Thermodynamics and Kinetics of Au(III) and Ag(I) Sorption on to Silicon-Organic Polymer

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Abstract: Sorption method is used for analysis of technological, geological and hydro-chemical samples with low content of precious metals and chemical pre-concentration of technological solution. Synthesized silicon-organic polymer containing thiocarbamide group, which named poly[bis -N,N'-(3-silsesquioxanilpropyl)-thiocarbamide]-(PSTM-3T) was used in this investigation. Sorption of Au(III) and Ag(I) ions from aqueous solutions of nitric acid has been studied using the silicon-organic polymer (PSTM-3T) under different experimental conditions. Better sorption was obtained at temperature 55 °C, 3 mol/L of nitric acid solution and contact time 300 min and 240 min for Ag(I) and Au(III). Thermodynamic parameters were calculated by Van't Hoff equation. The negative values of ΔG^0 at different temperatures indicate the feasibility of the process and the values become more negative with increase in temperature. The positive values of ΔH^0 and ΔS^0 indicate that the sorption process is endothermic and determine the disorderliness of the sorption at solid-liquid interface. Experimental data were evaluated to find out kinetic characteristics and found that the sorption of Au(III) followed pseudo-second order model and the sorption of Ag(I) followed pseudo-first order model. The sorption capacity increased with the increase in temperature and reached maximum value at 323 K and 328 K for Au(III) and Ag(I). The maximum sorption capacity of PSTM-3T for Au(III) and Ag(I) evaluated 333 and 129 mg/g.

Key words: Isotherm, sorption capacity, thiocarbamide.

1. Introduction

The variety of processes is used in the recovery and refining of precious metals and can be classified into two major categories. These are based on the differences of the raw material sources: one of the categories is process of refining of precious metals from concentrates of mined ores; and the other is process of recovering of precious metals from secondary materials sources such as recycled technological and industrial scraps. Examples of the latter include spent catalysts, electronic scrap, spent electrolytes and jewellery scraps. The separation of metal ions from solutions using sorbents has gained more attention due to their availability and costs. Sorption of precious metals (Au, Ag, Pt, Pd and Rh) on

to silicon organic sorbents with groups of thiocarbamide, thioacetamide, aminosulfide and dioxothiocarbamide has been investigated [1-7]. Synthesized silicon-organic polymer containing thiocarbamide group, which named poly[bis -N,N'-(3-silsesquioxanilpropyl)-thiocarbamide]-(PSTM-3T) was used in this work. There is report on preliminary study of Au(III) sorption thermodynamics on this sorbent [8], but sorption thermodynamics of Ag(I) and sorption kinetics of Au(III), Ag(I) have not detailed. This work focused on study of thermodynamics and kinetics of Au(III) and Ag(I) sorption onto PSTM-3T from aqueous solutions of nitric acid. Effect of parameters such as concentrations of nitric acid solution, initial concentration of Au(III) and Ag(I), time of contacts and temperatures was studied to find optimal sorption condition. Moreover, SEM/EDX and FT-IR analysis are used to confirm that Au(III) and Ag(I) are interacted with functional groups of

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PSTM-3T.

2. Experimental Procedure

2.1 Materials Preparation and Characterization

PSTM-3T polymer was produced from silicon-organic monomer: bis-N, N'-(3-triethoxysilylpropyl) thiocarbamide by hydrolytic poly-condensation reaction in aqueous media with pH 8-9 at the boiling temperature of the reaction mixture during 5-10 hours [7]. The synthesis reaction can be briefly expressed by Scheme 1.

The surface area and total pore volume of PSTM-3T were 490 m²/g and 3.53 cm³/g, respectively. This polymer is stable at 270 °C of heating [7].

2.2 Sorption Studies

In the present investigation, sorption of Au(III) and Ag(I) ions on PSTM-3T was treated in a temperature controlled shaker (PC-620D, CORNING). In a typical experimental run, 0.05 g of the sorbent was shaken together with 50 mL of solution with different concentration of Au(III) which was prepared from standard solution of Au(III). Agitation speed of the shaker was fixed at 500 rpm for all experiments. After equilibrium, the mixture was filtered and filtrate was analysed to determine the remaining metal ion concentrations. Au(III) and Ag(I) were analysed in a spectrophotometer at fixed wavelength of 490 nm for Au(III) and 416 nm for Ag(I) using dithizone and o-phenylenediamine as the complexing reagent. The analysis was carried out according to the procedure given by Ref. [9]. The same procedure has been used to study the effect of initial concentration, contact time and temperature.

2.3 Mathematical Procedures

The results of adsorbed Au(III) and Ag(I) on

PSTM-3T were quantified by mass balance. To test the system of equilibrium, the following parameters were used: sorption capacity of PSTM-3T (q_e); and sorption efficiency of the system (R). These parameters have been calculated as indicated in Eqs. (1) and (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R\% = \left(\frac{C_0 - C_e}{C_0} \right) * 100 \quad (2)$$

where C_0 , C_e are the initial and equilibrium concentrations of Au(III) and Ag(I) in the solution (mg/L); V is the volume of aqueous phase (L); m is the dry weight of the sorbent (g).

The sorption kinetic data of Au(III) and Ag(I) on the sorbent were analysed by pseudo-first and pseudo-second order rate equation [10]. The linearized form of pseudo-first order rate equation is given as:

$$\lg(q_e - q_t) = \lg q_e - \frac{K_1 t}{2.303} \quad (3)$$

The linearized form of pseudo-second order rate equation is given as:

$$\frac{t}{q_t} = \frac{1}{q_e} + \frac{1}{K_2 q_e^2} \quad (4)$$

where K_1 (min⁻¹) and K_2 (g/mg·min) are rate constants of pseudo-first order, pseudo-second order rate equation, respectively, t is the sorption period (min).

The thermodynamic parameters of the sorption, i.e. the changes of standard Gibbs free energy ΔG^0 (kJ/mole), standard enthalpy ΔH^0 (kJ/mole) and entropy ΔS^0 (J/mol·K), were calculated from the Van't Hoff equation.

$$\Delta G^0 = -RT \ln K_c; \quad K_c = \frac{C_A}{C_e} \quad (5)$$

$$\ln K_c = \frac{\Delta H^0}{-RT} + \frac{\Delta S^0}{R} \quad (6)$$

where R is the gas constant (8.314 J/mol·K), T(K) is the absolute temperature and C_A and C_e are the equilibrium concentration (mg/L) of metal ion, sorbed and left in the solution, respectively.

The activation energy of the process E_a (kJ/mole) was calculated by following formula [11].

$$\Delta H = E_a - RT \quad (7)$$

The data for the uptake of Au(III) and Ag(I) at different temperatures were processed in accordance to the linearized form of the Langmuir and Freundlich isotherm in Eqs. (8) and (9):

$$\frac{c_e}{q_e} = \frac{1}{Q \cdot b} + \frac{c_e}{Q} \quad (8)$$

$$\ln q_e = \ln K_f + n \ln C_e \quad (9)$$

where Q (mg/g) is the maximum sorption capacity, b (L/mg) is the Langmuir isotherm constant, n and K_f (l/g) are Freundlich isotherm constants.

3. Results and Discussion

3.1 Effect of Experimental Condition

The sorption experiments at 1-5 mol/L of nitric acid concentration range were carried out to study the effect of experimental condition. From the results as shown in Fig. 1, the highest sorption efficiency was observed around 3 mol/L of nitric acid solution. When the nitric acid concentration was increased from 4 to 5 mol/L, the sorption efficiency decreased. 3 mol/L of nitric acid solution was therefore chosen as suitable solution for next experiments.

3.2 Effect of Contact Time

Gold and silver uptake at different initial concentrations of Au(III) and Ag(I) were evaluated as a function of time (1-6 h) to determine an optimal contact time. Fig. 2 shows the time course of the sorption equilibrium of Au(III) and Ag(I) onto PSTM-3T.

Fig. 2 Effect of contact time on sorption capacity. Au(III) sorption (a) and Ag(I) sorption (b). (Solution volume of 50 mL with initial Au(III) concentration of 160, 320 and 480 mg/L at 293 K and with initial Ag(I) concentration of 20, 40 and 60 mg/L at 298 K, sorbent dosage of 0.05 g, 500 rpm).

As shown in Fig. 2a, sorption of Au(III) reaches the maximum value around at 240 min when initial concentrations of Au(III) are 160 mg/L, 320 mg/L and 480 mg/L, but sorption of Ag(I) reaches the maximum value around at 300 min when initial concentrations of Ag(I) are 20 mg/L, 40 mg/L, 60 mg/L and 80 mg/L (Fig. 2b). The sorption capacity of the sorbent increases by increasing an initial concentration of metal ion.

3.3 Thermodynamic Parameters

The values of ΔG^0 were calculated at each temperature, using Eq. (5) for the initial concentrations 160, 320 and 480 mg/L of Au(III) and 80, 100 and 140 mg/L of Ag(I) (Table 1). The negative values of ΔG^0 at different temperatures indicate the feasibility of the process and the values decrease with increase in temperature (Table 1). This suggests that the sorption process is spontaneous in nature and spontaneity decrease with the increase in temperature. The other

Fig. 1 Effect of nitric acid concentrations on sorption efficiency. (Solution volume of 50 mL with initial Au(III) and Ag(I) concentration of 20 mg/L, respectively, sorbent dosage of 0.05 g, 298 K, 500 rpm, 1 h).

thermodynamic parameters such as change in standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated by Eq. (6). ΔH^0 and ΔS^0 were calculated from the slope and intercept of the Vant Hoff's plot of $\ln K_c$ verses $1/T$. Positive values of ΔH^0 and (ΔS^0) indicate that the sorption process is endothermic and determine the disorderliness of the sorption at solid-liquid (sorbent PSTM-3T and nitric acid solution, containing Au(III) and Ag (I)) interface. Table 1 summarizes the results.

The activation energy of the sorption was calculated by Eq. (7). The values of the activation energy (E_a) were evaluated as 11.5-77.5 kJ/mol. These values suggest that the sorption of Au(III) and Ag(I) onto PSTM-3T is a chemical sorption, which is in accordance with the magnitude of activation energy for chemical adsorption. The activation energy of chemical adsorption is usually between 8.4 to 83.7

kJ/mol [12, 13].

3.4 Sorption Kinetics

The kinetics of Au(III) and Ag(I) on the PSTM-3T were analysed by pseudo first-order and pseudo second-order models. The experimental data and model predicted data are shown in Table 2.

The kinetics plots were made for sorption of Au(III) and Ag(I) on the PSTM-3T at different initial concentrations indicating that sorption reaction can be approximated with the second-order kinetics model. The correlation coefficient in this case was between 0.960 and 0.998, which is better than the first-order reaction model and calculated values of q_e are in good agreement with the results of experiments.

3.5 Sorption Isotherm

Two commonly used isotherms namely, Langmuir

Table 1 Sorption thermodynamic parameters.

T(K)	C_{Ag} (mg/L)	C_{Au} (mg/L)	ΔG^0 , kJ/mol		ΔH^0 , kJ/mol		ΔS^0 , J/mol·K		E_a , kJ/mol	
			Ag(I)	Au(III)	Ag(I)	Au(III)	Ag(I)	Au(III)	Ag(I)	Au(III)
293	80	160	-1.2910	-1.4410	8.68	13.06	98.85	70.60	11.50	15.8
303			-1.6043	-1.8052						
313			-2.2780	-2.0520						
323			-3.5591	-3.8471						
333			-5.3518	-3.9663						
293	100	320	-1.559	-0.9245	68.02	10.81	224.56	39.08	70.70	13.57
303			-2.3057	-1.2030						
313			-4.1460	-1.3292						
323			-5.0905	-1.8301						
333			-5.1425	-2.5980						
293	140	480	3.0137	1.408	74.83	11.09	256.32	24.95	77.50	13.4
303			1.9167	1.287						
313			-0.3813	1.100						
323			-4.6396	0.568						
333			-0.8574	0.521						

Table 2 Sorption kinetic parameters of Au(III) and Ag(I) sorption on to sorbent. (Solution volume of 50 mL, sorbent dosage of 0.05 g, 500 rpm, T = 303 K)

Ion	C_0 (mg/L)	$q_e(\text{exp})$ mg/g	Pseudo first-order			Pseudo second-order		
			$K_1 \cdot 10^{-2}$ (L/min)	$q_e(\text{cal})$ (mg/g)	R^2	$K_2 \cdot 10^{-4}$ (g/mg·min)	$q_e(\text{cal})$ (mg/g)	R^2
Au(III)	160	146.0	55.27	66.30	0.869	7.98	113.6	0.998
	320	117.5	69.09	70.76	0.969	1.57	125.0	0.978
Ag(I)	20	18.7	5.93	14.78	0.985	1.80	30.0	0.928
	60	42.3	8.49	32.31	0.893	0.75	70.0	0.960

Table 3 Isotherm constants.

Ion		Ag(I)	Au(III)
T (K)		328	323
Langmuir	Q (mg/g)	86.90	333.3
	b	4.60	0.033
	R ²	0.841	0.955
Freundlich	K _f (l/g)	1.76	1.63
	n	4.68	0.98
	R ²	0.902	0.914

Fig. 3 FT-IR spectra of PSTM-3T. Before (a), after gold (b) and silver (c) sorption.

and Freundlich isotherm were applied to explain or predict their equilibrium parameters for Au(III) and Ag(I) sorption onto PSTM-3T. The Langmuir isotherm is based on the monolayer sorption and expressed in the linear form as Eq. (8). The Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption and is expressed in linear form as Eq. (9). Constants and correlation coefficients are summarized in Table 3. The regression coefficient of Langmuir isotherm model is higher than Freundlich for Au(III) sorption. Freundlich isotherm constant n is 4.68 and regression coefficient of Freundlich isotherm model higher than Langmuir for Ag(I) sorption (Table 3). If the value of n is in the range of $1 < n < 10$, the sorption is favourable for Freundlich isotherm model [14]. From the all results, it can be concluded that the sorption of Au(III) and Ag(I) on to PSTM-3T followed Langmuir and Freundlich isotherm model, respectively. The maximum sorption capacity of the

sorbent for Au(III) and Ag(I) evaluated 333 and 129 mg/g.

3.6 Binding Mechanism

The change in morphology of the sorbent surface and amount of metal ion (7.66% of gold and 7.24% of silver) are determined by SEM/EDX analysis. It is confirmed that the structure of the sorbent changed after the sorption. To discuss the binding mechanism, FT-IR (Fourier Transform Infrared Spectroscopy) was used (Fig. 3).

As shown in Fig. 3a, which were obtained before the sorption, the peak at $3,300\text{ cm}^{-1}$ was attributed to N-H group, the peaks at $2,940$ and $2,880\text{ cm}^{-1}$ were due to the C-H stretching vibration of CH, CH₂, CH₃ groups, the peaks at $1,630$ and $1,560\text{ cm}^{-1}$ indicated the amide I (NH) and amide II (NH₂) bending vibration. Absorption peaks at $1,390$, $1,360$, 750 and 690 cm^{-1} were attributed to sulfo groups (CS), the peak at $1,140$ was attributed to Si-O-Si group and the peak at $1,030$ indicated CN stretching vibration, respectively. After gold and silver sorption (Figs. 3b and 3c), there were no changes at $2,940$, $2,880$, $1,140$ and $1,030\text{ cm}^{-1}$ but there were some changes at range of $3,500$ - $3,000$, $1,700$ - $1,500$ and $1,400$ - $1,300\text{ cm}^{-1}$ which related to NH, NH₂, CS and CN groups. Especially intensity of NH ($3,300\text{ cm}^{-1}$), NH ($1,630$) and NH₂ ($1,560\text{ cm}^{-1}$) groups decreased and the peak of NH₂ ($1,560\text{ cm}^{-1}$) shifted to the peak of $1,580\text{ cm}^{-1}$. Also lower peak of C = S ($1,390\text{ cm}^{-1}$) became very strong. All the results are signified that Au(III) and Ag(I) interacted with N and S atoms of functional groups of the sorbent.

4. Conclusion

It can be concluded from this investigation that synthesized sorbent, PSTM-3T can be used for the removal of Au(III) and Ag(I) from aqueous solution. Sorption Au(III) and Ag(I) is found to be effective in 3 mol/L of nitric acid solution and at higher temperatures. Sorption kinetics of Ag(I) follow pseudo-first order model and sorption kinetics of Au(III) follow pseudo-second order model. The values of activation energy suggest that the processes are chemical adsorption. The sorption isotherms of Ag(I) and Au(III) follow Freundlich and Langmuir model, respectively.

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