 1-naphthol and 1-naphthylamine on nonpolar XAD-4 occurs presumably due to the direct competition for their similar adsorption sites, the experimental uptakes of 1-naphthol and 1-naphthylamine in equimolar binary-solute system are obviously higher than the corresponding uptakes predicted by ELM, as shown in Fig. 2, indicating that the synergistic effect exists in 1-naphthol/1-naphthylamine equimolar co-solute adsorption system in the other point of view. It can also be seen that the notable larger synergistic response factors (a) of 1-naphthol or 1-naphthylamine on XAD-4 than NDA-100 indicate the greater

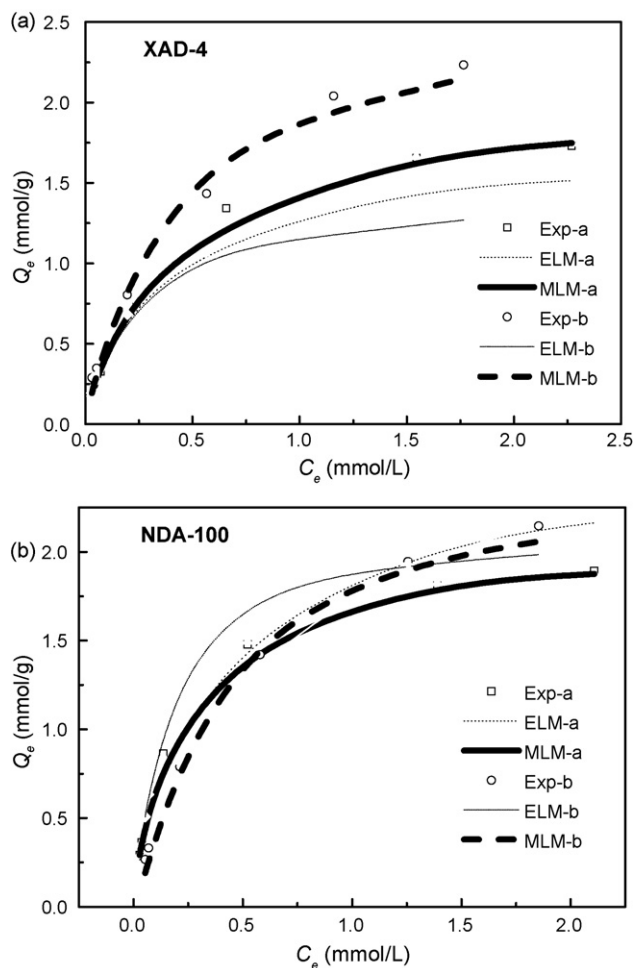


Fig. 2. Correlated (MLM) and predicted (ELM) vs. experimental equimolar binary-solute amounts adsorbed on (a) XAD-4 and (b) NDA-100 at 293 K. Exp-a: experimental 1-naphthol amounts adsorbed; Exp-b: experimental 1-naphthylamine amounts adsorbed.

adsorption enhancement on XAD-4 as discussed in the previous preload and primary-coexist binary-solute adsorption systems. It is probably due to the larger pore size of XAD-4, which is helpful for the adsorbed 1-naphthol and 1-naphthylamine molecules to interact with each other inside the resin particles. Table 3 displays that the synergistic response factors of 1-naphthylamine are always greater than 1-naphthol, indicating the larger enhancement of 1-naphthylamine adsorption by the coexist 1-naphthol. These phenomena are also identical with the experimental results of the greater synergistic adsorption effect of 1-naphthylamine as the primary solute in co-solute and preload adsorption systems. It can be explained that though

Table 3

Optimized a and b values from the MLM, and χ^2 values from the ELM and MLM for equimolar binary adsorption equilibriums at 293 K

Adsorbent	1-Naphthol				1-Naphthylamine			
	MLM		χ^2		MLM		χ^2	
	a_a	b_a	MLM	ELM	a_b	b_b	MLM	ELM
XAD-4	0.066	0.006	0.0022	0.0244	0.557	-0.245	0.0128	0.3679
NDA-100	-0.127	0.140	0.0002	0.0279	0.412	-0.742	0.0079	0.1205

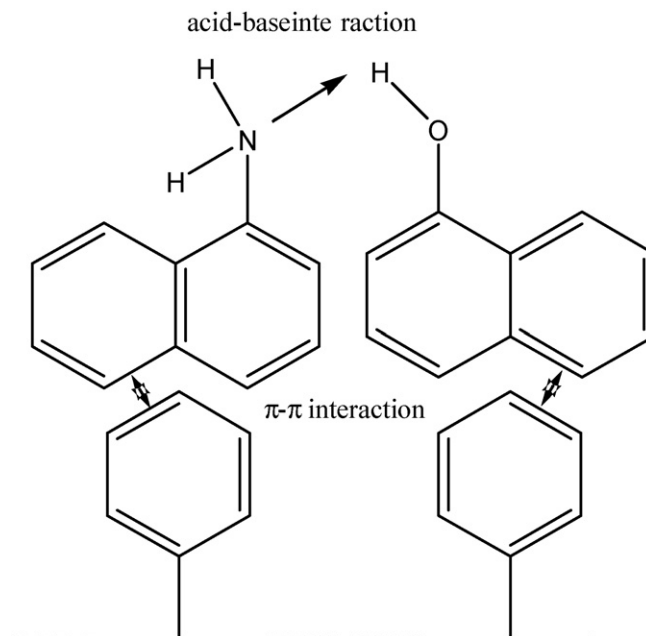


Fig. 3. Schemes for the proposed interactions between adsorbates as well as adsorbate and adsorbent.

the enhancement adsorption capacity of both 1-naphthylamine and 1-naphthol is caused by the lateral attractive interaction between the adsorbed acidic and basic adsorbates, due to the greater affinity of 1-naphthylamine to nonpolar adsorbents than 1-naphthol, some adsorbed 1-naphthol molecules are displaced by 1-naphthylamine molecules in solution, causing the augment of 1-naphthylamine synergistic adsorption and the decrement of 1-naphthol synergistic adsorption. Specially, the synergistic response factor of 1-naphthol on NDA-100 is too low to be positive, illustrating that the synergistic efficiency of 1-naphthol adsorption on NDA-100 is decreased with an increase in the amount adsorbed 1-naphthylamine attributed to two passive factors of the smaller pore size of NDA-100 and the weaker adsorption affinity of 1-naphthol.

All in all, though the synergistic adsorption mechanism is not very clear to us, the hydrogen bonding (acid–base) interaction between the lone pair of electrons on nitrogen atom of tertiary amino group in 1-naphthylamine and the hydrogen atom of hydroxyl group in 1-naphthol should not be ignored [16]. This synergistic effect also can be more easily explained if we also take into account the chemical characteristics change of the adsorbent caused by the adsorbed adsorbates discussed in previous sections. Additionally, due to the acid–base interaction, the electrostatic repulsion among the adsorbed 1-naphthol or

1-naphthylamine molecules could be counteracted each other, resulting in a closer packing of the aromatic molecules on the hydrophobic surface and then an increase in adsorption capacity [10]. The proposed interactions between adsorbates as well as adsorbate and adsorbent are listed in the schematic representation of Fig. 3.

4. Conclusions

This work has studied the adsorption isotherms of 1-naphthol and 1-naphthylamine in aqueous phase onto polymer adsorbents in single-solute, binary-solute, and the preloading adsorption systems. Adsorption capacity of one solute was enhanced in the presence of the other, which may be attributed to the synergistic effect arising from the lateral acid–base interaction of the adsorbed 1-naphthol and 1-naphthylamine molecules.

MLM based on the lateral attractive interaction of the adsorbed molecules was correlated successfully in these 1-naphthol/1-naphthylamine binary adsorption equilibria. The MLM parameters indicate that the synergistic coefficient of one adsorbate is linearly correlated with the adsorbed amount of the other. Moreover, the greater synergistic efficiencies of adsorbates are due to the larger average pore size of adsorbents, which probably allows the movement of 1-naphthol and 1-naphthylamine molecules and the formation of their lateral acid–base interaction inside the resin particles more easily.

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