

## ADSORPTION STUDIES OF TANNIC ACID BY COMMERCIAL ESTER RESIN XAD-7\*

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**Abstract** Tannic acid and its related compounds are known as refractory organic pollutants, and it can create serious problems for the environment. The adsorption and desorption studies of tannic acid on commercial resins XAD-7 and D-201 are performed, and all data indicates resin XAD-7 can be used as an effective adsorbent for removing tannic acid during water/wastewater treatment. Furthermore, adsorption thermodynamics studies indicate different adsorption mechanisms for TA on XAD-7 and D-201. FT-IR and solid state <sup>13</sup>C-NMR spectroscopy are used to explain the adsorption force between XAD-7 and TA. It suggests that hydrogen bonding is the main adsorption force for TA. Finally, XAD-7's adsorption capacity in the presence of different metal ions is investigated, which indicates that heavy metal ions in solutions can decrease the adsorption capacity for TA on ester resin XAD-7.

**Keywords:** Adsorption; Tannic acid; Resin; XAD-7; Metal ion.

### INTRODUCTION

Tannic acid (TA) is a natural organic acid and present in most surface and ground water. As a raw material and additives, TA is found in the wastewater of the coir and cork processing industries. Previous studies have demonstrated that TA has toxicity for aquatic organisms such as algae, phytoplankton, fish and invertebrates, which can create serious problems for the environment. Recently, it has also been found that trihalomethanes (THMs) can be formed in the presence of TA during the chlorine disinfection. So many researchers chose it as the major medium molecular weight disinfection by-products (DBPs) in their studies<sup>[1–3]</sup>. The current technologies to remove dissolved organic matter (DOM) from water/wastewater include coagulation, adsorption, nano-filtration (NF) and biological methods<sup>[4–8]</sup>. But it is well known that the traditional coagulation process can't remove low or media molecular weight DBPs effectively, and the NF has limited TA removal capacity in practice because TA tends to foul membrane severely. Though biological methods can remove 30%–50% DOM and avoid using chemicals, complex plant configurations and operating conditions are required. Among these technologies, adsorption is a common approach for removing pollutants from water with high efficiency and simple operation conditions<sup>[9, 10]</sup>.

Though acrylic ester resin XAD-7 and strong basic ion-exchange resin D-201 have been widely studied to remove DOM from water/wastewater for their perfect adsorption capacity<sup>[11, 12]</sup>, few researchers used these two

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adsorbents to remove TA from water. In this paper, adsorption of TA by resin XAD-7 and D-201 is studied. As a result, ester resin XAD-7 shows better adsorption capacity and higher adsorption rate for TA than D-201. Furthermore, solid state  $^{13}\text{C}$ -NMR, FT-IR spectroscopy and thermodynamics of XAD-7 are undertaken, which can illustrate the adsorption mechanism of TA. Finally, the effect of different metal ions on XAD-7's adsorption capacity for TA is also investigated.

## METHODS AND MATERIALS

### Chemicals

The acrylic ester resin XAD-7 was purchased from Rohm & Hass (USA), its specific surface area and average pore diameter were  $540\text{ m}^2\cdot\text{g}^{-1}$  and  $7.4\text{ nm}$  respectively. Strong basic ion-exchange resin D-201 was supplied by Nan&Ge (China), and its total exchange capacity was more than  $3.8\text{ mmol}\cdot\text{g}^{-1}$ . The molecular structure of XAD-7 and D-201 are shown in Figs. 1(a), 1(b). TA was obtained from Sigma (America), and its molecular structure was shown in Fig. 1(c). TA stock solution was prepared by dissolving TA in deionized water (DDW) without pH adjustment.

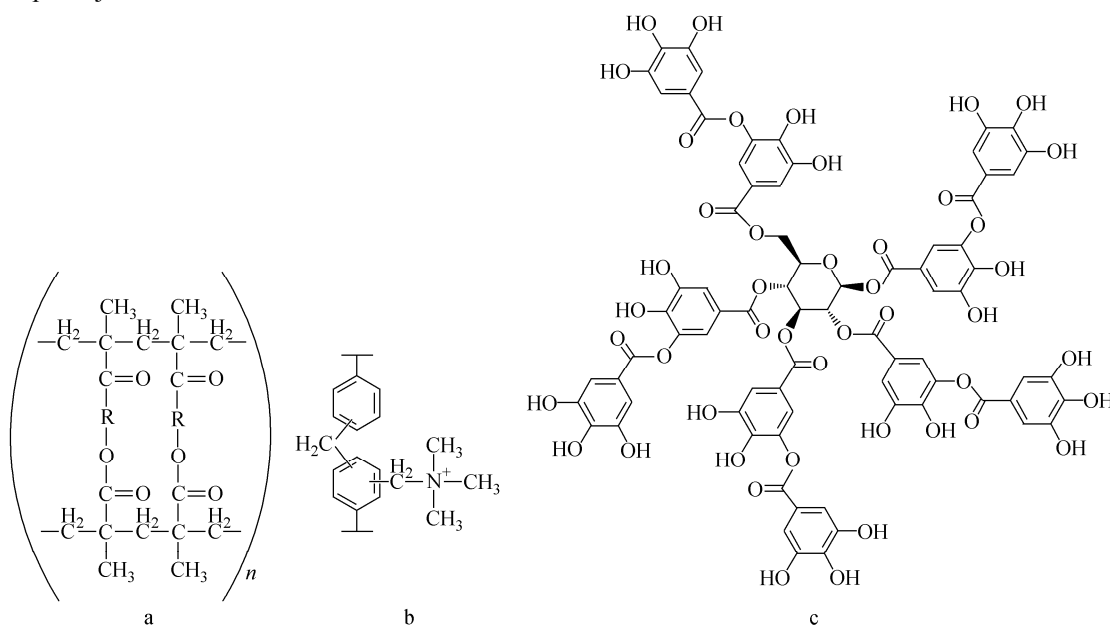


**Fig. 1** Molecular structure of (a) XAD-7, (b) D-201 and (c) tannic acid ( $\text{C}_{76}\text{H}_{52}\text{O}_{46}$ )

### Dynamic Adsorption Assay

Prior to their initial use, resins were extracted with acetone for 8 h and then dried for 8 h under vacuum at 333 K.

As shown in Fig. 2, mini column adsorption studies were conducted using a  $10\text{ cm} \times 1\text{ cm}$  I.D. stainless-steel column packed with 4.000 g resin and connected with a 6672 reciprocating pump (Beijing Analytical Instrument Plant) at 303 K. A  $100\text{ mg}\cdot\text{L}^{-1}$  TA solution was passed through the column at a flow rate of  $12\text{ mL}\cdot\text{h}^{-1}$ . Adsorption capacity of resin was evaluated in two ways: (1) the working capacity, that is, the total amount of tannic acid adsorbed until the effluent concentration reached  $5\text{ mg}\cdot\text{L}^{-1}$ , (2) the total capacity, that is, the total amount of adsorbed TA until the elute concentration reached the influent concentration. The adsorption capacity ( $q_1$ ) of resin was calculated with Eq. (1):

$$q_1 = V_2 (c_1 - c_2) / W \quad (1)$$

where  $V_2$  is the volume of solution through column (L),  $c_1$  is the initial concentration of solution ( $\text{mmol}\cdot\text{L}^{-1}$ ),  $c_2$  is the average concentration of the effluent, and  $W$  is the weight of dry resin (g). The concentration of TA was measured by a TOC analyzer.

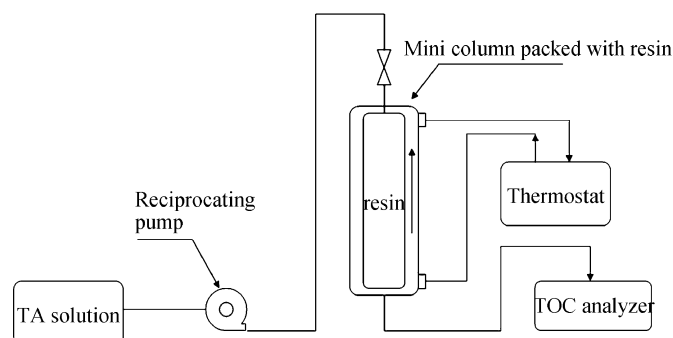


Fig. 2 Mini-column adsorption instrument

### Static Adsorption Assay

Equilibrium adsorption of TA was conducted at a certain temperature. For this purpose, aqueous solutions with different initial concentrations were used. Adsorption isotherms were determined using stoppered flasks containing 0.200 g resin per 100 mL solution. They were kept in a thermostat shaker bath at 303 K for 5 days, and then the equilibrium concentration was determined by TOC. The adsorption capacity was calculated according to Eq. (2):

$$q_e = V(c_0 - c_e)/W \quad (2)$$

where  $q_e$  is the adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ ), the  $V$  is the volume of solution (L),  $c_0$  is the initial concentrations of the solutions ( $\text{mg}\cdot\text{L}^{-1}$ ),  $c_e$  is the concentration of adsorption equilibrium solution ( $\text{mg}\cdot\text{L}^{-1}$ ), and  $W$  is the weight of dry resin (g). Then the adsorption isotherms of the above acids were obtained.

### FT-IR Spectroscopy and Solid State NMR Spectroscopy Characterization of XAD-7 before and after Adsorption

#### FT-IR spectroscopy

The FT-IR spectroscopy experiments of resin XAD-7 before and after adsorption of TA were performed on an FT-IR spectrometer (MAGNA 560, Nicolet Co.), and the spectra were recorded in the wave number range from  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  with the KBr pellet method.

#### Solid state NMR spectroscopy

Solid-state  $^{13}\text{C}$ -NMR experiments were performed at 298 K. The  $^{13}\text{C}$ -NMR spectra were recorded on a Varian Infinity Plus-300 spectrometer equipped with a 4 mm double-resonance magic angle spinning probe head, operating at 75.47 MHz.

### Effect of Metal Ions on XAD-7's Adsorption Capacity

The effects of different metal ions on XAD-7's adsorption capacity for TA were tested as follows: 100 mL solutions containing TA of different concentrations, XAD-7 resin (0.2 g), and certain metal ion (concentration =  $10\text{ mg}\cdot\text{L}^{-1}$ ) were prepared and kept in a thermostated shaker bath at 303 K for 5 days, and then the TA concentration was measured, and the amounts of TA adsorbed by XAD-7 were calculated.

## RESULTS AND DISCUSSION

### Dynamic Adsorption Assay

Mini-column adsorption and de-sorption curves of TA on resins at 303 K are shown in Figs. 3(a), 3(b) respectively. As shown in Fig. 3(a), at a flow rate of  $12\text{ mL}\cdot\text{h}^{-1}$  and the initial TA concentration of  $100\text{ mg}\cdot\text{L}^{-1}$ , the breakthrough adsorption capacities for TA were tested as  $15.39\text{ mg}\cdot\text{g}^{-1}$  on XAD-7 and  $8.87\text{ mg}\cdot\text{g}^{-1}$  on D-201, the total capacities were  $19.42\text{ mg}\cdot\text{g}^{-1}$  for XAD-7 and  $18.91\text{ mg}\cdot\text{g}^{-1}$  for D-201. 8% NaOH solution was used to desorb TA from the column. As shown in Fig. 3(b), at a flow rate of  $3\text{ mL}\cdot\text{h}^{-1}$ , within 6 h, adsorbed TA could be completely desorbed from XAD-7 and D-201 resins. It can indicate that high adsorption capacity of XAD-7

does not ‘trap’ the adsorbed TA molecules or prolong the de-sorption procedure. The concentration of de-sorption effluent from XAD-7 is higher than that from D-201, and the volume of desorption agent is comparatively less, so adsorption and de-sorption capacity for TA on XAD-7 are better than those on D-201 in practice.

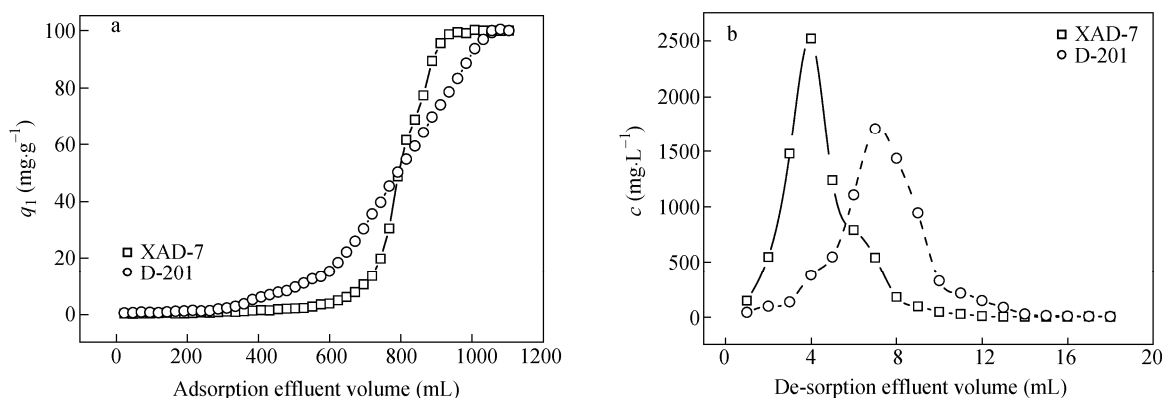


**Fig. 3** Dynamic adsorption and de-sorption curves of TA on resins at 303 K  
a) Adsorption curves; b) De-sorption curves

#### Static Adsorption Assay

Adsorption isotherms of TA on XAD-7 and D-201 at different temperatures are shown in Figs. 4(a), 4(b). All data are analyzed by Freundlich equation<sup>[13]</sup>:

$$\ln q_e = \ln K_F + 1/n \ln c_e \quad (3)$$

where  $K_F$  and  $n$  are characteristic constants. The regression equations at 283, 303 and 323 K along with the constants  $K_F$ ,  $n$  and the correlation coefficient  $R^2$  are listed in Table 1.

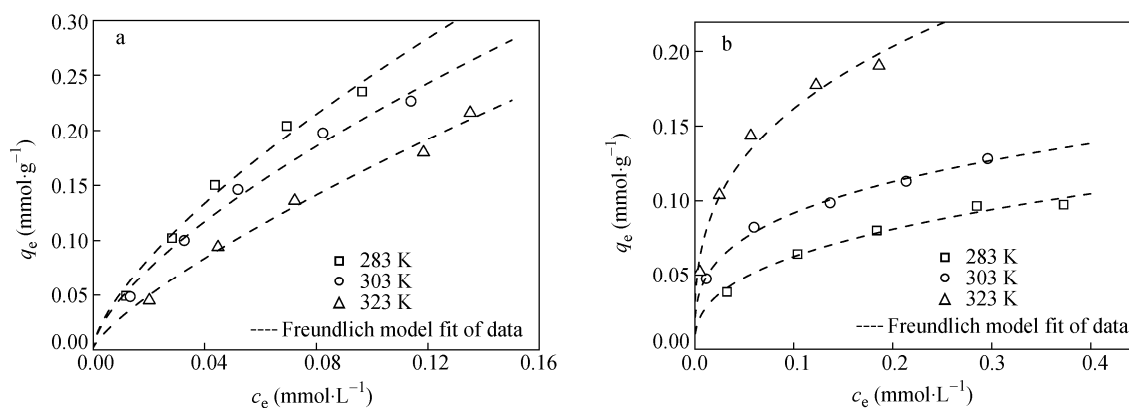


**Fig. 4** Adsorption isotherms of TA on resins at different temperatures: (a) XAD-7, (b) D-201

All equations are reliable because all the correlation factors ( $R^2$ ) were larger than 0.98. The values of  $K_F$ , a relative indicator of adsorption capacity in the Freundlich theory, indicate that the adsorption capacities of XAD-7 are higher than those of D-201 for TA. The constant  $n$  is larger than 1 in all cases, indicating favorable adsorptions.

At 283, 303 and 323 K, and the same residual concentrations ( $c_e$ ) of 0.1 and 0.4 mmol·L<sup>-1</sup>, the adsorption capacities ( $q_e$ ) on two adsorbents are calculated and listed in Table 2.

**Table 1.** Regression equation of  $\ln q_e$  versus  $\ln c_e$  for Freundlich isotherms at 283, 303 and 323 K

| Adsorbent | Temperature | Regression equation                 | Constant of Freundlich equation |       |       |
|-----------|-------------|-------------------------------------|---------------------------------|-------|-------|
|           |             |                                     | $n$                             | $K_F$ | $R^2$ |
| XAD-7     | 283 K       | $\ln q_e = 0.7696 \ln c_e + 0.4347$ | 1.30                            | 1.545 | 0.990 |
|           | 303 K       | $\ln q_e = 0.7661 \ln c_e + 0.2802$ | 1.31                            | 1.323 | 0.985 |
|           | 323 K       | $\ln q_e = 0.7597 \ln c_e - 0.0764$ | 1.32                            | 0.926 | 0.988 |
| D-201     | 283 K       | $\ln q_e = 0.3945 \ln c_e - 1.8792$ | 2.53                            | 0.153 | 0.988 |
|           | 303 K       | $\ln q_e = 0.3010 \ln c_e - 1.6980$ | 3.23                            | 0.183 | 0.995 |
|           | 323 K       | $\ln q_e = 0.3721 \ln c_e - 0.9524$ | 2.69                            | 0.386 | 0.983 |

**Table 2.** Equilibrium adsorption capacity  $q_e$  ( $\text{mmol}\cdot\text{g}^{-1}$ ) for TA on XAD-7 and D-201 at 303 K

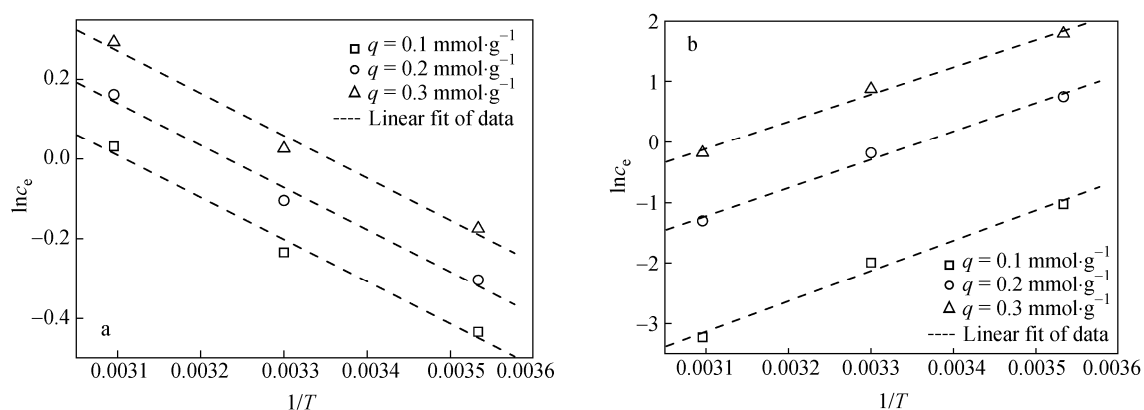
| Adsorbent | Temperature | Adsorption capacity                        |                                            |
|-----------|-------------|--------------------------------------------|--------------------------------------------|
|           |             | $c_e = 0.1 \text{ mmol}\cdot\text{L}^{-1}$ | $c_e = 0.4 \text{ mmol}\cdot\text{L}^{-1}$ |
| XAD-7     | 283 K       | 0.26                                       | 0.76                                       |
|           | 303 K       | 0.23                                       | 0.66                                       |
|           | 323 K       | 0.16                                       | 0.46                                       |
| D-201     | 283 K       | 0.06                                       | 0.11                                       |
|           | 303 K       | 0.09                                       | 0.14                                       |
|           | 323 K       | 0.16                                       | 0.27                                       |

When  $c_e = 0.1 \text{ mmol}\cdot\text{L}^{-1}$  (283 K), XAD-7's adsorption capacity for TA is more than three times as much as D-201's, when  $c_e = 0.4 \text{ mmol}\cdot\text{L}^{-1}$ , XAD-7's adsorption capacities is more than five times as much as D-201's. And higher adsorption capacity for TA on XAD-7 than that on D-201 at 303 K or 323 K is also observed.

The isosteric enthalpies of adsorption are calculated with a derivative Van't Hoff equation [14]:

$$\ln(1/c_e) = \ln K_0 + (-\Delta H/2.303RT) \quad (4)$$

where  $\Delta H$  is the isosteric enthalpy of adsorption,  $R$  is the gas constant,  $c_e$  is the equilibrium concentration of solute in moles per liter at the absolute temperature  $T$ , and  $K_0$  is a constant. At different temperatures (283, 303, and 323 K),  $c_e$  was obtained from the well-fitted isotherms.  $\Delta H$  was calculated from the slope of lines plotted by  $\ln c_e$  versus  $1/T$ , as shown in Figs. 5(a), 5(b).

**Fig. 5** (a) Determination of the isosteric enthalpy changes for TA on XAD-7; (b) Determination of the isosteric enthalpy changes for TA on D-201

The calculated isosteric adsorption enthalpies for TA on XAD-7 and D-201 are summarized in Table 3. Values of the enthalpy changes (always negative) on XAD-7 are indicative of an exothermic reaction, and their magnitudes ( $< 43 \text{ kJ}\cdot\text{mol}^{-1}$ ) show the adsorption of TA on XAD-7 at low  $c_e$  is led by physical adsorption, indicating physical adsorption force such as hydrogen bond may play an important role in adsorption process.

**Table 3.** Isosteric enthalpy of adsorption  $\Delta H$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) evaluated at different adsorption capacities in the temperature range 283–323 K

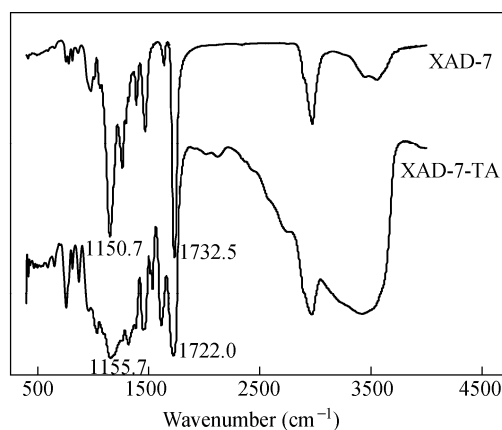
| Adsorbent | Isosteric enthalpy change ( $\text{kJ}\cdot\text{mol}^{-1}$ ) |                                          |                                          |
|-----------|---------------------------------------------------------------|------------------------------------------|------------------------------------------|
|           | $q = 0.1 \text{ mmol}\cdot\text{g}^{-1}$                      | $q = 0.2 \text{ mmol}\cdot\text{g}^{-1}$ | $q = 0.3 \text{ mmol}\cdot\text{g}^{-1}$ |
| XAD-7     | −20.29                                                        | −20.36                                   | −20.44                                   |
| D-201     | 106.89                                                        | 96.59                                    | 90.27                                    |

Values of the adsorption enthalpy changes for TA on D-201 are positive, which indicate an endothermic process. Their magnitudes ( $> 43 \text{ kJ}\cdot\text{mol}^{-1}$ ) show adsorption of TA at low  $c_e$  on D-201 to be a chemical process, and ion-exchange may be the main adsorption force.

### <sup>13</sup>C-NMR and FTIR Spectroscopy Characterization of XAD-7

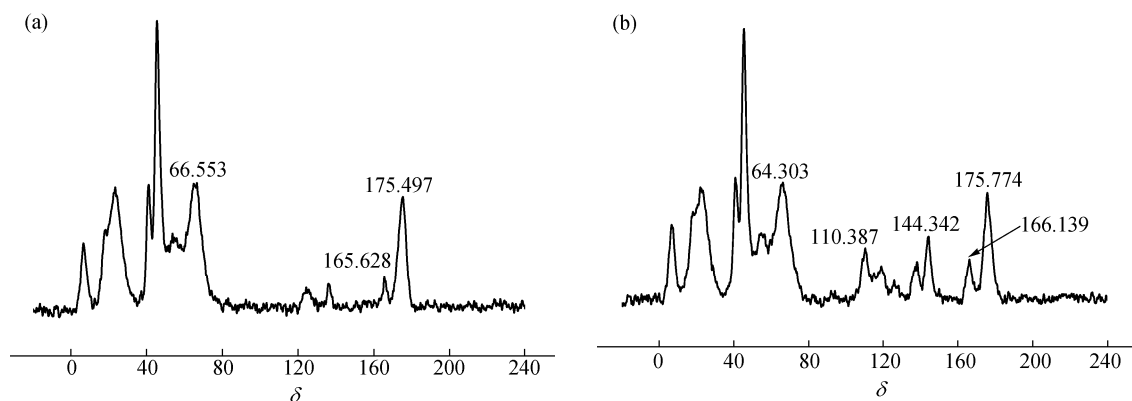
#### FT-IR spectroscopy characterization of XAD-7

In Fig. 6, the band at  $1732.5 \text{ cm}^{-1}$  of XAD-7 is due to  $\text{C}=\text{O}$  stretching, and  $1150.7 \text{ cm}^{-1}$  is due to the stretching of  $-\text{C}-\text{O}-$ . It is found that the absorption band of  $\text{C}=\text{O}$  decreases from  $1732.5 \text{ cm}^{-1}$  to  $1722.0 \text{ cm}^{-1}$ , a shift of  $\Delta\delta 10.5 \text{ cm}^{-1}$ , which suggests that adsorption of TA gets involved in the formation of hydrogen bonds.

**Fig. 6** IR spectra of XAD-7 before and after adsorption of TA

#### <sup>13</sup>C-NMR spectroscopy characterization of XAD-7

Figures 7(a), 7(b) show the <sup>13</sup>C-NMR spectroscopy characterization of XAD-7 before and after adsorption of TA. In Fig. 7(a), the peak at  $\delta = 66.533$  is the signal of  $-\text{CH}_2-\text{O}-$  groups, and the peaks at  $\delta = 175.497$  and

**Fig. 7** <sup>13</sup>C-NMR spectra of resin XAD-7  
a) Before adsorption of TA; b) After adsorption of TA

165.628 are signals of  $-\text{CO}-\text{O}-$  groups. As shown in Fig. 7(b), after adsorption of TA, peak of  $\text{O}=\text{C}-\text{O}-\text{C}$  moves from  $\delta = 175.497$  to  $175.774$ , and another peak of  $\text{O}=\text{C}-\text{O}-\text{C}$  moves from  $\delta = 165.628$  to  $166.139$ . It is due to the forming of hydrogen bonds between XAD-7's ester groups and TA-OH. However, the new peaks at  $\delta = 144.342$  and  $110.387$ , are the signals of aromatic C of TA which has been adsorbed by XAD-7.

#### Effect of Metal Ions on Resin's Adsorption Capacity for TA

As shown in Fig. 8, though XAD-7's adsorption capacity for TA isn't affected by  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  obviously,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  make a significant decrease in XAD-7's adsorption capacity for TA. All data are fitted by Langmuir equation<sup>[13]</sup>:

$$1/q_e = 1/bc_e + 1/q_m \quad (5)$$

From it, the monolayer saturation adsorption capacity of adsorbate,  $Q_m$  ( $\text{mg}\cdot\text{g}^{-1}$ ), the constant,  $b$  ( $\text{L}^{-1}$ ) and the adsorbent-adsorbate relative affinity in the adsorption process are obtained and listed in Table 4.

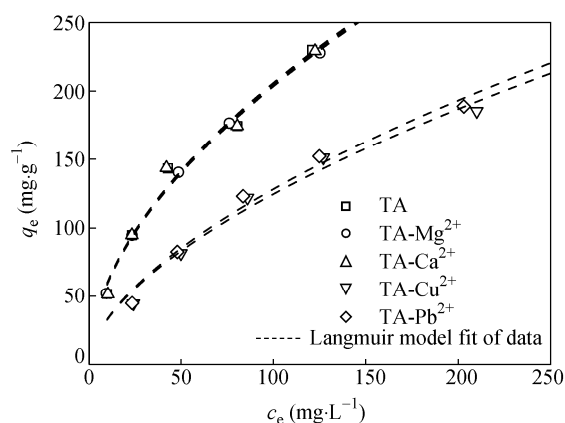


Fig. 8 Adsorption isotherms of TA on XAD-7 in the presence of metal ions

Table 4. Results obtained from the Langmuir equation applied to the adsorption isotherms of TA on XAD-7 at 303 K in the presence of metal ions

| Metal ions                          | Regression equation           | Constant of Langmuir equation |        |       |
|-------------------------------------|-------------------------------|-------------------------------|--------|-------|
|                                     |                               | $b$                           | $Q_m$  | $R^2$ |
| Without of metal ion                | $1/q_e = 0.1616/c_e + 0.0034$ | 6.19                          | 294.12 | 0.997 |
| In the presence of $\text{Ca}^{2+}$ | $1/q_e = 0.1709/c_e + 0.0032$ | 5.85                          | 312.5  | 0.998 |
| In the presence of $\text{Mg}^{2+}$ | $1/q_e = 0.1517/c_e + 0.0037$ | 6.59                          | 270.27 | 0.996 |
| In the presence of $\text{Cu}^{2+}$ | $1/q_e = 0.4731/c_e + 0.0029$ | 2.11                          | 344.82 | 0.999 |
| In the presence of $\text{Pb}^{2+}$ | $1/q_e = 0.4558/c_e + 0.0028$ | 2.19                          | 357.14 | 0.999 |

It is seen that the constant  $b$  decreased significantly in the presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , which indicates the adsorbent-adsorbate relative affinity in the adsorption process is weakened by these metal ions. It can be explained by the mechanism that  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  can form complex compounds ( $\text{Cu}^{2+}\cdots\text{HO-TA}$ ,  $\text{Pb}^{2+}\cdots\text{HO-TA}$ ) with HO— of TA<sup>[15]</sup>, occupying the active adsorption sites of TA, as a result, the adsorption force is weakened. On the other hand, it is possible for the occurrence of interaction between heavy metal ions and XAD-7's  $-\text{O}-$  groups or TA-OH, which increases the XAD-7's active adsorption sites or active adsorption layer, so the monolayer saturation adsorption capacity of XAD-7  $Q_m$  is slightly higher than that without these heavy metal ions.

Figure 9 shows the IR spectra of XAD-7 after adsorption of TA in the presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , which can confirm the above inference. In the presence of  $\text{Cu}^{2+}$  or  $\text{Pb}^{2+}$ , the adsorption band of  $\text{O}=\text{C}-\text{O}-$  moves from  $1155.7\text{ cm}^{-1}$  to  $1158.7\text{ cm}^{-1}$  and  $1161.9\text{ cm}^{-1}$  respectively. The red shift is due to the interactions between heavy metal ions and resin's ester groups  $-\text{O}-$ . Since  $-\text{O}-$  of resin's ester groups can serve as electron donor, and

heavy metal ions can serve as the electron donator, so it is possible for the occurrence of attraction between these species.

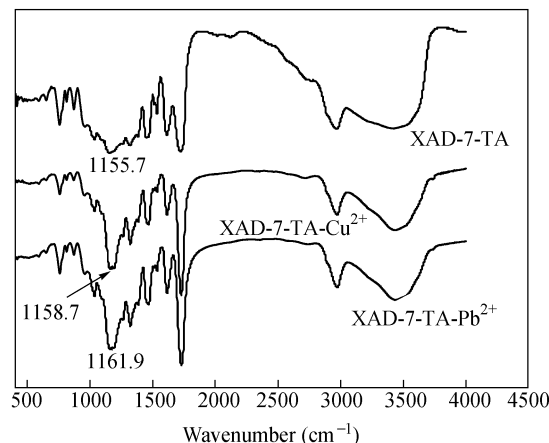


Fig. 9 IR spectra of XAD-7 after adsorption of TA in the presence of heavy metal ions

## CONCLUSIONS

Adsorption of TA by acrylic ester resin XAD-7 and strong basic ion-exchange resin D-201 is investigated. In the mini-column adsorption assay, at a flow rate of  $3 \text{ mL} \cdot \text{h}^{-1}$  and initial concentration of  $100 \text{ mg} \cdot \text{L}^{-1}$ , the breakthrough adsorption capacity for TA was  $15.39 \text{ mg} \cdot \text{g}^{-1}$  on XAD-7 and  $8.87 \text{ mg} \cdot \text{g}^{-1}$  on D-201, the total adsorption capacity was  $19.42 \text{ mg} \cdot \text{g}^{-1}$  on XAD-7 and  $18.91 \text{ mg} \cdot \text{g}^{-1}$  on D-201. However, TA adsorbed by XAD-7 could be desorbed using NaOH solutions completely. So XAD-7 may be used as an effective adsorbent to remove TA from water/wastewater in the future.

In static adsorption assay, XAD-7 also shows perfect adsorption capacity for TA. The values of the enthalpy for TA adsorbed by XAD-7 are negative, indicating an exothermic reaction, and their magnitudes ( $< 43 \text{ kJ} \cdot \text{mol}^{-1}$ ) manifest the process to be a physical adsorption. But the values of the enthalpy for TA adsorbed by D-201 are positive, which indicate an endothermic reaction, and their magnitudes ( $> 43 \text{ kJ} \cdot \text{mol}^{-1}$ ) manifest the process to be a chemical adsorption.

$^{13}\text{C}$ -NMR and FT-IR spectroscopy characterization of XAD-7 indicates that the hydrogen bonding between resin's  $\text{C}=\text{O}$  and TA's  $\text{HO}-$  groups is the main adsorption force.

XAD-7's adsorption capacity for TA is measured in the presence of metal ions. Though  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , affect XAD-7's adsorption capacity for TA slightly,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  decrease XAD-7's adsorption capacity significantly.

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