Syntheses and Properties of Carboxymethyl Chitosan/Urea–Formaldehyde Snake-Cage Resins

RONGJUN QU,[1,2] YANZHI SUN,[2] CHUNHUA WANG,[2] SHULAI LU,[1] HUIMEI YU,[2] GUOXIANG CHENG[1]

[1] School of Material Science & Engineering, Tianjin University, Tianjin 300072, People's Republic of China

[2] Department of Chemistry, Yantai Normal College, Shandong 264025, People's Republic of China

ABSTRACT: A series of novel snake-cage resins were synthesized using carboxymethyl chitosan (CM-CTS) as the snake resin and urea–formaldehyde resin (UF) as the cage resin. Such factors as the optimal synthesis conditions, content of the crosslinking agent, and sorption capacities for metal ions of the above-mentioned resins were investigated. The experimental results show that these resins have appropriate swelling properties and good mechanical stability. They do not run off in water, HCl, and NaOH aqueous solutions. To form a stable network system, NH_4Cl was used as a crosslinking agent to crosslink urea and formaldehyde in synthesis. The sorption experiment showed that the sorption properties of the resins in the presence of the crosslinking agent NH_4Cl are better than those without a crosslinking agent. The investigation of the FTIR spectra indicated that the chelate groups, such as —OH, —CO_2^- and $NHCH_2CO_2^-$, in snake-resin molecules participated in the coordination with the metal ions, but the —C=O bonds in the cage resin UF did not. The snake resin CM-CTS in the snake-cage resins was the major contributor of sorption. The sorption dynamics showed that the sorption was controlled by liquid film diffusion. The isotherms can be described by Freundlich and Langmuir equations. The saturated sorption capacities of the resins for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} were 1.48, 0.78, 0.13, and 0.02 mmol g^{-1}, respectively. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 310–317, 2002; DOI 10.1002/app.10331

Key words: adsorption; ion exchangers; networks; swelling

INTRODUCTION

Snake-cage resins can also be called "snake-cage polyelectrolytes." This type of exchanger consists of a crosslinked polymer matrix cage and a linear polymer snake which is physically trapped inside the cage. The concept of "snake-cage resin" was put forward first by Hatch et al. in 1957.[1] In recent years, these kinds of resins were developed quickly[2–6] and widely used in separating metal ions,[7] such as in removing salts from sugar[3] and purifying glycerin.[8] Generally, there are two methods for synthesizing snake-cage resins: (1) let monomers absorb and stay in the cage resin, then make the monomers polymerize into a linear "snake" resin by an appropriate method; and (2) mix the snake resin with monomers, then make these monomers crosslink each other into a "cage" resin. Regardless of which method is adopted, the snake resin must be tightly twisted inside the cage resin or it will be leached out. Carboxy-

Table I   Syntheses of UF Series Resins

UF	UF_1	UF_2	UF_3	UF_4	UF_5
Formaldehyde (mL)	100	100	100	100	100
Urea (g)	31	35	39	43	47
Formaldehyde/urea (molar ratio)	2.53 : 1	2.24 : 1	2.01 : 1	1.82 : 1	1.67 : 1

methyl chitosan (CM-CTS) has excellent chelate properties for metal ions[9] because it contains —OH, —NH_2, etc., chelate groups and an EDTA-like molecular structure. However, it is a linear molecule and easy to run off in water; hence, it must be chemically crosslinked before being used as a chelate resin. It is the difficulty of a crosslinking reaction that confines the application of CM-CTS. In this article, through a method we named "mix-co-polymerization," a series of novel chelate resins, which have a snake-cage structure, were synthesized by using CM-CTS as the snake resin and crosslinked urea–formaldehyde (UF) resin as the cage resin. This method solved the problem of the crosslinking difficulty of CM-CTS successfully and offered a new way to apply CM-CTS. The swelling feature and sorption properties of the above-mentioned resins for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} were also studied.

EXPERIMENTAL

Materials

CM-CTS was purchased from the Chengdu Zhida Ltd. Chemical Co. (Chengdu, China). The molecular weight and degree of carboxymethylation was found to be 1.2×10^6 and about 0.82, respectively. It was refluxed and extracted in 95% ethanol for 4 h before using. UF (38%), $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 7H_2O$, $ZnCl_2$, $PbNO_3$, EDTA, and xylenol orange were analytical-grade reagents.

Methods

Preparation of Prepolymer of Urea–Formaldehyde (Typical Synthesis)

An aqueous solution of formaldehyde (100 mL, 38%) was placed into a 250-mL three-necked flask. When the pH value was regulated to 7–7.5 with sodium hydroxide, 35 g urea was added while stirring at room temperature. After the urea dissolved, the temperature of the reactant mixture was gradually increased to 90°C for 1 h and 95–98°C for 1.5 h. When the pH value of the mixture was about 5–5.5, the reaction was finished. With the the pH regulated at 7–8, a colorless sticky liquid product was produced. The other products UF_1–UF_5 were obtained by changing the ratio of urea and formaldehyde (see Table I).

Preparation of Snake-Cage Resin I (Typical Synthesis)

An aqueous solution of CM-CTS, 40 mL, 2.02%, was mixed with 1 mL UF_1 solution and 0.215 g NH_4Cl at 40–50°C until a large quantity of gel appeared. Then, the gel was moved to a clean glass pane and dried under infrared light. The dried sample was ground, sieved, and moved to a Soxhlet extraction apparatus for reflux extraction in 95% ethanol for 12 h. Then, it was dried up again and called resin I. Resins II–XI were synthesized by the same method as was resin I (see Table II).

Table II   The Synthesis of Resins I–XI

Resin	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
UF_1 (mL)	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UF_2 (mL)	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UF_3 (mL)	0.00	0.00	1.00	0.00	0.00	1.00	1.00	0.00	1.00	1.00	1.00
UF_4 (mL)	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UF_5 (mL)	0.00	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	0.00
CM-CTS (mL)	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	60.00	80.00	100.0
NH_4Cl (g)	0.215	0.215	0.215	0.215	0.215	0.00	0.00	0.00	0.215	0.215	0.215

Table III Swelling Coefficients *K* of I–XI in Different Solvents

Solvent	Resin										
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Water	1.35	1.35	1.38	1.38	1.43	1.30	1.41	1.34	1.78	2.00	3.25
5% HCl	4.75	4.85	5.00	5.23	5.20	2.03	2.05	2.11	5.00	5.60	6.10
1% HCl	4.51	4.51	4.19	4.50	4.52	2.03	2.03	2.10	4.30	4.80	4.92
5% NaOH	1.44	1.62	1.82	1.96	1.92	1.55	1.55	1.56	2.58	3.18	3.71
1% NaOH	1.36	1.35	1.38	1.38	1.40	1.35	1.38	1.40	1.98	3.01	3.52

Swelling conditions: 0.1000 g sample of resin; 10 mL water; standing 12 h; tests three times every sample.

Properties of the Snake-cage Resin

The swelling properties, sorption dynamics, isothermal sorption, and effects of the pH of the resins were tested by the methods of Qu.[10] The sorption capacities and swelling coefficients were calculated,[11] respectively, according to the following equations:

$$Q = (C_0 - C)V/W \qquad (1)$$

$$K = \sum V / \sum V_0 \qquad (2)$$

where in eq. (1) Q (mmol g^{-1}) is the sorption capacity; C_0 and C (mmol L^{-1}), the initial and final concentration of metal ions in the solution; W (g), the weight of the dried resin; and V (mL), the volume of the solution, and in eq. (2), K is the swelling coefficient, and V and V_0, the volume of the resin before and after swelling, respectively.

RESULTS AND DISCUSSION

Synthesis of the Resin

In the common synthesis of snake-cage resins, as the linear molecule, the snake resin must be fully mixed with the prepolymer of the cage resin to prevent it from running off from the cage resin. Thus, it can be twisted tightly inside the cage resin when the crosslinking reaction has finished. Because CM-CTS is a huge water-soluble polymer and will extremely expand in water, the presence of a large amount of water will seriously disturb the crosslinking reaction. For the sake of solving this problem, resins I–IX were prepared by the following procedure: First, an aqueous solution of CM-CTS was fully mixed with UF, then the mixture was crosslinked by NH$_4$Cl, and, finally, the gel was evaporated slowly. The experiments revealed that snake-cage resin with good physical properties could be achieved by the above-mentioned synthetic method.

Table III shows that resins I–IX only swell but do not run off in water, acidic, and basic aqueous solutions of different concentrations, which reveal that all the resins contain a crosslinking structure, and a crosslinking reaction could occur even without the crosslinking agent (NH$_4$Cl). However, from Table IV, the sorption capacities of resins VI–VIII for metal ions are less than those of the other resins. A possible reason for this would be that a resin without the crosslinking agent NHCONHCH$_2$OH and its linear polymer,

Table IV Sorption Capacities of Resins I–IX for Metal Ions (mmol g^{-1})

Metal Ion	UF	Resin										
		I	II	III	IV	V	VII	VII	VIII	IX	X	XI
Cu^{2+}	0.014	0.776	0.799	0.892	0.908	0.905	0.189	0.220	0.243	1.280	1.412	1.482
Ni^{2+}	0.010	0.218	0.240	0.390	0.456	0.457	0.104	0.148	0.152	0.683	0.751	0.779
Pb^{2+}	0.001	0.020	0.020	0.023	0.023	0.020	0.021	0.072	0.096	0.103	0.107	0.132
Zn^{2+}	0.001	0.021	0.018	0.038	0.022	0.023	0.028	0.012	0.020	0.009	0.007	0.021

Sorption conditions: 25°C; shaking for 7 h; standing 8 h; weight of resin W = 0.1000 g; V = 5 mL; pH 4.0–6.0.
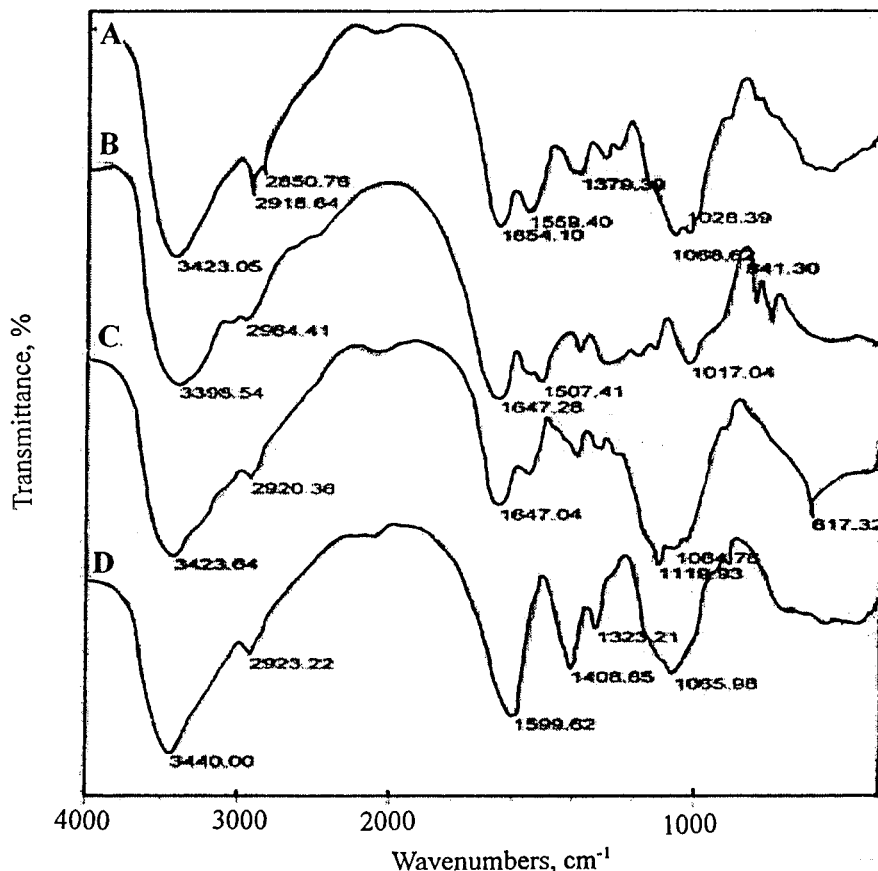
Figure 1 Spectra of resins after and before adsorption for Cu(II): (A) Resin I; (B) UF resin; (C) Resin I after sorption Cu(II); and (D) CM-CTS.

besides self-crosslinking and becoming cage resin, may crosslink with —OH and —NH$_2$, etc., groups in the CM-CTS molecule. This deduction can be proven by the following fact from Table III: The swelling coefficients of resins VI–VIII were much less than were those of the others in all the studied solutions. Considering that increasing the amount of formaldehyde will make a UF gel, the ratio between formaldehyde and urea is limited to about 2.53:1–1.67:1 (see Table I). To a certain extent, it is more exact to call this snake-cage resin prepared by the above method a "net-cage" resin.

From the FTIR spectra (which were determined with a Nicolet MAGNA IR-550 Series II infrared spectrophotometer made in the USA) (Fig. 1), it is clear that (1) in the spectrum of the CM-CTS resin a strong absorbing peak at 3440 cm^{-1} and a medium peak at 1066 cm^{-1} indicates the existence of —OH in the molecule. The high peaks at 1599.6 and 1408.7 cm^{-1} indicates that

there is —CO$_2^-$ of a —NHCH$_2$COO$^-$ group in the molecule. The weak absorbing peak at 2923.2 cm^{-1} that is the characteristic absorption of C—H indicates there are few C—H bonds in the molecule. A series of high peaks around 1066 cm^{-1} was due to the stretching vibration of C—OH and C—O—C bonds. (2) In the spectrum of the UF resin, the strong absorption at 3398.5 cm^{-1} proved the existence of —OH and —NH— groups. The absorbing peak at 1647 cm^{-1} is characteristic of comprehensive absorption of —NHCONH—. A series of peaks at 1100–1200 cm^{-1} reveal the existence of the C—O—C bond in the molecule. The absorbing peak at 2964.4 cm^{-1} proved the existence of the C—H bond in the molecule. (3) In the spectrum of resin I, the peaks at 1654.1 and 1559.4 cm^{-1} were the composite absorption of —COO— and —NHCONH—, and 1152.8, 1068.6, and 1028.4 cm^{-1} were the comprehensive absorption of C—O—C and C—OH. The other resins' structures are similar to that of resin I.
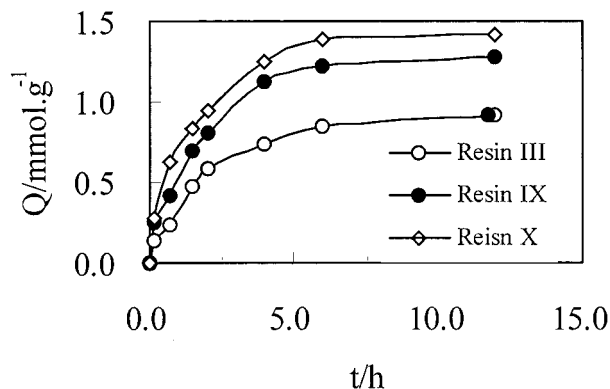
Figure 2   Sorption kinetic curves of resin for Cu^{2+}.

Swelling Properties

Since the sorption and regeneration of resins usually happens in acidic and basic aqueous solutions of different concentrations, it is necessary to study the swelling rate and swelling coefficient of resins in acidic and basic solutions. The quicker the swelling is, the less time it will take to re-treat the resins. The experimental result shows that in only about 16–20 min resins I–XI will sufficiently swell. The swelling property will directly influence the mechanical strength of the resins and the diffusion rate of metal ions inside the resins. The larger the swelling coefficient, the quicker diffusion will occur. Nevertheless, too high a swelling coefficient will lead to low mechanical strength of the resin. In this study, the swelling coefficients of the synthesized resins were within 2–6, and all the resins have satisfactory mechanical properties after swelling. Therefore, they are suitable to be used as a chelate resin.

Some conclusions can be drawn from Table III: (1) For the same type of resins, there is a basic rule, that is, the swelling coefficient in different solutions lies in the following order: 5% HCl > 1% HCl > 5 % NaOH > 1% NaOH > water, although they have different swelling properties in different solvents. This is because the acid and base will lead to the protonation of —N— and the ionization of —COOH in the snake resin CM-CTS, respectively. (2) The swelling coefficients increased with the amount of CM-CTS in the snake-cage resins, so proving that CM-CTS is the major contributor of the swelling. (3) The swelling coefficients of resins I–V in different solutions lies in the following order: V > IV > III > II > I, meaning that the swelling coefficients of the resins were related to the amount of formaldehyde in the synthesizing UF resin. The more formalde-

hyde used, the lower is the swelling coefficient. The possible reason for this is that an excess of the formaldehyde in synthesizing UF resins makes the molecular chains of UF shorten. The tighter the snake resins were entwined with the cage resin, the more difficult it was for the snake-cage resins to swell in the solutions. The fact that the above-mentioned resins just swell but do not dissolve in a solution proved that they had a crosslinking structure in the cage resin and the snake resin fully twined around inside the cage resins. With this result, the goal for synthesis of the snake-cage was achieved.

Sorption Properties

Sorption Capacity

The sorption capacity is an important parameter to judge a resin. The sorption capacities of resins I–IX for four metal ions were studied. From Table IV, some conclusions were made: (1) From resin I to resin V, the sorption capacities for the four metal ions decreased with the amount of formaldehyde in UF. The reason for this is similar to the swelling properties. (2) From resin III and resins IX–XI, the sorption capacities increased with the amount of CM-CTS in the snake-cage resin, showing that CM-CTS was the major contributor to chelate with the metal ions, which supported the deduction that the UF resin has almost no sorption for metal ions. The chelate mechanism investigation revealed a similar result. (3) The sorption capacities of resins VI–VIII were much lower than were those of the other resins. This is because a large amount of —NH_2 and —OH in CM-CT, which will be major contributors to chelate

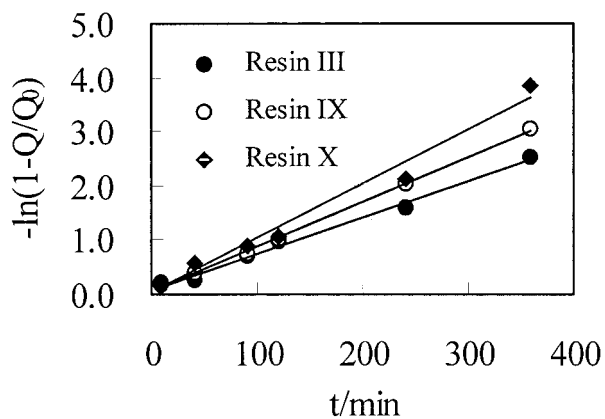**Figure 3**   Relationship between $-\ln(1 - Q/Q_0)$ and t (Cu^{2+}).

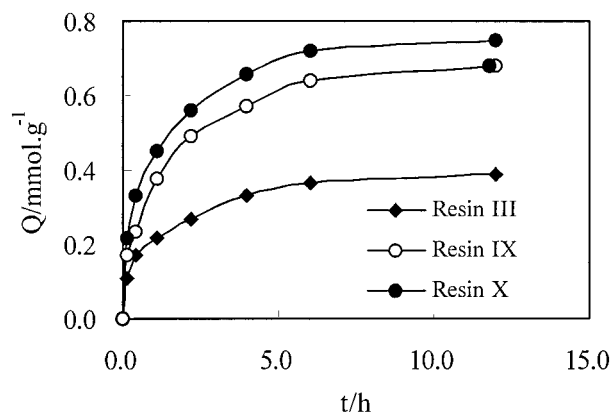**Figure 4** Sorption kinetic curves of resin for Ni^{2+}.

Table V   Rate Constants k and Regression Coefficients r

| Resin | Cu^{2+} | | Ni^{2+} | |
	k $(\times 10^{-2})$	r	k $(\times 10^{-2})$	r
Resin III	0.70	0.9945	0.79	0.9762
Resin IX	0.85	0.9982	0.81	0.9817
Resin X	1.01	0.9889	0.92	0.9822

with the metal ions, were missed by the crosslinking reaction. For all the resins, the order of the sorption capacity is usually $Cu^{2+} > Ni^{2+} > Pb^{2+} \approx Zn^{2+}$, indicating the higher sorption selectivity of the resin for Cu^{2+} and Ni^{2+} than for Pb^{2+} and Zn^{2+}.

Sorption Dynamics

As representatives, resins III and X were chosen to study the dynamics of static sorption for Cu^{2+} and Ni^{2+} (see Figs. 2–5). Although there are snake resins and cage resins, two kinds of structures in the snake-cage resins (Figs. 2 and 4) show that there is only "one platform" in every dynamic curve of resins III, IX, and X for Cu^{2+} and Ni^{2+}. This indicates that only a single mechanism is involved in the sorption. This conclusion had been proven in the section Sorption Capacity
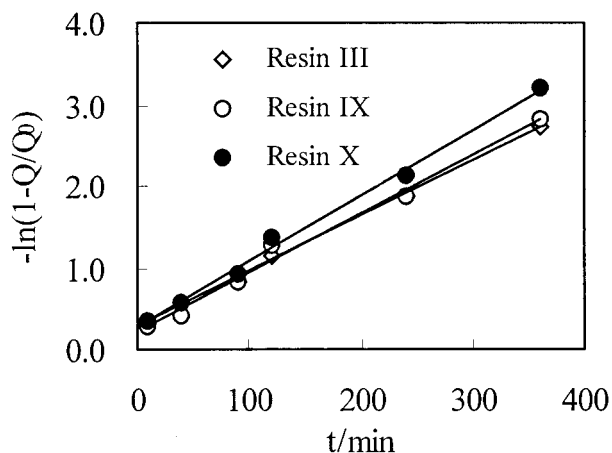
above. In this respect, these resins are different from the previous snake-cage resins synthesized using CM-CTS as the snake resin and the B-62 resin crosslinked by triethylenetetramine as the cage resin.[7]

Figures 3 and 5 show that all the sorption processes could be precisely described by the equation of G. E. Boyd: $-\ln(1 - Q - Q_0) = kt$, where Q is the sorption amount when the time is t; Q_0, the saturated sorption capacity; k, the constant rate of sorption; and t, the sorption time, meaning that the sorption of these resins for Cu^{2+} and Ni^{2+} belong to the mechanism of liquid film diffusion control[7] (for the k and r values, see Table V).

k is the constant of the sorption rate. From Table IV, a conclusion can be drawn that the greater the content of CM-CTS in the snake-cage resin the quicker the sorption is, no matter whether the sorption is for Cu^{2+} or for Ni^{2+}.

Isothermal Sorption

As a representative, the isothermal sorption of Cu^{2+} in resins III, IX, and X was studied. The
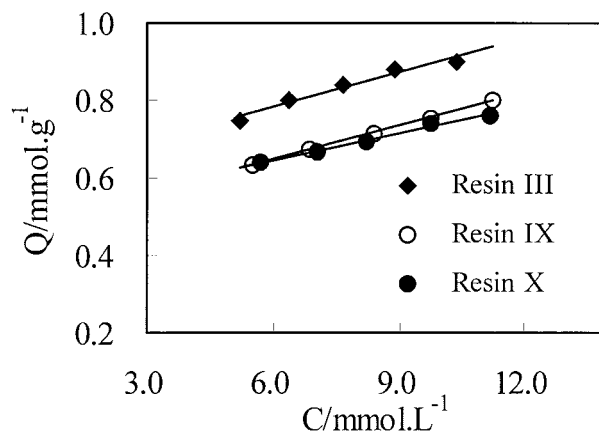

Figure 5 Relationship between $-\ln(1 - Q/Q_0)$ and t (Ni^{2+}).

Figure 6 Sorption isotherms of resins for Cu^{2+} (25°C).

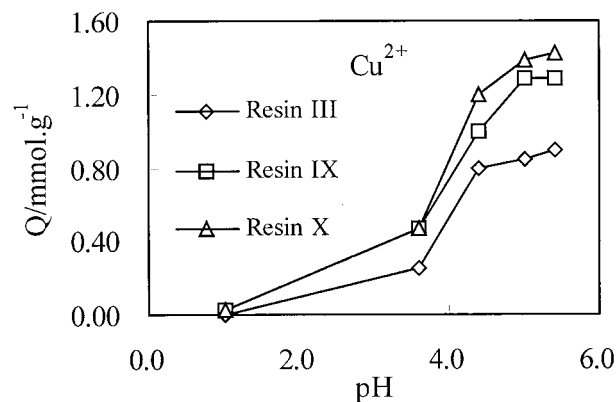**Table VI   Constants of Langmuir and Freundlich for Cu^{2+} (25°C)**

Resin	Q_0	b	r_L	n^{-1}	k	r_F
Resin III	0.9596	0.3351	0.9992	0.2517	0.4135	0.9917
Resin IX	1.0420	0.2572	0.9970	0.3236	0.3623	0.9993
Resin X	1.1340	03746	0.9996	0.2562	0.4962	0.9952

results are shown in Figure 6. The isotherms reveal that the sorption capacities increase with the equilibrium concentration. This is Brunauer I-type[12] sorption and has typical Langmuir characteristics. While treating the data in Figure 6 with Langmuir and Freundlich isothermal equations, respectively,

$$CQ^{-1} = CQ_0^{-1} + (Q_0 b)^{-1} \qquad (3)$$

$$\lg Q = n^{-1}\lg C + \lg k \qquad (4)$$

where the parameters of the equations (Table VI) are the following: Q is the sorption capacity; C, the equilibrium concentration; Q_0, the saturated sorption capacity; b, an empirical parameter; n, the Freundlich constant; and k, the binding energy constant reflecting the affinity of the resin to metal ions. Table VI shows that both r_L and r_F are above 0.9 and approach 1.0, indicating that all sorption processes could be described with the Langmuir and Freundlich formulas.[10] The values of n are within 2–10, indicating that the sorption of the three resins for Cu^{2+} is very easy.[13] Since k is a parameter representing the binding energy between metal ions and resins, then there is the order of binding energy between the resins and Cu^{2+} as follows: resin IX > resin III > resin IX.

This order is not in coincidence with that of the content of CM-CTS in snake-cage resins, so this phenomenon is difficult to explain (see Table VI).

Effect of pH on Sorption Ability

Figures 7 and 8 show that pH has a great effect on the sorption properties. When the pH is low, $-CO_2^-$ and $-NH-$ will be protonated into $-COOH$ and $-NH_2^+-$ and thus lose the chelating property for metal ion. When the pH is below 1.0, the sorption capacities are nearly equal to zero, so acid can be used to release the metal ions from the resins. When the pH is more than 4.0, the resins retain good sorption properties, but if the pH is too high, the metal ions will be hydrolyzed. So, no experiment with pH > 5.4 (for Cu^{2+}) and pH > 6.4 (for Ni^{2+}) conditions have been done in this work.

Sorption Mechanism

The infrared spectra in Figure 1 shows that the comprehensive peaks of $-CO_2^-$, $NHCH_2COO^-$, and $-NHCONH-$ at 1654 and 1500.6 cm^{-1} disappeared after sorption, whereas at 1647 cm^{-1}, the $-NHCONH-$ peak reappeared. This indicates that $-CO_2^-$ and $NHCH_2COO^-$ participated in the coordination with the metal ion and the

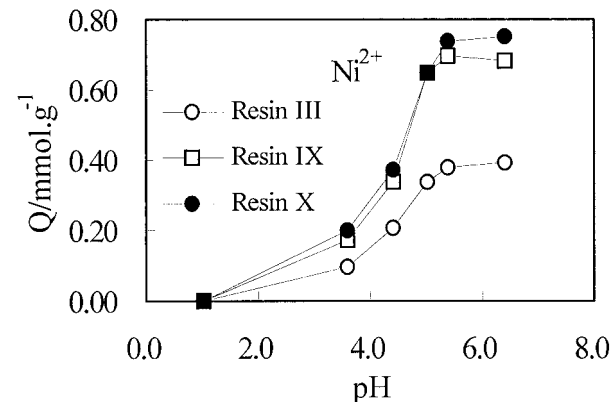**Figure 7** Effects of pH value on sorption capacities for Cu^{2+} (25°C).

Figure 8 Effects of pH value on sorption capacities for Ni^{2+} (25°C).

Table VII   Regeneration Properties of Resins III and X for Cu^{2+}

Measurement	Resin III					Resin X				
	Regeneration Times									
	1	2	3	4	5	1	2	3	4	5
Sorption capacities (mmol g^{-1})	0.89	0.87	0.87	0.83	0.85	1.41	1.34	1.34	1.36	1.35

—NH— and —C—O bonds in —NHCONH— did not. This result conforms to that from Table IV. The changes of absorption of the peak around $3400 \ cm^{-1}$ indicate that —OH participated in the coordination with the metal ion. This proves that snake resin CM-CTS is the major contributor of sorption for the metal ion.

Regeneration Properties

As an example, the regeneration properties of resin III were studied and are shown in Table VII. Table VII indicates that the sorption capacities are little changed after five times regeneration.

CONCLUSIONS

Several novel chelating resins with snake-cage structures were synthesized based on CM-CTS and UF resin using "mix-co-polymerization." CM-CTS/UF resins showed many characteristics such as the perfect mechanical stability, good sorption properties, and high selectivity for metal ions. CM-CTS in snake-cage resins will not leach out in acidic and basic aqueous solutions. The FTIR spectra revealed that only CM-CTS enlisted the chelating process with metal ions and the UF resin did not. The isotherms indicated that there was only one chelating mechanism, although there were two kinds of structures in the resins (CM-CTS and UF). CM-CTS/UF resins will prob-

ably be used in separating metal ions in analytical chemistry and environmental sciences.

REFERENCES

1. Hatch, M. J.; Dillon; J.; Smith, H. Ind Eng Chem 1957, 49, 1812.
2. Rollins; C.; Jensen; L.; Schwartz, A. N. Anal Chem 1962, 34, 711.
3. Walf, F.; Mlytz, H. J Chromatogr 1968, 34, 59.
4. Bogoczek, J. Chromatogram 1974, 102, 131.
5. Kaczmar, B. U.; Tasar, S. Macromol Chem 1976, 177, 1981.
6. Grote, M.; Schumacher, U. React Func Polym 1997, 35, 179.
7. Qu, R. J.; Wang, C. H.; Nie, Z. J.; Yang, S. T.; Wang, J. L.; Wang, S. Chin J React Polym 1999, 8, 28.
8. Hatch, M. J. J Am Oil Chem Soc 1961, 38, 470.
9. Qu, R. J.; Liu, Z. Q.; Wang, C. H.; Zhang, P. J. Acta Sci Circumstan 1997, 17, 121.
10. Qu, R. J. Polym Mater Sci Eng 1997, 13(4), 49.
11. He, H. J.; Wang, X .J.; Yang, Z. C. J Shanxi Normal Univ 1994, 22, 48.
12. He, B. L.; Huang, W. Q. Resins of Ion Exchange and Sorption; Press of Science and Technology and Education: Shanghai, 1995; p 395.
13. Wang, N. D.; Xong, C. H. Chem J Chin Univ 1996, 7, 767.