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RESEARCH ARTICLE

EXPERMENTAL AND THEORETICAL STUDY OF GOLD ADSORPTION ONTO POLYMERIC SORBENT.

***Odonchimeg. S.[1], *Javkhlantugs. N. [2], Tegshjargal. Kh.[2] , and Oyun. J. [3].**
1. Central Laboratory of Chemistry, Erdenet Mining Corporation, Orkhon 22100, Mongolia.
2. School of Engineering and Applied Sciences, National University of Mongolia, Ulaanbaatar 14201, Mongolia.
3. Department of Chemistry, Ulaanbaatar University, Ulaanbaatar 13374, Mongolia.

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Abstract

Polystyrene-azo-thiazandithion-2,4 (PSTDT) polymer was used to increase the gold content for analysis of waste copper, copper ore and concentrate. The optimum conditions of the sorption capacity of sorbent, [H^+], temperature and time dependence enrichment of gold content were examined to increase analysis efficiency by using treatment of PSTDT polymer. The moleculer structure of PSTDT polymer with gold were successfully determined using by FT-IR and theoretical calculations.

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Introduction:-

The atomic absorption spectroscopy (AAS) method is usefully for determination of low-content precious elements in biological (Olmedo et all.,2013), and geological samples (Hoffman., et all 1998). One of the precious metals is gold. Comparison of different gold recovery methods as amalgamatoin, cyanidation was investigated previously (Hylander et all., 2007). Hoffman et al. (Hoffman., et all 1998), describedthe gold analysis in geological samples by fire-assaying methods which includes instrumental neutron activation, AAS, graphit furnace-atomic absorption or inductively coupled plasma emission mass spectroscopy. The functional polymers can been used for determination of low-concentration gold in ores and minerals by using AAS such as silicon organic adsorbent PSTM-3T (Pozhidaev et all., 2013). The PSTM-3T polymer also had been investigated for removal of copper and chromium ions from aqueous solution (Narantsogt et all., 2014). PSTM-3T polymer includes thiocarbamide functional group which forms the metal complexes.

The Erdenet Mining Corporation (EMC) is one of the largest copper and molybdenum mining and processing factories in the world that located on the northern of Mongolia . The copper is concentrated by using flotation method of sulfide minerals. The concentration of gold in waste copper, copper ore and copper concentrate has been determined by using the AAS in Central Laboratory of Chemistry of EMC which method is not efficiency. The enrichment of precious metals is very useful for recovery and analytical chemistry. Monitoring the gold concentration in waste copper, copper ore and concentrate is important for mining. In recent, the polymer compound is treated into ores to increase the concentration of plate and precious metals. One of the polymer is the poly-styrene-azo-thiazondithion-2,4 (PSTDT) which firstly synthesized by Basargin et al (Basargin et all., 1995). The PSTDT polymer can been selectively determine the low-content gold samples by using enrichment method. In this present work, we determined the gold content in waste copper, copper ore and concentrate of EMC.

Corresponding Author:- Javkhlantugs. N, Odonchimeg. S.
Address:- School of Engineering and Applied Sciences, National University of Mongolia, Ulaanbaatar 14201, Mongolia.
Central Laboratory of Chemistry, Erdenet Mining Corporation, Orkhon 22100, Mongolia.

Materials and Methods:-

Materials:-

Poly-styrene-azo-thiazandithion-2,4 (PSTDT) polymer (Astralabor, Russia) was used to determine the gold content in waste copper, copper ore and concentrate. The PSTDT polymer (Fig. 1a) is not dissolve in water, acid, base and organic solvents that includes nitrogen and sulfur atoms at ortho-position which forms a stable chelate complex with gold. Gold atom substitutes a hydrogen atom of imine group and connects with sulfur atom by coordination bond(Fig. 1b) (Pozhidaev et all., 2013). Standard solution and certified reference sample were used 1 mg/ml gold solution (ACROS Organics) and 0.211 ppm gold contend (OREAS 13b), respectively.

Optinum condition gold adsorption

In order to define the optimum condition as temperature (20 °C, 50 °C and 100 °C), time (5–30 minutes) and HCI (0.5, 1.0, 1.5 N), HNO_3 (0.5, 1.0, 1.5 N) affecting to the gold adsorption, 25 mg PSTDT with 500 ppb gold standard solution were taken for 100 ml solution and stirred on the magnetic mixer. Gold contents in the solution were measured by spectrophotometry (MAPADA V-1600PC) to form the color complex with rodasol-XC. Adsorption efficiency of the gold was calculated as following equation:

$$R = \frac{q_a - q_f}{q_a} \times 100\% \qquad (1)$$

Where, R, q_a, and q_f are the adsorption efficiency (%), concentrations (ppb) of the gold in the standard solution and filtrate solution, respectively.

A. Sorption capacity of sorbent

The solutions of gold with concentrations of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55 ppb were prepared from the standard solution to determine the maximum amount of gold per adsorbent. 50 mg PSTDT added into each solutions at optimum condition then filtrate solutions were analyzed to adsorption efficiency. Sorption capacity of sorbent is calculated following equation:

$$SCS_{Au} = \frac{(C_0 - C)*V}{m} \qquad (2)$$

Where, C_0, C -gold concentration in initial and remained solution, respectively, V -50 ml standard solution, m- 50 mg sorbent

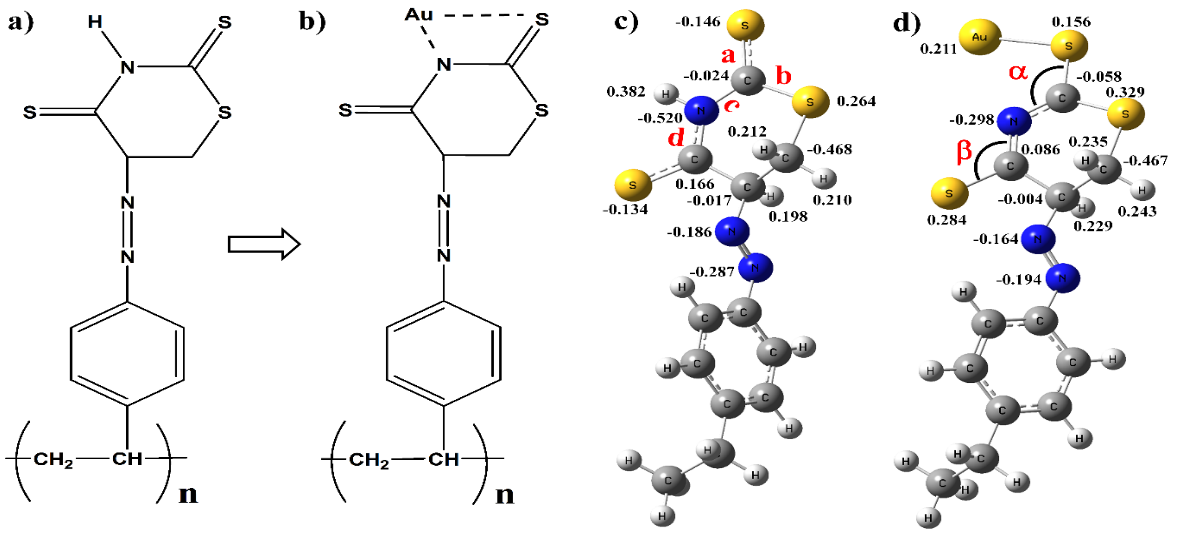

Fig. 1: Representation of molecular structure of PSTDT polymer (a) and PSTDT-Au (b). The optimized structures of PSTDT(c) and PSTDT-Au (d) with Mulliken atomic charges for selected atoms. Sulfur, nitrogen, carbon, hydrogen, and gold atoms are shown by yellow, blue, dark grey, light grey and yellow, respectively.

Determination of gold content in samples:-
Experimental procedures were applied to gold determination can be broadly divided into three stages as the sample decomposition, enrichment and analysis stages which were summarized as a scheme in Figure 2

Sample decomposition stage Samples were calcinated at 650 °C then were dissolved in nitric acid and were evaporated the solution. The powder had been calcinated at 450 °C to form the copper oxide. The formed oxide was dissolved in solution of H_2SO_4 : H_2O_2(3 %) with ratio 1 : 10. The excess solution of hydrogen peroxide was added and boiled the solution then was added NaCl and KI with concentration of 10 % to separate the gold, platinum, silver and palladium. This procedure was repeated twice. The precipitate was filtered and calcinated at 600 °C. The precipitate was dissolved in "Aqua regia" solution and evaporated then dissolved in 1 N hydrochloric acid. (A solution).

Enrichment stage 50 mg sorbent(PSTDT) were added into "solution A" to enrich the gold in the optimum condition by mixing. After the formation of chelate complex, the solids were filtered and were calcined at 550 °C then dissolved in 100 ml hydrochloric acid (1 N) then filtrate.

Analysis stage The sample burned by air-acetylene flam at 2125 - 2400 °C and measured the gold content at 242.7 nm wavelength using flame atomic absorption spectroscopy (FAAS) (Perkin Elmer AAnalyst 800).

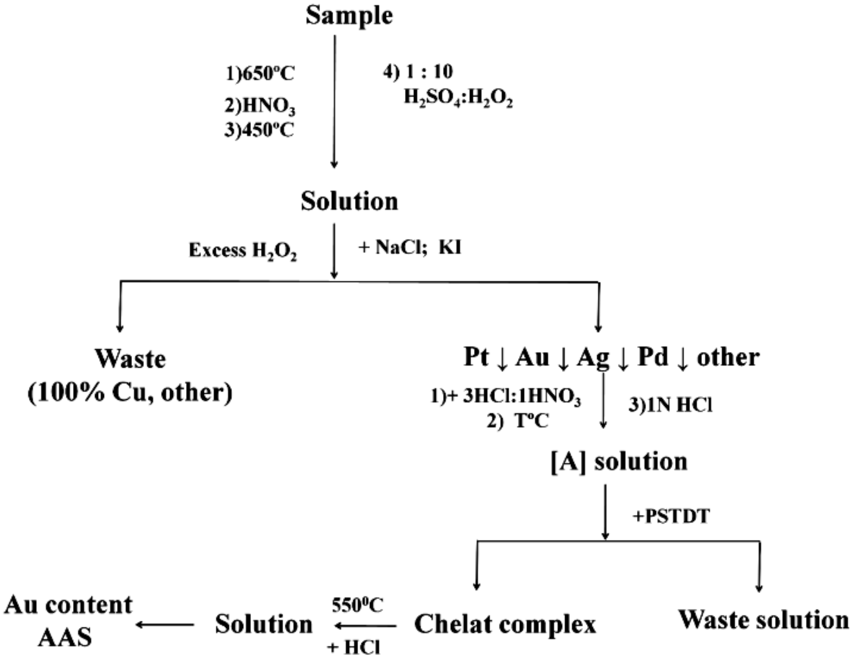

Fig. 2:- Scheme of experimental procedures for determination of gold content.

Fronter-Transform Infrared (FT-IR) spectroscopy:-
The chemical bond frequencies of functional groups of polymer before and after treatment of sample were analyzed by using Frontier-Transform Infrared (FT-IR) spectrophotometer (IRPrestige-21, Shimadzu, Tokyo, Japan). The powdered samples were mixed with KBr and made the pellets. The FT-IR spectra were obtained with frequency range of 4000 – 400 cm^{-1}.

Computational method:-
The optimization and frequency calculations of PSTDTand PSTDT-Au (Fig. 1c and d) complex were carried out using density functional theory (DFT) with Becke three parameter method (Becke .,1993), (Becke., 1988)and (Lee Yang Parr et all., 1988), correlation exchange with 6-31G(d) (Hehre et all., 1987) and LanL2DZ basis sets by Gaussian09 program. (Barone et all., 2009) 6-31G(d) basis set was applied for H, C, N, and S atoms, and LanL2DZ was applied for Au cation. Spin multiplicity of PSTDT and PSTDT-Au complex was singlet and doublet, respectively. All the convergent precisions were the system default values, and the all calculations were carried out

on the standard lab-level workstations with AMD Opteron 285 dual core CPU. Data visualization was carried out using Gauss View 03 (Frish et all., 2007).

Result and Discussion:-

Firstly, the adsorption optimum conditions of the sorption capacity of sorbent, [H^+], temperature and time dependence of PSTDT polymer for gold adsorption were established as <45 mg/g, 1 N, 20 °C and 15 min, respectively (Fig. 3 and Fig. 4).

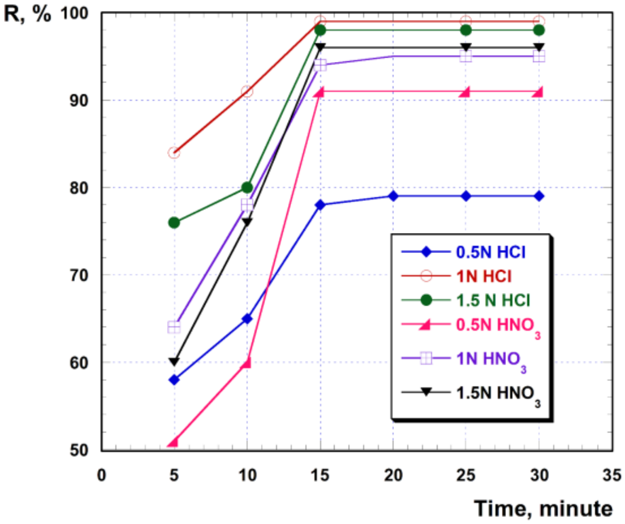

Fig. 3:- Time dependence of adsorption efficiencyfor the different acids.

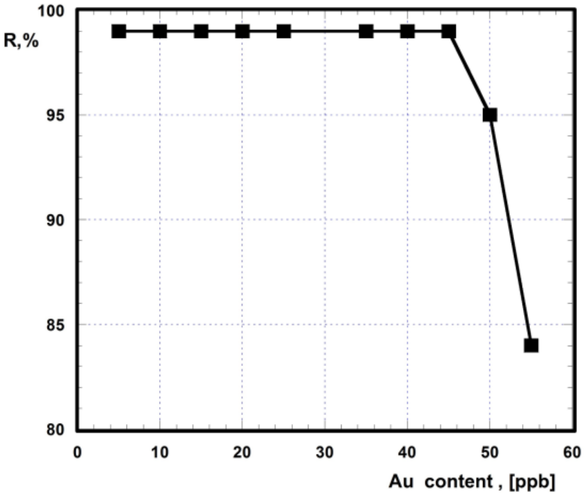

Fig. 4:- Adsorption efficiency of PSTDT polymer depends on the gold concentration.

Table 1 shows that the determined gold contents in copper ore, copper concentrate and waste copper by using our chemical treated (CT) flame atomic absorption spectroscopy (FAAS) to compare with assay analysis (AA) FAAS and inductively coupled plasma (ICP) mass spectrometry (MS) methods. The gold contents in copper concentrate and waste copper by using CT-FAAS were higher than by using ICP-MS method which mean that the low-content gold determination is enriched by the PSTDT polymer are higher efficiency in analysis of copper industry.

Table 1:- The Comparison of Gold Content by Using Different Methods of Chemical Treatment (CT), Assay Analysis (AA) Flame Atomic Absorption Spectroscopy (FAAS) and Inductively Coupled Plasma (ICP) Mass Spectrometry (MS).

Samples	Gold content, ppm		
	CT-FAAS	AA-FAAS	ICP-MS
Copper ore	0.004	NA	0.005
Copper concentrate	0.048	0.040	0.044
Waste copper	0.005	NA	0.002
OREAS 13b (0.211 ppm)	0.214	0.210	0.213

The functional groups of PSTDT polymer before and after treatment of gold samples were identified using FT-IR experiment and the spectrum is shown in Fig. 5.

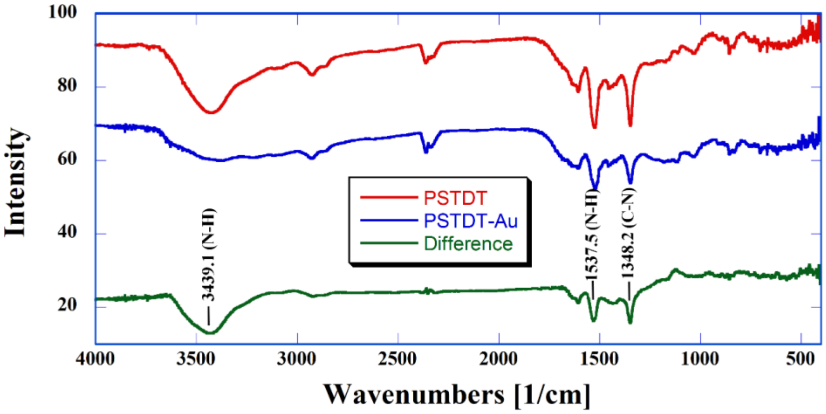

Fig. 5:- FT-IR spectra of PSTDT polymer before (red) and after (blue) treatment of gold sample and their difference (green).

In Fig. 5, the observable IR signals for PSTDT polymer were 1521.8 and 3375.4 cm^{-1} for N-H, 1348.2cm^{-1} for C-N (Table 2).

Table 2:- The Comparison of Theoretical and Experimental Frequencies of PSTDT and PSTDT-Au. The Percentage of Relative Deviation of Model in Different Frequencies is Shown In Parenthesis.

Groups	Wavenumbers, [1/cm]					
	PSTDT	Exp.	Δ [%]	PSTDT-Au	Exp.	Δ [%]
N-H	3518.5	3375.4	-4.0	-	-	-
	1514.6	1521.8	0.5	-	1525.7	-0.3
C-N	1367.9	1348.2	-1.5	1487.7	1348.2	-10.3
	1292.8	-	-	1268.6	1348.2	5.9

The intensities at these wavenumbers were decreased after the treatment of PSTDT to copper samples. The differences of the intensities of –NH group are shown in the figure which means that the gold was adsorbed onto PSTDT polymer. The -CS group shows the important for the sorption of the metal (Narantsogt et all., 2014) therefore the vibration intensity of C-N bond was decreased in Fig. 5. The IR signals were similar with the group frequencies (Coates ., 2004) vice versa the frequencies do not shown for PSTDT polymer after treatmentsof the gold sample. It shows that the gold atom substituted the hydrogen atom of imine group and connected with sulfur atom by coordination (Fig. 1b) Pozhidaev et all., 2013). The theoretical calculations were carried out by B3LYP method with 6-31G(d) basis set and optimized PSTDT polymer and PSTDT-Au structures are shown in Fig. 1c and d with Mulliken atomic charges for selected atoms. After the Au adsorption “a” bond length, “α” and “β” bond angles were increased (Fig. 1c and d). Au-S and Au-N bond lengthsare 2.338 Å and 3.089 Å, respectively, which are similar results with previous report. In this study, the frequency calculations of optimized structures of PSTDT polymer and PSTDT-Au (Fig. 1c and d) were investigated using the B3LYP method with 6-31G(d) basis set to compare the experimental IR results.. In theoretical calculations, the values for N-H bond frequencies have relative deviation less than 4 % and the deviations of values for C-N bond frequency are 1.5 % (Table 2). Calculated frequencies of CN bond in PSTDT-Au were 1487.7 cm^{-1} and 1268.6 cm^{-1} and deviated by 10.3 % and 5.9 % from experimental value of PSTDT polymer. The experimental IR spectrum of PSTDT-Au system had shifted intensities of CN bond vibration. The theoretical frequency result of NH bond disappeared on IR spectrum of PSTDT-Au structure and N=N bond intensity was increased from IR spectrum of PSTDT (Fig. 6).

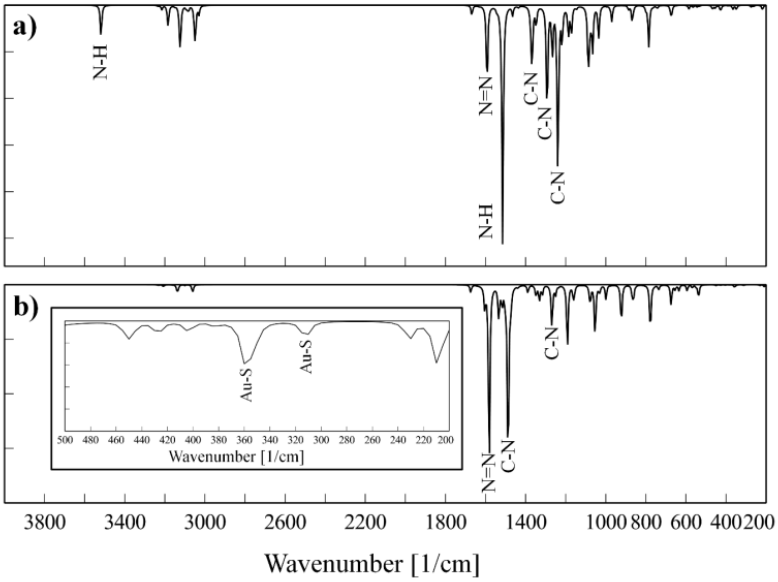

Fig. 6:- Calculated IR spectra of PSTDT (a) and PSTDT-Au (b). IR spectrum of PSTDT-Au between 200 cm^{-1} and 500 cm^{-1} (b, inset).

The calculated frequencies of Au-S were 314.3 cm^{-1} and 356.8 cm^{-1} (Fig. 6b). N=N bond characteristic was dramatically changed and indicated in HOMO orbitals (Fig. 7a and c). LUMO orbitals are shown in Fig. 7b and d where Au-S bond had partial occupation of LUMO orbital. The theoretical frequency values are in good agreement with experimental values, the same as previous reports (Narantsogt et all., 2014), (Pousti et all., 2013). Finally, the PSTDT polymer is a good enrichment of gold content to use the analysis of gold in copper samples.

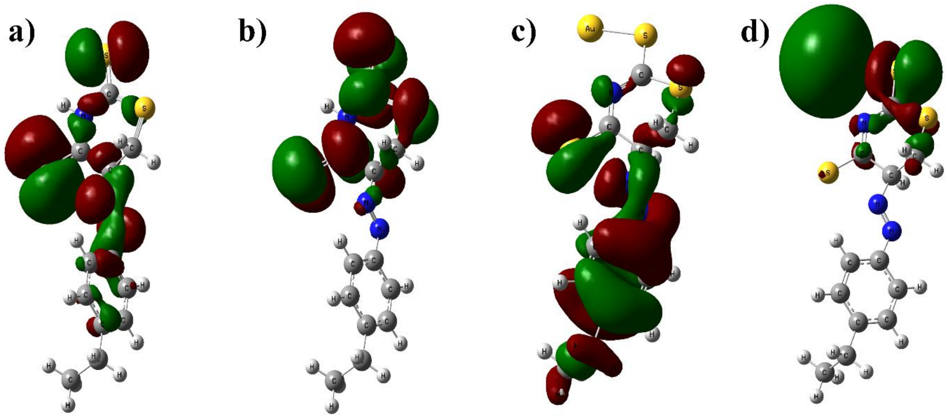

Fig. 7: HOMO (aand c) and LUMO (b and d) orbitals of PSTDT and PSTDT-Au, respectively.

CONCLUSION:-

The low-content gold determination in samples of copper industry was clearly examined using CT-FAAS, FT-IR and theoretical calculations. The optimum conditions of the sorption capacity of sorbent, [H$^+$], temperature and time dependence of PSTDT polymer for gold adsorption were <45 mg/g, 1 N, 20 °C and 15 min, respectively. The analysis efficiency of gold determination was increased after treatment of PSTDT polymer. The chemical interactions and moleculer structure of PSTDT polymer with gold were successfully determined using by FT-IR and theoretical calculations.

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