Adsorption of Copper Complexes on Anion Exchange Resin in Non-Ammoniacal and Ammoniacal Thiosulfate Leaching Systems

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Abstract

The leaching of copper using thiosulfate reagent as an alternative reagent to cyanide has been investigated since it is almost present in gold thiosulfate leaching. This paper addressed the investigation of adsorption of copper complexes on anion exchange resin in non-ammoniacal and ammoniacal thiosulfate leaching systems. The work provided the experimental procedures for the adsorption of copper complexes on strong based anion exchange resin in non-ammoniacal and ammoniacal resin-solution systems. The result showed that increasing ammonia in the solution resulted in the diminishing total copper complexes on the resin. As the solution pH of resin-solution systems was maintained by the ammonia solution added in the system, the same effect of ammonia on the total copper complexes on resin was also shown. Overall, non-ammoniacal resin-solution system gave much better adsorption isotherm of copper complexes on resin, and the dominant species copper complexes on the strong based anion exchange resin was expected to be Cu(S₂O₃)₅²⁻ based on leaching modelling.

Keywords: Adsorption; Copper; Leaching modelling; Resin

Introduction

The leaching of copper using thiosulfate reagent as alternative reagent to cyanide has been investigated since it is almost present in gold thiosulfate leaching. In general, copper is found in the gold leaching of complex ores [1,2]. The present of copper reduces the efficiency of gold leaching and consumes additional reagent [3,4]. To improve the recovery of gold, ammonium thiosulfate and oxygen under pressure was used [5] because copper ions can be catalysts for the oxidation of thiosulfate by oxygen or other oxidant, there should only be sufficient copper present to maximize leaching of gold and minimize thiosulfate consumption, and it only improves the initial rate of gold extraction [6,7].

The chemistry of gold leaching involving thiosulfate, ammonium and copper ions are complex due to the oxidation by dissolved oxygen [8-10]. Using ammoniacal thiosulfate in the gold leaching is typically much more economical than cyanidation to lixiviate significant quantities of copper without consuming excessive reagent [11]. The leaching of gold linearly increases with the Cu(II) concentration at low concentration (less than 5 mM) while the higher Cu(II) concentration almost does not affect the gold leaching rate [12]. The oxidation of thiosulfate in the presence of copper(II) and oxygen is very complex wherein oxygen increases the rate of copper(II) reduction to copper(I) by thiosulfate [13]. Hence, limiting the presence of oxygen and ammonia in the leach solution would be worthy to investigate the adsorption of copper complexes on anion exchange resins. Anion exchange resin had been intensively used in the quantification of thiosulfate and polythionates in gold leach solution on the resins [14]. The loading of gold using strong base anion exchange resin in non-ammoniacal resin-solution (NARS) systems has been studied, and polythionate concentration affects gold loaded on the resins [15]. However, there are still limited studies on the adsorption of copper complexes onto the resin at the equilibrium stage.

Therefore, the main objective of this work was to investigate the adsorption of copper complexes on strong based anion exchange resin in the present and the absent of ammonia. The specific objectives of the work were to provide the experimental procedure for the adsorption of copper complexes on strong based anion exchange resin in the resin-solution systems; to investigate the equilibrium adsorption of copper complexes in the resin-solution systems; to investigate the effect of ammonia concentration and the solution pH on the equilibrium adsorption of total copper complexes onto resin; to highlight the adsorption isotherm of total copper complexes in the resin-solution systems; and to obtain the dominant species of copper complexes in the resin-solution systems.

Experimental Methods

Apparatus and chemicals

The concentration of thiosulfate, polythionates and the total copper complexes in the experiments was analysed using the Waters 2695 HPLC separation module. For HPLC analysis, the copper must be masked with ethylenediamine [16], as copper thiosulfate peak interferes with the analysis of thiosulfate and polythionates. The HPLC separation was achieved using a Dionex IonPac AS16 ion exchange column equipped with an IonPac AG16 guard column. The mobile phase was a solution...
of sodium perchlorate (0.075 –0.2 M). The species detection was via a Waters 2996 Photodiode Array Detector (UV). Empower software was used for the calculation of peak area [17]. Details about the mobile solution and the wavelengths of UV adsorption and peak retention times of the involved species are described in the literature [14]. For the ICP analysis of total copper complexes, the samples were treated with NaCN (0.0167 M).

Copper was introduced as cupric sulphate (CuSO\(_4\cdot5H_2O\)). Ammonia-containing solutions were prepared using a 2 M NH\(_3\) stock solution standardised by acid-base titration [18]. Purolite A500/2788 in the chloride form with a macrospore structure was also used. The wet form of the resin contained 53-58 % moisture, the resin capacity is 1.15 meq/mL, and the specific gravity is 1.08 g/mL [19].

Procedures

All the experiments of the adsorption of copper complexes on strong based anion exchange resin in the resin-solution systems without and with ammonia were conducted at the ambient temperature (~23 °C) and variety pH. The concentration on the resin for a particular species was calculated from the change in its solution concentration in the system. The steps for the experiments were described as follow:

1. Leaching solution 200 ml was prepared, consisting of 20 mM (NH\(_4\))S\(_2\)O\(_3\) (ammonium thiosulfate), 5 mM sodium trithionate (Na\(_2\)S\(_3\)O\(_6\)), 2 mM cupric sulphate (CuSO\(_4\cdot5H_2O\)) and 50 mM ammonia in a 200ml volumetric flask. In dealing with ammonia loss, the ammonia solution was quickly added last before rapidly putting DI water into the flask to reach the 200 ml level. Then, it was quickly closed the flask with the cap.
2. Resin 0.5 g was prepared, and placed in a conical flask. It was then place in a 130 ml and sealed with plastic bottle.
3. The leaching solution was quickly placed in the bottle until it was full (130 mL total volume), and tightly sealed.
4. The bottle then placed on a roller at 35 rpm. Following that, the adsorption time is started using stopwatch.
5. The solution sample 1 mL was taken for HPLC analysis at just after 2 hours adsorption time started, and the solution pH was measured using pH probe.
6. After 2 hours adsorption, the resin was decanted and washed 4 times with DI water into a large vial. The remaining H\(_2\)O was sucked using pipette.
7. NaClO\(_4\) 50 mL (0.5M) was added into the vial for the dilution of copper complexes from resin, it was shaked at 130 U/minute on a Jubalo SW-20°C shaker for 30 minutes. The timer was started at the time of the 1st dilution started.
8. The solution sample 1 mL at 30 minutes was taken for HPLC analysis as the 1st dilution sample.
9. Following that, the resin was decanted and washed 4 times with DI water in the vial. The remaining H\(_2\)O was sucked.
10. NaClO\(_4\) 50 mL (0.5M) was re-added into the vial for the 2nd dilution of thiosulfate from resin, and it was also shaked at 150 U/minute for 30 minutes.
11. The 2nd dilution sample was taken for HPLC analysis at 30 minutes.
12. The resin was then decanted and washed 4 times with DI water in the vial. Before placing the resin in a small glass vial, the empty vial mass was measured.
13. The resin was placed in a small glass vial, and the remaining H\(_2\)O was also sucked.
14. Finally, the resin was dried at 60°C in an oven for about 16 hours.
15. The mass of vial with resin was measured to obtain the dried resin mass; the dried resin mass = the mass of vial with resin – the empty vial mass.

The 1st to 15th steps were repeated for the resin-solution systems with the initial ammonia concentration in the range of 0-400 mM and ammonium thiosulfate concentration in the range of 20-100 mM. For the ICP analysis of total copper complexes, 2 mL NaCN (0.0167 M) was added to each sample to stabilize the copper complexes in the sample.

Results and Discussion

Effect of ammonia concentration on equilibrium adsorption of copper complexes on resin

The effect of ammonia concentration in solution on total copper complexes adsorbed on resin in the resin-solution systems with the various initial concentration of thiosulfate in solution was viewed in Figure 1. As can be clearly seen in Figure 1, the total copper complexes adsorbed on resin sharply decreased from approximately 22.322 g copper/kg dry resin for the solution without ammonia to approximately 10.7122 g copper/kg dry resin for the solution with 50 mM ammonia.
(see the top graph of leaching with the 20 mM initial concentration of thiosulfate). Then, as the ammonia concentration in solution increased to 200 and 400 mM, the total copper complexes adsorbed on resin gradually decreases to 7.688 and 6.552 mM, respectively.

Compared to the total copper complexes adsorbed on resin in the system with the initial concentration of thioulate being 20 mM, the profile of total copper complexes adsorbed on resin with the 100 mM initial concentration of thioulate was decreased moderately from approximately 10.646 g copper/kg dry resin for the solution without no ammonia to approximately 7.881 g copper/kg dry resin for the solution with 50 mM ammonia (see the bottom graph in Figure 1). The same shape of graphs was also shown between the one with 20 mM thioulate and the one with 100 mM thioulate. But for the one with 100 mM thioulate, the total copper complexes adsorbed on resin was lower proportionally, which was 6.079 and 5.097 g copper/kg dry resin for the ammonia concentration in solution of 200 and 400 mM, respectively as shown by the bottom graph in Figure 1.

**Effect of pH on equilibrium adsorption of copper complexes on resin**

Meanwhile, the relationship between the total copper complexes adsorbed on resin and the solution pH was sighted in Figure 2. Because the pH solution was generated by the concentration of ammonia in the solution, it was not surprising that the profile of the total copper complexes adsorbed on resin over the solution pH was almost the same as Figure 1. The more pH in the solution was applied, the less total copper complexes adsorbed on resin was obtained.

**Adsorption isotherm of total copper complexes on resin**

The adsorption isotherm of total copper complexes in non-ammoniacal and ammoniacal resin-solution systems was clearly shown in Figure 3. The ammonia concentration applied in the system for the adsorption isotherm of total copper on resin was obtained. The adsorption isotherm of total copper complexes on resin shown by the bottom plots of the equation $Y_a = -494.84x + 66491$, and the equilibrium concentration of thioulate in solution being in the range of 6.932-85.841 mM. Meanwhile, when there was no ammonia applied, the system for the adsorption isotherm of total copper on resin are shown by the top plots of the equation $Y_a = -674.15x + 81630$ with the equilibrium concentration of thioulate in solution being in the range of 9.016-143.073 mM. Increasing ammonia concentration in the system resulted in the lower total copper complexes adsorbed on resin.

Overall, although the slope of the bottom linear fitting line was less than the top linear fitting line, the adsorption of total copper complexes with the addition of ammonia in the system was not be lifted up to the one without the addition of ammonia because the total copper adsorbed on the top plot (see the G plot in Figure 3) of the bottom line consists 50 mM ammonia. Therefore, non-ammoniacal resin-solution (NARS) system gave much better adsorption isotherm of copper on the resin as clearly highlighted in the previous results and discussions.

**The Dominant Species of Copper Complexes Based on Leaching**

The leaching and adsorption of copper in non-ammoniacal and ammoniacal resin-solution systems can be a simultaneous complex process. Copper (I) in solution reacted with thioulate as the leaching reagent in excessive amount to form copper thioulate complexes in solution. In the same time, copper (I) in solution also reacted with ammonia being added to form copper amine complexes. The equilibrium reactions in the resin-solution systems for the leaching could be modelled by the following equations:

1. $\text{Cu}^{+} + \text{S}_2\text{O}_3^{2-} \leftrightarrow \text{CuS}_2\text{O}_3^{-}$
2. $\text{Cu}^{+} + 2\text{S}_2\text{O}_3^{2-} \leftrightarrow \text{Cu(S}_2\text{O}_3)^{+}$
3. $\text{Cu}^{+} + 3\text{S}_2\text{O}_3^{2-} \leftrightarrow \text{Cu(S}_2\text{O}_3)^{-}$
4. $\text{Cu}^{+} + \text{NH}_3 \leftrightarrow \text{CuNH}_3^{+}$
5. $\text{Cu}^{+} + 2\text{NH}_3 \leftrightarrow \text{Cu(NH}_3)_2^{+}$
Concentration of copper complexes in the leaching solution over
been adopted. The column vector, 
in Equation (12):

\[
\begin{bmatrix}
\ln[\text{Cu}^+] \\
\ln[\text{CuS}_2\text{O}_3^{2-}] \\
\ln[\text{Cu(NH}_3\text{S}_2\text{O}_3^{3-}]) \\
\ln[\text{Cu(NH}_3\text{S}_2\text{O}_3^{2-}]) \\
\ln[\text{NH}_3] \\
\ln[\text{S}_2\text{O}_3^{2-}] \\
\end{bmatrix} = \mathbf{J} \mathbf{x}
\]  

where the stability constant for Equations (1), (2), (3), (4), (5), (6), (7) and (8) can be presented in \(\log \beta_1\), \(\log \beta_2\), \(\log \beta_3\), \(\log \beta_4\), \(\log \beta_5\), \(\log \beta_6\), \(\log \beta_7\), \(\log \beta_8\), respectively. The value of stability constant is 9.29, 12.17, 14.48, 5.8, 10.37, 9.93, 12.67 and 14.02 respectively [20].

Due to the competitive adsorption of thiosulfate and trithionate, and trithionate is strongly loaded on resin [15], the copper thiosulfate complexes and the copper amine complexes was expected to react with trithionate more than thiosulfate on the strong based anion exchange resin. Meanwhile, non-ammoniacal resin-solution system resulted in the higher adsorption isotherm of copper on the resin as stated in the previous discussion. From these reasons and it can be expected from the value of stability constant, \(\text{Cu(S}_2\text{O}_3\text{)}^3\text{−}\) was the dominant species in the leaching which was then adsorbed on resin to be the dominant species on resin.

However, further investigation was needed to obtain the most dominant species in the resin-solution system.

From Equations (1) to (8), there were 11 unknowns established with regards to the concentration of each species in leaching which are namely; \([\text{Cu}^+]\), \([\text{CuS}_2\text{O}_3^{2−}]\), \([\text{Cu(S}_2\text{O}_3\text{)}^3\text{−}]\), \([\text{CuNH}_3\text{S}_2\text{O}_3^{2−}]\), \([\text{CuNH}_3\text{S}_2\text{O}_3^{3−}]\), \([\text{CuNH}_3]\), \([\text{Cu(NH}_3\text{S}_2\text{O}_3^{2−}]\), \([\text{Cu(NH}_3\text{S}_2\text{O}_3^{3−}]\), \([\text{NH}_3]\), and \([\text{S}_2\text{O}_3^{2−}]\). In order to be able to solve the 11 unknowns, at least 3 other equations were required. The required 3 equations were the 3 mass balance equations for each species, Equations (9) to (11):

\[
\begin{align*}
[\text{Cu(I)}]_{\text{total}} & = [\text{Cu}^+] + [\text{CuS}_2\text{O}_3^{2−}] + [\text{Cu(S}_2\text{O}_3\text{)}^3\text{−}] + [\text{CuNH}_3] + [\text{Cu(NH}_3\text{S}_2\text{O}_3^{2−}] + [\text{Cu(NH}_3\text{S}_2\text{O}_3^{3−}] + [\text{CuNH}_3\text{S}_2\text{O}_3^{2−}] + [\text{CuNH}_3\text{S}_2\text{O}_3^{3−}] + [\text{NH}_3] \quad (9) \\
[S_2\text{O}_3^{2−}]_{\text{total}} & = [\text{CuS}_2\text{O}_3^{2−}] + 2[\text{Cu(S}_2\text{O}_3\text{)}^3\text{−}] + 3[\text{Cu(S}_2\text{O}_3\text{)}^3\text{−}] + 2[\text{CuNH}_3\text{S}_2\text{O}_3^{2−}] + [\text{S}_2\text{O}_3^{2−}] \quad (10) \\
[\text{NH}_3]_{\text{total}} & = [\text{CuNH}_3] + 2[\text{Cu(NH}_3\text{S}_2\text{O}_3^{2−}] + 3[\text{Cu(NH}_3\text{S}_2\text{O}_3^{3−}] + [\text{CuNH}_3\text{S}_2\text{O}_3^{2−}] + 3[\text{CuNH}_3\text{S}_2\text{O}_3^{3−}] + [\text{NH}_3] \quad (11)
\end{align*}
\]

To solve the 11 unknown, a numerical method utilising the multi-dimensional Newton-Raphson [21] approach in Excel software has been adopted. The column vector, \(\mathbf{x}\) for the unknown was presented in Equation (12):

\[
\begin{bmatrix}
\ln[\text{Cu}^+] \\
\ln[\text{CuS}_2\text{O}_3^{2−}] \\
\ln[\text{Cu(NH}_3\text{S}_2\text{O}_3^{3−}]) \\
\ln[\text{Cu(NH}_3\text{S}_2\text{O}_3^{2−}]) \\
\ln[\text{NH}_3] \\
\ln[\text{S}_2\text{O}_3^{2−}] \\
\end{bmatrix} = \mathbf{J} \mathbf{x}
\]

\[
\begin{align*}
\text{Figure 4: Concentration of copper complexes in the leaching solution over ammonia concentration based on leaching modeling.} \\
\text{Figure 5: The relationship between the calculated copper concentration on resin and the measured copper concentration on resin.}
\end{align*}
\]

The column vector, \(\mathbf{F}\) for the eleven functions to solve was expressed as Equation (13), and the Jocobian matrix \(\mathbf{J}\) was then expressed as Equations (14). As the result of leaching modelling for 100 mM thiosulfate, the concentration of copper complexes species in the solution can be predicted as shown in Figure 4. The species \(\text{Cu(S}_2\text{O}_3\text{)}^3\text{−}\) was the dominant species in the solution of non-ammoniacal resin-solution system, which was approximately 1.899 mM. When ammonia concentration was increased to be 50 mM and 200 mM, this species was still the highest among others, which is approximately 1.515 mM and 0.944 mM, respectively (see Figure 4).
However, the dominant species in the solution was changed to be CuNH₃(S₂O₃)₂⁻ which was approximately 0.906 mM when ammonia concentration was increased to be 400 mM as can be seen in Figure 4. Meanwhile, the Cu(S₂O₃)₃⁻ concentration was approximately 0.628 mM.

The total copper complexes adsorbed on resin can be calculated based on the initial copper concentration in leaching solution and the relationship between the total copper complexes on resin was compared to the measured equilibrium copper concentration in leaching solution. The calculated result was in a good agreement with the measured result the correlation coefficient, R² being 0.994.

**Conclusions**

The proposed experimental procedures were considerable method for the adsorption of copper complexes on strong based anion exchange resin in non-ammoniacal and ammoniacal solution systems. The effect of ammonia presence and pH was investigated. Increasing ammonia in the solution resulted in the decrease of total copper complexes on resin. Other result showed that the solution pH of resin-solution systems was maintained by the ammonia solution added in the resin-solution system where in the higher pH was applied, the lower amount of copper complexes on resin was adsorbed.

Compared to the ammoniacal resin-solution system, non-ammoniacal resin-solution (NARS) system gave much better adsorption isotherm of copper on resin. The dominant species copper complexes in solution of the NARS system was obtained to be Cu(S₂O₃)₂⁻ based on leaching modelling, and this species was expected to be the dominant species copper complexes adsorbed on resin.

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**References**


