
## Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Separation and Recovery of Silver(I) Ions from Base Metal Ions by Thiourea- or Urea-Formaldehyde Chelating Resin

Serap Kırcı[a]; Mustafa Gülfen[a]; Ali Osman Aydın[a]
[a] Department of Chemistry, Faculty of Arts & Sciences, Sakarya University, Esentepe Campus, Sakarya, Turkey

**To cite this Article** Kırcı, Serap , Gülfen, Mustafa and Aydın, Ali Osman(2009) 'Separation and Recovery of Silver(I) Ions from Base Metal Ions by Thiourea- or Urea-Formaldehyde Chelating Resin', Separation Science and Technology, 44: 8, 1869 — 1883

**To link to this Article: DOI:** 10.1080/01496390902885163

**URL:** http://dx.doi.org/10.1080/01496390902885163

*Separation Science and Technology*, 44: 1869–1883, 2009

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390902885163

# Separation and Recovery of Silver(I) Ions from Base Metal Ions by Thiourea- or Urea-Formaldehyde Chelating Resin

**Serap Kırcı, Mustafa Gülfen, and Ali Osman Aydın**
Department of Chemistry, Faculty of Arts & Sciences, Sakarya University, Esentepe Campus, Sakarya, Turkey



**Abstract:** In the present work, thiourea-formaldehyde (TF) and urea-formaldehyde (UF) chelating resins have been synthesized and they have been used in the adsorptions of Ag(I), Cu(II), and Zn(II) metal ions by batch and column methods. The effect of initial acidity of Ag(I) solution and the adsorption capacities of TF and UF resins by batch method and the separation of Ag(I) ions from Cu(II) and Zn(II) base metal ions by the column method were examined experimentally. The adsorption capacities of TF and UF resins were found as 58.14 and 47.39 mg Ag(I)/g by batch method and 30.7 and 4.66 mg Ag(I)/g, 0.80 and 0.121 mg Cu(II)/g, and under 0.002 mg Zn(II)/g by the column method, respectively. It was found that Ag(I) ions showed higher affinity towards TF resin than UF resin, compared with Cu(II) or Zn(II) ions, and Ag(I) could be separated more effectively by TF resin from Cu(II)and Zn(II) ions.

**Keywords:** Adsorption, chelating resin, separation, silver(I), thiourea-formaldehyde (TF), urea-formaldehyde (UF)

## INTRODUCTION

Silver is a heavy, noble, and precious metal. It has wide applications and usage in different areas; jewelry, catalyst, dentistry, electricity, medicine,

Received 11 May 2008; accepted 9 January 2009.
Address correspondence to Dr. Mustafa Gülfen, Department of Chemistry, Faculty of Arts & Sciences, Sakarya University, Esentepe Campus, Sakarya, TR-54187, Turkey. Tel.: +90 264 2956051; Fax: +90 264 2955950. E-mail: mgulfen@sakarya.edu.tr

and photography etc. It has been reported that 25% of the world's silver needs are supplied by recycling. The recycling of silver also includes the recovery or separation of Ag(I) ions. Ag(I) ions can be recovered selectively using chelating resins (1,2).

Chelating or coordinating resins are polymers with covalently bound functional groups containing one or more donor atoms which are capable of forming complexes directly with metal ions. These polymers can also be used for a specific separation of one or more metal ions from solutions with different chemical environment (3). In chelating resins, functional group atoms most frequently used are nitrogen (e.g., N presents in amines, azo groups, amides, nitriles), oxygen (e.g., O presents in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g., S presents in thiols, thiocarbamates, thioethers). The nature of the functional group will give an idea of the selectivity of the ligand towards metal ions (1,4–8).

Ag(I) is a good soft metal ion which forms stable complexes with the ligands including (N) and (S) donor atoms, in solutions or on the surface of solids. It has the effective ionic radii of 2.5 $A^0$, in aqueous solutions. A lot of metal ions have bigger effective ionic radii (For examples, Cu(II):6, Zn(II):6, Mg(II):8, Fe(III):9, Al(III):9, Zr(IV):11 $A^0$) (9). The fact that Ag(I) has low effective ionic radii is that it has low ionic and high chelating interactions according to the hard-soft acid-base (HSAB) theory by Pearson (10). Hence, the chelating resins containing sulfur and nitrogen as donor atoms have great attention due to their selectivity towards Ag(I) ions as soft metal ion (11–14).

Many researchers have studied the recovery, preconcentration, and separation of Ag(I) ions as well as other metal ions in different samples. There are a number of reports of different types of chelating resins used in the separation, preconcentration, or recovery of Ag(I) ions and including functional groups; 2-mercaptobenzothiazole (12), thiol, purolite thiomethyl, spheron thiol (13), thiourea (2,3,14), amino-mercapto (15), polythiazaalkane (16), thioureas, dithiocarbamate (17), and bisthiourea (18).

Thiourea-formadehyde (TF) including (N) and (S) and urea formaldehyde (UF) including (N) and (O) donor atoms are examples of chelating resins. They can be prepared easily in aqueous media and have high thermal stability and selectivity. In the present work, TF resin containing (S) donor atom was compared with UF resin containing (O) donor atom in the separation and recovery of Ag(I) ions from Cu(II) and Zn(II) base metal ions. For this aim, TF and UF resins were synthesized. The uptake and elution behaviors of these resins towards Ag(I) were investigated by batch and column methods to separate and recover Ag(I) ions from Cu(II) and Zn(II) base metal ions.

## EXPERIMENTAL

### Chemicals

The stock solutions of Ag(I), Cu(II), and Zn(II) were prepared from $AgNO_3$, $Cu(CH_3COO)_2$ and $Zn(NO_3)_2$ (Merck Co. Germany) respectively. Thiourea, urea, and formaldehyde (37% wt. solution) used in the syntheses of TF and UF resins were supplied from Fluka Co. Switzerland. The other reagents used in the experimental studies were of analytical grade and supplied from Merck Co. Germany.

### Synthesis of TF and UF Resins

TF and UF resins were synthesized according to amine-formaldehyde reactions (2,6,19–28). The molar ratio of thiourea or urea to formaldehyde was used as 1:1 in this study. In a beaker, 15.2 g of thiourea (0.2 mol) or 12.0 g of urea (0.2 mol) was mixed with 16.2 g of formaldehyde solution (0.2 mol). NaOH was added into the mixture so that the pH was increased to 8–10. The mixture was heated at around 353 K until all reactants were dissolved. The syntheses were continued by acid-catalyzed condensation reaction by adding HCl solution, and then UF or TF condensates began to precipitate. The condensates were filtered and washed with acid and water. Then the resins were dried at 378 K and powdered below the particle size of 150 μm. These powdered resins were used in the experimental studies. They were characterized by elemental analysis (20–28).

### Batch Method Studies

Ag(I) solutions used in the experimental studies were prepared by diluting stock $AgNO_3$ solution. Initial pH or acidity of Ag(I) solutions was adjusted with acetate buffer, $HNO_3$ or NaOH solution and Cu(II) and Zn(II) ions were added into Ag(I) solutions.

The uptake tests of the metal ions by batch method were performed to determine the optimum initial acidity and Ag(I) adsorption capacities of the resins. The effect of the initial acidity or pH was studied at 1 M $HNO_3$ concentration and pH 1–6. Therefore, 0.1 g of TF or UF resin was placed into 100 mL Ag(I) solution in a beaker. The uptake studies were carried out with 100 mL of Ag(I) solutions at initial concentration of 100 mg/L in the competitive conditions with 100 mg/L Cu(II) and Zn(II) ions.

Ag(I) adsorption capacities of the resins were studied with 0.1 g TF resin in 100 mL Ag(I) solutions at 75, 100, 125, and 150 mg/L concentrations, or

0.1 g UF resin in 100 mL Ag(I) solutions at 10, 20, 30, 40, and 50 mg/L concentrations in the competitive conditions with Cu(II) and Zn(II) at similar concentrations. The all batch method studies were performed at 298 K temperature. The concentrations of the metal ions in the samples collected before adsorption and at equilibrium time of 30 min. were determined by an atomic absorption spectrophotometer. The adsorption values were calculated according to initial concentrations.

### Column Method Studies

A glass column of 10 cm length and 0.8 cm inner diameter was packed with 1.0 g UF or TF resin. The column bed was conditioned firstly with 0.1 M $KNO_3$ for ionic effect exposure. The feed solutions including 200 mg/L Ag(I), Cu(II), and Zn(II) metal ions were passed through the column. The adsorption and the elution studies of the metal ions were carried out at a constant flow rate (1 mL/min.) using a peristaltic pump and at 298 K temperature. Ag(I), Cu(II), and Zn(II) ions loaded onto the resins were eluted by acidified thiourea solution (0.5 M thiourea +0.5 M $HNO_3$). The concentrations of the metal ions in each 10 mL solution passed through from the column were determined by the atomic absorption spectrophotometer.



### Instruments

The elemental analyses of UF and TF resins were performed with the use of a LECO CHNS 932 elemental analyzer (Leco Co. USA) by Tubitak in Ankara, Turkey. The column studies were performed with a column of 10 cm length and 0.8 cm inner diameter. A constant flow rate during adsorption or elution in the column studies was provided with a peristaltic pump (Masterplex, Cole-Polmer Ins. Co. UK). The concentrations of the metal ions were determined by an atomic absorption spectrophotometer (Shimadzu, AAS-6701 F, Japan). All pH measurements were made with a Hanna pH211 pH meter (Italy). In addition, ionic species were calculated with MINTEQA2 computer program for Windows by Allison Geoscience Consultants, Inc. and HydroGeoLogic, Inc.

## RESULTS AND DISCUSSION

### Elemental Analysis

The elemental analysis was carried out on the synthesized TF and UF chelating resins in order to determine C, N, H and S contents. The

**Table 1.** Elemental analyses of TF and UF resins

| | TF | UF |
|---|---|---|
| C | 26.77 | 30.34 |
| N | 28.69 | 32.35 |
| H | 4.158 | 5.902 |
| S | 33.26 | – |
| O (from difference) | 7.122 | 31.4 |

obtained results are given in Table 1. The elemental analyses confirmed nearly the compositions of resins. It was found from the elemental analyses of the resins that there were oxygen contents in TF and as extra in UF resins.



## Batch Method Studies

### Effect of Initial Acidity on the Uptake of Silver(I) Ions

The effect of initial acidity on the uptake of Ag(I) ions was performed with 100 mL 100 mg/L Ag(I) solutions at 1 M $HNO_3$ concentration and pH 1–6. Since Ag(I) begins to precipitate as silver hydroxide, it was not studied at higher or alkaline pH values. The initial acidities of the solutions were adjusted with acetate buffer, $HNO_3$, or NaOH solutions. Also Cu(II) and Zn(II) were added into the Ag(I) solutions, to provide the competitive conditions at 100 mg/L concentrations for each metal ion.

The experimental results of the initial acidity effect obtained with TF and UF resins are given in Figs. 1 and 2, respectively. It was found that the maximum Ag(I) sorption onto TF was at pH 3. On the other hand, UF resin was the best at pH 2. It can be seen from Figs. 1 and 2 that TF will show a good performance at pH 3–5 and UF will at pH 1–2. In other words, UF resin requested to be more protonated than TF resin. TF resin had more Ag(I) uptake values at high pH, while UF was less uptake at low pH.

Ag(I) ions may interact with $(R_1R_2)NH_2^+$ functional group through ionic interaction or with (S) or (N) donor atoms through chelation. Ag(I) ions in an acidic solution including $NO_3^-$ and $CH_3COO^-$ anions, form $Ag^+_{(aq)}$ and $Ag^+CH_3COO^-_{(aq)}$ as major species, and $Ag^+NO^-_{3\,(aq)}$ and $Ag(CH_3COO)_2^-$ as minor species. These species were calculated with MINTEQA2 for Windows by Allison Geoscience Consultants, Inc. and HydroGeoLogic, Inc. Ionic interactions and chelation reactions may be expressed by Eqs. 1–4 (2,6,26–29).

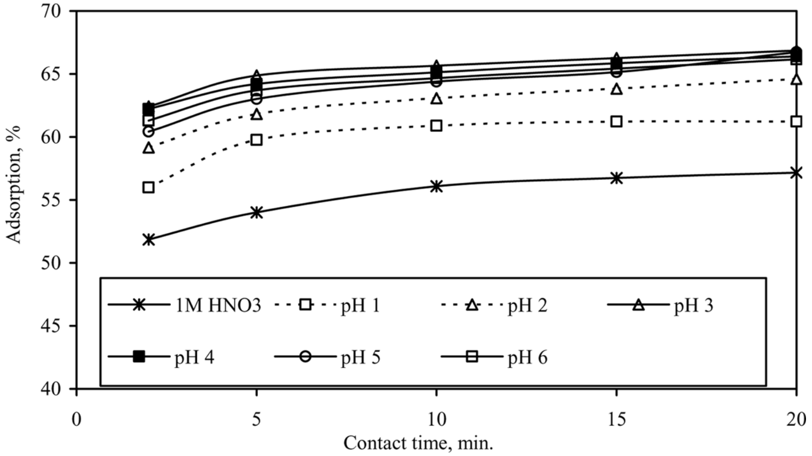


*Figure 1.* The effect of initial acidity on the uptake of Ag(I) onto TF (0.1 g resin; 100 mL solution; 100 mg/L Ag(I), Cu(II), and Zn(II); 298 K).

## Ionic Interactions

$$(R_1R_2)NH_2^+NO^-_{3\,(s)} + Ag^+_{(aq)} = (R_1R_2)NH_2^+NO_3^-Ag^+_{(s)} \tag{1}$$

$$(R_1R_2)NH_2^+NO^-_{3\,(s)} + Ag(CH_3COO)^-_{2\,(aq)} = (R_1R_2)NH_2^+Ag(CH_3COO)^-_{2\,(s)} + NO^-_{3\,(aq)} \tag{2}$$

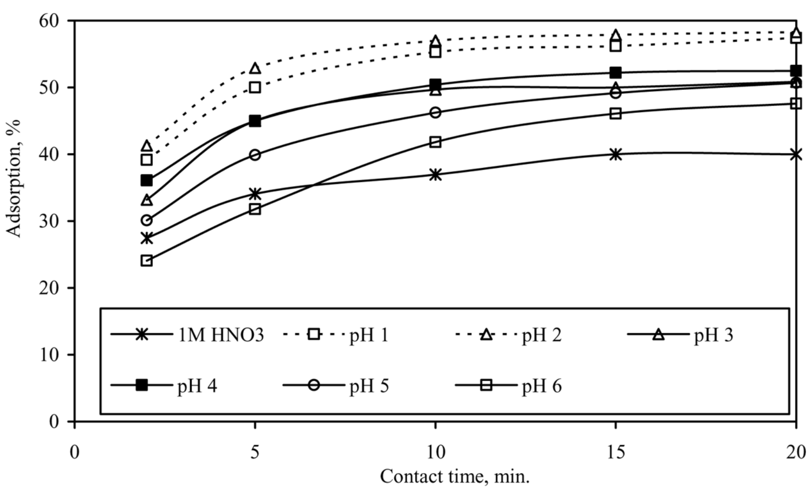


*Figure 2.* The effect of initial acidity on the uptake of Ag(I) onto UF (0.1 g resin; 100 mL solution; 100 mg/L Ag(I), Cu(II), and Zn(II); 298 K).

Chelation:

$$(R_1R_2)NH^+_{2\,(s)} + Ag^+_{(aq)} = (R_1R_2)HN\ldots Ag^+_{(s)} + H^+_{(aq)} \tag{3}$$

$$(R_1R_2)C = S_{(s)} + Ag^+_{(aq)} = (R_1R_2)C = S\ldots Ag^+_{(s)} \tag{4}$$

TF resin showed high Ag(I) uptake at pH values of 3–5 and UF resin was at pH values of 1–2. The fact that more Ag(I) uptake with TF at higher pH values confirms that sulfur atoms in TF resin contributed Ag(I) uptake by chelation. On the other hand UF resin requested more protonation. This shows that the uptake of Ag(I) ions onto UF resin is governed by more ionic interaction.

According to the experimental results, the optimum pH values of 3 and 2 were selected for TF and UF, respectively. So Ag(I) solutions adjusted to pH 3 or 2 were used in the later experimental studies.



## Silver(I) Adsorption Capacities of the Resins

It was as though a monolayer adsorption with the functional groups on the chelating resins occurred. Therefore, the Langmuir equation was used to determine Ag(I) adsorption capacities of TF and UF resin. Linear Langmuir equation is given by Eq. 5,

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}}\frac{1}{C_e} \tag{5}$$

where $Q_{max}$ and $q_e$ are the maximum adsorption capacity (mg/g) and the concentration of Ag(I) ions on the resin (mg/g), respectively; Ce is the equilibrium concentration of Ag(I) ions in the solution (mg/L), and b is a constant related to the energy of adsorption (L/mg) (26,29).

Ag(I) adsorption capacities of the resins were studied by batch method, by putting 0.1 g resin into 100 mL of Ag(I) solution containing Cu(II) and Zn(II) metal ions at the different concentrations, and stirring for 30 min. contact time at 298 K temperature. The prepared Ag(I) solutions had 75, 100, 125 and 150 mg/L concentrations with TF resin, or 10, 20, 30, 40, and 50 mg/L concentrations with UF resin in the competitive conditions with Cu(II) and Zn(II) at similar concentrations. Ag(I) adsorption capacities of TF and UF resins were calculated from the plots of $1/q_e$ versus $1/C_e$ in Fig. 3. It was found that Ag(I) adsorption capacities of TF and UF resins were 58.14 and 47.39 mg Ag(I)/g, respectively. The values of b constant for the adsorption of Ag(I) were also calculated as 0.0043 L/mg with TF and 0.0291 L/mg with UF resin. The experimental results showed that TF resin had more Ag(I) adsorption capacity than UF resin.

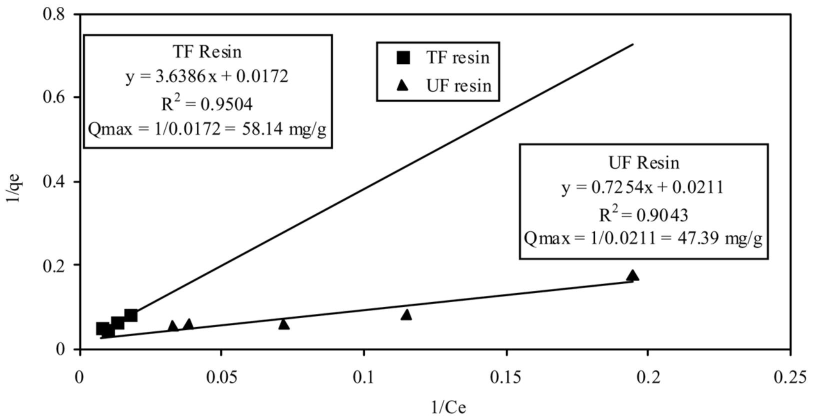


***Figure 3.*** Langmuir isotherms with TF and UF resins (0.1 g resin; 100 mL solution; 75, 100, 125 and 150 mg/L Ag(I), Cu(II) and Zn(II) with TF; 10, 20, 30, 40, and 50 mg/L Ag(I), Cu(II), and Zn(II) with UF; 298 K).



## Column Method Studies

### Adsorption of Silver(I) Ions

In the column studies, first the adsorption of the Ag(I) ions was examined. The breakthrough curves obtained for Ag(I) ions with TF and UF resins were plotted as $C/C_0$ dimensionless concentration factor (where C is the concentration of the metal ion in the solution at the outlet of the column and $C_0$ is the initial concentration of the metal ion in the feed solution) versus to bed volume (BV) (Fig. 4). The breakthrough curves agree with the results obtained from batch method experiments. It was found that TF resin was more efficient in the breakthrough point ($C/C_0$:0.05), the chromatographic point ($C/C_0$:0.50) or the dynamic capacity ($C/C_0$:90) than UF resin.

### Elution of Silver(I) Ions

Ag(I) ions adsorbed onto TF or UF resin were eluted by the use of 0.5 M thiourea in 0.5 M $HNO_3$ solution. The elution results are given Fig. 5. In the adsorption study, the solution having 200 mg/L Ag(I) ions had been used. At the end of elution, it was found that the first 10 mL-elution solution included 3020 mg/L Ag(I) concentration with TF and 450 mg/L Ag(I) concentration with UF resin. In other words, the TF resin had more Ag(I) adsorption capacity or Ag(I) ions can be more concentrated with TF resin than UF resin.

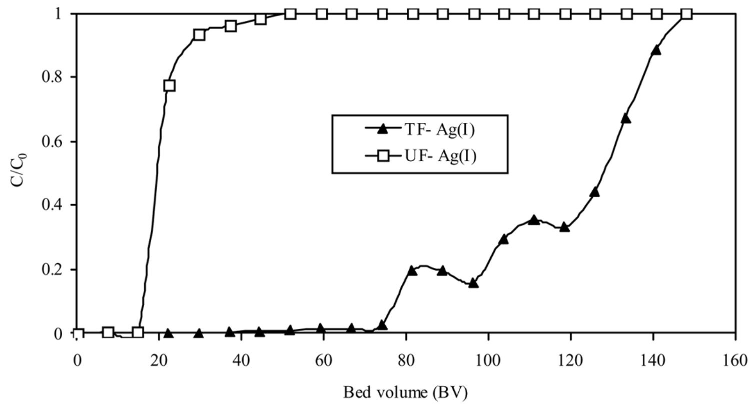


***Figure 4.*** The breakthrough curves for the adsorption of Ag(I) onto TF and UF (1 g resin; Dry BV: 1.35 mL; 200 mg/L Ag(I); pH = 3 with TF, pH = 2 with UF; Flow rate: 1 mL/min.; 298 K).



## Separation of Silver(I) from Copper(II) and Zinc(II) Ions

The separation of Ag(I) ions from the base metal ions is attractive since silver is a precious metal. In the experimental studies, Cu(II) and Zn(II) ions were selected as base metal ions. Their properties are near the soft metal ions and they occur together with precious metals in ores or wastes. All the adsorption studies were in the competitive conditions. In the column studies, Cu(II) and Zn(II) ions were also analyzed and the results are

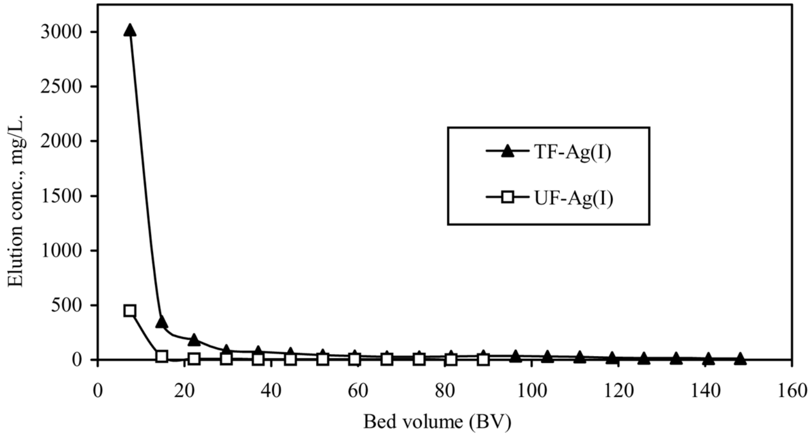


***Figure 5.*** The elution of Ag(I) from TF and UF (Feed solution: 0.5 M thiourea +0.5 M $HNO_3$; Flow rate: 1 mL/min.; 298 K).

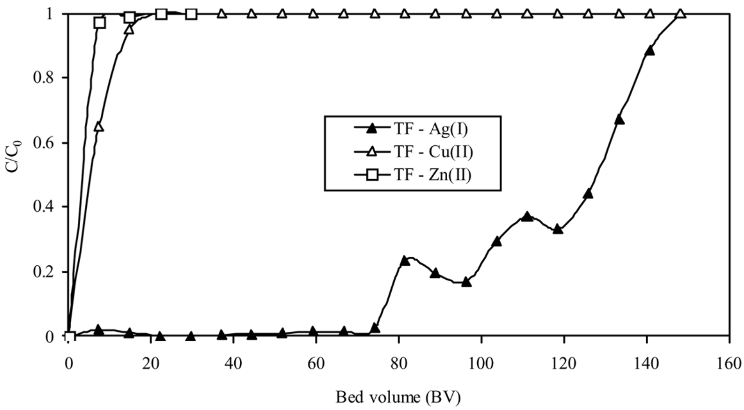


***Figure 6.*** The breakthrough curves for the adsorptions of Ag(I), Cu(II) and Zn(II) onto TF (1 g resin; Dry BV: 1.35 mL; 200 mg/L for each metal ions; pH = 3; Flow rate: 1 mL/min.; 298 K).

given together with Ag(I) as breakthrough curves in Figs. 6 and 7, and as elution profiles in Figs. 8 and 9. Both of the two resins showed more affinity towards Ag(I) ions. Ag(I) ions were concentrated after first adsorption-elution cycle. However, Cu(II) and Zn(II) ions were diluted. These results showed that Ag(I) will be separated and concentrated from the solutions containing Cu(II) and Zn(II) base metal ions. Moreover, in the column studies, the TF chelating resin showed better

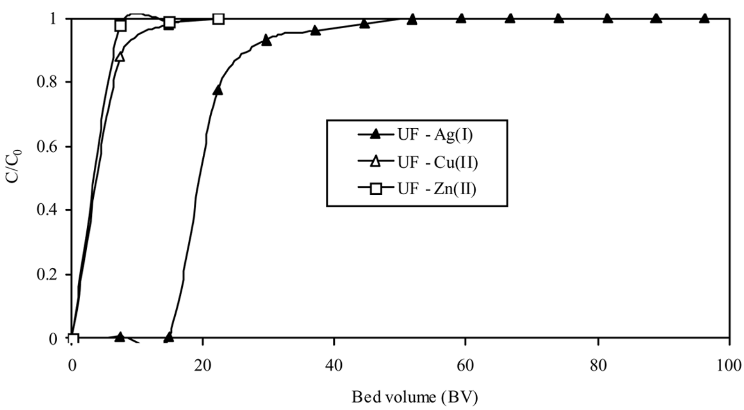


***Figure 7.*** The breakthrough curves for the adsorptions of Ag(I), Cu(II) and Zn(II) onto UF (1 g resin; Dry BV: 1.35 mL; 200 mg/L for each metal ions; pH = 2; Flow rate: 1 mL/min.; 298 K).

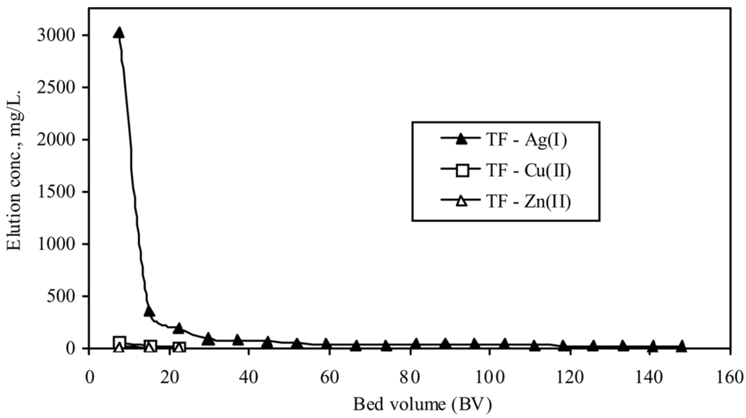


***Figure 8.*** The elutions of Ag(I), Cu(II) and Zn(II) from TF (Feed solution: 0.5 M thiourea +0.5 M $HNO_3$ Flow rate: 1 mL/min.; 298 K).



results in the separation and concentration of Ag(I) ions compared to UF chelating resin.

## Elution Efficiency and Reuse Tests

Ag(I) elution efficiencies from TF and UF resin were calculated for first adsorption-elution cycle. It was found that the elution ratios of Ag(I) ions from TF resin were 98.40% and 96.57% from UF resin. In addition, the

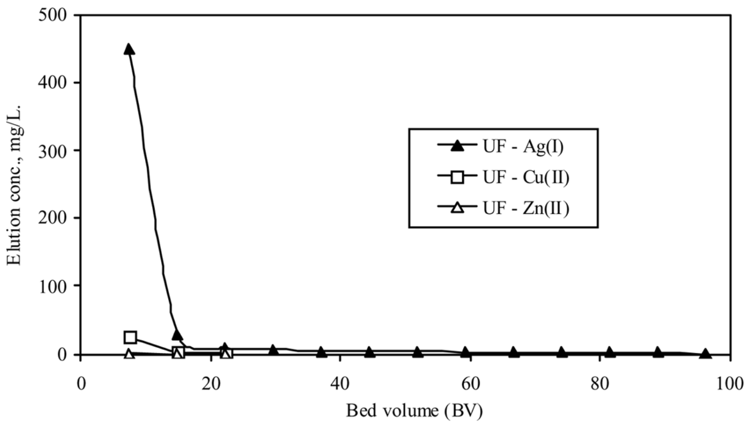


***Figure 9.*** The elutions of Ag(I), Cu(II) and Zn(II) from UF (Feed solution: 0.5 M Thiourea +0.5 M $HNO_3$ Flow rate: 1 mL/min.; 298 K).

reuse tests were examined for three adsorption-elution cycles. After the first cycle, Ag(I) adsorption capacities of the both resins increased a little more. This increase may be due to increase in contact surface of the resins with the solution.

## Column Adsorption Capacities of TF and UF Resins

The dynamic adsorption capacities ($C/C_0$:0.90) of TF and UF resins for Ag(I), Cu(II) and Zn(II) ions were examined by column method. The results are given in Fig. 10 for TF and Fig. 11 for UF. It was found that the dynamic adsorption capacities of the TF resin were 30.7 mg Ag(I)/g, 0.80 mg Cu(II)/g and under 0.002 mg Zn(II)/g and the capacities of TF resin were 4.66 mg Ag(I)/g, 0.121 mg Cu(II)/g and under 0.002 mg Zn(II)/g.

In an acidic solution including $NO_3^-$ and $CH_3COO^-$ anions, Cu(II) ions form $[Cu(CH_3COO)]^+$, $[Cu(CH_3COO)_2]_{(aq)}$ and $[Cu(CH_3COO)_3]^-$ as major species and, $Cu^{2+}$ or $[Cu(H_2O)_4]^{2+}$ as minor species. Zn(II) ions are $[Zn(CH_3COO)]^+$, $[Zn(CH_3COO)_2]_{(aq)}$ and, $Zn^{2+}$ or $[Zn(H_2O)_4]^{2+}$ as major species, and $[ZnNO_3]^+$ as minor species. These species were calculated with MINTEQA2 for Windows by Allison Geoscience Consultants, Inc. and HydroGeoLogic, Inc. Anionic complexes can interact with protonated amines on the resins at the beginning of the adsorption. Cationic complexes can not interact. Moreover, Ag(I) is a very good soft acid. It can be coordinated easily by soft base ligands or sulfur and nitrogen atoms on the resins. Ag(I) is very competitive in the adsorption by TF



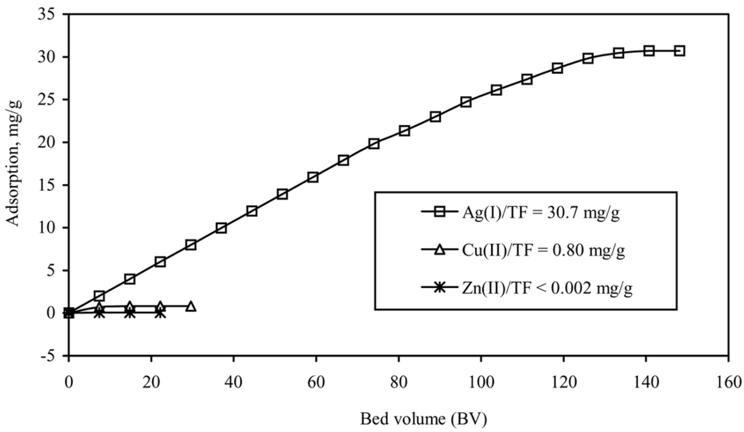


***Figure 10.*** Ag(I), Cu(II) and Zn(II) adsorption capacities of TF resin.

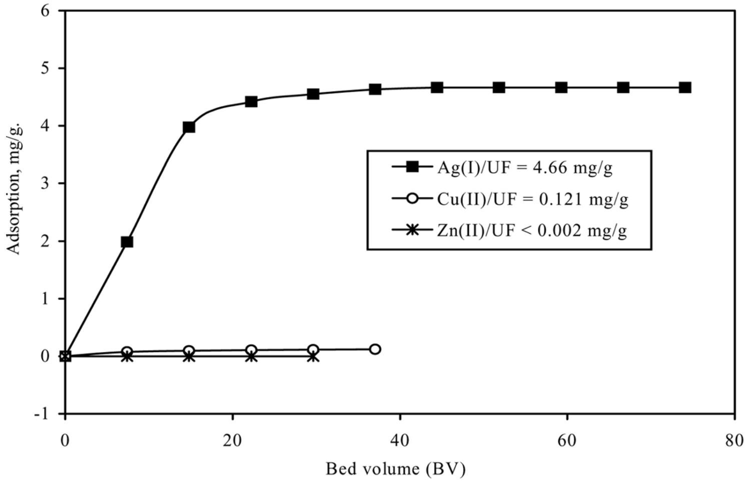


***Figure 11.*** Ag(I), Cu(II) and Zn(II) adsorption capacities of UF resin.



and UF resins when it is together with Cu(II) and Zn(II) ions. Similarly, Ag(I) will be competitive in the adsorptions by chelating resin containing sulfur or nitrogen in case of many other hard acids and cationic complexes.

TF chelating resin containing sulfur and nitrogen donor atoms showed more Ag(I) adsorption capacity in both batch and column experiments than UF resin containing oxygen and nitrogen atoms. Sulfur is a softer base than oxygen. Sulfur atoms contributed the adsorption of Ag(I) ions by chelating mechanism.

## CONCLUSIONS

The separation and recovery of Ag(I) ions over Cu(II) and Zn(II) base metal ions by thiourea-formaldehyde (TF) and urea-formaldehyde (UF) chelating resins were investigated by the batch and column methods. The adsorption capacities of TF and UF resins were found as 58.14 and 47.39 mg Ag(I)/g by batch method and 30.7 and 4.66 mg Ag(I)/g, 0.80 and 0.121 mg Cu(II)/g and under 0.002 mg Zn(II)/g by column method, respectively. Ag(I) ions showed higher affinity towards TF resin than UF compared with Cu(II) or Zn(II). It was found that Ag(I) ions could be separated more effectively by TF resin from Cu(II)and Zn(II) ions. It was concluded that sulfur atoms contributed the adsorption of Ag(I) ions by chelation mechanism.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the Scientific Research Commission at Sakarya University in Turkey for the financial support of this work *(Project No: 2007-50-01-29)*.

## REFERENCES

1. Hasany, S.M.; Ahmad, R. (2004) Removal of traces of silver ions from aqueous solutions using coconut husk as a sorbent. *Separ. Sci. Technol.*, *39* (15): 3509.
2. Yirikoglu, H.; Gulfen, M. (2008) Separation and recovery of silver(I) ions from base metal ions by melamine-formaldehyde-thiourea (MFT) chelating resin. *Separ. Sci. Technol.*, *43* (2): 376.
3. Zuo, G.; Muhammed, M. (1995) Thiourea-based coordinating polymers: synthesis and binding to noble metals, *React. Polym.*, *24* (3): 165.
4. Camel, V. (2003) Solid phase extraction of trace elements. *Spectrochim. Acta B*, *58* (7): 1177.
5. Bilba, D.; Bejan, D.; Tofan, L. (1998) Chelating sorbents in inorganic chemical analysis. *Croat. Chem. Acta*, *71* (1): 155.
6. Aydin, A.; Imamoglu, M.; Gulfen, M. (2008) Separation and recovery of gold(III) from base metal ions using melamine-formaldehyde-thiourea (MFT) chelating resin. *J. Appl. Polym. Sci.*, *107* (2): 1201.
7. Donia, A.M.; Atia, A.A.; Elwakeel, K.Z. (2005) Gold(III) recovery using synthetic chelating resin with amine, thio and amine/mercaptan functionalities. *Sep. Purif. Technol.*, *42* (2): 111.
8. Donia, A.M.; Atia, A.A.; Elwakeel, K.Z. (2007) Recovery of gold(III) and silver(I) on a chemically modified chitosan with magnetic properties. *Hydrometallurgy*, *87* (3–4): 197.
9. Dean, J.A. (1999) *Lange's Handbook of Chemistry,* 5th Ed; McGraw-Hill, Inc.: New York, p. 8.83.
10. Pearson, G.R. (1963) Hard and soft acids and bases. *J. Amer. Chem. Soc.*, *85* (22): 3533.
11. Donia, A.M.; Atia, A.A.; El-Boraey, H.A.; Mabrouk, D.H. (2006) Adsorption of Ag(I) on glycidyl methacrylate/N,N '-methylene bis-acrylamide chelating resins with embedded iron oxide. *Sep. Purif. Technol.*, *48* (3): 281.
12. Absalan, G.; Mehrdjardi, M.A. (2003) Separation and preconcentration of silver ion using 2-mercaptobenzothiazole immobilized on surfactant-coated alumina. *Sep. Purif. Technol.*, *33* (1): 95.
13. Iglesias, M.; Antico, E.; Salvado, V. (2001) The characterisation of silver sorption by chelating resins containing thiol and amine groups. *Solvent Extr. Ion Exc.*, *19* (2): 315.
14. Ni, C.; Yi, C.; Feng, Z. (2001) Studies of syntheses and adsorption properties of chelating resin from thiourea and formaldehyde. *J. Appl. Polym. Sci.*, *82* (13): 3127.

15. Zhang, C.; Li, X.; Pang, J. (2001) Synthesis and adsorption properties of magnetic resin microbeads with amine and mercaptan as chelating groups. *J. Appl. Polym. Sci.*, *82* (7): 1587.
16. Sakamoto, H.; Ishikawa, J.; Koike, M.; Doi, K.; Wada, H. (2003) Adsorption and concentration of silver ion with polyrner-supported polythiazaalkane resins. *React. Funct. Polym.*, *55* (3): 299.
17. Trochimczuk, A.W.; Kolarz, B.N. (2000) Synthesis and chelating properties of resins with methylthiourea, guanylthiourea and dithiocarbamate groups. *Eur. Polym. J.*, *36* (11): 2359.
18. Atia, A.A. (2005) Adsorption of silver(I) and gold(III) on resins derived from bisthiourea and application to retrieval of silver ions from processed photo films. *Hydrometallurgy*, *80* (1–2): 98.
19. Pascault, J.P. (2002) *Thermosetting Polymers*; Marcel Dekker Inc: New York.
20. Schanzer, F.H.; Bühner, H.G. (2002) Investigation the curing amino resins with TGA-MS and TGA-FT-IR. *Spectrosc. Eur.*, *14* (6): 21.
21. Christjanson, P.; Pehk, T.; Siimer, K. (2006) Hydroxymethylation and polycondensation reactions in urea-formaldehyde resin synthesis. *J. Appl. Polym. Sci.*, *100* (2): 1673.
22. Nalwa, H.S.; Vasudevan, P. (1983a) Electrical properties of melamine-thiourea-formaldeyhde. *Makromol. Chem-Rapid.*, *4* (1): 45.
23. Nalwa, H.S.; Vasudevan, P. (1983b) Thermally stimulated depolarization effect in thiourea-formaldehyde condensate. *Polymer*, *24* (9): 1197.
24. Nalwa, H.S.; Vasudevan, P. (1983c) Thiourea-formaldehyde condensate – Synthesis characterization and electrical-resistivity. *Mater. Res. Bull.*, *18* (7): 897.
25. Philbrook, A.; Blake, C.J.; Dunlop, N.; Eastona, C.J.; Kenirya, M.A.; Simpsona, J.S. (2005) Demonstration of co-polymerization in melamine-urea-formaldehyde reactions using N-15 NMR correlation spectroscopy. *Polymer*, *46* (7): 2153.
26. Birinci, E.; Gulfen, M.; Aydın, A.O. (2009) Separation and recovery of palladium(II) from base metal ions by melamine formaldehyde-thiourea (MFT) chelating resin. *Hydrometallurgy*, *95* (1–2): 15.
27. Ertan, E.; Gulfen, M. (2009) Separation of gold(III) ions from copper(II) and zinc(II) ions using thiourea-formaldehyde or urea-formaldehyde chelating resins. *J. Appl. Polym. Sci.*, *111* (6): 2798.
28. Ebewele, R.E.; Myers, G.E.; River, B.H. (1991) Polyamine-modified urea-formaldehyde resins. I. Synthesis, structure, and properties. *J. Appl. Polym. Sci.*, *42* (11): 2997.
29. Atia, A.A.; Donia, A.M.; Yousif, A.M. (2005) Comparative study of the recovery of silver(I) from aqueous solutions with different chelating resins derived from glycidyl methacrylate. *J. Appl. Polym. Sci.*, *97* (3): 806.