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Recovery of Gold from Aqueous Solution Containing Au(III) by Silicon Organic Polymer

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Abstract: The silicon organic polymer containing PSOT-3 (dioxothiocarbamide groups) has been synthesized and characterized, and the adsorption of Au(III) on PSOT-3 was investigated. The results showed that PSOT-3 had good adsorption capacity for Au(III), and the adsorption of Au(III) was found to be the most effective in 0.1~0.3 mol/dm^3 hydrochloric acid solution. The adsorption is physical and the process is endothermic, and Freundlich isotherm fits the data better than the Langmuir isotherm. The adsorption can be generally described by electrostatic interaction (Coulomb's force) between the adsorbent and the adsorbate. The high adsorption capacity of this sorbent has significant potential for gold recovery from aqueous solutions.

Key words: Gold, adsorption, adsorption kinetics, silicon organic polymer, thermodynamic parameters.

1. Introduction[1]

Gold is used in wide variety of fields such as in electrical and electronic industries, in chemical processes, in medicine, in health food and in jewellery. In Mongolia, gold production has gone up in recent years to 14.5 ton in 2015 from 5.9 ton in 2012. Mongolia holds an estimated over 1,353.1 tons in gold reserves which consists of 27.6 tons of placer deposits, 224.2 tons of hard rock deposits and 1,103.3 tons of other metals deposits with gold [1]. A hard rock deposit mining has received significant attention because of decrease in resource of placer deposits.

A variety of methods are found in literature to recover precious metals from aqueous solutions. These methods include cementation [2], solvent extraction [3-5], ion exchange [6], precipitation [7] and adsorption on activated carbon [8, 9]. Now, activated carbons are used as main adsorbent in hard rock gold mining.

There are several gold adsorption studies about different adsorbents [10-17]. But these techniques are low selectivity and efficiency for gold in dilute solution.

In this study, the authors used synthesized silicon organic polymer containing PSOT-3 (dioxothiocarbamide groups) for the investigation of Au(III) adsorption. PSOT-3 was obtained from silicon-organic monomer: bis-N, N'-(3-triethoxysililpropyl) thiocarbamide by hydrolytic poly-condensation reactionsuggested by Boronkov et al. [15, 18]. The synthesis reaction can be briefly expressed by Scheme 1.

$$\mathrm{N[(C_2H_5O)_3Si(CH_2)_3NH]_2CS} \xrightarrow[-6n\mathrm{C_2H_5OH}]{2n\mathrm{H_2O_2}} \rightarrow$$

$$\rightarrow \mathrm{[O_{1.5}Si(CH_2)_3(NH)_2CSO_2]n}$$

Scheme 1

This polymer (PSOT-3) is not commercialized at present and adsorption experiment was carried out only silver [18] and lanthanides [15].

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The main objective of this work was to evaluate the Au adsorption capacity of synthesized PSOT-3 from aqueous solution with Au(III) depending on varying concentration of hydrochloric acid solution, agitation time, initial concentration of Au(III) and temperature. Furthermore, the adsorption thermodynamics, kinetics, isotherms and adsorption mechanism have been discussed in this paper.

2. Experimental

2.1 Polymer Characterization

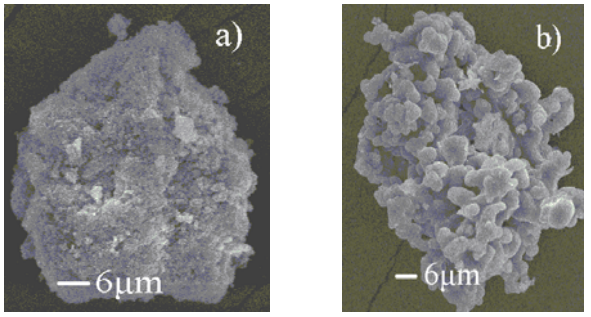
PSOT-3 was characterized by SEM (Scanning Electron Microscopy), EDX (EnergyDispersive X-ray Spectrometer) and BET (Brunauer-Emmett-Teller) method with N_2 adsorption/desorption test.

Structural changes of PSOT-3 after the adsorption were confirmed by the results from SEM images (Fig. 1) and EDX composition (Table 1).

The difference of the weightloss between pure and gold adsorbed PSOT-3 was about 10% which relates to adsorbed gold. The surface area of PSOT-3 was 36.4 m^2/g.

2.2 Adsorption Experiment

In the present investigation, the adsorption of Au(III) onto PSOT-3 was conducted in a temperature controlled shaker (PC-620D, CORNING). In a typical experimental run, 0.05 g of the adsorbent was shaken together with 0.5 dm^3 of adsorptive solution. Au(III) solution with different concentration 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 the filtrate was analysed to determine the remaining metal ion concentrations. Au(III) were analysed in a spectrophotometer at fixed wavelength of 490 nm using o-phenilendiamine as the complexing reagent [15]. To test the system of equilibrium, the following parameters were used: adsorption capacity of PSOT-3 (q_e); and sorption efficiency of the system (R). These parameters have been calculated as indicated below



MAG x2000; ACCV 15kV MAG x2000; ACCV 15kV

Fig. 1 SEM images of pure a) and gold adsorbed ; b) PSOT-3.

Table 1 EDX composition of PSOT-3.

Elements	Weight (%)	
	Pure sorbent	Sorbent, after adsorbed gold
Silica (Si)	14.3	14.7
Carbon (C)	34.3	31.4
Oxygen (O)	28.7	23.4
Sulfur (S)	6.4	1.8
Nitrogen (N)	16.3	14.9
Chlorine (Cl)	-	3.8
Gold (Au)	-	10.0

Eq. (1) and Eq. (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_o and C_e (mg/dm^3) are the initial and equilibrium concentrations of Au(III) in the solution, V (dm^3) is the volume of aqueous phase, m (g) is the dry weight of the adsorbent.

3. Results and Discussion

3.1 Effect of the Concentration of Hydrochloric Acid

The adsorption of Au(III) onto PSOT-3 has been performed at different concentrations of hydrochloric acid solution with initial concentration of 20 mg/dm^3 Au(III) and at temperature of 298 K (Fig. 2). While the acid concentration range is 0.01-0.1 mol/dm^3, the adsorption efficiency of Au(III) is increased from 98.1% to about 99.9%. There is no change in adsorption efficiency when acid concentration is between 0.1 and 0.3 mol/dm^3. By more increasing the

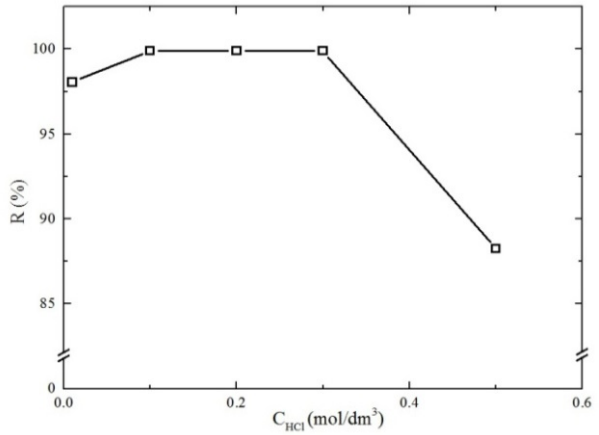


Fig. 2 Effect of the concentration of hydrochloric acid solution on gold sorption efficiency. ($V_{solution}$ = 0.5 dm^3, $m_{sorbent}$ = 50 mg, [Au(III)]$_{initial}$ = 20 mg/dm^3, 298 K, 500 rpm).

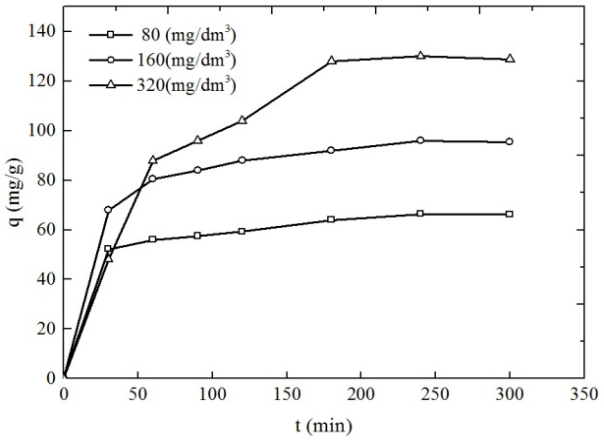


Fig. 3 Effect of initial concentrations of Au(III) and contact time on gold sorption capacity. ([HCl] = 0.1 mol/dm^3, $V_{solution}$ = 0.5 dm^3, $m_{sorbent}$ = 50 mg, 298 K, 500 rpm).

acidic concentration up to 0.5 mol/dm^3, the adsorption efficiency decreased from 99.9% to 88.3%. This decrease in the adsorption efficiency of Au(III) may have been caused by changes in chemical species of Au(III) (Scheme 2).

$$[AuCl_2]^+ + 2Cl^- \leftrightarrow [AuCl_4]^-$$

Scheme 2

Therefore, 0.1 mol/dm^3 of hydrochloric acid solution was chosen as suitable solution in this study.

3.2 Effect of Contact Time and Initial Concentration of Au(III)

The adsorption of Au(III) onto PSOT-3 was carried out from 30 min to 300 min with changing initial concentrations of 80, 160 and 320 mg/dm^3 of Au(III) (Fig. 3).

As shown in Fig. 3, the adsorption capacity increased with increasing initial concentration of Au(III) and with time. The maximum value (96.3-99.6%) was obtained at 240 min when initial concentrations of Au(III) are 80, 160 and 320 mg/dm^3. Hence, the optimized contact time was taken 4 hours for Au(III) adsorption onto PSOT-3.

The change of adsorption capacity with varying initial concentration is shown in Fig. 4. The experimental result shows an increase in value of the adsorption capacity with increasing initial concentration of Au(III).

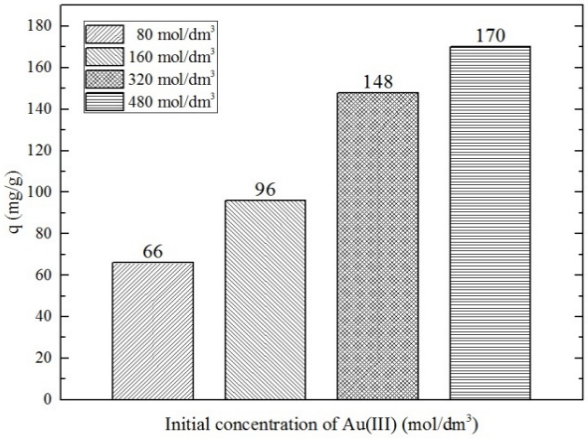


Fig. 4 Effect of initial concentrations of Au(III) on gold sorption capacity. ([HCl] = 0.1 mol/dm^3, $V_{solution}$ = 0.5 dm^3, $m_{sorbent}$ = 50 mg, 298K, 4 hrs, 500 rpm).

3.3 XRD Analysis of PSOT-3

The samples were characterized by XRD. Fig. 5 shows XRD pattern of PSOT-3 after the Au(III) adsorption (4 hr and 328 K).

The sharp peaks observed at 2θ values of around 37, 45, 65, 77, 82 degree in Fig. 5 was identified as the crystal structure of elemental gold. These results verify the generation of metallic gold on PSOT-3 after the adsorption of Au(III).

3.4 Investigation of Adsorption Thermodynamics

The thermodynamic parameters of the adsorption, i.e. the changes in standard Gibb's free energy ΔG^0

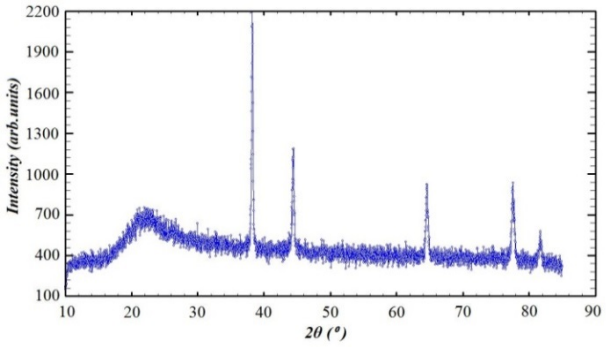


Fig. 5 XRD pattern of PSOT-3, after Au(III) adsorption (328 K and 4 hrs).

(kJ/mole), standard enthalpy ΔH^0 (kJ/mole) and entropy ΔS^0 (J/mol·K), were calculated from the Van't Hoff equation (Eq. (3) and Eq. (4)).

$$\Delta G^0 = -RT\ln K_c;\ K_c = \frac{C_A}{C_e} \quad (3)$$

$$\ln K_c = \frac{\Delta H^0}{-RT} + \frac{\Delta S^0}{R} \quad (4)$$

where, R is the gas constants (8.314 J/mol·K), T (K) is the absolute temperature, K_c is the equilibrium constant, C_A and C_e are the equilibrium concentration (mg/dm^3) of gold (III) adsorbed and left in the solution, respectively.

The slope and intercept of the plot of $\ln K_c$ versus 1/T were used to determine the values of ΔH^0 and ΔS^0. ΔG^0 was calculated at each temperature using the Eq. (4) for the initial concentrations 80 mg/dm^3, 160 mg/dm^3, 320 mg/ dm^3 and 480 mg/dm^3 of Au(III). The results are summarized in Table 2.

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 indicate that the adsorption process is endothermic, and ΔS^0 determine the disorderliness of the adsorption at solid-liquid (adsorbent PSOT-3 and hydrochloric acid solutions containing Au(III)) interface.

As presented in Table 2, the values of the Gibbs free energy were evaluated as -0.2 ~ -10.9 kJ/mol. These values suggest that the adsorption of Au(III) onto PSOT-3 is a physisorption. The Gibbs free energy of physical adsorption is usually between -20 to 0 kJ/mol.

Table 2 Thermodynamic parameters. ([HCl] = 0.1 mol/dm^3, $V_{solution}$ = 0.5 dm^3, $m_{sorbent}$ = 50 mg, 4 hrs, 500 rpm).

T(K)	C_{Au}(mg/L)	ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/mol·K
298		-5.6		
308		-6.2		
318	80.0	-7.1	35.7	137.0
328		-9.6		
338		-10.9		
298		-2.7		
308		-3.5		
318	160.0	-3.8	39.7	140.8
328		-7.4		
338		-7.9		
298		-1.3		
308		-1.8		
318	320.0	-2.2	21.0	74.5
328		-3.6		
338		-4.2		
298		-0.2		
308		-0.5		
318	480.0	-0.7	17.0	57.0
328		-1.4		
338		-2.7		

3.5 Adsorption Isotherm

Adsorption equilibrium data were correlated to the Freundlich and Langmiur isotherms at 298K.

The Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption, and is expressed in linear form as Eq. (5) shows.

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (5)$$

where, K_f (dm^3/g) and n are an empirical parameter related to the intensity of adsorption, which varies with heterogeneity of the adsorbent. K_f and n are determined from the linear plot. It is generally stated that the values of n in the range $1 < n < 10$ represent favourable adsorption [19].

The plots of $\log q_e$ versus $\log C_e$ for Au(III) adsorption onto PSOT-3 are shown in Fig. 6. From Fig. 6, Au(III) adsorption onto PSOT-3 conforms to the Freundlich isothermal adsorption equation well, and K_f and n are determined as shown in Table 3.

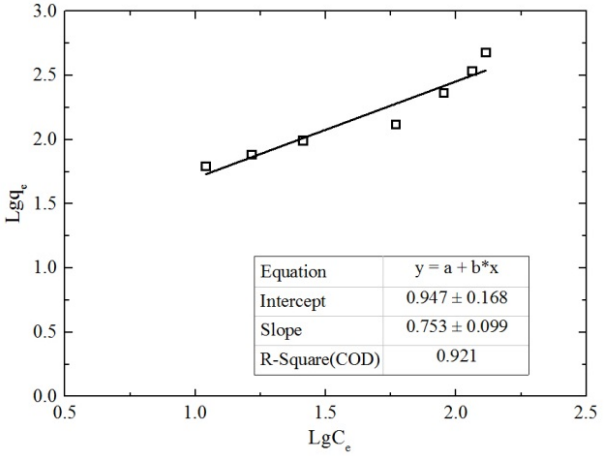


Fig. 6 Freundlich isotherm of Au(III) adsorption onto PSOT-3. ([HCl] = 0.1 mol/dm^3, $V_{solution}$ = 0.5 dm^3, $m_{sorbent}$ = 50 mg, [Au(III)]$_{initial}$ = 320 mg/dm^3, 4 hrs, 298 K, 500 rpm).

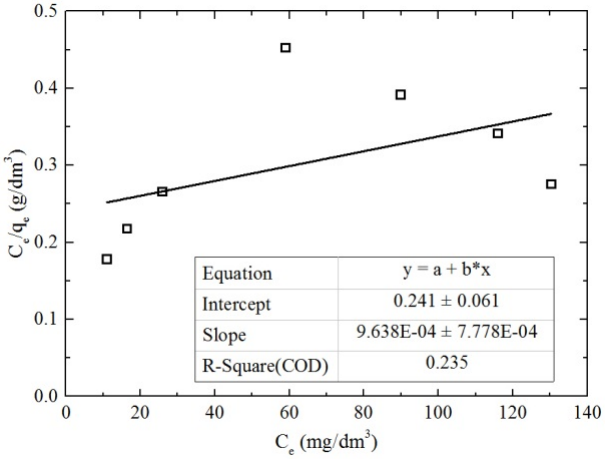


Fig. 7 Langmiur isotherm of Au(III) adsorption onto PSOT-3. ([HCl] = 0.1 mol/ dm^3, $V_{solution}$= 0.5 dm^3, $m_{sorbent}$ = 50 mg, [Au(III)]$_{initial}$ = 320 mg/dm^3, 4 hrs, 298 K, 500 rpm).

Table 3 Adsorption isotherm parameters of Au(III) onto PSOT-3.

Freundlich isotherm model	K_f (dm^3/g)	0.946
	n	1.33
	R^2	0.921

The Langmiur isotherm is based on the monolayer adsorption of Au(III) ions onto the surface of PSOT-3, and is expressed in the linear form as Eq. (6).

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \quad (6)$$

where, C_e (mg/dm^3) is the equilibrium concentration, q_e (mg/g) is adsorption capacity at equilibrium, Q_{max} (mg/g) is the maximum adsorption capacity, b (dm^3/mg) is the Langmuir isotherm constant. Q_{max} and b are determined from linear plot. The Langmuir adsorption isotherm plot of C_e/q_e versus C_e is shown in Fig. 7. From Fig. 7, it is found that Au(III) adsorption onto PSOT-3 is not well fitted by Langmiur adsorption isotherms models. Comparing two isotherm models, experiment data were relatively fitted to Freundlich isotherm than Langmuir isotherm.

The adsorption isotherm obtained from this work is compared with that calculated based on Freundlich isotherm as shown in Fig. 8. This result shows that Freundlich isotherm model is not necessarily adaptable to experimental data even though poor prediction at high concentration.

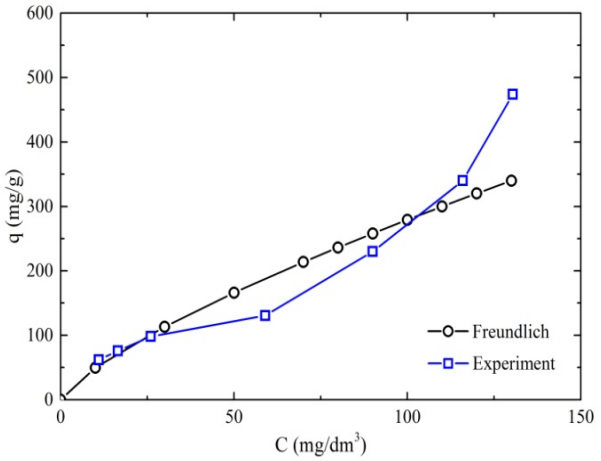


Fig. 8 Adsorption isotherm. ([HCl] = 0.1 mol/dm^3, $V_{solution}$ = 0.5 dm^3, $m_{sorbent}$ = 50 mg, [Au(III)]$_{initial}$ = 320 mg/dm^3, 4 hrs, 298 K, 500 rpm).

3.6 Comparison with Alternative Sorbents

Table 4 shows the adsorption of gold by other adsorbents reported in the literature. It is clear that the PSOT-3 shows better values and higher affinity for the effective adsorption of Au(III).

3.7 Adsorption Mechanism

For discussing the adsorption mechanism, PSOT-3 of before and after gold adsorption was characterized by FT-IR (Fourier Transform Infrared Spectroscopy). According to Ref. [22], the IR spectrum of pure adsorbent (Fig. 9a) can be assigned as follows.

Table 4 Comparison of PSOT-3 with other reported adsorbents for the adsorption capacity of Au(III).

Sorbents	Q_{max} (mg/g)	Ref.
L-214	108.7	[10]
ARH	93.5	[10]
Alugnate cross-linked with $CaCl_2$	290.0	[11]
Dealginated seaweed waste	78.0	[12]
Chitosan (L-lysine modified)	129.3	[13]
Eggshell membrane	147.0	[20]
Resin duolite GT-73	114.3	[21]
PSOT-3	474.0	In this study

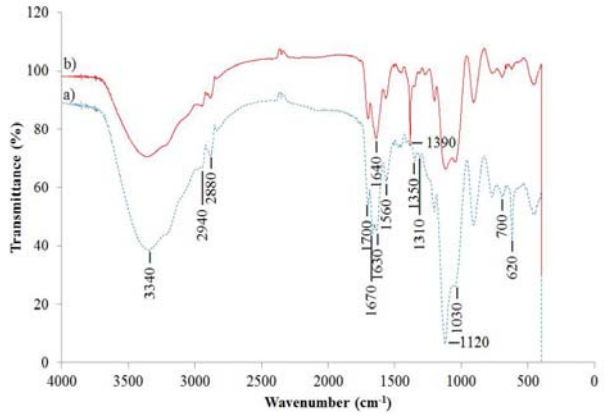


Fig. 9 FT-IR spectra of PSOT-3 (a) before and (b) after gold adsorption.

The peak at 1,700, 1,670, 1,630 and 1,560 cm^{-1} were indicated as the (CN) stretching vibration and amide I (NH), amide II (NH_2) bending vibration. Absorption peaks at 700, 620 and 1,120 cm^{-1} were attributed to C-S groups and Si-O-Si group. The peak at 1,030 cm^{-1} showed (SO) stretching vibration.

After the adsorption (Fig. 9b), the intensity of (CN) stretching vibration and amide I (NH), amide II (NH_2) bending vibration at range of 1,700-1,560 cm^{-1} was decreased. The peak at 1,670 cm^{-1} (C=N) and 620 cm^{-1} (C-S) were disappeared and new strong peak of C=S group was detected at 1,390 cm^{-1}. Also there were changes at range of 1,200-1,000 cm^{-1} which related to stretching vibration of Si-O-Si and SO groups.

The results are signified that Au(III) ion interacted with functional groups of the adsorbent.

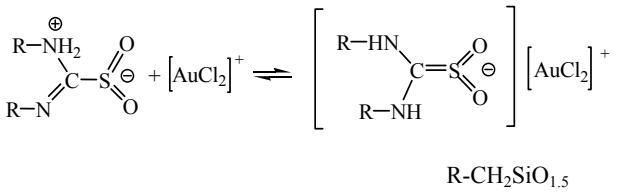
By using results of EDX, the ratio of metal ion to chloric ion (Me:Cl) was calculated by following Eq. (7) [23]:

$$n = \frac{C_{Cl}\% \cdot A_{Au}}{C_{Au}\% \cdot A_{Cl}} \quad (7)$$

where, C_{Cl}% and C_{Au}% are concentration of chlorine and gold in the adsorbent phase, A_{Au} and A_{Cl} are atomic weight of chlorine and gold.

According to Eq. (8), the ratio of metal to chlorine Me:Cl = 1:2 can be proved the sorption mechanism. Based on all the results, sorption reaction can be expressed by scheme 3.

Therefore, it can be concluded that the adsorption of Au(III) onto PSOT-3 can be generally described by electrostatic interaction (Coulomb's force) between the adsorbent and the adsorbate.



Scheme 3

4. Conclusion

The present study investigated the efficiency of PSOT-3 as adsorbent for Au(III) by batch techniques. The following results could be obtained:

(1) PSOT-3 is able to adsorb Au (III) from aqueous solutions.

(2) Adsorption of Au(III) was found to be effective in 0.1 ~0.3 mol/dm^3 hydrochloric acid solution.

(3) The adsorption capacity increased with increasing initial concentration of Au(III).

(4) The adsorption is physical in nature and the process is endothermic, which confirmed by evaluated thermodynamical parameters.

(5) Freundlich isotherm fits the data better than the Langmuir isotherm.

(6) The adsorption can be generally described by electrostatic interaction (Coulomb's force) between the adsorbent and the adsorbate.

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