



Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 1: Isotherms

P.J. Tauetsile^a, E.A. Oraby^{a,b}, J.J. Eksteen^{a,*}

^a Western Australian School of Mines: Minerals Energy and Chemical Engineering, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia

^b Faculty of Engineering, Assiut University, Egypt

ARTICLE INFO

Keywords:

Glycine-cyanide system
Gold
Copper
Carbon
Adsorption isotherms

ABSTRACT

Cyanide-starved alkaline glycine solutions have been shown to have distinct advantages in terms of lower reagent consumption and detoxification needs, or leach rate and recovery, over cyanide- only and glycine-only leach systems respectively for gold ores with nuisance copper. Activated carbon has been shown to be suitable for gold adsorption from alkaline glycine systems, and is well established for cyanide based systems. Activated carbon being an effective substrate for the adsorption of gold thus offers a possible downstream carbon-in-pulp (CIP) recovery route for alkaline glycine leach systems and hybrid systems in the presence of cyanide. Given the frequent occurrence of gold deposits with high levels of nuisance copper, the equilibrium loading of gold and copper onto activated carbon from cyanide-starved alkaline glycine solutions containing copper and gold has been studied. Adsorption efficiency was studied in terms of equilibrium loading isotherms. Results showed that while copper adsorption is more sporadic based on goodness of fit, gold adsorption is more consistent and clearly follows the Freundlich isotherm model (good linear correlation of $\log Q$ vs $\log C$ values). The adsorption isotherms were obtained using a gold concentration of 2 ppm. In the presence of copper, the equilibrium gold loading increases with increasing glycine and calcium ion concentrations, decreases with increasing cyanide concentration and is not affected by initial gold concentration. The cuprous cyanide and cupric glycinate complexes lowered gold loading through a competitive adsorption with the copper (I) cyanide complexes adsorbing more rapidly on the carbon than their glycinate counterparts. The equilibrium gold loading capacity in cyanide-starved glycine solutions containing 2 ppm Au and 300 ppm Cu, at pH 11 was found to be 9.95 kg_{Au}/ton_{carbon} in 24 h, which is almost four times higher than the gold loading capacity in a pure cyanide system (2.7 kg_{Au}/ton_{carbon}) under similar conditions. The study revealed that activated carbon was an effective adsorbent for removal gold from cyanide-glycine aqueous solutions.

1. Introduction

The powerful synergistic effects of glycine-cyanide as reported by Eksteen et al. [13] and Oraby and Eksteen [28] presents a possible alternative leaching process to conventional cyanidation for the leaching of copper-gold ores. Glycine cyanide-starved mixtures can be used to reduce cyanide consumption for complex polymetallic ores which contain other minerals readily soluble in cyanide. The presence of glycine serves as a suitable receptor of both base and precious metals and allows the recycling of the glycine after metal recovery from solution, thereby significantly reduces reagent consumption. Copper mi-

nerals more especially, when present in large quantities, are notorious for excessive consumption of cyanide through the formation of stable copper cyanide complexes (Eqs. (1) and (2)). This in turn adversely affect both process economics and efficiency of the conventional cyanidation process by yielding poor gold recoveries. It has been reported that every 1% reactive copper present in ore consumes 30 kg/t NaCN [24]. The presence of copper sulphides such as covellite (CuS) and chalcocite (Cu₂S) also increase cyanide consumption by forming cyanate (OCN⁻) and thiocyanate (SCN⁻) in addition to copper cyanide complexes according to Eqs. (3) and (4) respectively.



* Corresponding author.

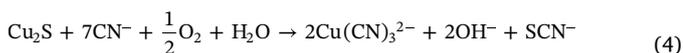
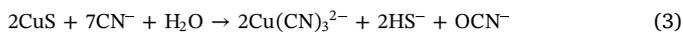
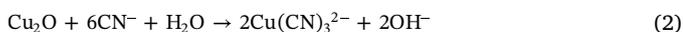
E-mail address: jacques.eksteen@curtin.edu.au (J.J. Eksteen).

<https://doi.org/10.1016/j.seppur.2018.09.024>

Received 4 July 2018; Received in revised form 8 September 2018; Accepted 9 September 2018

Available online 11 September 2018

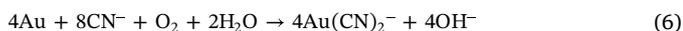
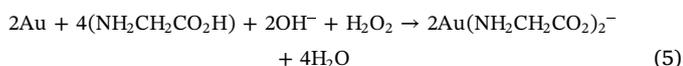
1383-5866/ © 2018 Elsevier B.V. All rights reserved.



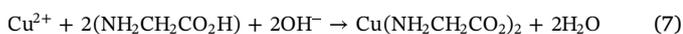
In this regard, the glycine cyanide mixture can be used as an alternative lixiviant, or a synergistic lixiviant with catalytic amounts of cyanide, for the treatment of copper-rich gold ores. On its own, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), the simplest amino acid, in an alkaline environment can selectively leach copper and gold from ores and/or concentrates. With leaching performed between pH 7 and 12, the leach system is the only alkaline benign system studied that allows for the selective leaching of copper in the presence of precious metals [26]. Glycine leaching can allow for reagent consumption reduction as glycine reduces interference from foreign cations with insignificant Fe, Mn, Cr, Mg, Al and Si dissolution and no interaction with acid consuming gangue observed [12].

Despite its environmental benign nature, alkaline glycine leaching suffers a major drawback of slow gold leaching. Unlike with cyanide, the pure (i.e. in the absence of a catalyst) alkaline glycine leaching process is significantly slower, with leach rates being slower than that of conventional cyanidation even at elevated temperatures of around 50–60 °C [28]. Sometimes, lixiviants can be combined to produce a synergistic effect [40]. Oraby and Eksteen [27] demonstrated that the slow leaching rate of glycine can be counteracted by adding small amounts of copper and cyanide (as cuprous-cyanide complex) to the glycine solution, resulting in leach rates as much as five times higher than those of cyanide-only leaching. In all cases where cyanide is present, it runs at starvation levels, i.e. where the cyanide is wholly insufficient to dissolve cyanide soluble copper minerals and free cyanide is not measurable at the end of the leach process, although low levels of weak acid dissociable (WAD) cyanide may remain. The use of small amounts of cyanide is often not problematic as environmental effects are minimised, safety for workers maximised and operating costs reduced significantly. In these cyanide-starved alkaline glycine systems, glycine acts as the main lixiviant since it makes up the bulk of the reagent mixture. The chemistry of the glycine cyanide leach system however is complex due to the presence of two complexing reagents glycine and cyanide, which interact with gold and copper according to Eqs. (5)–(11). As a result, different gold and copper species are present in the leach solution. Depending on process conditions, the interaction of copper and cyanide species can result in various copper cyanide complexes whose equilibrium is described by Eqs. (8)–(11). However, for a cyanide starved solution the predominant species is $\text{Cu}(\text{CN})_2^-$.

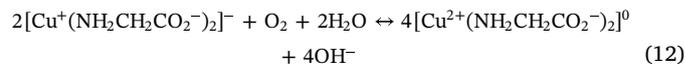
Gold complexes



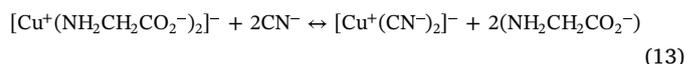
(b) Copper complexes



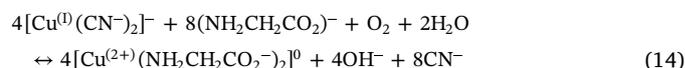
The ratio of WAD cyanide versus Cu glycinate in the system depends on the redox cycling between cuprous (Cu(I)) copper and cupric (Cu(II)) copper (Eqs. (12)–(15)).



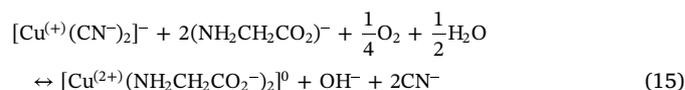
Interchange reaction:



Combined reaction:



Or:



With the majority of the world production of gold obtained by the carbon adsorption processes, activated carbon adsorption remains the preferred and dominant technique for gold recovery from alkaline cyanide leach solutions because of its simplicity, effectiveness and economic importance [37,39]. Some authors have recently shown that activated carbon is able to extract the gold glycinate complex in the presence and absence of copper from alkaline solutions [28,35,36]. The activated carbon adsorption technique therefore represents a conventional route for gold recovery from glycine cyanide leach solutions and no change would be adopted to the downstream processing. To date, there is no literature evaluating gold adsorption onto active carbon for alkaline cyanide-starved glycine solutions containing copper.

With carbon as its major component, activated carbon is a porous, amorphous carbonaceous material with a large internal surface area [7,22,25]. In addition to carbon, its elemental composition which to a large extent depends on the source raw material, comprises hydrogen, nitrogen, sulfur and oxygen [4,6,33]. Active carbons have a tridisperse microcrystalline structure comprising pores of varying sizes classified as, micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm) [10,41]. Macropores found on the outer surface of the active carbon particles act as a gateway for adsorbate molecules to pores in the innermost part of the active carbon. Mesopores also known as transitional pores, branch directly off macropores and their function is to channel the adsorbate into the micropores. Micropores which make up about 95% of the total surface area of the active carbon largely affect the adsorption capacity of a given active carbon. Most activated carbon adsorbents used commercially have a specific surface area of the order 800–1500 m²/g. The adsorption efficiency of active carbons is also determined by the chemical structure of the carbon's surface. The carbon's ability to adsorb metal cations is due to the inherent ion exchange properties resulting from the presence of heteroatoms bonded to the carbon surface in the form of carbon-oxygen, carbon-nitrogen, and carbon-sulfur surface functional groups. The carbon-oxygen groups are the most important as oxygen has a major effect on the adsorption capacity of the active carbon [5,15,38]. This particular surface group can exist in three forms, acidic, neutral and basic. The acidic carbon-oxygen surface group renders the carbon surface hydrophilic and thus increase the adsorption of metal cations.

The mechanism of the interaction between the carbon surface and gold cyanide complex is not well understood with different researchers reporting different mechanisms to explain their results. All suggested theories to date can be summarised under four categories (i) the reduction theory with carbon as the reducing agent, (ii) the ion pair adsorption theory where gold is suggested to adsorb on the carbon surface not in its metallic state but by formation of a carbonyl aurocyanide compound $[\text{AuCN}\cdot\text{CO}(\text{CN})_2]$ through chemical precipitation, (iii) adsorption of gold as the aurocyanide complex $[\text{Au}(\text{CN})_2]^-$ through the simple anion exchange mechanism resulting from the electrostatic interaction between positive and negative charges and (iv) cluster compound adsorption theory which involves adsorption of gold complex alongside that of other metallic ions [23]. Adsorption isotherms are the most extensively used methods for obtaining useful information about the adsorbate, adsorbent and the adsorption process. This information can in turn be used for the effective design of any new adsorption system i.e. carbon-in-pulp (CIP) and carbon-in-leach (CIL) processes for gold. The Freundlich isotherm in particular has successfully been used to give insights on the adsorption of gold, silver and mercury cyanide complexes on carbon using synthetic solutions.

The objective of this work is to evaluate the adsorption behaviour of activated carbon to recover gold from cyanide-starved glycine solutions in the presence of copper. Moreover, through the use of equilibrium adsorption isotherms validated through laboratory experimental results, the influence of some analytical parameters on the activated carbon adsorption of gold in the presence of copper from a cyanide catalysed glycine system are investigated in detail.

2. Material and methods

2.1. Sorbent characterisation

The adsorbent used in this work was a fresh activated carbon: PICAGOLD® G210AS produced by Jacobi Carbons. The sorbent was manufactured from raw high grade coconut shell as per specifications from the manufacturer. Prior to use, the activated carbon was pulverised to reduce the time needed to reach equilibrium [29], using the Ro-Tap® apparatus, oven dried at 70 °C for 16 h and preserved at ambient temperature in a desiccator. The surface area of the carbon as determined by the N_2 BET (Nitrogen Brunauer-Emmett-Teller) method was $840.69 \pm 46.55 \text{ m}^2/\text{g}$. The BET surface area of the carbon enables the loading capacity to be presented as grams of gold per metre squared of carbon (g/m^2). The particle size distribution of the pulverised carbon is depicted in Fig. 1.

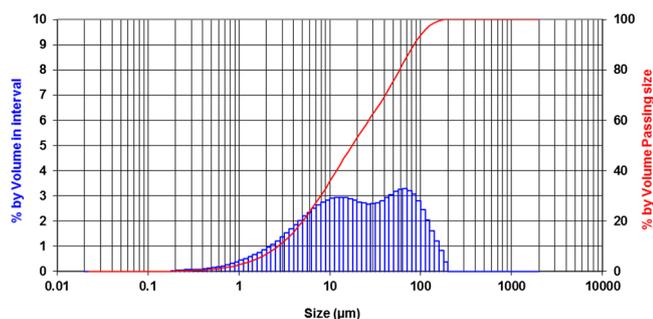


Fig. 1. Particle size distribution of pulverised carbon.

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 glycinate cyanide-starved alkaline 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 the required amounts of CuCN (Ajax FineChem) and 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 Meter) by the addition of $\text{Ca}(\text{OH})_2$ (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 5 g/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. A Supor® 0.45 µm 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 the figure captions and in the text. A fresh solution was prepared for each experimental run.

2.3. Adsorption experiments

The traditional bottle-on-rolls method was employed for the metal complexes adsorption onto activated carbon. The experimental runs were carried out in sealed 2.5 L Winchester bottles (OD 44 cm and L 30 cm) at room temperature (circa 23 °C). The development of equilibrium isotherms was effected by contacting accurately weighted five different concentrations of powdered activated carbon samples of 0.080, 0.256, 0.512, 0.800 and 1.280 g/L powdered activated carbon with 250 ml of gold and copper synthetic standard solution. The initial pH of the solutions was adjusted to 11 and maintained during the experiments by using $\text{Ca}(\text{OH})_2$ or H_2SO_4 . The mixture was bottle rolled for 24 h at 100 rpm. Preliminary tests were conducted for 72 h and the results indicated that 24 h is sufficient to reach equilibrium conditions. Once the equilibrium time was reached, samples were filtered using a 0.22 µm FilterBio® CA syringe filter to remove any present carbon fines and prevent further adsorption. Total metals concentration in solution were determined by atomic adsorption spectrophotometry by using an Agilent 55B AAS.

3. Results and discussion

3.1. Freundlich isotherm

The Freundlich isotherm is often used to represent equilibrium states of systems in which the adsorbate adsorbs onto the adsorbent through chemisorption, physisorption or both, two mechanisms through which the gold cyanide complex adsorbs onto activated carbon as previously suggested by some researchers. The kinetic approach was used in this work for deriving the Freundlich adsorption isotherms. In the kinetic approach it is assumed that, at equilibrium the rates of adsorption and desorption are equal. Adsorption isotherms can also be derived through the statistical and thermodynamic theoretical approaches. The Freundlich equation that was used to fit the gold experimental adsorption data at a temperature range from 22 °C to 25 °C and equilibrium pH 11 from a glycine cyanide starved solution containing copper is:

$$Q_e = kC_e^n \quad (16)$$

Where Q_e is the adsorbate quantity per unit mass of adsorbent at equilibrium (mg g^{-1}), C_e the equilibrium concentration of adsorbate in solution (mg L^{-1}), n the Freundlich equation constant parameter used for quasi-Gaussian energetic heterogeneity characterisation of the adsorption surface and k the equilibrium gold loading capacity. The linear form of the equation is:

$$\log Q_e = \log k + n \log C_e \tag{17}$$

A plot of $\log Q_e$ against $\log C_e$ gives a straight line with an intercept on the y-axis. The intercept and slope of this linear plot corresponds to the values of k and n respectively.

The effects of glycine concentration, solution pH, cyanide concentration, initial gold concentration, calcium chloride concentration, ionic strength of the solution on the gold loading capacity of activated carbon are evaluated in the following sections.

3.2. Effect of glycine concentration

3.2.1. In the presence of copper

Adsorption isotherms in Fig. 2, were obtained from experiments carried out from solutions at different glycine concentrations of 1.0, 5.0, 10.0 and 15.0 g/L. As the glycine concentration increases, the isotherms progressively show higher gold loadings. This is also reflected by the k values in Table 1 which indicate that the gold adsorption increases by increasing the glycine concentration up to 10 g/L and no major affect was observed beyond 10 g/L. This result may attributed to the various dominating copper complex species at different glycine levels but constant copper and cyanide concentrations. At 1.0 g/L glycine, there is increased competitive adsorption between gold and copper complexes as a high proportion of the copper exists as CuCN_2^- , a complex known to adsorb rapidly onto activated carbon [9,14,17]. Increased glycine concentration increases the formation of copper (II) glycinate ($\text{Cu}(\text{H}_2\text{NCH}_2\text{COO})_2$) complex which has less affinity for adsorption onto active carbon thereby depressing copper adsorption and increasing gold selectivity. This is verified in Fig. 3 which shows that copper adsorption decreases with increasing glycine concentration.

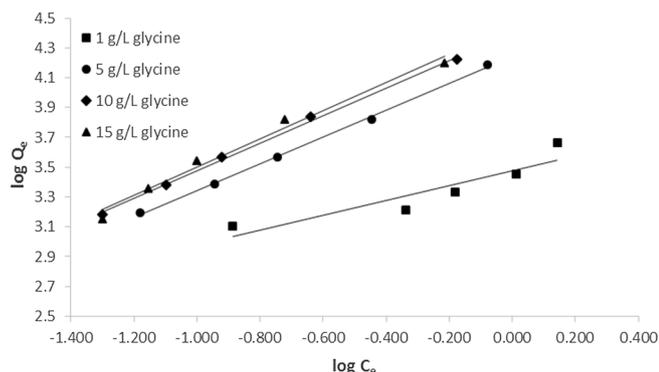


Fig. 2. Gold loading isotherms as a function of glycine concentration (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

Table 1

Numerical Freundlich isotherm constants for different glycine concentrations for gold.

Glycine conc g/L	Freundlich k		n	R^2
	Kg/t	g/m^2		
1	3.0	3.94×10^{-6}	0.50	0.83
5	17.4	2.28×10^{-5}	0.90	0.99
10	25.2	3.31×10^{-5}	0.93	0.99
15	27.9	3.66×10^{-5}	0.95	0.98

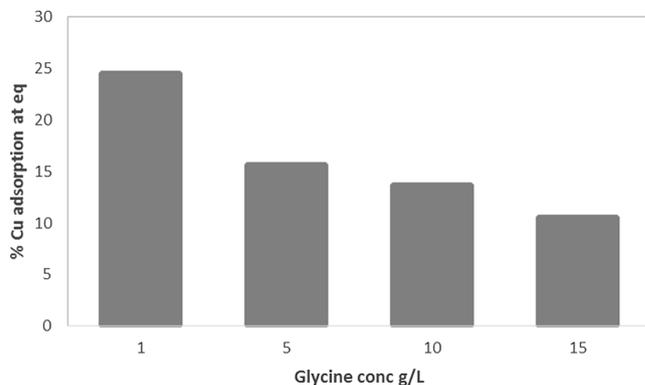


Fig. 3. Effect of glycine concentration on copper adsorption. Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

3.2.2. In the absence of copper

It is interesting to see even in a copper-free system, the presence of glycine enhances gold loading as depicted by gold loading isotherms in Fig. 4. This suggests that generally, glycine may be used to enhance gold loading onto activated carbon. The gold loading capacity, k values, for a copper free system are considerably higher (Table 2) which is expected as there are no copper complexes in solution competing with gold during the adsorption.

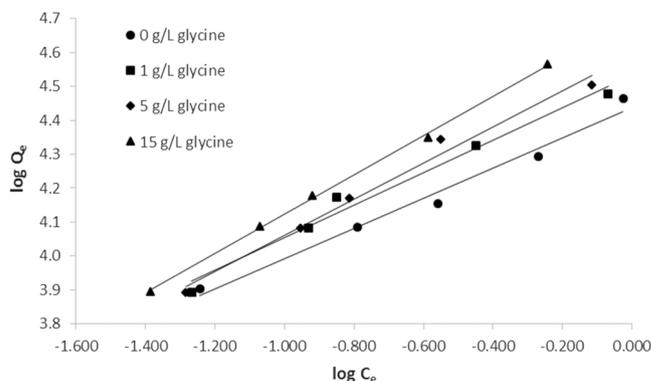


Fig. 4. Gold loading isotherms as a function of glycine concentration (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 0 ppm, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

Table 2

Numerical Freundlich isotherm constants for different glycine concentrations for gold in the absence of copper.

Glycine conc g/L	Freundlich k		n	R^2
	Kg/t	g/m^2		
0	27.3	3.58×10^{-5}	0.44	0.98
1	34.0	4.46×10^{-5}	0.48	0.98
5	39.4	5.16×10^{-5}	0.53	0.99
15	50.5	6.63×10^{-5}	0.58	0.99

3.3. Effect of pH

It has been reported by different studies that solution pH is considered as one of the most important variables affecting gold adsorption

onto activated carbon [1,19]. For glycine based systems, a change in pH also implies a gradual transition between different glycine forms, the zwitterion ($^+H_3NCH_2COO^-$ (HL)) and the glycinate anion ($H_2NCH_2COO^-$ (L)) [32]. Previous investigations on alkaline glycine leaching confirmed that a pH of around 11 was optimal for gold extraction [28]. To study the influence of pH on gold adsorption, four tests were performed at initial solution pH values of 9, 10, 11 and 12. Isotherms for the adsorption of the gold complex at these pHs are presented in Fig. 5. There is no clear trend on the effect of pH on gold adsorption from a cyanide starved glycine solutions containing 300 ppm copper. The corresponding gold loading data in Table 3 suggests gold loading to be optimal at pH 10. A similar behaviour has been reported by Barbetti and Bax [2] who found out that the presence of copper alters the trend observed for copper-free gold cyanide systems in an unpredictable way where gold loading capacity increases with decreasing pH [21].

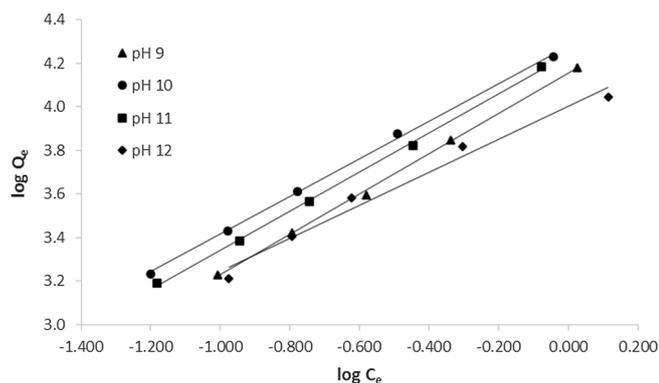


Fig. 5. Gold loading isotherms as a function of solution pH (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [CN] 123 ppm, [Glycine] 5 g/L, 23 °C, 24 h contact time.

Table 3 Numerical Freundlich isotherm constants at various solution pHs for gold.

pH	Freundlich k		n	R ²
	Kg/t	g/m ²		
9	14.2	1.87 × 10 ⁻⁵	0.92	0.99
10	19.1	2.51 × 10 ⁻⁵	0.87	0.99
11	17.4	2.28 × 10 ⁻⁵	0.90	0.99
12	10.1	1.32 × 10 ⁻⁵	0.76	0.98

3.4. Effect of cyanide concentration

3.4.1. Glycine-cyanide system

In order to evaluate the effect of cyanide concentration, copper was added as CuCN powder and NaCN used to adjust the cyanide concentration as needed while maintaining the copper concentration constant. It was observed from experimental data in Fig. 6 and Table 4 that increasing cyanide concentration decreases the overall gold loading capacity. The dependence of gold sorption on cyanide concentration is attributed to a number of factors. Free cyanide species readily adsorbs onto activated carbon [3,11] and hence compete with gold for adsorption sites on the carbon. More importantly, where copper is present, the speciation of the cyanocuprate (I) complex at any given pH is governed by [Cu(I)]/[CN⁻] ratio. Under the studied CN:Cu molar ratios, most of the copper cyanide species is present as Cu(CN)₂⁻ and these species have high affinity to be adsorbed on the activated carbon

[20]. Increasing the cyanide concentration in a glycine-cyanide system tends to favour the formation of [Cu⁺(CN)₂]⁻ over [Cu²⁺(Gly)₂]. The copper glycinate differs from its cyanide counterpart in two important aspects:

- the glycinate complex is neutral (zero charge) whereas the cyanide complex is anionic and
- the glycinate complex has copper in its cupric (2+) state whereas the cyanide complex has copper in its cuprous (+1) state.

The dicyanocuprate complex of copper and cyanide therefore appear similar in many ways to the dicyanoaurate complex of gold and cyanide, whilst the same cannot be said of the glycinate system where both the complex charge and metal oxidation state of the two metals differs. Carbon is known to have a greater selectivity for mono anionic complexes and as such anionic [Cu⁺(CN)₂]⁻ is more readily adsorbed and competes more with gold during adsorption than neutral [Cu²⁺(Gly)₂]. The UV-Vis Spectrophotometer (Agilent Cary 60 UV-Vis) was used to confirm initial copper speciation at different cyanide concentrations and the results are also shown in Table 4. Visually, a colour change from deep to pale blue was observed with increasing cyanide concentration, further confirming that increasing cyanide concentration favours formation of the readily adsorbed mono cyanocuprate complexes over that of the copper glycinate complex.

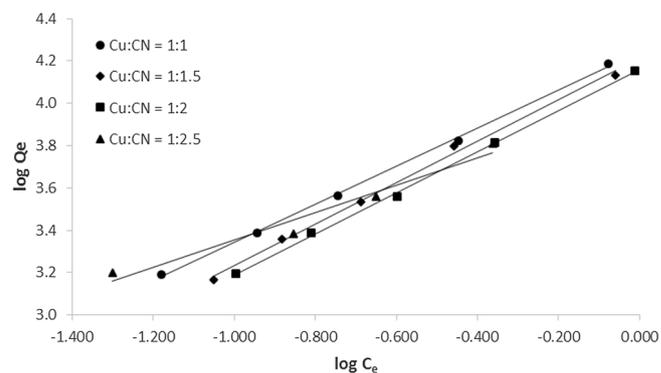


Fig. 6. Gold loading isotherms as a function of cyanide concentration (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [Glycine] 5 g/L, pH 11, 23 °C, 24 h contact time.

Table 4 Numerical Freundlich isotherm constants at different cyanide concentrations for gold and initial [Cu²⁺] in solution.

Cu:CN	[CN] ppm	Freundlich k		n	R ²	[Cu ²⁺] mg/L
		Kg/t	g/m ²			
1:1	123.0	17.4	2.28 × 10 ⁻⁵	0.90	0.99	290
1:1.5	237.1	16.3	2.14 × 10 ⁻⁵	0.98	0.99	190
1:2	352.2	14.5	1.90 × 10 ⁻⁵	0.97	0.99	120
1:2.5	467.3	9.95	1.31 × 10 ⁻⁵	0.64	0.96	60

3.4.2. Cyanide-only system

As a control, the effect of free cyanide on gold loading was conducted for a pure cyanide system in the absence of glycine. Gold loading capacity increased with increasing free cyanide concentration for a solution containing 2 ppm Au and 300 ppm Cu as shown by Freundlich isotherms in Fig. 7 and coefficient k values in Table 5. The carbon adsorption of the cyanocuprate complexes decreases in the order Cu(CN)₂⁻ > Cu(CN)₃²⁻ > Cu(CN)₄³⁻. Excess free cyanide drives equilibrium towards the tetracyano cuprate species which does not

significantly adsorb on carbon hence reducing competition for the active sites on carbon and improving the extent to which gold is loaded. Interesting results that can be drawn here is that glycine addition enhances gold loading significantly. For the same cyanide concentration (467.3 ppm), the gold loading capacity in a glycine-cyanide system is three times more than in a cyanide only system under similar conditions as shown by *k* values in Tables 4 and 5 respectively.

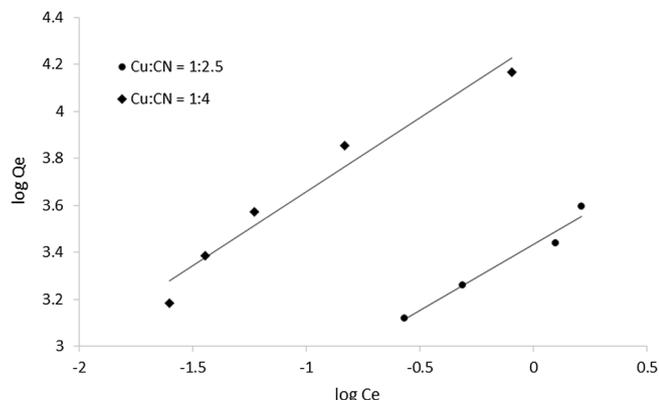


Fig. 7. Gold loading isotherms as a function of cyanide concentration for a pure cyanide system (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [Glycine] 0 g/L, pH 11, 23 °C, 24 h contact time.

Table 5 Numerical Freundlich isotherm constants at different cyanide concentrations for gold for a pure cyanide system.

Cu:CN	[CN] ppm	Freundlich <i>k</i>		<i>n</i>	R ²
		Kg/t	g/m ²		
1:2.5	476.3	2.7	3.55 × 10 ⁻⁶	0.56	0.97
1:4	813.6	19.3	2.53 × 10 ⁻⁵	0.63	0.96

3.5. Effect of initial gold-concentration in solution

Gold adsorption isotherms (Fig. 8) and corresponding *k* values (Table 6) obtained using various initial gold concentrations for the cyanide-starved glycine system indicated that, the effect of initial gold concentration in the range of 2–16 ppm on gold loading is insignificant. Increasing the initial gold concentration does not affect loading capacity. A similar trend was reported by Barbetti and Bax [2] for the Au-Cu-cyanide system but was not studied in detail. For the Au-cyanide (copper free) system, equilibrium loading capacity increases with increasing gold concentration in solution [21].

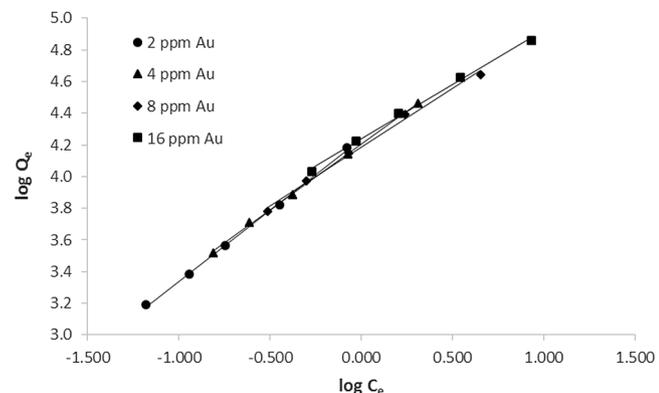


Fig. 8. Gold loading isotherms as a function of initial gold concentration (Freundlich model). Initial [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

Table 6 Numerical Freundlich isotherm constants for gold at various initial gold concentrations.

Initial gold conc ppm	Freundlich <i>k</i>		<i>n</i>	R ²
	Kg/t	g/m ²		
2	17.4	2.28 × 10 ⁻⁵	0.89	0.99
4	16.0	2.10 × 10 ⁻⁵	0.83	0.99
8	15.3	2.01 × 10 ⁻⁵	0.74	0.99
16	17.3	2.27 × 10 ⁻⁵	0.69	0.99

3.6. Effect of pH modifier (Ca²⁺ versus Na⁺)

Equilibrium loading was determined from glycine-cyanide-copper solutions by using different pH modifiers, caustic soda (NaOH) and lime (Ca(OH)₂). Adsorption solutions containing Ca²⁺ has a higher ionic strength than Na⁺ due to the high charges concentration in the solutions in the presence of divalent Ca. The results shown in Fig. 9 indicates that increasing the ionic strength improves gold loading capacity significantly, also confirmed by the corresponding *k* values given in Table 7. Increasing loading capacity with increasing ionic strength can be explained by the difference between the radius to charge ratio of the two ions, Ca²⁺ and Na⁺. For a coordination number of 6, the Ca²⁺ has a radius of 1 Å while Na⁺ has a radius of 1.02 Å. This means Ca²⁺ is smaller but it also has a higher charge compared to Na⁺ thereby exhibiting a higher columbic force per molecule that keeps the gold glycinate/cyanide complex firmly attached to the carbon surface better than its Na⁺ ion counterpart.

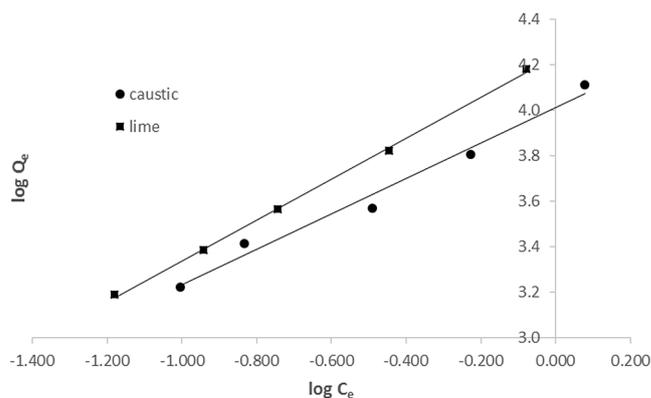


Fig. 9. Gold loading isotherms as a function of ionic strength of the solution (Freundlich model). Initial [Au] 2 ppm, initial [Cu] 300 ppm, [CN] 123 ppm, [Glycine] 5 g/L, pH 11, 23 °C, 24 h contact time.

Table 7 Numerical Freundlich isotherm constants for gold adsorption at varying ionic strength of solution.

pH modifier	Freundlich <i>k</i>		<i>n</i>	R ²
	Kg/t	g/m ²		
Caustic	10.3	1.35 × 10 ⁻⁵	0.90	0.99
Lime	17.4	2.28 × 10 ⁻⁵	0.90	0.99

3.7. Effect of CaCl₂

Inorganic salts of calcium, magnesium and sodium are known to generally enhance the adsorptive capacity of adsorbents including that of activated carbon [8,16,18,30,34]. Calcium salts are the most

effective followed magnesium salts with sodium salts being the least effective [31]. The effect of changing the concentration of calcium chloride salt on gold loading onto activated carbon is presented in Fig. 10. It can be seen that even addition of small amounts (0.5 g/L) of calcium chloride significantly increased the adsorptive capacity of activated carbon for gold more than fivefold as shown by Freundlich k values in Table 8. According to Randtke and Jepsen [30], the increasing of adsorptive capacity as a result of higher concentration of various salts is due to the interaction of calcium ions Ca^{2+} (in the case of calcium salts) and adsorbate and adsorbent likely resulting in:

- (i) Formation of complexes more absorbable than species which are uncomplexed.
- (ii) Increased intermolecular hydrophobic interactions by neutralisation of the hydrophilic functional surface groups.
- (iii) Reduction of the repulsive electrostatic forces between the surface

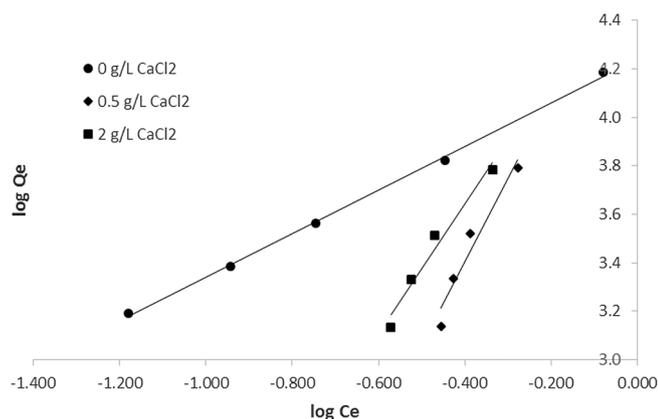


Fig. 10. Gold loading isotherms as a function of ionic CaCl_2 concentration (Freundlich model). Initial $[\text{Au}]$ 2 ppm, initial $[\text{Cu}]$ 300 ppm, $[\text{CN}^-]$ 123 ppm, $[\text{Glycine}]$ 5 g/L, pH 11, 23 °C, 24 h contact time.

Table 8

Numerical Freundlich isotherm constants for gold adsorption at varying Ca^{2+} concentrations.

CaCl_2 Conc g/L	Freundlich k		n	R^2
	Kg/t	g/m^2		
0.0	17.4	2.28×10^{-5}	0.90	0.99
0.5	60.9	7.99×10^{-5}	3.46	0.94
2.0	50.3	6.60×10^{-5}	2.65	0.97

of the active carbon and adsorbate.

4. Conclusions

In this study, equilibrium adsorption experiments for the recovery of gold from alkaline cyanide-starved glycine synthetic solutions in the presence of copper have been carried out using activated carbon as adsorbent. The Freundlich isotherm was used to evaluate gold adsorption at different glycine concentrations, pH values, cyanide concentrations, initial gold concentration, and calcium chloride concentration. It has previously been shown by the authors that cyanide starved glycine leach system significantly improves the extraction of the precious metals from copper-gold ores and concentrates. The results obtained from this research study can be summarised as follows:

- Gold adsorption from glycine-cyanide solution in the presence of copper was in good correspondence with the Freundlich isotherm.

- Glycine addition to cyanide increases gold loading capacity both in the presence and absence of copper. When copper was present, the loading capacity increased sixfold between glycine concentrations of 1 and 5 g/L.
- In the pH range (9–12) studied, there was no obvious trend with maximum gold loading capacity observed at pH 10.
- Maintaining a low free cyanide concentration increased the carbon's selectivity of gold over copper. Increasing the CN:Cu molar ratio from 1:1 (i.e. 123 ppm cyanide) to 2.5:1 (i.e. 476.3 ppm cyanide) reduced the gold loading capacity by half due to increased adsorption competition of CN^- ions and copper. This is related to the presence of the WAD cyanide $\text{Cu}(\text{CN})_2^-$. It is better to minimise the WAD cyanide in glycine-cyanide-copper in order to have higher gold adsorption. This may be done by sulphide precipitation, solvent extraction or ion exchange [13].
- Using lime ($\text{Ca}(\text{OH})_2$) rather than caustic (NaOH) as a pH modifier almost doubled the gold loading capacity. Ca^{2+} ion has a higher coulombic force per molecule and hence attaches gold more firmly onto active carbon.
- By positively altering the interaction mechanism of the gold complex and carbon surface, calcium chloride salt significantly increased gold loading capacity.

Acknowledgements

The financial support by Curtin University and the government of the Republic of Botswana through the University of Botswana is greatly appreciated.

References

- [1] M. Adams, G. McDougall, R.D. Hancock, Models for the adsorption of aurocyanide onto activated carbon. Part III: comparison between the extraction of aurocyanide by activated carbon, polymeric adsorbents and 1-pentanol, *Hydrometallurgy* 19 (1) (1987) 95–115.
- [2] K. Barbetti, A. Bax, *Competitive Copper/Gold Adsorption – SIMCIL Modelling Developments*, WA School of Mines, Curtin University, 2016.
- [3] A. Behnamfard, M.M. Salarirad, Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon, *J. Hazard. Mater.* 170 (1) (2009) 127–133.
- [4] S. Biniak, G. Szymański, J. Siedlewski, A. Świątkowski, The characterization of activated carbons with oxygen and nitrogen surface groups, *Carbon* 35 (12) (1997) 1799–1810.
- [5] H.P. Boehm, Chemical identification of surface groups, *Adv. Catal.* 16 (1966) 179–274.
- [6] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, *Carbon* 32 (5) (1994) 759–769.
- [7] R.H. Bradley, B. Rand, On the physical adsorption of vapors by microporous carbons, *J. Colloid Interface Sci.* 169 (1) (1995) 168–176.
- [8] R.W. Coughlin, F.S. Ezra, R.N. Tan, Influence of Chemisorbed Oxygen in Adsorption onto Carbon from Aqueous Solution, *Hydrophobic Surfaces*, Elsevier, 1969, pp. 44–54.
- [9] X. Dai, A. Simons, P. Breuer, A review of copper cyanide recovery technologies for the cyanidation of copper containing gold ores, *Miner. Eng.* 25 (1) (2012) 1–13.
- [10] M.A. Daley, D. Tandon, J. Economy, E.J. Hippo, Elucidating the porous structure of activated carbon fibers using direct and indirect methods, *Carbon* 34 (10) (1996) 1191–1200.
- [11] R.R. Dash, C. Balomajumder, A. Kumar, Removal of cyanide from water and wastewater using granular activated carbon, *Chem. Eng. J.* 146 (3) (2009) 408–413.
- [12] J.J. Eksteen, E.A. Oraby, The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: effect of catalytic ions, sulphide minerals and amino acid type, *Miner. Eng.* 70 (2015) 36–42.
- [13] J.J. Eksteen, E.A. Oraby, B.C. Tanda, P.J. Tauetsile, G.A. Bezuidenhout, T. Newton, I. Bryan, Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores, *Can. Metall. Q.* 57 (4) (2018) 390–398.
- [14] M. Fleming, The absorption of gold cyanide onto activated carbon. III. Factors influencing the rate of loading and the equilibrium capacity, *J. South Afr. Inst. Min. Metall.* 84 (4) (1984) 85–93.
- [15] V.A. Garten, D.E. Weiss, J.B. Willis, A new interpretation of the acidic and basic structures in carbons. II. The chromene-carbonium ion couple in carbon, *Aust. J. Chem.* 10 (3) (1957) 309–328.
- [16] R. Gustafson, J. Paleos, Interactions responsible for the selective adsorption of organics on organic surfaces, *Organ. Comp. Aquat. Environ.* (1971) 213–238.
- [17] A. Ibrado, D. Fuerstenau, Adsorption of the cyano complexes of Ag (I), Cu (I), Hg (II), Cd (II) and Zn (II) on activated carbon, *Miner. Metall. Process.* 6 (1) (1989) 23–28.

- [18] M.C. Lee, V.L. Snoeyink, J.C. Crittenden, Activated carbon adsorption of humic substances, *J. (Am. Water Works Assoc.)* (1981) 440–446.
- [19] J. Lu, D. Dreisinger, W. Cooper, Thermodynamics of the aqueous copper–cyanide system, *Hydrometallurgy* 66 (1) (2002) 23–36.
- [20] S.A. Manktelow, J.G. Paterson, J.A. Meech, Removal of copper and cyanide from solution using activated carbon, *Miner. Environ.* 6 (1) (1984) 5–9.
- [21] J. Marsden, I. House, *The Chemistry of Gold Extraction*, Ellis Horwood Limited, Sussex, 1992, p. 568.
- [22] K.J. Masters, B. McEnaney, The development of structure and microporosity in cellulose carbon, *Carbon* 22 (6) (1984) 595–601.
- [23] D.J. McDougall, R.D. Hancock, M.J. Nicol, O.L. Wellington, R.G. Copperthwaite, The mechanism of the adsorption of gold cyanide on activated carbon, *J. S. Afr. Inst. Min. Metall.* 80 (9) (1980) 344–356.
- [24] D. Muir, A review of the selective leaching of gold from oxidised copper–gold ores with ammonia–cyanide and new insights for plant control and operation, *Miner. Eng.* 24 (6) (2011) 576–582.
- [25] A. Oberlin, M. Villey, A. Combaz, Influence of elemental composition on carbonization: pyrolysis of kerosene shale and kuckersite, *Carbon* 18 (5) (1980) 347–353.
- [26] E.A. Oraby, J.J. Eksteen, The selective leaching of copper from a gold–copper concentrate in glycine solutions, *Hydrometallurgy* 150 (2014) 14–19.
- [27] E.A. Oraby, J.J. Eksteen, Gold leaching in cyanide-starved copper solutions in the presence of glycine, *Hydrometallurgy* 156 (2015) 81–88.
- [28] E.A. Oraby, J.J. Eksteen, The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon, *Hydrometallurgy* 152 (2015) 199–203.
- [29] R.G. Peel, A. Benedek, Attainment of equilibrium in activated carbon isotherm studies, *Environ. Sci. Technol.* 14 (1) (1980) 66–71.
- [30] S.J. Randtke, C.P. Jepsen, Chemical pretreatment for activated-carbon adsorption, *J. (Am. Water Works Assoc.)* (1981) 411–419.
- [31] S.J. Randtke, C.P. Jepsen, Effects of salts on activated carbon adsorption of fulvic acids, *J. (Am. Water Works Assoc.)* (1982) 84–93.
- [32] N. Rega, M. Cossi, V. Barone, Structure and magnetic properties of glycine radical in aqueous solution at different pH values, *J. Am. Chem. Soc.* 120 (23) (1998) 5723–5732.
- [33] R.A. Shawabkeh, D.A. Rockstraw, R.K. Bhada, Copper and strontium adsorption by a novel carbon material manufactured from pecan shells, *Carbon* 40 (5) (2002) 781–786.
- [34] V.L. Snoeyink, W.J. Weber Jr, H.B. Mark Jr, Sorption of phenol and nitrophenol by active carbon, *Environ. Sci. Technol.* 3 (10) (1969) 918–926.
- [35] P.J. Tauetsile, E.A. Oraby, J.J. Eksteen, Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 1: Isotherms, *Hydrometallurgy* 178 (2018) 202–208.
- [36] P.J. Tauetsile, E.A. Oraby, J.J. Eksteen, Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 2: Kinetics, *Hydrometallurgy* 178 (2018) 195–201.
- [37] Z. Tu, S. Lu, X. Chang, Z. Li, Z. Hu, L. Zhang, H. Tian, Selective solid-phase extraction and separation of trace gold, palladium and platinum using activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate, *Microchim. Acta* 173 (1–2) (2011) 231–239.
- [38] R.D. Vidic, C.H. Tessmer, L.J. Uranowski, Impact of surface properties of activated carbons on oxidative coupling of phenolic compounds, *Carbon* 35 (9) (1997) 1349–1359.
- [39] R. Wan, J. Miller, Research and development activities for the recovery of gold from alkaline cyanide solutions, *Miner. Proces. Extract. Metall. Rev.* 6 (1–4) (1990) 143–190.
- [40] X. Yang, M.S. Moats, J.D. Miller, X. Wang, X. Shi, H. Xu, Thiourea–thiocyanate leaching system for gold, *Hydrometallurgy* 106 (1) (2011) 58–63.
- [41] B. Zdravkov, J. Čermák, M. Šefara, J. Janků, Pore classification in the characterization of porous materials: a perspective, *Open Chem.* 5 (2) (2007) 385–395.