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Synthesis of a novel dithiooxamide–formaldehyde resin and its application to the adsorption and separation of silver ions

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ABSTRACT

In this study, a new chelating resin of dithiooxamide (rubeanic acid)–formaldehyde (DTOF) has been synthesized by the reaction of dithiooxamide and formaldehyde. Also a well-known chelating resin of thiourea (thiooxamide)–formaldehyde (TUF) has been prepared by the reaction of thiourea and formaldehyde. DTOF and TUF chelating resins were used in the adsorption, separation and concentration of silver ions by batch and column techniques. These resins were characterized using FTIR and elemental analysis. It was found that DTOF resin has silver adsorption capacity of 3333.3 mg g^{-1} or 30.86 mmolg g^{-1} and TUF resin has the capacity of 1428.6 mg g^{-1} or 13.22 mmol g^{-1}. DTOF resin showed more affinity to silver ions according to Cu(II), Zn(II), Ni(II) and Co(II) base metal ions than TUF resin. It was also demonstrated that DTOF resin can be used in the separation and concentration of silver ions.

1. Introduction

Silver is generally found together with copper and lead mineralization in nature. Silver metal is used in jewelry, silverware, food and beverage-processing, and metal alloy industries. Silver compounds are used in mirroring, photographic, electroplating, catalyst, antimicrobial materials, batteries and ink-formulation industries. In case of a solution including silver ions in a hydrometallurgical, recycling or wastewater process, preliminary separation of silver ions from the solutions containing alkaline, earth alkaline or base metal ions may be more profitable than other metal ions. The chelating resins can be used in the concentration and selective separation of silver ions. Also, the ion exchange resins can be used for silver ions, but the chelating resins are preferred instead of the ion exchange resins because of their selectivity [1–8].

The chelating resins have different functional groups and matrix or support. Functional groups in these resins may include N, O, S and P donor atoms. Chelating resins are used widely in the separation, concentration or analytical pre-concentration of metal ions [9,10]. For silver ions, N and/or S atoms in functional groups are preferred due to the Hard-Soft Acid Base (HSAB) theory by Pearson [11]. Silver ion is known as a soft Lewis acid and it has smaller effective ionic radii (2.5 Å) in aqueous solution (O donor atom media) than a lot of metal ions [12]. On the other hand, N and S atoms are softer ligand than oxygen atom. Silver ion shows affinity to N atom and especially S atom in a functional group. Chelating resins containing N and/or S atoms as donor atoms have great attention due to their selectivity towards silver(I) ions [6,7,13–17].

Many researchers have studied the adsorption, separation or concentration of silver ions using chelating resins with different functional groups including N and/or S atoms. Some examples of these functional groups in chelating resins studied for the adsorption, separation or concentration of silver ions are thiourea [6,7,18–20], dithiocarbamate [1,20–23], bisthiourea [24], thiol and amine [1,3,4], thiosemicarbazide [25], polythiazaalkane [26], 2-mercaptobenzothiazole [27], thiophene [28] and amberlite XAD-16 resin [29].

Thiourea functional group has been widely used in chelating resins for the adsorption of silver ions and other precious metal ions. Rubeanic acid (dithiooxamide) has similar molecular structure to thiourea (thiooxamide) molecule and it includes more S donor atoms. A few examples of the polymers or chelating resins functionalized with dithiooxamide are 2,4-dihydroxyacetophenone–dithiooxamide–formaldehyde terpolymer for Fe(III) Cu(II) Ni(II) Co(II) and Zn(II) ions adsorption by Rahangdale et al. [30], polystyrene–divinylbenzene functionalized

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with dithiooxamide for Cu(II), Zn(II), Cd(II) and Pb(II) ions by Dutta and Das [31], and dithiooxamide groups incorporated into a matrix of polystyrene–divinylbenzene for Pd(II) by Dutta et al. [32]. DTOF chelating resin has not been used for the adsorption of any metal ion or silver. DTOF can be synthesized similar to TUF resin and it can be used in the separation or concentration of silver ions. In this study, a new DTOF resin has been synthesized and both DTOF and TUF chelating resins were used in the adsorption and selective separation of silver ions. The results obtained with DTOF resin including more S donor atoms were compared with the results of TUF resin.

2. Experimental

2.1. Reagents

All the chemicals were of analytical grade and used as received. Dithiooxamide, formaldehyde (37%, 1.09 gm L^{-1}, solution) and thiourea for the synthesis of DTOF and TUF resins were purchased from Fluka (Switzerland). $AgNO_3$, $Cu(NO_3)_2$, $ZnSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}7H_2O$ and $Co(NO_3)_2{\cdot}7H_2O$ used as sources for the solutions of Ag(I), Cu(II), Zn(II), Ni(II) and Co(II) ions, respectively, were obtained from Merck (Germany).

2.2. Apparatus

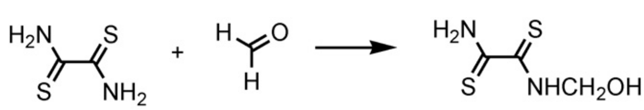
The elemental analysis of DTOF or TUF resin was performed using a LECO CHNS 932 elemental analyzer (Leco Co. USA) by Tubitak in Ankara, Turkey. FTIR spectra were recorded on a Shimadzu-IRPrestige-21 FTIR spectrophotometer. A Shimadzu model AA-6701F atomic absorption spectrophotometer (AAS) was used for the determination of concentrations of metal ions. A hollow cathode lamp and air–acetylene flame was used for all measurements. The operating conditions for silver ions were as follows: wavelength 328.3, slit width 0.5 nm, lamp current 10 mA and lighting mode BGC-D2. pH values of solutions were measured with a Hanna model pH211 pH-meter. Column studies were performed with a column of 10-cm length and 0.37-cm inner diameter. A constant flow rate during adsorption or elution by column technique was provided with a Masterplex, Cole-Polmer Ins. Co., peristaltic pump.

2.3. Synthesis of the chelating resins

TUF is a well-known resin and synthesized at 80 °C by amine–formaldehyde reactions. It has been used in different areas. However, DTOF resin has not been explored. Dithiooxamide as molecule structure is similar to thiourea including two primary amines. Amine–formaldehyde reactions can be carried out for the synthesis of DTOF resin. These reactions include hydroxymethylation (Eqs. (1) and (2)) and condensation steps (Eqs. (3)–(6)). The hydroxymethylation reactions are faster in basic aqueous solutions, while the condensation reactions are in acidic solutions. TUF has very complex structure. The condensation of the hydroxymethyl compounds can result in dimethylene ether or only methylene bridges. A highly cross-linked resin may be produced using higher formaldehyde:amine mole ratio before the hydroxymethylation [6,7,14,15,33–37].

DTOF resin was prepared by condensing dithiooxamide and formaldehyde solution by similar reactions in the synthesis of TUF resin. It was aimed to more linear or less branched copolymer for adsorption. Hence, low formaldehyde/thiooxamide mole ratio was used in the syntheses of the resins. DTOF resin was synthesized with a 12 g of dithiooxamide (0.1 mmol) and a 12 mL of formaldehyde solution (37%) (0.15 mmol) were taken as initial reagents. On the other hand, TUF resin was with a 7.6 g of thiourea (0.1 mmol) and a 12 mL of formaldehyde solution (0.15 mmol).

Hydroxymethylation reactions:



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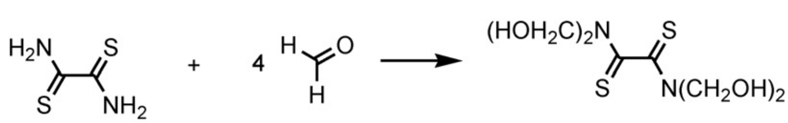

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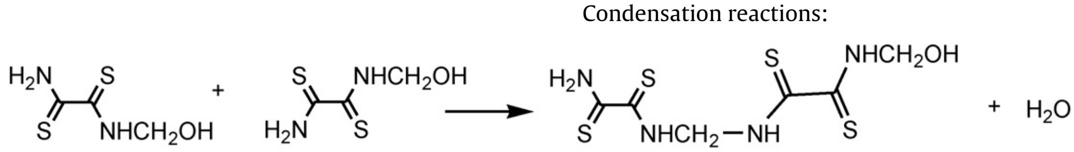
Condensation reactions:



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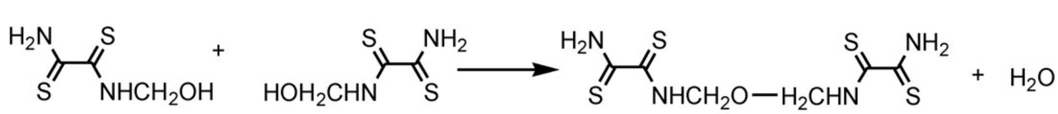

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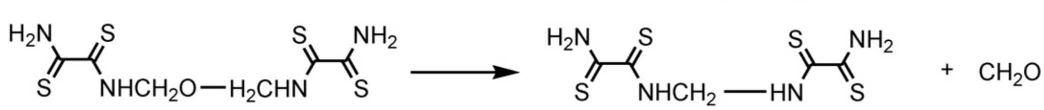

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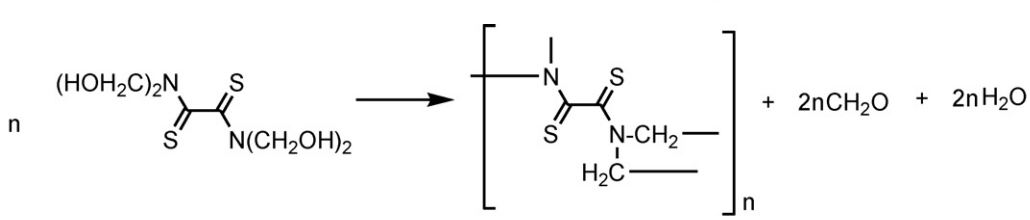


(6)

In the synthesis of DTOF resin, dithiooxamide was dissolved in 30 mL 0.1 mol L^{-1} NaOH solution and then the mixture was poured into formaldehyde solution. pH was adjusted to 10 with NaOH solution (0.1 mol L^{-1}) and temperature was to 80 °C. After complete dissolution, pH was adjusted to 2 with HCl solution (10%) while the mixture was stirred at temperature of 80 °C. After orange colored DTOF resin condensates began to precipitate, the reaction was carried out for 6 h. The obtained condensates were filtered, washed with acid and water, dried at 80 °C and the resin were ground to below particle size of 150 μm. TUF resin was also synthesized similarly with above mentioned quantities of the reagents and it was also washed, dried and powdered. These powdered resins were used in the all experimental studies. They were characterized by elemental analysis and FTIR [14–16,34,37].

2.4. Batch adsorption studies

2.4.1. Effect of initial pH on silver uptake

To examine the effect of initial pH on the adsorption of silver ions, the adsorption experiments were carried out using 0.1 g DTOF or 0.1 g TUF resin in 200 mL 1000 mg L^{-1} silver solutions in the pH range of 0–6. The desired pH was controlled using 0.1 mol L^{-1} HNO_3 or 0.1 mol L^{-1} NaOH solution. Silver ion concentrations in the sample solutions taken at predetermined time intervals of 1, 3, 24, 48 and 72 h were analyzed by AAS. The adsorption density, q_e (mg g^{-1}), of silver ions onto DTOF or TUF resin was calculated from the following relation (Eq. (7)),

$$q_e = \frac{(C_i - C)}{m} \times V \qquad (7)$$

where C_i and C are the concentrations (mg L^{-1}) at initial and different adsorption periods, respectively, m is the mass of resin (g) and V is solution volume (L).

2.4.2. pH change during the adsorption

Acidity or pH during the silver adsorption onto DTOF or TUF resin may change because of the protonation or proton release. Therefore, pH change during the adsorption was examined with 1 g resin in 100 mL 1000 mg L^{-1} silver solution at near pH 4. pH changes during the silver adsorption were noted for both DTOF and TUF resins, and the obtained results with DTOF and TUF resins were compared with 1 g resin in 100 mL water at near pH 4 again.

2.4.3. H^+ ion capacity

H^+ ion can bind to DTOF and TUF resins including N, O and S atoms. In other words, these resins can be protonated. This protonation affects the adsorption properties of these resins. To examine the H^+ ion capacity, 1 g DTOF or TUF resin was stirred in 100 mL 0.1 mol L^{-1} HCl solution for 30 min. Then the resins were filtered, washed with distilled water, dried at 50 °C temperature and titrated with standardized 0.02 mol L^{-1} NaOH solution. H^+ ion capacities of DTOF and TUF resins were calculated as mmol g^{-1}, to estimate the protonable sites on the resin.

2.4.4. Silver ion adsorption capacity

To examine silver adsorption capacities of DTOF and TUF resins, the experimental studies were carried out using 0.1 g DTOF resin in 250 mL silver solutions at 1000, 1500, 2000 and 2500 mg L^{-1} concentrations or 0.1 g TUF resin in 250 mL silver solutions at 500, 750, 1000 and 1250 mg L^{-1} concentrations by stirring for 120 h, equilibrium time. The sample solutions were taken at predetermined time intervals of 24, 48, 72, 96 and 120 h and silver ion concentrations in these solutions were analyzed by AAS. The adsorption data were plotted according to Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \qquad (8)$$

where C_e (mg L^{-1}) is the equilibrium concentration of silver ions in solution, q_e (mg g^{-1}) the adsorbed value of metal ions at equilibrium concentration, Q_{max} (mg g^{-1}) is the maximum adsorption capacity and b (L mg^{-1}) is the binding constant which is related to the energy of adsorption. Silver adsorption capacities of the resins were calculated using Langmuir isotherm [6,7,18].

2.5. Column studies

2.5.1. Adsorption and elution of silver ions

A glass column of 10-cm length and 0.37-cm inner diameter was packed with 0.15 g DTOF or TUF resin. The column bed was conditioned with acidified thiourea solution (1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} thiourea) before metal ion adsorption. The feed solution including 200 mg L^{-1} Ag(I) was passed through the column at a constant flow rate (0.3 mL min^{-1}) using a peristaltic pump. The concentrations of silver ions in each 10 mL solution passed through from the column were determined by AAS and the adsorbed silver quantities were calculated according to non-adsorbed silver and initial silver concentrations. Elution studies were carried out with acidified thiourea solution (1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} thiourea) at same flow rate with adsorption. Silver ion concentrations in each 10 mL solution eluted from the column were determined by AAS again.

2.5.2. Separation of silver ions from base metal ions

To examine the separation of silver ions from base metal ions, the feed solution including Ag(I), Cu(II), Ni(II) and Zn(II) ions at 200 mg L^{-1} concentrations was passed through the column at 0.3 mL min^{-1} flow rate. The metal ions adsorbed onto DTOF or TUF resin were eluted by acidified thiourea solution (1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} thiourea). All the concentrations of the metal ions in each 10 mL solution eluted from the column were determined by AAS.

3. Results and discussions

3.1. Synthesis and characterization of DTOF and TUF resins

Both DTOF and TUF chelating resins were synthesized by hydroxymethylation reactions (Eqs. (1) and (2)) in basic aqueous solution and then by condensation reactions (Eqs. (3)–(6)) in acidic aqueous solution. The synthesized resins were tested by elemental analysis and the results are given in Table 1. The nitrogen and sulfur contents were found to be 9.86 and 13.28 mmol g^{-1} in DTOF and 19.38 and 9.73 mmol g^{-1} in TUF, respectively. As expected, it was found that DTOF included more S donor atoms.

The synthesized DTOF and TUF resins were characterized by FT-IR and their spectra are given in Fig. 1. The characteristic peaks of DTOF resin were assigned at 3271 cm^{-1} for secondary amine, ⟩N–H stretching; at 1666 cm^{-1} for ⟩N–(C=S)– stretching; at 1084 cm^{-1} for ⟩C=S and at 947 cm^{-1} for ⟩C–S–. On the other hand, the peaks

Table 1
Elemental analysis of the chelating resins (O% was calculated from difference).

Resin	C (w/w%)	H (w/w%)	N (w/w%)	N (mmol g^{-1})	S (w/w%)	S (mmol g^{-1})	O (w/w%)	O (mmol g^{-1})
DTOF	30.29	4.344	13.80	9.86	42.49	13.28	9.076	5.67
TUF	23.87	4.661	27.14	19.38	31.15	9.73	13.18	8.23

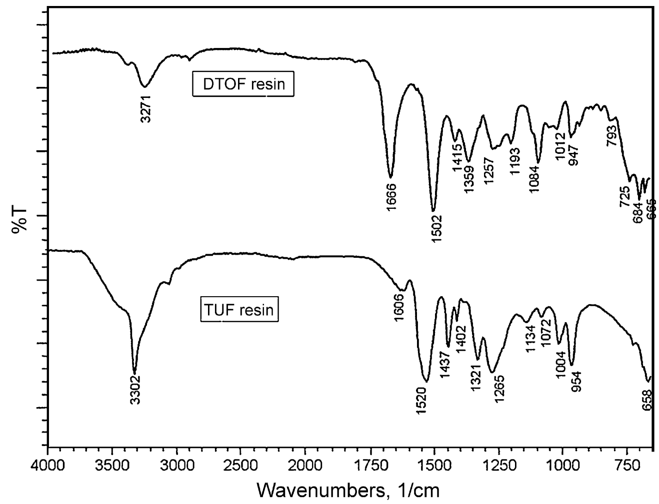


Fig. 1. FT-IR spectra of DTOF and TUF resins.

of TUF resin were at 3302 cm^{-1} for secondary amine, ⟩N–H stretching; at 1606 cm^{-1} for ⟩N-(C=S)– stretching; at 1072 cm^{-1} for ⟩C=S and at 954 cm^{-1} for ⟩C–S–. Additionally, C–O–C stretching peaks were noted at 1193 cm^{-1} with DTOF and at 1134 cm^{-1} with TUF. Ni et al., studied thiourea–formaldehyde resin and they assigned a peak at 1540.6 cm^{-1} for ⟩C=NH. Similarly, the peaks at 1502 cm^{-1} with DTOF and at 1520 cm^{-1} with TUF may be belong to ⟩C=NH [15,18,19,30–32,38].

Considering elemental analysis, FTIR spectra, the synthesis reactions, the suggested structures of TUF and DTOF chelating resins are given in Fig. 2. Thiourea–formaldehyde resin or similarly dithiooxamide–formaldehyde resin may show complexity and alternative bounding combinations according to synthesis conditions.

3.2. Batch method studies

3.2.1. Effect of initial pH on silver uptake

DTOF and TUF resins were used for the silver uptake at the different initial pH values of 0–6. The further experiments above pH 6 were not carried out, due to the precipitation of silver ions in alkaline media. The experimental results obtained at the different initial pH values are given in Fig. 3 with DTOF resin and Fig. 4 with TUF. It was found that DTOF resin has the saturated adsorption capacity of 1826 mg g^{-1} at pH 1, while TUF resin has 786 mg g^{-1} at pH 4. DTOF resin required more acidic silver solution than TUF resin. TUF resin reached the equilibrium sharply at pH 1 and 2, while it was slow at the pH range of 3–6. DTOF resin showed similar adsorption curves at all pH values. In general, both resins can be used in silver adsorption at pH values of 0–6, according to matrix ion types. For the later experimental studies, the optimum pH values were selected as pH 1 with DTOF resin and pH 3 with TUF resin considering other metal ions and the maximum adsorption values.

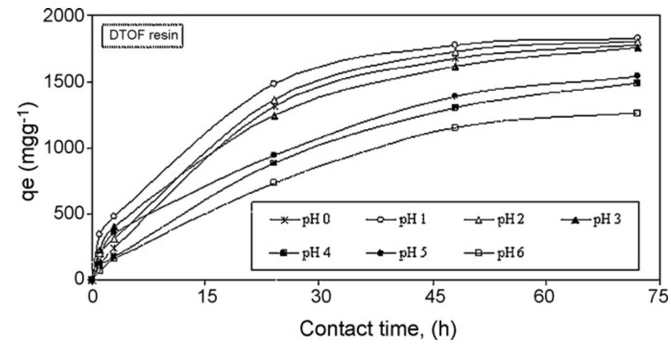


Fig. 3. Effect of initial pH on the sorption of silver ions by DTOF resin.

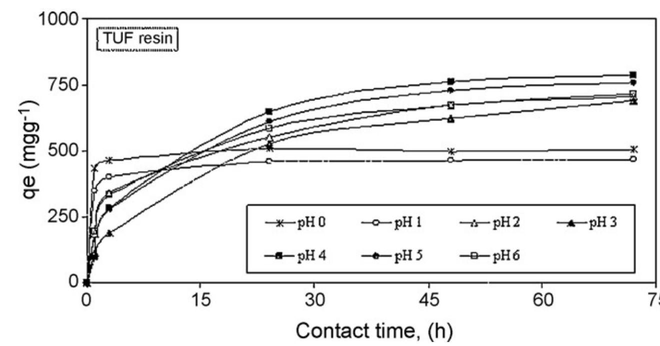


Fig. 4. Effect of initial pH on the sorption of silver ions by TUF resin.

The adsorption of silver ions onto a chelating resin is a pH dependent process due to both the chemistry of silver ions in solution and the protonation of functional groups such as ⟩NH and ⟩C=S. Silver ions can be adsorbed onto DTOF or TUF resin by ionic interaction (Eq. (9)) or chelation (Eqs. (10) and (11)) or the both mechanism. In the chelation mechanism, nitrogen and sulfur atoms are effective due to the HSAB theory [1,6,7,11,13,18].

Ionic interaction:

$$\rangle NH_2{}^+ + NO_3{}^- + Ag^+ \rightleftharpoons NH_2{}^+NO_3{}^-Ag^+ \tag{9}$$

Chelation:

$$\rangle NH_2{}^+ + Ag^+ \rightleftharpoons \rangle HN:\ldots Ag^+ + H^+ \tag{10}$$

$$\rangle C{=}S + Ag^+ \rightleftharpoons \rangle C{=}S:\ldots Ag^+ \tag{11}$$

3.2.2. pH change during silver uptake

pH change during the adsorption of silver ions onto DTOF and TUF resins were examined and compared with water at near pH

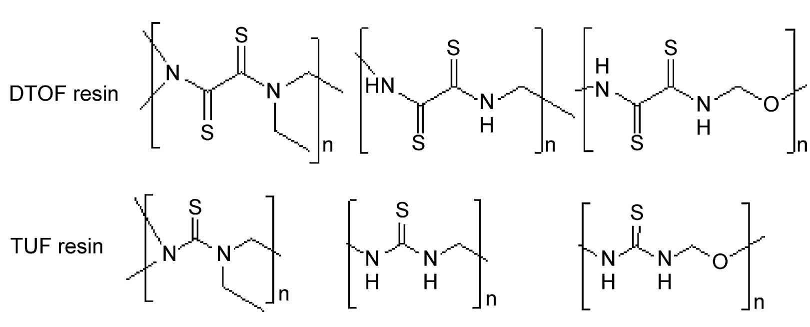


Fig. 2. The suggested structures of DTOF and TUF resins.

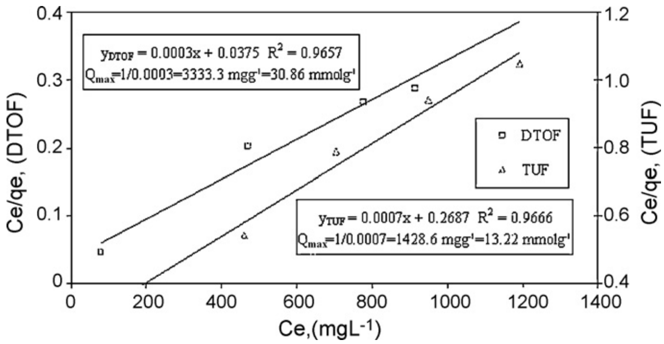
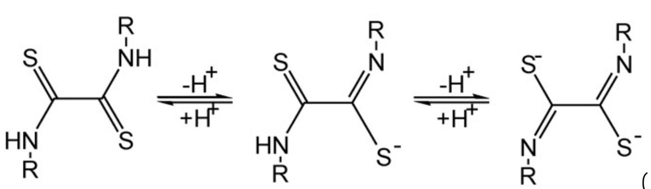


Fig. 5. The Langmuir adsorption isotherms of silver ions onto DTOF and TUF resins.

4. It was seen that DTOF resin in water at near pH 4 did not cause pH to change, while TUF resin caused the pH change from 4.5 to 3.65. Moreover it was found that pH values during silver uptake decreased from 4.14 to 2.40 with DTOF and from 4.50 to 2.60 with TUF. It can be said that TUF resin had been more protonated during the synthesis. H^+ ions were released from both resins during the silver adsorption according to Eq. (10). This result shows that the mechanism of silver adsorption on the resins changes from the ionic interaction to the chelation mechanism. In addition, TUF resin reached the protonation equilibrium in a shorter period of time.

3.2.3. H^+ ion capacity

DTOF and TUF resins including N, O and S atoms can be protonated and this affects the adsorption properties of these resins. For example, DTOF resin can be equilibrated with the protons in a solution (Eq. (12)) [31,39]. The protonation capacities of DTOF and TUF resins were measured by acid–base titration method. It was found that DTOF resin could be bound with more H^+ ion (0.60 mmol g^{-1} H^+) than TUF resin (0.31 mmol g^{-1} H^+). In other words, DTOF resin is more protonable than TUF resin due to the presence of more ligand atoms.



(12)

3.2.4. Silver ion adsorption capacity

The silver adsorption capacities of DTOF and TUF resins were examined using the Langmuir isotherm (Eq. (8)). The Langmuir isotherm assumes that any adsorption occurs as a monomolecular layer onto an adsorbent. In this adsorption process, it was considered that ionic or chelation adsorption was a monolayer chemical adsorption.

The plots of C_e/q_e versus C_e over the concentration range of silver ions are given in Fig. 5, for the used resins. It was found that DTOF resin has the silver adsorption capacity of 3333.3 mg g^{-1} or 30.86 mmol g^{-1} and TUF resin has the capacity of 1428.6 mg g^{-1} or 13.22 mmol g^{-1}. Moreover, b constants were calculated as 0.0080 L mg^{-1} with DTOF resin and 0.0026 L mg^{-1} with TUF. When the adsorption capacities of many chelating resins and TUF resin by previous studies in literature and of TUF resin in this study are examined, it is seen that DTOF resin has achieved the best silver adsorption capacity (Table 2). High sulfur content is effective in silver adsorption due to soft metal ion–soft ligand interaction according to the HSAB theory [6,10,17].

Table 2
Some examples of silver adsorption capacities with different resins.

Resin	Silver adsorption capacity (mmol g^{-1})	References
Melamine–formaldehyde–thiourea	0.95	[18]
Melamine–formaldehyde–EDTA	0.05	[18]
Bisthiourea–formaldehyde (1:1)	6.10	[18]
Bisthiourea–formaldehyde (2:1)	7.31	[24]
Thiourea–formaldehyde	13.1	[19]
Amino-bearing resin	1.2	[1]
Amino/thiol-bearing resin	2.8	[1]
Melamine–formaldehyde–thiourea	0.556	[6]
Thiourea–formaldehyde	13.22	In this study
Dithiooxamide–formaldehyde	30.86	In this study

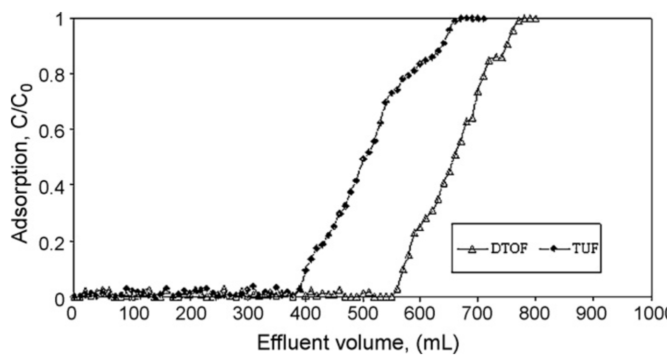


Fig. 6. The breakthrough curves with DTOF and TUF resins.

3.3. Column studies

3.3.1. Adsorption and elution of silver ions

In the column adsorption studies, the feed solution containing 200 mg L^{-1} silver ions was allowed to pass through the column packed with DTOF or TUF resin at a constant flow rate. The breakthrough curves were plotted as a dimensionless concentration factor C/C_0 (C: the concentration of silver ions in the solution coming out of the column and C_0: is the concentration of silver ions in the feed solution) versus effluent volume. Fig. 6 shows the breakthrough curves obtained using DTOF and TUF resins. According to the results, DTOF resin is better than TUF resin at column adsorption capacity. Silver ions can form strong complexes with thiourea in an aqueous solution (log K_1:7.4; log K_2:13.1) [12]. Therefore, silver ions were eluted using acidified thiourea solution (1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} thiourea) from DTOF and TUF resins (Fig. 7), after loading silver ions onto the resins. The elution results showed that

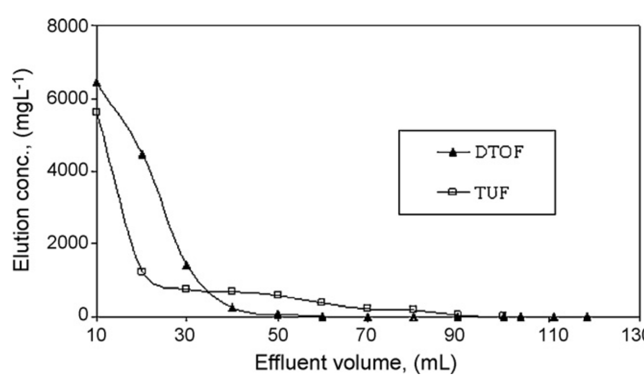


Fig. 7. Elution of silver ions.

silver ions adsorbed onto DTOF and TUF resins could be separated or concentrated into a new solution. For an adsorption–elution cycle, 200 mg L^{-1} silver concentration can be concentrated up to 6450 mg L^{-1} with DTOF, while up to 5600 mg L^{-1} TUF. In the case of lower silver concentration in a feed solution, effluent silver solutions at similar concentrations can be obtained at the end of elution. The column adsorption capacities from the breakthrough curves were calculated as 880 mg g^{-1} (8.15 mmol g^{-1}) for DTOF and 667 mg g^{-1} (6.18 mg g^{-1}) for TUF resin. The recoveries were found above 95%. DTOF resin is better than TUF resin to separate and concentrate silver ions by column technique.

3.3.2. Separation of silver ions from base metal ions

The separation of silver ions from the base metal ions is attractive since silver is a precious metal. To examine the separation of silver ions, Cu(II), Zn(II), Co(II) and Ni(II) ions as base metal ions were added into silver solution and the competitive adsorption of silver ions with these ions was studied and than they were eluted. The selected base metal ions have near properties with soft metal ions or they are borderline metal ions in the Pearson's HSAB theory and they occur together with precious metals or silver ions in ores or wastes. The synthesized DTOF resin was used in the selective separation of silver ions by column technique. The results obtained from the column adsorption in the competitive conditions are given in Fig. 8 as breakthrough curves (C/C_0 versus effluent volume) and in Fig. 9 as elution profiles. DTOF resin showed more affinity towards silver ions according to the selected base metal ions. Silver ions were concentrated from 200 to 6450 mg L^{-1} after first adsorption–elution cycle. However, other metal ions were diluted from 200 mg L^{-1} to less concentration. These results showed that silver ions will be separated and concentrated from the solutions containing Co(II), Ni(II), Cu(II) and Zn(II) base metal ions. This adsorption column experiments were studied to saturate the DTOF resin in the column. Therefore high silver and base metal ions concentrations were selected. In case of lower initial concentrations before the adsorption, an effluent solution including more concentrated silver ions and more diluted ions can be obtained. However, at trace level concentrations, similar recoveries for both silver and nickel ions were obtained by Tuzen and Soylak [40]. At trace level concentrations, non-adsorbed surface area on an adsorbent would be expected and the competitive adsorption would not have been started. However, a good separation can be achieved at high concentrations.

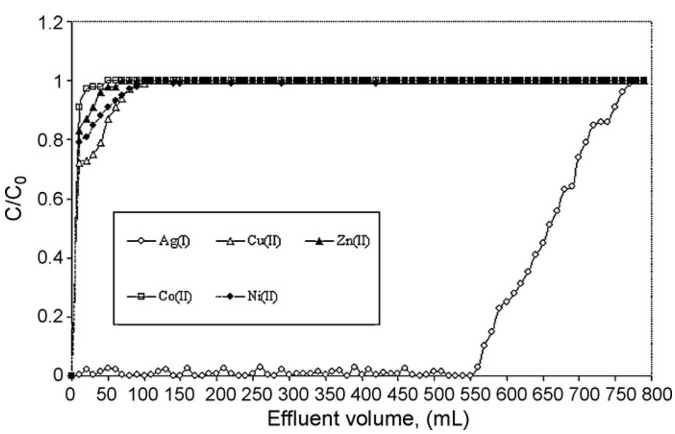


Fig. 8. The breakthrough curves of competitive adsorption of metal ions by DTOF resin.

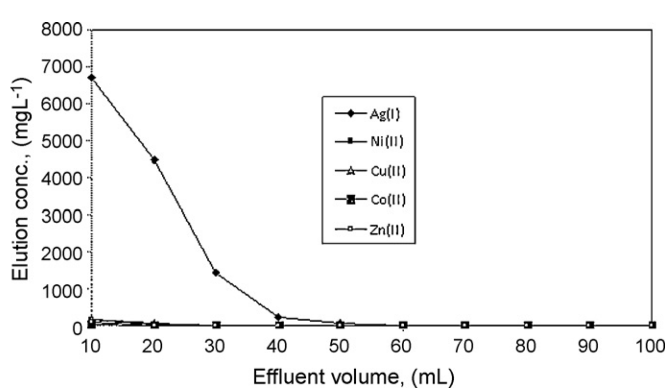


Fig. 9. Elution of metal ions from DTOF resin.

3.3.3. Reusability of DTOF resin

DTOF resin was used in second adsorption–elution cycle and similar breakthrough curve and elution profile with first adsorption–elution cycle was obtained. Third or later adsorption–elution cycles by saturating the DTOF resin in the column were not studied as it required more time. If the resin is coated on an inert material, it may be examined in the experiments of adsorption–elution cycles.

4. Conclusions

DTOF chelating resin derived from dithiooxamide (rubeanic acid) and formaldehyde and TUF resin from thiooxamide (thiourea) and formaldehyde have been prepared, and these resins were used in the adsorption, separation and concentration of silver ions. It was found that DTOF resin has the silver adsorption capacity of 3333.3 mg g^{-1} or 30.86 mmol g^{-1} and TUF resin has the capacity of 1428.6 mg g^{-1} or 13.22 mmol g^{-1} by batch method. DTOF resin is more protonable resin than TUF. The silver adsorption capacities of the resins in the column were found as 880 mg g^{-1} (8.15 mmol g^{-1}) for DTOF and 667 mg g^{-1} (6.18 mg g^{-1}) for TUF resin. Compared with TUF resin, DTOF resin showed more affinity to silver ions than Cu(II), Zn(II), Ni(II) and Co(II) base metal ions. It was concluded that the adsorption of silver ions onto DTOF or TUF resin is governed by both ionic interaction and chelation mechanism.

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