Separation and Recovery of Gold(III) From Base Metal Ions Using Melamine–Formaldehyde–Thiourea Chelating Resin

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ABSTRACT: Melamine–formaldehyde–thiourea (MFT) chelating resin has been prepared. Au^{3+} ions uptake behavior and selectivity of the chelating resin were investigated by both batch and column methods. MFT resin showed higher affinity toward Au^{3+} compared with base metal ions, Cu^{2+} and Zn^{2+}. The highest Au^{3+} uptake values were obtained at pH 2 and Au^{3+} adsorption capacity of the resin was calculated as 48 mg Au^{3+}/g resin (0.246 mmol Au^{3+}/g resin) by batch method. It was concluded that Au^{3+} ions could be selectively concentrated from the solution including Cu^{2+} and Zn^{2+} base metal ions by column method. J Appl Polym Sci 107: 1201–1206, 2008

Key words: melamin–formaldehyde–thiourea resin; chelating resin; gold(III); adsorption; elution

INTRODUCTION

Recovery of gold as a precious element attracted the attention of many researchers over many years. Gold is recovered from a wide variety of sources such as primary sources constituted by ores, and also secondary sources usually more complex such as copper nickel sulfide leach residues, copper and silver anode slimes, as well as recycled scraps. Methods which have been applied to the recovery of gold from its solutions include zinc-dust cementation,[1] carbon adsorption,[2] solvent extraction,[3] and ion exchange.[4–8] Carbon adsorption and ion exchange processes are less selective, and solvent extraction techniques cause the loss of solvent, which may be hazardous for the environment. For this reasons, chelating resins have been developed, taking advantage of the intrinsic selectivity provided by the grafted functional groups. Recently, chelating resins with various functionalities have also been widely used for concentrating and retrieving of gold.[9–27]

A chelating resin or polymer essentially consists of two components: the chelate forming functional group and the polymeric matrix or the support; the properties of both components determine the features.[14,27] Chelating or coordinating resins are polymers with covalently bound functional groups containing one or more donor atoms that 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. In these 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).[10,13,14,22,27] A number of sulfur-containing chelating resins were synthesized and used widely in preconcentration, separation, purification, and recovery of noble metals as well as gold. Polymers with covalently bonded functional groups containing donor sulfur atoms such as thiol,[10,21,23] thiourea,[22] bisthiourea,[13] dithizone,[25] thiosemicarbazide,[20,28] and other sulfides[19,24] have been applied for the selective sorption of noble metal or gold ions.

The chelating resins with functional groups including sulfur and nitrogen donor atoms are very efficient at chelating with precious metals according to hard–soft acid–base (HSAB) theory by Pearson.[29] Soft metal ions, for instance Au^{3+}, Ag^{+}, and Pd^{2+}, show affinity to soft bases with donor atoms as O $<$ N $<$ S. On the other hand, hard metal ions, for instance Cu^{2+}, Fe^{3+}, and Al^{3+}, show affinity to hard bases with donor atoms as O $>$ N $>$ S. Moreover, amino resins as chelating resins have ionic interaction properties by protonated amines.[12,14,27]

In the present work, melamine–formaldehyde–thiourea (MFT) resin containing S and N donor atoms

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were prepared and characterized. The uptake and elution behaviors of the MFT resin toward Au^{3+}, Cu^{2+}, and Zn^{2+} were investigated by both batch and column methods, to separate and recover Au^{3+} ions from base metals.

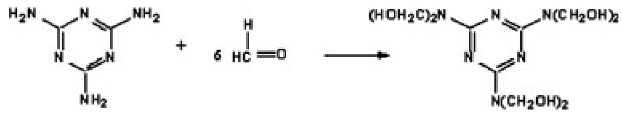
EXPERIMENTAL

Melamine (2,4,6-triamino-1,3,5-triazine), formaldehyde (formalin as solution), thiourea, and the other chemicals were obtained from Merck Company (Dermstadt, Germany). Gold solutions were prepared by dilution from standard solution ($HAuCl_4$, in 1*M* HCl). Initial pH values of the solutions were adjusted with either hydrochloric acid or sodium hydroxide solutions after adequate chloride (0.01*M* HCl) addition for $AuCl_4$. Cu^{2+} and Zn^{2+} solutions were prepared from, $Cu(CH_3COO)_2$ and $Zn(NO_3)_2$, respectively.

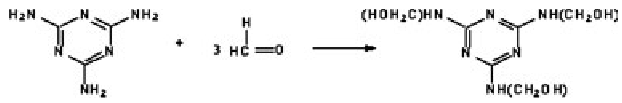
MFT resin can be synthesized by hydroxymethylation (Schemes 1–3) and condensation (Schemes 4–6) reactions.[30] Melamine, formaldehyde and thiourea at 1 : 5 : 1 molar ratio were taken into a 500-mL beaker. First, melamine and thiourea and then formaldehyde solution were added to reaction beaker. pH was increased with NaOH until solid reactants dissolved at 353 K temperature. At the same time, magnetic stirrer was used during synthesis. After dissolution of solid reactants or oligomers of melamine–metylol–thiourea, HCl solution was added as acid catalyst. Reaction mixture started developing the MFT polycondensates. For polycondensation by release of water, heating at 353 K was carried out. The obtained resin was collected by filtration and washed with HCl solution and then with distilled water. It was dried at 378 K and was grinded. Then the powder resin was washed with distilled water and dried at 378 K temperature several times. Resin ground to below 212 μm particle size, not processed for porosity, was used in the experimental studies.[30–32]

For batch tests, 1 g of the MFT resin was stirred in 100 mL solution including 100 ppm Au^{3+} ions examining pH effect and including 100–200 ppm Au^{3+}, Cu^{2+}, and Zn^{2+} ions examining selective or competitive adsorption for a certain period at room temperature. In the Au^{3+} adsorption capacity, experimental study was provided by equilibrating 0.1 g of the resin with 100 mL 250 ppm Au^{3+} solution for 120-min contact time. The amounts of the all metal ions on the resin were calculated from the analysis of the aqueous phase.

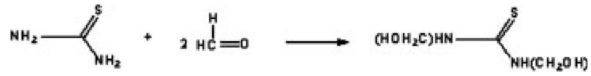
For column studies, a column with 0.80 cm inner diameter and 10 cm high was charged by 1 g of the resin. In all column studies, a peristaltic pump was used to pump the feed solution or the elution solution down flow through the column at 0.2 or 3.0 mL/min flow rate. The feed solution having 100 ppm Au^{3+}, Cu^{2+}, and Zn^{2+} metal ions at pH 2 was used. In the elution experiments were carried out using the 0.1*M* thiourea + 0.1*M* HNO_3 solution. The metal ions in the effluent was periodically collected and analyzed. The column studies were done at room temperature.



Scheme 1 MF(1 : 6) hydroxymethylation.



Scheme 2 MF (1 : 3) hydroxymethylation.



Scheme 3 TF(1 : 2) hydroxymethylation.

In the characterization of the resin, elemental analysis was performed by TUBİTAK, Marmara Research Center in Turkey, and FTIR spectra were recorded by a Mattson FTIR 60R spectrophotometer in KBr disk. A Shimadzu Model 6700 flame atomic absorption spectrophotometer (FAAS) was used for the determination of the metal ions in aqueous solutions before and after adsorption or elution.

RESULTS AND DISCUSSION

Characterization of the MFT resin

Elemental analysis

The elemental analysis was carried out on the synthesized MFT resin in order to determine C, N, H, and S content. The obtained results are given in Table I. It is seen that the prepared resin includes N and S donor atoms as chelating resin. In addition, the ligand concentrations were calculated as 25.57 and 3.28 mmol/g for N and S donor atoms, respectively. Moreover oxygen content was calculated from difference of all the other composition.

FTIR spectra

The obtained MFT resin was also characterized by FTIR analysis. FTIR spectra of the resin are given in Figure 1. The peak around 2930 cm^{-1} shows the C—H stretching absorption of methylene. The char-

Scheme 4 Polycondensation.

Scheme 5 Polycondensation.

Scheme 6 Polycondensation.

acteristic FTIR absorption band at 1592 cm^{-1} in the spectrum of the MFT resin is taken for the thiourea functional group. N—H stretching in secondary amines occurs at 3500–3300 cm^{-1} area. The peak at 1143 cm^{-1} was assigned for C—O—C.[9,32–35] Hence it was found that thiourea reacted within the resin. However, oxygen could not release completely. It was thought that N and S donor atoms on the surfaces of resin particles may be effective in adsorption. The structural formula of the resin was confirmed from the FTIR spectra and structure of the MFT resin is given in Figure 2.

Metal ions uptake using batch method

Effect of pH on gold(III) uptake

The investigation of the effect of pH on uptake of Au^{3+} was performed at pH 1–8, by mixing 1 g of the MFT resin in 100 mL 100 ppm Au^{3+} solution. Initial pH values of the solutions were adjusted with either hydrochloric acid or sodium hydroxide solutions after adequate chloride (0.01*M* HCl) addition for $AuCl_4^-$. The coexistence of hydroxide, chloride, and hydroxide–chloride complexes makes gold speciation very complex. At low chloride concentrations (below 10^{-6} M), gold is present in the solution in hydroxide forms: $Au(OH)_2^+$ (below pH 1), $Au(OH)_3$ (between pH 1 and pH 12), and $Au(OH)_4^-$ (above pH 12). For high chloride concentrations (above 0.01*M*), $AuCl_4^-$ predominates in acidic solutions, while in alkaline solutions, both $Au(OH)_4^-$ and $Au(OH)_3$, $Au(OH)_3Cl^-$ coexist and/or predominate. In the near neutral region, the existence of $AuOHCl_3^-$ (pH 3.5–6.5) and $Au(OH)_2Cl_2^-$ (pH 4.5–8) is debatable. In the case of intermediate chloride concentrations (between 0.01 and 10^{-6} M), many species may coexist depending on the pH: In acidic solutions (below pH 5), $AuCl_4^-$, $Au(OH)Cl_3^-$, $Au(OH)_2Cl_2^-$, $Au(OH)_3$, $AuCl_3$, $AuOHCl_2$, and $Au(OH)_2Cl$ may be present in the solution.[12] In the experimental studies, the solutions having 100 ppm

TABLE I
Theoretical and Experimental Elemental Compositions of MFT Resin

	Experimental		Theoretical [% (wt)]	
Component	% (wt)	mmol/g	Figure 2a	Figure 2b
C	38.10	–	32.00	36.12
N	35.80	25.57	49.97	37.45
H	4.80	–	4.00	5.00
S	10.50	3.28	14.00	10.70
O	10.80 (from difference)	–	–	10.70

($5.10^{-4}M$) Au^{3+} and $10^{-2}M$ chloride concentrations were used at different pH values. At these conditions, $AuCl_4^-$ is predominant in acidic solutions. Above pH 4, formations of chloride–hydroxide complexes of Au^{3+} begin.

MFT resin includes S and N donor atoms. Gold forms $AuCl_4^-$ complex ions in acidic chloride solution. In acidic medium, N atoms are protonated and $AuCl_4^-$ may interact with protonated amines, $(R_1R_2)NH_2^+$ by ionic interaction [eqs. (1–3)]. Otherwise gold may interact with electron pair on N and S by chelation [eqs. (4) and (5)] during adsorption.

Ionic interaction;

$$(R_1R_2)NH + HCl \rightleftarrows (R_1R_2)NH_2^+Cl^- \quad (1)$$

$$(R_1R_2)NH_2^+X^- + AuCl_4^- \rightleftarrows RNH_2 + AuCl_4^- + X^- \quad (2)$$

$$(R_1R_2)NH + HAuCl_4 \rightleftarrows (R_1R_2)NH_2^+AuCl_4^- \quad (3)$$

Chelation;

$$(R_1R_2)C{=}S + AuCl_4^- \rightleftarrows (R_1R_2)C{=}S\cdots AuCl_3 + Cl^- \quad (4)$$

$$(R_1R_2)HN + AuCl_4^- \rightleftarrows (R_1R_2)HN\cdots AuCl_3 + Cl^- \quad (5)$$

Figure 3 shows the sorption results at different pH values. In the experimental studies, the highest

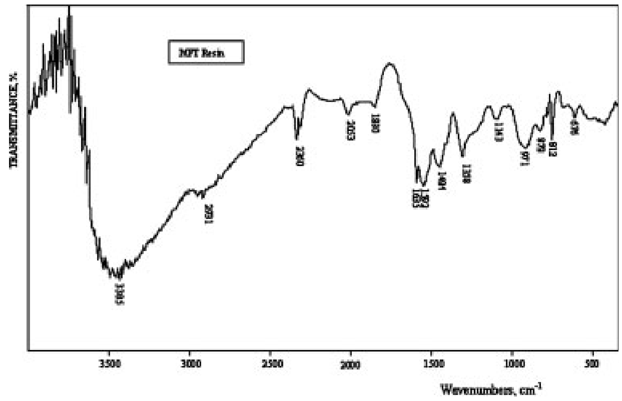


Figure 1 FTIR spectra of MFT resin.

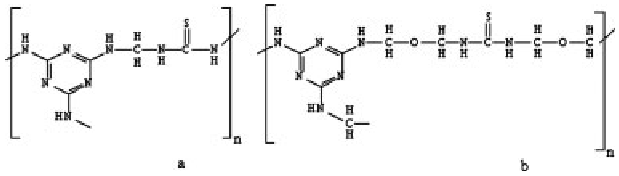


Figure 2 Melamine–formaldehyde–thiourea resin.

adsorption values were obtained at pH 2. The gold sorption decreased at pH 1. It may be explained by Cl^- competition with $AuCl_4^-$. Metal ion chelation with sulfur compounds is weakly sensitive to the pH. At pH 8, the resin does not include protonated amines but gold adsorption was seen at this pH. Chelation may also govern the sorption, but it is less effective. It was concluded that ionic interaction by protonated amines governs effectively the adsorption mechanism of gold ions together with chelation. In other words, ionic interaction and chelation have synergistic effect. Hence, the optimum initial pH of 2 was determined by batch technique for Au^{3+} uptake. Under selected experimental conditions and with pH 2, gold is present in the solution as $AuCl_4^-$.[10,12,13,33,36,37]

Gold(III) adsorption capacity of the resin

Gold(III) adsorption capacity of the MFT resin was determined by batch experimental technique, by equilibrating 0.1 g of the resin with 100 mL 250 ppm Au^{3+} solution for 120-min contact time. It was found using eq. (6) that the resin had gold adsorption capacity as 0.246 mmol Au^{3+}/g resin or 48 mg Au^{3+}/g resin at pH 2.

$$\text{Adsorption capacity} = \frac{Au^{3+}\ (\text{mmol})\ \text{on the resin}}{\text{Resin (g)}} \qquad (6)$$

Selective adsorption

The selective adsorption of Au^{3+} ions together with Cu^{2+} and Zn^{2+} base metal ions was investigated at

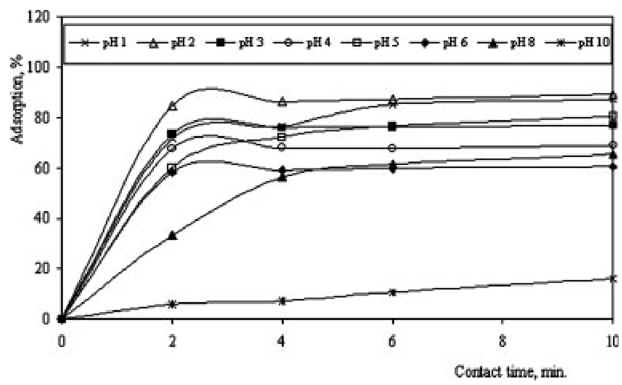


Figure 3 Effect of pH on Au^{3+} ions uptake (1 g resin, solution: 100 mL 100 ppm Au^{3+}. Temperature: 298 K.).

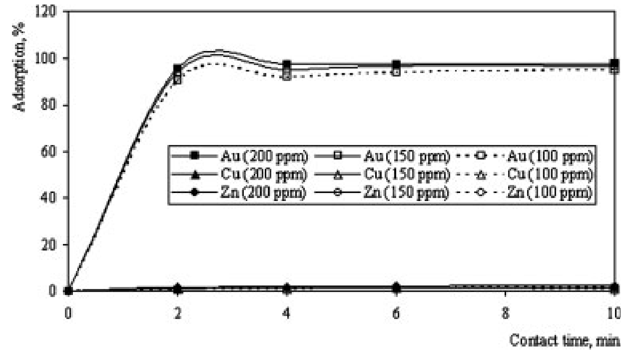


Figure 4 Selective adsorption of Au^{3+} ion by batch method (1 g resin, solution: 100 mL including Au^{3+}, Cu^{2+}, and Zn^{2+} at pH 2. Temperature: 298 K.).

different initial concentrations. The obtained results are given in Figure 4. It was found that higher Au^{3+} uptake than the other ions occurred at same initial concentrations. While copper and zinc ions were adsorbed about 3–5%, gold was adsorbed about 80–97% by batch method. Gold forms anionic $AuCl_4^-$ complex in the solution including acid and chloride while copper and zinc form cationic $Cu(H_2O)_4^{2+}$ and $Zn(H_2O)_4^{2+}$, respectively.[12] Moreover gold shows affinity to N and S donor atoms, copper and zinc are to O atoms. Gold is present together with copper and zinc in mining, jewellery, etc. Gold can be separated selectively from copper and zinc ions by batch technique.

Metal ions uptake using column method

Adsorption

In the column studies, first the adsorptions of the metal ions were examined. Figure 5 gives the breakthrough curves for adsorption. The initial and the down flow metal ion concentrations were indicated

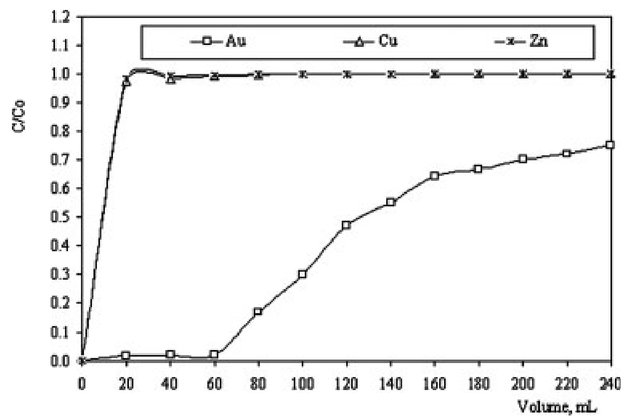


Figure 5 Adsorption of metal ions by column method (Resin bed: 0.8 cm, 1 g resin. Feed solution: 100 ppm Au^{3+}, Cu^{2+}, and Zn^{2+} at pH 2. Flow rate: 0.2 mL/min, Temperature: 298 K).

TABLE II
Separation Factors for Gold Ions Over Copper and Zinc Ions

Volume (mL)	0–20	20–40	40–60	60–80	80–100	0–100
K(Au/Zn)	2817	6023	9751	2436	1164	4438
K(Au/Cu)	1894	2900	5395	972	2331	2698

by C_0 and C, respectively. As it can be seen from Figure 5, it was found that the resin had very high uptake behavior for gold ions, but hardly ever uptake the others. When a solution having 100 ppm concentrations for Au^{3+}, Cu^{2+}, and Zn^{2+} ions passed through column, C/C_0 ratios were obtained as 0.018–0.02 for Au^{3+}, 0.972–0.991 for Cu^{2+}, and 0.981–0.995 in 0–60 mL volume. That means very selective separation.

Separation factor

The separation factors for gold ions over copper and zinc ions were calculated from the column adsorption data using eq. (7).[9] The obtained results are given in Table II. It was found very high separation factors by column method.

$$\text{Separation factor } (K_{A/B}) = \frac{(C_{A1} - C_{A2})\, C_{B2}}{(C_{B1} - C_{B2})\, C_{A2}} \quad (7)$$

where, C_{A1}, the concentration of A metal ions before adsorption; C_{A2}, the concentration of A metal ions after adsorption; C_{B1}, the concentration of B metal ions before adsorption; C_{B2}, the concentration of B metal ions after adsorption.

Elution

The elution studies of adsorbed gold and the other metal ions, with 0.1*M* thiourea solution acidified with 0.1*M* HNO_3, from a column packed with the MFT resin were carried out at a flow rate of 0.2 mL/min. The elution curves are given in Figure 6.

Before adsorption, the solution having 100 ppm gold ions had been used. At the end of elution, it was seen that the first 10 mL elution solution included 120 ppm Au^{3+} concentration and below 5 ppm Cu^{2+} and Zn^{2+} ions. In other words, gold ion concentration increased from 100 to 120 ppm and copper and zinc concentrations decreased less than 5 ppm. Hence it was found that gold ions could be concentrated and recovered selectively over base metal ions.

Reuse tests

The resin stability was examined by four-times adsorption experiments. The obtained results are given in Figure 7. It was seen that the resin adsorbed gold ions again. It shows that nitric acid solution used the elution process does not damage the resin. However, the efficiencies in the adsorptions after first cycle are lower in general. This situation may

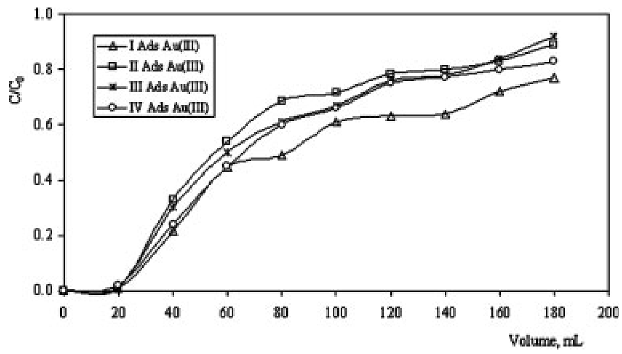


Figure 7 Re-use tests (Resin bed: 0.8 cm, 1 g used resin. Feed solution: 100 ppm Au^{3+} at pH 2. Flow rate: 3 mL/min, Temperature: 298 K).

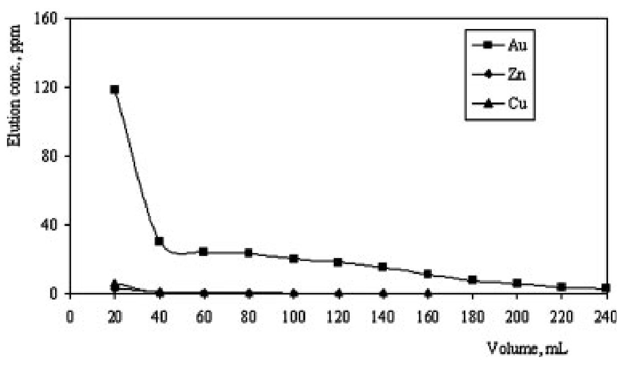


Figure 6 Elution of metal ions (Resin bed: 0.8 cm, 1 g resin loaded with metal ions. Elution solution: 0.1*M* thiourea and 0.1*M* HNO_3. Flow rate: 0.2 mL/min, Temperature: 298 K).

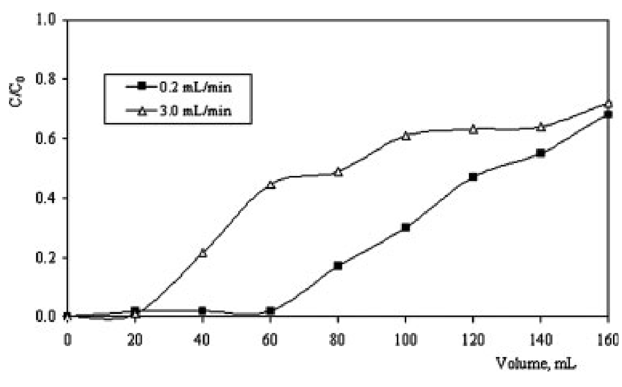


Figure 8 Effect of flow rate on the adsorption (Resin bed: 0.8 cm, 1 g resin. Feed solution: 100 ppm Au^{3+} at pH 2. Temperature: 298 K).

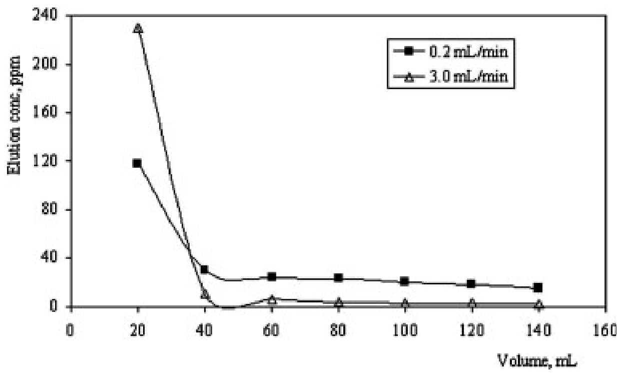


Figure 9 Effect of flow rate on the elution (Resin bed: 0.8 cm, 1 g resin. Feed solution: 0.1*M* thiourea and 0.1*M* HNO_3 elution solution. Temperature: 298 K).

be due to passivization of the sites on the surface of the resin.

Effect of flow rate

The effect of flow rate on adsorption and elution of gold ions (at flow rates 0.2 and 3 mL/min) were examined and the obtained results are given in Figures 8 and 9. Different adsorption ratios were obtained at different flow rates in general. In adsorption process by column method, low flow rate is recommended, but high flow rate is in elution.

CONCLUSIONS

MFT chelating resin is very efficient at removing gold ions from the solutions including copper and zinc. The optimum pH is determined as pH 2 for the adsorption of gold ions. The gold adsorption capacity of the MFT resin has been found to be 48 mg Au^{3+}/g or 0.246 mmol/g. Protonated amines contributes effectively the adsorption of gold. It was concluded that ionic-interaction by protonated amines governs effectively the adsorption mechanism of gold ions together with chelation. The resin shows less affinity to copper and zinc base metal ions. The MFT resin, which is producible easily in aqueous media, can be used in separation, recovery, or preconcentration of gold ions.

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