Synthesis of Chelating Resin PETU and Its Adsorption to Ag(I)

ZHONG Hong(钟 宏), WANG Shuai(王 帅), QIU Yun-ren(邱运仁), WANG Ai-ping(王爱萍)

(*Department of Chemistry & Chemical Engineering, Central South University, Changsha, Hunan 410083, China*)

Abstract: A novel chelating resin (PETU) with thiourea groups in its main chain was synthesized by the reaction of O,O'-butane-1,4-diyl dicarbonisothiocyanatidate and triethylene tetraamine. The adsorption of Ag(I) on PETU was investigated by batch tests. The results showed that adsorption data fitted Boyd's diffusion equation of liquid film and the adsorption was controlled by liquid film diffusion. Under the temperatures between 15~60℃, the adsorption capacity decreased with the increase of temperature, and increased with the increase of initial concentration of Ag(I). The experimental data fitted Langmuir and Freundlich equations, and the correlation coefficients for Langmuir equation were between 0.9965~0.9998, and those for Freundlich equation were between 0.8211~0.9810, and increased with the adsorption temperature. ΔH, ΔG and ΔS calculated by thermodynamic formulae were all negative, which meant that the adsorption process was exothermic and spontaneous, and the entropy decreased during the process. XPS results showed that N, S and O atoms were the electron donors to coordinate with Ag.

Key words: chelating resin; Ag(I); adsorption

CLC No.: TQ425.2; O647.3 **Document Code:** A **Article ID:** 1009−606X(2007)04−0689−05

1 INTRODUCTION

With the development of industrial technology, noble metals are playing a more and more important part in aviation, rocketry, electronics, chemical engineering, metallurgy, environmental protection, energy resources, and medicine, etc. There are many methods to extract precious metals, such as replacement precipitation, activated carbon adsorption, solvent extraction and resin-in-pulp (RIP) methods. RIP process has the advantages of high adsorption capacity, good selectivity to noble metals, rapid adsorption rate and easy wash-out, so it has attracted much attention in recent years[1,2]. There have been many reports about preparation of chelating resins and their high adsorption capacity and good selectivity to noble metal ions including Au, Ag, Pt and Pd[3−7].

As an excellent ligand to noble metal ions, thiourea is widely used in extraction, separation and recovery in precious metal hydrometallurgical field. Chelating resins with thiourea groups are expected to be new type functional materials for separation and recovery of precious metals. Thiourea resins can be obtained in two ways: one is to graft thiourea groups onto the main chains of polymers, which usually have thiourea groups in the branches, another is to polymerize the monomers to homopolymers or copolymers with thiourea groups, which usually have thiourea groups in their main chains. At present, thiourea chelating resins are mostly synthesized in the first way, so the reaction efficiency and content of thiourea groups are low and the adsorption performance of the resins is limited[8].

In this work, a novel polymeric ester thiourea resin (PETU) with ordered structure and high content of thiourea groups was synthesized by the reaction of isothiocyanatidate and triethylene tetraamine (TETA). The adsorption behavior of Ag(I) on PETU was investigated.

2 EXPERIMENTAL

2.1 Synthesis of PETU Resin

Figure 1 shows the synthesis route of the resin PETU. First, 1,4-butanediol bischloroformate was prepared by the reaction of 0.073 mol triphosgene and 0.10 mol 1,4-butanediol in 20 mL toluene for 10 h under the temperature of 5℃, catalyzed by 0.0035 mol N,N-dimethylaniline (DMA), then 1,4-butanediol bischloroformate reacted with 0.25 mol NaSCN for 3.5 h under the temperature of 5℃, using 0.0010 mol PEG-400 as phase transfer catalyst, from which O,O'-butane-1,4-diyl dicarbonisothiocyanatidate was synthesized. At last, isothiocyanatidate reacted with 0.05 mol TETA to obtain PETU resin.

Received date: 2006−09−18; **Accepted date:** 2006−10−27
Foundition item: Supported by National Natural Science Foundation of China (No. 20476105)
Biography: ZHONG Hong(1961−), male, native of Longquan City, Zhejiang Province, Ph.D., professor, major in chemical engineering; WANG Shuai, corresponding author, E-mail: hgwangshuai@163.com.

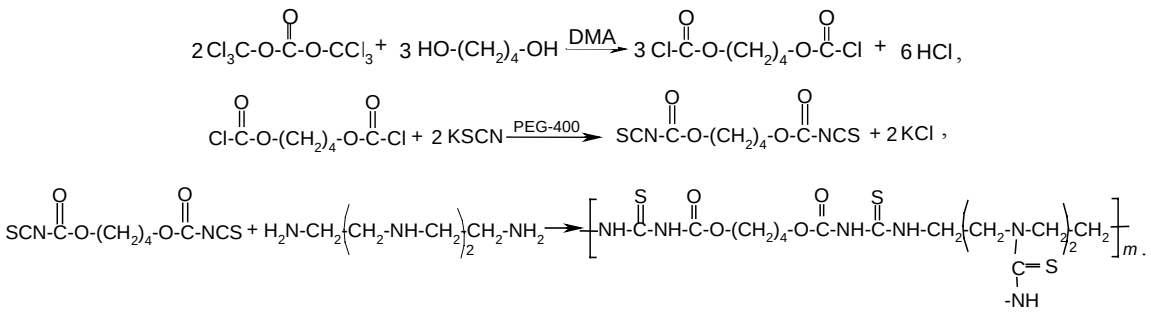

Fig.1 The synthesis route of PETU

2.2 Adsorption Experiment

The adsorption performance of metal ions on PETU was investigated by batch tests. 250 mg resin was suspended in 25 mL solution (1 mol/L HNO_3) in an iodometric flask, which was placed in the thermostatic vibrator. At a desired temperature, the flask was shaken for 10 h, which was proved to be enough to reach adsorption equilibrium. The solution was filtrated, and the concentration of metal ions in the filtrate was determined by Volhard method. Adsorption capacity could be calculated by the following equation:

$$Q=(C_0-C_e)V/m, \quad (1)$$

where Q is the adsorption capacity (mmol/g), C_0 the initial concentration of solution (mol/L), C_e the concentration after adsorption (mol/L), V the volume of the solution used for adsorption (L), and m the mass of the dry resin (g).

3 RESULTS AND DISCUSSION

3.1 Characterization of PETU

Infrared spectrum of PETU was obtained by KBr method. The result is shown in Fig.2. The characteristic peaks of N—H appear at 3358.2 and 771.9 cm^{-1}, C—N 1375.0 cm^{-1}, C═O 1703.2 and 1654.89 cm^{-1}, C═S 1074.1 and 1051.0 cm^{-1}, and —NH—CS—NH— 1529.1 cm^{-1}. It is justified that the resin contains the functional groups of amidocyanogen, ester and thiourea.

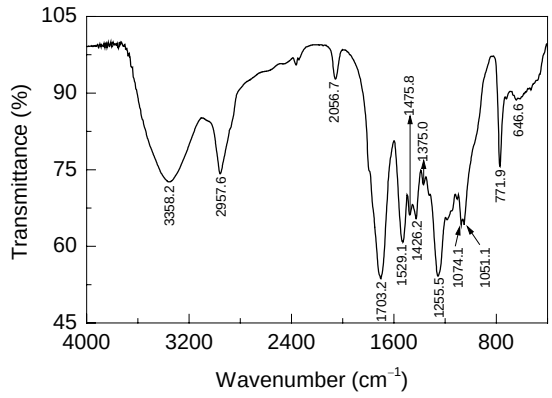

Fig.2 FT-IR spectrum of PETU

Elemental analysis results were obtained as follows (%): C 47.1, N 16.3, S 16.9, O 15.2, H 4.5.

3.2 Adsorption of Metal Ions on PETU

Adsorption of various metal ions on PETU were carried out under the following conditions: T=30℃, t=24 h, C_0=0.1 mol/L, and C_{HNO_3}=1 mol/L. The obtained adsorption capacities were 3.53 mmol/g for Ag(I), and 0.230 mmol/g Cu(II), 0.160 mmol/g Zn(II), 0.030 mmol/g Fe(III), <0.010 mmol/g Ca(II), Mg(II), Pb(II). So PETU had good adsorption performance for Ag(I).

3.3 Adsorption Kinetics for Ag(I)

The effect of contact time on the adsorption of Ag(I) on PETU was studied by taking 250 mg resin with 25 mL $AgNO_3$ solution, the result is shown in Fig.3. The adsorption conditions are: temperature 30℃, initial concentration of $AgNO_3$ solution 0.1 mol/L, and concentration of HNO_3 1 mol/L. The adsorption process could reach equilibrium in 10 h, and the equilibrium adsorption capacity was 3.527 mmol/g.

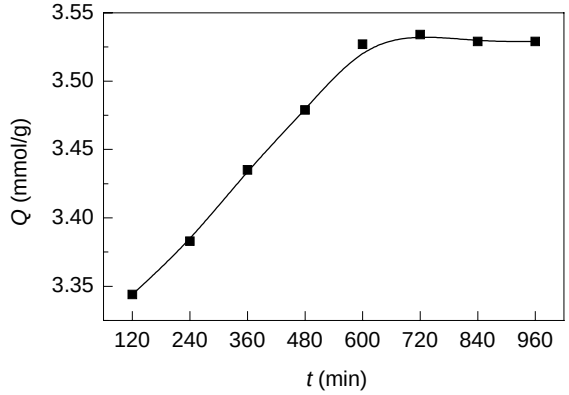

Fig.3 Adsorption kinetics of PETU for Ag(I)

The data before equilibrium are in good accordance with Boyd's diffusion equation of liquid film[9,10], expressed as Eq.(2).

$$-\ln(1-F)=kt, \quad (2)$$

where F is the fractional attainment of equilibrium at time t, obtained by the expression $F=Q/Q_m$, where Q_m is the maximum adsorption capacity, and k the adsorption rate constant.

The curve of $-\ln(1-F)$ vs. t is shown in Fig.4. The linear equation is $-\ln(1-F)=0.000202t+0.95781$, and the correlation coefficient R^2 is 0.9979. It suggests that the kinetics of the adsorption process was controlled by diffusion through the liquid film surrounding the solid adsorbent, and adsorption kinetics constant k at 30℃ was 0.000202 min^{-1}.

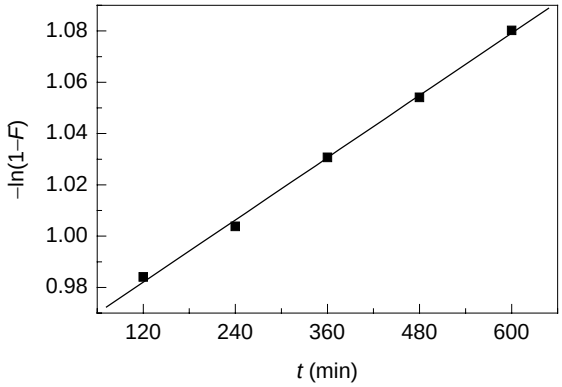

Fig.4 $-\ln(1-F)$ vs. t plot of PETU for Ag(I)

3.4 Adsorption Isotherms for Ag(I)

The effect of initial concentration C_0 of Ag(I) on adsorption capacity is presented in Fig.5. C_0 varied from 0.02 to 0.18 mol/L and temperature from 15 to 60℃. At the same temperature, adsorption capacity Q increased with the increase of C_0, when C_0 was greater than 0.10 mol/L, Q changed slowly, close to the maximum adsorption capacity at this temperature. When C_0 was the same, Q decreased with the increase of temperature, which implies that the process was exothermal and low temperature was favorable for the adsorption. The adsorption capacity reached the maximum 4.077 mmol/g, while temperature was 15℃ and C_0 0.18 mol/L.

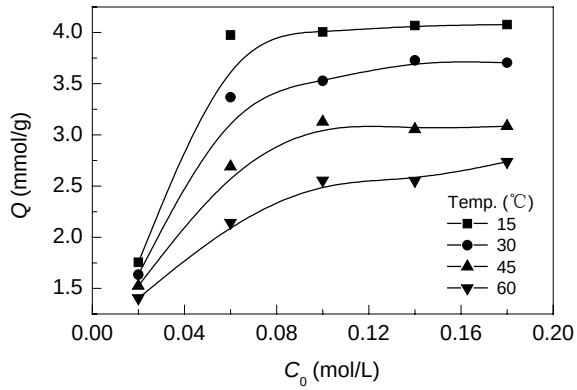

Fig.5 Adsorption isotherms of PETU for Ag(I)

Langmuir and Freundlich equations are usually used to describe adsorption of the metal ions on the absorbent surface[11−13]. The isotherms are given by the following equations:

$$C_e/Q=C_e/Q_m+1/(Q_mK_L), \quad (3)$$

$$\ln Q=n^{-1}\ln C_e+\ln K_F, \quad (4)$$

where K_L is the equilibrium constant, n the Freundlich constant and K_F the binding energy constant reflecting the affinity of resin to metal ions. The data in Fig.5 were analyzed with the above two equations, and results were presented in Fig.6 and Table 1.

It can be seen from Table 1 that correlation coefficients for Langmuir isothermal model are all close to 1, and decrease with the increase of temperature, so Langmuir isothermal model fits the results preferably, especially at low temperatures. Correlation coefficients for Freundlich isothermal model increase with the increase of the temperature, so Freundlich isothermal model fits the results better at high temperatures. Correlation coefficients for Langmuir isothermal model are closer to 1, being more fitted than that for Freundlich model, indicating that Langmuir equation is better than Freundlich equation to describe the adsorption on PETU for Ag(I).

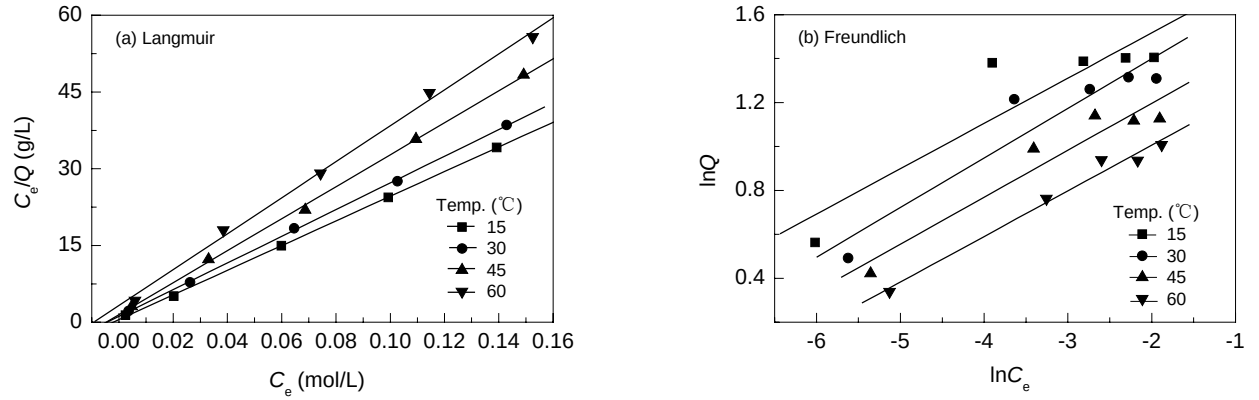

Fig.6 Langmuir and Freundlich isotherms of PETU for Ag(I)

Table 1 Langmuir and Freundlich equations of PETU and parameters

T (℃)	Langmuir equation	Q_m (mmol/g)	K_L (L/mol)	R^2	T (℃)	Freundlich equation	n	K_F	R^2
15	C_e/Q=241.0C_e+0.519 5	4.149	464.0	0.999 8	15	ln$Q$=1.930+0.2062lnC_e	4.850	6.887	0.821 1
30	C_e/Q=260.6C_e+1.162	3.837	224.3	0.999 6	30	ln$Q$=1.851+0.2259lnC_e	4.427	6.368	0.891 6
45	C_e/Q=312.5C_e+1.488	3.200	210.0	0.999 0	45	ln$Q$=1.624+0.2139lnC_e	4.675	5.076	0.921 3
60	C_e/Q=351.4C_e+3.258	2.846	107.9	0.996 5	60	ln$Q$=1.421+0.2077lnC_e	4.815	4.141	0.981 0

3.5 Adsorption Thermodynamics of Ag(I)

The changes of enthalpy ΔH and entropy ΔS during the adsorption process could be calculated by the following equation[14,15], fitting the data in Fig.5.

$$\ln D=-\Delta H/(RT)+2.303\Delta S/R, \quad (5)$$

where D, known as the distribution coefficient of the adsorbate, is equal to $(C_0-C_e)V/(mC_e)$, R is the universal gas constant, being 8.314 J/(mol·K).

The change of Gibbs free energy ΔG could be calculated by

$$\Delta G=\Delta H-T\Delta S. \quad (6)$$

The results are shown in Fig.7 and Table 2. It can be seen from the values of minus ΔH and ΔS, the adsorption process was exothermic, and entropy decreased fore-and-after the process. Therefore low temperature was beneficial to the adsorption. ΔG being negative justifies that the adsorption was a spontaneous process. At the same initial concentration of Ag(I), the higher the temperature was, the smaller the absolute value of ΔG became, and the more difficult the adsorption took place. At the same temperature, the absolute value of ΔG decreased with the increase of initial concentration of Ag(I). The surface of the resin was covered gradually by Ag ions, so the potential of adsorption became weak and ΔG became small.

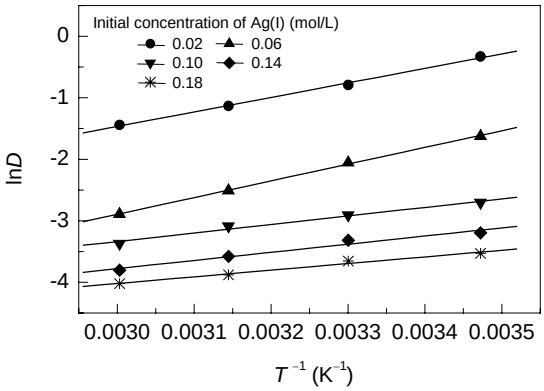

Fig.7 ln$D$ vs. T^{-1} plots of PETU for Ag(I)

Table 2 Result of fitting for ln$D$ vs. T^{-1}

C_0 (mol/L)	Fitting equation	R^2	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)			
					15 ℃	30 ℃	45 ℃	60 ℃
0.02	ln$D$=2361T^{-1}−8.550	0.996 8	−19.63	−30.86	−10.74	−10.28	−9.815	−9.352
0.06	ln$D$=2717T^{-1}−11.05	0.999 1	−22.59	−39.88	−11.11	−10.51	−9.910	−9.311
0.10	ln$D$=1386T^{-1}−7.494	0.981 8	−11.52	−27.05	−3.729	−3.323	−2.917	−2.511
0.14	ln$D$=1326T^{-1}−7.758	0.969 4	−11.03	−28.01	−2.963	−2.543	−2.122	−1.702
0.18	ln$D$=1081T^{-1}−7.262	0.982 8	−8.988	−26.22	−1.437	−1.044	−0.650 8	−0.257 5

3.6 XPS Spectra of PETU before and after Adsorbing Ag(I)

X-ray photoelectron spectroscopy (XPS) was performed on XSAM800 System. Electron binding energies of PETU before and after adsorption of Ag(I) were shown in Table 3.

Table 3 Electron binding energies of PETU (eV)

Orbit	$AgNO_3$	PETU	PETU−Ag	Change
Ag $3d_{3/2}$	374.6	–	373.5	−1.1
Ag $3d_{5/2}$	368.5	–	367.4	−1.1
N 1s	–	401.8	403.3	+1.5
S 2p	–	165.0	166.5	+1.5
O 1s	–	535.3	536	+0.7

During the adsorption, the binding energies of N 1s, S 2p and O 1s increased obviously, which suggests that they were all electron donors. The binding energies of both Ag $3d_{3/2}$ and Ag $3d_{5/2}$ were reduced by 1.1 eV, implying that Ag(I) was an electron acceptor.

4 CONCLUSIONS

(1) A novel polymeric ester thiourea resin (PETU) containing O, N and S atoms was synthesized using O,O'-butane-1,4-diyl dicarbonisothiocyanatidate and TETA as raw materials. FT-IR spectroscopy and elemental analysis were employed to characterize its structure.

(2) The adsorption of PETU for metal ions was investigated. Adsorption capacity sequence was: Ag(I)≫Cu(II)>Zn(II)>Fe(III)>Ca(II), Mg(II), Pb(II).

(3) The adsorption of PETU for Ag(I) fit Boyd's diffusion equation of liquid film, Langmuir model and Freundlich model. ΔH, ΔS and ΔG of the adsorption for

Ag(I) were all negative, implying that the adsorption was exothermic and spontaneous, and entropy decreased during the process.

(4) XPS analysis showed that the coordination between N, S, O and Ag took place during the adsorption for Ag(I).

REFERENCES:

[1] Fu J G, Liu L B, Xiong Q F, et al. A Review of Resin-in-pulp for Recovering Gold [J]. Gold, 2006, 27(1): 41–44(in Chinese).

[2] Fleming C, Wells J, Thomas K G. Process for Recovering Gold from Thiosulfate Leaching Solutions and Slurries with Ion Exchange Resin [P]. US Pat.: 6344068 B1, 2002–02–05.

[3] Garg B S, Sharma R K, Bhojak N, et al. Chelating Resins and Their Applications in the Analysis of Trace Metal Ions [J]. Microchem. J., 1999, 61: 94–114.

[4] Dorota J B, Bo Zena N K. Gold Sorption on Weak Base Anion Exchangers with Aminoguanidyl Groups [J]. Eur. Polym. J., 2002, 38: 2239–2246.

[5] Zhu X L, Wang L H, Zhang Z B, et al. Synthesis of Thiourea-resin by Microwave Irradiation and Its Adsorption Properties [J]. J. Chem. Eng. Chin. Univ., 2004, 18(1): 62–66(in Chinese).

[6] Atia A A. Adsorption of Silver(I) and Gold(III) on Resins Derived from Bisthiourea and Application to Retrieval of Silver Ions from Processed Photo Films [J]. Hydrometallurgy, 2005, 80: 98–106.

[7] Donia A M, Atia A A, Elwakeel K Z. Gold(III) Recovery Using Synthetic Chelating Resins with Amine, Thio and Amine/Mercaptan Functionalities [J]. Sep. Purif. Technol., 2005, 42: 111–116.

[8] Xu Y W, Yang Y H, Li H P. Study on Chelating Resins XXX: Syntheses and Adsorption Properties of Thiourea Type Resins [J]. J. Wuhan University (Natural Science Edition), 1999, 45(2): 129–134(in Chinese).

[9] Boyd G E, Adamson A W, Myers L S. The Exchange Adsorption of Ions from Aqueous Solution by Organic Zeolites: II. Kinetics [J]. J. Am. Chem. Soc., 1947, 69(3): 2836–2848.

[10] Bhattacharyya K G, Gupta S S. Pb(II) Uptake by Kaolinite and Montmorillonite in Aqueous Medium: Influence of Acid Activation of the Clays [J]. Colloids Surf., A: Physicochem. Eng. Aspects, 2006, 277: 191–200.

[11] Abou-Mesalam M M. Sorption Kinetics of Copper, Zinc, Cadmium and Nickel Ions on Synthesized Silico-antimonate Ion Exchanger [J]. Colloids Surf., A: Physicochem. Eng. Aspects, 2003, 225: 85–94.

[12] Demirba A, Pehlivan E, Gode F. Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from Aqueous Solution on Amberlite IR-120 Synthetic Resin [J]. J. Colloid Interface Sci., 2005, 282: 20–25.

[13] Wang L N, Qi T, Zhang Y. Synthesis of Novel Chelating Adsorbents for Boron Uptake from Aqueous Solutions [J]. The Chinese Journal of Process Engineering, 2006, 6(3): 375–379.

[14] Maity N, Payne G F, Ernest M V, et al. Caffeine Adsorption from Aqueous Solutions onto Polymeric Sorbents: The Effect of Surface Chemistry on the Adsorptive Affinity and Adsorption Enthalpy [J]. Reactive Polymers, 1992, 17(3): 273–287.

[15] Xia C F, Xing D Y, Chen B R. Study of Chloroethanoic and Trichloroethanoic Acid Thermodynamics with Cross-linked Chitosan Resin [J]. Ion Exchange and Adsorption, 2004, 20(2): 125–130(in Chinese).