Adsorption thermodynamics and kinetic investigation of aromatic amphoteric compounds onto different polymeric adsorbents

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Abstract

The adsorption behavior of p-aminobenzoic acid and o-aminobenzoic acid onto the different polymeric adsorbents was systematically investigated as a function of the solution concentration and temperature. Experimental results indicated that the equilibrium adsorption data of the four polymeric adsorbents fitted well in the Freundlich isotherm. The adsorption capacity of multi-functional polymeric adsorbent NJ-99 was the highest, which might be attributed to the strong hydrogen-bonding interaction between the amino groups on the resin and the carboxyl group of aminobenzoic acid. The adsorption capacity of o-aminobenzoic acid onto any adsorbent was higher than p-aminobenzoic acid. Thermodynamic studies suggested the exothermic, spontaneous physical adsorption process. Adsorption kinetics results showed that the adsorption followed the pseudo-second-order kinetics model and the intraparticle mass transfer process was the rate-controlling step.

Key words: aromatic amphoteric compound; aminobenzoic acid; polymeric adsorbents; adsorption; thermodynamics; kinetics

Introduction

Wastewater containing aromatic compounds presents a serious disposal problem because of its toxicity and poor biodegradation as well as good solubility in water. Especially for the aromatic amphoteric compounds involving both Lewis acid and Lewis base functional groups, their particular physicochemical characteristics bring more difficulties for the treatment of wastewater. A lot of methods, such as biological degradation and oxidation (Zhang et al., 1999; Lin et al., 2001), applied for the purification of water contaminated by aromatic amphoteric compounds, are often with limited success. Resin adsorption technology has been used as a more attractive alternative for removing aromatic pollutants from wastewater (He and Huang, 1995; Zhang et al., 2001). Many studies (Pan et al., 2005; Cai et al., 2005) have been conducted on the removal of phenols and aromatic amines involving one kind of functional group. However, the concerned research on the resin adsorption techniques of aromatic amphoteric compounds has not been systematically investigated.

Mass transfer within the resin particles can be complex, as adsorption is inherently a transient process involving some short-range diffusion in both the fluid and the adsorbed phases. Both intraparticle and external diffusion may play a role in the liquid phase adsorption on porous adsorbents. Although a large number of studies on the adsorption kinetics have been reported (Annadurai and Krishnan, 1997; Ho and Mckay, 1999; Mckay and Ho, 1999; Li and Arup, 2000), few of them addressed the adsorption thermodynamics and kinetics of aromatic amphoteric compounds on polymeric adsorbents.

The current study aimed at identifying the significance of intraparticle and external diffusion of the aromatic amphoteric compound aminobenzoic acid inside the water-compatible hypercrosslinked multi-functional polymeric adsorbent NJ-99 and NG-10 in comparison with the hypercrosslinked adsorbent CHA-111 and the hydrophobic macroporous adsorbent XAD-4. Thermodynamic investigations have been performed to elucidate the equilibrium adsorption behavior of aminobenzoic acid onto polymeric adsorbents.

1 Materials and methods

1.1 Materials

Two kinds of aminobenzoic acid (p-aminobenzoic acid and o-aminobenzoic acid) were purchased from Shanghai...


1.2 Characterization of adsorbents

The special hypercrosslinked polymeric adsorbent CHA-111 was prepared by controlling the post-crosslinking reaction, whereas NJ-99 and NG-10 were obtained by introducing some amino groups and sulfonic groups, respectively, to the surface of porous polystyrene-divinylbenzene beads during the post-crosslinking process.

The specific surface area and the pore structure of the four polymeric adsorbents were measured using a Micromeritics apparatus (ASAP-2010 Micromeritics Instrument Corporation, USA) with nitrogen as sorbate following the Brunauer Emmett Teller (BET) method. Infrared spectra of the polymeric adsorbents were obtained from a Nicolet 170 SX IR spectrometer (USA) with a pellet of powdered potassium bromide and resin. The amounts of amino groups on adsorbent NJ-99 and the sulfonic groups on adsorbent NG-10 matrix were measured as reported in the reference (He and Huang, 1995).

1.3 Adsorption static test

Prior to their initial use, the four polymeric adsorbents were first extracted by ethanol in a Soxhlet apparatus for 8 h and then dried under vacuum at 333 K for 8 h. The static adsorption of the aromatic amphoteric compound aminobenzoic acid on the adsorbents at three different temperatures (283, 298 and 313 K) was conducted as follows: 0.100 g of the dry resin was introduced into 100 ml aqueous solution of aminobenzoic acid into an airproof flask. 100 ml aqueous solution of aminobenzoic acid or 224 nm (p-aminobenzoic acid) or 224 nm (o-aminobenzoic acid). The equilibrium adsorption capacities \( Q_e \) (mmol/g) were thus calculated with Eq. (1):

\[ Q_e = \frac{V_c(C_0 - C_e)}{W M} \]

where, \( V_c \) is the volume of solution (L), \( W \) is the mass of dry resin (g), and \( M \) is the molecular weight of the adsorbate.

1.4 Adsorption kinetic test

Adsorption kinetic test of aminobenzoic acid on the four adsorbents was carried out in a way similar to the static adsorption test, except that 0.100 g of the dry resin was introduced into 100 ml aqueous solution of aminobenzoic acid with initial concentrations (\( C_0 \)) of 1000 mg/L. The instantaneous adsorbates uptakes on the resin were calculated by measuring the concentrations of adsorbates in solution with UV-Vis spectrometer (UK) at different contact time.

2 Results and discussion

2.1 Characteristics of the polymeric adsorbents

Table 2 lists the characteristics of the adsorbents employed in the current study. Table 2 shows that the hypercrosslinked resin CHA-111 has the largest surface area, micropore area and micropore volume among the four resins but without functional groups on the matrix. The presence of the amino groups on NJ-99 is confirmed by its stronger symmetrical stretching vibration absorbance peaks of C–N at the range 1175–1363 cm\(^{-1}\) in the IR spectra in Fig.1b. The presence of the sulfonic group on NG-10 is confirmed by the stronger asymmetrical and symmetrical stretching vibration absorbance peaks of S=O at 1346 and 1265 cm\(^{-1}\), respectively, in Fig.1a. Therefore, it is reasonably considered that the amino group or sulfonic group had been introduced to the surface of the NJ-99 and NG-10, respectively. From Fig.1d, the stronger stretching vibrations of S=O at 1346 and 1265 cm\(^{-1}\) confirm the presence of the sulfonic group on NG-10.

### Table 1 Physical properties of the adsorbates

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Water solubility (wt%)</th>
<th>pK_a1</th>
<th>pK_a2</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Aminobenzoic acid</td>
<td>0.59</td>
<td>2.38</td>
<td>4.89</td>
</tr>
<tr>
<td>o-Aminobenzoic acid</td>
<td>0.16</td>
<td>2.11</td>
<td>4.95</td>
</tr>
</tbody>
</table>

* Liu et al., 2002.

### Table 2 Physical properties of the four adsorbents

<table>
<thead>
<tr>
<th>Property</th>
<th>XAD-4</th>
<th>CHA-111</th>
<th>NJ-99</th>
<th>NG-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Polystyrene</td>
<td>Polystyrene</td>
<td>Polystyrene</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Polarity</td>
<td>Non-polar</td>
<td>Weak polar</td>
<td>Moderate polar</td>
<td>Moderate polar</td>
</tr>
<tr>
<td>BET surface area (m(^2)/g)</td>
<td>880.2</td>
<td>934.0</td>
<td>819.1</td>
<td>673.7</td>
</tr>
<tr>
<td>Micropore area (m(^2)/g)</td>
<td>3.1</td>
<td>561.3</td>
<td>463.3</td>
<td>406.5</td>
</tr>
<tr>
<td>Micropore volume (ml/g)</td>
<td>0.0051</td>
<td>0.2530</td>
<td>0.209</td>
<td>0.1862</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>5.83</td>
<td>1.20</td>
<td>1.20</td>
<td>1.26</td>
</tr>
<tr>
<td>Quantitative functional groups (mmol/g)</td>
<td>0</td>
<td>0</td>
<td>1.51</td>
<td>1.235</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
<td>Brown</td>
<td>Light brown</td>
<td>Dark brown</td>
</tr>
</tbody>
</table>
vibration absorbance peak of C=O at 1704 cm\(^{-1}\) for CHA-111 demonstrates the presence of C=O in the surface of adsorbent CHA-111, which demonstrates the weak polarity of the adsorbent.

2.2 Equilibrium adsorption

Figure 2 shows the equilibrium adsorption isotherms of \(p\)-aminobenzoic acid and \(o\)-aminobenzoic acid on the four adsorbents at 298 K. The adsorption isotherms at other temperatures (283 K and 313 K) are similar to the isotherms at 298 K. The data are fitted with the empirical Freundlich isotherm equation (Lin and Cheng, 1999):

\[
Q_e = K_f C_e^{1/n}
\]

(2)

where, \(K_f\) and \(n\) are the characteristic constants. The correlative isotherm equations along with the relevant parameters are listed in Table 3. The Freundlich isotherm equation can all represent the adsorption data well because all the correlative factors \(R\) are larger than 0.99. According to the Freundlich theory (Slejko, 1985), the parameter \(K_f\) is taken as a relative indicator of adsorption capacity and \(n > 1\) indicates the favorable adsorption. From Table 3, all the exponents \((n)\) in all cases are larger than 1, which demonstrates the adsorption of \(p\)-aminobenzoic acid and \(o\)-aminobenzoic acid onto the adsorbents are favorable.

As can be seen from Fig.2 and the fitted Freundlich parameters (Table 3), the order of adsorption capacities of the four polymeric adsorbents for two kinds of aminobenzoic acid is: NJ-99 > CHA-111 > NG-10 > XAD-4.

For an adsorption of aromatic compounds onto polymeric adsorbent from aqueous solutions, the adsorption capacity towards a given adsorbate increases generally

<table>
<thead>
<tr>
<th>Adsortent</th>
<th>(p)-Aminobenzoic acid</th>
<th>(o)-Aminobenzoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n)</td>
<td>(K_f)</td>
</tr>
<tr>
<td>CHA-111</td>
<td>2.6309</td>
<td>0.8968</td>
</tr>
<tr>
<td>NJ-99</td>
<td>3.9370</td>
<td>1.2402</td>
</tr>
<tr>
<td>NG-10</td>
<td>2.3821</td>
<td>0.5146</td>
</tr>
<tr>
<td>XAD-4</td>
<td>1.7097</td>
<td>0.2383</td>
</tr>
</tbody>
</table>
Fig. 2 Adsorption isotherms of aminobenzoic acid on different adsorbents (298 K). (a) p-aminobenzoic acid; (b) o-aminobenzoic acid.

as the micropore content and specific surface area of the resin increase (Li et al., 2001, 2002). It is evident from Table 2 that the specific surface area of NJ-99 is not the largest, but demonstrates the best adsorption property for aminobenzoic acid. Whereas the adsorbent XAD-4 possesses the bigger surface area and exhibits the smallest adsorption capacity. Hence, the difference may by no means be explained simply by the specific surface area and micropore content. Compared with XAD-4, the hypercrosslinked adsorbents CHA-111, NJ-99 and NG-10 possess the stronger adsorption affinity to aminobenzoic acid, which is primarily attributed to the micropore volume and weak or moderate polarity of the latter three adsorbents. The matching of polarity between adsorbents and adsorbate is an important factor affecting the adsorption of aromatic compounds (Li et al., 2001, 2002; Sun et al., 2005). For the adsorption of aminobenzoic acid onto NJ-99 and NG-10, the functional groups on the resin may be assumed to play the dominant role. Thus, not only should π–π interactions between the aromatic rings of the adsorbate and the matrix of the resin be taken into account, but also the hydrogen bonding between the functional groups on the resin and the carboxyl or amino groups of aminobenzoic acid (Crittenden et al., 1999; Rojas and Voilley, 1996). From Table 2, the amino group content of adsorbent NJ-99 is 1.51 mmol/g. Therefore, the largest adsorption capacity of NJ-99 may be attributed to the amino groups associated with the structure of NJ-99. The amino groups on the resin may undergo the stronger hydrogen bonding with the carboxyl of aminobenzoic acid. Thus, it increases the adsorption capacity of NJ-99 towards the aromatic amphoteric compound containing carboxyl group and simultaneously compensates for the decrease in the adsorption capacity brought out by a decrease in the specific surface area and micropore volume. For NG-10, the stronger hydrogen-bonding interaction occurs between the sulfonic groups of the resin and amino groups of amphoteric adsorbate, but NG-10 presents a smaller adsorption capacity than NJ-99 and CHA-111. This can be explained qualitatively in terms of the functional group content of polymer and specific surface area as well as micropore volume. The functional group content of NG-10 is smaller than NJ-99 (1.235 and 1.51 mmol/g, respectively). All the specific surface area, micropore volume and micropore area of NG-10 are lower than NJ-99 and CHA-111. Therefore, although the formation of hydrogen bonding can increase the adsorption capacity of NG-10, it cannot compensate for the decrease in adsorption capacity owing to the loss of the specific surface area and micropore volume. In a word, specific surface area, micropore structure and content of functional groups together dominate the adsorption property of the polymers.

As seen from $K_f$ in Table 3, the adsorption capacities of o-aminobenzoic acid on the same adsorbent are all larger than p-aminobenzoic acid. The difference in adsorbability can be explained in terms of the adsorbate’s solubility, acidity and basicity as well as the position of carboxyl and amino groups on the benzene ring. The solubility of o-aminobenzoic acid in water is much lower than p-aminobenzoic acid (Table 1) and thus it shows stronger hydrophobicity. This may be one of the possible reasons for its higher adsorption capacity. Further, o-aminobenzoic acid possess the lower $pK_a$, and the higher $pK_a$ than p-aminobenzoic acid (Table 1). Therefore, the Lewis acid-base interaction between the functional groups of o-aminobenzoic acid and the polymers is expected to be stronger than that between p-aminobenzoic acid and the resins according to the Lewis acidity and basicity. In addition, some researches (Kumar et al., 2003; Sun et al., 2005) revealed that the same functional group but at the ortho position greatly enhanced the adsorption energies of such compound as o-aminobenzoic acid used in the current study. Thus, cumulative effects of solubility and position of the (–COOH) and (–NH₂) functional group at the ortho position may probably account for higher adsorbability of o-aminobenzoic acid than p-aminobenzoic acid onto not only multi-functional polymers but also CHA-111 and XAD-4.

2.3 Adsorption thermodynamics of aminobenzoic acid

To elucidate the adsorption mechanism of aminobenzoic acid onto polymeric adsorbents better, the calculated adsorption thermodynamics parameters according to Eqs. (3)–(5) (Garcla-Delgado et al., 1992; John and Tsezos,
free energy change of adsorption, \( \Delta G \) of the Freundlich equation, and \( \Delta S \) of the integrated adsorption mechanism involving the enthalpy changes are in the 10–30 kJ/mmol range indicating the strongest affinity occurs for XAD-4 towards the same adsorbate. The negative entropy changes suggest that more ordered arrangement of solute molecules is shaped on the surface of the adsorbent, which are indicative of an enthalpy-driven adsorption process (Pan et al., 2002). The absolute \( \Delta S \) values decrease with the increase of temperature, which elucidates the rise of temperature augments the randomness at the solid-solution interface during the adsorption process resulting in the increase of entropy after adsorption (Li et al., 2001, 2002; Pan et al., 2002; Sun et al., 2005).

### 2.4 Adsorption kinetics of aminobenzoic acid

The adsorption kinetics was carried out to explore the practicability in removing aromatic amphoteric compounds from water streams. The effect of contact time \( t \) on the uptake \( (Q_v) \) of \( p \)-aminobenzoic acid and \( o \)-aminobenzoic acid onto the four adsorbents in the condition of \( C_0 = 1000 \) mg/L at 298 K is shown in Fig 3.

The mass transfer effect on the adsorption kinetics can be analyzed by the following Eqs. (6)–(9) (Boyd et al., 1947; Reichenberg, 1953; Hao, 1983).

\[
\ln(1 - F) = -R^e t \tag{6}
\]

\[
F = \frac{Q_v}{Q_e} = 1 - 6 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 B_t) \tag{7}
\]

when \( F > 0.85 \)

\[
B_t = -\ln(1 - F) - 0.4977 \tag{8}
\]

when \( F < 0.85 \)

\[
B_t = \left( \sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F}{3}} \right)^2 \tag{9}
\]

where, \( F \) is the fractional attainment of equilibrium, \( R^e \) and \( B_t \) are the mass transfer coefficients (min\(^{-1}\)). The linearity of the plot of \( \ln(1-F) \) and \( t \) indicates the role of the external mass transfer in the adsorption process. According to Eqs. (8) and (9), the linearity of the plot of

![Fig. 3 Adsorption rate curves of aminobenzoic acid onto the four adsorbents at 298 K.](jesc.ac.cn)
The apparent adsorption rates (\(K_a\)) relatively rapid approach to equilibrium. In addition, nature indicating that higher temperature could make for attaining equilibrium tends to follow the pseudo-second-order kinetics model because of its larger correlation coefficients. The rate constants increase with the temperature, which can be explained by the stronger hydrogen-bonding interaction between the amino groups on the resin and the carboxyl group of aminobenzoic acid as well as micropore volume. The adsorbility of any adsorbent towards \(o\)-aminobenzoic acid is larger than \(p\)-aminobenzoic acid owing to cumulative effects of the more hydrophobicity of \(o\)-aminobenzoic acid as well as the position of carboxyl and amino groups on the benzene ring.

The isotherm data were well fitted with the Freundlich isotherm equation in the conditions of the current study. The thermodynamic results show the exothermic, spontaneous physical adsorption process. Adsorption kinetic studies show that the adsorption conforms to the pseudo-second-order kinetics model and the intraparticle mass transfer process is a rate-controlling step. The quicker attainment of sorption equilibrium (within 4 h) for aminobenzoic acid on NJ-99 is helpful for practical use, and the adsorbent NJ-99 has, therefore, exhibited good potential in removing the aromatic amphoteric compounds from aqueous solutions for industrial purposes.

### References


