

SYNTHESES AND ADSORPTION PROPERTIES OF PHENOL-FORMALDEHYDE-TYPE CHELATING RESINS BEARING THE FUNCTIONAL GROUP OF TARTARIC ACID*

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Abstract Several kinds of novel chelating resins bearing the functional group of tartaric acid (TTA-FQ-12, TTA-FQ-23, and TTA-FQ-34) were synthesized by reacting epoxy maleic anhydride, which was prepared through the oxidization reaction of maleic anhydride by hydrogen peroxide, with phenol-formaldehyde resin containing polyamine (FQ resins series). The effects of such factors as reaction time, reaction temperature and pH value on the loading capacity of TTA in resins were investigated. The results showed that the optimum reaction conditions are as follows: time 9–12 h; temperature 90–105°C; pH value 6–10. The loading capacities of TTA can reach 0.15, 0.14, and 0.11 mmol/g⁻¹ when the functional group of FQ resin was $-\text{OCH}_2\text{CH}_2\text{NHC}_2\text{H}_4\text{NH}_2$, $-\text{O}(\text{CH}_2\text{CH}_2\text{NH})_2\text{C}_2\text{H}_4\text{NH}_2$ and $-\text{O}(\text{CH}_2\text{CH}_2\text{NH})_3\text{C}_2\text{H}_4\text{NH}_2$, respectively. The structures of resins were characterized by FTIR spectra. The primary study on the adsorption properties of the resins for metal ions showed that there are two kinds of adsorption mechanisms *i.e.* ion exchange and chelate in the adsorption process. TTA-FQ resins have much higher adsorption selectivity for Pb^{2+} and Zn^{2+} than for Cu^{2+} and Ni^{2+} . These resins can probably be used for separating Pb^{2+} or Zn^{2+} in the mixture of metal ions or for treating wastewater containing heavy metal ions.

Keywords Tartaric acid, Chelating resin, Synthesis, Adsorption, Heavy metal ion

INTRODUCTION

Chelating resins have been widely used for separating and treating industrial wastewater which contains heavy metal ions^[1–4]. There are a large number of hydrophilic groups such as $-\text{CH}_2\text{OCH}_2-$ and $-\text{CH}_2\text{OH}$ in the structure of phenol-formaldehyde, which confer excellent hydrophilic and swelling properties upon the resin in water and other polar solvents. Therefore, phenol-formaldehyde resin is more suitable than those hydrophobic polymers such as crosslinked polystyrene and crosslinked polyacrylate for preparing ion-exchangers or chelating agents used in polar solvents^[5]. Qu and coworkers^[6–8] reported the syntheses of several chelating resins containing different polyamine group based on phenol-formaldehyde resin and their adsorption properties for Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , Ag^+ , and Au^{3+} . Xu^[9] reported that chelating resin containing amino acid structure had good adsorption selectivity for divalent metal ion. Generally, this type of resin was synthesized by the carboxymethylation of amino-resin. In this paper, a series of new chelating resins containing amino acid structure were synthesized by introducing tartaric acid (TTA) into the previously reported resins^[7] that containing different polyamine. TTA is a common analytical reagent and is generally used as masking agent of metal ions because it can form stable chelate complexes with many kinds of metal ions. The incorporation of TTA into amino-resin

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makes the resin have both amino and amino acid functional groups; hence good adsorption selectivity for divalent metallic ion can be anticipated.

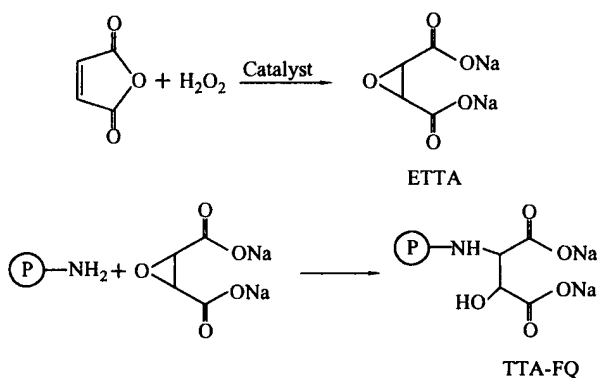
EXPERIMENTAL

Instruments and Reagent

FQ series resins (the functional groups of FQ-12, FQ-23, FQ-34 were $-\text{OCH}_2\text{CH}_2\text{NHC}_2\text{H}_4\text{NH}_2$, $-\text{O}(\text{CH}_2\text{CH}_2\text{NH})_2-\text{C}_2\text{H}_4\text{NH}_2$ and $-\text{O}(\text{CH}_2\text{CH}_2\text{NH})_3\text{C}_2\text{H}_4\text{NH}_2$) were synthesized according to Ref. [6]; maleic anhydride, sodium tungstate dihydrate, hydrogen peroxide, xlenol orange, NaOH, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and ZnO were AR grade. Infrared spectrometer (Nicolet MAGNA-IR 550), gas thermostat oscillator (THA-S) and pHS-2 pH-meter were used for characterization.

Synthesis of Resin

The general synthetic route for resins is shown in Scheme 1.



Scheme 1

Preparation of ETNA resin

To a three-necked round flask, 25 mL hydrogen peroxide and 19.8 g maleic anhydride were added. When the mixture was dissolved completely, 0.5 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to the mixture after a desired amount of 20% aqueous NaOH solution was added to adjust the pH to 3.5. After reaction for 4 h at 58–60°C, the mixture was cooled to room temperature, then the solid product was filtered off, dried, and re-dissolved in deionized water. A desired amount of 30% aqueous NaOH solution was added to adjust the pH to 6.5. Aqueous ETNA was thus obtained.

Syntheses of target resin TTA-FQ (typical procedure)

A desired amount of FQ resin was suspended in excess 20% aqueous ETNA solution and swollen for 12 h at 25°C, then refluxed for 12 h. After reaction, the resin was filtered and washed thoroughly with deionized water to pH = 7, then extracted in a Soxhlet apparatus with 95% ethanol for 12 h. A primrose-colored powder product was obtained after drying.

Structural Characterization and Function Determination

FTIR measurements of the resins were carried out by using KBr pellets with 32 scans and a resolution of 4 cm^{-1} .

The determination was carried out according to Ref. [1] and adsorption capacities were calculated using the following equation:

$$Q = (c_0 - c) \times V/W$$

where Q (mmol/g^{-1}) is the adsorption capacity, c_0 and c (mmol/mL^{-1}) are the initial and final concentration of the metal ion in the solution, V (mL) is the volume of the solution and W (g) is the weight of the dry resin.

RESULTS AND DISCUSSION

Synthesis of TTA-FQ

There are many methods to attach TTA to a polymeric resin frame causing (1) the TTA's carboxyl group to react with polymeric resin frames containing active functional groups, such as $-\text{OH}$ or $-\text{NH}_2$ and (2) the TTA's $-\text{OH}$ to react with the polymeric resin frames containing carboxyl group. If the first method were adopted, one molecule of TTA would consume one carboxyl group, which has not only good chelating capacity but also good ion-exchange capacity for metal ions. To ensure the resin maintains its optimum adsorption capacity, it is necessary to avoid the consumption of carboxyl group. In the second method, the consumption of carboxyl group could be avoided, the ester bond ($-\text{COOC}-$) formed in the reaction would be easily hydrolyzed under alkaline or acidic conditions, and then the stability of resin would be seriously affected. Generally, epoxy compounds can react with $-\text{NH}_2$ or $-\text{OH}$ very easily and form ring-opening addition product. The method of introducing TTA into polymeric structure by the reaction of epoxy group with $-\text{NH}_2$ can completely overcome the above-mentioned disadvantage. This work focuses on the influences of reaction time, temperature, pH value, and concentration of solution on the loading capacities of TTA in the FQ series resins.

Effect of reaction time on loading capacity of TTA

The effect of reaction time on loading capacity of TTA was investigated by taking FQ-12 resin as an example. The results are shown in Fig. 1. When the reaction time exceeds 9 h, further prolonging reaction time could hardly influence the loading capacity of TTA. In order to ensure that the reaction proceeds sufficiently, all the reactions were run for 12 h. The loading capacities of the three resins of TTA after 12 h are shown in Table 1. From Table 1, it can be seen that although the nitrogen content in FQ-34 is the highest among the three resins, its loading capacity of TTA is the lowest.

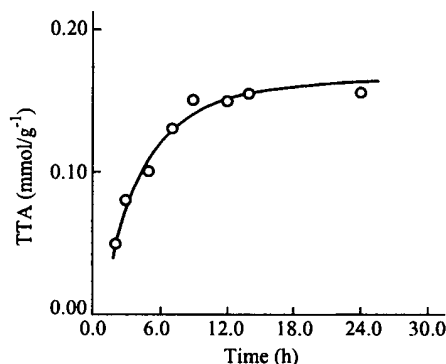


Fig. 1 Effect of time on the content of TTA in resin

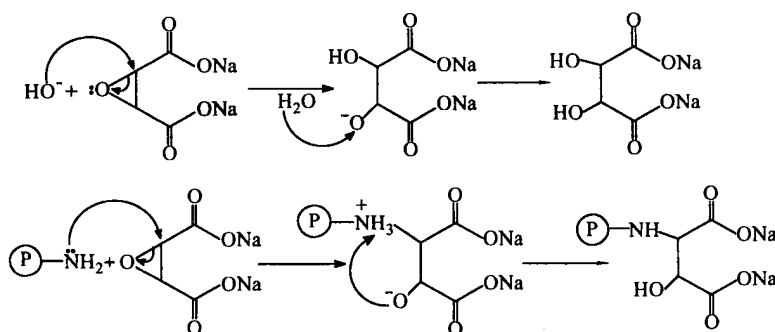
Table 1. The loading capacities of TTA in TTA-FQ series resins (temperature = 25°C)

Resins	TTA-FQ-12	TTA-FQ-23	TTA-FQ-34
Nitrogen content in original resin (mmol/g)	0.60	0.74	0.88
Loading capacity of TTA (mmol/g)	0.15	0.14	0.11
The molar ratio of TTA with nitrogen	0.25	0.19	0.13

It is inferred that this phenomenon may be related to the crosslinking degree of polyamine in the resin. Triethylenetetramine has the longest chain among the three polyamines, therefore, the crosslinking degree of polyamine in FQ-34 is the highest among the three resins^[6]. The increase of crosslinking degree hinders the diffusion of ET TA into resin and prevents the inner amino group of resin from reacting completely. On the contrary, the crosslinking degree of polyamine in FQ-12 is the lowest; the ET TA molecule can enter the inside of resin easily, so the loading capacity of TTA-FQ-12 is the highest. Table 1 reveals that the utilization ratio of amino group in TTA-FQ-12 is the highest among the three resins and reaches 25%. The remaining 85% amino group does not take part in the reaction because the size of the ET TA molecule is too big for it to be able to enter the resin.

Effect of pH value on loading capacity

Figure 2 shows that the pH value has significant effect on the loading capacity of the resins. The loading capacity is highest at pH 6–10. However, the loading capacity declines when the pH value is lower than 6 or higher than 10. The probable reasons are: (1) under higher pH conditions, the concentration of OH^- is higher, the following probable competitive reactions (Scheme 2) may occur.



Scheme 2

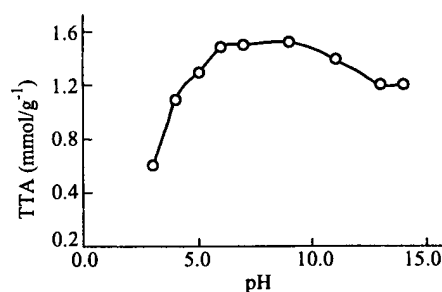
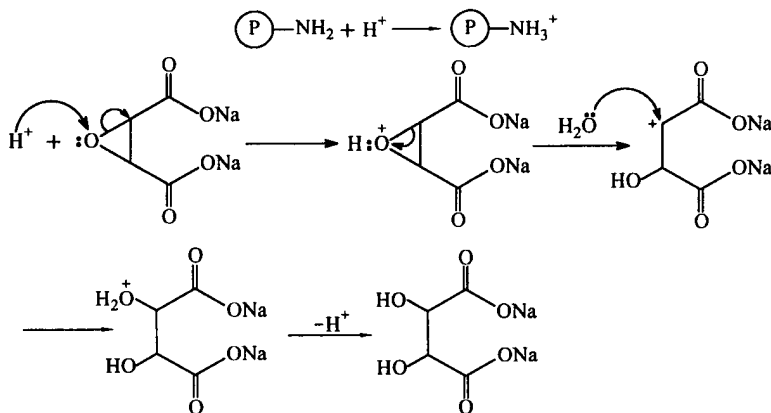


Fig. 2 Effect of pH value on the capacities of TTA

(2) Under lower pH conditions, amino group is protonated and its nucleophilic capacity becomes weak, so the following reactions (Scheme 3) occur:



Scheme 3

Effect of temperature on loading capacity

The effects of temperature between 40–105°C on the loading capacities were investigated using FQ-12 as an example. The experimental results in Fig. 3 show that there are evident differences in TTA loading capacities of the products when the temperature is within 40–105°C. A satisfactory result can be obtained when the reaction

temperature is between 95–105°C. It was noticed that the color of the resins becomes deeper and deeper when the experimental temperature is over 110°C (the general refluxed temperature was about 105°C); however, the loading capacity does not increase evidently.

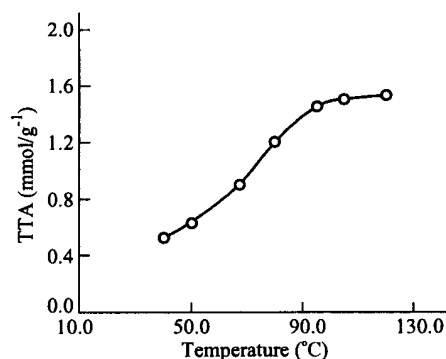


Fig. 3 Effect of temperature on the capacity of resin

Characterization of Resin

FTIR was employed to characterize the structure of the resin. The spectral results are shown in Table 2. The vibrational absorption bands at 1600, 1500, and 1450 cm^{-1} in all resins indicate the presence of benzene ring. The absorption bands at 1245 and 1030 cm^{-1} prove the existence of Ph—O—C structure. The absorption bands of amino group at 3300–3400 cm^{-1} indicate that there are some residual —NH— groups in the resin after reaction with ET TA. This result tallied with that of determination of loading capacity. The absorption band at 1770 cm^{-1} in the spectra of TTA-FQ-12(B), TTA-FQ-23(B), TTA-FQ-34(B) indicates the existence of —COOH which disappears after the resin has been treated with dilute NaOH aqueous solution. This further proves the existence of —COOH. Aforementioned facts confirm that TTA has been introduced successfully into the structure of resins and the desired resins were obtained.

Table 2. FTIR spectral data of resins

Resins	FQ-12	TTA-FQ-12(B)*	TTA-FQ-34(A)**	FQ-23	TTA-FQ-23(B)	TTA-FQ-23(A)	FQ-34	TTA-FQ-23(B)	TTA-FQ-34(A)
$V_{\text{N-H}}$	3373	3386	3368	3365	3422	3429	3363	3409	3418
$V_{\text{C-H}}$	3061	3061	3061	3060	3060	3060	3061	3060	3060
$V_{\text{as C-H}}$	2924	2924	2923	2924	2927	2927	2928	2925	2926
$V_{\text{s C-H}}$	2871	2872	2872		2875		2875	2875	2873
$V_{\text{C-C, ph}}$	1609	1609	1609	1609	1611		1609	1637	
	1585	1585	1585	1585		1580	1585	1611	1583
	1508	1508	1508	1508	1508	1508	1508	1508	1508
	1455	1449	1449	1450	1449	1450	1450	1449	1449
$V_{\text{C=O}}$	—	1702	1650		1700			1702	1650
		1609	1609		1636	1618		1638	1611
$V_{\text{ph-o-c}}$	1246	1245	1244	1246	1244	1243	1246	1243	1243
	1034	1033	1028	1033	1029	1033	1035	1028	1029
$\delta_{\text{C-H, ph}}$	840	840	838	838	840	841	841	839	839
		732	731	731	732		732	732	731
	689	689	688	688	687	688	670	688	688

* B represents the resin before being treated with 10% NaOH solution

** A represents resin after being treated with 10% NaOH solution

Adsorption Properties of Resins

The static adsorption capacities of TTA-FQ(A) series resins for metal ions are shown in Table 3. TTA-FQ has higher selectivity for Zn^{2+} and Pb^{2+} than for Cu^{2+} and Ni^{2+} . This adsorption property is entirely different from the

general polyamine-typed chelating resin, therefore this resin may probably be useful for the separation of Zn^{2+} and Pb^{2+} .

Table 3. The adsorption capacities of TTA-FQ(A) series resins (mmol/g)*

Resins**	TTA-FQ-12	TTA-FQ-23	TTA-FQ-34
Cu^{2+}	0.72	0.73	0.85
Ni^{2+}	0.35	0.37	0.64
Zn^{2+}	1.74	0.41	0.37
Pb^{2+}	1.35	0.82	0.62

* Adsorption conditions: 0.1000 g resin, 20 mL metal ion solution, 30°C, shaking 4 h and settling for 4 h

** All resins were treated with 10% NaOH aqueous solution.

The adsorption dynamics of TTA-FQ resin for Cu^{2+} and Pb^{2+} were investigated and the results are shown in Fig. 4 and Fig. 5. From Fig. 4, the existence of “inflections” in the dynamics curves of two resins for Cu^{2+} shows that the mechanism involved in the whole adsorption process is not a simple one. In the early 0.5 h, the adsorption process was very quick; may be it is an ion exchange reaction from Na^+ to Cu^{2+} occurring on COO^-Na^+ and is the major adsorption process. This is because TTA is mainly attached on the surface of resin and has preferential contact with metallic ion during adsorption. When the adsorption time was within 0.5–1.5 h, the adsorption rate curve becomes flat because, within this period, the chelating adsorption of Cu^{2+} with $-\text{NH}-$ is the major process as $-\text{NH}-$ groups are generally located inside of the resin and the entry of Cu^{2+} into the resin is controlled by liquid film diffusion. The adsorption equilibrium time is about 2 h. A similar phenomenon can be seen in the adsorption for Pb^{2+} , that is, there are two adsorption mechanisms involved in the adsorption. Only the adsorption rate for Pb^{2+} was slightly faster than for Cu^{2+} . The adsorption for Pb^{2+} was carried out within about 1.5 h.

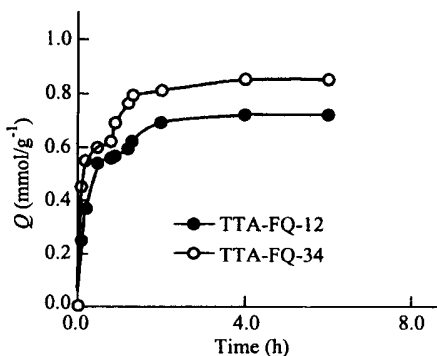


Fig. 4 Adsorption dynamics curves of TTA-FQ resins for Cu^{2+}

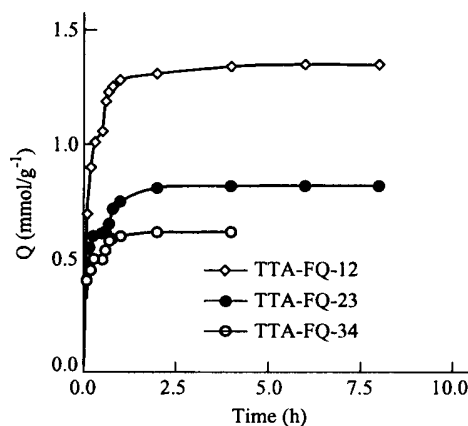


Fig. 5 Adsorption dynamics curves of TTA-FQ resins for Pb^{2+}

CONCLUSIONS

Series of TTA-FQ resins synthesized in this work have excellent adsorption properties for Cu^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} . Their optimum adsorption capacities are 0.85, 0.64, 1.35 and 1.74 mmol/g, respectively. The adsorption selectivity of TTA-FQ-12 for Pb^{2+} and Zn^{2+} is the best among all the resins. Ion exchange and chelating mechanisms are involved in the adsorption process of series of TTA-FQ resins for metal ions.

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