# Comparative Study of the Recovery of Silver(I) from Aqueous Solutions with Different Chelating Resins Derived from Glycidyl Methacrylate

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**ABSTRACT:** Glycidyl methacrylate (GMA) was polymerized in the presence of divinylbenzene (DVB). The GMA/DVB resin was immobilized with different chelating moieties containing nitrogen or sulfur donor atoms. The resins obtained [an amino-bearing resin (RI), an amino/thiocarbamate-bearing resin (RII), a triazole-bearing resin (RIII), and an amino/thiol-bearing resin (RIV)] were tested toward the recovery of Ag(I) from its aqueous solutions. The adsorption behavior of Ag(I) and the resin regeneration were studied. The sulfur-containing resins showed higher uptake and lower elution efficiency than those containing nitrogen.

The maximum uptake values were 1.20, 1.33, 1.40, and 2.86 mmol/g for RI, RII, RIII, and RIV, respectively. The mechanism of interaction between Ag(I) and the resins is also suggested. Regeneration was achieved with a 0.5$N$ thiourea solution, acidified thiourea, or 0.5$N$ $H_2SO_4$, where the resins were stable over five cycles. Elution efficiencies of 94–96 and 90–93% were achieved for the nitrogen- and sulfur-containing resins, respectively. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 806–812, 2005

**Key words:** resins

## INTRODUCTION

Silver is used in the jewelry, silverware, metal alloy, and food and beverage-processing industries. Little soluble silver waste would be expected to result from use of the solid metal. Silver nitrate is the most common soluble salt used in the porcelain, mirroring, photographic, electroplating, and ink-formulation industries. Recovery of silver from waste streams is more profitable than that for most other metals.[1–5] The main technologies used for silver removal from wastewaters include precipitation, ion exchange, reductive exchange, and electrolytic recovery.[6] Chelating resins with various functionalities have also been widely used for the concentration and retrieval of silver.[7–13]

In this study, a glycidyl methacrylate (GMA)/divinylbenzene (DVB) resin was prepared. The obtained resin was anchored with different chelating moieties containing nitrogen and sulfur. The adsorption/desorption behavior of the obtained resins toward silver(I) from its aqueous solutions was investigated. Applications in a flow system and the regeneration of the resins were also evaluated.

## EXPERIMENTAL

### Chemicals

GMA, DVB, benzoyl peroxide ($B_2O_2$), ethylenediamine (en), carbon disulfide ($CS_2$), and thiourea were Aldrich products. 3-Amino-1,2,4-triazole-5-thiol (AZ) was supplied by Organica Co. (Germany). Silver nitrate was used as a source for Ag(I).

### Preparation of the studied resins

#### Preparation of the GMA/DVB resin

The resin was prepared through the polymerization of GMA in the presence of DVB as a crosslinker and at molar ratio of 9.5:0.5, respectively. The preparation procedure was carried out as described elsewhere.[14] The resin obtained was immobilized with different chelating groups to give the corresponding chelating resins according to Scheme 1.
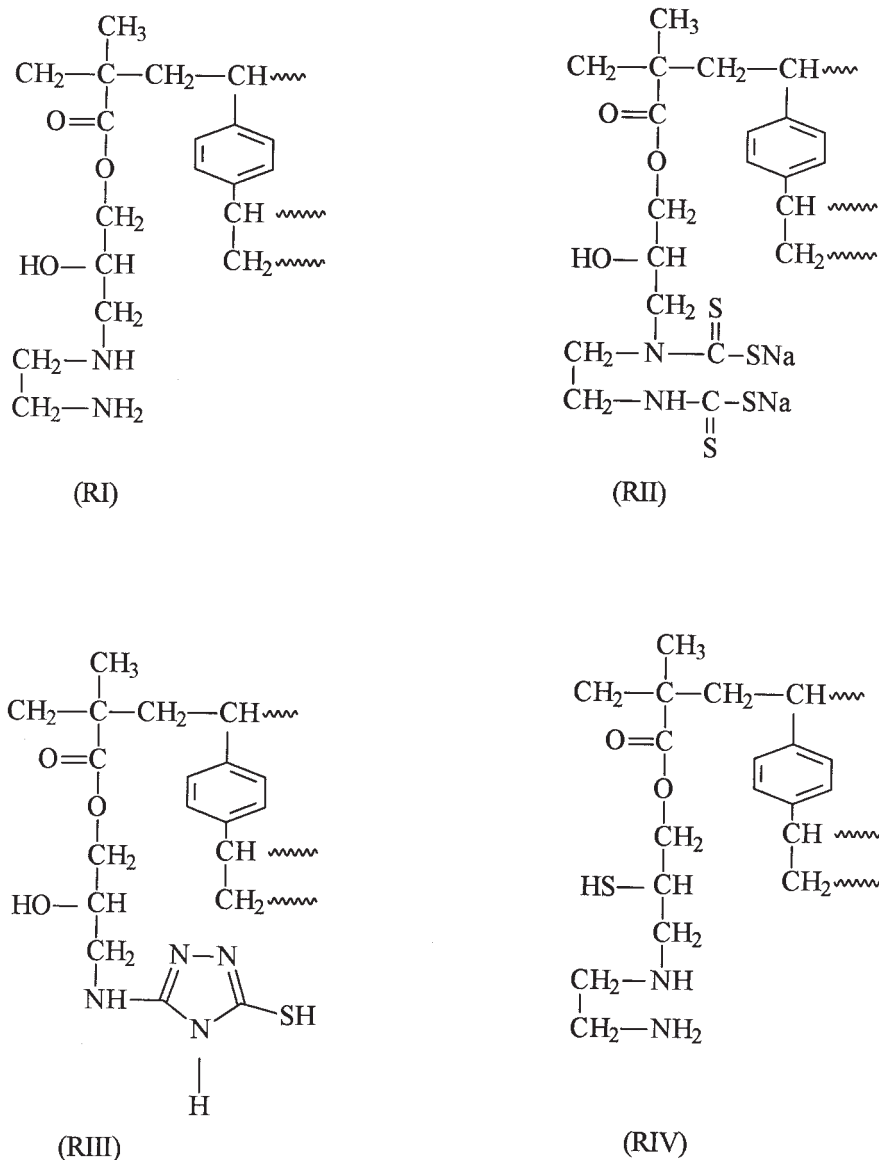
#### Amino-bearing resin (RI)

The method of preparation was described in detail in one of our previous articles.[14] The obtained resin was anchored with amino groups.

#### Amino/thiocarbamate-bearing resin (RII)

The reaction was carried out as previously reported.[15] Sodium metal (1.4 g) was carefully dis-

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Triazole resin ←——(AZ)—— GMA/DVB ——(en)——→ Amino resin ——EtONa+ CS$_2$——→ Amino/thio resin
(RIII)                              (RI)                              (RII)

GMA/DVB │ Thiourea + (en) ↓

Amino/thiol resin
(RIV)

**Scheme 1**

solved into 20 mL of dried ethanol in a flask. RI (1 g) was added to the flask along with 3 mL of CS$_2$. The contents were stirred at 50°C for 7 days. The obtained product was filtered off, washed subsequently with distilled water and methanol, and then kept to dry.

Triazole-bearing resin (RIII)

GMA/DVB resin (1 g) and AZ (4 g) were dissolved in 12 mL of dimethylformamide (DMF). The reaction mixture was refluxed at 60°C for 72 h in an oil bath. The product was filtered off, washed with cold methanol, and dried.

Preparation of the thiirane intermediate

A methyl thiirane methacrylate intermediate was prepared according to a method reported earlier.[16] Thiourea (3 g) were dissolved in a mixture of DMF/ethanol at a ratio of 3:1 v/v. Three grams of the resin (GMA/DVB) were added to the thiourea solution, and then the contents were refluxed in an oil bath at 60°C with continuous stirring for 72 h. The product was filtered off, washed subsequently with cold methanol and acetone, and then dried in air.

Amino/thiol-bearing resin (RIV)

The thiirane methacrylate (1 g) obtained in the previous step and en (4 g) were dissolved in 12 mL of DMF. The reaction mixture was refluxed at 75–80°C for 72 h in an oil bath. A pale yellow product was formed, filtered, washed with cold methanol, and then dried.

The IR spectra of the synthesized resins were performed with a PerkinElmer 550 S spectrophotometer.

**Uptake measurements**

Preparation of the solutions

A stock solution ($2 \times 10^{-2}$ M) of silver nitrate was prepared in twice-distilled water. A stock solution of ethylenediaminetetraacetic acid (EDTA; $5 \times 10^{-3}$ M) was prepared and standardized against a solution of MgSO$_4$ · 7H$_2$O with Eriochrome Black-T as an indicator.[17] Buffers of acetic acid/acetate and ammonium hydroxide/ammonium chloride were used for the experiments carried out in controlled acidic or basic conditions. H$_2$SO$_4$ was used to study the effect of strong acidic media on the uptake of Ag(I) by the studied resins.

Metal-ion-uptake experiments done with the batch method

Metal-ion-uptake experiments done with the batch method were performed by the placement of 0.1 g of dry resin in a flask containing 100 mL of Ag(I) solution at a desired initial concentration and pH. The contents of the flask were equilibrated on a Vibromatic 384 shaker at 300 rpm and at about 28 ± 1°C for a definite time period. A sample of the solution (5 mL) was taken after the equilibration time and then filtered, and the residual concentration of metal ion was determined via titration against $5 \times 10^{-3}$ M EDTA with the Volhard method.[17]

Effect of pH on the uptake of Ag(I)

Uptake experiments under controlled pH were carried out following the previous procedures for uptake experiments. The pH was controlled with a suitable buffer. To study the effect of the conjugate anion on the uptake, HCl, HNO$_3$, or H$_2$SO$_4$ were used. The equilibrium time was fixed at 3 h and 28 ± 1°C.

Uptake experiments done with the column method

The resin (0.1 g) was placed in a glass column (10 cm in length and 1 cm wide). The Ag(I) solution (100 mL) at an initial concentration of $5 \times 10^{-3}$ M was allowed to flow gradually through the column under the force of gravity at different rates. The underflow solution (10 mL) was taken, and the residual concentration for Ag(I) was determined.

Elution experiments

Elution experiments were performed by the placement of 0.1 g of the resin in the column; we then

CH₃
CH₂—C—CH₂—CH〜
O=C
O
CH₂
HO—CH
CH₂
CH₂—NH
CH₂—NH₂

CH 〜
CH₂〜

(RI)

CH₃
CH₂—C—CH₂—CH〜
O=C
O
CH₂
HO—CH
CH₂  S
CH₂—N—C–SNa
CH₂—NH-C–SNa
S

CH 〜
CH₂〜

(RII)

CH₃
CH₂—C—CH₂—CH〜
O=C
O
CH₂
HO—CH
CH₂  N—N
NH          SH
N
H

CH 〜
CH₂〜

(RIII)

CH₃
CH₂—C—CH₂—CH〜
O=C
O
CH₂
HS—CH
CH₂
CH₂—NH
CH₂—NH₂

CH 〜
CH₂〜

(RIV)

**Scheme 2**

loaded Ag(I) by allowing 100 mL of a silver ion solution to flow at rate of 1 mL/min. After the maximum uptake in the first run was reached, the resin was washed carefully by the flow of distilled water through the column. The resin loaded by Ag(I) was then subjected to elution with 100 mL of thiourea, acidified thiourea, and $H_2SO_4$ at different concentrations. After the resin was treated with the eluent, the resin was carefully washed with distilled water, dilute alkali, and finally, with distilled water prepare it for reuse in the second uptake run. The elution efficiency was calculated by the division of the total uptake in the second run by that of the first run.

## RESULTS AND DISCUSSION

The IR spectra of the studied resins showed that the epoxy band at 1265 cm$^{-1}$ in the spectrum of the GMA/DVB resin disappeared in those of RI, RII, RII, and RIV. Moreover, the spectra of these resins were characterized by $\nu$ N—H at 3442/3250 cm$^{-1}$ and $\nu$ C—H at 1439 and 1327 cm$^{-1}$. The observed peak at 2529 cm$^{-1}$ was characteristic for S—H in RIII and RIV. The suggested structural formulas of the studied resins are given in Scheme 2.

## Uptake of Ag(I) with the batch method

The uptake of Ag(I) from its aqueous solutions at pH 6.5 (natural pH) as a function of time by the four resins is shown in Figure 1. The equilibrium was achieved within nearly 80 min for resins RI, RII, and RIII, whereas for resin RIV, the equilibrium was attained within 4 h. Levels of 50, 78, 88, and 63% of total uptake of Ag(I) were obtained within 40 min for resins RI, RII,
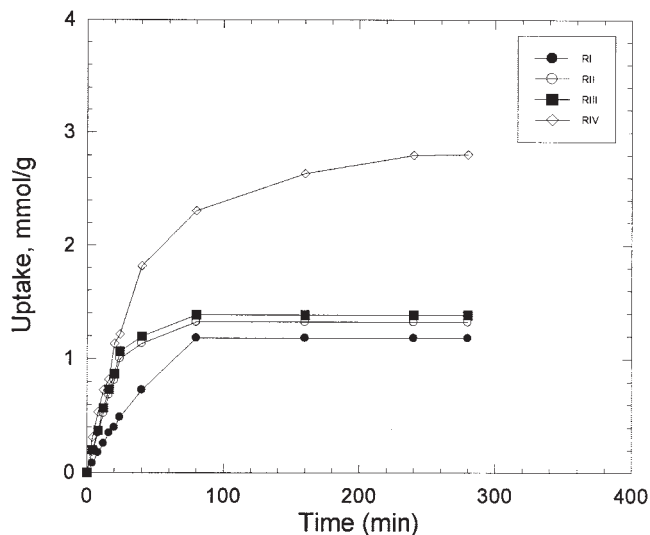
**Figure 1** Uptake of Ag(I) by the resins as a function of time at natural pH at an initial concentration of $5 \times 10^{-3}$ $M$ and a temperature of $28 \pm 1°C$.

RIII, and RIV, respectively. The maximum uptake at the equilibrium times followed the order RIV $\gg$ RIII > RII > RI. This order was dependent on the type and the concentration of chelating groups.

**Effect of pH on the uptake of Ag(I)**

The effect of the acidity of the medium on the up-take of Ag(I) by the studied resins is shown in Figure 2. Figure 2 indicates that the highest uptake was obtained at natural pH. This may have been due to
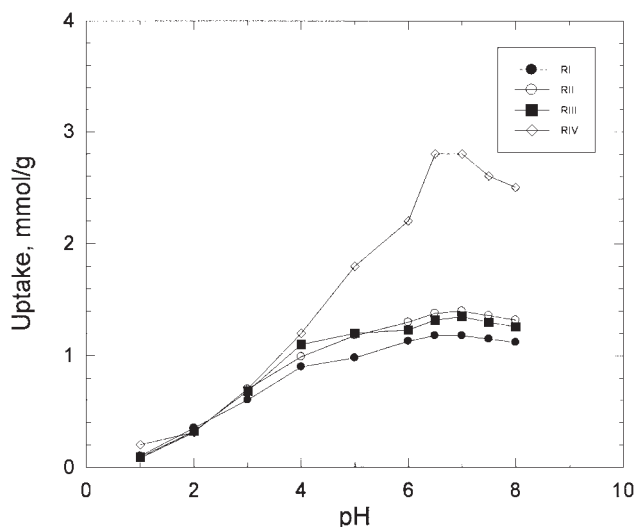


**Figure 2** Effect of pH on the uptake of Ag(I) by the resins at an initial concentration of $5 \times 10^{-3}$ $M$ and a temperature of $28 \pm 1°C$.
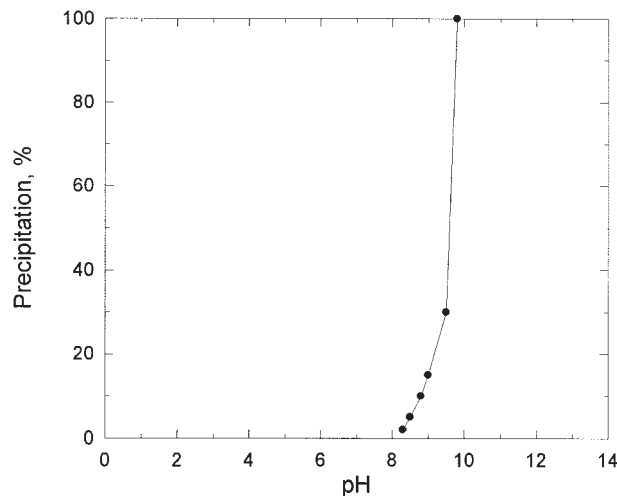


**Figure 3** Precipitation of Ag(I) as a function of pH at $28 \pm 1°C$.

1. The presence of a free lone pair of electrons on nitrogen or sulfur atoms that was suitable for coordination with the metal ion to give the corresponding resin–metal complex.
2. Ion exchange between —SH groups and the Ag ion:

$$R–SH + Ag^+ \rightarrow R–SAg + H^+ \qquad (1)$$

The decrease in the uptake in the acidic media may have been due to the protonation of the lone pair of electrons on nitrogen and/or the undissociation of the —SH group, which hindered complex formation or ion exchange. The decrease in the uptake of Ag(I) prior to pH 8 may have been due to the masking of Ag ions in the form of soluble anions such as silver–hydroxide or silver–ammonia complexes. At pH 8, almost all of the Ag ions precipitated in the form of Ag(OH), as shown by the pH–precipitation data in Figure 3. In the range of pH of 4–7 (Fig. 2), RII and RIII gave close uptake values. This indicated that both resins may have had the same content of interaction sites and the same uptake mechanism through the ion exchange of R—SH groups to give R—SAg. On the other hand, the observed higher uptake value of RIV than those of the other three resins in the same pH range may have been due to the formation of a stable silver complex with two fused chelate rings. For RI, the uptake took place through complex formation, with one chelate ring displaying a lower stability than that of RIV. Therefore, lower uptake values were observed.

Table I reports the effect of the conjugate anion on the uptake of Ag(I) by the resins with HCl, HNO$_3$, and H$_2$SO$_4$. In the case of HCl and HNO$_3$, a minor decrease in the uptake was reported with decreasing pH. These findings may be explained by the formation of com-

| | Uptake (mmol/g) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | RI | | | RII | | | RIII | | | RIV | | |
| pH | HCL | $HNO_3$ | $H_2SO_4$ | HCL | $HNO_3$ | $H_2SO_4$ | HCL | $HNO_3$ | $H_2SO_4$ | HCL | $HNO_3$ | $H_2SO_4$ |
| 1.1 | 0.98 | 0.94 | 0.10 | 1.10 | 1.02 | 0.09 | 1.13 | 1.06 | 0.08 | 1.80 | 1.86 | 0.20 |
| 1.3 | 1.00 | 0.97 | 0.30 | 1.15 | 1.05 | 0.20 | 1.20 | 1.08 | 0.20 | 1.93 | 1.88 | 0.23 |
| 1.5 | Precipitation | 0.98 | 0.30 | Precipitation | 1.10 | 0.24 | Precipitation | 1.12 | 0.25 | Precipitation | 1.89 | 0.26 |
| 1.8 | Precipitation | 1.00 | 0.31 | Precipitation | 1.13 | 0.28 | Precipitation | 1.15 | 0.30 | Precipitation | 1.92 | 0.28 |
| 2.0 | Precipitation | 1.05 | 0.35 | Precipitation | 1.16 | 0.32 | Precipitation | 1.18 | 0.31 | Precipitation | 1.94 | 0.31 |
| 3.0 | Precipitation | 1.12 | 0.60 | Precipitation | 1.19 | 0.68 | Precipitation | 1.20 | 0.70 | Precipitation | 2.19 | 0.70 |

plex anions, such as $AgCl_2^-$ and $Ag(NO_3)_2^-$, in the presence of HCl and $HNO_3$, respectively. These soluble anions may have been able to undergo exchange adsorption with the anions located on the resin surface according to the following routes:[18]

$$R_3NH^+Cl^- + AgCl_2^- \leftrightarrow R_3NH^+AgCl_2^- + Cl^- \quad (2)$$

$$R_3NH^+NO_3^- + Ag(NO_3)_2^- \leftrightarrow$$
$$R_3NH^+Ag(NO_3)_2^- + NO_3^- \quad (3)$$
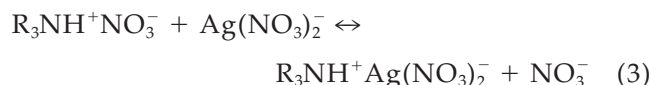
The ion-exchange mechanism required the formation of $AgCl_2^-$ and $Ag(NO_3)_2^-$. The range of pH greater than 1.3–3.0 was avoided in case of with HCl due to the precipitation of silver as AgCl. At lower pH ranges, the precipitated AgCl interacted with excess HCl to give the soluble anion $AgCl_2^-$, which became able to undergo the ion-exchange process.

For $H_2SO_4$, the uptake of Ag(I) on all of the studied resins dramatically decreased with decreasing pH. The lower uptake may have been due to the formation of a resin–sulfate salt, which did not furnish ion exchange with other anions:[18]

$$R_3N + H_2SO_4 \leftrightarrow [R_3NH^+]_2SO_4^{-2} \quad (4)$$

Figure 4 shows the adsorption isotherm of Ag(I) by the four resins at natural pH and 28 ± 1°C. For all resins, the uptake increased with increasing initial concentration until a plateau was reached. Afterward, the increase of the metal-ion concentration did not affect the uptake capacity. The maximum uptake values were 1.20, 1.33, 1.40, and 2.86 mmol/g for RI, RII, RIII, and RIV, respectively. The adsorption data of Ag on the four resins were applied to the Langmuir isotherm:[19]

$$\frac{C_e}{q_e} = \frac{C_e}{q_s} + \frac{1}{Kq_s} \quad (5)$$

where $C_e$ is the equilibrium concentration of the metal ion (mmol/L), $q_e$ is the adsorbing capacity in equilib-

rium state (mmol/g), $q_s$ is the saturated uptake capacity on the resin (mmol/g), and $K$ is the binding constant (L/mmol). The plotting of $C_e/q_e$ versus $C_e$ gave straight lines, indicating that the adsorption was simple and complied with the Langmuir isotherm, as shown in Figure 5(a–d). Each straight line had intercept and slope values equal to $1/Kq_s$ and $1/q_s$, respectively. The values of $K$ and $q_s$ were obtained and are reported in Table II. As indicated in Table II, RIV showed a higher $q_s$ value (2.9 mmol/g) and a higher $K$ value (1.7 L/mmol). This explained the higher chelating power of the RIV resin toward the Ag ions.

## Uptake of Ag(I) with the column method

The uptake of Ag(I) by the four resins as done with the column method is reported in Table III. The data indicated that the uptake was closely related to the flow rate. As the flow rate increased, the uptake decreased. This could be explained by the fact that increasing the flow rate decreased the contact time be-
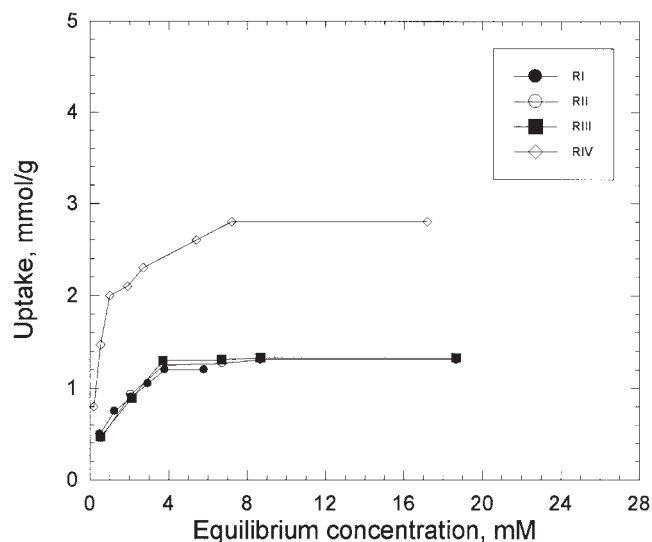


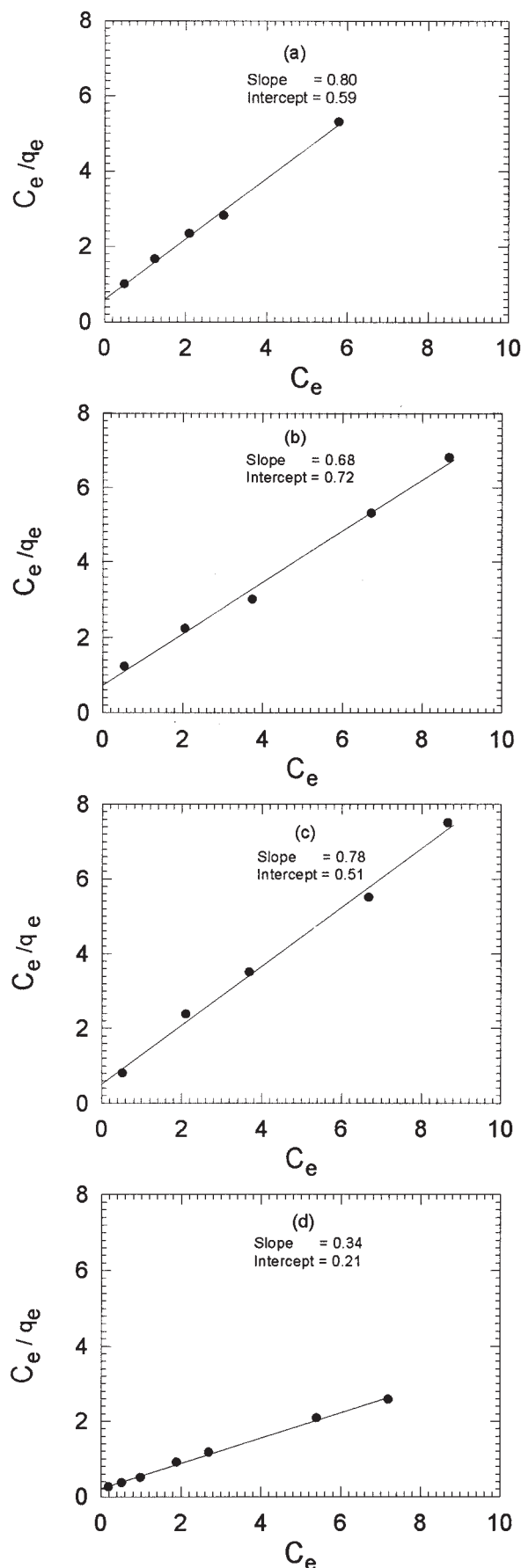**Figure 4** Adsorption isotherms of Ag(I) by the resins at natural pH and 28 ± 1°C.

**Figure 5** Langmuir plots for the adsorption data of Ag(I) on the resins: (a) RI, (b) RII, (c) RIII, and (d) RIV.

**TABLE II**
**Parameters of the Langmuir Adsorption**
**Isotherm for Ag(I) on the Resins**

| Resin | $q_s$ (mmol/g) | $K$ (L/mmol) |
|-------|----------------|--------------|
| RI | 1.2 | 1.3 |
| RII | 1.4 | 0.9 |
| RIII | 1.3 | 1.5 |
| RIV | 2.8 | 1.7 |

tween the Ag ions and the resin. In practical application, the management between the extent of uptake and the time must be taken into consideration.

**Elution**

The elution of Ag(I) from the resins was performed with thiourea, acidified thiourea, and $H_2SO_4$ at different concentrations and a flow rate of 1 mL/min. The elution data are given in Table IV. The elution efficiency (%) was verified with the following equation:

Elution efficiency (%)

$$= \frac{\text{Total uptake in the second run}}{\text{Total uptake in the first run}} \times 100\% \quad (6)$$

The elution of Ag(I) from all of the studied resins improved as the initial concentration of the acid increased. With $0.5N$ $H_2SO_4$, elution efficiencies of 96, 93, 94, and 90% were achieved for the RI, RII, RIII and RIV resins, respectively. Moderate concentrations of the acid could be used for blending with thiourea. An elution efficiency of $91 \pm 2\%$ was reached with the $0.1N$ $H_2SO_4/0.5N$ thiourea mixture. The elutions of Ag(I) from resins RII and RIV were less efficient than those of RI and RIII. This again explained the higher binding of Ag(I) with the resins containing sulfur compared to those containing nitrogen (see the $K$ values; Table II). We recommend the use of $H_2SO_4$ and the avoidance of HCl or $HNO_3$ for the elution of Ag(I) due to the possibility of the formation of exchangeable anions of $AgCl_2^-$ and $Ag(NO_3)_2^-$.

Repeated elution did not significantly affect the efficiency of the resins. The maximum uptake of the

**TABLE III**
**Effect of Flow Rate on the Uptake of Ag(I) on the Resins**

| Flow rate (mL/min) | Uptake (mmol/g) | | | |
|---|---|---|---|---|
| | RI | RII | RIII | RIV |
| 1 | 1.18 | 1.35 | 1.40 | 2.73 |
| 2 | 1.18 | 1.30 | 1.38 | 2.61 |
| 3 | 1.00 | 1.18 | 1.20 | 2.02 |
| 4 | 0.90 | 1.08 | 1.10 | 1.64 |
| 5 | 0.78 | 1.00 | 1.05 | 1.08 |

**TABLE IV**
**Elution Efficiency of the Resins with**
**$H_2SO_4$ and Thiourea**

| Eluent | Concentration ($N$) | Elution efficiency (%) | | | |
|---|---|---|---|---|---|
| | | RI | RII | RIII | RIV |
| $H_2SO_4$ | 0.1 | 79 | 78 | 76 | 70 |
| | 0.2 | 83 | 82 | 81 | 79 |
| | 0.5 | 96 | 93 | 94 | 90 |
| Thiourea | 0.5 | 45 | 50 | 51 | 46 |
| Thiourea + $H_2SO_4$ | 0.5 | 91 | 93 | 91 | 89 |
| | 0.1 | | | | |

recycled resins was 97% of the fresh resins over five cycles.

## CONCLUSIONS

The uptake of Ag(I) by the obtained resins was investigated with the batch and column methods. Resin RIV showed a high affinity toward the Ag ion, with an uptake up to 2.85 mmol/g. The uptake of Ag(I) in the presence of HCl and $HNO_3$ was attributed to the formation of the anions $Ag(Cl)_2^-$ and $Ag(NO_3)_2^-$, respectively. These anions were able to exchange with conjugate anions on the resin surface. The elution of the Ag(I) loaded on the resin surface was successfully done with $H_2SO_4$ or acidified thiourea. We do not recommend the use HCl or $HNO_3$ for the elution of Ag(I). The obtained resins were stable over five cycles.

## References

1. Absalan, G.; Mehrdjardi, M. A. Sep Purif Technol 2003, 33(1), 95.
2. Ajiwe, V. I. E.; Anyadiegwu, I. E. Sep Purif Technol 2000, 18(2), 89.
3. Tunçeli, A.; Türker, A. R. Talanta 2000, 51, 889.
4. Trochimczuk, A. W.; Kolarz, B. N. Eur Polym J 2000, 36, 2359.
5. Cárdenas, G.; Muñoz, C.; Rodriguez, M.; Morales, J.; Soto, H. Eur Polym J 1999, 35, 1017.
6. Patterson, J. W. Industrial Wastewater Treatment Technology, 2nd ed.; Butterworth: London, 1985.
7. Das, D.; Das, A. K.; Sinha, C. Talanta 1999, 48, 1013.
8. Sakamotoa, H.; Ishikawab, J.; Koikeb, M.; Doib, K.; Wadab, H. React Funct Polym 2003, 55, 299.
9. Iglesias, M.; Antico, E.; Salvado, V. Solvent Extr Ion Exch 2001, 19, 315.
10. Dong, S.; Zhang, W.; Hu, Y.; Xu, Y. Nat Sci 2000, 5(1),98.
11. Geckeler, K. E.; Bayer, E.; Spivakov, B. Y.; Shkinev, V. M.; Vorob'eva, G. A. Anal Chim Acta 1986, 189, 285.
12. Maeda, H.; Egawa, H. Anal Chim Acta 1984, 162, 339.
13. Ni, C.; Yi, C.; Feng, Z. J Appl Polym Sci 2001, 82, 3127.
14. Atia, A. A.; Donia, A. M.; Abou-El-Enein, S. A.; Yousif, A. M. Sep Purif Technol 2003, 33(3), 295.
15. Atia, A. A.; Donia, A. M.; Yousif, A. M. React Funct Polym 2003, 56, 75.
16. Xu, Y. W.; Zhang, C. C.; Dong, S. H. Acta Polym Sinica 1989, 1, 109.
17. West, T. S. Complexometry with EDTA and Related Reagents, 3rd ed.; BDH Chemicals: 1969.
18. Kawamura, Y.; Mitsuhashi, M.; Tanibe, H. Ind Eng Chem Res 1993, 32, 386.
19. Qi, T.; Sonoda, A.; Makita, Y.; Kanoh, H.; Ooi, K.; Hirotsu, T. Ind Eng Chem Res 2002, 41, 133.