Investigation on sorption of Au(III) onto silicon-organic polymers with thioacetamide, thiocarbamide, and dioxothiocarbamide groups

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Abstract. Silicon-organic polymers containing thioacetamide, thiocarbamide, and dioxothiocarbamide groups were used in this investigation. The polymers were produced by the hydrolytic poly-condensation reaction of silicon-organic monomer, 3-triethoxysilylpropylamine. Au(III) sorption onto the polymers has been studied. The optimal condition of the sorption is confirmed by sorption experiments which were carried out at various times and in acidic solution conditions. Based on the result of the instrumental analysis and the values of thermodynamic parameters, such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ can be concluded that Au(III) can be connected with the electro-donor nitrogen and sulfur atoms of the functional group of the polymer by chemical and coordination bonds.

Keywords: precious metal, thermodynamic parameters, functional groups.

1   Introduction

The usage of precious metals is rapidly increasing based on their properties, such as oxidation and corrosion resistance, high melting point, good electrical conductivity, catalytic activity, and biological inactivity. For example, the chemical industry, electrical engineering, automobile industry, electronic engineering, medicine, cosmetics, painting processing, etc. [1]. In the last years, the use of precious metals in the electronics industry rapidly. Therefore, the research on separating precious metals from electronic and electrical waste (secondary raw materials) and industrial wastewater is of great interest to researchers [2]. The content of precious metals in electronic boards is 10 times higher than in natural deposit ore. According to the research on chemical content of electronic boards, content of Cu, Pb, Zn, Au, Ag, Pt,

and Pd are 10.0-26.8%, 0.99-4.19%, 0.16-2.17%, 80-1000 g/t, 110-3301 g/t, 4.6-30 g/t and 10-294 g/t, respectively.

There are many conventional methods for separating precious metals from various solutions, such as cementation [3,4] extraction [5,6,7,8] adsorption with activated carbon and ion exchange [9,10,11], and precipitation. However, these methods lack selectivity for precious metals, are not suitable for dilute solutions, and are expensive [12].

Nowadays, the research work of precious metals adsorption onto polymer materials with the following properties, good selectivity, resistance to an acidic environment, high specific surface area, and high adsorption capacity, takes a significant interest.

Therefore, in this research work, the sorption of gold onto organic silicon polymer PSOT-3, PTAS-3, and PSTM-3T polymers with dioxothiocarbamide (-NHC(SO$_2$)NH-), thioacetamide (-NHC(S)CH$_3$), and thiocarbamide (-NHC(S)NH-) group, respectively. The objective of this work is to confirm the optimal condition of the sorption Au(III) onto the polymers and determine the thermodynamic parameters of the process. Moreover, we focused on the interaction between Au(III) and the functional group of the polymers.

2   Experimental details

2.1   Materials

This investigation used 3 types of silicon-organic polymers containing diokcotiocarbamide, thioacetamide and thiocarbamide functional groups which are named poly[bis-N,N^I-(3-silseskvioksanilpropyl) dioxothio-carbamide] PSOT-3, poly[bis-N,N^I-(3-silseskvioksanilpropyl) tioacetamide] PTAS-3 and poly[bis-N, N^I-(3-silseskvioksanilpropyl) tiocar-bamide] PSTM-3T. All the polymers were produced by the hydrolytic poly-condensation reaction of silicon-organic monomer: 3-triethoxysilylpropylamine [13,14,15]. The characteristics of the sorbents are summarized in Table. 1

2.2   Sorption experiment

The sorption experiments are based on the reaction between the polymers (0.05 g) and metal ion solution (50 ml) with different concentrations. The experiments were conducted in a temperature-controlled shaker. Then, we filtered the suspension, and the filtrate was analysed by a spectrophotometer using a complexing reagent to determine the remaining metal ion concentration.

The sorption efficiency is calculated by the following equation:

$$R\% = \left(\frac{C_0 - C_e}{C_e}\right) * 100 \qquad (1)$$

where R is sorption efficiency (%), c$_o$ and c$_e$ are the initial and equilibrium concentrations of metal ion in the solution (mg/l).

Table 1. The characteristics of the PSOT-3, PTAS-3, and PSTM-3T

Name of the polymers and chemical formula	Functional groups of the polymers	Temperature of stability, ^0C	FT-IR spectra of the sorbents	Pore volume, cm^3/g and surface area, m^2/g
PSOT-3, $[O_{1.5}Si(CH_2)_3NH\text{-}C(SO_2)\text{-}NH]n$	$R{-}NH{-}\overset{\overset{O\;\;\;O}{\diagdown\!S\!\diagup}}{\underset{\parallel}{C}}{-}NH{-}R \rightleftharpoons R{-}NH{-}\overset{\overset{O\;\;\;OH}{\diagdown\!S\!\diagup}}{\underset{}{C}}{=}N{-}R$ dioxothiocarbamide	270	$\nu_{Si\text{-}O\text{-}Si}$ 1050, ν_{NH} 3400, δ_{NH} 1640, $\nu_{C=N}$ 1690, ν_{SO} 1100, ν_{CS} 610	1.17 410
PTAS-3, $[O_{1.5}Si(CH_2)_3\text{-}NH\text{-}C(S)\text{-}CH_3]n$	$\left[R{-}NH{-}\underset{\underset{S}{\parallel}}{C}{-}CH_3\right]_n \rightleftharpoons \left[R{-}N{=}\underset{\underset{SH}{\mid}}{C}{-}CH_3\right]_n$ thioacetamide	230	$\nu_{Si\text{-}O\text{-}Si}$ 1145, $NC(S)NH$ 3220, δ_{NH} 1570	0.93 510
PSTM-3T, $[O_{1.5}Si(CH_2)_3NHC(S)NH\text{-}(CH_2)_3SiO_{1.5}]n$	$\left[R{-}NH{-}\underset{\underset{S}{\parallel}}{C}{-}NH{-}R\right]_n \rightleftharpoons \left[R{-}NH{-}\underset{\underset{SH}{\mid}}{C}{=}N{-}R\right]_n$ thiocarbamide	270	$\nu_{Si\text{-}O\text{-}Si}$ 1140, ν_{NH} 3300, δ_{NH} 1570, $\nu_{C=S}$ 1350	3.53 490

2.3 Characterization

To discuss the interaction between the polymers and Au(III), the elemental analysis of samples was determined an energy-dispersive spectrometer (EDS, JED-2300, JEOL, Akishima, Tokyo, Japan) and surface functional groups of the polymers before and after adsorption of Au(III) were identified using the KBr pellet method, with wavenumbers from 400 to 4000 cm^{-1} on Fourier transform infrared spectroscopy (FTIR-4200, JASCO, Hachioji, Tokyo, Japan).

3 Result and discussion

3.1 Interaction between Au(III) and functional group of the polymers

According to the EDS analysis results shown in Table 2, the main elements of the polymers were silicon, carbon, and oxygen. Compared with the composition before sorption, the amount of Au(III) was determined after sorption. It confirms that the sorption was performed successfully. The content of oxygen, nitrogen, and sulfur changed after sorption, which suggests that the Au(III) reacted with the oxygen, nitrogen, and sulfur in the functional groups of the polymers.

We present the FT-IR spectra of the PSOT-3, PTAS-3, and PSTM-3T in Fig. 1, 2, and 3. We found the FT-IR spectra of the PSOT-3 peaks at 3340 (vN-H), 2940 (vCH), 2880 (vCH), 1700 (vC=N), 1670 (vC=N), 1630 (δNH), 1560 (δNH$_2$), 1120 (vSiOSi), 1030 (vSO) 6a 620 (vCS) (Fig. 1) [15]. After the Au(III) sorption, we detected the following changes in the FT-IR spectra: the intensity of the deformation bond of CN group (1700 cm^{-1}) and valence bond of amine groups (NH and NH$_2$) (1630 and 1560 cm^{-1}) decreased, the peaks corresponding to C=N (1670 cm^{-1}) and

Table 2. Elemental composition of the polymers

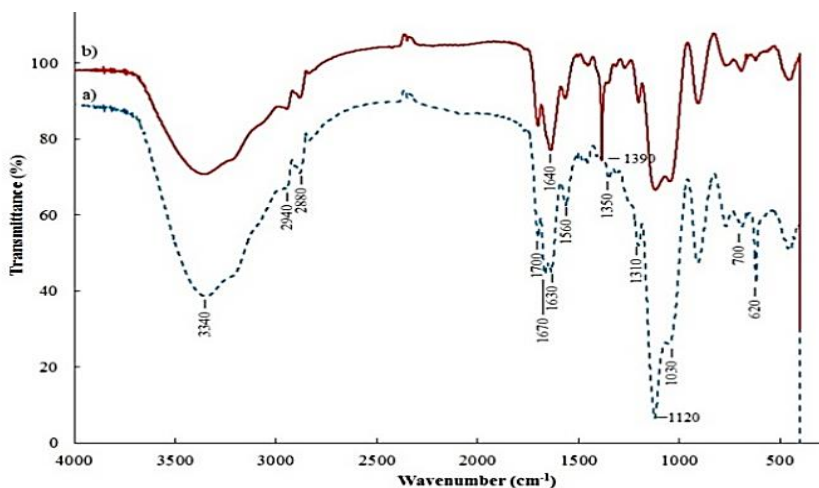| Polymers		Elements, weight %					
		Silica (Si)	Carbon (C)	Oxygen (O)	Sulfur (S)	Nitrogen (N)	Gold (Au)
PSOT-3	Before sorption	14.3	34.31	28.72	6.42	16.25	-
	After sorption	16.86	31.41	23.37	1.77	14.85	11.71
PTAS-3	Before sorption	14.66	47.84	18.34	11.71	7.45	-
	After sorption	9.67	36.66	15.98	6.56	9.75	21.37
PSTM-3T	Before sorption	18.31	36.94	23.16	14.23	7.27	-
	After sorption	22.4	40.56	23.48	3.96	1.93	7.66

Figure 1. FT-IR spectra of PSOT-3, before (a) and after (b) sorption of Au(III)

C-S (620 cm^{-1}) groups disappeared, a new peak corresponding to adsorption of C=S group at 1390 cm-^{1} was detected. As shown in Fig. 2, the following peaks are noted in the FT-IR spectra of the PTAS-3; 3220 (vNH), 3070 (vCH$_3$), 2920 (vN+H), 2880 (vCH), 1670 (vC=N), 1550 (δNH$_2$), 1460 (δNH), 1400 (vC=S), 1330 (vCH3), 1310 (vCN), 1120 (vSiOSi), 1020 (vCN), 750 (δCH$_2$), 690 (vCS) and 470 (vCN) cm^{-1}. However, after the sorption, the intensity of the CN deformation bond (1670, 1310, and 1020 cm^{-1}) increased and the intensity of the peaks at 3220, 2920 and 1560 cm^{-1} decreased. It indicates that Au(III) is connected to the amino group by chemical bond.
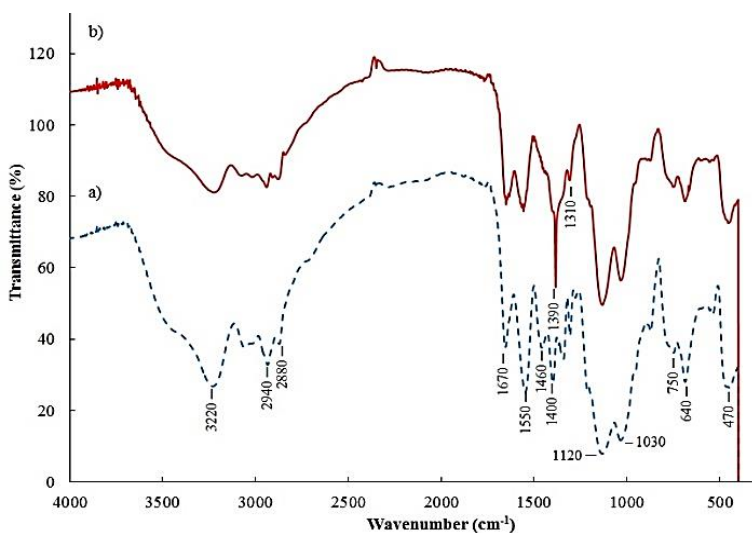

Figure 2. FT-IR spectra of PTAS-3, before (a) and after (b) adsorption of Au(III)

According to the results of FT-IR analysis of PSTM-3T (Fig. 3), the peaks at 3320 (vNH), 2920 (vN-H), 2880 (vCH), 1630 (δ NH), 1560 (δNH$_2$), 1305 (vCN), 1200 (vCN), 1120 (vSi-O-Si), 1000 (vCN), 760 (δCH$_2$), and 690 (vCS) cm^{-1} were detected in the spectra. After sorption (Fig. 3b), the intensity of NH (3320 cm^{-1}) and NH$_2$ (1570 cm^{-1}) groups decreased and a new peak of the C=S group was detected at 1390 cm^{-1}. These changes prove that the Au(III) ion interacts to the nitrogen and sulfur atoms of the functional group of the polymer.
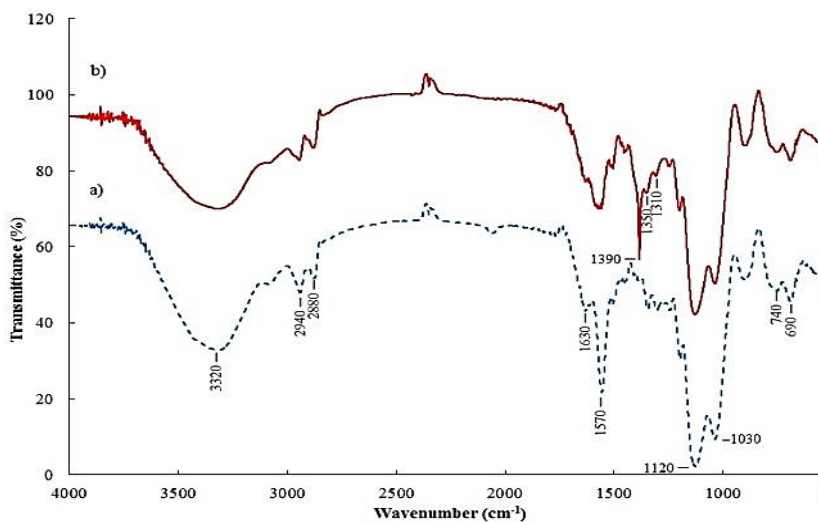
Figure 3. FT-IR spectra of PSTM-3T, before (a) and after (b) adsorption of Au(III)

3.2   The optimal condition of Au(III) sorption

To confirm the optimal condition of the Au(III) sorption onto the polymers we studied the effect of the concentration of hydrochloric and nitric acids. Au(III) sorption experiments were conducted in hydrochloric acid conditions with a concentration range of 0.01-0.5 mol/L and 0.1-5.0 mol/l for PSOT-3 and PTAS-3 polymers. Au(III) sorption experiments were conducted in nitric acid conditions with concentration range of 1-5 mol/L for PSTM-3T polymer. Results are shown in Table 3.

Table 3. The relation between acid concentration and sorption efficiency (R, %)

Polymer	Initial concentration of Au(III), mg/l	C_{HCl}	R, %
PSOT-3	21.9	0.01	98.1
		0.10	99.9
		0.20	99.9
		0.30	99.9
		0.50	88.3
PTAS-3	219.0	0.10	90.5
		0.50	90.9
		1.00	88.7
		3.00	86.3
		5.00	86.3
PSTM-3T	160.0	1.00	82.0
		2.00	84.0
		3.00	87.0
		4.00	87.5
		5.00	81.8

To study the effect of contact time on the Au(III) sorption onto PSOT-3, PTAS-3, and PSTM-3T polymers, the experiments were carried out from 60 - 300 minutes at 298K. The sorption equilibrium was reached after 240 minutes for all the cases. Based on all these results the optimal condition of the sorption is chosen as shown in Table 4.

Table 4. The optimal condition of Au (III) sorption onto silicon organic polymers

| Polymer | The optimal condition | | |
	Concentration of acidic solution	Time, min	$R\%$
PSOT-3	0.1 mol/L of HCl		98.0
PTAS-3	0.5 mol/L of HCl	240	90.9
PSTM-3T	3 mol/L of HNO_3		88.0

3.3   Thermodynamic Studies

We evaluated the standard thermodynamic parameters (the standard Gibbs-free-energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$)) for the sorption of Au(III) onto the polymers at a temperature of 25 °C. $\Delta G°$, $\Delta H°$ and $\Delta S°$ are derived from Eq. (2) and Eq. (3):

$$\Delta G^0 = -RTlnK_c \tag{2}$$

$$lnK_c = \left(\frac{\Delta H^0}{-RT}\right) + \left(\frac{\Delta S^0}{R}\right) \tag{3}$$

where K_c is the equilibrium constant ($K_c = C_{Ae}/C_e$); C_{Ae} is the concentration of adsorbed Au(III) (mg/L); C_e is the equilibrium concentration of Au(III) (mg/L); T is the temperature (K); R is the universal gas constant (8.314 J/mol·K).

We found the $\Delta H°$ and $\Delta S°$ from the slope and intercept of the linear plot (lnK_c versus 1/T). We summarized the results in Table 5. The values of the $\Delta G°$ were determined in the temperature of 298K to be between -0.924 and -7.446 kJ/mol. According to the negative values of the $\Delta G°$, the adsorption of Au(III) onto the PSOT-3, PTAS-3, and PSTM-3T are favored and spontaneous.

The standard enthalpy change $\Delta H°$ values are positive, a characteristic of an endothermic process. Moreover, the positive value of the standard entropy change $\Delta S°$ indicates the increased randomness at the solid-liquid interface.

Table 5. The thermodynamic parameters of the sorption

Polymer	C_{Au} (mg/L)	ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/mol·K
PSOT-3	160.0	-2.722	39.490	140.756
	320.0	-1.345	21.060	384.500
PTAS-3	160.0	-12.942	63.953	360.600
	320.0	-7.446	103.925	384.500
PSTM-3T	160.0	-1.441	13.060	70.600
	320.0	-0.924	10.810	39.080

4   Conclusions

In this study, we successfully studied the sorption properties of PSOT-3, PTAS-3, and PSTM-3T polymers for Au(III) and discussed the results through FT-IR and EDS instrumental analyses. We determined the maximum sorption efficiency to be 98.0, 90.9, and 88% under optimal conditions for PSOT-3, PTAS-3, and PSTM-3T, respectively. According to sorption thermodynamics sorption process is endothermic and spontaneous. Based on the result of the instrumental analysis and the values of thermodynamic parameters, such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ can be concluded that Au(III) can be connected with the electro-donor nitrogen and sulfur atoms of the functional group of the polymer by chemical and coordination bonds. These polymers could be an effective material for the recovery of Au(III) from aqueous solutions.

Acknowledgments

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