Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: Kinetics

P.J. Tauetsile\textsuperscript{a}, E.A. Oraby\textsuperscript{a,b}, J.J. Eksteen\textsuperscript{a,}\textsuperscript{⁎}

\textsuperscript{a} Western Australian School of Mines: Minerals Energy and Chemical Engineering, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia
\textsuperscript{b} Faculty of Engineering, Assiut University, Egypt

\textbf{A R T I C L E  I N F O}

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\textbf{A B S T R A C T}

The downstream processing of leachates arising from the dissolution of copper bearing gold ores in cyanide-starved alkaline glycine solutions is imperative for the successful implementation of the new leach system at industry level. This study investigates the behaviour of gold adsorption onto activated carbon in the presence of copper from cyanide-starved glycine solutions. The adsorption behaviour was kinetically investigated using the Fleming k,n model. The model had a high consistency with experimental data (up to 6h) for both gold and copper as evidenced by the regression coefficient (R\textsuperscript{2}) values which were close to 1. The effects of important parameters including glycine concentration, solution pH, cyanide concentration, initial gold concentration, adsorbent concentration and ionic strength of the solution were studied. The results showed that, except for initial gold and carbon concentrations, a variation of these major factors had a pronounced effect on copper adsorption and slightly affected the gold adsorption, both in terms of adsorption rate and overall recovery. It was also seen that the active carbon had a high adsorption tendency towards gold over copper. The gold and copper extraction from a cyanide-glycine solution containing 2mg/L gold, 300mg/L copper, pH 11, 5g/L glycine, Cu:CN of 1:1 (123mg/L CN) and 8g/L carbon using lime as a pH modifier reached 99.0% and 52.8% respectively. Most copper and gold was recovered in the first 6h. The corresponding initial adsorption rates are 1263.8h\textsuperscript{-1} for gold and 19.0h\textsuperscript{-1} for copper.

1. Introduction

The synergistic effect of glycine and cyanide on the leaching of gold ores has been shown [10,22,24]. Cyanide remains the predominant lixiviant used in the hydrometallurgical treatment of copper-gold ores. The conventional cyanidation process is therefore well researched, understood and established. The process owes its prevalence to its technical simplicity, efficiency and cost-effectiveness [14]. The use of glycine as a gold lixiviant was recently developed [9,23,25]. Besides the environmental concerns on the use of cyanide, the main impetus in seeking alternative gold lixiviants is the exploration shift towards gold ores, more especially cupriferous ores, that are considered as complex to cyanidation [7]. The copper dissolution during cyanidation, which to a large extent depends on the copper mineralogy of the ore, leads to high cyanide consumption, adversely affecting both the process efficiency and economics [6,8,19,21,26].

The presence of cyanide soluble copper during the leaching of gold using glycine cyanide mixture has been found to be beneficial. In the presence of glycine, gold leaching in solutions containing cuprous cyanide at very low or zero free cyanide concentration was found to be on average six times higher than of a solution containing cuprous cyanides in the absence of glycine). According to Oraby et al. [22], the presence of glycine is believed to aid gold dissolution in any of the following ways: (i) by complexing with the cupric and cuprous ions [3], thereby increasing the concentration of free cyanide which in turn complexes the gold into solution; (ii) forming cupric glycinate which then acts as an additional oxidant to the system; (iii) leaching gold in cyanide-starved solutions containing cuprous cyanide precipitates copper as Cu(OH)\textsubscript{2} which passivates the gold. Glycine has the ability to dissolve this and other passivation layers; (iv) freeing gold particles locked in copper sulfide matrices through glycine dissolution of copper; (v) glycine acts as an additional gold lixiviant. It should be noted that in this glycine cyanide system, cyanide which is mostly present as cuprous cyanide runs at starvation levels. Glycine leaching offers the advantages of lower toxicity and the potential to effectively leach gold from some cyanide-refractory ores. In the presence of an oxidant in solution, gold can be leached by glycine at alkaline pHs and slightly elevated temperatures (50–60 °C) to form the gold glycinate complex according to

\begin{equation}
\text{[CuGly]_n} + \text{H}_2\text{O} \rightarrow \text{CuGly} + \text{H}_2\text{O} + \text{Gly}
\end{equation}
the following reaction:

\[
2Au + 4(NH_2CH_2CO_2H) + 2OH^- + O_2 \rightarrow 2[Au(NH_2CH_2CO_2)]^{2+} + 3H_2O
\]

(1)

Early research by [24] confirmed that in its pristine form, activated carbon adsorbs the gold glycinate complex. This was further validated during recent studies by [29,30] who showed that the gold glycinate complex adsorbs very strongly onto carbon. However, the solutions resulting from glycine cyanide leaching contain a variety of metal-ligand complexes including, gold-glycinate (Eq. (1)), gold cyanide (Eq. (2)), copper-cyanides (Eq. (3)–(6)) and copper-glycinate (Eq. (7)) in different proportions as a function of the concentrations of copper, cyanide, glycine and pH.

4Au + 8CN\(^{-}\) + O\(_2\) + 2H\(_2\)O \rightarrow 4[Au(CN)]\(^{2+}\) + 4OH\(^{-}\)

(2)

\[
Cu^+ + CN^- \leftrightarrow CuCN
\]

(3)

CuCN + CN\(^{-}\) \rightarrow Cu(CN)\(^{2+}\)

(4)

\[
Cu(CN)\(^{2+}\) + CN\(^{-}\) \rightarrow Cu(CN)\(^{2+}\)
\]

(5)

\[
Cu(CN)\(^{2+}\) + CN\(^{-}\) \leftrightarrow Cu(CN)\(^{2+}\)
\]

(6)

\[
Cu^2+ + 4(NH_2CH_2CO_2H) + 2OH^- \rightarrow Cu(NH_2CH_2CO_2)^{2+} + 2H_2O
\]

(7)

The oxidation reactions of Cu\(^{+}\) to Cu\(^{2+}\) which determines the WAD cyanide to copper glycinate ratio occurs through the following equilibrium where Gly\(^{-}\) is anionic glycinate (NH\(_2\)CH\(_2\)CO\(_2\)):\n
\[
4[Cu^{(3)}(CN)^{2-}]^2 + 8Gly^- + O_2 + 2H_2O \leftrightarrow 4[Cu^{(2+)}(Gly)^{-}]^2 + 4OH^- + 8CN^-\]

(8)

Or

\[
[Cu^{(2+)}(CN)^{2-}]^2 + 2Gly^- + \frac{1}{4} O_2 + \frac{1}{2} H_2O \leftrightarrow [Cu^{(2+)}(Gly)^{-}]^2 + OH^- + 2CN^-\]

(9)

The objective of the presented work is to investigate the use of activated carbon as an adsorbent material for gold recovery in the presence of copper from aqueous alkaline glycine cyanide-starved solutions using kinetic equation modelling. The Fleming k,n model was used to correlate and evaluate the adsorption kinetics. It was also of interest to elucidate the effect of various parameters on the adsorption rate of gold and copper from glycine-cyanide systems. The solutions contained a very low concentration of gold (2μgL\(^{-1}\)) in the presence of 300μgL\(^{-1}\) copper.

2. Material and methods

2.1. Carbon characterisation

Fresh activated carbon, PICAGOLD® G210AS produced by Jacobi Carbons derived from coconut shell was used in the study. Prior to use, the carbon was mechanically sized to \(-2.36 + 2.00\) mm and stored in a sealed container at ambient temperature. The carbon was used as it is with no further treatment. The surface area of the granular carbon as determined by the N\(_2\)BET method was 894.13 ± 46.69 m\(^2\)/g.

2.2. Adsorbates

All experiments were carried out using synthetic solutions. Reagents of analytical grade and distilled water were used for the preparation of gold in cyanide-starved glycine solutions, by the dissolution of a gold powder assaying 99.9% Au on a metal basis (spherical, -200 mesh) supplied by Alfar Aesar – Thermo Fisher Scientific. The standard glycine copper cyanide solution was prepared by dissolving 0.445 g/L CuCN (Ajax FineChem) and 1.058 g/L glycine (\(>99\%\), Sigma-Aldrich) in distilled water. The pH of the solution was buffered and maintained at pH 11 with a pH meter (Model AQUA-PH Cube pH-mV-Temperature Meter) by the addition of Ca(OH)\(_2\) (Chem-Supply Pty Ltd). The solution was agitated with Teflon magnetic stirrer bars at 400 rpm. Leaching of the gold powder was done at room temperature in a beaker left open to the atmosphere. A standard leaching solution contained 5g/L glycine, 123 ppm cyanide added as copper cyanide complex. Thus the ratio of copper to cyanide in the leach solution was 1. Gold powder by mass was added as needed and dissolved in this leach solution over a 24 h period. This resulted in solutions containing 2 ppm gold, 300 ppm copper and no free cyanide. The evaporation effect during leaching was managed by adding distilled water as needed. The evaporation effect during leaching was managed by adding distilled water as needed. A Supor®-450 47 mm 0.45μm membrane disc filter (Pall Corporation) was used to filter the alkaline gold solution prior to each adsorption experiment. Variations from these standard conditions are clearly noted in figure captions and in the text. A fresh solution was prepared for each experimental run.

2.3. Adsorption experiments

Loading tests were performed with the sized fresh carbon to provide a carbon concentration of 8 g/L (1.6 g carbon in 200 mL of solution). The solution contained an initial gold and copper concentration of 2 mgL\(^{-1}\) and 300 mgL\(^{-1}\), respectively unless otherwise stated. The traditional bottle-on-rolls method was used for the experiments. The experimental runs were carried in sealed 2.5L Winchester bottles (OD 44 cm and L 30 cm) at room temperature (approx. 23 °C). The mixture was bottle rolled for 24 h at 105 rpm with 5 ml samples taken at times, 0, 0.5, 1, 2, 4, 6 and 24 h. At the time of sampling, all samples were taken using the 10 ml Terumo syringe and filtered using a 0.22μm FilterBio® CA syringe filter to remove any present carbon fines and prevent further adsorption. The copper and gold concentrations in solution were determined by an atomic adsorption spectrometer (Agilent 55B AAS model).
3. Results and discussion

3.1. Adsorption kinetic model

The semi-empirical Fleming $k,n$ adsorption model was used to simulate the Au and Cu adsorption kinetics on activated carbon. This model that has been widely used assumes that the adsorption rate is independent on the loading capacity of the carbon [31]. The model uses a single pseudo mass transfer coefficient to describe the rate of adsorption from the liquid phase across the boundary layer between carbon and solution phases into the pores of the carbon particles. The model also assumes an equilibrium relationship between metal in solution and metal on carbon at the carbon-solution boundary. This assumption is valid for early stages of CIP plants which are usually operated under conditions in which gold concentration in solution is low ($< 1$ ppm) for most stages. The mathematical representation of the model is given as:

$$\Delta \text{Au}_{\text{c}} = k \times \text{Au}_{\text{t}} \times t^n$$  

Where $k$ and $n$ are model parameters, $k$ being the rate constant, $1/\text{h}$, and $n$ a model parameter, $t$ is the adsorption time (h), Au$_t$ is gold concentration in solution (ppm) at time $t$, $\Delta \text{Au}_{\text{c}}$ is gold adsorbed on carbon (ppm) from $t = 0$ up to a certain time $t$.

The model assumes the adsorption process operates at steady state and that all adsorption stages occur in perfectly mixed reactors and the parameter value $k$ is constant throughout. Many years of experience have proved the Fleming $k,n$ model sufficient for the task they were developed for. According to Fleming et al. [11], using simple and cheap laboratory batch tests, this modelling tool can be utilized to accurately predict steady-state adsorption behaviour and assess how plant upset conditions can affect the adsorption process.

The adsorption kinetics of gold and copper were conducted in an alkaline glycine-cyanide solution containing 2 mg L$^{-1}$ gold and 300 mg L$^{-1}$ copper at pH 11 in the following sections. The effects of glycine concentration, Cu:CN molar ratio, pH, initial gold concentration, carbon concentration and ionic strength are evaluated below.

3.2. Effect of glycine concentration

3.2.1. In the presence of copper

At a fixed cyanide concentration, the kinetics investigation of gold adsorption onto activated carbon was conducted at four initial glycine concentrations (1, 5, 10 and 15 g/L) in the presence of 300 ppm copper and the results are presented in Fig. 1 and Table 1. The observations indicate that when copper is present, increasing free glycine concentration accelerates the gold adsorption rate between glycine concentrations of 1 and 10 g/L as indicated by the increasing model parameter $k$. Beyond 10 g/L glycine, the increase in glycine concentration is of no effect on the gold adsorption rate. However, the overall gold recoveries are quite insensitive to free glycine concentration with 98% Au recoveries observed within six hours at various glycine concentrations. Increasing glycine concentration requires more time to reach the targeted pH of the solution thereby increasing Ca$^{2+}$ ion (ionic strength) in solution. In order to ascertain that the rapid initial Au adsorption is not the result of the effect of calcium ion, caustic was used as a pH modifier for a glycine concentration of 5 g/L (Section 3.7) and the results compared. The effect of increased Ca$^{2+}$ concentration (high ionic strength) was also investigated at varying CaCl$_2$ concentration but constant glycine concentration (Section 3.8). As will be discussed later, unlike is the case with other leaching systems, increasing the solution’s ionic strength by either using lime instead of caustic retards gold adsorption for the glycine-cyanide system. It can be concluded therefore that increased Au adsorption rate in this instance was solely due to increasing free glycine concentration.

In the case of copper, the effect of free glycine concentration on the competitive adsorption of copper is very significant both in terms of adsorption rate and overall recoveries. Increasing glycine concentration decreases both Cu adsorption rate and overall recovery. Glycine has a tendency to keep copper in solution as it favours the formation of copper glycinate complex ((Cu(H$_2$NCH$_2$COO)$_2$) which is not readily absorbed on the activated carbon. In the glycine only system, all the copper exists as Cu$^{2+}$. However, in the glycine cyanide system, there is both Cu$^{+}$ and Cu$^{2+}$. It is important to monitor this ratio in order to maximise Au adsorption and minimise Cu adsorption. Adjusting the free glycine concentration is a key factor in optimising the ratio between Cu(I) and Cu(II).

3.2.2. In the absence of copper

When preparing a copper-free low cyanide gold glycinate solution, NaCN (Rowe Scientific) was used as the cyanide source in place of CuCN. In the absence of copper, glycine concentration affected gold loading kinetics dramatically. As can be seen from Table 2, the initial gold adsorption rate (model parameter $k$) is highest for a cyanide only system (0 g/L glycine) and decreases with increasing glycine concentration. It is stated in literature that for a pure cyanide system, the loading rate of gold onto carbon sites between free cyanide species and gold. Overall gold recovery is not affected by varying glycine concentration as shown in Fig. 2. Within a six-hour time frame, > 99% Au was recovered at different glycine concentrations in the absence of copper.

![Fig. 1. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different glycine concentrations ([Au] 2 ppm, [Cu] 300 ppm, [CN] 123 ppm, pH 11, [Carbon] 8 g/L, 23 °C, 24 h contact time).](image-url)

Table 1

<table>
<thead>
<tr>
<th>Glycine Conc (g/L)</th>
<th>$k$ (h$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>1</td>
<td>557</td>
<td>59</td>
<td>1.3</td>
</tr>
<tr>
<td>5</td>
<td>1264</td>
<td>19</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>1842</td>
<td>24</td>
<td>1.1</td>
</tr>
<tr>
<td>15</td>
<td>1758</td>
<td>24</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different glycine concentrations ([Au] 2 ppm, [Cu] 300 ppm, [CN] 123 ppm, pH 11, [Carbon] 8 g/L, 23 °C, 24 h contact time).
3.3. Effect of pH

In Fig. 3, the effect of pH on the competitive adsorption of gold and copper was studied in the range between pH 9–12. A scan can be observed from the results shown in Fig. 3 and Table 3, the pH variation did not affect the gold adsorption; there was no significant variation on the adsorption rate with increasing pH. The overall gold recovery after 24 h of adsorption is also not pH dependent. Over 99% of gold was recovered at all pH values after 24 h, with the majority (> 97%) recovered within the first 6 h. The dependence of copper on pH, however, is more pronounced. At high solution pHs, there is lower copper recovery and initial adsorption rate. The pH at which copper recovery was lowest and lowest is pH 11. The results suggested pH 11 as the optimum pH of adsorption as it is at this value where gold recovery is maximised (99%) and copper recovery minimised (52%). Previous investigations on gold leaching confirmed that a pH value near 11 was optimal for gold leaching and optimum gold adsorption takes place in the next stage at pH 11.

3.4. Effect of cyanide concentration

3.4.1. Glycine-cyanide system

Fig. 4 shows the gold and copper loadings over time at various copper-to-cyanide ratios. It can be seen that in general, the rate of adsorption for both gold and copper increases with increasing cyanide concentration as evidenced by increasing k values in Table 4. The copper speciation in solution is greatly dependant on the Cu:Cn ratio and therefore the change in adsorption behaviour of copper can simply be represented by the change in the Cu(CN)2− speciation as cyanide concentration is increased [32]. A 1:1 copper-to-cyanide ratio means Cu(CN)2− was dissolved in glycine solution and there was no free cyanide. This means the concentration of the readily

<table>
<thead>
<tr>
<th>Glycine conc (g/L)</th>
<th>k (h⁻¹)</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.269</td>
<td>1.3</td>
<td>0.97</td>
</tr>
<tr>
<td>1</td>
<td>8320</td>
<td>1.2</td>
<td>0.96</td>
</tr>
<tr>
<td>5</td>
<td>4159</td>
<td>0.8</td>
<td>0.99</td>
</tr>
<tr>
<td>10</td>
<td>4190</td>
<td>0.5</td>
<td>0.98</td>
</tr>
<tr>
<td>15</td>
<td>5190</td>
<td>0.8</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 2

Fleming Kinetic model constants for Au at different free glycine concentrations in the absence of copper.

<table>
<thead>
<tr>
<th>pH</th>
<th>k (h⁻¹)</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Cu</td>
<td>Au</td>
<td>Cu</td>
</tr>
<tr>
<td>9</td>
<td>1215</td>
<td>44</td>
<td>1.6</td>
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<tr>
<td>10</td>
<td>1556</td>
<td>37</td>
<td>1.1</td>
</tr>
<tr>
<td>11</td>
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<td>19</td>
<td>1.2</td>
</tr>
<tr>
<td>12</td>
<td>1152</td>
<td>28</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 3

Fleming Kinetic model constants for Au and Cu at different solution pHs.

Fig. 2. Adsorption of Au in cyanide starved glycine solutions at different glycine concentrations ([Au] 2 ppm, [Cu] 0 ppm, [CN] 123 ppm, pH 11, [Carbon] 8 g/L, 23 °C, 24 h contact time).

Fig. 3. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different pH levels ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, [Carbon] 8 g/L, 23 °C, 24 h contact time).

Fig. 4. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions as a function of cyanide concentration ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [Carbon] 8 g/L, pH 11, 23 °C, 24 h contact time).
adsorbed $\text{Cu(CN)}_2^-$ was less than that of $\text{Cu}^{2+}$ glycinate species. By increasing the cyanide concentration, more copper is converted to Cu(I) which leads to the increase in the amount of copper recovered. $\text{Cu(CN)}_2^-$ adsorbs more than $\text{Cu}^{2+}$ glycinate.

### 3.4.2. Cyanide-only system

Fig. 5 and Table 5 show copper and gold adsorption from a pure cyanide solution containing 2 mg/L gold and 300 mg/L copper at different concentrations of cyanide. From Fig. 5, increasing the cyanide concentration increased the overall gold recovered in 24 h but decreased copper recovery. The adsorption curves flattened beyond 6 h indicating that a steady state was achieved between the adsorbed metals on the carbon and the metal complexes in solution. The model $k$ values from Table 5 shows that for a pure cyanide system, an increase in cyanide concentration increases initial gold adsorption rate but decreases the initial copper adsorption rate. The gold adsorption behaviour noted here is directly opposite for that of a pure cyanide system without copper. In the absence of copper, Marsden and House [18] observed that in a pure cyanide system, the gold loading rate decreased with increasing cyanide concentration. The authors attributed this behaviour to increased competition from free cyanide species.

### 3.5. Effect of initial gold-concentration in solution

As seen from Fig. 6, the initial gold concentration does not have an effect on the overall gold adsorption. However, the data shown in Table 6 shows a slight effect of the initial gold on the adsorption rate. The rate of gold adsorption increases with increasing gold concentration in solution up to 8 mg L$^{-1}$ then it decreases. For a cyanide glycine system, increasing initial gold concentration depresses copper adsorption thereby affecting overall copper recovery negatively. The copper recovery is lowest at 16 mg L$^{-1}$. This is expected as there is increased competition between copper and gold at high gold concentrations. Activated carbon has a high affinity for gold than copper complexes. The initial copper adsorption rate is highest between gold concentrations of 4 and 8 mg L$^{-1}$.

---

**Table 4**

<table>
<thead>
<tr>
<th>Cu:CN</th>
<th>[CN] ppm</th>
<th>$k$ (h$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Au</td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>1:1</td>
<td>123.0</td>
<td>1264</td>
<td>19</td>
<td>1.2</td>
</tr>
<tr>
<td>1:1.5</td>
<td>237.1</td>
<td>1380</td>
<td>30</td>
<td>1.1</td>
</tr>
<tr>
<td>1:2</td>
<td>352.2</td>
<td>1370</td>
<td>37</td>
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</tr>
<tr>
<td>1:2.5</td>
<td>467.3</td>
<td>1571</td>
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</table>

**Table 5**

<table>
<thead>
<tr>
<th>Cu:CN</th>
<th>[CN] ppm</th>
<th>$k$ (h$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Au</td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>1:2.5</td>
<td>467</td>
<td>872</td>
<td>45</td>
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<tr>
<td>1:4</td>
<td>814</td>
<td>7987</td>
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</table>

**Table 6**

<table>
<thead>
<tr>
<th>Initial gold conc ppm</th>
<th>$k$ (h$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
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</thead>
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<td></td>
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<td>Au</td>
</tr>
<tr>
<td>2</td>
<td>1215</td>
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<td>4</td>
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</tr>
<tr>
<td>16</td>
<td>1295</td>
<td>11</td>
<td>1.3</td>
</tr>
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</table>

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3.6. Effect of carbon concentration

The adsorbent amount is another important parameter that affects metal loading. The effect of carbon concentration on the adsorption of gold and copper from aqueous solutions was investigated at various concentrations of 2, 4, 8 and 12 g/L at constant gold and copper concentrations of 2 and 300 mg/L respectively. As shown in Fig. 7, the removal efficiency of both gold and copper increased with increasing carbon concentration. This is due to the increase in the effective surface area of the adsorbent and adsorbent/adsorbate ratio. The adsorption efficiency was maximum at a carbon concentration of 8 g/L, after that the removal was not significantly enhanced. This is the reason why a carbon concentration of 8 g/L was chosen as the optimum concentration for all other experiments. Increasing carbon concentration increases the gold adsorption rate but decreased the copper adsorption rate as shown by k constant values in Table 7.

![Fig. 7. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different carbon concentrations ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time).](image)

![Fig. 8. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions as a function of ionic strength of the solution ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, [Carbon] 8 g/L, pH 11, 23 °C, 24 h contact time).](image)

### Table 7

Fleming Kinetic model constants for Au and Cu at different carbon concentrations.

<table>
<thead>
<tr>
<th>Carbon conc g/L</th>
<th>k (h⁻¹)</th>
<th>n</th>
<th>R²</th>
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</thead>
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<td></td>
<td>Au</td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
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<td>853</td>
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<td>4</td>
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<tr>
<td>12</td>
<td>2424</td>
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</tr>
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</table>

3.7. Effect of pH modifier

The effects of two alkaline medium sodium hydroxide (caustic) and calcium hydroxide (lime) on gold and copper adsorption from a glycine-cyanide system were compared and the results are as shown in Fig. 8 and Table 8. Both can be used to adjust the solution pH to the desired alkaline value of 11. When lime was used the overall gold and copper recovered and the corresponding initial adsorption rates were lower. Usage of lime tends to foul carbon as calcium is precipitated. However, at industrial scale, lime is preferred and used as it is much cheaper than caustic. It also has the added advantage of stabilising the solution pH value owing to its slow dissolution tendency.

### Table 8

Fleming Kinetic model constants for Au and Cu at different pH modifiers.

<table>
<thead>
<tr>
<th>pH modifier</th>
<th>k (h⁻¹)</th>
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<th>R²</th>
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<td>Cu</td>
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</tr>
<tr>
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<td>25</td>
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</tr>
<tr>
<td>Lime</td>
<td>1264</td>
<td>19</td>
<td>1.2</td>
</tr>
</tbody>
</table>

3.8. Effect of CaCl₂

CaCl₂ slightly increases the adsorption rate but has no significant impact on the overall recovery of both gold and copper as clearly depicted by rate constants and recovery time graphs in Table 9 and Fig. 9 respectively. However, it should be noted that the presence of high concentrations of CaCl₂ may lead to the formation of calcium hydroxide which can essentially block off carbon pores resulting in a slight reduction on metals recovery. Though gold and copper recovery increased with the addition of 0.5 g/L CaCl₂, increasing CaCl₂ concentration from 0.5 g/L to 2.0 g/L lead to slightly lower recoveries. The calcium hydroxide layer formed on the carbon surface blocks both Au and Cu from adsorbing equally hence the trend for Cu and Au are similar. The calcium hydroxide layer is a physical not a chemical hindering block.
The effect of studied parameters on the initial gold concentration reached a magnitude of gold concentration reached a result in gold yields of 98% or more. Copper, though present in solution at 4, 8, and 12 g/L carbon concentrations, the gold recoveries were 97.9%, recovery significantly. At 2 g/L carbon, 91.8% gold was recovered while all studied parameters, only carbon concentration affected overall gold recovery significantly. The model previously used to describe the kinetic adsorption behavior of copper and gold from cyanide-starved glycine solutions. The theoretical constants of the Fleming k,n model was used to describe the adsorption of gold cyanide onto activated carbon. Part III: comparison between the extraction of aurocyanide by activated carbon, polynamic adsorbents and 1-pentanol, Hydrometallurgy 19 (1) (1987) 95–115.

### Table 9

**Fleming Kinetic model constants for Au and Cu at different free calcium chloride concentrations.**

<table>
<thead>
<tr>
<th>CaCl₂ conc g/L</th>
<th>k (h⁻¹)</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>0.0</td>
<td>1264</td>
<td>19</td>
<td>1.2</td>
</tr>
<tr>
<td>0.5</td>
<td>1275</td>
<td>46</td>
<td>0.7</td>
</tr>
<tr>
<td>2.0</td>
<td>1744</td>
<td>36</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Fig. 9.

Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different concentrations of calcium chloride ([Au] 2 ppm, [Ca] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, [Carbon] 8 g/L, pH 11, 23°C, 24 h contact time).

#### 4. Conclusions

The theoretical constants of the Fleming k,n model was used to describe the kinetic adsorption behavior of copper and gold from cyanide-starved glycine synthetic solutions. The model previously used to describe gold loading onto carbon was a good match to the experimental data. Of all studied parameters, only carbon concentration affected overall gold recovery significantly. At 2 g/L carbon, 91.8% gold was recovered while at 4, 8, and 12 g/L carbon concentrations the gold recoveries were 97.9%, 99.0% and 99.4% respectively. The variation of all other parameters resulted in gold yields of 98% or more. Copper, though present in solution in more than a hundredfold magnitude of gold concentration reached on average only 50% recovery. The effect of studied parameters on the initial rate of adsorption, k, are summarised below:

- At a Cu:CN ratio of 1:1, increasing glycine concentration increased gold adsorption but decreased copper adsorption rate. The highest copper adsorption rate (58.9 h⁻¹) occurred at 1 g/L glycine which is the same concentration at which the overall copper recovered was highest (70.4%).
- In the absence of copper, the gold adsorption rate decreased with increasing glycine concentration. For a glycine-free solution, (0 g/L glycine) the adsorption rate was 10266.8 h⁻¹ and 8319.5 h⁻¹ for a solution containing 1 g/L glycine. Increasing the glycine concentration to 5 g/L reduced the adsorption rate by more than half to 4159.0 h⁻¹. Beyond 5 g/L glycine, the rate constant was not affected by increasing the glycine concentration.
- There was no obvious trend on the effect of pH on gold adsorption rate. The highest rate was at pH 10. Further pH increments beyond 10 decreased the adsorption rate. For copper, increasing the solution pH generally decreases adsorption rate.
- Increasing the CN:Cu ratio while keeping copper concentration constant increased the adsorption rate of both gold and copper.
- A higher initial gold concentration resulted in a high gold and copper adsorption rate.
- High adsorbent concentration increased gold but reduced initial copper adsorption rate.

#### Acknowledgements

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2018.09.022.

#### References


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