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Extraction of Silver From Photographic Waste

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Abstract- **The waste photographic films/X-ray contains 1.5 - 2 % (w/w) black metallic silver which is recovered and reused. Around 18-20% of the world's silver needs are supplied by recycling photographic waste. Silver is a precious metal, further silver has wide uses like in jewellery, dentistry, photography, mirrors, optics, industries, etc. So the recovery of silver is beneficial in industrial, chemical and economical aspects. Recovery of silver from photographic wastes is interesting because of the economic value of silver and also from environmental point of view. In photographic industry, silver is recovered from development and fixing solution, spent rinse water and scrap films. Electrolysis is a commonly used method to recover silver from photographic wastes but it is not suitable for dilute silver concentration (less than 100 ppm) because the plating efficiencies are very low. This process requires high initial capital investment and high operating cost, and critical operating conditions that need to be constantly supervised. The 100 ppm of silver concentration in effluent is relatively high compared to recommended allowable discharge level of 0.1 to 1.0 mg/dm^3, which means that further treatment is required before it can be discharged to water stream. The oldest and conventional method of silver recovery, precipitation, could not achieve the recommended discharge level although it has provided an effective technique for silver recovery. This is because an industrial effluent contains complexing agents which might bind to the silver metal. This metal complex is sometime very stable and not able to be precipitated by precipitation process. To overcome the problem our method has a great potential and has been reported as an advanced technique for recovery of silver.**

Keywords- **Silver, extraction, photographic waste.**

I. Introduction

Increasing industrialization and urbanization worldwide had caused serious pollution all around the world, especially in the aquatic environment. Wastewaters produced by humans are frequently laden with toxic heavy metals such as copper, silver, mercury, etc. The soluble form of these heavy metals is very dangerous because it is easily transported and more readily available to plants and animals. For humans, poisoning by these metals can result in severe dysfunction of kidney, reproduction system, liver, brain and central nervous systems [1]. Hence, to remove the toxic heavy metals from wastewaters has become increasingly focused. Furthermore, recovery of the precious metals like silver, gold and platinum will not only solve the environmental problems but also have profitable potential.

Silver is a precious metal widely used in the photographic, electrical, electronics, chemical and jewelry industries. Even though it is not as expensive as gold or platinum, silver is still only present in limited amounts in nature, which contributes to the need for efficient methods of recycling silver from waste generated by the above industries [2]. Most world silver is recovered from scraps such as photographic films, X-ray films and jewelry [3]. During the past three decades, many methods have electrolysis [4], precipitation [5], ion flotation [6], ion-exchange [7], adsorption [8] and reverse osmosis [9], etc. Among all the above methods, adsorption using low-cost adsorbents is recognized as an emerging technique and a large variety of adsorbents have been developed and tested. For instance, activated carbon [10], polymeric adsorbents [11], clarified sludge [12] and biomaterials such as chitosan [13–15], konjac glucomannan [16], seaweed [17] and lignin [18], etc. Chitosan, as one of the most frequently reported biosorbents, has been investigated by many researchers for recovery of heavy metals from aqueous solution. Modifications of chitosan can make it more selective and effective for several metal ions, especially heavy metal ions. Carboxymethylation was regarded as a simple and efficient way to facilitate the adsorption capacity of chitosan for many heavy metals [19]. In addition, grafting new functional groups such as thiourea [20], thiourea/rubeanic acid [21], l-lysine [22] and glycine [23] onto cross-linked chitosan backbone can also improve its selectivity and adsorption ability. To date, no report has been identified on chitosan resin modified by using the two methods carboxymethylation and grafting sulfur groups (thiourea) together. In this work, a thiourea-modified chitosan resin was synthesized and characterized by Fourier transform infrared (FT-IR) spectroscopy. The adsorption behavior of the resin towards silver in aqueous solution was investigated and examined by ICP-OES. Both kinetic and thermodynamic analyses for adsorption process were reported.

II. Experimental Work

A. Instrumentation

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo-Fisher) was used to determine the concentration of metal ions. Fourier transform infrared spectroscopy was used to analyze the functional groups in the synthesized resin and the original chitosan.

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B. Chemicals

Chitosan with 80 mesh, 96% degree of deacetylation and average-molecular weight of 6.36×10^5 was purchased from National Chemicals, India, Glutaraldehyde, thiourea and other chemicals and reagents were purchased from Merck, India. All the other reagents were analytical grade and distilled water was used to prepare all the solution. Standard solution of silver (1000 mg/l) for ICP-OES was obtained from National Chemicals, India. Metal ions of nitrate form was used and 0.1M HNO_3 and 0.1M NaOH were used for pH adjustment.

C. Synthesis of the Thiourea-Modified Chitosan Resin

O-carboxymethyl-chitosan was prepared following the method of Zhu et al. [23]. 2 g chitosan was immersed in 25 ml of 50 wt% NaOH solution to swell and alkalize for 24 h. Five grams of monochloroacetic acid was dissolved in 25 ml of isopropanol, and then added drop-wise to the flask containing the alkalized chitosan after filtration for 20 min. The reaction continued 8 h at room temperature and then the mixture was filtered to remove the solvent. The filtrate obtained was dissolved in 100 ml of water, and 2.5M HCl was added to it to adjust its pH to 7. After this solution was centrifuged to remove the precipitate, 400 ml of anhydrous ethanol was added to it and the precipitate was O-carboxymethyl-chitosan. 3.0 g of thiourea was dissolved in 60-ml distilled water. 17.1 ml of (50%) glutaraldehyde solution was added to thiourea solution in a round flask. The mixture was heated on a water bath for 3 h at 323 K. After completion of the reaction, 1.36 g of carboxymethyl-chitosan was dissolved in 30-ml distilled water, and the solution was then added to the mixture of the flask and heated for 8 h at 343 K. A large quantity of resin was formed, and washed several times with dilute sodium hydroxide, distilled water and acetone respectively. The resin was dried at 333K for 3 h and weighed about 2.96 g, and then sieved where the particle size fraction 0.1–0.4mm was used in this study.

D. Characterization of the Resin

FT-IR-spectra were used to identify the structure of the synthesized resin. The sample was prepared mixing 1mg of the material with 100mg of spectroscopy grade KBr. The FT-IR-spectra were recorded using Nicolet Magne-Avatar 360 equipment.

E. Preparation of Solution

A stock solution of silver nitrate (1×10^{-2} M) was prepared in distilled water.

0.1M HNO_3 and 0.1M NaOH were used to change the acidity of the medium.

F. pH Study of Ag(I) Adsorption onto the Modified Chitosan Resin

The experiments performed to determine the effect of pH on Ag (I) adsorption were carried out by placing 0.1 g of dry resin in a series of flasks containing 100 ml 1×10^{-2} M metal ion solution. The desired pH was adjusted using 0.1M HNO_3 and 0.1M NaOH. The flasks were shaken at 300rpm for 12 h at 298 K. After adsorption, the filtrate of each flask was obtained and the metal ion concentration was determined by ICP-OES.

G. Adsorption Kinetics

The effect of contact time on the uptake of Ag (I) by the resin was done by placing 0.1 g of dry resin in a series of flasks. To each flask, 100 ml of Ag (I) at pH 4.0 with initial concentration of 1×10^{-2} M was added. The flasks were shaken at 298 K. Samples of 5ml solution were withdrawn at scheduled time intervals and analyzed for Ag (I) concentration.

H. Adsorption Isotherms

0.1 g dry resin was swelled in a series of 250-ml flasks containing 50mL of distilled water for 1 h. In each flask, 50mL of metal ion solution at desired concentration was added to the flask, and the pH value was recorded. The flasks were shaken at 300rpm while keeping the temperature at 298, 308, 318 and 328K for 12 h. Later on, the concentration of solution was determined by ICP-OES and the metal ion uptake was calculated.

I. Metal Ions Co-adsorption Experiment

The selective separation of Ag(I) from binary mixtures with Cu(II), Ni(II), Cd(II), Zn(II) and Ca(II) was carried at pH 1.0 with the same other adsorption conditions in Section 5.2.6. After adsorption equilibrium, the concentration of each metal ion in the solution was measured by ICP-OES.

J. Desorption and Reusability

Ag (I)-loaded modified chitosan resin was collected and washed with deionized water to remove any unabsorbed metal ions. Then batch desorption experiments were carried out using various concentrations of thiourea, HCl and thiourea–HCl solutions. The resin after desorption was rinsed with deionized water, dried and then reused in adsorption experiment. The process was repeated for five times.

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III. Results And Discussions

A. Characteristics of the Resin

As seen from Fig. A., the adsorption band around 3300cm^{-1} in all spectrums, revealed the stretching vibration of $^{-}NH_2$ and ^{-}OH groups in chitosan, and the bands near 1641 and 1555cm^{-1} in the spectrum of the resin are assigned to C=N of Schiff's base moiety and C–N of thiourea moiety, respectively.

The spectrum of the resin also displays new bands near 1108 and 1053cm^{-1} corresponding to C–O, one of the characteristics of O-carboxymethyl-chitosan. Besides, a lot of differences in the spectra before and after silver sorption were observed. The bands at 2917cm^{-1} strengthened. The intensity of the band around 1400cm^{-1} which is assigned to >N–C S group was substantially decreased after Ag (I) binding, which confirms that sulphur groups were involved in silver binding. In the spectrum of silver adsorbed onto the modified resin, the peak at 1641cm^{-1} disappeared and a new peak around 1703cm^{-1} came out. Additionally, the changes in the spectra around 3300cm^{-1} and the decreasing intensity at 1053cm^{-1} also indicated that the nitrogen atoms as well as oxygen atoms in the –OH and –CO groups were involved in silver adsorption.

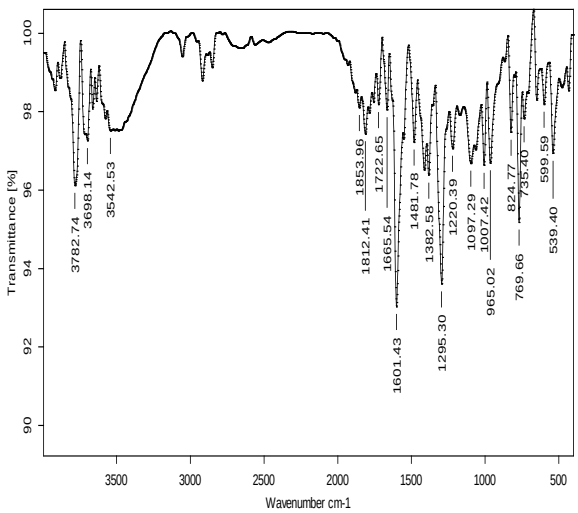

Fig. A. FT-IR spectra of thiourea-modified chitosan resin after Ag (I) adsorption.

B. The pH Effect on Ag (I) Sorption

In Fig. B., it is clearly seen that the uptake of Ag (I) increases as the pH increases till reaching a maximum value around pH 4.0. The pH value of solution increased after adsorption equilibrium. At the initial pH< 4.0, the increase of pH was more obvious and the final pH could reach above 6.0, while at the initial pH> 4.0, the final pH slightly elevated and did not go beyond 8.0.

As reported by Chassary et al. [20], at lower pH, part of metal sorption can be explained by electrostatic attraction of anion metal complexes by protonated amine groups. With pH reaching about 4.0, the higher adsorption capacity might be due to the presence of free lone pairs of electrons on nitrogen and sulfur atoms that are suitable for coordination with Ag (I) to give the corresponding resin–metal complex. At higher pH, the decreased adsorption of precious metals observed maybe due to precipitation and the electrostatic repulsion between surface sites of adsorbent and metal ions.

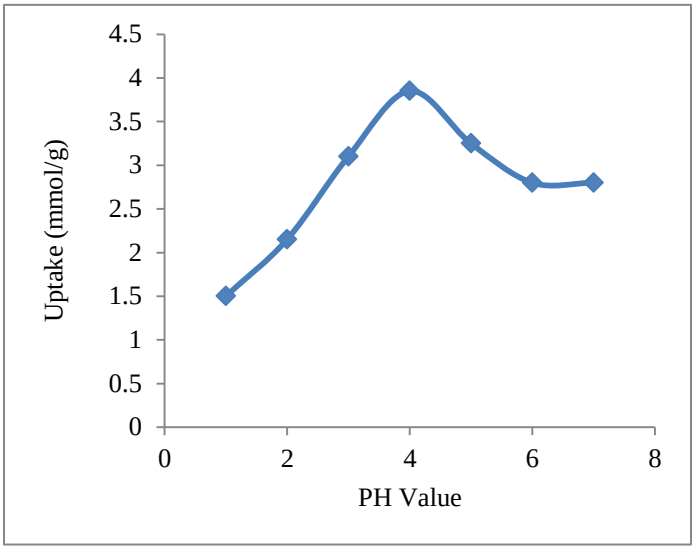

Fig. B. Effect of the initial pH on the uptake of Ag (I) by the studied resin.

Table A.
Parameters of the pseudo-first-order, pseudo-second-order kinetic models and intra-particle diffusion model for recovery of Ag (I) on the studied resin.

Metal ion	Pseudo-first-order		
	K_1 (min^{-1})	q_e (mmol/g)	R^2
Ag (I)	0.016	1.87	0.9857
Metal ion	Pseudo-second-order		
	K_2 (g/mmol min)	q_e (mmol/g)	R^2
Ag (I)	0.126	4.1	0.9979
Metal ion	Intra-particle diffusion		
	K_{id} (mmol/gmin $^{0.5}$)	Intercept	R^2
Ag (I)	1.368	0.313	0.99

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C. Adsorption Kinetics

The effect of contact time on the adsorption of Ag (I) is shown in Fig. C(I). Experimental results suggested that the silver adsorption could reach equilibrium within 4 h. The reaction kinetic parameters for the adsorption process were studied by batch method. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were selected to elucidate the adsorption kinetic process in this work. The Lagergren pseudo-first-order kinetic model is represented as:

$$Log\ (q_e - q_t) = log\ q_e - \left(\frac{k_1}{2.303}\right) \qquad _____(1)$$

Where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption, q_e and q_t (m mol/g) are the amounts of metal ion adsorbed at equilibrium and time t (min), respectively. The q_e and rate constant k_1 were calculated by plotting the log (q_e - q_t) versus t. The plots for pseudo-first-order model are presented in Fig. C(II). The pseudo-second order model can be written as:

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

Where k_2 is the pseudo-second-order rate constant of adsorption (g/(mmolmin^{-1})). The kinetic parameters for pseudo-secondorder model are determined from the linear plots of (t/q_t) versus t. The plots for pseudo-second-order model are presented in Fig. C(III). The parameters for pseudo-first and pseudo-second order models were all shown in Table 5.1. Accordingly as shown in Table 5.1, the calculated qe value of pseudo-second-order kinetic model is in good agreement with experimental q_e value (3.77 m mol/g) and could fit the adsorption of Ag (I) on the resin very well. To further test whether the adsorption rate is controlled by intra-particle diffusion, the intra-particle diffusion model was used. The initial adsorption rate (h) can be determined from k_2 and q_e values using

$$h = k_2 q_e^2 \qquad _____ (3)$$

The linear form of the intra-particle diffusion equation can be

Described as:

$$\ln q_t = \ln k_{id} + 0.5 \ln t \qquad _____ (4)$$

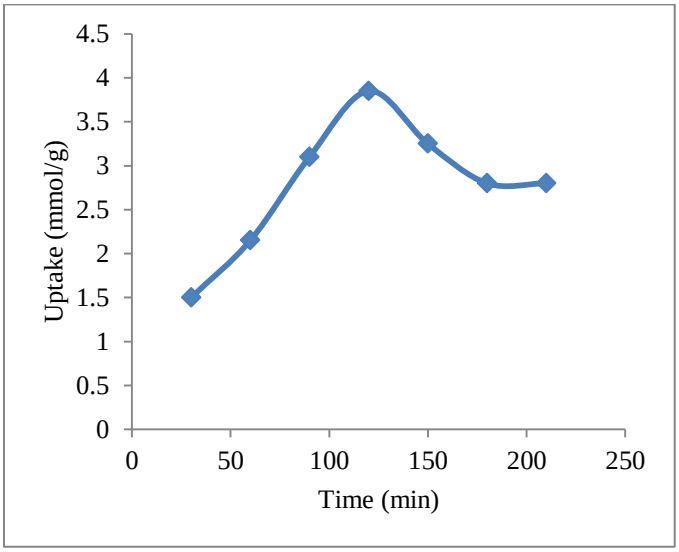

Fig. C (I)

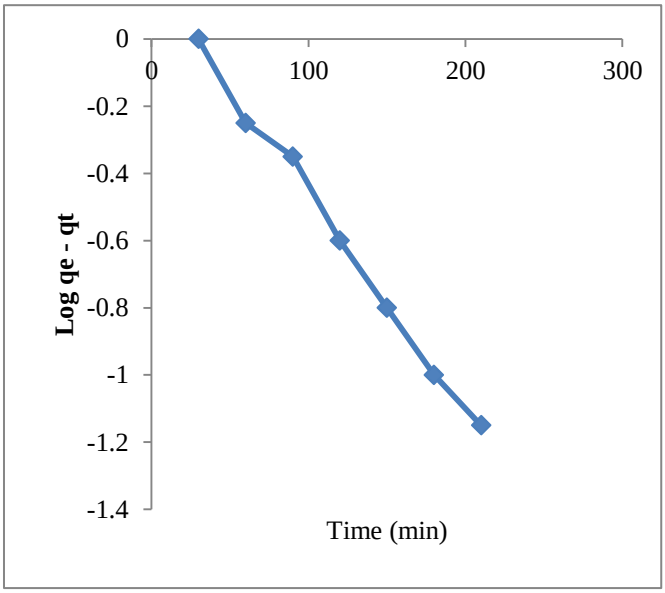

Fig. C (II)

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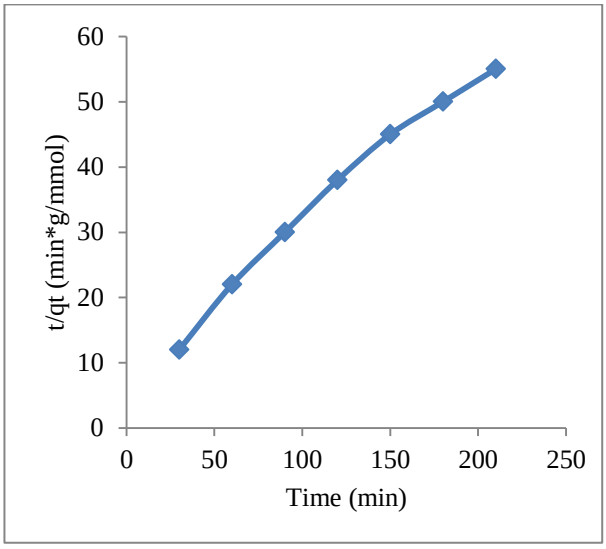

Fig. C (III)

Fig. C. (I) Effect of adsorption time on the uptake of Ag (I). (II) Pseudo-first-order kinetic plots for the adsorption of Ag (I). (III) Pseudo-second-order kinetic plots for the adsorption of Ag (I).

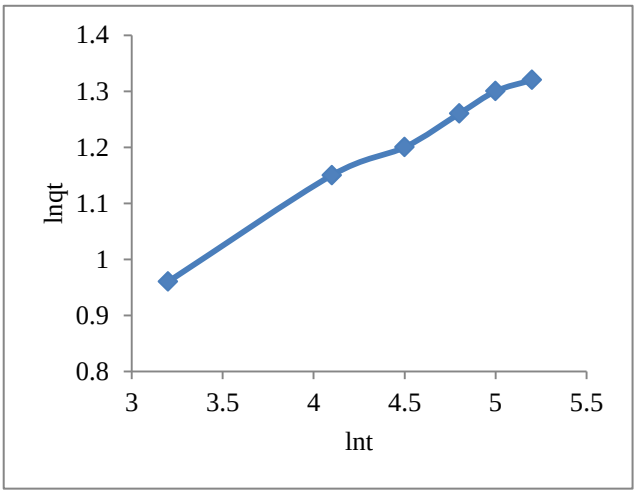

Fig.D. Plots for intra-particle diffusion.

D. Adsorption Isotherms

Where kid (m mol/ (g min$^{1/2}$)) is the intra-particle diffusion rate constant, which can be obtained from the slope of the plot ln q_t versus ln t in Fig. D. The kinetic parameters from this model are also given in Table A. From the experimental results, the main adsorption mechanism may be chemical sorption and consist of the external surface adsorption and the gradual adsorption stage. In gradual adsorption stage, intra-particle diffusion is rate controlling step. Adsorption capacity decreased with elevated temperature. To interpret the adsorption experimental data, the Langmuir and Freundlich isotherm models were used.

The Langmuir model can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \qquad (5)$$

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} (mmol/g) and K_L (l/mmol) are the Langmuir constants which are related to the adsorption capacity and energy of adsorption, respectively, and can be calculated from the intercept and slope of the linear plot, with C_e/q_e versus C_e. The values of K_L and Q_{max} at different temperatures for adsorption of Ag (I) were reported in Table B. It is seen that the value of Q_{max} at 298K (obtained from Langmuir plots) is consistent with that experimentally obtained (3.77 mmol/g), indicating that the adsorption process mainly monolayer. The adsorption curves showed that the maximum uptake value for Ag (I) was 3.77 mmol/g. In former study, chitosan's maximum uptake value for Ag (I) was 42.0 mg/g. Compared to chitosan, the higher maximum adsorption capacity obtained for Ag (I) on this resin is because of the fact that the carboxymethylation and incorporation of thiourea in chitosan increase the number of sorption sites, which enhances the adsorption capacity. The degree of suitability of resin towards Ag (I) was estimated from the values of the separation factor constant (R_L) which can be calculated from the equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (6)$$

Where K_L (l/mmol) is the Langmuir equilibrium constant and C_0 (mmol/l) is the initial concentration of metal ion. $R_L > 1.0$ unsuitable; $R_L = 1$ linear; $0 < R_L < 1$ suitable; $R_L = 0$ irreversible. The values of R_L lie between 0.151 and 0.298 confirming the suitability of the resin for the recovery of Ag (I). The Freundlich model assumes heterogeneous adsorption due to the diversity of the adsorption sites or the diverse nature of the metal ions adsorbed, free or hydrolyzed species.

Table B.
Langmuir and Freundlich constants for adsorption of Ag (I) by resin.

Temperature (K)	Langmuir model		
	Q_{max} (mmol/g)	K_L (L/mmol)	R^2
298	4.09	0.564	0.9963
308	3.40	0.506	0.9975
318	2.98	0.335	0.9954
328	2.41	0.236	0.9928

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Temperature (K)	Freundlich model		
	k_f (l/g)	N	R^2
298	1.64	3.140	0.9902
308	1.30	3.065	0.9813
318	1.05	2.732	0.9866
328	1.79	2.134	0.9310

The Freundlich model is expressed as:

$$q_e = k_f C_e^{1/n} \qquad (7)$$

Where k_f ($l^{(1-1/n)}$/g) is the Freundlich constant related to adsorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity. k_f and n can be calculated from the slope and intercept of the linear plot of log q_e versus log C_e. The adsorption data fit with Freundlich isotherm model is also shown in Table B.

Table C
Thermodynamic parameters at different temperatures

Temperature (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol K)
298	-14.13	-24.77	-35.70
308	-13.77		
318	-13.41		
328	-13.06		

That the Langmuir model fits the experimental data better than the Freundlich model.The values of K_L at different temperatures were treated according to van't Hoff equation,

$$\ln K_L = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (8)$$

Where ΔH◦ (J/mol) and ΔS◦ (J/mol K) 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 -ΔH◦/R and ΔS◦/R, respectively. Gibbs free energy of adsorption (ΔG◦ (J/mol)) was calculated from the following relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (9)$$

The values of ΔH◦, ΔS◦ and ΔG◦ were reported in Table C. The negative values of ΔH◦ confirm the exothermic nature of adsorption process.

The observed decrease in negative values of ΔG◦ with increasing temperature implies that the adsorption becomes less favorable at higher temperature.

Table D. compares the maximum adsorption capacity of the hiourea-modified chitosan resin for Ag (I) with other adsorbents reported in the literature. The result demonstrated that the adsorption capacity of this resin was relatively higher than several other adsorbents.

E. Metal Ions Co-adsorption

Selective separation of Ag (I) from binary mixtures with Cu (II), Ni (II), Cd (II), Zn (II) and Ca(II) was studied at pH 1.0 and the other adsorption conditions was following Section 5.2.6. The uptake obtained for Ag (I) in the presence of Cu (II), Ni (II), Cd (II), Zn (II) and Ca (II) was 2.26, 0.3, 0.1, 0.02, 0.5 and 0.0 mmol/g, respectively. The especially higher uptake of Ag (I) compared to other metal ions at relatively lower pH value (1.0) may be useful in the selective separation of Ag (I) from other metal ions.

F. Desorption and Reusability

Desorption efficiency of the modified resin was studied by the batch method using various concentrations of thiourea, HCl and thiourea–HCl solutions. The results are presented in Table 5. It was found that 0.5M thiourea–2.0M HCl solution can effectively desorbed the Ag(I) (>98%) from adsorbent material.

Table D.
Maximum adsorption capacities for adsorption of Ag (I) onto various adsorbents

Absorbent	Adsorption capacity (mmol/g)
Surface moleculer-imprinted biosorbent [24]	1.846
Chemically modified melamine resins [25]	0.95
Chemically modified chitosan with magnetic properties [26]	2.1
Resin derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde [27]	3.6
Thiourea-modified chitosan resin (this work)	3.77

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Table E.
Desorption process.

Desorption agent	Desorption efficiency (%)
0.1 M Thiourea	32.37
0.3 M Thiourea	71.25
0.5 M Thiourea	86.31
1.0 M Thiourea	92.60
0.5 M HCl	33.72
1.0 M HCl	60.14
1.5 M HCl	67.29
2.0 M HCl	72.38
0.5 M Thiourea-2.0 M HCl	99.23

The high desorption efficiency obtained when 0.5M thiourea–2.0M HCl solution was used may be explained by the electrostatic interactions between the silver(I) species and charged species from elution, through the comparison of the electric double layer, which would weaken the interaction between the adsorbent and silver(I), promoting desorption. Also the resin can be reused after desorption with 0.5M thiourea–2.0M HCl solution. The resin reused for 5 cycles and the uptake of Ag (I) was 3.73, 3.71, 3.66, 3.65 and 3.63 mmol/g, respectively. These results showed that the adsorption capacity of this modified chitosan resin was not significantly changed up to 5 cycles and the desorption efficiencies were above 95%. Therefore, the resin had good durability and could be successfully applied for the recovery of Ag (I).

IV. Conclusion

As a result from the above method we get the silver free ion which is useful. Further modified thiourea chitosan resin has better yield of extraction, further it have higher selectivity of the silver. This type of resin can be reused after the regeneration and have long lasting characteristics. This resin is cheaper, thus the extraction cost is decreased. Further the operating conditions are normal which also reduce the process cost and ease of operation. It is the better method then other method technically, chemically, & economically.

The recovery of silver (I) from aqueous medium was studied using a thiourea-modified chitosan resin. The FT-IR picture confirmed the efficient modification of this chitosan resin.

The results suggested that the adsorption process was dependent on contact time, initial metal ion concentration, solution pH and temperature. The data also indicated that the adsorption reaction followed the pseudo-second-order kinetic model and fit well with the Langmuir isotherm equation as well as the simplified intra-particle diffusion equation. The 0.5M thiourea–2.0M HCl solution can effectively desorb silver (I) from the resin and this resin could be reused up to 5 times without obvious change in the uptake of silver (I).

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