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Adsorption of silver(I) on synthetic chelating polymer derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde

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A B S T R A C T

New types of polymer condensation adducts were synthesized through the reaction of 3-amino-1,2,4-triazole-5-thiol (AZ) with glutaraldehyde in the absence and in the presence of thiourea at different molar ratios. The adsorption behavior of the chelating polymers towards Ag(I) from aqueous solutions was studied. Better adsorption behavior was achieved for Ag(I) by thiourea polymeric adducts. The chelating matrix obtained from a molar ratio of 2:1:3 of AZ, thiourea and glutaraldehyde, respectively, showed uptake capacity of 3.6 mmol/g. These polymers were evaluated for their recovery of Ag(I) from aqueous solutions using batch methods. The obtained polymers achieved promising results in the selective separation of Ag(I) from other metal ions. Both kinetics and thermodynamic parameters of the adsorption process were obtained. The data indicated that the adsorption process is an endothermic reaction and kinetically proceeds according to pseudo-first-order model. These parameters indicated that the polymers can be applied in the recovery of Ag(I).

1. Introduction

Precious metals are widely used in industry, agriculture and medicine, because of their specific physical and chemical properties. Economically, the precious metals have been historically important as currency, and remain important as investment commodities. Silver is considered of special economic interest compared with other metals. Silver nitrate is the most common soluble salt that is used in porcelain, mirroring, photographic, electroplating, and ink formulation industries [1]. Most world silver is recovered from scraps such as photographic films, X-ray films and jewellery [2]. Thus it is necessary to treat the waste aqueous solutions and try to recover them economically. Environmental poisoning due to the emission of waste metals from the mineral processing industry in the last few decades has been and continues to be of growing concern, also recent developments in environmental quality standards highlight the need for improved wastewater treatment of dilute metal-bearing effluents. Many studies have been recently focused on the extraction and separation of precious metals due to both increasing industrial need for these metals and their limited sources. The conventional methods for the removal of metal ions from water and wastewater include zinc-dust cementation [3], carbon adsorption [4], solvent extraction [5,6], ion exchange and adsorption [7]. Among all the above methods, adsorption is recognized as an emerging technique for the depollution of heavy-metal polluted streams. A number of adsorbents have been developed and tested for the removal and recovery of silver(I) (e.g., activated carbon [8,9], cellulose nitrate membrane [10] and chelating resins [11]). Large improvements have been achieved in the last few years through the development of several chelating resins [12–14]. The selectivity for a specific metal ion depends on what kind of complexing agent is introduced into the polymeric chain. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for complexing with ligands that have more or less electronegative donor atoms. Chelating agents with nitrogen and sulphur groups are highly efficient for the selective sorption of precious metal ions. Chelating resins with amine [15], mercaptan [16,17], and thiourea groups [18] are widely used in extraction, separation and recovery of precious metals in hydrometallurgical field.

The ultimate goal of this study is to develop a simple method for preparation of new chelating polymers bearing N and S as a donor atoms. In this paper, a simple method for the preparation of a new chelating polymers were reported. The application of the obtained polymers for recovery of Ag(I) from aqueous solutions was also investigated. The studied polymers showed high efficiency and

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selectivity towards Ag(1) ions. Thermodynamic and kinetic analysis for adsorption process was reported.

2. Experimental

2.1. Chemicals

3-Amino-1,2,4-triazole-5-thiol (AZ) was Organica product (Feinchemie GmbH Wolfen, Germany), glutaraldehyde and thiourea were Aldrich products (Aldrich Chemical Co., Milwaukee, WI, USA). All other chemicals were BDH Prolabo products (VWR International GmbH, Germany) and were used as received. Silver nitrate was used as a source of Ag(I). Potassium tetracyanonickelate(II) was prepared as reported elsewhere [15].

2.2. Preparation of the chelating polymers

Polymer P1 was prepared from the reaction of AZ with glutaraldehyde at molar ratios 1:1 and the other polymers P2, P3, P4 and P5 were prepared from the reaction of AZ and thiourea with glutaraldehyde (25%) at molar ratios 1:1:1, 1:1:2, 1:2:3 and 2:1:3, respectively. The required weights of AZ and thiourea were dissolved in 40 mL of warm water. The corresponding volume of glutaraldehyde was added and the reaction mixture was heated at 90 °C for 3 h with stirring. Yellow products were formed, filtered off and subsequently washed with hot water, cold water, ethanol then acetone, The polymers having (m.p. >300 °C), were then air dried and collected for subsequent studies. The yield percent of each reaction was calculated using the following relation:

$$\text{yield percent}(\%) = \frac{m_P}{m_T + (V_G \times D_G \times 0.25)} \times 100 \qquad (1)$$

where m_p is the mass of the obtained dried polymer (g), m_T is the mass of the required thiourea (g), V_G is the volume of the required glutaraldehyde solution (mL) and D_G is the density of glutaraldehyde solution (g/mL).

2.3. Characterization of the polymers

2.3.1. FT-IR analysis

Infra red spectra were performed using Nicolet IR200 FT-IR Spectrometer.

2.3.2. Water regain

Water regain factor, W%, represents the percentage of water held intrinsically by the polymer. For water regain determination, polymer samples were centrifuged for 30 min at 1000 rpm to remove excess water and then weighed. These samples were then dried at 50–60 °C until complete dryness then weighed again. To calculate this factor, the following equation was applied:

$$W\% = \frac{100(m_w - m_d)}{m_w} \qquad (2)$$

where m_w and m_d are masses (g) of the wet and dried polymer, respectively. Water regain values are (10 ± 2%) and (14 ± 2%) for P1 and P5, respectively, with insignificant differences when changing conditions. This value reflects an increase of the hydrophilic character of P5 polymer.

2.3.3. Surface area

The surface area of the prepared polymers was measured by methylene blue adsorption as this material is known to be adsorbed as a monolayer only on solid sorbents [20]. A standard solution of this material was prepared (0.02 g/L). A calibration curve for methylene blue was drawn ($\lambda = 660$ nm) by measuring diluents from standard stock. To calculate the surface area, 0.1 g of resin was treated with 25 mL of methylene blue of concentration 0.02 g/L. The treatment lasted until there was no further decrease in absorbance. The amount of methylene blue adsorbed was calculated based on concentration difference between the initial and equilibrium values, which were measured by DR 5000 spectrophotomer (HACH) USA. The surface area of the polymers were calculated using the following equation [21]:

$$A_s = \frac{G N_{Av} \O\, 10^{-20}}{M M_W} \qquad (3)$$

where A_s is the polymer surface area in m^2/g, G the amount of methylene blue adsorbed (g), N_{Av} the Avogadro's number (6.02×10^{23}), $\O$ the methylene blue molecular crosssection (197.2 Å^2), M_W the molecular weight of methylene blue (373.9 g/mol) and M is the mass of adsorbent (g). The surface area of the prepared polymers was calculated to be 560 and 687 m^2/g for P1 and P5, respectively.

2.4. Preparation of solutions

A stock solution of silver nitrate (1.2×10^{-2} M) was prepared. A stock solution of EDTA (5×10^{-3} M) was also prepared and standardized against a solution of $MgSO_4 \cdot 7H_2O$ using Eriochrome Black-T (EBT). HNO_3 and NaOH were used to change the acidity of the medium. Thiourea (0.5 M) acidified by H_2SO_4 (0.01 M) was used as an eluent for stripping Ag(I) adsorbed on the resin.

2.5. Uptake measurements

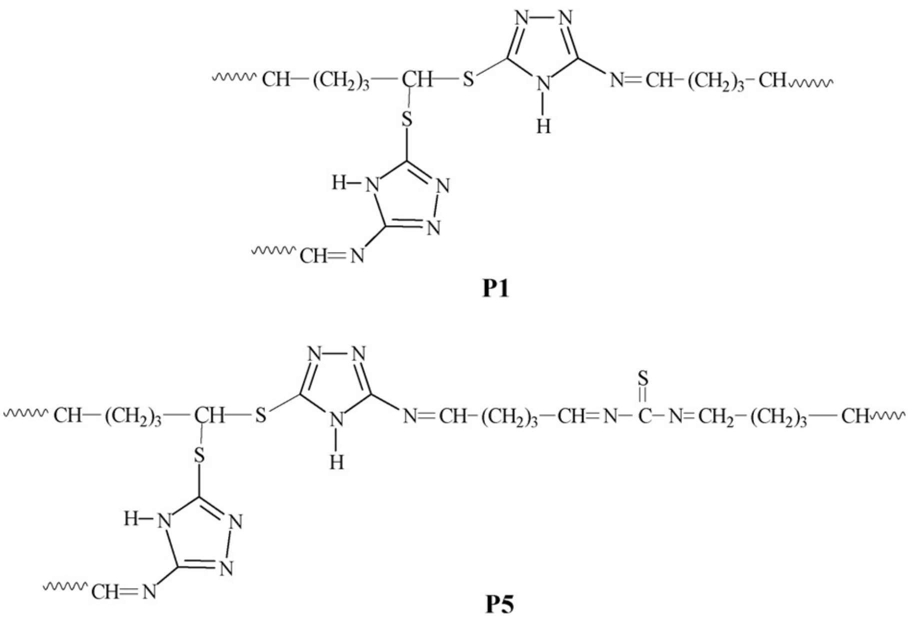
2.5.1. Batch method

The effect of contact time on the polymer uptake of Ag(I) was done using a batch method. 0.1 g of dried polymer was placed in a flask containing 100 mL of metal ions. Initial concentrations of 8×10^{-3} M were used. The flasks were shaken on a Vibromatic-384 shaker at 300 rpm and at 25 ± 1 °C. Five milliliters of the solution were taken at different time intervals then centrifuged at 3000 rpm. The residual concentration of Ag(I) was determined complexmetrically with EDTA (5×10^{-3} M) by the replacement titration method using potassium tetracyanonickelate(II) and murexide indicator [19,22]. Each data point was taken as the average of three measurements.

Adsorption of metal ions on the chelating polymer obtained under controlled pH was carried out following the above methods. The desired pH was controlled using HNO_3 and NaOH while the equilibrium time was fixed at 6 h and 25 ± 1 °C. Studying the adsorption of Ag(I) in strong basic media was avoided due to the precipitation of metal hydroxide.

Complete adsorption isotherms were obtained by placing 0.1 g portions of dried resin in a series of flasks containing 100 mL of Ag(I) ions at natural pH. The flasks were shaked at 300 rpm while keeping the temperature at 25, 40, 50 or 55 °C for 6 h. Later on, the residual concentration was determined where the metal ion uptake was calculated.

Selective separation of Ag(I) from binary mixtures with Cu(II), Pb(II), Cd(II), Zn(II) or Ca(II) was studied at pH 2 using P5 resin. Therefore 0.1 g of dry resin was introduced in a series of flasks, each flask containing 100 mL of 8×10^{-3} M Ag(I) solution in a binary mixture with 8×10^{-3} M Cu(II), Pb(II), Cd(II), Zn(II) or Ca(II). Five milliliters of the solution was taken after 6 h, and then filtered off, where the residual concentration of metal ion was determined via the titration against 5×10^{-3} M EDTA using murexide as an indicator for Cu(II). EBT was used as an indicator for Ca(II), Mg(II), Cd(II), Zn(II) and Pb(II).



Scheme 1. Proposed structures of the studied chelating polymers.

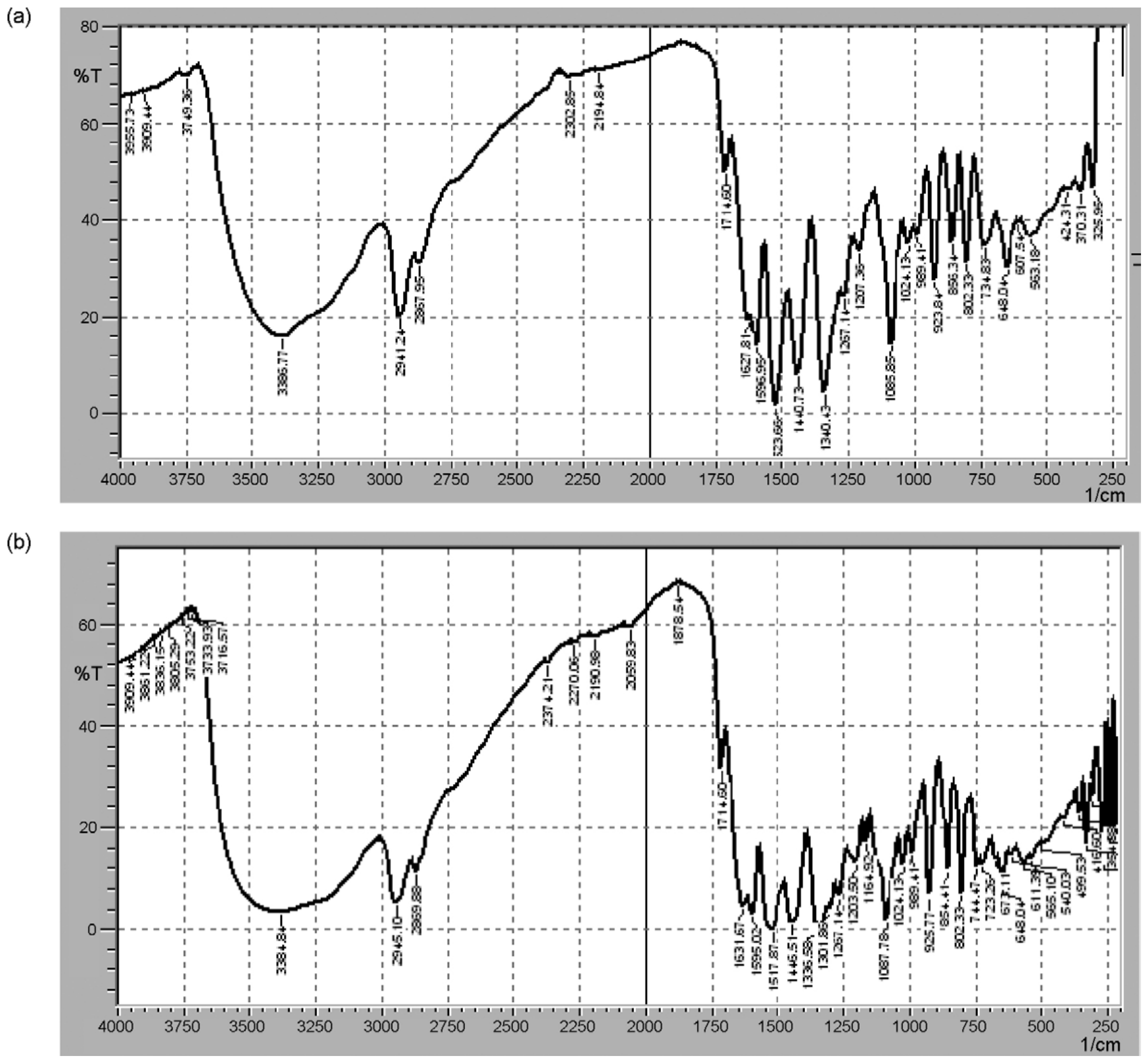


Fig. 1. FTIR spectra of the studied chelating polymers ((a) P1 chelating polymer; (b) P5 chelating polymer).

Table 1
Preparation of triazole polymers at different molar ratios and its uptake capacity for Ag(I) ions.

Polymer	Molar ratio			Yield (%)	Uptake (mmol/g)
	AZ	Thiourea	Glutaraldehyde		
P1	1	0	1	90	1.53
P2	1	1	1	80	4.32
P3	1	1	2	83	3.74
P4	1	2	3	61	3.72
P5	2	1	3	86	3.60

2.5.2. Elution

One gram of the polymer P5 was placed in a plastic column (5 cm length and 1.0 cm diameter). A solution of (4×10^{-3} M) Ag(I) was allowed to flow gradually through the column under the force of gravity at flow rate of 0.5 mL/min. Five milliliters of the underflow solution was removed every 25 min where the residual concentration of the metal ion was determined. The experiment was terminated when the concentration of the underflow matches its initial concentration. Thereafter the column was washed carefully by flowing distilled water through it. The polymer loaded by Ag(I) was then subjected for elution using 50 mL of thiourea (0.5) acidified with H_2SO_4 (0.01 M). After elution the polymer was carefully washed with water, dilute alkali and finally with distilled water to become ready for reuse. This process was repeated for 4 cycles.

3. Results and discussions

3.1. Characterization of the prepared polymers

The suggested structures of polymers P1 and P5 shown in Scheme 1 were confirmed from IR spectral measurements. The spectra of prepared polymers (shown in Fig. 1) display bands near 3391, 1627, 673 and 648. These bands are assigned to ν N–H, ν N=C, ν C–S and ν C=S, respectively. These bands and also the presence of a band characteristic for thioacetal bond confirm the condensation reaction adducts (polymers) obtained from the reaction of AZ with glutaraldehyde, and AZ with glutaraldehyde and thiourea, respectively.

3.2. Uptake studies using batch method

Table 1 lists the polymer P1 obtained from the reaction of AZ with glutaraldehyde at molar ratios 1:1 and polymer P3, P4 and P5 were prepared from the reaction of AZ and thiourea with glutaraldehyde (25%) at molar ratios of 1:1:2, 1:2:3 and 2:1:3. As shown in Table 1, the increase of thiourea content in the resin is associated with a corresponding decrease in yield, this may be due to side reaction between thiourea and glutaraldehyde forming water-soluble liquid polymer that is removed by filtration leading to a reduction in the yield of the produced chelating polymer. The higher uptake of thiourea containing polymers may be due to the decrease in the steric hindrance obtained from the presence of triazole moiety in the polymer structure, which facilities the diffusion of Ag(I) into polymer structure. While the increase in glutaraldehyde content is associated with a high degree of crosslinking, this high crosslinker concentration cause a significant decrease in metal uptake efficiency [23] and enhance the reaction yield. So the addition of thiourea increases Ag(I) uptake in P2 and decreases the yield due to the removal of the formed soluble thiourea–glutaraldehyde polymer.

Thus the adsorption of Ag(I) ions into the prepared polymers can be affected by the amount of thiourea and glutaraldehyde in two ways:

Table 2
Elemental analysis of the studied chelating polymers.

Polymer	Elemental analysis			
	C%	H%	N% (mmol/g)	S% (mmol/g)
P1	43.00	3.98	25.32 (17.99)	14.24 (4.45)
P5	43.34	3.59	27.86 (19.90)	16.92 (5.28)

(a) The increase of thiourea concentration results in higher uptake and lower yield.
(b) The increase of glutaraldehyde concentration results in lower uptake and higher yield.

Therefore, the amount of Ag(I) adsorbed and the reaction yield is basically the combined effect of each precursor content (AZ, thiourea, and glutaraldehyde).

The elemental analysis was carried out on the synthesized P1 and P5 polymers in order to determine C, H, N and S content. The obtained results are given in Table 2. The reported data in Table 2 indicates an increase in N and S content in case of P5, this increase is due the presence of thiourea moiety in P5 structure. In addition the ligand concentration was calculated as 22.4 mmol/g and 25.18 for P1 and P5, respectively. The fact that the polymers include N and S donor atoms, shows that the chelating polymers formed are amenable to uptake Ag(I). The coordination number of Ag(I) is 2. One Ag(I) atom needs two electron pairs to form a complex, thus the ligand occupation (%) of the chelating polymer towards Ag(I) could be verified using the relation:

$$\text{ligand occupation}\,(\%) = \frac{\text{uptake of Ag(1) in mmol/g} \times 2}{\text{concentration of active sites in mmol/g}} \times 100 \qquad (4)$$

The ligand occupation (%) in P1 chelating polymer is 12% at 25 °C and natural pH. This low value of ligand occupation (%) may be due to the steric hindrance obtained from the presence of triazole moiety in the polymer structure. While ligand occupation (%) in P5 chelating polymer is 28.59% at 25 °C and natural pH. The observed increase in ligand occupation (%) for P5 chelating polymer may be due to the presence of the less steric hindrance thiourea moiety in the polymer structure.

3.2.1. Effect of pH on the uptake

The data of the effect of the acidity of the medium on the uptake of Ag(I) is shown in Fig. 2. It is clearly seen that the uptake of Ag(I)

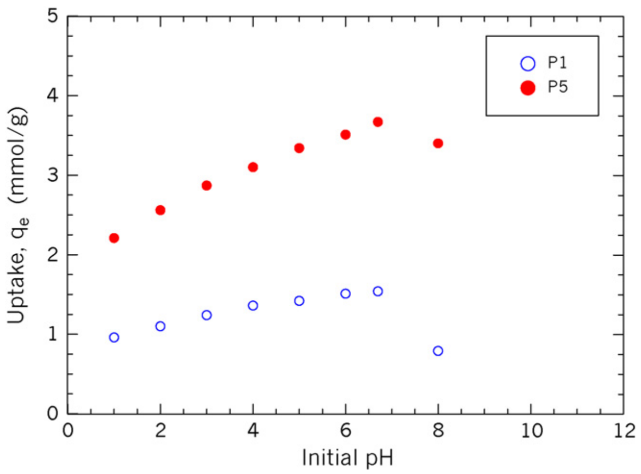


Fig. 2. Effect of pH on the uptake of Ag(I) by polymers at 25 °C and initial concentration of 8×10^{-3} M.

increases with increasing pH till reaching a maximum value around pH 6.7. The dominant mechanism of interaction is probably due to the presence of free lone pairs of electrons on nitrogen or sulphur atoms that are suitable for coordination with Ag(I) to give the corresponding resin–metal complex.

polymeric matrix-(N/S)+$AgNO_3$=polymeric matrix-(N/S)$AgNO_3$

This behavior indicates the complex formation mechanism between Ag(I) and the donor atoms (N and/or S) on the polymer. These findings are in agreement with that early reported in previous results [15,16].

The slow decrease in the uptake of Ag(I) below pH 6.7 may be due to the competition between protons and Ag(I) ions to coordinate with free lone pairs of electrons on nitrogen or sulphur atoms. While the decrease in the uptake of Ag(I) prior to initial pH 8 may be due to the masking of Ag(I) ions in the form of soluble hydroxide anions. At pH >8, almost all of the Ag(I) ions are precipitated in the form of AgOH [15].

The recorded appreciable uptake of Ag(I) at lower pH values may be useful in the selective separation of Ag(I) from other metal ions.

3.2.2. *Selectivity studies*

Selective separation of Ag(I) from binary mixtures with Cu(II), Pb(II), Cd(II), Zn(II) or Ca(II) using P5 chelating polymer was studied at pH 2 and same other adsorption conditions. Their uptake in the presence of Ag(I) were in following order <0.06, <0.04, 0.1, <0.05 and 0.0 mmol/g, respectively. This data indicate very weak adsorption for the mentioned metal ions relative to that of Ag(I). The separation factors for Ag(I) ions over Cu(II), Pb(II), Cd(II), Zn(II) or Ca(II) ions were calculated from the adsorption data using the following equation [18]:

$$\text{separation factor}(S_{A/B}) = \frac{(C_{A1} - C_{A2}) \times C_{B2}}{(C_{B1} - C_{B2}) \times C_{A2}} \qquad (5)$$

where C_{A1} and C_{A2} stand for the concentrations of metal ion A (Ag(I)) before and after adsorption, respectively, and C_{B1} and C_{B2} stand for the concentrations of metal ion B (Cu(II), Pb(II), Cd(II), Zn(II) or Ca(II)) before and after adsorption. The values of the separation factor ($S_{A/B}$) are 61.20, 92.03, 36.53 and 73.53 for the separation of Ag(I) from Cu(II), Pb(II), Cd(II) and Zn(II), respectively. This indicates that P5 chelating polymer has high selectivity for Ag(I) ions over the studied other metal ions.

It is reported that thiourea and nitrogen or sulphur containing compounds forms complexes with several metal ions such as Ag(I), Cu(II), Pb(II), Cd(II), Zn(II), etc. [22], therefore the observed weak adsorption of Cu(II), Pb(II), Cd(II), Zn(II) on P5 (nitrogen or sulphur containing polymer) is astonishing phenomena, this phenomena may be attributed to the nature of the formed AZ–thiourea–glutaraldehyde polymer (i.e. types of the new formed chelating moieties). Similar behavior was observed in the adsorption properties studies of a chelating resin from thiourea and formaldehyde done by Ni et al. [18].

3.2.3. *Kinetic studies*

Fig. 3 shows the change in the uptake of Ag(I) by the polymer as a function of time at initial concentration of 4×10^{-3} M and pH 6.8. Obviously, about 90% of the maximum uptake capacity was achieved within 375 and 400 min for P1 and P5, respectively.

The uptake-time data obtained were treated in the form of four simplified kinetic models including pseudo-first-order, pseudo-second-order, diffusion model (Fickian diffusion low) and (Elovich equation).

The pseudo-first-order model is expressed as [24]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad (6)$$

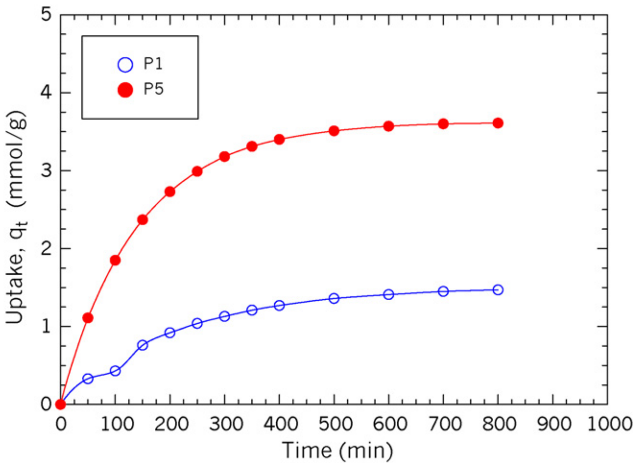


Fig. 3. Effect of time on the uptake of Ag(I) from initial concentration of 8×10^{-3} M by the studied polymers at 25 °C and pH 6.7.

where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption and q_e and q_t (mmol/g) are the amounts of metal ion adsorbed at equilibrium and time t, respectively. On the other hand, the pseudo-second-order model is expressed as [25]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (7)$$

where k_2 is the pseudo-second-order rate constant of adsorption (g mmol^{-1} min^{-1}). The aforementioned two models basically consider external film diffusion, intraparticle diffusion and interaction step for adsorption process. The rate determining step of the adsorption reaction may be one of the above three steps. Shaking eliminates the external film diffusion. So, the adsorption rate may be controlled by intraparticle diffusion or interaction step. The kinetic parameters for the pseudo-first and pseudo-second models are determined from the linear plots of $\log(q_e - q_t)$ versus t (Fig. 4) or (t/q_t) versus t (Fig. 5), respectively. The validity of each model could be checked by the fitness of the straight lines (r^2 values). Accordingly, as shown in Table 3, the adsorption of Ag(I) on the obtained resins is perfectly fit pseudo-first-order model rather than pseudo-second-order one. In addition, the experimental and theoretical values of q_e (obtained from pseudo-first-order model) are closely similar, confirming the validity of that model for the adsorption system under consideration. It was observed from Fig. 5 that the adsorption of Ag(I) correlates with pseudo-second-order in case of

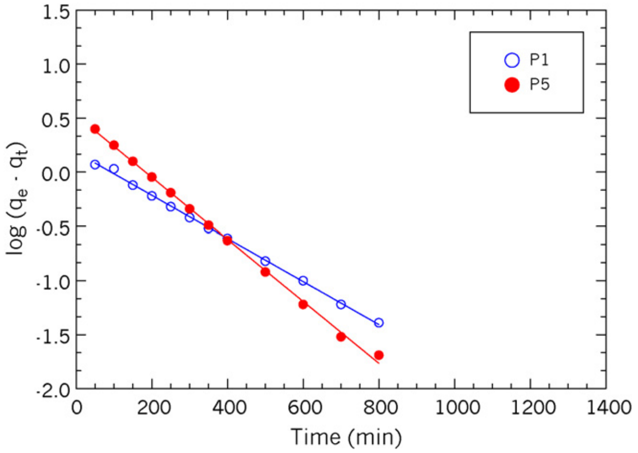


Fig. 4. Pseudo-first-order kinetics of the uptake of Ag(I) by the studied polymers at 25 °C and pH 6.7.

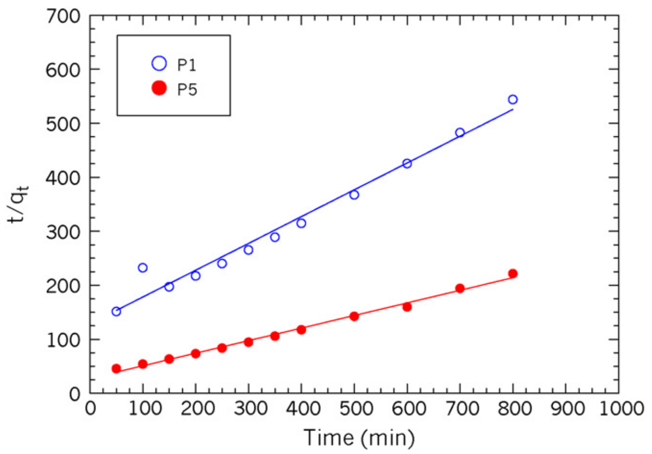


Fig. 5. Pseudo-second-order kinetics of the uptake of Ag(I) by the studied polymers at 25 °C and pH 6.7.

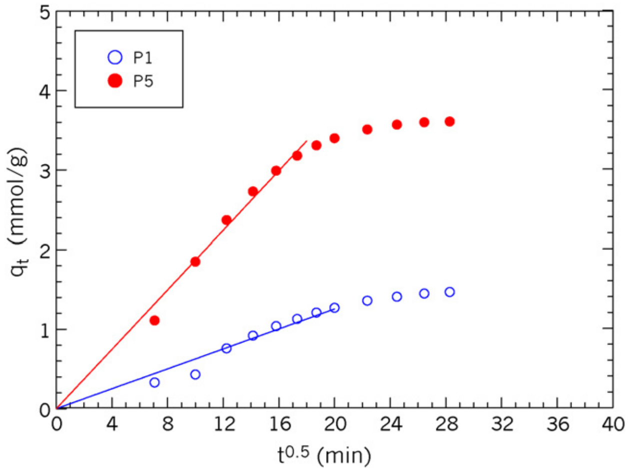


Fig. 6. The intraparticle diffusion kinetics model of the uptake of Ag(I) by the studied polymers at 25 °C and pH 6.7.

P5 ($r^2 = 0.993$) better than P1 ($r^2 = 0.974$), this may be due to the less steric hindrance obtained from the presence of thiourea in the resin structure. This implies that the rate determining step of the adsorption reaction depends on both the concentration of the active sites and the textural properties of the resin. The intraparticle diffusion rate can be described as reported by Chang and Juang [26]:

$$q_t = K_i t^{0.5} \tag{8}$$

where K_i is intraparticle diffusion rate (mmol/g min$^{-0.5}$). The K_i is the slope of straight line portions of the plot of q_t versus $t^{0.5}$ (Fig. 6). The K_i values are 0.063 and 0.187 (mmol/g min$^{-0.5}$) for P1 and P5, respectively. These values of K_i mean that P5 polymer has better diffusion properties than P1. It was observed that the adsorption of Ag(I) correlates with Fickian diffusion low in case of P5 ($r^2 = 0.998$) which is better than P1 ($r^2 = 0.991$), this again confirms the role of thiourea in enhancing the diffusion properties of the metal ion onto P5 polymer.

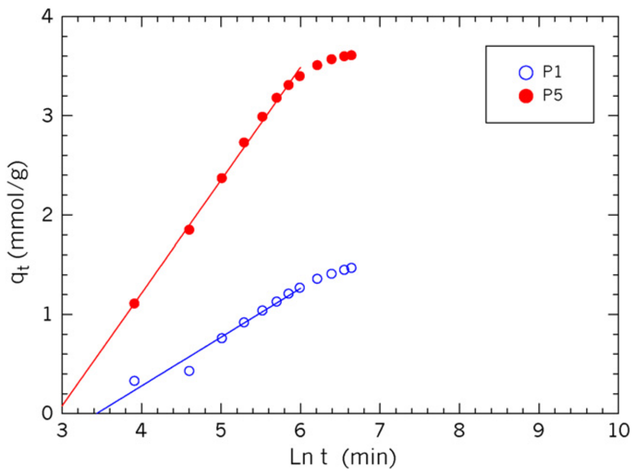


Fig. 7. The Elovich kinetics model of the uptake of Ag(I) by the studied polymers at 25 °C and pH 6.7.

The Elovich equation was also applied to the sorption of Ag(I) by the obtained polymers. The Elovich equation is given as follows [27]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q) \tag{9}$$

where q is the sorption capacity at time t and α is the initial sorption rate (mmol g^{-1} min^{-1}) and β is the desorption constant (g/mmol). To simplify the Elovich equation, it is assumed that $\alpha\beta t \gg 1$ and by applying the boundary conditions $q = 0$ at $t = 0$, this equation becomes:

$$q_t = \frac{1}{\beta}(\ln \alpha\beta) + \frac{1}{\beta}(\ln t) \tag{10}$$

Thus, the constants can be obtained from the slope and intercept of a straight line plot of q versus $\ln t$. The linearization of the equation giving the rate of reaction allows obtaining the initial sorption rate, α (mmol g^{-1} min^{-1}) from the intercept of a straight line plot of q_t versus $\ln t$ (Fig. 7). The values of α for the adsorption of Ag(I) on polymers P1 and P5 are 0.016 and 0.060 (mmol g^{-1} min^{-1}), respectively. The values of β were also obtained and are found to be 2.03 and 0.88 (g/mmol) for P1 and P5, respectively. This data suggest the applicability of Elovich kinetic model for the adsorption of Ag(I) on the studied resins, the values of r^2 are found to be 0.964 and 0.996 for P1 and P5, respectively, this indicates that the film diffusion and the sorption reaction are the rate limiting steps for the adsorption of Ag(I) on the studied resins and confirms the role of thiourea in enhancing the adsorption kinetics of Ag(I) onto the P5 chelating polymer.

3.2.4. Adsorption isotherms

Fig. 8 shows the isotherms of adsorption of Ag(I) on resin, respectively at different temperatures. The adsorption curves show maximum uptake values of 1.6 mmol/g, respectively. The adsorption data were plotted according to Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \tag{11}$$

Table 3

Parameters of the pseudo-first order and pseudo-second order for the adsorption of Ag(I) on the studied polymers.

Polymer	$q_{e,\exp}$	Pseudo-first order			Pseudo-second order		
		k_1 (min^{-1})	$q_{e,\mathrm{calc}}$ (mmol/g)	r^2	k_2 (g mmol^{-1} min)	$q_{e,\mathrm{calc}}$ (mmol/g)	r^2
P1	1.50	0.0043	1.52	0.991	0.0019	2.01	0.974
P5	3.61	0.0064	3.34	0.998	0.0020	4.29	0.993

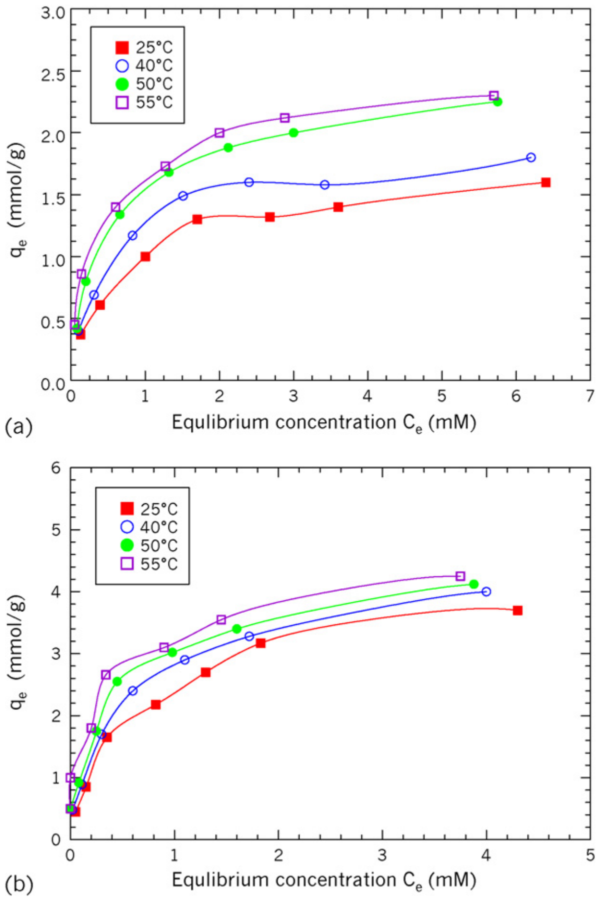


Fig. 8. Adsorption isotherms for the adsorption of Ag(I) by the studied polymers at different temperatures and pH 6.7 ((a) P1 chelating polymer; (b) P5 chelating polymer).

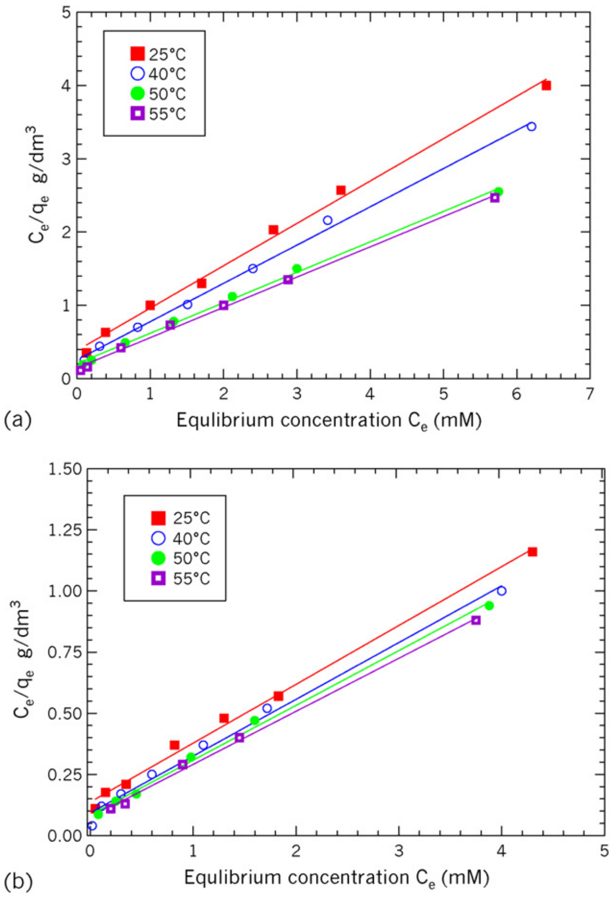


Fig. 9. Langmuir isotherms for the adsorption of Ag(I) by the studied polymers at different temperatures and pH 6.7 ((a) P1 chelating polymer; (b) P5 chelating polymer).

where C_e is the equilibrium concentration of metal ions in solution (mmol/L), q_e the adsorbed value of metal ions at equilibrium concentration (mmol/g), Q_{max} the maximum adsorption capacity (mmol/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption (L/mmol). Plotting C_e/q_e against C_e gives straight lines, indicating that the adsorption complies with the Langmuir isotherm as shown in Fig. 9. Each straight line has slope and intercept equal to $1/Q_{max}$ and $1/K_LQ_{max}$, respectively. The values of K_L and Q_{max} at different temperatures for adsorption of Ag(I) were reported in Table 4. It is seen that the value of Q_{max} (obtained from Langmuir plots) at 25 °C is mainly consistent with that experimentally obtained, indicating that the adsorption process is mainly monolayer. The observed r^2 values indicate that the adsorption of Ag(I) correlates well with Langmuir model.

The degree of suitability of resin towards metal ions was estimated from the values of separation factor constant (R_L) that gives an indication for the possibility of the adsorption process to proceed. $R_L > 1.0$ unsuitable; $R_L = 1$ linear; $0 < R_L < 1$ suitable; $R_L = 0$ irreversible [28]. The value of R_L could be calculated from the relation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{12}$$

where K_L is the Langmuir equilibrium constant and C_0 is the initial concentration of metal ion. The values of R_L lie between 0.063 and 0.568 indicating the suitability of the studied polymers as adsorbent for Ag(I) from their aqueous solutions.

The observed increase in both values of Q_{max} and K_L at elevated temperature indicates the endothermic nature of the adsorption process. The values of K_L at different temperatures were treated according to van't Hoff equation [29]:

$$\ln K_L = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{13}$$

where ΔH° and ΔS° are enthalpy and entropy changes, respectively, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (in Kelvin). Plotting $\ln K_L$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of ΔH° and ΔS° were calculated from Fig. 10

Table 4
Langmuir constants for adsorption of Ag(I) on the studied polymers.

Temperature (°C)	P1			P5		
	Q_{max} (mmol/g)	K_L (L/mmol)	r^2	Q_{max} (mmol/g)	K_L (L/mmol)	r^2
25	1.73	1.52	0.968	4.16	1.84	0.994
40	1.91	2.08	0.995	4.34	2.55	0.996
50	2.40	2.08	0.990	4.54	2.75	0.991
55	2.43	2.92	0.978	4.76	3.00	0.994

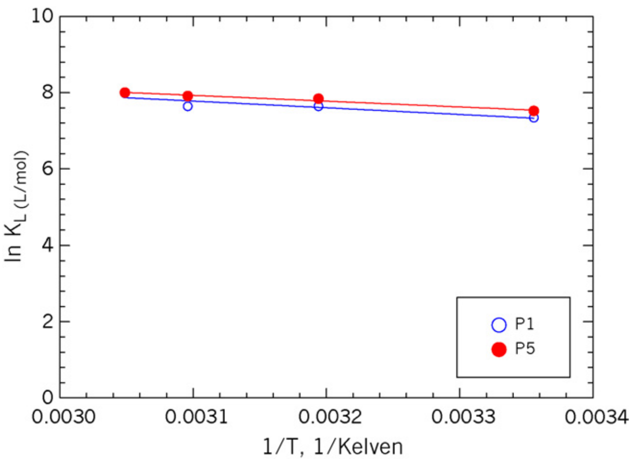


Fig. 10. Van't Hoff plots for the uptake of Ag(I) on the studied polymers.

and reported in Table 5. The positive values of ΔH° confirming the endothermic nature of adsorption process, whereas the positive values of ΔS° indicates an increase in the degree of freedom of the system which means a more random state that mostly encountered in metal chelation. The chelation mechanism for Ag(I) is a substitution reaction of water of hydration bonded to the metal ion by active sites. The liberation of water molecules of chelation suggests the high orderness of adsorption system at equilibrium due to the interaction between active sites and metal ion. Gibbs free energy of adsorption (ΔG°) was calculated from the following relation:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \qquad (14)$$

The values of ΔG° at different temperatures were calculated and reported in Table 6. The negative value of ΔG° indicates a spontaneous reaction. The observed increase in negative values of ΔG° with increasing temperature implies that the adsorption becomes more favorable at higher temperatures [16]. The data given in Table 6 also show an increase in the values of $T\Delta S^\circ$ at all temperatures.

3.3. *Elution and regeneration cycles*

Sorption/desorption cycle runs were carried out for Ag(I) on P5 polymer . The elution of the metal ions was performed using 50 mL of 0.5 M thiourea acidified with 0.01 M H_2SO_4. As shown in Fig. 11, the breakthrough curves for recovery of Ag(I) showed no characteristic changes during successive cycles. This indicates that P5 chelating polymer has good performance for repeated use up to four cycles.

Table 5
Enthalpy and entropy changes for adsorption of Ag(I) on studied polymers.

Polymer	ΔH° (kJ/mol)	ΔS° (J/mol K)
P1	14.62	110.00
P5	12.60	104.99

Table 6
Free energy change for adsorption of Ag(I) on polymers at different temperatures.

Temperature (K)	P1		P5	
	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)
298	−18.16	32.78	−18.68	31.28
313	−19.81	34.43	−20.26	32.86
323	−20.91	35.53	−21.31	33.91
328	−21.46	36.08	−21.83	34.43

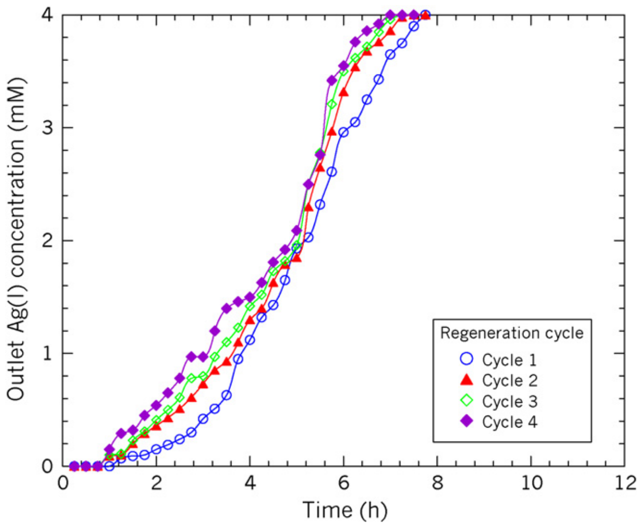


Fig. 11. Effect of successive desorption cycles on the breakthrough curves for the recovery of Ag(I) at flow rate of 0.5 mL/min using P5 chelating polymer.

3.4. *Conclusions*

Recovery of Ag(I) from aqueous solutions was studied using resin derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde. The recovery process was carried out through batch and column methods. The chelating thiourea polymer showed good selective adsorption of Ag(I) from binary mixtures of different metal ions. Kinetic studies indicated that the adsorption reaction follows the pseudo-first-order kinetics. Thermodynamic parameters obtained indicated that the adsorption process is spontaneous and endothermic reaction.

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