

# Preparation and Adsorption Properties of Chelating Resins from Thiosemicarbazide and Formaldehyde

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**ABSTRACT:** A novel chelating resin was synthesized in just one step under mild synthetic conditions. The synthesis was carried out through the copolymerization of thiosemicarbazide and formaldehyde in an aqueous solution. The adsorption properties for some noble metal ions were investigated. The results showed that the resin had high adsorption selectivity for Au(III) and Ag(I). The adsorption capacities for the two metal ions reached up to 7.3 and 11.8 mmol/g, respectively. The adsorption rate for the two metal ions in a dilute solution was 99.9%. The adsorption fit first-

order kinetics, and an isothermal adsorption study indicated that it corresponded to Langmuir monomolecular layer adsorption. The change in the bonding energy during the chelating process was investigated with X-ray photoelectron spectroscopy. The study revealed that nitrogen and sulfur atoms of the resins were electron donors and metal ions were electron acceptors in the process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2455–2461, 2009

**Key words:** adsorption; ESCA/XPS; ion exchangers; resins

## INTRODUCTION

Noble metals are precious resources in industry. Using chelating resins to retrieve these noble metals from aqueous solutions is always an interesting project for chemistry researchers.<sup>1–3</sup> Chemists are trying to enhance the adsorption capacity and adsorption selectivity of chelating resins.<sup>3–5</sup> Thus, the development of novel chelating resins has attracted much attention from scientists.<sup>4–10</sup>

It has been reported that chelating resins containing nitrogen and sulfur atoms possess particularly good adsorption properties for noble metals such as Au(III), Ag(I), Pd(II), and Pt(IV).<sup>5–10</sup> In particular, chelating resins made of thiourea have unique adsorption selectivity for the noble metals. Masoedova et al.<sup>11</sup> synthesized an isothioureia resin that selectively adsorbed Au(III), Pd(II), and Pt(IV). Xu et al.<sup>5</sup> prepared chelating resins containing mercapto and thiourea groups and studied the chelating properties for Au(III), Ag(I), Pd(II), and Pt(IV). There are some other reports about thiourea resins.<sup>12–16</sup> However, in the reported studies, the chelating resins were usually prepared through

reactions of polymer matrices with small molecules containing functional groups. This often requires a complicated synthetic procedure, and the concentration of applicable chelating groups in the resins is low. Consequently, the adsorption capacity is limited.<sup>17</sup>

Thiosemicarbazide (TSC) is a derivative of thiourea. There are high percentages of nitrogen and sulfur in the TSC molecule. Meanwhile, the amino groups in TSC are active functional groups that easily react with formaldehyde (FA). It is expected that chelating resins made from TSC will have excellent adsorption capacities for noble metal ions. To our knowledge, there are very few reports of chelating resins made from TSC.<sup>18</sup>

To improve the adsorption property and to simplify the synthetic procedure, in this study, we chose TSC as a material to design the preparation of a novel chelating resin because of its reactive activity with FA and the abundant chelating groups in its molecule. A novel chelating resin was prepared in one step under mild conditions in this work. The adsorption capacities of the resins for Au(III) and Ag(I) were much higher than those in reported studies. The mechanism of adsorption was studied with X-ray photoelectron spectroscopy (XPS).

## EXPERIMENTAL

### Materials

TSC and an aqueous FA solution (36%) were purchased from Aldrich and National Chemical Groups

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of China, respectively. TSC was recrystallized with water before use.

### Preparation of the chelating resin

TSC (9.10 g, 0.1 mol) was dissolved in 100 mL of water, which was placed in a three-necked flask equipped with a mechanical stirrer and a condenser. An aqueous FA solution (with various molar ratios of TSC) was added to the mixed solution. The pH value was adjusted to 6.0 with dilute hydrochloric acid. The copolymerization was performed via refluxing at 60°C for 6 h. The solid product was filtered and purified via refluxing with acetone for 24 h. The product was sequentially washed with 10% HCl, 10% NaOH, and distilled water. The white powder resin was obtained after 10 h of drying (40°C) at reduced pressure. A series of chelating resins were obtained with various TSC and FA molar ratios. The compositions of the chelating resins were determined with elemental analysis (Rario EL III, Elementar Analysensysteme GmbH, Germany). The structure of the resin was confirmed with an infrared spectrophotometer [Nexus 470 Fourier transform infrared (FTIR) spectrometer, Nicolet] and <sup>13</sup>C-NMR (Unity Plus 400, Varian, United States).

### Determination of the adsorption properties

The adsorption properties were examined with a static adsorption method. The adsorption capacity was calculated as follows:

$$Q = \frac{(C_0 - C)V}{W} \quad (1)$$

where  $Q$  is the adsorption capacity (mmol/g);  $C_0$  and  $C$  are the concentrations of the metal ions before and after adsorption (mol/L);  $V$  is the volume of the metal-ion solution used in adsorption (mL); and  $W$  is the weight of the resin used in adsorption (g).

### Adsorption capacities for Ag(I)

A resin (0.125 g) was placed in a small conical flask containing 25.0 mL of an aqueous AgNO<sub>3</sub> solution (0.1 mol/L). The flask was wrapped in black paper to exclude all light. After being motionless for 22 h, the mixture was vibrated for 2 h and then filtered. The concentration of Ag(I) in the solution was measured with the Volhard method; the concentration of Ag(I) was titrated with a potassium thiocyanate solution with ammonium iron sulfate hexahydrate as an indicator.

### Adsorption capacities for Au (III)

A resin (25.0 mg) and a 50.0-mL aqueous metal-ion solution (1 mg/mL) were mixed in a conical flask.

The aforementioned static adsorption procedure was followed. The concentration of Au(III) was measured with atomic adsorption spectrometry (TAS 990, Puxi General Instrument Co., Ltd., Beijing, P.R. China).

### Adsorption capacities for Hg(II), Pb(II), and Zn(II)

A metal-ion solution (0.025 mol/L) was mixed with 0.125 g of a chelating resin in a conical flask. After static adsorption for 22 h and vibration for 2 h, the concentrations of the metal ions were determined by EDTA titration.

### Adsorption rates for Ag(I) and Au(III)

A resin (25.0 mg) was placed in a conical flask, and a very diluted aqueous metal-ion solution (0.1 mg/mL) was added for adsorption. The concentration was measured according to the method described previously.

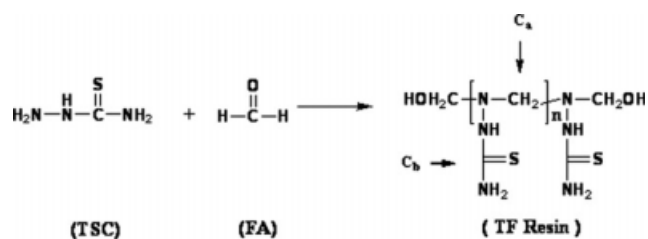
### XPS analysis

The electron binding energies of some atomic orbits of the resins and metal ions Au(III) and Ag(I) were measured with XPS KRATOS AXIS-ULTRA DLD (Shimadzu International Trading, Shanghai Co., Ltd., China).

## RESULTS AND DISCUSSION

### Preparation of the chelating resins

In this work, we directly reacted TSC with an aqueous FA solution (Fig. 1). The reaction can be carried out under very mild conditions because of the high reactivity of the reactants. The amino groups of TSC react with FA by a mechanism of nucleophilic addition followed by the elimination of water between hydroxyl methyl and amino groups. The amino groups adjacent to C=S are also able to react with FA, and this results in a crosslinked condensation copolymer. The effect of the feed ratio on the preparation has been investigated, and the results are shown in Table I. In terms of the elemental analysis of Table I, when the molar ratio of TSC to FA in the feed is 2 : 1 (TF1), the composition of the resin (S, 30.6%; N, 40.2%) is close to that of the calculated



**Figure 1** Scheme for the preparation of the chelating resins.

**TABLE I**  
Preparation of TSC-FA Chelating Resins

No.	TSC (g)	FA (mL)	TSC/FA (mol/mol)	Analysis	
				N (%)	S (%)
1	18.20	8.33	2 : 1	40.2	30.6
2	9.10	8.33	1 : 1	37.8	28.9
3	9.10	16.67	1 : 2	31.5	24.0
4	9.10	41.67	1 : 5	30.1	22.8

The copolymerization was carried out at 60°C for 6 h.

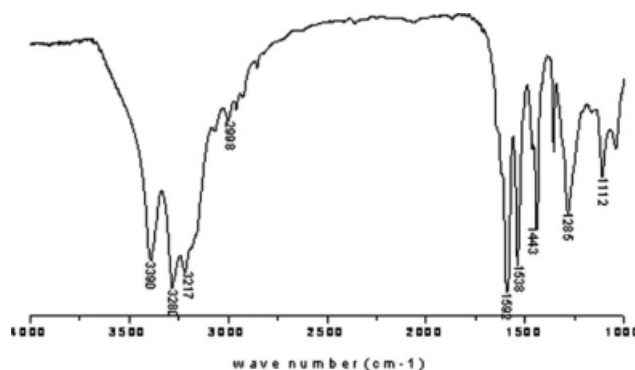
alternate copolymer (S, 31.1%; N, 40.8%). The sulfur and nitrogen percentages decrease as FA increases in the feed, and this indicates that there is more of the FA component in the copolymer. This is because there are three nitrogen atoms and five N—H bonds in each TSC molecule. All the N—H bonds are potentially able to react with FA. Therefore, one TSC molecule may consume more than one FA molecule if FA is in excess in the feed. Meanwhile, homopolymer segments of FA may form by self-polymerization. Both factors cause the increase in the FA content in the copolymers. Consequently, sulfur and nitrogen percentages decrease. However, when TSC is in excess in the feed, the content of TSC in the copolymer is not more than that of the alternate copolymer. Obviously, TSC is unable to homopolymerize by itself. In this work, we have also investigated the effect of the pH value on the copolymerization. The copolymerization of TSC and FA can take place and crosslinked resins can be produced in aqueous solutions with a broad range of pH values. Additionally, we used water as the reacting medium because water is a cheap and nontoxic solvent and has good dissolving properties for reactants.

### Stability of the resins

When the resins are immersed in different solvents such as HCl (2.0 mol/L), NaOH (2.0 mol/L), acetone, ethanol, methanol, and benzene for 72 h, no linear polymers or monomers are found in these solvents. This proves that the chelating resins are highly stable in acidic, alkaline, and organic solutions. Usually, chelating resins are used at room temperature, at which they are very stable.

### FTIR spectrum of resin TF2

Figure 2 presents the spectrum of resin TF2. The peaks can be analyzed as follows. The strong adsorption peaks at 3280 and 3217  $\text{cm}^{-1}$  belong to the adsorption peaks of the secondary and tertiary amino groups, and the peak at 3390  $\text{cm}^{-1}$  is evidence of a few hydroxyl groups. The peak at 2998  $\text{cm}^{-1}$  indicates the existence of  $\text{CH}_2$  in the copolymer. The peaks at 1592 and 1538  $\text{cm}^{-1}$  can be attrib-



**Figure 2** FTIR spectrum of resin TF2.

uted to the bending adsorption of N—H, and the peaks at 1443 and 1112  $\text{cm}^{-1}$  show C—N bond stretching. The peak at 1285  $\text{cm}^{-1}$  is the C=S vibration peak, and the peak at 1112  $\text{cm}^{-1}$  indicates N—N adsorption. Therefore, the structure of the resin can be confirmed by the FTIR spectrum.

### $^{13}\text{C}$ -NMR spectrum of resin TF2

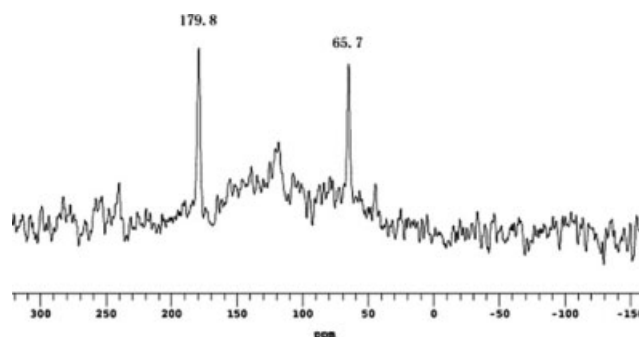
To further study the structure of the chelating resin, the  $^{13}\text{C}$ -NMR spectrum of resin TF2 has been determined, and the results are shown in Figure 3. Two peaks at 65.7 and 179.8 ppm can be found in Figure 3. They correspond to the information for  $\text{C}_a$  and  $\text{C}_b$  indicated in Figure 1, respectively.  $\text{C}_b$  has a higher  $^{13}\text{C}$ -NMR chemical shift than  $\text{C}_a$  because it connects with more electronegative atoms than  $\text{C}_a$ .

### Studies of the adsorption properties

#### Adsorption capacity

By using the static adsorption method, we have measured the adsorption capacities of the resins for noble metal ions [Au(III) and Ag(I)] and some transition-metal ions [Hg(II), Pb(II), and Zn(II)]. The results are shown in Table II.

Table II shows that the adsorption capacities of resin TF1 for Au(III) and Ag(I) are significantly high, reaching up to 7.3 and 11.8 mmol/g, respectively.



**Figure 3**  $^{13}\text{C}$ -NMR spectrum of resin TF2.

**TABLE II**  
**Adsorbing Capacities for Metal Ions of the Chelating Resins at 25°C**

Resin	Adsorbing capacity for metal ions (mmol/g)					
	Au(III) in HCl (2M)	Ag(I)		Hg(II) <sup>a</sup>	Pb(II) <sup>a</sup>	Zn(II) <sup>a</sup>
		HNO <sub>3</sub> (1M)	pH 7			
TF1	7.3	10.5	11.8	3.3	0.3	0.6
TF2	6.5	9.3	10.6	2.8	0.2	0.5
TF3	4.3	8.0	8.8	1.8	0.1	0.2
TF4	3.1	7.8	8.1	0.9	0.1	0.1

<sup>a</sup> pH 5.6 according to a pH meter (PHS-25, Shanghai, China).

They are even higher than those of other thiourea resins in a previously reported work,<sup>5</sup> which indicated adsorption capacities of 4.0 mmol/g for Au(III) and 5.3 mmol/g for Ag(I). According to the Lewis acid–base theory, Au(III) and Ag(I) belong to soft acids, and sulfur and nitrogen belong to soft bases. The same kinds of acids and bases have excellent affinity. Resin TF1 contains very high sulfur and nitrogen percentages, which indicate abundant functional chelating groups in the resin. Therefore, the adsorption property is considerable. The adsorption capacities for the two ions decrease as the TSC content decreases in the resins. The TSC component in the resin plays an important role in the adsorption for the two metal ions. The adsorption capacity of the resins for Hg(II) are of a middle level. However, the adsorption capacities for Pb(II) and Zn(II) are very low.

#### Adsorption rates for Ag(I) and Au(III)

To investigate the recovery efficiency of the resins, we have studied the adsorption rates of the resins for Ag(I) and Au(III) in very diluted solutions. In the study, a resin in slightly more excess was put into a metal-ion solution for adsorption. The changes in concentrations of the metal ions were determined, and the adsorption rate was calculated with the following formula:

$$R(\%) = \frac{100(C_1 - C_2)}{C_1} \quad (2)$$

where  $R$  is the adsorption rate and  $C_1$  and  $C_2$  are the concentrations of the metal ions before and after

adsorption, respectively. The experimental results show that resin TF1 has excellent adsorbing rates for Ag(I) and Au(III), which reach up to 99.9%. This implies that the resin has a strong adsorbing ability for the two metal ions. It adsorbs the ions almost completely as long as a sufficient amount of the resin is used for the adsorption. This suggests that resin TF1 has potential applications in concentrating and retrieving Au(III) and Ag(I) even in very diluted solutions. The adsorption rate slightly decreases with the decrease in the TSC content in the copolymer. For example, the adsorption rates of resins TF2, TF3, and TF4 for Au(III) ions are around 97.5, 95.3, and 92.8%, respectively.

#### Adsorption selectivity

Three groups of mixed metal-ion solutions were made to test the adsorption selectivity of resin TF2. The separating factor ( $K$ ) was calculated with the following formula<sup>12</sup>:

$$K = \frac{C_{B2}(C_{A1} - C_{A2})}{C_{A2}(C_{B1} - C_{B2})} \quad (3)$$

where  $C_{A1}$  and  $C_{A2}$  are the concentrations of metal ion A before and after adsorption, respectively, and  $C_{B1}$  and  $C_{B2}$  are the concentrations of metal ion B before and after adsorption, respectively. Tables III and IV provide the results for adsorption selectivity. From  $K$ , we find that resin TF2 has an adsorption priority for Au(III) and Ag(I) when they are mixed with Pb(II), Zn(II), and Hg(II). This property can be used for separating Au(III) or Ag(I) from some

**TABLE III**  
**Adsorption Selectivity for Mixed Solutions Containing Au(III)**

Concentration (mg/mL)	Mixed solutions of metal ions		
	Au(III)–Pb(II)	Au(III)–Zn(II)	Au(III)–Hg(II)
$C_{A1}/C_{B1}$	1.00/2.70	1.00/1.30	1.00/2.50
$C_{A2}/C_{B2}$	0.23/2.35	0.25/1.12	0.28/2.16
$K^a$	22.5	18.6	16.3

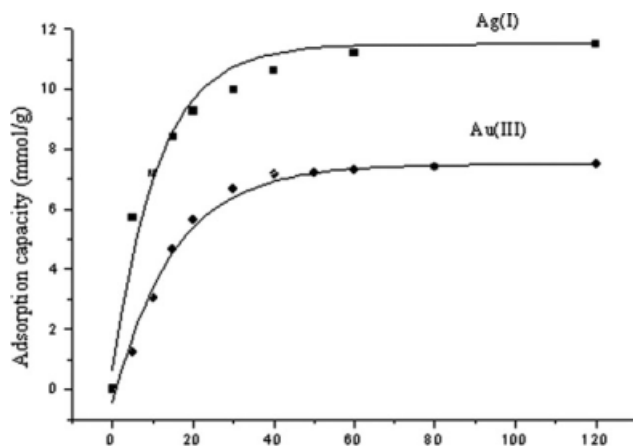
$$^a K = \frac{C_{B2}(C_{A1} - C_{A2})}{C_{A2}(C_{B1} - C_{B2})}$$

**TABLE IV**  
**Adsorption Selectivity for Mixed Solutions Containing Ag(I)**

Concentration (mol/L)	Mixed solutions of metal ions		
	Ag(I)–Pb(II)	Ag(I)–Zn(II)	Ag(I)–Hg(II)
$C_{A1}/C_{B1}$	0.10/0.025	0.10/0.025	0.10/0.025
$C_{A2}/C_{B2}$	0.02/0.021	0.03/0.022	0.03/0.021
$K^a$	21.0	17.1	12.3

$$^a K = \frac{C_{B2}(C_{A1} - C_{A2})}{C_{A2}(C_{B1} - C_{B2})}$$





**Figure 4** Adsorption speed of resin TF2 for Ag(I) and Au(III).

mixed solutions containing other coexisting metal ions.

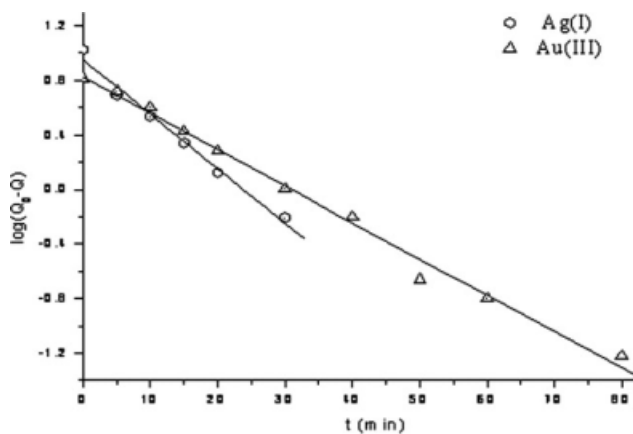
#### Adsorption kinetics

Taking resin TF2 as an example, we have studied the relationship between the adsorption capacity and time. The resin was put in metal-ion solutions, and the adsorption capacity at various times was measured. It is clear that the initial adsorption is fast, and the adsorption gradually slows down. The equilibrium adsorption is reached after 1 h. The kinetic adsorption patterns for Ag(I) and Au(III) are shown in Figure 4.

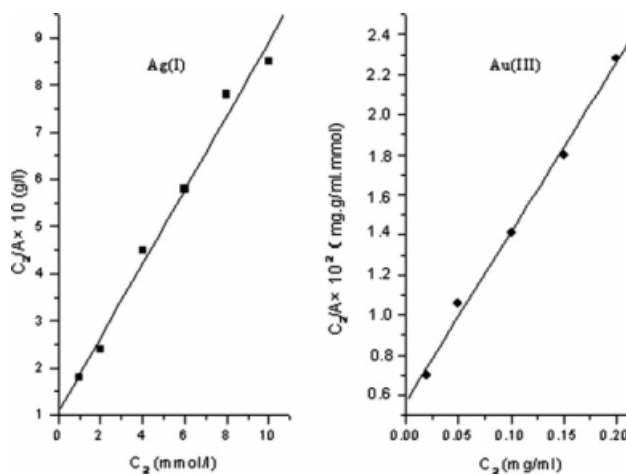
The adsorption kinetics can be described by the Lagergren adsorption equation<sup>19</sup>:

$$\text{Log}(Q_0 - Q) = \text{Log}Q_0 - \frac{k_a}{2.303}t \quad (4)$$

where  $Q_0$  and  $Q$  are the adsorption capacities at equilibrium and at adsorption time  $t$  (min), respectively, and  $k_a$  is the adsorption constant ( $\text{s}^{-1}$ ). Plots of  $\log(Q_0 - Q)$  against  $t$  for Au(III) and Ag(I) are



**Figure 5** Relationship between  $\log(Q_0 - Q)$  and  $t$ .



**Figure 6** Isothermal adsorption curves for Ag(I) and Au(III).

shown in Figure 5. The plots show good linear relationships with regression coefficients of 0.9933 and 0.9959 for Ag(I) and Au(III), respectively. The  $k_a$  values for Ag(I) and Au(III) are 0.092 and 0.061, respectively. This reveals that the adsorption corresponds to first-order kinetics.

#### Adsorbing isotherm

To investigate the relationship between the amount of adsorption and the equilibrium concentration of the metal ions at a certain temperature ( $25^\circ\text{C}$ ), we have studied the adsorbing isotherm of resin TF2 for Ag(I) and Au(III). Langmuir proposed a monomolecular layer adsorption model when studying the adsorption of solids for gases.<sup>20</sup> If the equation is employed to describe the adsorption of resins for a metal ion in solution, the equation is expressed as follows:

$$\frac{C}{Q} = \frac{C}{Q_m} + \frac{1}{k_1 Q_m} \quad (5)$$

where  $C$  is the concentration of a metal ion in the equilibrium adsorption state,  $Q$  is the adsorption capacity,  $Q_m$  is the maximum adsorption capacity of the resin, and  $k_1$  is the Langmuir constant. Linear relationships between  $C/Q$  and  $C$  are observed, and

**TABLE V**  
Binding Energy of Resin TF2 Before and After Chelation (eV)

Orbit	TF2	TF2-Au(III)	$\Delta^a$	TF2-Ag(I)	$\Delta^a$
$C_{1s}$	282.78	282.77	-0.01	282.79	0.01
$N_{1s}$	397.61	398.76	1.15	398.25	0.64
$S_{2p}$	159.73	160.96	1.23	160.62	0.89

<sup>a</sup> Binding-energy difference between the resin metal and resin.

**TABLE VI**  
Binding Energy of Metal Ions Before and After Chelation

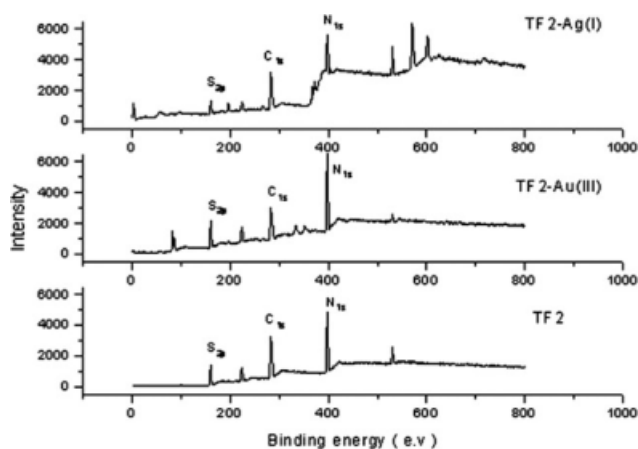
Orbit	H <sub>2</sub> AuCl <sub>4</sub>	TF2-Au(III)	$\Delta^a$	AgNO <sub>3</sub>	TF2-Ag(I)	$\Delta^a$
Au-4f <sub>5/2</sub>	87.31	86.49	-0.82			
Au-4f <sub>7/2</sub>	83.65	82.79	-0.86			
Ag-3d <sub>3/2</sub>				372.96	372.20	-0.76
Ag-3d <sub>5/2</sub>				366.97	366.20	-0.77

<sup>a</sup> Binding-energy difference between the resin metal and resin.

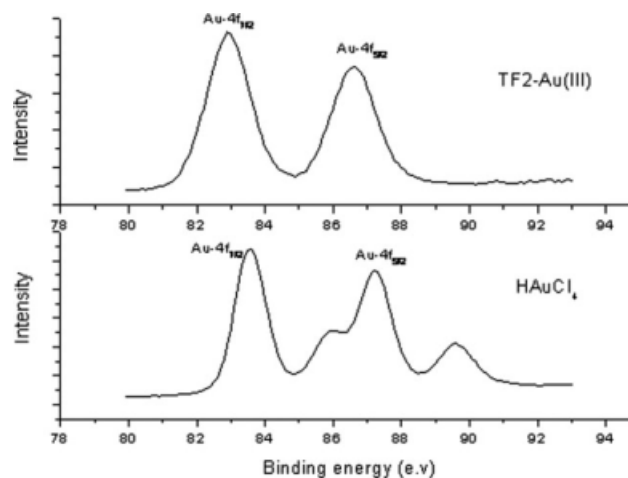
the coefficients are 0.9930 and 0.9974, respectively. This indicates that the adsorption corresponds to the Langmuir monomolecular layer adsorbing mechanism. The curves of the isothermal adsorption are shown in Figure 6.

#### XPS analysis

To study the mechanism of the adsorption process, we have measured binding-energy changes for some atomic orbits of the resins and metal ions. It is well known that the binding energy increases with the loss of electrons and decreases with the gain of electrons.<sup>13</sup> Through the analysis of binding-energy changes before and after adsorption, we can understand that electrons flow from nitrogen and sulfur atoms to metal ions during the adsorption process. The results are shown in Tables V and VI. The binding energies of the N<sub>1s</sub> and S<sub>2p</sub> orbits rise 1.15 and 1.23 eV, respectively, after resin TF2 chelates Au(III) (Table V). Thus, we deduce that nitrogen and sulfur atoms of the resin donate electrons, whereas Au(III) accepts electrons in the chelating process, because the binding energies of the Au-4f<sub>5/2</sub> and Au-4f<sub>7/2</sub> orbits decrease by -0.86 and

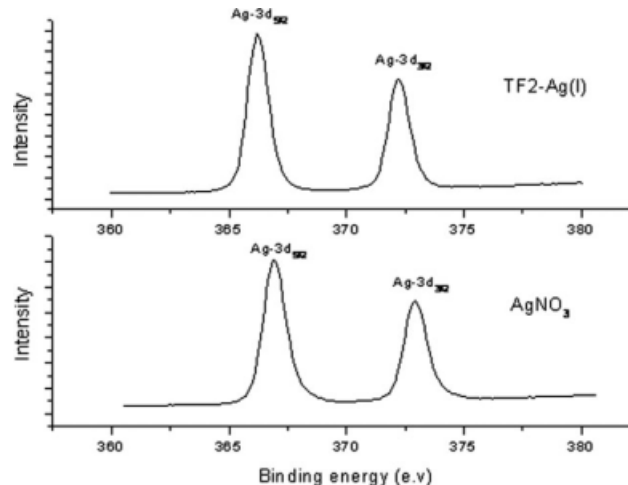


**Figure 7** Binding energies of nonmetal atomic orbits of resin TF2 and its chelates with Au(III) and Ag(I), respectively.



**Figure 8** Binding energies of metal atomic orbits of Au(III) and its chelate with resin TF2.

-0.82 eV, respectively (Table VI). The sulfur atom shows a greater increase in the binding energy than the nitrogen atom, probably because sulfur is a better electron donor than nitrogen. Meanwhile, we also found that when resin TF2 chelates Ag(I), the binding energies of the N<sub>1s</sub> and S<sub>2p</sub> orbits rise 0.64 and 0.89 eV, respectively (Table V), and the binding energies of the Ag-3d<sub>3/2</sub> and Ag-3d<sub>5/2</sub> orbits decrease by -0.75 and -0.68 eV, respectively (Table VI). The binding energy of C<sub>1s</sub> changes very little (Table V), and this means that the carbon atoms are not involved in the chelating process. We can conclude that the stable chelates are formed through the flow of electrons from the nonmetal atoms (sulfur and nitrogen) to the metal ions Au(III) and Ag(I). The binding-energy changes of resin TF2 and the metal ions Au(III) and Ag(I) are shown in Figures 7–9, respectively.



**Figure 9** Binding energies of metal atomic orbits of Ag(I) and its chelate with resin TF2.

## CONCLUSIONS

Novel chelating resins can be prepared in one step through a reaction between TSC and FA in an aqueous solution under mild synthetic conditions. The nearly alternate copolymer is obtained if TSC is in slight excess with respect to FA in the feed. The new resins have demonstrated a significantly high adsorption capacity, adsorption rate, and selectivity for Au(III) and Ag(I). The adsorption kinetics correspond to first-order absorption. XPS has revealed that electrons flow from sulfur and nitrogen atoms to metal ions during the chelating process. The resins have the advantages of a simple synthetic method, cheap raw materials, and excellent adsorption properties for metal ions Au(III) and Ag(I). They have potential applications for concentrating and retrieving noble metals such as Au(III) and Ag(I) in aqueous solutions.

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