

Competitive and cooperative adsorption behaviors of phenol and aniline onto nonpolar macroreticular adsorbents

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Abstract: The adsorption behaviors of phenol and aniline on nonpolar macroreticular adsorbents (NDA100 and Amberlite XAD4) were investigated in single or binary batch system at 293K and 313K respectively in this study. The results indicated that the adsorption isotherms of phenol and aniline on both adsorbents in both systems fitted well Langmuir equation, which indicated a favourable and exothermic process. At the lower equilibrium concentrations, the individual amount adsorbed of phenol or aniline on macroreticular adsorbents in single-component systems was higher than those in binary-component systems because of the competition between phenol and aniline towards the adsorption sites. It is noteworthy, on the contrast, that at higher concentrations, the total uptake amounts of phenol and aniline in binary-component systems were obviously larger than that in single-component systems, and a large excess was noted on the adsorbent surface at saturation, which is presumably due to the cooperative effect primarily arisen from the hydrogen bonding or weak acid-base interaction between phenol and aniline.

Keywords: macroreticular adsorbent; phenol; aniline; competitive adsorption; cooperative adsorption

Introduction

Contamination of surface water and groundwater with aromatic compounds is one of the most serious environmental problems human being faces today. Owing to their acute toxicity and good solubility, phenol and aniline, representatives of aromatic compounds, are of top priority contaminants and also the most important substructures of potentially carcinogenic pollutants discharged from pharmaceutical, dyestuff, photographic, agrochemical, and metal plating industries (Li, 2001; Zhu, 2000). Therefore, the efficient removal of phenol and aniline from waste streams has increasingly become a significant environmental concern (Lee, 1996; Liu, 2003). Among lots of available techniques, adsorption on activated carbon has been extensively employed for the removal of trace organic contaminants. However, due to the inability of activated carbons to completely desorb the uptake components (Motonobu, 1986), in the past two decades, polymeric adsorbents, which possess wider variations on functionality, surface area, and porosity than activated carbons, have been used as an alternative in industrial applications for efficiently removing and recovering the valuable aromatic compounds from wastewater (Gusler, 1993; Juang, 1999; Xu, 1999; Karan, 1999a). Generally, contaminated water contains more than one organic compound species. It is thus of industrial interest and of significance to investigate the adsorption behaviors of multiple organic compounds from aqueous solutions with polymeric adsorbents. In dependence upon the repulsive or attractive interactions between the adsorbates and the surface of adsorbents or among the adsorbates, the adsorption process of the binary components assayed is expected to be competitive or cooperative. Although a small amount of work has been published on the competitive adsorption of organic pollutants (Liu, 2004; Damien, 2000; Jia, 2003) and less work focused on the cooperative adsorption of organic, particularly aromatic compounds on polymeric adsorbents (Faisal, 1996; Kazuhiko, 2000), the mechanisms behind the competitive

and cooperative properties of aromatic compounds are not clear. Hence, through the adsorption behaviors of phenol and aniline on nonpolar polymeric adsorbents in single or binary batch systems, the present work was aimed at achieving a better qualitative and quantitative understanding on the interactions between phenol and aniline species and elucidating the mechanisms of competitive or cooperative adsorption.

1 Materials and methods

1.1 Adsorbates and adsorbents

The aqueous solutions of adsorbates were prepared by dissolving phenol and aniline (Shanghai Chemical Reagent Station, China) into deionized water without further pH adjustment. Some physical properties of phenol and aniline are presented in Table 1.

Table 1 Physical properties of phenol and aniline at 298K

Solute	Cross-sectional distance ^a , m	Volume ^a , m ³ /mol	Saturated concentration in water ^b , mol/m ³	pK _a
Phenol	4.20×10^{-10}	87.8×10^{-6}	912	9.99 ^b
Aniline	5.15×10^{-10}	91.7×10^{-6}	376	4.6 ^c

Notes: ^a. Taken from software ChemSketch of Advanced Chemistry Development Inc.; ^b. taken from Lange's handbook of chemistry; ^c. taken from the conjugate acid of aniline

Two nonpolar polymeric adsorbents, Amberlite XAD4 and NDA100, were adopted in this study. The former was supplied by Rohm and Haas (Philadelphia, PA, USA) and the latter was supplied by Jiangsu N & G Environmental Technology Co. Ltd. (Jiangsu, P. R. China). The specific surface area and the pore size distribution of XAD4 and NDA100 were measured by ASAP-2010C Micromeritics Instrument (USA) using nitrogen adsorption.

1.2 Adsorption isotherms

Single component adsorption isotherms were performed using the conventional bottle-point technique at two temperatures (293K and 313K). Batch adsorption runs were carried out in 100 ml glass flasks. Prior to use, XAD4 and NDA100 adsorbents were extracted with ethanol for 8 h in a

Soxhlet apparatus and vacuum desiccated at 325K for 24 h. Fixed adsorbent dosages of 0.050 g were directly introduced into a 100 ml glass flask. Owing to their non-polarity, XAD4 and NDA100 were necessarily wetted with 0.5 ml of methanol and then rinsed three times with deionized water before use. Subsequently 50 ml of an aqueous solution of phenol or aniline with an initial concentration ranging from 0.15 to 2 mmol/L was added into each flask. The batch factor (ml/g) was maintained at 1000 throughout this study.

The adsorption isotherms for binary-component system were conducted by following the above procedures except that the initial individual concentrations of aqueous solutions were varied from 0.15 to 2 mmol/L with a 1:1 molar ratio of phenol and aniline.

The flasks were then transferred into a G25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 150 r/min for 24 h, in which the adsorption is sufficient to attain equilibrium according to preliminary kinetics studies, at the given temperature. The amount adsorbed of phenol and aniline can be calculated by the following equation:

$$Q_e = V_1(C_0 - C_e)/1000 W, \quad (1)$$

where C_0 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 phenol or aniline on the adsorbents (mmol/g), V_1 is the volume of the aqueous solution (ml), and W is the mass of dry adsorbents (g).

The solution concentrations were determined using high performance liquid chromatography (HPLC), which was connected to Waters 600 controller, Waters 600 pump and Waters 2487 Dual Absorbance UV detector at 274 nm (Waters, USA). Mobile phase was 0.1% $\text{KH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$: methanol = 70:30 (V/V) and flow rate was 1 ml/min.

2 Results and discussion

2.1 Characterization of polymeric beads

Characteristic properties of XAD4 and NDA100 employed in this study are listed in Table 2. It can be seen that the chemical structures of both Amberlite XAD4 and NDA100 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 (Coughlin, 1968;

Juang, 1999). In addition, the specific surface area and micropore volume of NDA100 are higher than those of XAD4. Especially, NDA100 has the micropore (pore diameter less than 2 nm) area of around 740 m^2/g , whereas XAD4 has only 74 m^2/g of micropore area, which might cause the different adsorption behaviors of nonpolar macroporous adsorbents (Xu, 1999).

Table 2 Characteristic properties of NDA100 and XAD4 adsorbents^a

Property	NDA100	XAD4
Structure	Polystyrene	Polystyrene
Polarity	Nonpolar	Nonpolar
BET surface area, m^2/g	1225	914
Micropore area, m^2/g	740	74
Micropore volume, ml/g	0.336	0.012
Average pore diameter, nm	3.0	5.8
Desorption average pore diameter, nm	16.7	8.4
Particle size, nm	0.4–0.6	0.4–0.6
Colour	Deep brown	White

Note: ^a. Value measured in the present study

2.2 Single-component adsorption

The adsorption isotherms of phenol or aniline in the single-component system on XAD4 and NDA100 at 293K(a) and 313K(b) are shown in Fig. 1. It can be seen that the amounts adsorbed of phenol and aniline on adsorbents increased with the increase of their equilibrium concentrations, indicating the spontaneous adsorption (Giles, 1974; Weber, 1991).

The adsorption of aromatic compounds on polymeric adsorbents has been successfully described qualitatively and quantitatively by adopting several models (Dabrowski, 2001; Fritz, 2001), one of which is the Langmuir approach based on the some assumptions, including the energetically homogeneous surface of adsorbents, no interaction between the adsorbed molecules, the identical mechanisms for adsorption, and a complete monolayer adsorption on the surface. Although the assumptions all are not typically met by aromatic compounds adsorption, the Langmuir model has been demonstrated to provide an accurate description of process. Langmuir model is represented by the Equation (2):

Langmuir equation

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

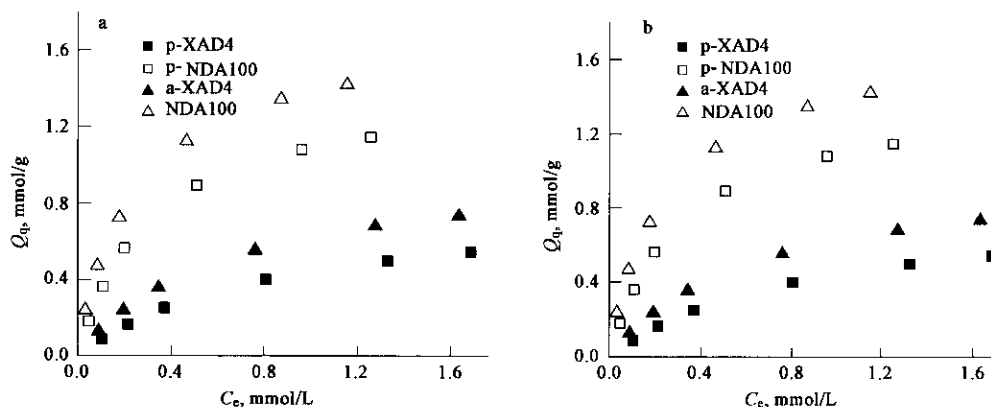


Fig.1 Equilibrium adsorption isotherms of phenol (■, □) and aniline (▲, △) on XAD4 (filled symbols) and NDA100 (open symbols) in single-component system at (a) 293K, (b) 313K

where Q_e is the amount adsorbed at equilibrium (mmol/g), C_e is the equilibrium concentration in bulk fluid phase (mmol/L), Q_m is the maximum adsorption capacity (mmol/g), namely complete coverage of available adsorption sites, K_1 is the affinity constant (Xu, 1999; Slejko, 1985). The results of the nonlinear least-squares regression analyses with the Langmuir equations are presented in Table 3. It can be seen that Langmuir isotherm models fit the adsorption data well since all the correlative factors R^2 are larger than 0.992 (Lide, 1991).

Table 3 Langmuir isotherms parameters for adsorption in single-component system

Adsorbent	Adsorbate	Temp., K	K_1	Q_m , mmol/g	R^2
XAD4	Phenol	293	0.910	0.926	0.995
		313	0.639	0.800	0.997
	Aniline	293	1.270	0.927	0.999
		313	0.723	1.042	0.997
NDA100	Phenol	293	2.823	1.501	0.995
		313	1.723	1.426	0.996
	Aniline	293	2.374	1.738	0.993
		313	1.874	1.740	0.992

As shown in Fig. 1 and Table 3, the affinity of phenol or aniline towards the nonpolar adsorbents declined as the equilibrium concentrations increase. This is probably due to the reduction in the adsorption sites and the augment of the electrostatic repulsion caused by the increase in the negative or positive charge of adsorbed phenol/aniline (Belmouden, 2001). It also can be seen that K_1 for the adsorption of phenol or aniline on NDA100 are higher than that on XAD4, showing that the adsorption affinity of adsorbates to NDA100 is greater than that to XAD4. Additionally, the maximum adsorption capacity (Q_m) of phenol or aniline on NDA100 is much higher than that on XAD4. The more excellent adsorption property of NDA100 than XAD4 may be attributed to its much higher specific surface area and pore volume (Xu, 1999). Owing to its greater hydrophobic property (Table 1), which is helpful for the adsorption on the nonpolar adsorbents, aniline exhibits higher adsorption affinity to and the maximum adsorption capacity on both NDA100 and XAD4 in comparison with phenol. Moreover, the electronic density of the aromatic ring of phenol and aniline plays another possible role in the difference in their adsorption behaviours.

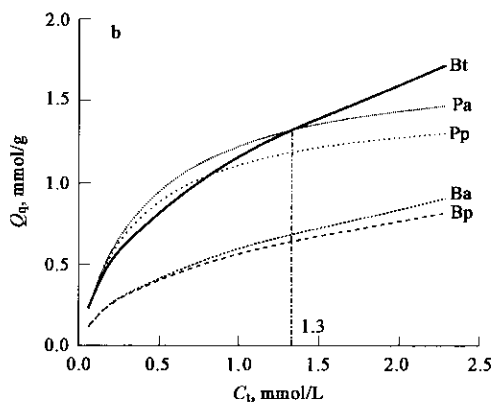
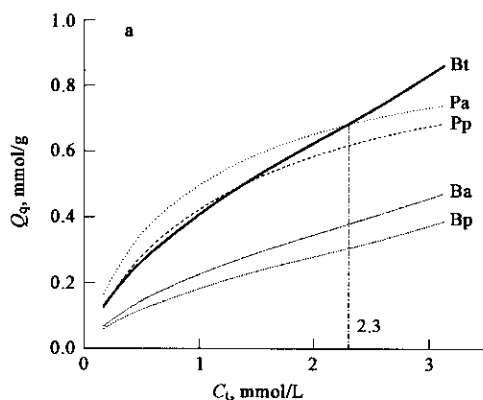


Fig. 2 Equilibrium adsorption isotherms of phenol and aniline on XAD4(a) and NDA100(b) in binary-component system at 293K. For each adsorbent, data lines correspond to the following: P_a —aniline absorbed in single system, P_p —phenol absorbed in single system, B_a —aniline absorbed in binary system, B_p —phenol absorbed in binary system, B_t —total of aniline and phenol absorbed in binary system

Because the two adsorbents absorb the both compounds by π - π dispersion interaction between the aromatic ring of phenol or aniline and the phenyl ring of the adsorbent, the greater electron density in the ring supplies more π -electrons to interact with the adsorbent and accordingly increase the affinity of aniline to adsorbents (Katrin, 2001). With respect to the effect of temperature, it is shown from Fig. 1 and Table 3 that the affinity constant (K_1) of both phenol and aniline towards the NDA100 and XAD4 is declined as the temperature increase, indicating the exothermic nature, but the greater water affinity of phenol and aniline at higher temperature cannot be ruled out.

2.3 Binary components adsorption

As mentioned in the previous section, phenol and aniline have similar adsorption behaviours on both adsorbents when plotted alone. Aniline has a slightly stronger adsorption affinity on the nonpolar adsorbents than phenol. This affinity as well as the possible interaction between the two types of adsorbates might be crucial factors in their competitive and cooperative adsorption behaviours. At high equilibrium concentrations, net attractive hydrogen bonding interaction between phenol and aniline at the interface could cause the higher adsorption capacity of them in binary-component system than the maximum loadings of the individual adsorbates in single-component system. 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 (P_1 or P_2) in single-component system at the same total equilibrium concentration ($C_t = C_1 + C_2$ in binary-component system; $C_i = C_1$ or C_2 in single-component system) (Faisal, 1996).

Fig. 2 depicts the adsorption isotherms of phenol/aniline on XAD4 and NDA100 in aqueous binary species system. Their adsorption isotherms can also be given a good fit with Langmuir model, and the results are listed in Table 4. Because the values of pH at adsorption equilibrium in the tested single or binary-component systems are kept from 5.5 to 8.0, it is assumed that the different values of pH would not significantly influence the adsorption behaviours of adsorbates. As shown in Fig. 2 and Table 4, the total uptakes ($B_t = B_p + B_a$) of phenol and aniline in binary-component system on XAD4 are lower than the individual uptakes (P_p or

P_a) in single-component system in the lower total concentration region, indicating the competitive effect. On the contrary, in the higher total concentration region (C_1 up to 2.3 mmol/L), the total uptakes (B_1) of the adsorbates in binary-component system are higher than the individual uptakes (P_p or P_a) in single-component system, indicating the expected cooperative effect. The competitive and cooperative adsorption behaviors of phenol and aniline on NDA100 are similar to those on XAD4, but the critical total concentration (C_1) is lowered to 1.3 mmol/L at 293 K.

Table 4 Langmuir isotherms parameters for adsorption in binary-component system

Adsorbent	Adsorbate	Temp., K	K_1	Q_m , mmol/g	R^2
XAD4	Phenol	293	0.426	0.649	0.986
		313	0.403	0.541	0.992
	Aniline	293	0.420	0.804	0.992
		313	0.479	0.588	0.995
	Phenol + aniline	293	0.423	1.453	0.990
		313	0.443	1.125	0.994
NDA100	Phenol	293	1.426	1.022	0.988
		313	1.088	0.994	0.993
	Aniline	293	1.137	1.197	0.987
		313	0.965	1.170	0.991
	Phenol + aniline	293	1.271	2.213	0.987
		313	1.023	2.162	0.992

2.3.1 Competitive adsorption of phenol and aniline on nonpolar adsorbents

As for the same kind of adsorption driving force by π - π dispersion interaction discussed in previous sections, because the sizes of phenol and aniline molecules (around 0.4 nm and 0.5 nm, respectively) are small enough to pass through the pore of XAD4 and NDA100 (around 5.8 nm and 3.0 nm, respectively), the competition for the adsorption sites instead of the pore size distribution of adsorbent should be involved in the predominant mechanism to account for the lower total amount adsorbed (B_1) of phenol and aniline in binary-component system than that in single-component system at the low equilibrium concentrations (Damien, 2000; Kazuhiko, 2000).

On the other hand, the formation of complex (Kazuhiko, 2000), phenol-aniline ($P^- - A^+$), through Lewis acid-base interaction between amino group of aniline and hydroxyl group of phenol at the near neutral value of pH in this study should be taken into account. Although the greater hydrophobic nature of the ($P^- - A^+$) complex is helpful to increase the adsorption uptake by hydrophobic interaction, its access to adsorption sites in micropores would be restricted by the larger size of the ($P^- - A^+$) complex molecule. Therefore, the reduction of free phenol and aniline molecules dissolving in aqueous solution after formation of the ($P^- - A^+$) complex results in the decrease of adsorption capacities of phenol and aniline in binary-component systems.

2.3.2 Cooperative adsorption of phenol and aniline on nonpolar adsorbents

Given two assumptions: monolayer coverage of phenol and aniline molecules on adsorbents and no interaction occurring between the two adsorbate species, the ratio of the amount adsorbed experimentally of phenol or aniline in binary-component systems over their theoretical adsorption

capacities, namely, the cooperative coefficients can be quantitatively achieved. It is of importance in the adsorption process for multiple components (Damien, 2000).

The theoretical number of phenol and aniline molecules absorbed on adsorbents in binary-component system at saturation in a monolayer without interaction can be described by

$$Q_{pm}^{the} \alpha_{pm} L + Q_{am}^{the} \alpha_{am} L = S \times 10^{21}, \quad (3)$$

where Q_{pm}^{the} and Q_{am}^{the} (mmol/g) denote the theoretical amount adsorbed of phenol and aniline molecules in binary-component system, α_{pm} and α_{am} (nm²/mol) respectively refer to the surface area occupied by one molecule of phenol and aniline on adsorbent surface calculated from single-component system, L is the Avogadro constant, and S is the specific surface area of adsorbent (m²/g).

Assume that the ratio (r) of Q_{pm}^{the} to Q_{am}^{the} at saturation is equal to the ratio of the experimental amount adsorbed of phenol $Q_{pm}^{exp'}$ (mmol/g) over that of aniline $Q_{am}^{exp'}$ (mmol/g) obtained from their adsorption isotherms in single-component system:

$$r = \frac{Q_{pm}^{the}}{Q_{am}^{the}} = \frac{Q_{pm}^{exp'}}{Q_{am}^{exp'}}. \quad (4)$$

By combining Eq. (3) and (4), the theoretical amount adsorbed of phenol (Q_{pm}^{the}) and aniline (Q_{am}^{the}) can be obtained:

$$Q_{pm}^{the} = \frac{S \times 10^{21} / L}{\alpha_{pm} + \alpha_{am} / r}, \quad (5)$$

$$Q_{am}^{the} = \frac{Q_{pm}^{the}}{r}. \quad (6)$$

Finally, the cooperative coefficients of phenol and aniline (e_p and e_a) on the adsorbent surface were calculated:

$$e_p = \frac{Q_{pm}^{exp}}{Q_{pm}^{the}} \times 100\%, \quad (7)$$

$$e_a = \frac{Q_{am}^{exp}}{Q_{am}^{the}} \times 100\%, \quad (8)$$

where Q_{pm}^{exp} or Q_{am}^{exp} are the maximum adsorption capacity (mmol/g) of phenol or aniline in binary-component system. The theoretical and experimental values for phenol and aniline on the both XAD4 and NDA100 at equilibrium are listed in Table 5. It can be seen that the experimental adsorption capacities of phenol and aniline exceed to a large or small extent their theoretical ones when they are adsorbed simultaneously, indicating the multilayer adsorption caused by the cooperative effect between phenol and aniline molecules (Damien, 2000).

Table 5 Comparison between the theoretical and experimental adsorbent surface coverage at saturation in the binary adsorption experiments

Experiment	XAD4		NDA100	
	293K	313K	293K	313K
S , m ² /g	914	914	1225	1225
α_{pm} , nm ² /molecule	1.64	1.90	1.36	1.43
Q_{pm}^{the} , mmol/g	0.463	0.400	0.750	0.713
Q_{pm}^{exp} , mmol/g	0.649	0.541	1.022	0.994
e_p , %	140.1	135.2	136.1	139.5
α_{am} , nm ² /molecule	1.64	1.46	1.17	1.17
Q_{am}^{the} , mmol/g	0.464	0.521	0.869	0.870
Q_{am}^{exp} , mmol/g	0.804	0.588	1.197	1.170
e_a , %	173.5	112.8	137.8	134.5
r	1.00	0.77	0.86	0.82

Several possible explanations can be proposed for this cooperative adsorption phenomenon. Because some hydrogen bonding interactions between phenol and aniline molecules on the adsorbent surface can decrease the free energy for adsorption, the electrostatic repulsion of phenol or aniline could be shielded and neutralized by each other, allowing a closer packing on the hydrophobic surface (Damien, 2000). On the other hand, the molecules of aromatic compounds may be adsorbed generally in flat orientation on the adsorbent surface at low concentrations, but mainly in vertical orientation at high concentrations (Barradas, 1965; Bertocini, 2000). As the surface packing is close at high concentrations (Hansen, 1949; Langmuir, 1917), the hydrophobic phenyl rings of adsorbates are close to the phenyl ring of the polymer matrix, but the hydrophilic functional groups of adsorbates are protruding into the aqueous phase. The outward amino group of aniline molecule or hydroxyl group of phenol molecule adsorbed can form some new "hydrogen bonding adsorption sites", so a second adsorption layer may be formed on the adsorbent surface. Hence, the cooperative adsorption mechanism in the tested binary-component system may be mainly attributed to the hydrogen bonding interaction, which occurs between the lone pair of electrons on nitrogen of tertiary amino group of aniline and the hydrogen of hydroxyl group of phenol which can be treated as a Lewis acid-base interaction (Anasthas, 2001). The proposed interactions between adsorbates as well as adsorbate and adsorbent are listed in the schematic representation of Fig.3.

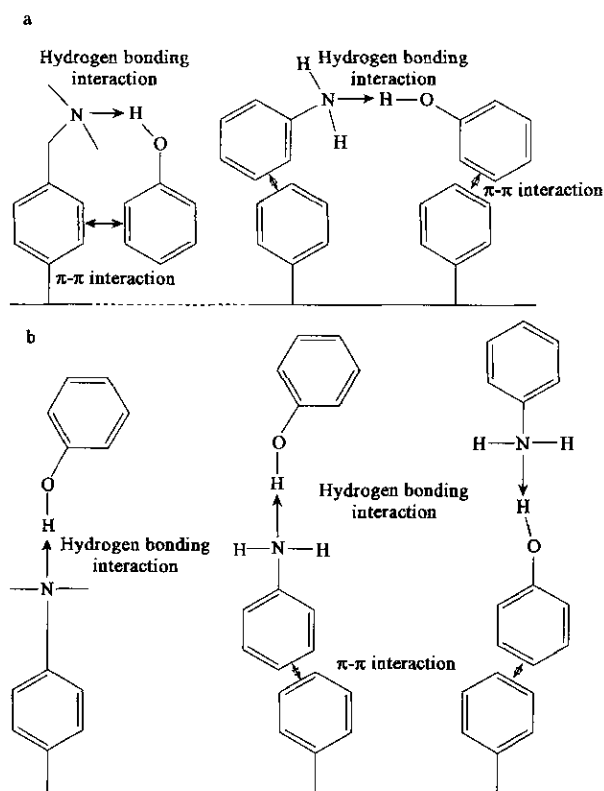


Fig.3 Schemes for the proposed interactions between adsorbates as well as adsorbate and adsorbent
(a) in low concentration region, (b) in high concentration region

3 Conclusions

The adsorption isotherms of both phenol and aniline on XAD4 and NDA100 in single and binary-component system can be excellent described by Langmuir equations, which indicates a favourable and exothermic process.

At the lower equilibrium concentrations, competitive adsorption behaviors of phenol and aniline are observed on nonpolar adsorbents XAD4 and NDA100 in binary adsorption system attributed to the reduction in the number of free adsorbates molecules after the formation of the complexes ($P^- - A^+$) with hydrogen bonding interactions as well as to the decrease in the number of accessible adsorption sites in small pores of adsorbent for the larger size of the ($P^- - A^+$) complex molecule. The competition for the adsorption sites is involved into the predominant adsorption mechanism at low equilibrium concentrations.

At the higher equilibrium concentrations, extra adsorption capacities of phenol and aniline can be quantitatively observed, which is due to the cooperative effect arisen from the hydrogen bonding interactions between adsorbates on the adsorbent surface.

Acknowledgements: The authors are also grateful for the Analytical Center at Jiangsu Petrochemical Institute for the measurements of surface area and pore parameters of the polymeric adsorbents and the Department of Chemical Engineering at Jiangsu Petrochemical Institute for the HPLC analysis.

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(Received for review September 30, 2004. Accepted November 10, 2004)