Studies of Syntheses and Adsorption Properties of Chelating Resin from Thiourea and Formaldehyde

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ABSTRACT: Chelating resins are useful substances in industry because of their extraordinary adsorption properties for specific metal ions. In this study, a new type of chelating resin is synthesized simply by reaction between thiourea and formaldehyde. The synthetic conditions and the structure of the product are approached and the adsorbing capacities for 11 metal ions, adsorbing rates, and selectivities investigated. The results of the experiments show that the resin has high adsorbing capacities for Ag(I): 13.1 mmol/g, and for Au(III): 6.95 mmol/g. Adsorbing rates are close to 100% in dilute solution. Isothermal adsorbing study reveals that the adsorption is monomolecular layer adsorption process. It is hopeful for the resin to be used for concentrating and retrieving Ag(I) and Au(III) ions from their dilute solutions in industry. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3127–3132, 2001

Key words: chelating resin; adsorption property; thiourea; formaldehyde

INTRODUCTION

Chelating resins have outstanding adsorption properties for some metal ions. Therefore, they have been widely used for removing heavy metal ions in waste water and for concentrating and retrieving noble metal ions. There are a number of reports of different types of chelating resins, such as polyethylene polyamine, polythioether, dithiocarboxylic acid, mercapto, mercaptoamine, thiourea, and heterocycle.[1–6] Thiourea resins have been found to adsorb some noble metal ions effectively. Mgasoedova et al.[7] synthesized isothiourea resin that quantitatively adsorbed Au(III), Pd(II), and Pt(IV) in acidic solution. Chen et al.[8] obtained macroporous resins with a reaction between crosslinked polychloromethylstyrene and thiourea. The resin was used for retrieving Au(III) in electroplated waste water. Chao and Shu[9] used polyvinylchloride and synthesized thiourea resins that showed high selective adsorbing capacities of noble metal ions.

We observed that in previous reports the chelating resins containing thiourea were manufactured by reactions between thiourea and some polymers, such as crosslinked polychloromethylstyrene or polyvinylchloride. The chelating functional groups in these resins were not high, resulting in low adsorption capacity. To improve adsorption properties and also to simplify the manufacturing process, we used thiourea directly to react with formaldehyde in an aqueous solution and synthesized thiourea–formaldehyde resins. We then investigated the adsorption properties of the resins for noble metal ions and some other metal ions. Preparation of the resins was simpler, and the adsorption properties were superior to those of the previous research efforts.

EXPERIMENTAL

Instruments

In this study, we used Perkin–Elmer 1600 Series FTIR; model 1106 Elemental Analyzer; U/V 1100 Spectrophotometer.

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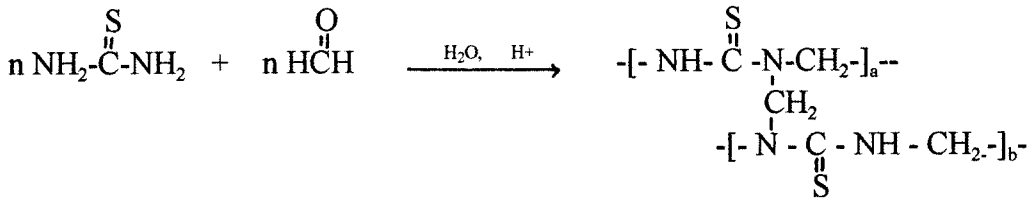


Scheme I

Synthesis of Chelating Resins

In a 250-mL two-necked flask equipped with a stirrer and condenser, 15.2 g (0.2 mol) of thiourea and 40 mL of distilled water were mixed. The flask was heated until thiourea was dissolved. Then, 15 mL of formaldehyde (37% aqueous solution, containing 0.2 mol formaldehyde) was added, adjusted pH was 3 with an acid. The reaction was carried out for 6 h with heating (95°C) and stirring. The product was washed with dilute NaOH solution, distilled water, ethanol, and acetone in turn. White powder resin was obtained after drying for 10 h at reduced pressure (60°C, 10 mmHg).

Measurements of Adsorption Properties

Adsorption Capacities for Ag(I)

In this study, 0.150 g resin was put in a 50-mL conical flask containing 25.0 mL (0.1 mol/L) of $AgNO_3$ aqueous solution (pH = 7 or 1N HNO_3). The conical flask was wrapped with black paper to exclude light. The mixture was vibrated for 2 h after remaining motionless for 20 h and was then filtrated. The concentration of Ag(I) was determined using the Volhard method. The adsorbing capacity was calculated as follows:

$$A = (C_1 - C_2) \times V/W$$

where A is adsorbing capacity, C_1 and C_2 are the concentrations of the metal ion before and after adsorption, V is the volume of metal ion solution used in adsorption, and W is the weight of resin used in adsorption.

Adsorption Capacities for Au(III), Pd(II), Pt(IV)

A 20.0-mg resin and a 30.0-mL metal ion solution (1N HCl) were placed in a 50-mL conical flask. The same procedure as used above was followed. The concentration of the metal ions was measured with an Ultraviolet/Visible Spectrophotometer.

Adsorption Capacities for Hg(II), Cu(II), Zn(II), Fe(III), Mg(II), Ni(II), and Pb(II)

A metal ion solution (0.025 mol/L) was mixed with 0.0625 mg of a chelating resin in a conical flask. After static adsorbing for 22 h, the concentration of the metal ion was measured by EDTA titration.

Adsorption Rates for Ag(I), Au(III), Pd(II), and Pt(IV)

A 0.025-mg resin was placed in a conical flask, a very dilute metal ion solution (0.1 mg/mL) was added, and again the concentration of the metal ion was determined according to the procedure described above after adsorbing for 22 h.

RESULTS AND DISCUSSION

Synthesis of Chelating Resins

Koichi et al.[10] reported that resins were prepared by reactions of HCHO with a reaction product (or

Table I Syntheses and Analyses of Resins*

	Thiourea		HCHO[a]			Analyses (%)			
Resin	g	mol	ml	mol	Yield (g)	S	N	C	H
PTF1	7.6	0.1	30.0	0.4	8.0	27.3	22.1	32.3	4.9
PTF2	7.6	0.1	7.5	0.1	6.6	35.4	30.8	27.7	5.2
PTF3	15.2	0.2	7.5	0.1	7.8	36.0	31.0	24.3	4.5

* Reactions were carried out for 6 H at 95°C and pH 3 aqueous solution.
[a] 37% HCHO.

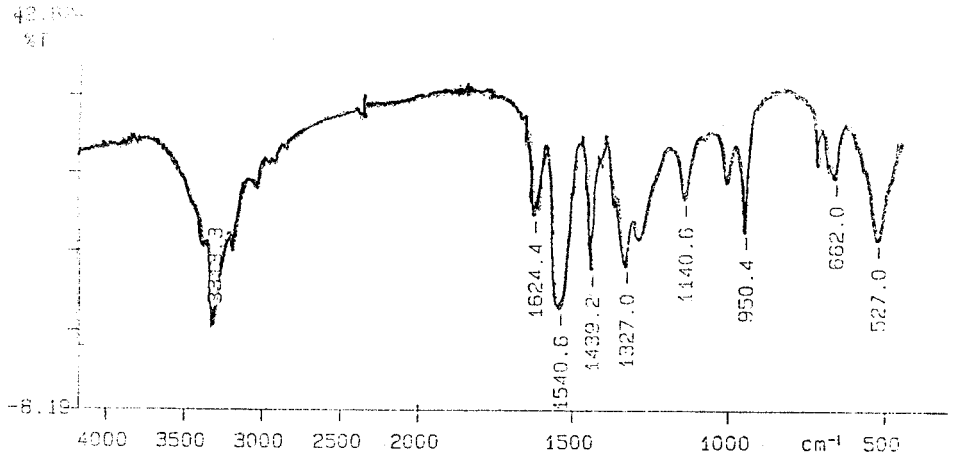


Figure 1 IR spectra of chelating resin PTF3.

its salt) of CS_2 and an amine such as urea, thiourea, or melamine in an acidic solution.[10] Qi[11] used suspension polymerization of thiourea, diphenol, and HCHO and manufactured a type of pearl resin. In this study, we used thiourea to react directly with formaldehyde in an acidic solution, with the expectation that the resin would be synthesized according to Scheme I.

To find the optimal synthetic condition, we investigated some factors that would affect the reaction.

Molar Ratio of Reactants

Different molar ratios of thiourea to formaldehyde were taken in our experiments. The synthetic and elemental analysis results are shown in Table I.

From analysis of resin PTF2 in Table I, it can be seen that if the molar ratio of thiourea to formaldehyde was 1 : 1, the analysis of the product was close to the composition of the alternate copolymer (calculated: S, 36.4%; N, 31.8%; C, 27.3%; H, 4.5%). If the amount of formaldehyde is in excess to thiourea (see resin PTF1), the analysis indicated that there was more formaldehyde component in the product compared with alternate copolymer. This was because part of formaldehyde polymerized by itself. When the molar number of thiourea was greater than that of HCHO (see resin PTF3), the analysis of the prod-

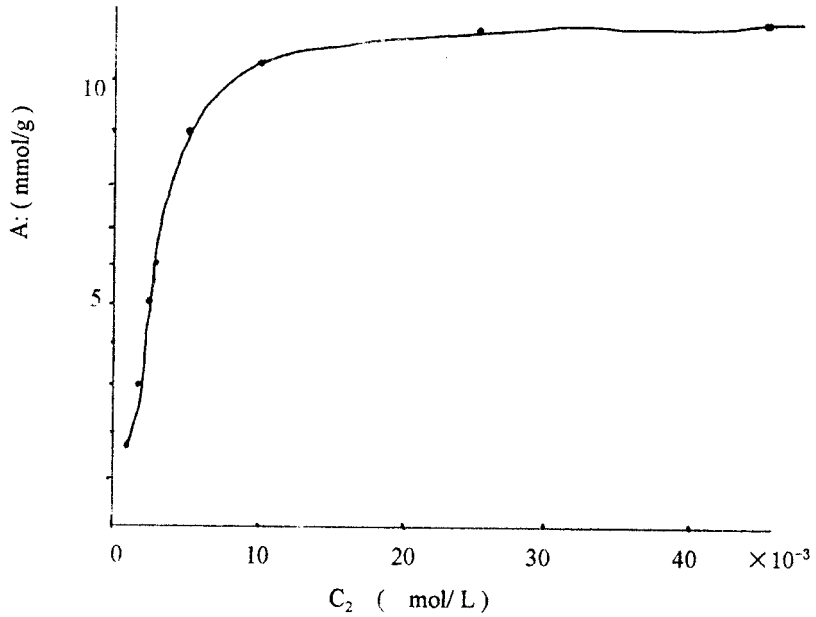
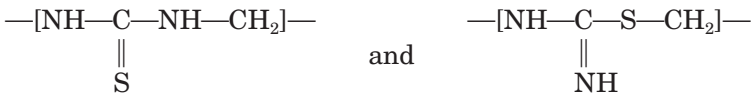


Figure 2 Adsorption capacity for Ag(I) at different concentrations.



Scheme II

uct was still close to that of the alternate copolymer. Obviously, thiourea was unable to be polymerized by itself under these conditions. But the particle size of PTF3 was thinner than that of PTF1 and of PTF2.

Reaction Time

The relationship between yield and reaction time was also examined in this study. The yields of the products at different reaction time were as follows: 1H, 2.9 g; 3H, 4.0 g; 6H, 5.8 g; and 12H, 6.0 g, respectively, if the following conditions were applied: molar ratio, 1 : 1; (thiourea 7.6 g, HCHO 7.5 mL); pH 3; temperature, 95°C.

pH Value of the Reaction System

The synthetic reaction was carried out at different pH values, respectively. We found that the synthetic reactions could take place easily when the solution was acidic, whereas in a neutral solution, no reactions were found within 24 h.

Tests of Solubility

The resins were placed in benzene, methanol, ethanol, acetone, 2N hydrochloric acid, 2N sodium hydroxide for 3 days, respectively; no solubility was found. These tests proved that the resins were crosslinked.

IR Spectra

Figure 2 was the IR spectra of chelating resin. The peaks could be analyzed as follows: 3313.3 cm^{-1} strong adsorption peak showed the existence of N—H in secondary amino; 1624.4 cm^{-1} (W) and 1140.6 were peaks of C═S—N— bond; 1540.6 cm^{-1} (s) was C═NH peak; 1439.2 cm^{-1} and 1327.0 cm^{-1} were peaks of C—N; 950.4 cm^{-1} and 527.0 cm^{-1} indicated thioether bonds S—C appeared. Thus, we inferred that there were two types of structural units in the copolymer at same time, as shown in Scheme II.

Adsorption Property Studies

Adsorbing Capacities

Using the static adsorbing method, we measured the adsorbing capacities of the three resins for some noble metal ions and part of transitional metal ions respectively. The results are shown in Table II.

We can see from Table II that the adsorbing capacities of the three resins for Ag(I) and Au(III) were considerable, and higher than those of other thiourea resins.[7–9,11–13] For Pd(II), Pt(IV), Hg(II), Cu(II), Fe(II), and Zn(II), the resins had much lower adsorbing capacities. And for Pb(II), Ni(II), and Mg(II), no adsorption was found. PTF3 had the highest capacity among the three resins. It could be explained that PTF3 had smaller particle size and had more contacting surface area with metal ions compared to PTF1 and PTF2.

Effect of Adsorbing Time on Adsorbing Capacity

Having taken resin PTF3 as an example, we investigated the relationship between adsorption time and the capacity. PTF3 resin was placed in a solution of $AgNO_3$ (1N HNO_3), and the capacities at different adsorption time were recorded. During the first 2 h, adsorption was fast; 1 h later, adsorbing capacity reached up to 9.5 mmol/g. Then, the capacity slowly increased with time, and saturated adsorption appeared after 22 h.

Table II Adsorbing Capacities of Resins (mmol/g)

	Ag(I)		Au(III)	Pd(II)	Pt(IV)	Hg(II)	Cu(II)	Fe(II)	Zn(II)
Resin	(pH = 7)	(HNO_3)		(1N HC1)			(pH = 5–6)		
PTF1	7.8	7.6	2.64	0.29	0.92	0.7	0.1	0.8	0.2
PTF2	11.3	11.9	5.24	0.47	1.35	2.5	0.3	1.6	0.5
PTF3	13.1	12.3	6.27	0.66	1.46	3.5	0.7	1.9	0.3

Table III Adsorbing Rates of Resins (%)

Resin	Ag(I) (pH 7)	Ag(I) (1N HNO_3)	Au(III)	Pd(II) (1N HCl)	Pt(IV)
PTF1	94.5	95.0	92.3	72.0	33.5
PTF2	99.5	99.8	98.2	85.0	36.1
PTF3	100	100	99.9	90.0	46.0

Adsorbing Rates

To find out how the resins concentrate metal ions in dilute solutions effectively, we examined the adsorbing rates of these resins in very dilute solutions. Thus, slightly more excess resin was put into a dilute solution for adsorption. The change in the concentrations of the metal ions was measured and adsorbing rate was calculated according to the formula

$$R\ (\%) = (C_1 - C_2) \times 100/C_1$$

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

Table III indicates that resins PTF2 and PTF3 adsorbed Ag(I) and Au(III) completely in very dilute solutions if the amount of resins used was sufficient. These results imply that the resins could be used to concentrate and retrieve some noble metal ions in industry.

Adsorbing Selectivity

To study the behavior of the resins in mixed solution of different metal ions, we prepared three mixtures of Au(III), Pd(II), and Pt(IV) ion solutions and investigated the adsorbing selectivities for specific metal ions. The separating factor (K) was calculated using the formula

$$K = (C_{A1} - C_{A2}) \times C_{B2}/(C_{B1} - C_{B2}) \times C_{A2}$$

where, C_{A1} and C_{A2} stand for the concentrations of metal ion A before and after adsorption, and C_{B1} and C_{B2} stand for the concentration of metal ion B before and after adsorption. Observing K in Table IV, we conclude that two resins have adsorbing priority for Au(III) and Ag(I). These adsorbing selectivities corresponded to their high capacities and rates for silver and gold.

Adsorbing Isotherm

Adsorbing isotherm is used to describe the relationship between amount of adsorption and equilibrium concentration of metal ions at a certain temperature. Thus, the adsorbing capacities of resin PTF2 for Ag(I) were measured when temperature was 25°C; see Table V for the results.

We see from the capacity–concentration curve in Figure 2 that the adsorption goes up with the increase of equilibrium concentrations of Ag(I) until it has reached saturated adsorption. After saturated adsorption, the concentration no longer affects the capacity.

When investigating adsorption of solids for gases, Langmuir proposed a monomolecular layer adsorption model, obtaining an adsorption equation.[14] If the equation is used to describe the adsorption of a resin for a metal ion in solutions, the equation is written as follows:

Table IV Adsorbing Selectivity of Resins

Resin	Concn (mg/mL)		Mixed Solutions of Metal Ions: Au(III)–Pd(II)		Au(III)–Pt(IV)		Pd(II)–Pt(IV)	
PTF1	C_{A1}	C_{B1}	0.525	0.455	0.525	0.460	0.455	0.460
	C_{A2}	C_{B2}	0.300	0.405	0.360	0.390	0.410	0.400
	K		6.08		2.55		0.73	
PTF3	C_{A1}	C_{B1}	0.525	0.455	0.525	0.460	0.455	0.460
	C_{A2}	C_{B2}	0.140	0.401	0.150	0.400	0.408	0.380
	K		20.42		16.67		0.55	

Table V Adsorption Isothermal Studies

Resin (g)	$AgNO^3$ (0.1N) (mL)	H_2O (mL)	C_1 (mol/L)	C_2 (mol/L)	A (mmol/g)	C_2/A
0.15	30	0	0.1000	0.0435	11.48	37.9×10^{-4}
0.15	25	5	0.0833	0.0259	11.30	22.9×10^{-4}
0.15	20	10	0.0667	0.0111	11.12	10.0×10^{-4}
0.15	15	15	0.0500	0.0037	9.26	4.0×10^{-4}
0.15	10	20	0.0333	0.0014	6.38	2.2×10^{-4}
0.15	8	22	0.0267	0.0009	5.15	1.8×10^{-4}
0.15	5	25	0.0167	0.0005	3.05	1.6×10^{-4}
0.15	3	27	0.0100	0.0003	1.94	1.4×10^{-4}

$$C_2/A = C_2/C_0 + 1/(K_1C_0)$$

where C_2 is equilibrium concentration of the metal ion, A is adsorbing capacity in equilibrium state, C_0 is saturated adsorbing capacity and K_1 is the Langmuir constant. Figure 3 plots C_2/A vs C_2 as a straight line, showing that the adsorption is monomolecular layer type and corresponded to Langmuir adsorbing isothermal when solutions are dilute.

CONCLUSIONS

The thiourea–formaldehyde chelating resin was synthesized in an acidic solution. Structural analysis proved that the resin was an alternate copolymer. The measurements of adsorption of resin for some metal ions showed that resins had higher adsorbing capacity, rate, and selectivity for Ag(I) and Au(III) than for the other ions. Isothermal adsorbing study showed that the adsorption belonged to Langmuir monomolecular layer adsorption. The PTF3 resin has potential application in industry for concentrating and retrieving A(I) and Au(III).

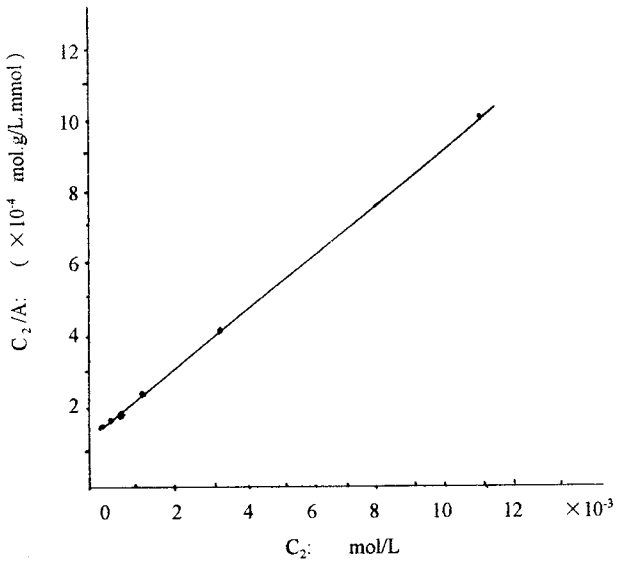


Figure 3 Isothermal adsorption curve for Ag(I).

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