Improved recovery of gold and silver from thiosulfate solution on activated carbon in presence of ammonium persulfate

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Abstract: Thiosulfate (TS) process for extraction of gold and silver is a promising alternative to the highly toxic cyanidation process. One of the main reasons caused limiting the practical application of the TS process is the poor recovery of gold and silver on the commonly used activated carbon (AC). Increasing amounts of TS ions greatly inhibited the adsorption of gold and silver from synthetic solutions. No adsorption was obtained when the TS concentration reached 0.8 M after 5 h. The adsorption efficiency from real leach liquor initially contained 0.2 M TS was as low as 40-50%, after a long time of 15 hours. We have suggested that the removal of the residual TS ions in leach liquor through an interaction with an oxidizing agent such as ammonium persulfate (APS) would improve the adsorption of gold and silver on AC. Increasing the APS concentrations from 0.0 M to 0.01 M drastically improved the gold adsorption efficiency from 5% to 85% after only 10 min. Almost 95% of both metals was adsorbed after 90 min. EDXRF chart confirmed the adsorption of gold and silver on AC. A process flowsheet was proposed for an integrated TS leaching and recovery of gold and silver from Al Amar tailing including adsorption on AC in presence of APS.

Keywords: activated carbon, adsorption, gold, silver, thiosulfate, ammonium persulfate

1. Introduction

Conventional cyanidation is commonly used for leaching of gold ores because of its great efficiency. Although several materials have been studied, the use of AC to separate gold from cyanide leaching solutions has become a standard process for gold adsorption (Grosse et al., 2003; Feldman et al., 2015; Tauetsile et al., 2019a,b). Activated carbon, a material produced from carbon-rich sources, offers an incredibly porous surface structure, which creates a vast surface area to adsorb materials. It possesses a unique set of properties: a well-developed reproducible microporous structure, a large internal surface area, and a high degree of surface reactivity (Yu et al., 2015). This porous structure, in combination with attraction forces, allows AC to capture material components for their later recovery. The benefits of this process in the gold industry are high selectivity, efficiency, purity of the product and relatively low cost. Moreover, the AC can be added directly to the cyanide pulp in the so-called CIP or CIL processes and then separated by simple screening, thereby avoiding filtration stage which may lead to losses of soluble gold in tailings (Bansal and Goyal, 2005; Muir and Aylmore, 2004).

The main disadvantage of the cyanidation is the extremely toxic character of the reagent (Mahmoud et al., 2015, 2016, 2018, Moussavi et al., 2018). The problem of gold ore processing became a separate issue when the European Parliament adopted Resolution No. P7_TA(2010)0145 on 5 May 2010, which was a general ban on the use of cyanide mining technologies in the European Union [Resolution EP 2010]. Internationally several countries have banned cyanide technology in gold and silver mining (Eisler and Wiemeyer 2004). Therefore, multiple non-cyanide lixiviants such as thiosulfate, thiourea,

thiocyanate, and halogens have been investigated (Konyratbekova et al., 2015). Among these non-cyanide lixiviants, thiosulfate is thought to be the most attractive alternative reagent to cyanide for processing gold ores because of its relatively cheap cost, nontoxicity, and high complex constant with gold. Moreover, thiosulfate can be used for leaching of gold from carbonaceous gold ores as gold-thiosulfate complex which is not preg-robbed by the carbonaceous component of the ores (Navarro et al., 2007).

Recovery of gold from thiosulfate solutions can be carried out by different procedures, namely; cementation, adsorption or solvent extraction (Navarro et al., 2004; Zhang and Dreisinger 2004; Jeffrey et al., 2010; Dong et al., 2017; Xu et al., 2019). It was stated that AC has a very low affinity for the gold thiosulfate $[Au(S_2O_3)_2]^{3-}$ complex and the effectiveness in adsorption of complexed gold from aqueous solutions decreases in the following ligand order: $SCN^- > SC(NH_2)_2 > CN^- >> S_2O_3^{2-}$ (Gallagher et al., 1990). The low affinity was explained to be due to the high anionic charge of the gold - thiosulfate complex $[Au(S_2O_3)_2]^{3-}$ and the bulkiness of the thiosulfate ions compared to gold cyanide $[Au(CN)_2]^-$, steric limitations due to molecular structure (Navarro et. al., 2007; Yu et al., 2015). However, Sitando et al. (2019), have indicated that the presence of free thiosulfate ion in solution was the reason for the low gold adsorption extent onto AC.

Practically, the poor recovery of gold and silver on AC is one of the main reasons those are limiting the application of the TS process. The TS system has progressed slowly towards commercial application. The only known thiosulfate gold processing plant is the one commissioned in November 2014 at Barrick's Goldstrike operation in the USA for treating double refractory ore [Choi et al., 2013]. The process utilizes 'resin-in-leach' circuit for recovering gold from leach liquor because AC was not the efficient commercial adsorbent.

Nevertheless, research on the adsorption of gold onto AC from thiosulfate solutions never stopped (Navarro et al., 2007; Vargas et al., 2006; Young et al., 2012; Alishahi et al., 2014; Yu et al., 2015). Several authors have proposed modification methods of AC to improve the gold and silver adsorption. Impregnated AC with cyano-cuprous species have been proposed through gold– copper exchange where better gold adsorption rate was attained (Young et al., 2012; Yu et al., 2015). The process uses cyanide component and needs long and tough preparation procedures. Yu et al. (2018) have used silver ferrocyanide impregnated AC, and the gold adsorption rate increase. Chen et al. (2019a) have suggested grafting sulfur containing groups to the AC using 2-Mercaptobenzothiazole where a strong affinity for $[Au(S_2O_3)_2]^{3-}$ was verified. The adsorption mechanism was not clear and the cost of preparation is expected to be high. These improving approaches would be better if their modification processes could be further simplified. Therefore, other effective, non-cyanide and simple adsorption methods of gold and silver on AC are quite essential.

So far, no work was reported on the treatment of thiosulfate in aqueous leach solution to improve the adsorption of gold and silver on AC. Oxidative removal of the residual TS ions in leach liquor was suggested to improve the adsorption of gold and silver on AC. Conversion of the thiosulfate anion into its producing ions through a reaction with a suitable oxidizing agent may improve the adsorption of gold and silver.

In this work, adsorption of gold and silver on AC from ammoniacal thiosulfate solution was investigated in the presence of APS. This study extends our previous work on gold and silver extraction from tailings to obtain an integrated thiosulfate process including leaching and recovery on AC [Mahmoud et al., 2018].

2.   Materials and methods

Synthetic and real leach liquors of gold and silver were used in adsorption tests. The synthetic solution was used to study the effect of a wide range of ATS concentrations. The real leach solution was used to generate the adsorption isotherms. Table 1 shows the summarized experimental conditions of leaching and adsorption tests.

2.1. Preparation of synthetic leach liquors

A stock solution of gold thiosulfate was prepared by dissolving one gram of gold sodium thiosulfate $Na_3[Au(S_2O_3)_2]$ (Alfa Aesar) in 1000 cm³ of deionized water. A stock solution of silver thiosulfate

$(NH_4)_3[Ag(S_2O_3)_2]$ was prepared by mixing 0.28 g of ammonium thiosulfate $(NH_4)_2S_2O_3$ (ATS) and 0.63 g of silver nitrate $AgNO_3$ (Sigma Aldrich) in 1000 cm^3 de-ionized water. A synthetic leach liquor containing 10 ppm each gold thiosulfate and silver thiosulfate in 0.3 M ammonium hydroxide was then prepared. In 1000 cm^3 volumetric flask, a 24.9 cm^3 of each gold and silver thiosulfate stock solutions were added followed by a 20.7 cm^3 of concentrated ammonium hydroxide solution. The mixture was completed to the mark with de-ionized water. To prepare synthetic leach liquors with different ATS concentrations (0.1, 0.2, 0.3, 0.6 and 0.8 M), the corresponding weights of ATS (1.48, 2.96, 4.45, 8.89, and 11.85 g) were added to every 100 cm^3 of the above-mentioned synthetic solutions.

Table 1: Summarized experimental conditions of leaching and adsorption tests

Item	Condition
1. Leaching	
Source of gold and silver	Al Amar tailing waste
Particle size	100 % - 100 mesh
Calcination temperature	400 °C
Calcination time	2 hr
ATS concn.	0.2 M
Ammonium hydroxide concn.	0.3 M
Solid/Liquid ratio	1/1.2 g/ cm^3
Leaching time	24 hr
Leaching Temperature	~ 25 °C
Shaking speed	480 rpm
2. Adsorption	
Effect of ATS concn.	
Type of soln.	Synthetic
Gold source	Sodium thiosulfate, Alfa Aesar
Silver source	Silver thiosulfate, prepared
ATS concn.	0 – 0.8 M
Ammonium hydroxide concn.	0.3 M
Adsorption time	300 min
Sampling times	0, 10, 25, 90, 180, 900 min
Kinetic and effect of ATS concn.	
Type of soln.	Real leach
ATS concn.	0.2 and 0.3 M
Ammonium hydroxide concn.	0.3 M
Sampling times	0, 10, 25, 90, 180, 900 min
Effect of APS concn.	
Type of soln.	Real leach
APS concn.	0 - 0.2 M
Temperature	~ 25 °C
Time	0 - 900 min
Sampling time	0, 10, 25, 90, 180, 900 min
Sample volume	1 cm^3
Weight of carbon	2 g
Volume of solution	0.045 L
Carbon to liquid ratio*	44.4 g/L
Shaking speed	480 rpm
Loading of Au and Ag on AC	
Type of soln.	Real leach
APS concn.	0.01 M
Adsorption time	90 min
Ratio of weight of carbon / volume of soln.	2.2 – 111.1 g/L

*Or otherwise mentioned

2.2. Preparation of real leach liquors

A stock thiosulfate real leach liquor loaded with gold and silver was prepared from the tailing waste of Al Amar mine in Saudi Arabia (calcined at 400 oC for 2 hours). The chemical composition of the sample was 6.8 ppm Au, 16.1 ppm Ag, 39%Si, 13.3% Zn, 6.5 Fe, 0.17% Cu. The applied leaching conditions were 0.3 M ammonium hydroxide, 0.2 M ATS, solid to liquid ratio 1/1.2 g/cm3, shaking time 24 h. At these conditions, almost 50% of each Au and Ag were extracted. The gold and silver contents in this leach liquor were 2.8 ppm and 6.7 ppm, respectively. The stability of the gold and silver was checked each time the adsorption experiments were carried out by analyzing their contents in synthetic and real leach solutions and were found almost unchanged during the period of tests in this work. Thiosulfate concentration was also checked in the used solutions from time to time and found almost stable.

2.3. Adsorption

A 2 g, or otherwise mentioned, of AC (National Chemicals Import and Export Corporation, China) surface area 150-300 m2/g, cylindrical shape (5.4 x 4 mm), density 0.45-0.55 g/ cm3, moisture 10%, ash content 7%, was placed in a 100 cm3 plastic bottle with tight lid. A 45 cm3 of the synthetic or real leach solution was added and the mixture was horizontally shaken at 480 rpm for the required period of time. At different time intervals, a 1 cm3 was taken from the liquid phase, and the concentrations of gold and silver were detected using Inductively Coupled Plasma - Atomic Optical Emission Spectrometer (ICP-AOS), Optima 2000 DV, Perkin Elmer. The adsorbed amounts of gold or silver were calculated by mass differences before and after the adsorption experiments. The effectiveness of the adsorption process was estimated from the percentage of metal adsorption, which was calculated by using equation 1:

$$R = ((C_o - C_t)/C_o) \times 100 \tag{1}$$

The loading capacity was measured using equation (2):

$$q = (C_o - C_t)\ V/\ W \tag{2}$$

where R is the percentage of gold or silver adsorption, q is the amount of gold or silver loaded (g/t), C_o is the initial metal concentration and C_t is the metal concentration at an elapsed time, after the addition of AC. V is the volume of solution and W is the weight of carbon (t). Calculations were based on the corrected volumes of solution (the exact volume of the solution after samples were taken). Thiosulfate ions were measured using High Pressure Liquid Chromatography (HPLC), Waters Alliance model 2695.

3.   Results and discussion

Leaching reaction of gold with thiosulfate has been proposed as presented in equation 3 [Aylmore and Muir, 2001, Mahmoud et al., 2015]:

$$Au + 5\ S_2O_3^{2-} + Cu(NH_3)_4^{2+} \ \rightarrow\ Au(S_2O_3)_2^{3-} + 4\ NH_3 + Cu(S_2O_3)_3^{5-} \tag{3}$$
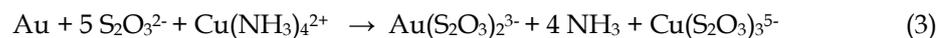
where the produced Cu(I) is then re-oxidized to Cu(II) by oxygen.

Silver coexists in most gold ores in the form of alloy electrum, acanthite (Ag_2S) or other minerals (Zhang, et. al, 2008). The Ag_2S can interact with thiosulfate ions according to equation 4 (Salinas-Rodríguez et al., 2016):

$$Ag_2S + O_2 + 4\ S_2O_3^{2-}\ + 4\ H^+ \rightarrow 2\ Ag(S_2O_3)_2^{3-} + S^{2-} + 2\ H_2O \tag{4}$$

The next stage is to recover the leached gold and silver on an adsorbent such as the commonly used AC. In the following sections, adsorption of gold and silver on AC will be studied focusing on the negative effect of TS ions and adsorption improvement in the presence of APS.

3.1. Effect of thiosulfate

The residual thiosulfate ions in solution may be the reason for the inhibition of gold and silver adsorption on AC. Adsorption of gold and silver from synthetic thiosulfate solution has been studied with various initial ATS concentrations (from 0.1 to 0.8 M) at 0.3 M ammonium hydroxide for 300 min. As shown in Fig. 1, the adsorption efficiency was in the range of 40-50% in 0.1 M ATS and the adsorption was continuously decreasing with increasing ATS concentrations for both metals. Almost no gold and silver were adsorbed when the ATS concentration reached 0.8 M. This behaviour may be related with

to competition of adsorption to active sites on AC between excess thiosulfate $(S_2O_3)^{2-}$ anions in one side and gold thiosulfate anion $[Au(S_2O_3)_2]^{3-}$ and silver thiosulfate anion $[Ag(S_2O_3)_2]^{3-}$ in the other side. This adversely influenced the adsorption efficiency. Sitando et al., have found that the adsorption of gold on carbon was significantly lower in the presence of free thiosulfate (Sitando et al., 2019). They have stated that free thiosulfate helps to stabilize Au(I) in two ways: (i) by stabilizing Au(I) as $[Au(S_2O_3)_2]^{3-}$ in solution or (ii) compete with gold(I)-thiosulfate for adsorption sites. These explanations are in consistence with our above-obtained results using ammoniacal thiosulfate solutions.
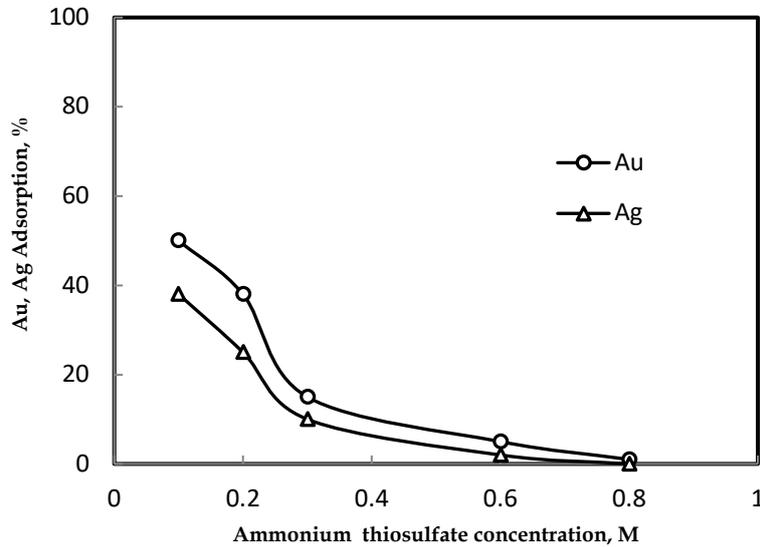
Fig. 1. Effect of ATS concentration on adsorption of Au and Ag from synthetic solutions on AC, 0.3 M ammonium hydroxide, 300 min

The existence of high ATS concentration would also decrease the adsorption kinetics. This phenomenon was confirmed by comparing the adsorption-time profiles of Au and Ag in two different real leach solutions using initial concentrations of 0.2 M and 0.3 M ATS. The results plotted in Fig. 2 show a remarkable drop in the adsorption of both metals at the higher ATS concentration of 0.3 M compared with those of 0.2 M ATS. These results indicated that efficient recovery of gold and silver could not be obtained in the presence of background TS ions in solution. Thus, improvement of adsorption may be
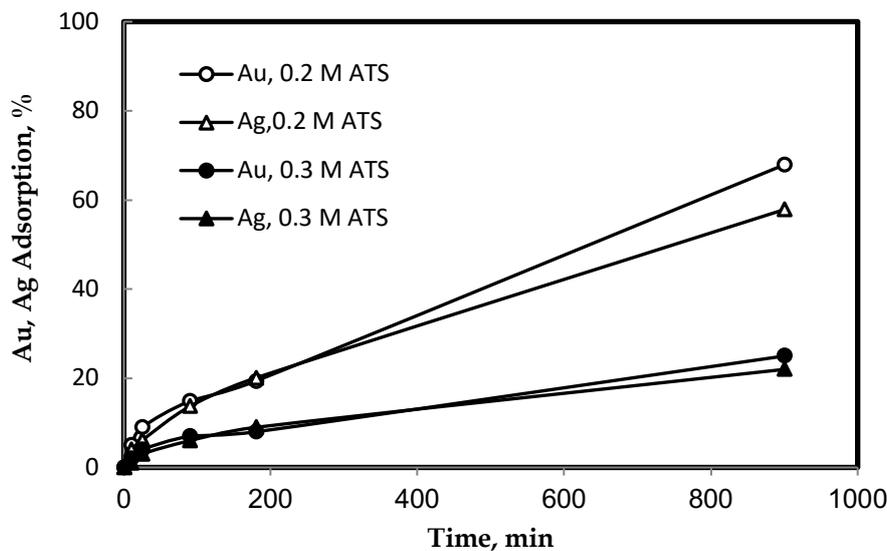
Fig. 2. Adsorption of gold and silver on AC from real leach solutions at different initial ATS concentrations

expected to occur through an interaction between the residual ATS in the leach liquor and an oxidizing agent. In this work we have selected APS as a suitable oxidizing agent.

3.2. Effect of ammonium persulfate

Thiosulfate ions can be oxidized using several oxidizing agents. Table 2 shows geometric structures of some sulfur-containing groups related to thiosulfate oxidation. Aerial oxidation of thiosulfate in the presence of UV light showed that 67% can be removed from the aqueous solution for one hour as shown in equation 5 (Ahmad et al., 2015).

$$S_2O_3^{2-} + 3O_2 + H_2O \rightarrow 2SO_4^{2-} + 2OH^- \tag{5}$$

Iodine oxidizes thiosulfate to form tetrathionate by the following redox reaction as shown in equation 6 (Mitchell, 1996).

$$2\,S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2\,I^- \tag{6}$$

Thiosulfate is oxidized with chlorine to sulfate during its use as a dechlorination agent as shown in equation 7 (Barbera et al., 2012).

$$S_2O_3^{2-} + 4\,Cl_2 + 5\,H_2O \longrightarrow 10\,H^+ + 2\,SO_4^{2-} + 8\,Cl^- \tag{7}$$

Other oxidants such as hydrogen peroxide, (Chatterjee et al., 2014; Ball and Brindley, 2016) and bacteria (Schreiber and Pavlostathis, 1998) can oxidize thiosulfate easily.

Persulfate (PS) ion has two oxygen atoms links two SO_3^- groups (table 2) and acts as an oxidizing agent by accepting two electrons and subsequent dissociation into two SO_4^{2-} groups according to the equation 8:

$$S_2O_8^{2-}\,(aq) + 2\,e^- \rightarrow 2\,SO_4^{2-}\,(aq) \tag{8}$$

The standard electrode potential $E°(S_2O_8^{2-}/SO_4^{2-}) = 1.96V$ [Bratsch, 1989, Wu et al., 2014]. The redox reaction between PS and TS ions produces sulfate and tetrathionate as shown in equation 9 [Sorum and Edwards, 1952]:

$$S_2O_8^{2-} + 2\,S_2O_3^{2-} \rightarrow 2\,SO_4^{2-} + S_4O_6^{2-} \tag{9}$$
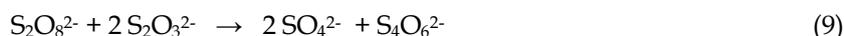
Table 2: Geometric structure of some sulfur containing ions

Sulfate SO_4^{2-}	Thiosulfate $S_2O_3^{2-}$	Persulfate $S_2O_8^{2-}$	Tetrathionate $S_4O_6^{2-}$

The persulfate ions are characterized by high redox potential (2.01 V) almost similar to that of ozone (2.07 V) and higher than that of hydrogen peroxide (1.8 V) and that of permanganate anion (1.7 V) which indicates its great oxidation reactivity (Kopczyński et al., 2017). Ammonium persulfate (APS) is an inexpensive, highly water-soluble, non-explosive and a nontoxic oxidizing agent. applications. APS finds many commercial widespread applications for groundwater and environmental remediation through organic chemical degradation as many of these reactions involve the destruction of environmental contaminants (Pino et al., 1998; Matzek and Carter, 2016).

A stock real leach solution was prepared by thiosulfate treatment of tailings collected from Al Amar plant, Saudi Arabia. The final diluted liquor contained 2.8 ppm Au and 6.7 ppm Ag and used in subsequent experiments.

A series of experiments were performed to study the effect of the addition of APS and its concentration on adsorption rate of gold and silver from real thiosulfate leach liquor that initially contained 0.2 M ATS. As shown in Fig. 3, in the absence of persulfate ions, the adsorption rate was slow and the adsorption slowly increased with time. After a long time of 15 h, only 67% of gold and 58% of silver were adsorbed without reaching equilibrium. On the other hand, a substantial increase in

adsorption of both metals with time was attained in the presence of 0.2 M APS. That is, about 90% and 75% of gold and silver were adsorbed after only 25 min, respectively. The adsorption of both metals was improved at a longer time, reaching about 95% after 90 min, and then very slightly increased. It seems that the APS interacted with the residual ATS in the leach liquor according to equation 9. This eliminated the harmful effect of ATS on adsorption efficiency and remarkably improved the adsorption rate of gold and silver. The produced tetrathionate and sulfate ions looks have no similar poisoning effect on active sites of carbon compared with TS ions (Aylmore et al., 2014).
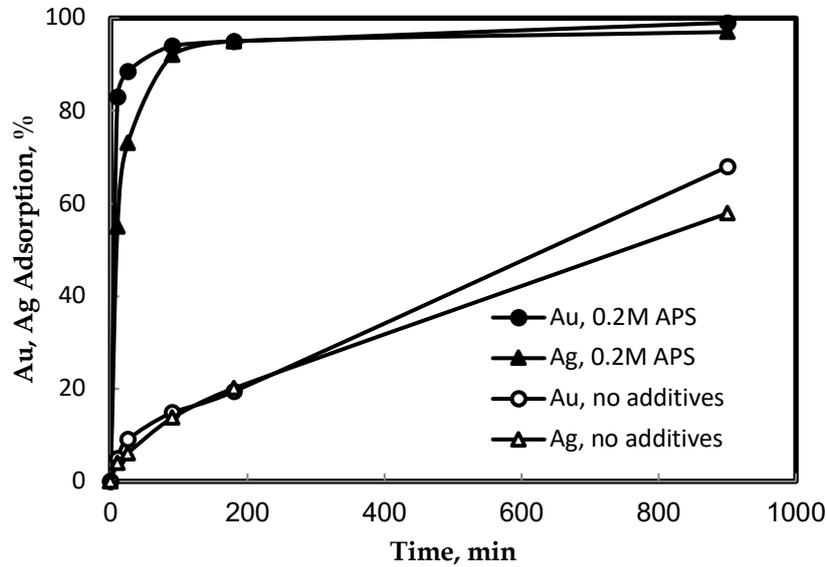
Fig. 3. Adsorption of gold and silver from real leach liquor on AC in absence and presence of 0.2 M APS

Adsorption rate of gold and silver, from real leach liquor on AC at different APS concentrations, from 0.0 M to 0.2 M, is presented in Fig. 4 and 5, respectively. In the presence of a low concentration such as 0.005 M APS, a slight increase in adsorption of both metals was observed compared with 0.0 M APS. About 15% and 19% of gold were adsorbed after 90 min in the absence and in the presence of 0.005 M APS, respectively. The adsorption of silver increased from 15% without APS to 25% in presence of 0.005 M APS. These results indicated that the effect of the little amount of 0.005 M APS, seems ineffective for the oxidation of all residual amount of ATS in solution, and thus little improvement was observed.
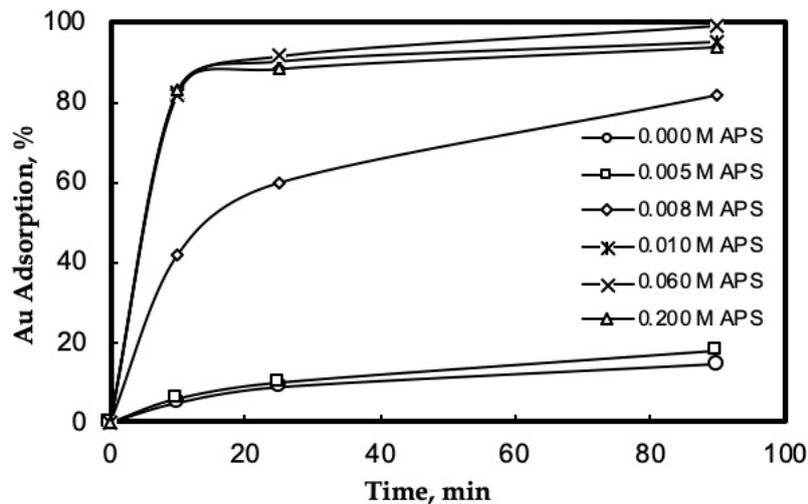
Fig. 4. Adsorption of gold on AC from real leach solution at different initial APS concentrations

A substantial improvement in adsorption rate of both metals was observed when the initial APS concentration reached 0.008 M and upward. That is almost 85% of both metals was adsorbed after 90

min. Higher APS concentrations, 0.01 and 0.2 M, showed compatible adsorption profiles with very fast kinetics of adsorption in the first 10 min and graduate improvement at longer contact times. Silver showed behavior of kinetics that is almost similar to that of gold. That is, near to the equilibrium value of adsorption (90%) was reached after 90 min.

Values of gold and silver adsorption efficiency after 90 min were plotted against the APS concentration and are shown in Fig. 6. Noticeable jumps in adsorption efficiency of both metals were observed around 0.01 M APS and then remained stable at higher concentrations till 0.2 M.
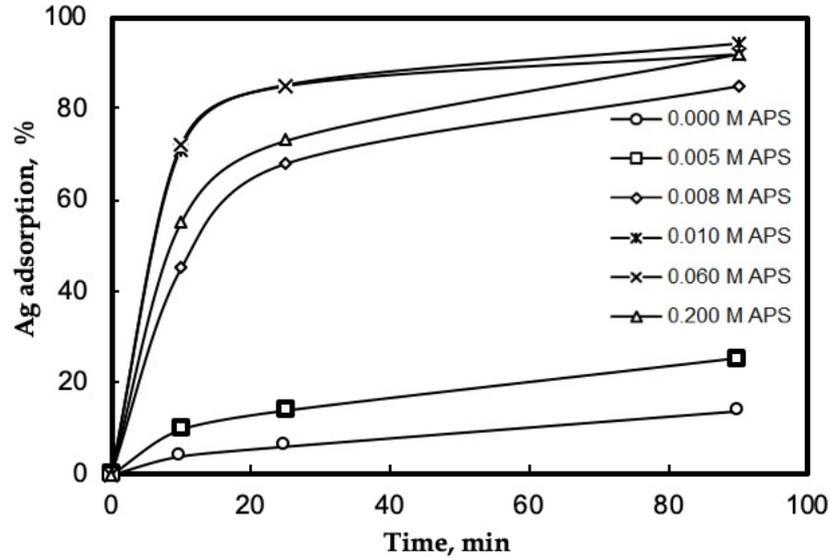
Fig. 5. Adsorption of silver on AC from real leach solution at different initial APS concentrations
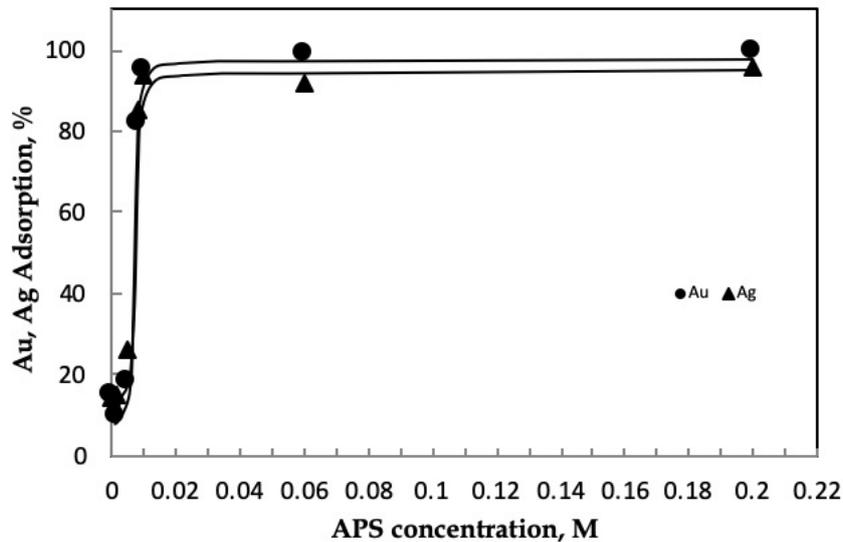
Fig. 6. Effect of initial APS concentration on adsorption of Au and Ag from real leach solution on AC, 90 min

The effect of initial APS concentration on free TS concentration remained in real leach solution after 90 min of adsorption on AC is shown in Fig. 7. The remained TS in real leach solution was close to 0.1 M when no AC or APS was added. This indicated that about half of the initial 0.2 M TS was consumed. It is clear that the required concentration of APS should be optimized to be adapted with the solution composition. Equation 9 shows that the stoichiometric values of APS and ATS are 1 : 2, respectively. The optimum value of APS concentration in the present study, 0.01 M, indicates that the corresponding ATS was around 0.02 M. It should be taken in consideration that a considerable portion of the starting 0.2 M ATS in the leaching experiment was consumed by complexing with the available aqueous metallic components (such as Au, Ag, Cu, Ni, Co...), by oxidation or by adsorption onto solid minerals. The

remained amount of free ATS deteriorates the adsorption efficiency of the AC (Abbruzzese et al., 1995; Aylmore and Muir 2001). It was reported that 50% of TS is lost during the leaching process (Zipperian et al., 1988; Abbruzzese et al., 1995; Xia C., 2001).
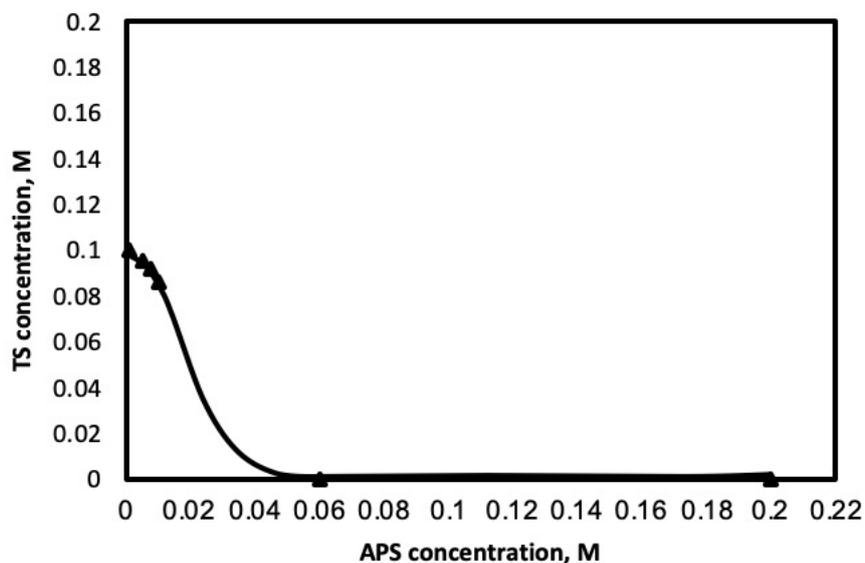
Fig. 7. Effect of initial APS concentration on free TS concentration remained in real leach solution after adsorption on AC, 90 min

3.3. Effect of amount of AC

A series of experiments were carried out using various amounts of AC; namely 0.1, 0.5, 1, 2, and 5 g in 0.045 L leach solution to examine their effect on both the capacity of gold and silver adsorption and on the adsorption kinetics in presence of 0.01 M APS, Table 3, Figs. 8 and 9. These carbon amounts were corresponding to ratios of the weight of carbon/the volume of the solution of 2.2, 11.1, 22.2, 44.4 and 111.1 g/L, respectively. It can be observed that the adsorption profiles noticeably improved with increasing the amount of AC. The adsorption of gold and silver was fast during the first 10 min and then slowed down at longer times. This behavior may indicate that the vacant adsorption sites on carbon surface are decreasing with time due to the competitive adsorption of other chemical components from the solution such as TS ions.

It can be observed from loading results in Table 3 that, the recovery of gold and silver increased continuously with increasing the amount of carbon. The recovery increased from 39.7 % to 98 % and from 44.7 % to 95.5 % when the weight of carbon increased from 0.1 g to 5 g for every 45 cm^3 of leach solution for gold and silver, respectively. The more amount of carbon used, the greater the surface area and active sites available for metals adsorption. The adsorption recovery after 90 min reached values close to completion (94% for Au and 92% for Ag) at a weight of carbon to volume ratio of 44.4 g/L. Abbruzzese et al., (1995) have reached almost similar recovery but after a long adsorption time of 6 hours. The better recovery of gold and silver is attributed to the advantageous effect of the added APS. Typical gold loadings of the carbon after the adsorption time of 90 min were found to be changed from 500 to 30 g Au/t carbon, when the ratio of the weight of carbon to the volume of the solution changed from 2.2 to 111.1 g/L, respectively. Under similar conditions, the silver loadings were changed from 1350 to 58 g Ag/t carbon.

3.4. Scanning electron microscope image, SEM, of AC

Scanning Electron Microscope image of the used AC after three adsorption experiments at 1000 magnification is shown in Fig. 10. The surface of the used AC looks has homogeneous and regular pore structure with almost similar size of sharp and round edges. The Energy Dispersive X-Ray Fluorescence, EDXRF, chart of the used AC is shown in Fig. 11. A small gold and silver peaks are shown sometimes overlapped with other elements like S. The EDXRF analysis shows impurities and adsorbed metals of

about 3% in the following descending order: O, Si, Al, Zn, Fe, K, Ca, Ag and Au. These low level of impurities seem to have no significant effect on the purity of adsorbed gold and silver.

Table 3. Loading of Au and Ag from real leach liquor, initially contained 0.2 M ATS, at different ratios of weight of carbon to volume of solution in presence of 0.01 M APS

Weight of carbon, g	Volume of solution, L	Weight of carbon / volume of soln. (g/L)	% Adsorption*		Metal Loading (g/t)*	
			Au	Ag	Au	Ag
0.1	0.045	2.2	39.7	44.7	500	1350
0.5	0.045	11.1	81.7	77.8	210	470
1.0	0.045	22.2	91.5	80.0	120	240
2	0.045	44.4	94.0	92.0	60	140
5	0.045	111.1	98.0	95.5	30	58

* After 90 min
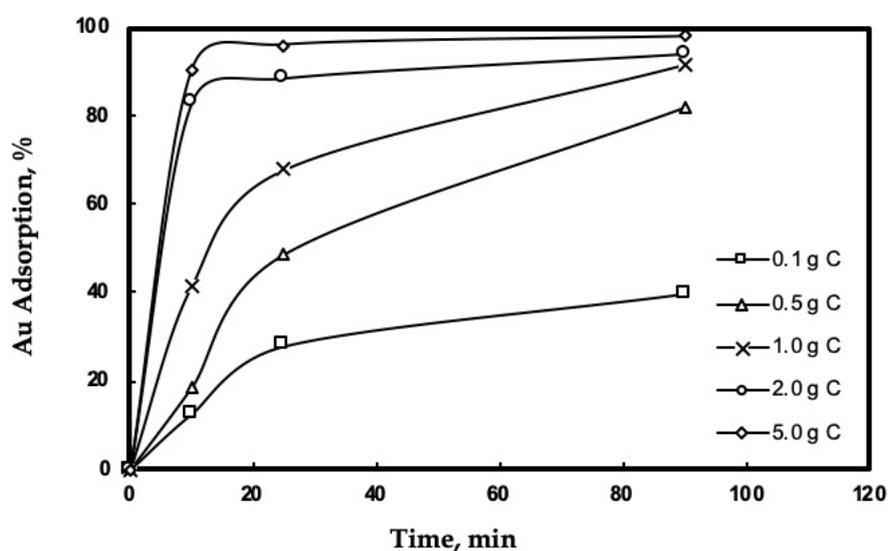
Fig. 8. Adsorption of Au from real leach solutions initially contained 0.2 M ATS in presence of 0.01M APS on different amounts of AC
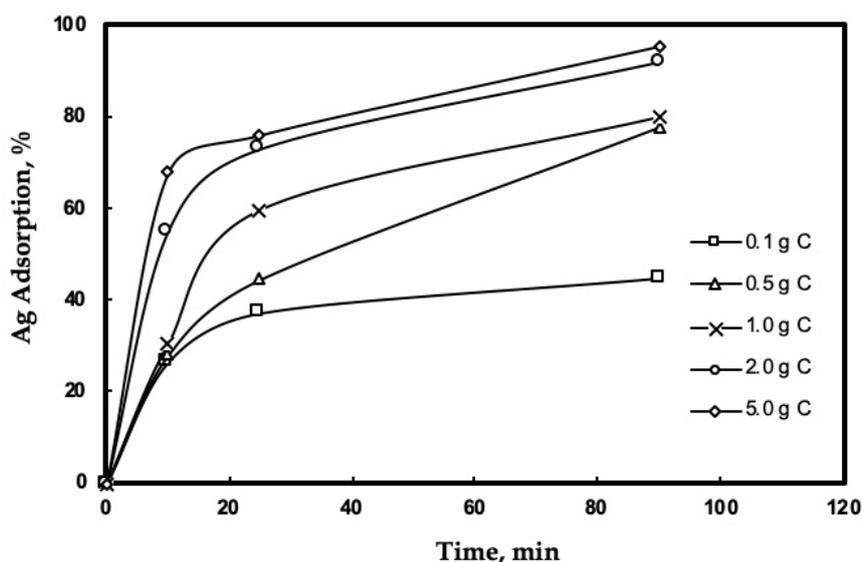
Fig. 9. Adsorption of Ag from real leach solutions initially contained 0.2 M ATS in presence of 0.01 M APS on different amounts of AC
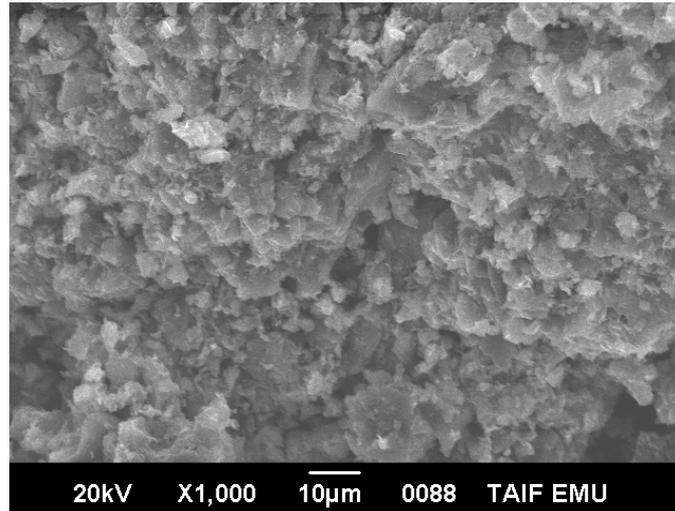
Fig. 10. Scanning Electron Microscope image of the used AC
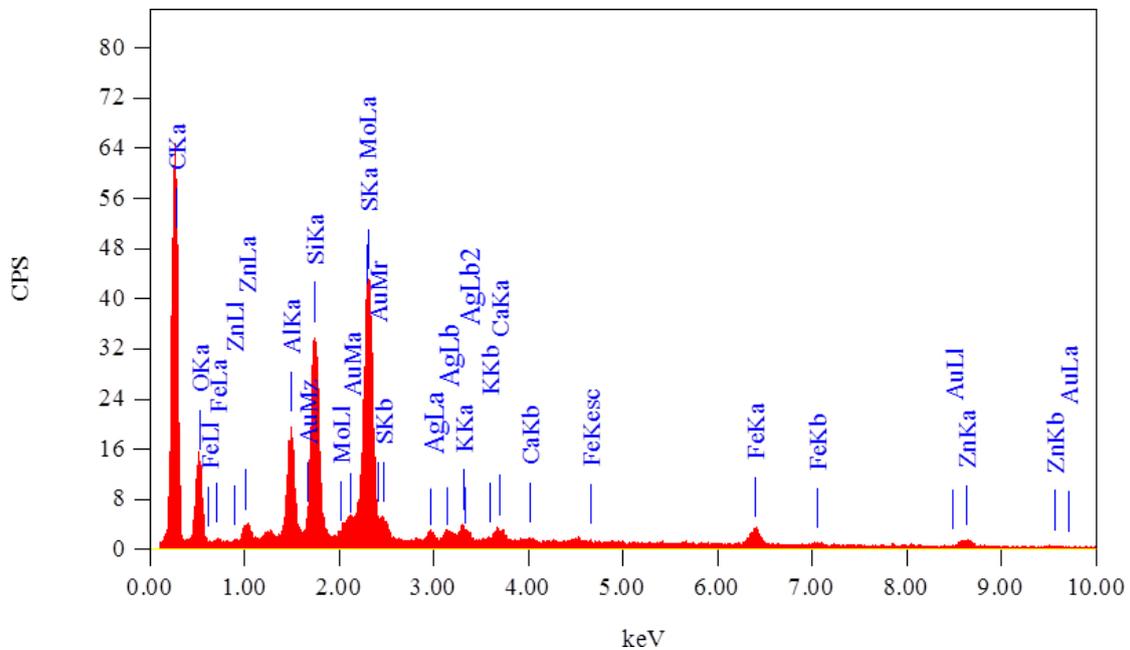
Fig. 11. EDXRF chart of the used AC after one adsorption from real leach liquor initially contained 0.2M ATS in presence of 0.01 M APS

3. 5. Application of the oxidative removal of thiosulfate using APS for recovery of gold and silver from Al Amar tailings

The hard sulfidic nature of Al Amar ore caused losses of appreciable amounts of precious metals wasted in tailings. In our previous work, we have studied the parameters affecting retreatment of Al Amar tailing waste with thiosulfate for extraction of gold and silver [Mahmoud et al., 2018]. In combination with the outcomes of the present work, Fig. 12 shows a proposed flowsheet describing the flow of suggested operations for recovering the lost precious metals in tailing waste and their recovery on AC modified by oxidative removal of thiosulfate using APS. The tailing waste is calcined at 400 °C for 2 hours to liberate the trapped gold and silver from the sulfide matrix. The calcined tailing is leached with ammoniacal thiosulfate solution, where ATS and ammonium hydroxide are added to maintain their concentrations at 0.2 M and 0.3M, respectively. The slurry is agitated for at least 12 hours. This is followed by subsequent adsorption on AC in presence of 0.01 M APS. After 2 hours, the loaded carbon

is separated from the slurry by screening and subjected to elution with hot caustic soda. The barren carbon is recycled to the adsorption stage and the concentrated gold and silver solutions are subjected to electrowinning to produce gold and silver dore. The solid residue is separated from the barren solution by filtration.

The present flowsheet is considered as a complementary proposed sequence of operations for leaching with TS process and recovery of gold and silver on AC. Regardless of the safe environmental impact of the thiosulfate route, the gold recovery from Al Amar CIL feed was improved to 70% compared with 60% with cyanidation process [Mahmoud et al., 2015]. In addition, 50% of the lost gold and silver was extracted with thiosulfate from tailings [Mahmoud et al., 2018]. Based on the outcomes of the present work, effective adsorption of gold and silver on AC in the presence of APS can further improve the TS process to be closer to industrial application.

In the known Zadra process a mixture of sodium hydroxide and sodium cyanide is used for gold desorption from AC (Soleimani and Kaghazchi 2008). However, there are several techniques for non-cyanide gold desorption using alkaline solutions, deionized water, organic solvents, and ultrasound (Davidson et al., 1970; Feng, et al., 2003; Soleimani and Kaghazchi 2008; Chen et al., 2019b). The elution is mainly enhanced at high temperature. Existence of cyanide is known to increase the rate and efficiency of elution. In this work, the elution was performed with hot NaOH solution. The cyanide was not used neither in leaching nor in elution procedures. The elution efficiency reached about 85% for gold and silver. However, detailed elution study is recommended.
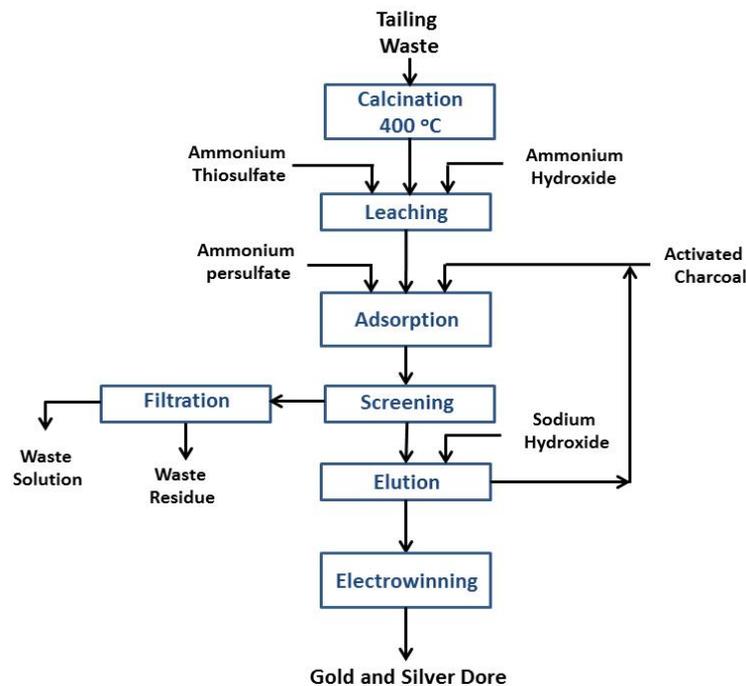
Fig. 12. Proposed flowsheet for retreatment Al Amar tailing waste by thiosulfate leaching of Au and Ag and their modified recovery on AC in presence of APS

4. Conclusions

Increasing amounts of background TS ions were found to have a sharp depressing effect on adsorption of Au and Ag on AC from synthetic solutions. No adsorption was obtained in 0.8 M TS after 5 h. Free TS ions was expected to stabilize the gold complex $[Au(S_2O_3)_2]^{3-}$ and the silver complex $[Ag(S_2O_3)_2]^{3-}$ in solution or to compete with these complexes for adsorption sites. Oxidative removal of the residual TS ions, in the presence of APS as an additive, drastically improved the adsorption of Au and Ag on AC. The adsorption profiles of the real leach liquor improved with increasing the APS concentration till 0.01 M. The adsorption capacity increased with increasing the AC. The metal loading reached 500 g/t for Au and 1350 g/t for Ag at a carbon/volume ratio of 2.2 g/L. The EDXRF images showed the characteristic peaks those are confirming the adsorption of gold and silver on AC. An integrated process flowsheet

was proposed for extraction and recovery of Au and Ag from Al Amar mine in Saudi Arabia using ammoniacal TS leaching and including the addition of APS as an adsorption aid.

Acknowledgment

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