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Gold Recovery from Thiosulfate Solutions using Hydrogen Peroxide

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Gold recovery from pregnant leach solutions like pregnant thiosulfate leach solutions from gold-containing solid wastes (e.g., e-waste) has gained considerable research attention in recent years due to the high market value and limited supply of gold. Although hydrogen peroxide (H_2O_2) is known as a green reducing agent since it liberates water and oxygen only as reaction by-products, recovery of gold from thiosulfate solutions via H_2O_2 reduction is still scarce. Hence, this work aimed to recover gold from thiosulfate solutions using H_2O_2 as a reducing agent. The reduction experiments were carried out by mixing gold(III)-containing thiosulfate solutions with H_2O_2, and the effects of different initial gold(III) concentrations (10-500 ppm), H_2O_2 concentrations (0.05-2 M), reaction temperatures (25-65°C) on the gold recovery yield were investigated. The highest gold yield of over 98% was achieved with an initial gold(III) concentration of 500 ppm and a H_2O_2 concentration of 2 M at 60°C. Therefore, H_2O_2 is a potential reducing agent for the recovery of gold from thiosulfate solution.

Keywords: Gold; recovery; thiosulfate; hydrogen peroxide; yield

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Gold has always been a valuable commodity from time to time. At present, there is a 4000-ton global yearly demand for gold, which is primarily used for national storage and product manufacturing, especially in the jewelry and electronics industries [1]. Nonetheless, the availability of natural gold has started to dwindle throughout the world, with the Earth's crust averaging a mere 5 ppb of gold [2]. Thus, secondary resources from solid waste are implemented to be reliable suppliers for gold to conserve natural deposit, eliminate environmental contamination, and promote sustainable utilization of resources [3]. According to statistics in 2016, out of 4570 tons of gold from world mining, 1334 tons of gold was obtained from electronics scrape (e-waste), scrap jewelry, bullion, and jewelry waste [4]. Furthermore, e-waste has shown contains approximately 10–10,000 g of gold/ton, which is higher than gold ores which only contains barely 0.5–13.5 g of gold/ton [5].

The process of recovering gold from gold-containing solid wastes like e-waste, jewelry scraps, waste dental crowns, spent catalysts, etc. through leaching has been considered to be innovative approach to obtain gold while also helps reducing solid wastes [6]. However, the current use of cyanidation techniques to leach gold from its various ores and solid wastes is undesirable from an environmental perspective. The usage of cyanide for leaching purposes has also been prohibited in many regions and countries due to toxicity and environmental concerns. The use of alternative gold leaching solutions has been investigated and discussed in numerous reviews [7-9]. One of the greener alternatives for cyanide is thiosulfate solution owing to the high complexing capacity of its thiosulfate ion ($S_2O_3^{2-}$) with gold to form stable gold-thiosulfate anionic complexes, i.e., ($[Au(S_2O_3)_2]^{3-}$) [8]. Thiosulfate group also exhibits lower reactivity and slower chemisorption kinetics than the thiol group, and thus provides opportunity to control the surface density of the monolayer ligand on metal nanoparticles [10]. After leaching, the gold-loaded thiosulfate solution is called the pregnant thiosulfate leach solution. Recovering gold from ores and solid wastes using thiosulfate solutions has been known for several decades, but extensive research has only started in the past few years.

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Numerous methods are available for metal recovery from aqueous solutions, including solvent extraction, ion exchange, liquid membrane processes, adsorption, reduction, and even micro/nanomotor-based strategies [11-20]. Brust-Schriffin methods also employed thiol ligands to utilize gold's high affinity to thiol ligands, which minimize gold nanoparticle from growing and makes average gold size lower than 10 nm [21]. Reduction of gold from pregnant thiosulfate leach solutions has been carried out with various reducing agents such as ascorbic acid, sodium borohydride and hydrogen peroxide [19,22,23]. For the most part, hydrogen peroxide (H_2O_2) is commonly used due to its being a green reagent that only liberates water and oxygen only as reaction by-products. While H_2O_2 has been widely used as reducing agent for other metals, recovery of gold using thiosulfate as leachant with H_2O_2 as reducing agent has only been shown by Huang Y, where H_2O_2 is used to oxidize gold thiosulfate complex, $Au(S_2O_3)_2^{3-}$ and result in precipitation efficiency of gold of approximately 95% [24].

Hence, this work aimed to recover gold from thiosulfate solutions using H_2O_2 as a reducing agent for gold(III). The parameters manipulated in this work include initial gold(III) concentration, H_2O_2 concentration, and temperature. The pregnant thiosulfate leach solutions were synthesized in the lab using gold and thiosulfate solutions, replicating the gold composition reported in various studies [25].

EXPERIMENTAL

Chemicals and Materials

The reagents used in this work were supplied from Sigma-Aldrich with analytical grade purity. No additional purification is needed. The reagent includes gold(III) chloride solution ($HAuCl_4$), ammonium thiosulfate ($(NH_4)_2S_2O_3$), H_2O_2 (30-32%), NaOH pellets and HCl.

Procedure

The experiment was conducted by using different parameters. The effects of initial gold(III) concentration (100, 200, 300, 400, 500 ppm) in ammonium thiosulfate solution, H_2O_2 concentration (0.05, 0.1, 0.5, 1, 2 M), temperatures (25, 35, 45, 55, 65°C), as well as gold nanoparticles yield was investigated.

As for the procedure of the experiment, 500 ppm of gold solution were prepared from stock solution ($HAuCl_4$) using ammonium thiosulfate (ATS) as diluter. A 25 mL of mixed gold-ATS solution was added into three necks round bottom flask. Then the solution was heated with water bath underneath until it reaches 65°C. 5 mL of 2 M H_2O_2 was then added into the solution drop by drop under constant stirring of 250 rpm for 10 minutes. This experiment was then triplicated with each different values of respective parameters of initial gold concentration (100, 200, 300, 400 ppm), H_2O_2 concentration (0.05, 0.1, 0.5, 1 M) and temperature (25, 35, 45, 55°C).

Characterization Methods

The gold-ATS solution (500 ppm) that had not undergone reaction before adding H_2O_2 was subjected to UV-Vis Spectrophotometry (Cary 60, Agilent) to ascertain the presence of gold thiosulfate complexes and gold nanoparticles. After that, the solution was analyzed by Atomic Absorption Spectrophotometer (AAS) (AA-7000, Shimadzu) to determine the gold ion contents. Before the AAS analysis, the samples were appropriately filtered and diluted to 10 factors in order to give accurate readings. The percentage recovery of gold was calculated by Equation 1:

$$\%\ Gold\ NP\ recovered = \frac{Initial\ gold\ content\ in\ the\ medium - Final\ gold\ content\ in\ the\ medium}{Initial\ gold\ content\ in\ the\ medium} \times 100\% \qquad (1)$$

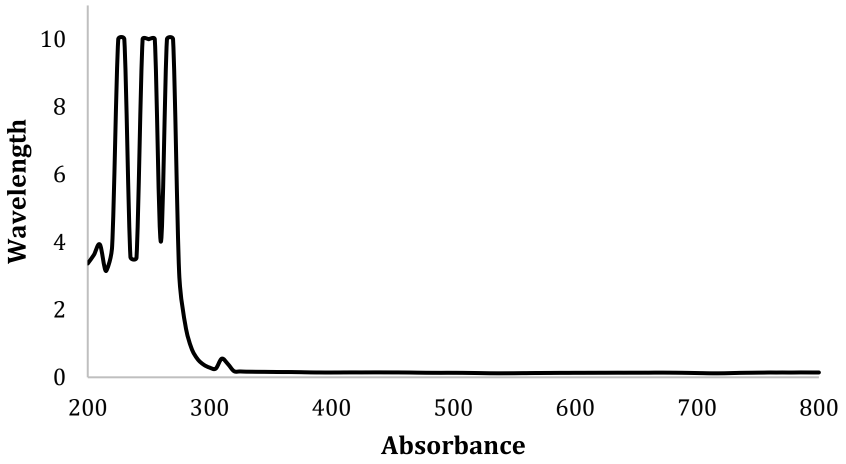

Figure 1. UV-Vis spectra of unreacted gold mixed with ATS solution at 500 ppm.

RESULTS AND DISCUSSION

UV-Vis Spectra

Figure 1 shows the UV-Vis spectra of unreacted gold mixed with ATS solution at 500 ppm. Based on previous reports, it was noted that gold thiosulfate complexes showed a strong absorbance peak at 312 nm [26–29]. As depicted in Figure 1, a noticeable peak is evident at 309.98 nm, while there is an absence of a peak within the 500-600 nm range. These suggest the existence of gold thiosulfate complexes but the absence of gold nanoparticles in the gold solution.

Initial Gold Concentration

Figure 2 shows the influence of initial gold ions. It was recognized that the total reduction overall sensitively changed in spite of small increase in initial gold ions from 100 ppm to 500 ppm. The optimum recovery is when the initial gold concentration is at 400 ppm which showcases the gold recovery of 99.92%. The rate increased by increasing the initial gold ions concentration up to 200 ppm, but it began to slow down up to 400 ppm and gradually decreased at 500 ppm of gold ions.

This result could be elucidated as initial gold concentrations increase; more gold ions are present in the solution to gain electrons. In this case, Au^{3+} will gain electrons release by decomposition of H_2O_2 and is then reduced to Au^0 which is the intended product. These reactions can be summed up in the following equations [30]:

$$\mathrm{AuCl_4^-} + 3\mathrm{e^-} \rightarrow \mathrm{Au} + 4\mathrm{Cl^-} \qquad E^o(\mathrm{V}) = +1.002 \quad (2)$$

$$\mathrm{H_2O_2} \rightarrow \mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \qquad E^o(\mathrm{V}) = -0.695 \quad (3)$$

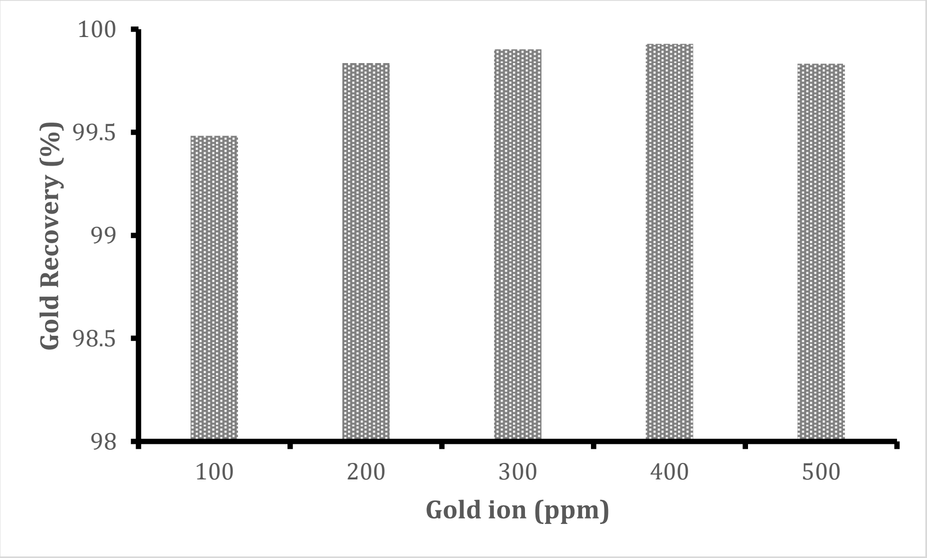

Figure 2. Reduction of gold in different initial gold ions concentration at 2M H_2O_2, 65°C.

As evident from the above, reactions (2) and (3) can be combined, resulting in the reduction of $AuCl_4^-$ to Au by H_2O_2,as shown in reaction (4).

$$2AuCl_4^- + 3H_2O_2 \rightarrow 2Au + 8Cl^- + 3O_2 + 6H^+ \quad (4)$$

Since the standard redox potential of the net reaction (Eq. 4) is +0.307 V [30], it is thermodynamically favorable. The overall reaction is also proven by changes in color in the solution. Figure 3 shows the photograph of 500 ppm gold solution before and after adding H_2O_2. The sample before reduction of H_2O_2 showed a crystal clear and transparent solution. After adding 2M of H_2O_2, the color changed to dark brown, indicating the formation of Au^0.

However, at 400 ppm to 500 ppm of gold concentration, the gold recovery (%) began to decrease gradually. It is possible that the Au^{3+} ions in the solution start to become excess and H_2O_2 present in the solution is not sufficient enough to provide electrons for most Au^{3+} ions. Theoretically by increasing the H_2O_2 concentration, the gold recovery (%) will increase as well [31]. However, this is not the case as will be explained subsequently.

H_2O_2 Concentration

Figure 4 shows the influence of different H_2O_2 concentrations. It was recognized that the total reduction overall sensitively changed in spite of a small increase in H_2O_2 concentration from 0.05 M to 1 M. The rate increased by increasing the initial H_2O_2 concentration up to 0.1 M, but it began to gradually decrease at higher concentrations of H_2O_2 concentration.

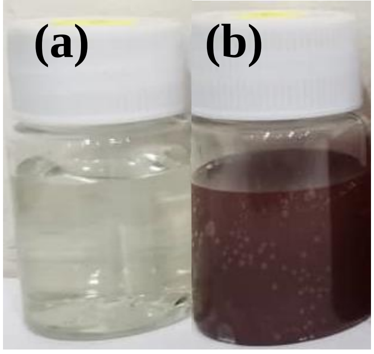

Figure 3. Photograph of 500 ppm gold solution before **(a)** and after **(b)** adding 2M H_2O_2.

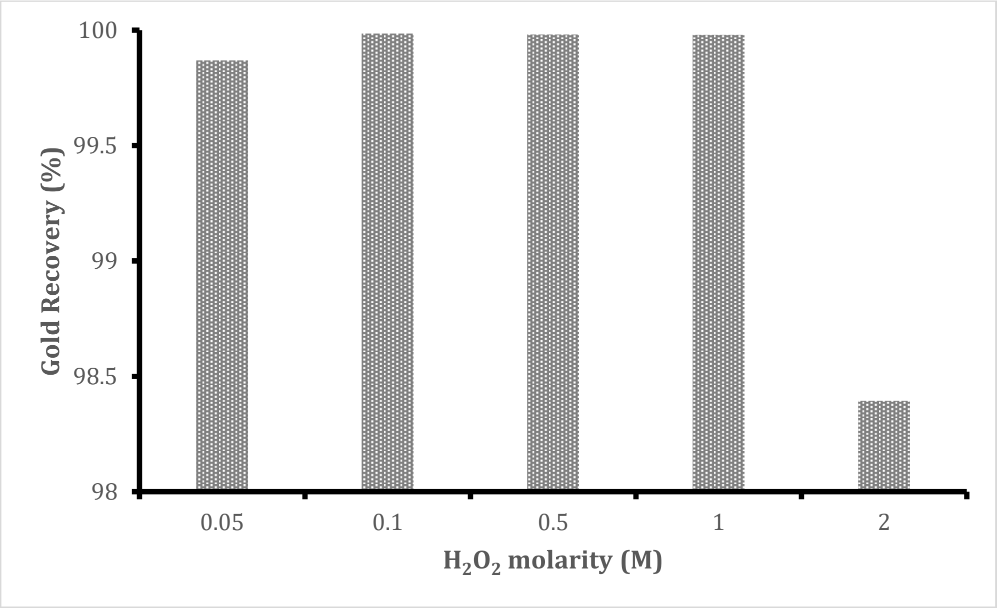

Figure 4. Reduction of gold in different H_2O_2 concentration at 500 ppm gold solution, 65°C.

It is shown that the optimum reduction is 99.98% at 1 M. The increase in gold reduction from 0.05 M up to 0.5 M is due to more concentrated H_2O_2 produced more oxygen bubbles and the reaction rate was faster. However, the gold reduction does decline slightly above 0.5 M to 1 M and massively to 2 M of H_2O_2. A possible reason for this to occur is due to the lack sufficient of gold ions presence in the solution to react with H_2O_2, which results in excess of overall H_2O_2 concentration. Another reason for the decrease in reduction percent is possibly due to abundance of OH^- ions causing increased hindrance to diffusion of Au^{3+} ions [32]. This is also supported by another study [33], where higher presence of H_2O_2 had a diminishing return since the excessive H_2O_2 could act as a scavenger for the OH radicals inside the solution, which results in reduced overall reduction of gold. H_2O_2 can also convert to OH radicals by the interaction with transition metal ions (Au^{3+}). While currently there is no study emphasizing formation of OH radicals through gold ion, formation through other metal ions such as iron (Fe) has been previously reported [34].

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow OH + Fe^{3+} + H_2O \qquad (5)$$

It is stated that metals such as Fe can be responsible for the formation of OH radicals through the Fenton reaction which is evident in equation (3) [34]. There is also another review that stated H_2O_2 can also convert to OH radicals by the interaction with transition metal ions (Au^{3+}) [35]. Hence, the decrease in gold reduction at higher H_2O_2 concentration due to formation of OH radicals is a plausible possibility.

Temperatures

Figure 5 shows the influence of varying temperatures. It was recognized that the total reduction of overall gold sensitively changed in spite of a small increase in temperature with interval of 10°C. While they show substantial increases from 25°C up to 45°C, they began to stagnant at 55°C and forward. The difference in reduction total from 55°C to 65°C is only about ± 0.001 which is a very minor increase. It is shown that 65°C has the highest reduction of all, which is 99.993%.

As expected, increasing the temperature accelerates hydrogen peroxide consumption which equals to increase in reaction rate [36]. This is because H_2O_2 decomposes rapidly at T>39.85°C and releases more scavenger electrons converting Au^{3+} ion to Au [30]. This is in line with rate of reaction theory where an increase in temperature will raise the average kinetic energy of the reactant molecules resulting in minimum energy necessary for an effective collision.

The stagnant curve at 55°C and 65°C can be explained due to frequent decomposition of H_2O_2. The OH radicals from H_2O_2 decomposition react with the newly formed hydrogen atoms or molecules and therefore reduce the amount of both H_2O_2 and H_2 [37]. This new formation consumed electrons needed for reduction of Au^{3+} ions. Although the decomposition of H_2O_2 can reduce the number of products, the lower production rates at higher temperatures are mainly due to OH and H recombination [37].

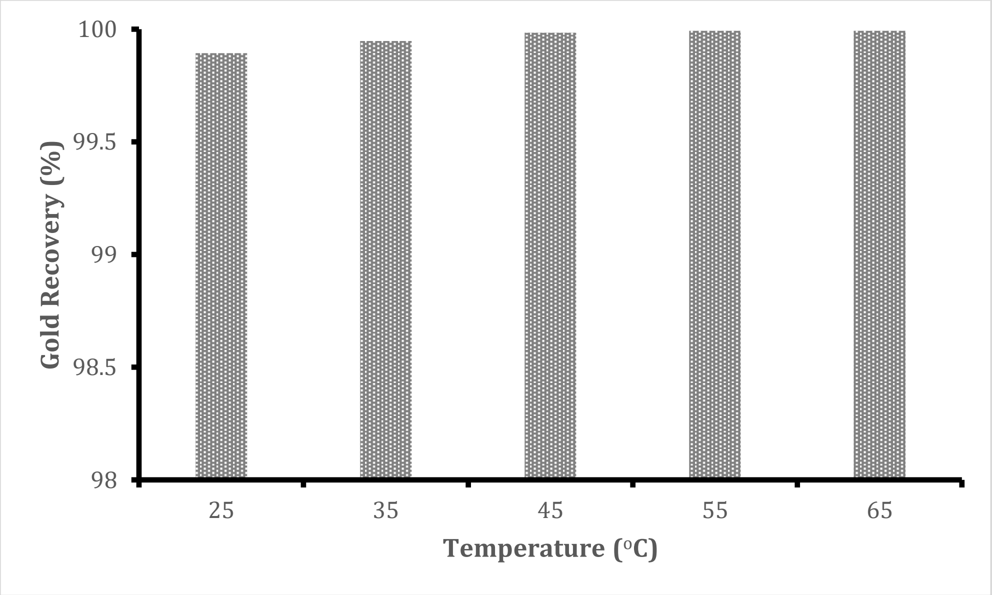

Figure 5. Reduction of gold in different temperatures at 500 ppm, 2M H_2O_2.

CONCLUSION

Recovery of gold from thiosulfate solution using H_2O_2 as reducing agent is an innovative approach which has been tried to minimize the environment adverse impact from usage of cyanide along with non-green reducing agent as well to recover the precious value of gold in pregnant leach solution originated from e-waste. Recovery of gold was found to be dependent on the concentration of gold initial present on the leach solution with optimum recovery of 99.92% at 400 ppm. The concentration of H_2O_2 also increases gold recovery up to 1 M which is observed to be optimum (99.98%), and massively decreases up to 2 M due to formation of OH radicals. Finally, temperature has also been shown to affect the gold recovery up positively to 65°C. Since decomposition reaction has been stated to be very slow at lower temperature and increase as temperature increases, further testing is required for temperatures above 65°C. Overall, this work has achieved the objective of recovering gold from thiosulfate solutions using H_2O_2 as a reducing agent with parameters of initial gold(III) concentration, H_2O_2 concentration, and temperature.

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