

WASM: Minerals, Energy and Chemical Engineering

**Adsorption of Gold and Copper from Alkaline Glycine-based
Leach Solutions using Activated Carbon**

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**This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University**

August 2019

Declaration

I declare that this thesis is an account of my own research (save to the extent explicitly otherwise stated) and contains work that has not previously been submitted for a degree at any any other educational institution.

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Abstract

The global challenge to find environmentally friendly cyanide alternatives, which are economically feasible for the exploitation of gold-copper ores continues to intensify. The increase in gold-copper ores of complex mineralogy which renders cyanidation ineffective and expensive plus public's environmental and health concerns regarding cyanide toxicity are the main drivers for the need to find an alternative process. Owing to its ability to form stable complexes with gold and copper, glycine has been proposed as a promising potential alternative lixiviant. Progress into the understanding of glycine leaching behaviour of copper minerals and gold-copper ores has been made. However, a comprehensive study on the subsequent treatment method of the resultant leachate has been lacking.

Activated carbon adsorption is popular in cyanide systems for gold recovery due to its relatively low capital and operating costs, its simplicity and its effectiveness. It is therefore proposed for glycine leach systems. Optimisation of the carbon adsorption process for any new system needs an understanding of the adsorption behaviour of the metals of interest. Adsorption behaviour of any new system is modelled and studied through the use of kinetics and isotherm studies.

This research, which is presented as a series of five published peer-reviewed journal articles plus additional unpublished sections, evaluates the adsorption behaviour of gold onto activated carbon from glycine-based solutions containing copper and gold. Through the use of bottle-on-roll tests, the metals adsorption was studied from synthetic alkaline glycine-only and cyanide-starved glycine solutions. The metals concentration of the standard solutions mimicked that of real leach solutions (2 ppm Au, 40 ppm Cu; glycine only solutions and 2 ppm Au, 300 ppm Cu; cyanide-starved glycine solutions). The basic kinetic and isotherm parameters, Fleming k constant and Freundlich constant respectively, were determined under varied process conditions at room temperature. The first order reaction Fleming k, n model was used to obtain the kinetic values while the Freundlich isotherm model was used to analyse experimental isotherm data.

It was found that, activated carbon is an effective adsorbent of gold complexes in both the glycine and cyanide-starved glycine systems, making the process a practical option for treating gold containing glycine leachates. Adsorption kinetics indicated rapid gold adsorption during the first 60 mins (with more than 80% gold recovery observed) and a gradual increase until pseudo equilibrium was reached. Under optimum conditions, overall gold recovery in 24 hours was greater than 98%. The results obtained have shown carbon to be highly selective for gold over copper.

Though the copper is present in solution in higher concentration amounts (over ten orders of magnitudes) than gold, the kinetics of copper exhibited a rather slow initial adsorption rate and lower overall recovery (~ 40%) within a similar time frame, suggesting that co-adsorption of gold and copper could be minimised by allowing a shorter adsorption residence time.

Isotherm studies showed that unlike free cyanide, glycine does not compete with gold complexes for active sites on the carbon and hence does not lower carbon loading capacity for gold. It is advisable therefore to maintain a low cyanide concentration in cyanide-starved glycine solutions to minimise the adsorption competition between the metal complexes and cyanide ions. The presence of copper in glycine only solutions enhances gold loading capacity on the carbon. Increasing copper concentration from 0 to 20 ppm increased the gold loading capacity on the carbon by 75% from 26.6 kg_{Au}/t_{carbon} to 46.5 kg_{Au}/t_{carbon}.

The feasibility of eluting gold loaded in glycine-only solutions from activated carbon was explored. After 20 bed volumes, 62% of gold was eluted from non-pre-treated loaded carbon using only pure deionised water heated to 130 °C in a single stage column elution. Sodium chloride solution eluted only 25% gold under similar conditions. The AARL elution technique resulted in an elution recovery of 88% after 20 bed volumes. The process involved first soaking the loaded carbon in 3% HCl solution at 80 °C for 30 minutes followed by pre-treatment with a hot caustic cyanide solution (3% NaCN and 1% NaOH at a temperature of 110 °C) for 30 minutes before elution with hot DI water (130 °C). While not demonstrated in this work, the recovery from recycled carbon (from elution to be reused in absorption) over a long term may be higher as there may be a recirculating load of gold that determines the baseline. This needs to be evaluated in further work and was not deemed within the scope and time of this thesis.

Acknowledgements

Dear Jesus, eternally grateful to thee for giving me the strength and wisdom needed to see this PhD to completion. Forever indebted to thee. Thank you.

Professor Jacques Eksteen and Dr Elsayed Oraby, my wonderful supervisors, your guidance, support and encouragement have been nothing short of amazing. You pushed me beyond limits I never knew I could reach. Thank you.

To members of Curtin University's Gold Technology Research Group, it's been a pleasure being a part of and working alongside you. You provided me with the most pleasant working and social environment one could ask for. Special thanks to Mr Jim Cupitt, our projects manager, Ms Karen Barbetti, the group's project hydrometallurgist and Ms Irlina Winata, our lab technician.

The government of the Republic of Botswana and Curtin University, thank you for funding this work.

Mom and Dad, a massive thanks for your love, moral and emotional support. Special gratitude to friends and family who supported me all the way.

List of publications included as part of the thesis

The following refereed published papers form the basis of this PhD by publication:

- **Full-text refereed conference proceedings**

1. Eksteen, J.J., Oraby, E.A., Tanda, B.C., Tauetsile, P.J., Bezuidenhout, G.A., Newton, T., Trask, F. and Bryan, I., 2018. Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores. *Canadian Metallurgical Quarterly*, 57(4), pp.390-398.

- **Journal Papers**

2. **Tauetsile, P. J.**, Oraby, E. A., & Eksteen, J. J. (2018). Adsorption behaviour of copper and gold glycinate in alkaline media onto activated carbon. Part 1: Isotherms. *Hydrometallurgy*, 178, 202-208.
3. **Tauetsile, P. J.**, Oraby, E. A., & Eksteen, J. J. (2018). Adsorption behaviour of copper and gold Glycinate in alkaline media onto activated carbon. Part 2: Kinetics. *Hydrometallurgy*, 178, 195-201.
4. **Tauetsile, P. J.**, Oraby, E. A., & Eksteen, J. J. (2019). Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 1: Isotherms. *Separation and Purification Technology*, 211, 594-601.
5. **Tauetsile, P. J.**, Oraby, E. A., & Eksteen, J. J. (2019). Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: Kinetics. *Separation and Purification Technology*, 211, 290-297.

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Author Contribution Statement

As the primary author of four out of five publications forming the body of this thesis, the PhD candidate conceived, planned and performed experiments, processed and interpreted experimental data and took lead in writing the manuscript of all four journal articles. Professor Jacques Eksteen and Dr Elsayed Oraby provided critical feedback throughout, aided in shaping the research, assisted in results analysis, edited and revised the manuscripts. Co-authors have given permission for the work to be included in the thesis and the contribution of each co-author to the published work arising from this thesis is detailed in a signed statement presented in Appendix A at the back of this volume.

For the fifth publication, the PhD student is co but not first author. The PhD candidate contributed to a subsection of the paper. This candidate planned and performed experiments, extracted and processed data relevant to their part of the publication. The PhD candidate was the fourth co-author from a total of eight authors.

Dedication

“To mum and dad with love...”

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1. General Introduction and Overview

1.1 Background to this study

Mining activities often result in the impairment of the environment. Though mining is mostly a small scale activity, the resultant environmental impacts are usually significant as they can extend beyond the actual mining site through various ways. Acid mine drainage, erosion and tailings deposits are some of the pathways through which mining waste may enter the extended environment. Mine wastes in their nature are notorious for containing toxic substances capable of contaminating soil and water supplies. This has, as a result, challenged the mining industry to find alternative processes that can minimise the environmental impacts of their mining activities. Cyanide, which is the main lixiviant used in the gold mining industry, is considered highly toxic and is also a fairly expensive reagent (e.g. compared to lime and sulfuric acid). In addition, it is seldom economically worthwhile to recover due to the formation of, and loss to, a range of toxic by-products such as thiocyanate, cyanate, HCN vapour losses and ferrocyanide as well as weak acid dissociable cyanides. As a result, the health and environmental concerns that come with cyanide usage has prompted some governments across the world to impose stringent regulatory laws on its use, or in extreme cases ban its usage entirely, thereby halting or eliminating gold mining in many parts of the world (DeVoto and McNulty, 2000; Laitos, 2012; Muezzinoglu, 2003).

Many new deposits are refractory and the popularity of cyanide as the lixiviant of choice for processing of these ores is gradually declining although it is still the predominant reagent used due to a lack of economic alternatives. According to Afenya (1991), an ore is classified as refractory if the gold contained therein is intertwined with sulphides, siliceous gangue, carbonaceous material and or other cyanide consuming minerals. These additional ore components are a nuisance to the conventional cyanidation process as they increase the cyanide consumption and by default the overall cost of the process. Refractory gold ores are found across the globe. In Western Australia for example, such deposits found in the Eastern Goldfields region, are mostly pyritic and contain roughly 42% refractory gold encapsulated in 3% and 1% pyrite and arsenopyrite respectively (Vaughan, 2004). Other refractory ores may be telluriferous, manganiferous, carbonaceous or cupriferous in nature (Abotsi and Osseo-Asare, 1986; Afenya, 1991; Climo et al., 2000; Guerra and Dreisinger, 1999; Valliant and Barnett, 1982; Zhang et al., 2010; Zipperian et al., 1988).

An attempt to address issues of cyanide toxicity and ineffectiveness has resulted in the study of over 25 solvents as potential alternatives. These include but are not limited to, thiosulphate ($\text{Cu(II)-NH}_3\text{-S}_2\text{O}_3$), thiourea (Fe(III)), ($\text{CS(NH}_2)_2$), halides (Cl_2 , Br_2 , I_2), synergies of cyanide with other reagents ($\text{NH}_3\text{-CN}^-$, BrCN , Ca(CN)_2), thiocyanate (SCN^-), ferric chloride, bacteria, natural acids and nitriles (Aylmore, 2005; Hilson and Monhemius, 2006; Molleman and Dreisinger, 2002). The commercial adoption of most of these cyanide alternatives has been hindered by a number of factors including 1) high process cost emanating from excessive reagent consumption and or cost of reagent, 2) complex process chemistry, 3) lack of compatible downstream processing techniques and 4) toxic or corrosive nature of the reagent (Hilson and Monhemius, 2006). For example, save for its use by Barrick Gold Corporation in its Goldstrike deposit (Fleming et al., 2003; Marchbank et al., 1996), the industrial application of the thiosulphate leach system, which is deemed the most viable alternative, is virtually non-existent. The complex thiosulphate leach chemistry and unstable nature of thiosulphate itself when dissolved in water, present technical challenges that have restricted its use in the gold industry (Fleming et al., 2003; Grosse et al., 2003; Muir and Aylmore, 2004; Senanayake, 2005). Therefore, the need for a more environmentally friendly gold processing route that is technically robust and economically advantageous remains.

In addition, many of these processes are not well suited to polymetallic systems with multiple cyanide consuming minerals. This is particularly problematic for fairly common polymetallic gold ores, namely gold-copper ores where copper is often a nuisance element and economic recovery of the copper can seldomly be justified. Such ores typically contain 1 ppm of gold or less, and up to 0.1% copper, which implies a copper to gold mass ratio of greater than 1000:1 (3000:1 molar ratio), causing high cyanide consumption by a metal of much lower value (Gold is valued at around USD 45,800 per kg versus copper valued at USD 6 per kg, thus a value ratio of greater than 7,600 to 1 at the time of writing). In addition copper (cuprous)-cyanide complexes can form tetracyano complexes whereas gold only forms the dicyanoaurate complex, further driving up cyanide consumption. The use of a non-toxic, stable, readily recoverable and recyclable reagent would be useful if such a reagent can partially or fully replace cyanide.

1.2 Glycine as a Lixiviant

Interest in the solubilisation of gold by organic acids dates back to the work of Brown et al. (1982) and Jingrong et al. (1996). Brown et al. (1982) confirmed that amino acids in bodily sweat dissolved gold thereby making gold jewellery a possible cause of skin allergies. Some of the amino acids found in bodily sweat include glycine, histidine, alanine, lysine and valine (Coltman Jr et al., 1966). Addition of glycine, histidine, alanine and valine to thiosulphate leaching systems has also been found to improve gold extraction substantially (Feng and Van Deventer, 2011).

The idea of using glycine as a gold and copper lixiviant was explored just recently (Eksteen and Oraby, 2015; Oraby and Eksteen, 2014; Tanda et al., 2017). Oraby and Eksteen (2015b) established that though not as powerful a lixiviant as cyanide, under neutral to alkaline conditions, ambient to moderately elevated temperatures (23–60 °C) and using hydrogen peroxide as an oxidant, glycine can leach gold and silver at a much faster rate compared to other alternatives. The authors reported a gold leaching rate of 0.322 $\mu\text{mol}/\text{m}^2\text{s}$ in 48 hours for alkaline glycine hydrogen peroxide solutions (0.5 M glycine, 1% peroxide, pH 11) which is higher than the gold leach rate (0.22–0.25 $\mu\text{mol}/\text{m}^2\text{s}$) of thiosulfate ferric oxalate systems after six days.

Under the same process conditions, the reaction rates of gold in glycine alone are at most 1/20th those of cyanide, making it more suited to in-situ and heap leaching as these processes require prolonged leach times (Eksteen and Oraby, 2015). Oraby and Eksteen (2015a) developed the GlyCat™ process, in which gold dissolution in glycine solutions is significantly enhanced by the presence of copper-cyanide species with no free cyanide present in solution. In solutions containing 10 mM $\text{Cu}(\text{CN})_2^{2-}$, gold dissolution rates in the presence and absence of glycine were 11.1 $\mu\text{mol}/\text{m}^2\text{s}$ and 0.65 $\mu\text{mol}/\text{m}^2\text{s}$ respectively.

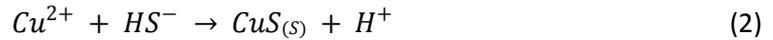
Glycine leaching is also applicable to copper minerals. The possibility of selectively leaching copper over gold using alkaline glycine systems was investigated (Eksteen and Oraby, 2015). At ambient temperature, 98.0% copper was recovered in just 48 hours. Analysis of the leach residue revealed that most of the undissolved copper was contained in covellite. Tanda et al. (2017) who investigated the leaching behaviour of various copper oxide minerals in glycine solutions at room temperature (average 22°C) reported that under optimum leaching conditions (pH 11 and glycine to copper ratio of 4:1), 95.0%, 91.0%, 83.8% and 17.4% of copper was extracted after 24 hours from azurite, malachite, cuprite, and chrysocolla mineral specimens respectively.

The contention that gold lixiviants should be economical, environmentally safe and have the ability to effectively process ores not amenable to cyanidation presents glycine as a potential cyanide alternative. In addition to its effectiveness in the leaching of gold, silver and copper, glycine is an environmentally benign reagent which can be cheaply purchased in bulk industrially (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015b). The above-mentioned literature on glycine leaching suggests that progress into the understanding of glycine leaching of gold and copper has been made. However, no previous study has dealt with the recovery of gold from glycine leach liquors using activated carbon.

1.3 Recovery of Gold from Glycine Leachates

Metals separation and solution purification, a critical hydrometallurgical step, links the leaching process with the final metal winning process. To date, less attention has been given to the upgrading and recovery processes suited to glycine leachates. One such method is activated carbon adsorption of gold complexes. Activated carbon still remains one of the most cost-effective and well known processes to recover gold from alkaline leachates. Other well established conventional techniques that can be used alongside active carbon adsorption for solution purification include precipitation, solvent extraction and sorption onto chelating exchange resins. Figure 1.1 shows images of a copper-gold GlyCat™ pilot plant that has demonstrated the process. The corresponding schematic of the flow configuration is illustrated in Figure 1.2.

The pilot plant comprises two main stages: leaching of the copper-gold concentrate (using an alkaline cyanide starved-glycine solution) and separation of dissolved metals, specifically gold and copper. After glycine cyanide leaching, the leachate and leach tails are separated in a solid-liquid separation step using a filter press. The leachate then proceeds to the copper removal step where it is contacted with sodium sulfide (Na_2S) and copper is precipitated as copper sulphide (CuS). The reaction proceeds successively according to equations 1 and 2. The liquor then goes to the carbon-in-column section for gold removal using activated carbon then back to the leach tanks to be recycled. The copper removal step only removes upto 80% copper depending on the amount of copper present and solution chemistry. For low copper systems, this step can be by-passed. The total cyanide requirements of the plant are split between points A and B (Figure 1.2). Adding cyanide at point B is advantageous in that it raises the copper to the tetra-cyano copper species which adsorbs poorly onto active carbon compared to the di-cyano copper species. This reduces the adsorption of copper complexes during the gold adsorption step.



Based on the work of Eksteen and Oraby (2015) who did scoping experiments on activated carbon adsorption of gold glycinate complexes, it was hypothesised that pregnant leach solutions from glycine systems could be processed in a similar manner as for cyanide leach systems using activated carbon adsorption for gold recovery. Carbon adsorption is a well-developed widely adopted process in the gold cyanide industry since it is fast, simple, cheap, selective, environmentally friendly and very effective (Tu et al., 2011). To date, literature on activated carbon adsorption of gold complexes from glycine solutions and the effect of various operating conditions on the process is non-existent. The main focus of the present study therefore, is to investigate very fundamentally, activated carbon adsorption of gold complexes from glycine only and GlyCat™ leach systems. As highlighted earlier, though there is an option of copper removal prior to carbon adsorption, copper is never removed in totality hence it will always be present to some degree in the leachate at the carbon adsorption step. This study will, therefore, include the effect on gold adsorption on activated carbon where copper is present.

Critical questions that the study will seek to address include:

- Will Au be adsorbed at low solution concentrations?
- What is the rate of adsorption of Au?
- How selective is the carbon for Au over Cu?
- In terms of total Au recovered, how effective is activated carbon to adsorb gold from glycine and glycine-cyanide solutions?
- What are the critical factors that affect Au adsorption?
- To what extent does gold elute from carbon under varied eluent compositions?

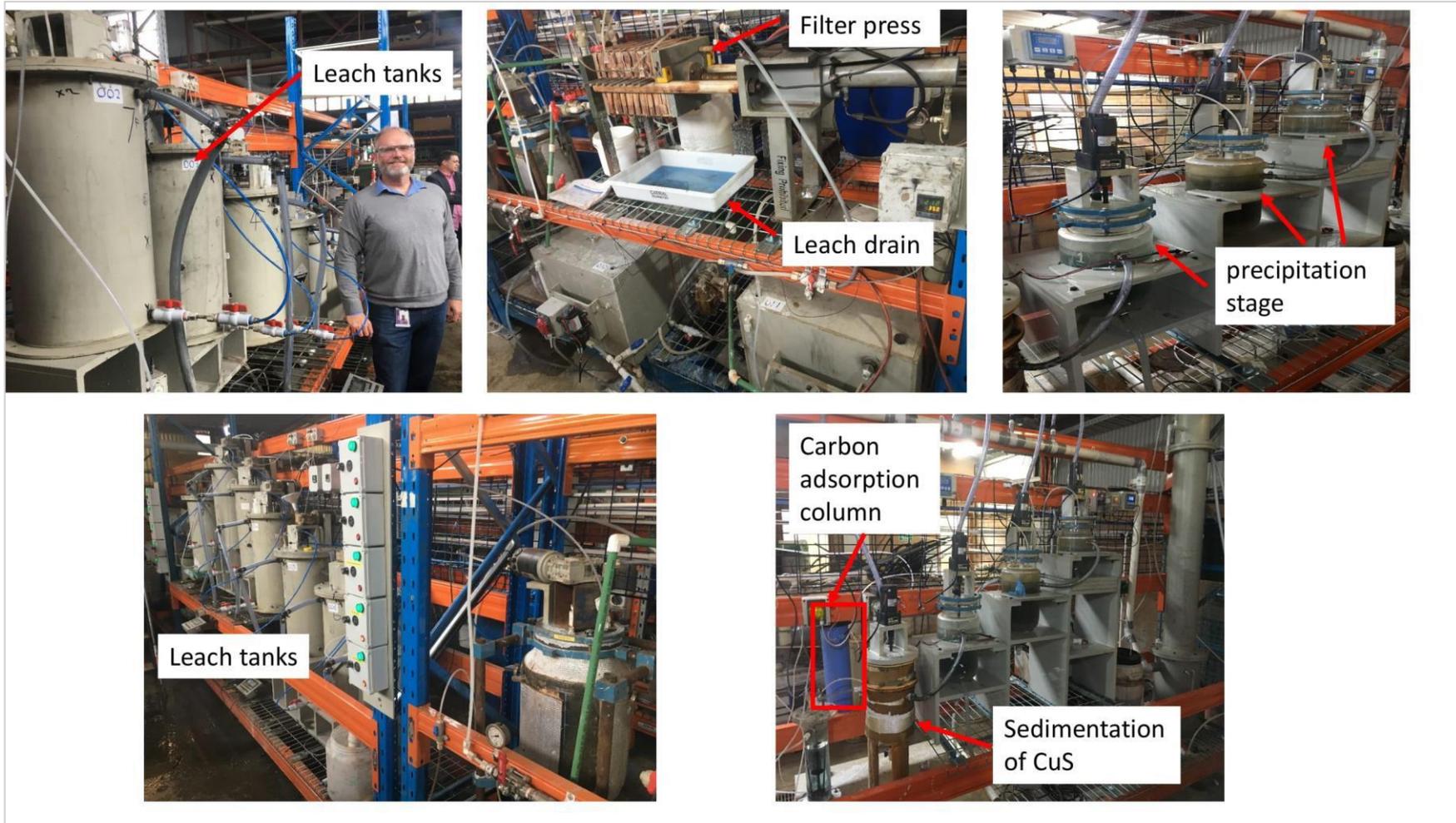


Figure 1.1: GlyCat leach and solution purification pilot plant

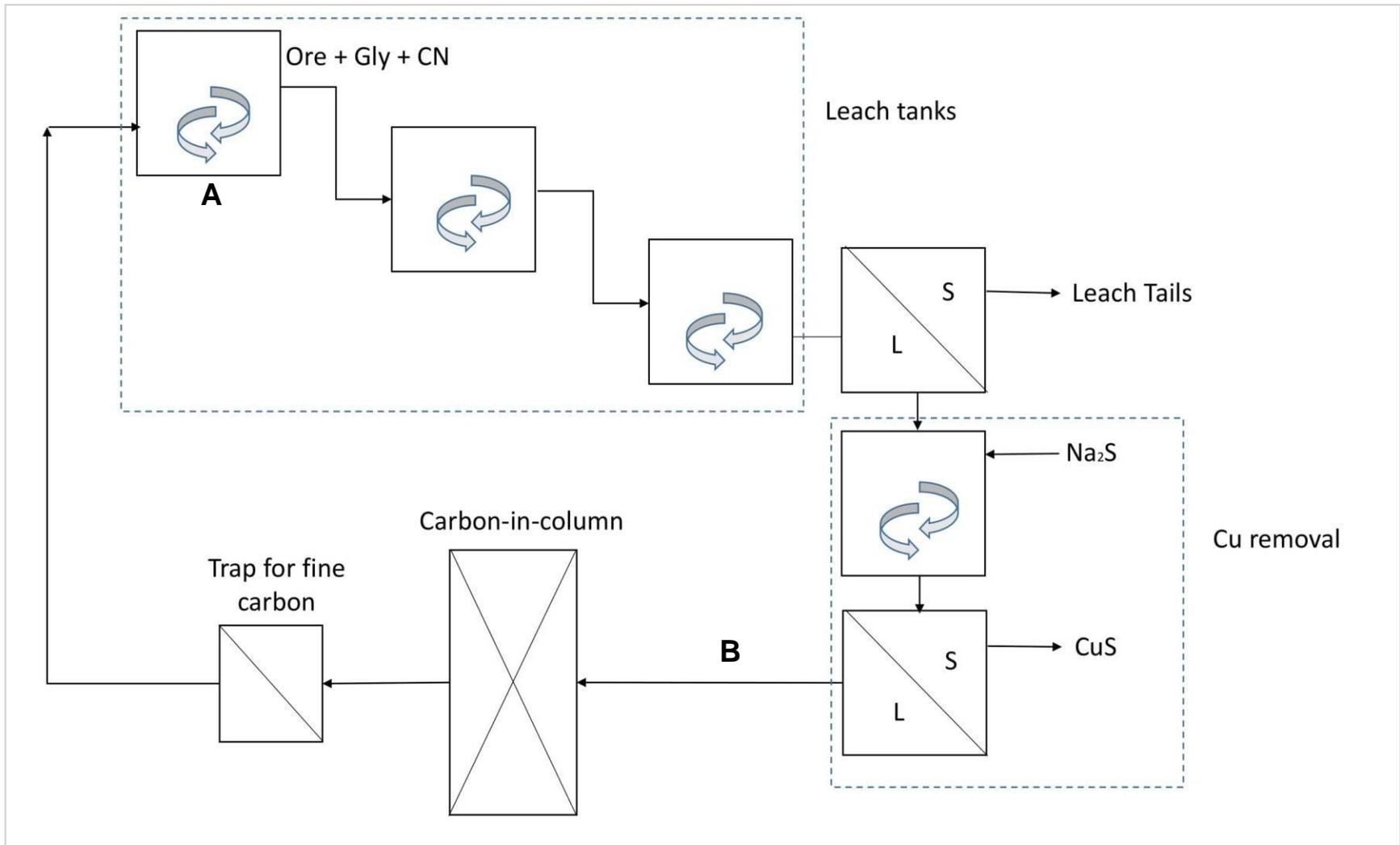


Figure 1.2: Schematic diagram of pilot plant

1.4 Thesis objectives

The application of carbon adsorption and elution to glycine systems for metals recovery from the leach solutions is of utmost importance as the industrial feasibility of the newly developed glycine leaching techniques is dependent on the availability of an effective downstream processing method. The main aim of this work was to evaluate if the carbon-in-leach (CIL) and carbon-in-pulp (CIP) methods, which are well established and most favoured in gold cyanide systems, can be used to recover gold from glycine and glycine-cyanide solutions containing some copper.

The study will, therefore, address the following specific questions:

- If activated carbon adsorption is used as an adsorbent for gold in alkaline glycine or glycine-cyanide solutions, what are the loading isotherms of gold both on its own and in a competitive loading environment where copper is present?
- What are the kinetics of activated carbon loading for gold and copper each on their own and in a competitive loading environment?
- Does gold and copper co-adsorb during carbon adsorption? If so to what extent?
- What are the major factors affecting gold adsorption? How does varying them affect adsorption?
- Can gold that was loaded from glycine systems be eluted from the loaded carbon? If yes, how effective is the elution?

1.5 Significance of study

Leaching of gold-copper ores with glycine has been proposed as a promising alternative gold ore lixiviant that can entirely or partially replace the highly toxic, expensive and sometimes ineffective cyanide which most times has hindered the economical processing of some refractory gold ores. The significance of the project was to research and develop a process for precious metals recovery from solutions in the presence of glycine, a study which has not been undertaken before.

The thesis is the first comprehensive study on activated carbon adsorption of gold from glycine solutions. The research will enable the selective recovery of gold from alkaline glycine solutions and provide an in-depth understanding of the factors influencing the recovery process. It will furthermore aid in selecting the process conditions for optimal gold recovery from a holistic design perspective. The isotherm and kinetic data generated from this research will enable the design and evaluation of carbon-in-pulp

(CIP), carbon-in-leach(CIL) and carbon-in-column (CIC) circuits for gold where copper may be present, paving the way for scale-up from laboratory to pilot plant testing.

1.6 Scope of the study

The study is limited to evaluating the feasibility of carbon adsorption process for gold complexes from glycine and glycine cyanide systems using laboratory batch kinetic and isotherm data generated from synthetic solutions whose metal concentration mimicked those of real solutions. The study primarily investigates how various process conditions such as solution pH, reagent concentration and metal concentration influence the gold adsorption process. Based on the results, optimum adsorption conditions for gold are suggested. The feasibility of eluting gold loaded from glycine only systems is also examined in an exploratory approach. Save for variation of eluent temperature and type of eluent, the effect of other parameters on elution were not investigated and hence process optimisation of the elution stage falls outside the scope of the present study.

1.7 Thesis Overview

This is a hybrid thesis presented as a combination of a series of published papers and work that has not been published. Published work is presented in the format in which it was published according to the style of the publishing journal. The experimental set-up for each part of study (where applicable) is detailed under each chapter. The thesis is in agreement with Curtin University's Doctor of Philosophy Rules for the content and format of a hybrid thesis. The organization of this thesis is as follows:

- **Chapter 1:** Introduction

This chapter introduces the research area and outlines the background and rationale for the present study. It briefly presents a general overview on challenges arising from cyanide usage and proposes glycine based systems as a viable alternative. The chapter subsequently describes the aims of the present study and provides a chapter by chapter overview of the thesis.

- **Chapter 2:** Literature Review

Gives a detailed literature review on glycine and cyanide leaching of gold-copper ores. The chemistry, limitations and advantages of each leach system is discussed. A detailed review on activated carbon adsorption of gold from cyanide solutions is also given. Associated adsorption mechanisms and factors

affecting gold adsorption are discussed in detail. Information regarding elution of loaded carbon is summarised.

- **Chapter 3:** Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores. (*Publication 1*)

Chapter 3 sets the context of the thesis by providing a review summary on work done on glycine leach systems particularly on leaching and metals recovery from solution. The chemistry, kinetics and extraction efficiency of leaching of copper and gold using glycine and cyanide starved glycine solutions was discussed and contrasted against that of the conventional cyanidation process. Purification of the resultant leachates (glycine only systems) using activated carbon and solvent extraction for gold and copper recovery respectively is also discussed. Based on the leaching and adsorption findings, the economics surrounding implementation of the process at industry level is scrutinised. It is the accumulation of the work from numerous co-authors.

- **Chapter 4:** Adsorption behaviour of copper and gold glycines in alkaline media onto activated carbon. (*Publication 2*)

Part 1 of a two-part publication series focusing on glycine only systems, this chapter evaluated the adsorption potential of coconut shell based activated carbon for gold from alkaline glycine solutions in the presence of copper through the use of isotherms. Liquid phase adsorption experiments were conducted and the maximum adsorptive capacity was determined. The effect of experimental parameters, namely, glycine concentration, pH and metal concentration and ionic strength of solution on gold adsorption were studied. Experimental data was mathematically modelled using the Freundlich equation, which according to literature is suited to both homogeneous and heterogeneous systems (Foo and Hameed, 2010). The Freundlich equation was reasonably applicable in all of the studied cases with correlation coefficients (R^2) in the range of 0.87–0.99. The isotherm constants were calculated and correlated with the adsorption behaviour.

The optimum conditions for removal of gold from solution are pH 10, 10 g/L glycine and upto 20 ppm copper in solution. The results showed that the

activated carbon used had a higher adsorption capacity for gold glycine complexes than for their cyanide counterparts.

Isotherm data is important in the design of an adsorption plant as it serves as a guide for carbon dosage requirements, one of the most important economic factors when designing and running a gold processing plant.

- **Chapter 5:** Adsorption behaviour of copper and gold glycinate in alkaline media onto activated carbon: Kinetics (**Publication 3**)

Part 2 of a two-part publication series extends the results of the previous chapter on glycine only systems by evaluating the kinetics of adsorption process. The contact time between carbon and leachate is also an important economic factor when operating an adsorption plant. Increased contact time can give higher degree of carbon saturation thus decreasing carbon dosage but increasing cost of the column (Westermarck, 1975). Kinetic studies are used to experimentally evaluate the optimum contact time suitable to a specific system. In this chapter, the Fleming k_n method was used to model and analyse the gold adsorption process in alkaline glycine solutions. The adsorption of Au (I) and Cu (II) ions from solutions by granulated coconut shell activated carbon was studied in a batch adsorption system. Factors influencing gold adsorption such as glycine concentration, pH, metal and carbon concentration and ionic strength of solution, were investigated. Adsorption process was relatively fast with maximum equilibrium established at about 120 min. Carbon exhibited a good selectivity for Au (I) over Cu (II) glycinate ions.

- **Chapter 6:** Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper: Isotherms (**Publication 4**)

As mentioned previously, in the presence of minute or low cyanide concentrations and copper in solution, glycine can readily leach gold in alkaline medium. The copper and cyanide exists as copper cyanide complexes with no free cyanide in the system. This leach system suited for agitated tank leaching, owing to its fast kinetics also warrants a suitable solution purification process. Activated carbon adsorption previously shown to be suitable for adsorption from alkaline glycine systems and cyanide systems was trialled for the hybrid glycine-cyanide system. This chapter examined the

technical feasibility of applying activated carbon adsorption for gold concentration from glycine solutions containing copper-cyanide complexes through the study of isotherms.

Effects of various variables on adsorption efficiency were studied using batch experiments. These include glycine concentration, copper concentration, copper to cyanide ratio and solution pH. The gold adsorption results exhibited a good consistency towards the Freundlich isotherm model. Under optimum conditions (pH 11, Cu:CN 1:1, 123 ppm cyanide, 5 g/L glycine) the equilibrium gold loading capacity of the carbon was 9.95 kg_{Au}/ton_{carbon}, which is four times higher than the loading capacity in a pure cyanide system under similar conditions. The chapter (publication) was Part 1 of a two-part publication series on cyanide-starved glycine systems.

- **Chapter 7:** Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper: Kinetics (**Publication 5**)

The second of a two-part series of publications, this chapter presents evaluation of chemical kinetic data, important for the detailed understanding of the adsorption of gold and copper on activated carbon from cyanide-starved glycine solutions. The chapter adds on the previous one by including kinetic studies to give a complete picture of the chemistry of activated carbon adsorption from cyanide-starved glycine solutions containing copper and gold. A summary of the specific contents of the chapter follows: (1) studies revealed that the experimental data had a high consistency with the Fleming k,n model. Kinetic parameters such as initial adsorption rate were calculated using the model; (2) the effect of important parameters similar to those in the preceding chapter were investigated for both copper and gold adsorption; (3) based on the results, a conclusion of how these factors affected the adsorption process in terms of effectiveness and overall recoveries were drawn.

The main factor that affected gold recovery significantly was the carbon concentration. Variation of all other parameters slightly affected gold adsorption. The granulated coconut shell based carbon was found to be very selective for gold over copper with gold adsorption of 99% or more under optimum conditions compared to 50% or less copper recovered notwithstanding that copper concentration in solution was more than hundred fold that of gold.

- **Chapter 8:** Elution of gold glycinate complex from loaded carbon

Presents the experiments and findings of exploratory work done on elution of carbon loaded from pure glycine systems in the absence of copper. Various eluting techniques, including the Anglo American Research Laboratory (AARL) carbon stripping system, commonly used for conventional cyanide systems were tested. The only variable whose effect was tested across the elution techniques was temperature of the eluant. Pressure was kept constant at 50 psi. Optimisation of the elution process was not within the scope of this study and therefore does not form part of this chapter as elution is predominantly a closed system.

- **Chapter 9:** Conclusions and recommendations

Based on the major results obtained during this study, the main conclusions drawn from adsorption and elution work are summarised in this chapter. Recommendations for future work are also outlined.

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2 Literature Review

2.1 Introduction

The processing of gold-copper or refractory ores is a multistep process made up of numerous unit operations. The chosen metallurgical process flowsheet which comprises of a combination of these unit operations, depends on the grade of the ore or concentrate and is usually unique to each orebody. An ideal flowsheet will aim for high metal recovery percentages at the lowest possible cost, whilst minimising environmental impact and safety risks. The chronology of the unit operations for the most widely accepted basic gold processing route is; crushing and grinding, leaching, activated carbon adsorption of leached gold, elution and electrowinning. Eluted or “spent” carbon from the elution unit operation undergoes thermal regeneration before being reintroduced back into the adsorption circuit for reuse. A thorough understanding of each unit operation is critical in accomplishing the aims highlighted in the previous chapter.

This chapter reviews the leaching of copper-gold ores by the following leach systems: 1) conventional cyanidation, 2) glycine leaching and 3) cyanide-starved glycine leaching known as GlyCat™. Following a review of the leaching techniques, this literature survey then focuses on the hydrometallurgical processes used to treat metal-laden solutions. An overview of the commonly used separation technique, activated carbon adsorption, which is the main focus of this study is presented. Particular attention is paid to its role in gold recovery, gold adsorption mechanism, carbon manufacture, fouling and regeneration. Elution of the loaded carbon has also been reviewed. Different elution methods, desorption mechanism of gold from activated carbon and factors affecting elution of loaded carbon are discussed.

2.2 Glycine and Cyanide Leaching of Gold-Copper Ores

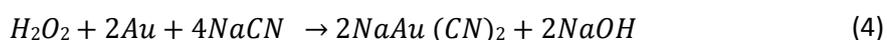
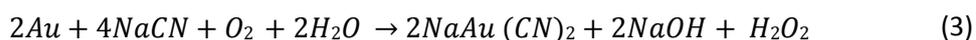
2.2.1 Cyanide Leaching of Gold Ores

Discovered in the 19th century, gold cyanidation is the most widely used technology in the processing of gold ores. The process replaced the previously used technologies of mercury amalgamation and chlorination as it offered better metallurgical performance and economic advantages. Though mercury amalgamation was applicable to high grade ores, gold recoveries were rather mediocre (80% at most). Chlorination on the other hand is quite cumbersome and expensive (Prasad et al., 1991), and led to gold plating onto carbon rather than adsorption of the chloro-aurate complex.

The industrial application of cyanidation has to date been a major milestone in gold ore processing. Cyanidation accounts for the processing of one billion tons of gold-bearing ores and more than 85% of gold extracted in the world (Abbruzzese et al., 1994). However, the depletion of free milling ores, the continuous decline in gold ore grades and the discovery of complex refractory deposits have challenged cyanide usage and inspired the search for techniques that can effectively deal with the technical challenges arising from this shift in gold ore mineralogy. Cyanidation has been extensively researched and continues to be researched as evidenced by the availability of a considerable amount of literature on diverse subject areas. One of the most notable well-researched areas has been the effective carbon-in-leach technology and elution processes for the recovery of gold from cyanidation liquors.

2.2.1.1 Mechanism of Gold Cyanidation

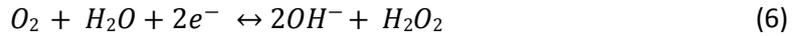
According to the Elsner equation, oxygen is required for the dissolution of gold. Gold is the noblest known metal and thus has a high standard reduction potential. Without appropriate complexing agents, the oxidation of gold to one of its predominant oxidation states, Au(I) and Au (III), by oxygen is not possible. The presence of a complexing ligand such as cyanide is necessary to reduce the reduction potential of gold, thereby enabling gold oxidation in mild oxidising conditions. After oxidation, the gold is dissolved to form the stable complex ion $[Au(CN)_2]^-$. It has been proposed that gold dissolution occurs in two successive steps according to Equations (3) and (4). Hydrogen peroxide is formed as an intermediate product. The two partial reactions reduce to form the Elsner equation represented by Equation (5).



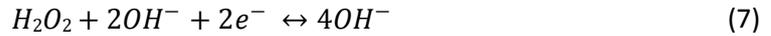
Marsden and House (1992) argued that, though stoichiometrically correct, the Elsner equation does not fully describe reactions taking place at the cathodes during gold dissolution. Kudryk and Kellog (1954) who confirmed the electrochemical nature of the gold dissolution process showed that in alkaline pH conditions, cyanidation is a result of two redox half reactions; oxidation of gold (anodic reaction) and reduction of oxygen (cathodic reaction).

The mechanism of oxygen reduction at the cathode is showed by Equations (6) and (7).

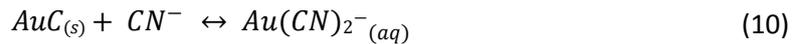
(a) Reduction of oxygen to hydrogen peroxide



(b) Hydrogen peroxide decomposition to hydroxide ions



The successive anodic reaction steps which lead to gold oxidation are represented by Equations (8) through (10).



It is generally proposed and accepted that a few sequential steps occur prior to and after the abovementioned electrochemical reactions. The first step in the gold dissolution process is the absorption and solubilisation of oxygen in a cyanide solution. The dissolved oxygen together with cyanide then migrate to the solid-liquid interface where they diffuse through the Nernst boundary layer onto the solid surface. The Nernst boundary layer is defined as the thin static liquid layer at the surface of the metal. The rate at which cyanide and oxygen diffuse onto the solid gold surface is the primary controlling step of the dissolution of gold (Kudryk and Kellogg, 1954). After the electrochemical reactions which lead to gold dissolution, the solubilised gold cyanide complex and other reaction products from the solid surface are desorbed and transported to the bulk of the solution.

2.2.1.2 Factors Affecting Gold Dissolution

2.2.1.2.1 Cyanide to Oxygen Molar Ratio

It is apparent from Elsner's equation that both cyanide and oxygen are necessary for gold dissolution to occur. The exact ratio value which yields maximum gold extraction has been an issue of debate among researchers. Habashi (1967) stated the optimal molar ratio of free CN^- to dissolved O_2 as 6. The author further pointed out that if the $[CN^-]$ to $[O_2]$ ratio is less than six then the rate of cyanidation becomes independent of

oxygen concentration and if the ratio is more than six the rate becomes independent of the cyanide concentration. Kudryk and Kellogg (1954) stated an optimum molar ratio of 6.4 which works out to a $[\text{CN}^-]$ concentration of 75 ppm. Cyanide control is vital during plant operation for cost optimisation and from an environmental point of view. Vorster and Flatman (2001) pointed out that since cyanide is the more expensive reagent of the two, from a financial point of view it is desirable to ensure cyanide is the rate-limiting reagent hence practically, a $[\text{CN}^-]$ to $[\text{O}_2]$ ratio that should be maintained should always be less than the calculated stoichiometric ratio. Optimisation of cyanide/oxygen ratios in CIP and CIL circuits is done by keeping track of the potential shift of the pulp, which is done to determine cyanide and oxygen deficiency, using a gold electrode (Heath and Rumball, 1998).

2.2.1.2.2 pH

Lime ($\text{Ca}(\text{OH})_2$) is usually used industrially as it is a low cost alkali to maintain a pH above 9 during cyanidation (Ellis and Senanayake, 2004; Ling et al., 1996). A pH below 9 leads to excessive cyanide loss through hydrolysis. A pH above 9 lowers cyanide consumption by minimising the formation of HCN gas since the pK_a of HCN in pure water is 9.2 (Ellis and Senanayake, 2004; La Brooy et al., 1994; Ling et al., 1996). Though the optimum leaching pH depends on the ore type, the majority of gold plants operate between pH 9 and pH 11 depending on other process conditions, particularly the nature of the process water and mineralogy of the ore. A pH above 11 tends to decrease the gold dissolution rate by increasing the concentration of OH^- ions which adsorb easily on the gold surface thereby occluding cyanide access by forming a passivating film on the gold surface (Kondos et al., 1995; Kudryk and Kellogg, 1954).

2.2.1.2.3 Temperature

Though temperature affects gold dissolution kinetics, cyanidation is usually carried out at ambient temperature. As mentioned earlier, one of the critical steps during the gold dissolution process involves diffusion of reagents (O_2 and CN^-) across the Nernst boundary. Therefore, to some extent temperature has a marked effect on the gold dissolution rate. Increasing the temperature (up to 85 °C) lowers the viscosity of the liquid and increases kinetics and diffusion rates (Marsden and House, 1992). Marsden and House (1992) mentioned that the dissolution rate reaches a maximum at 85 °C after which further increase becomes detrimental. Beyond 85°C oxygen solubility is decreased while the dissolution of undesirable minerals is increased. Practically, the benefit of using higher than ambient temperatures is too insignificant to warrant running gold cyanidation at elevated temperatures, hence ambient temperatures are deemed best more especially from an economic point of view.

2.2.1.2.4 Ore Mineralogy

The mineralogy of gold ores is such that in most instances gold is found in contact and association of minerals such as pyrite, chalcopyrite, pyrrhotite, sphalerite and other gangue minerals. These sulphide minerals leach alongside gold during the metal extraction process and negatively affect leaching by consuming cyanide and forming passivating films on gold (Aghamirian and Yen, 2005; Dai and Jeffrey, 2006; Filmer, 1982; Lorenzen and Van Deventer, 1992). According to Weichselbaum et al. (1989), sulphide ion concentration as low as 1 mg/L in solution can negatively affect gold leaching by forming an aurous sulphide layer on the surface of the gold. The extent of the effect of sulphide ions on gold dissolution depends on the amount of oxygen dissolved in solution and solubility of the sulphide minerals (Liu and Yen, 1995). Lorenzen and Van Deventer (1992) showed that pyrite, chalcopyrite and pyrrhotite were the most detrimental to gold dissolution.

2.2.1.2.5 Agitation

To attain sufficient leaching rates a certain minimum rate of agitation is allowable. The level of agitation affects among other things the thickness of the Nernst boundary layer, the diffusion rate of reagents, and to some extent the concentration of dissolved oxygen in solution. Agitation by the use of an efficient sparging system has been used to increase oxygen uptake (Bodnaras et al., 1993). A balance between agitation rate and the need to increase leach recoveries is vital as it can affect the overall economics of the process by dictating the overall power requirements (Marsden and House, 1992).

2.2.2 Glycine Leaching of Gold and Copper Ores

The dissolution of gold, copper and silver in alkaline glycine solutions has recently been reported. Eksteen and Oraby (2014) developed and patented an alkaline glycine leaching process for treating ores, ore concentrates and tailings comprising copper and precious metals. It was discovered during the early stages that glycine leaching at ambient temperatures was sufficient for copper recovery while elevated temperatures were required to leach precious metals. Oraby and Eksteen (2015) investigated the gold and silver dissolution behaviour in pH modified glycine solutions under various temperature, solution pH and reagent concentrations using rolled metal sheets of 99.9% purity. From their results, it was inferred that the optimum condition for gold dissolution is 60°C, 1M (75 g/L) glycine and a pH of 11. Eksteen and Oraby (2015) suggested that the same conditions could be employed for gold extraction in a heap leaching setting. The authors noted that an oxidant (like hydrogen peroxide) was essential for gold dissolution in glycine systems.

Tanda et al. (2017) demonstrated the ambient copper leaching capability of alkaline peroxide-glycine systems. The authors investigated the leaching behaviour of copper oxide minerals at ambient temperature and pressure and determined the optimum leaching conditions as pH 11 and glycine to copper ratio of 4:1. Copper plays a significant role in glycine leach systems. It was noted during the study that the Cu(I) in solution gets oxidized to Cu(II) which improves the stability of copper as metal glycine complexes. Addition of Cu²⁺ ions was also found to catalyse gold extraction for glycine leach systems (Eksteen and Oraby, 2015).

2.2.2.1 Chemistry of Glycine

Glycine is a nonpolar amino acid with the formula NH₂CH₂COOH. The basic structure of all α-amino acids is characterised by a carboxyl acid group (COOH) and an amino group (NH₂) and a side group (R) unique to a particular amino acid (Figure 2.1). Glycine, the smallest α-amino acid has its side chain as a hydrogen atom.

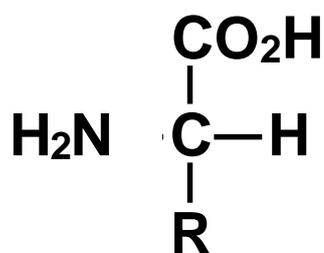


Figure 2.1: Basic structure of amino acid

The presence of an amine and carboxylic group implies that glycine is amphoteric in nature. An amphoteric molecule can exist as an acid (proton donor) and or a base (proton acceptor) when dissolved in water depending on the pH of the aqueous solution. Glycine is most stable in solution in its zwitterionic form (Hoyau et al., 2001). In this state (Figure 2.2), glycine carries both positive and negative charges in equal proportions such that the net electric charge of the molecule is zero. The pH range in which glycine is present chiefly in its zwitterionic form is 2.35 to 9.78.

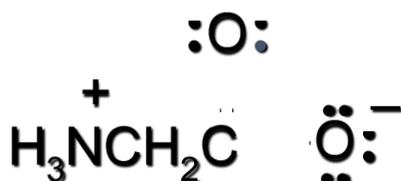


Figure 2.2: Zwitterion structure of glycine

The isoelectric point (pI) is the specific pH at which the amino acid molecule is neither negative nor positive and carries no net electric charge. Glycine has a pI of 6.0 at room

temperature. At a pH solution below 6, glycine exists mostly in its protonated form as a monocation (Figure 2.3). In this state, there is an excess of H⁺ ions in solution which get attracted to the negatively charged carboxylate ion thus leaving only a positive charge (+1) on the amine group.

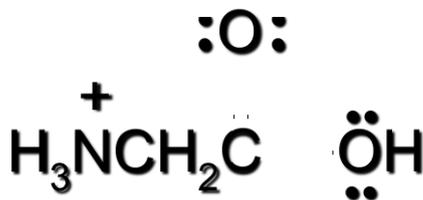


Figure 2.3: Positively charged glycine ion

When the solution pH is above 6.0, the excess OH⁻ ions in solution are attracted and attached to the amine (NH₃⁺) group resulting in the loss of H⁺. The amine group then has a neutral charge leaving the overall charge of glycine molecules as negative (Figure 2.4).

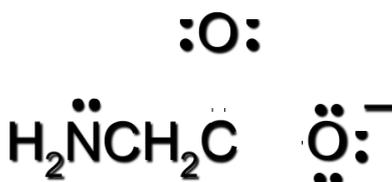


Figure 2.4: Negatively charged glycine ion

Glycine is widely used in various industries like pharmaceuticals, food, feed additives and chemical industries. Due to its zwitterionic character, glycine has a high aqueous solubility in water at ambient temperature as in this form, it is attracted to the dipolar water molecules (Yang et al., 2008). In organic solvents, however, glycine solubility is quite low due to the low polarity of these solvents (Bouchard et al., 2007). The degree to which glycine is solubilised depends upon the polarity of the solvent. A decrease in polarity of any solvent system translates to a reduction in the solubility of glycine.

Elevated temperatures are known to promote the decomposition of glycine in oxidising environments. Yablokov et al. (2009) observed that the noticeable decomposition of glycine occurs at 210°C, a temperature which is considerably lower than its melting point of 262°C. During thermal degradation of glycine, a range of products are formed including amines, organic and carbonic acids. These products can be formed from glycine via two pathways, decarboxylation and deamination (Sato et al., 2002).

The electrochemical oxidation of glycine leads to the formation of iminocarboxylic acid, which then undergoes hydrolysis before forming ammonia and aldehyde via decarboxylation. The oxidation of glycine by permanganate is an autocatalytic process that is autocatalysed by soluble colloidal manganese dioxide, a product of the reaction (Insausti et al., 1992; Perez-Benito et al., 1987). Glycine oxidation by iron (III) at 55°C results in the formation of formaldehyde (HCHO), carbon dioxide (CO₂) and ammonia (NH₃) (Sarathi et al., 2005). It was noted during the study that the zwitterionic form of glycine was more reactive to iron (III) than its protonated counterpart. Berger et al. (1999) investigated the oxidation of glycine by ozone and hydroxyl radicals. The by-products of glycine ozonation were nitrites and nitrates while glycine decomposition by hydroxyl ions resulted in the production of ammonia, oxamic, oxalic and formic acids. Glycine oxidation by ferricyanide, potassium bromate and aquamanganese (III) has also been reported (Sarathi et al., 2005). Generally, during oxidation, glycine decomposes and forms products like formaldehyde, ammonia, carbon dioxide and glyoxalic acid depending on the type of oxidant and presence of other reagents. It must be noted that glycine degradation by dissolved oxygen has not been reported anywhere in the literature.

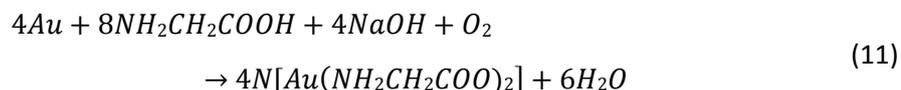
Various bacteria have also been reported to oxidise glycine (Campbell, 1955). Early studies on the breakdown of glycine by *Bacillus Proteus* and *Bacillus Coli* bacteria was done by Bernheim et al. (1935). The authors showed that in the presence of sufficient oxygen, the bacteria completely oxidised glycine to carbon dioxide, water and ammonia. The bacteria was reported to decompose glycine via decarboxylation. Other bacteria capable of degrading glycine include *Pseudomonas fluorescens* which also convert glycine to ammonia, carbon-dioxide and water. The intermediate products of the reaction were identified as glyoxylic and formic acids.

Glycine, like other amino acids, tends to form metal complexes. Glycine, a bidentate ligand, bonds to metal ions by donating two pairs of electrons. Complexation of glycine with metals may occur via three ways: (i) chelation between the nitrogen atom of the amino group and an oxygen atom of the carbonyl group, (ii) carboxyl attachment of neutral glycine and (iii) carboxylate attachment of zwitterionic glycine (Hoyau et al., 2001). Early investigations on metal complexation with amino acids reported the ability of glycine to complex with various metal ions such as platinum, copper, silver, nickel, vanadium, cadmium and gold (Bertran et al., 1999; Brown et al., 1982; Gharie and Zare, 1995; Kieft and Nakamoto, 1967; Komorita et al., 1968; Shoeib et al., 2001). The presence of amino acids in thiosulphate leaching systems also improves gold extraction by stabilising the leaching system and reducing thiosulphate consumption

(Feng and van Deventer, 2011). The interaction of gold with various amino acids including glycine has been studied by various researchers (Bogdanovskaya et al., 1986; Brown et al., 1982; Jingrong et al., 1996).

2.2.2.2 Glycine Leaching of Copper and Gold

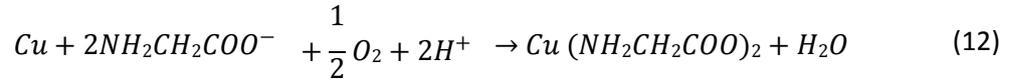
The use of glycine as a leaching agent for copper and gold from their resources was proposed by Oraby and Eksteen (2015) and Oraby and Eksteen (2014). Leaching studies for gold recovery found that after two days, alkaline (pH 11) glycine (0.5 M / 37.5 g/L) peroxide (1%) leaching resulted in leach rates (0.322 $\mu\text{m}/\text{m}^2$) comparable to those of thiosulphate-EDTA or thiosulphate oxalate systems after six days (0.25 $\mu\text{m}/\text{m}^2$). The presence of silver in the glycine leach solution accelerated the gold leach rate by six times within the same time frame. During leaching, zwitterionic form of glycine has been found to adsorb on gold surfaces and form a thin film. The oxygen and carbon atoms of the glycine molecules remain oriented perpendicular to the gold surface, an indication that zwitterionic glycine remains structurally invariant upon adsorption on the gold surface (Liedberg et al., 1985). Pakiari and Jamshidi (2007) utilised the Density Functional Theory (DFT) to study the binding of gold and silver clusters to glycine. The N-Au(Ag), O-Au(Ag) and S-Au(Ag) bonds were found to dominate the interaction of these metals with amino acids with the Ag cluster exhibiting a weaker bond with glycine than its Au counterpart. The reaction between gold and glycine is described by Equation (11).



As can be seen from Equation (11), oxygen plays a major role during the formation of the gold glycinate complex. Oxidising agents such as potassium permanganate and hydrogen peroxide have previously been used as oxidants during leaching of gold ores by mixed amino acids produced by micro-organisms (Groudev et al., 1996).

In their study on the leaching behaviour of copper oxide minerals, Tanda et al. (2017) reported that, in the presence of glycine, Cu(I) rapidly oxidises to Cu(II) which is the most stable copper glycinate complex. Addition of glycine to reactive slurries used in copper chemical mechanical polishing (Cu CMP) also increases the removal rates of excess copper significantly (Du et al., 2004). It was suggested that the enhanced copper dissolution was due to the catalysis of hydrogen peroxide decomposition by copper Cu(II)-glycine complexes. The decomposition reaction yields hydroxyl radicals which in turn oxidises the copper to its stable water-soluble glycinate complex.

The overall reaction of copper dissolution in glycine solutions is shown by Equation (12).



The electrochemical studies of copper in aqueous glycine solutions revealed the copper glycinate complex to be stable over a pH range of 2.6 to 12 at room temperature. The stability diagram of the system is shown in Figure 2.5 (Aksu and Doyle, 2001).

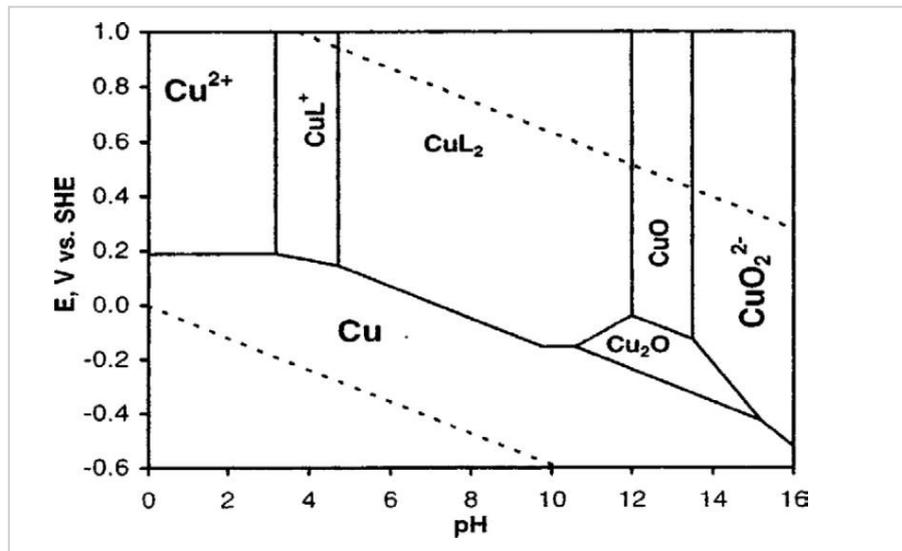
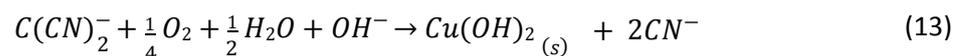


Figure 2.5: Eh-pH Diagram for Copper-Glycine system at 25°C and 1 atm, 10^{-5} copper activity, 10^{-2} glycine activity.

According to Oraby and Eksteen (2015a) it has been experimentally shown that copper (I) cyanide can be used to enhance gold dissolution in glycine. The process involves using alkaline glycine solutions containing cuprous cyanide at low to zero cyanide concentrations. Leaching of gold using cuprous cyanide in the absence of glycine at a pH of 12.5 precipitates copper as $\text{Cu}(\text{OH})_2$ (Equation 13) which passivates the gold surface and hinders further gold dissolution (Vukcevic, 1997).



Addition of glycine to the cuprous leach system enhances gold dissolution by dissolving the $\text{Cu}(\text{OH})_2$ passivation layer. Glycine is believed to generate free cyanide ions CN^- by forming complexes with cupric and cuprous ions according to Equations

(14) through to (16) i.e. glycine displaces cyanide by complexing copper (Oraby and Eksteen 2015a). The free CN⁻ ions are then available to complex the gold according to Equation 11.



2.3 Activated Carbon Adsorption

Activated carbon is used in carbon in leach, carbon in pulp and carbon in column for the recovery of gold from alkaline cyanide solutions. These methods, of which carbon in pulp is the most common, utilise the adsorption properties of activated carbon to recover gold from leach pulps. The successful commercial application of glycine leaching depends primarily on a viable technology similar to that of cyanidation which would enable gold recovery from metal laden alkaline glycine solutions.

Recovery techniques that have previously been applied for gold recovery from cyanide solution include carbon dioxide, precipitation/cementation, ion exchange and solvent extraction (Adams, 1994; Fleming et al., 2011; Gomes et al., 2001; Harris et al., 1992; Khosravi et al., 2017; Kordosky et al., 1992; Mooiman and Miller, 1986; Oo and Tran, 1991; Riveros, 1990; Riveros, 1993; Vilchis-Carbajal et al., 2000; Wadnerkar et al., 2015). Early studies by Oraby and Eksteen (2015b) proved activated carbon as an effective substrate in recovering the gold glycinate complex. Therefore, a technology similar to the well-known carbon in pulp/leach/column processes is proposed for the recovery of gold from glycine leachates or pulps.

2.3.1 Carbon-In-Pulp Circuit (CIP)

Since the 1950's, the carbon-in-pulp process is the preferred and widespread used process for the recovery of gold from cyanide pulps. Low capital and operating costs, high gold recoveries, low sensitivity to variation in process conditions and ability to handle clayey ores are some of the positive reasons why this process has a competitive advantage over other recovery methods (Bailey, 1987; Stanley, 1990). The main unit operations of the process (Figure 2.6) include leaching, carbon adsorption, carbon acid washing and elution, zinc precipitation or electrowinning and carbon regeneration or reactivation.

A discussion of each unit operation follows.

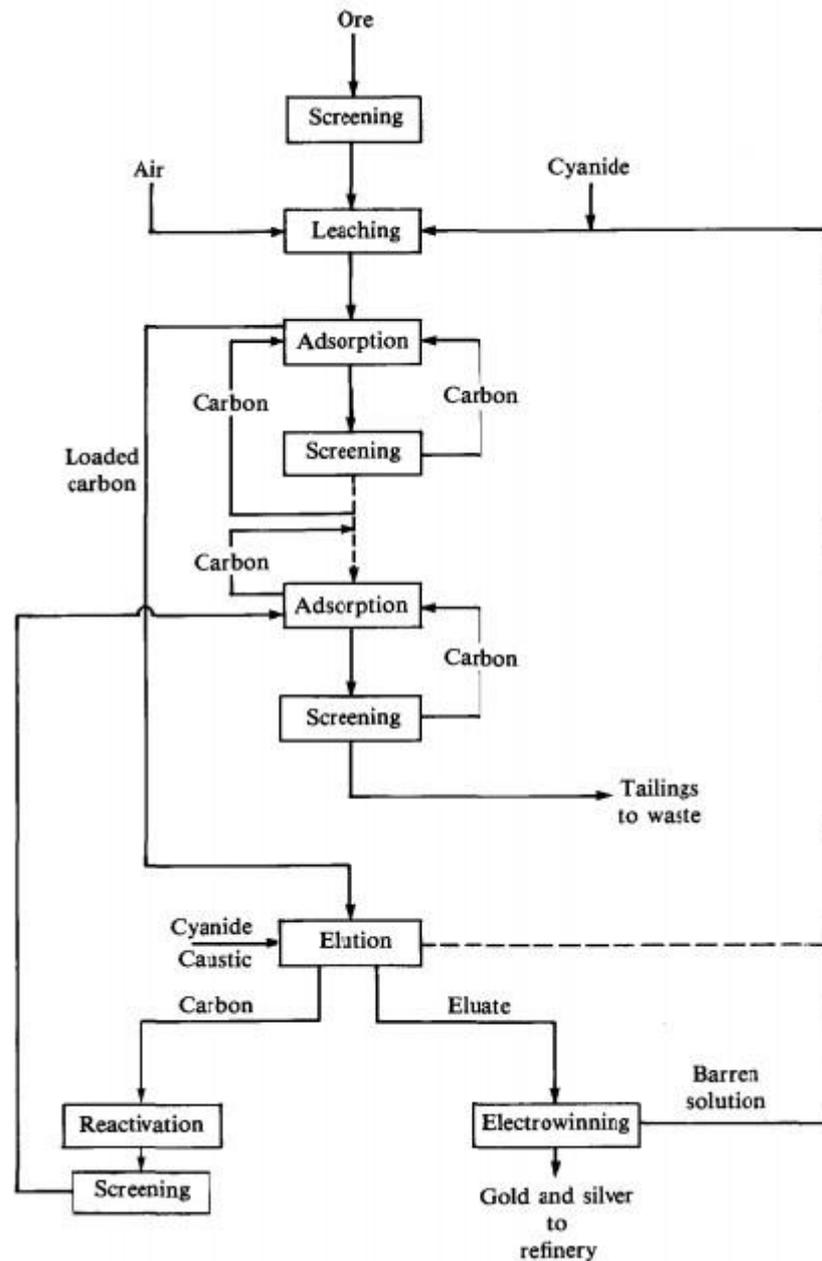


Figure 2.6: CIP plant flowsheet for gold recovery (McDougall and Fleming, 1987)

2.3.1.1 Leaching

Ore is first crushed and ground to a particle size of typically 80% under 75 μ m to achieve gold liberation (La Brooy et al., 1994). The crushed gold bearing ore is then contacted with a solution of sodium cyanide (approximately 0.01 mol/ or 500 ppm) in the presence of oxygen. Prior to cyanidation of the gold bearing material, a thickener is used to maintain a correct solid to liquid ratio of the pulp (Bailey, 1987; Stanley, 1990). The anodic oxidation (dissolution) of gold and cathodic reduction of oxygen, create an optimum E_h (mixed potential) in solution at which gold leaching occurs.

The presence of carbonaceous material and reactive constituents such as heavy metal impurities in the pulp, lead to a reduction in the gold dissolution rate and overall percentage recovered through depleting the reagent (cyanide) in the pulp and re-adsorbing the already dissolved aurocyanide ions.

2.3.1.2 Adsorption

From the leach tanks, the cyanided pulp is screened before being pumped to a series of adsorption tanks. During screening, woodchips and other oversized materials that may block interstage screens are removed (Bailey, 1987; Dahya and King, 1983; Laxen and Becker, 1979). The adsorption tanks are arranged in a cascading pattern to utilise gravity for pulp movement (Yannopoulos, 2012). Each tank contains roughly 25 g/l granulated activated carbon which is retained in the tank by the interstage screens as the pulp flows freely from one tank to another. The carbon and pulp move in a counter current flow where the gold in solution decreases downstream while gold loading of carbon increases upstream (Bailey, 1987; Dahya and King, 1983; Laxen and Becker, 1979).

The number of tanks, size of each and residence time in each all depend on the feed rate and targeted plant performance. Mechanical agitation is commonly utilised to maintain sufficient contact between the pulp and the carbon. Mechanical agitation is preferred over other types as it gives higher adsorption kinetics overall (Menne, 1982). The choice of a type of mechanical mixer depends on the relative density of the slurry. It is sometimes necessary to maintain low densities to ensure sufficient suspension of fast settling particles. The mechanism of gold adsorption will be dealt with later in the thesis (Section 2.4.2).

2.3.1.3 Elution

A hot strong sodium hydroxide cyanide solution is used to elute the loaded carbon. The concentration of the solution depends on the elution method used. The Zadra and Anglo American Research Laboratories (AARL) techniques are the most popular elution methods in gold processing. The Zadra process involves the stripping of loaded carbon with a 2% NaOH and 0.1% NaCN solution at elevated temperatures of 85-95 °C and atmospheric pressure. The process has low capital cost but long stripping times lasting anywhere between 24 to 60 hours (Zadra et al., 1952). With the AARL technique, the carbon is preconditioned in half a bed volume of 5% NaOH and 1% NaCN solution for about one hour. The pre-treated carbon is then eluted using high quality softened hot water (110 °C) and high pressures (50-100 kPa) at 3-bed volumes per hour (Banini and Stange, 1994; Van Deventer and Van der Merwe, 1994). The process shortens the stripping cycle times to approximately 9 hours (in total). The

two methods differ in that there is no carbon pre-treatment in the Zadra technique. Generally, elution produces a concentrated solution of 50-1000 mg/l Au from which gold is electrowon or precipitated. Prior to elution, the loaded carbon is usually acid washed with a (10% v/v) hot hydrochloric acid solution to remove fines, slimes and precipitated calcium carbonate (CaCO₃) from the carbon pores. This ensures fewer contaminants are transferred to the electrowinning circuit. Calcium carbonate is known to clog carbon pores and lead to poor elution and adsorption. Acid washing also makes the carbon less sensitive to the quality of water used in the succeeding steps of the AARL process. The chemistry of elution and the mechanism by which gold complexes are eluted are discussed in the proceeding sections (Section 2.5.3).

2.3.1.4 Electrowinning and Merrill Crowe Process

Gold from eluates resulting from the elution of active carbon is often recovered by either electrowinning or zinc cementation. During electrowinning, an electric potential is applied between inert conductive metal anodes and cathodes immersed in a gold electrolyte solution. Pure gold electroplates onto the cathodes which are later digested in hydrochloric acid then calcined or smelted (Bhappu, 1990). The gold depleted electrolyte is then returned to the elution circuit where it is reused for stripping gold from the loaded carbon. The typical electrowinning cells used in industry contain cathodes made out of stainless steel mesh or wool. These cathodes can be reused but they are usually replaced after each strip. Stainless steel provides a large surface area for deposition of metals (Dahya and King, 1983; Laxen, 1984). The chemistry of the process is well researched and understood. The electrowinning reactions that occur at the cathode are shown in Equations (17) through (19).



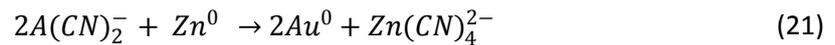
At the anode, water is decomposed and oxygen evolved according to Equation (20).



The electrowinning process employed at a particular operation depends on the elution method used prior. For Zadra elution, electrowinning is integral with elution. The eluate

is recirculated until the carbon gold content is low. For AARL elution, the electrowinning circuit is operated as a batch sub-process independent of the elution process. The eluate is recirculated in the electrowinning cell until enough gold is depleted from solution.

The Merrill Crowe process precipitates gold from solution using zinc dust or shavings. The process is preferred where the silver to gold ratio is high (exceeds 2) or when the eluate contains high concentrations of other chemicals such as flotation reagents. The cementation of gold using zinc is an electrochemical reaction described as follows:



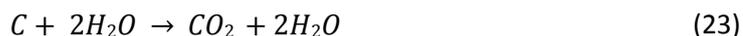
During the redox reaction, the gold is reduced to its metallic state by accepting an electron while the zinc is oxidised to its (+2) state from its metallic (0) state by donating two electrons (Navarro et al., 2004). In their chronological order, the main steps in the process include clarification, deaeration, zinc precipitation and filtration. The main aim of clarification is to reduce the concentration of suspended solids to 1 ppm or less, a condition critical for effective precipitation to occur. The clarified solution is then deaerated to remove dissolved oxygen from solution before zinc dust is added to precipitate gold according to Equation (21). Excessive dissolved oxygen tends to keep gold in solution. The precipitate is recovered using a filter press.

2.3.1.5 Carbon Regeneration

The practical application of active carbon for precious metals recovery, particularly from an economic point of view, is dependent on the reuse of carbon in multiple adsorption cycles. Various organic and inorganic species present in the pulp adsorb alongside gold during the CIP process, causing excessive poisoning of the carbon (Bradshaw et al., 1997). Most of these contaminants do not elute, resulting in loss of activity of the carbon by blocking active sites for gold adsorption. Carbon reactivation, the frequency of which depends on the pulp makeup, is therefore mandatory before the carbon is returned to the adsorption circuit for reuse.

Carbon may be regenerated thermally, chemically, by using solvents or biological methods. The most effective and common regeneration method is thermal regeneration. During thermal regeneration, the carbon bed is heated to about 550 - 900 °C in the presence of steam in a non-oxidising environment for 15 to 30 minutes to vaporise and burn off volatile and non-volatile adsorbates. The steam ensures the carbon is surrounded by an inert environment thus preventing oxidation of the carbon. The moisture content of the carbon entering the kiln is very critical for

successful reactivation. A 20% moisture by weight is optimum and any excess water should be removed before the carbon enters the kiln. The activity of the carbon decreases with each cycle as regeneration leads to partial combustion of the carbon each time according to Equations (22) and (23). This is the reason the carbon is periodically discarded.



After regeneration, the reactivated carbon is cooled, screened and conditioned then sent back to the adsorption circuit.

2.3.1.6 Conclusion

Though the fundamental chemistry of the carbon in pulp process is well researched and understood, a few grey areas concerning the process exist. The decomposition chemistry of cyanide as it flows through the process remains unknown. The understanding of the effect of acid wash on the carbon and the adsorption mechanism of other complexes (non-metals) found in the pulp is lacking. Research around the complex surface chemistry on how carbon absorbs metal ions is also not conclusive.

2.4 Activated Carbon

Activated carbon is a group of amorphous carbon materials with a highly porous internal structure. Because of their polydisperse porous structure, activated carbons are versatile and excellent adsorbents which have found varied applications in many industries. Their most common application relate to their use in the adsorptive removal of odour, colour and other impurities during water purification; air purification; purification in food, chemical and pharmaceutical industries and in medicine for the removal of toxins (Dąbrowski et al., 2005; Malik, 2003; Margot et al., 2013; Otowa et al., 1997; Selvi et al., 2001; Sircar et al., 1996; Spahis et al., 2008). The use of activated carbons in the field of hydrometallurgy for the recovery of precious metals, particularly gold, is the basis of the present study.

2.4.1 Manufacture and Structure of Activated Carbon

Activated carbon can be produced from a variety of carbon raw materials such as coal, coconut husks peat and petroleum. The carbons are made by the pyrolysis of solid carbon materials such that a portion of the solid is removed and small voids commonly known as pores are formed (Akash and O'Brien, 1996). The methods of producing

activated carbon can be divided into two processes, physical or chemical (Adinata et al., 2007; Bouchelta et al., 2008; Williams and Reed, 2006). The physical activation process involves two main steps, carbonisation and activation. During carbonisation, the carbonaceous material undergoes thermal decomposition under inert atmosphere to eliminate volatiles and produce a primary pore structure ready for activation. The carbonisation temperature ranges between 400°C and 1000°C. In the second activation step, the resulting char is activated using activating agents such as steam or carbon dioxide. The activation temperature ranges between 600°C and 900°C. Chemical activation, on the other hand, is a single step method which involves impregnating the source raw material with chemicals and heat-treating the impregnated material under inert conditions. During chemical activation, carbonisation and activation of the raw material occur simultaneously. Chemicals widely used in industry include zinc chloride, phosphoric acid and potassium hydroxide (Adinata et al., 2007; Gao et al., 2013; Sudaryanto et al., 2006; Yagmur et al., 2008).

The main advantages that chemical activation presents include lower activation temperatures, less activation times and development of a better porous structure (Ahmadpour and Do, 1996; Maciá-Agulló et al., 2004). However, economically, the chemical method is more expensive as activating agents are more expensive, plus there is a necessary additional washing step (Maciá-Agulló et al., 2004). Adsorption efficiency of activated carbons depends on the source raw material and activation process (Akash and O'Brien, 1996; Rivera-Utrilla et al., 1991).

2.4.1.1 Pore Structure of Activated Carbon

Granular activated carbons for gold adsorption exhibit a heterogeneous tri disperse pore structure made up of macropores, mesopores and micropores (Dubinin and Stoeckli, 1980; Gergova and Eser, 1996; Lei et al., 2001; Williams and Reed, 2006). These pores, whose size and distribution can be controlled by changing the carbonisation conditions, are classified based on size of their diameter. The pores give the carbon its porosity and high internal surface area of about 500-2500 m²/g, which is predominantly contained within the micropores. The complex pore network of active carbons is classified according to size as follows; (a) micropores (< 2nm D_p), (b) mesopores (2 - 50 nm D_p), and (c) macropores (> 50 nm D_p) where D_p is the pore diameter (Deventer, 1986; Hu et al., 2001; Jia et al., 1998; Mays, 2007).

Micropores contribute the highest adsorption capacity of active carbons as their specific surface area constitutes approximately 95% of the total surface area of the active carbon (Branton and Bradley, 2011; Cho et al., 1979; McDougall, 1991; Seke et al., 2000). The surface area of mesopores also known as transitional pores, does

not exceed 5% of the total surface area of the carbon. Mesoporosity of a carbon can however be enhanced during the manufacturing process. Mesopores acts as a passage to the micropores, which lie in the innermost parts of the carbon. Macropores open directly to the external surface and act as conduits for the adsorbate into the internal structure of the carbon. The contribution of macropores to the total surface area of the carbon is very small (<1%).

The pore structure has a significant bearing on the adsorption capacity of active carbons. Purification of alkaline cyanide leachates is achieved by the use of coconut shell based carbon. Coconut shell-based carbon is preferred as it has a thinner pore structure and thus a higher retention rate (Ahmedna et al., 2000; Daud and Ali, 2004; Khosravi et al., 2017). The coconut activated carbon also has a large surface area emanating from the predominance of micropores in its structure. The high microporosity in turn gives the carbon its tight structure creating a mechanically strong carbon that is resistant to attrition.

2.4.1.2 Chemical Structure of Activated Carbon

The chemical structure of active carbon influences its adsorptive capacity. The surface chemistry of active carbon is determined by its heterogeneity which is related to the presence of heteroatoms. These heteroatoms may originate from the source raw material or becomes part of the carbon structure during activation (El-Sayed and Bandosz, 2004; Snoeyink and Weber, 1967). Active carbons are associated with carbon, oxygen and heteroatoms such as sulfur and nitrogen. These atoms are bonded to the edges of the carbon to form carbon-oxygen, carbon-nitrogen or carbon-sulfur surface groups. The carbon-oxygen surface groups are the most important as these affect the chemical reactivity and adsorption capacity of the carbon.

Activated carbons are classified into two: H-carbons and L-carbons. H-carbons, formed at temperatures of 1000°C absorb H⁺ ions when in contact with water while L-carbons which are formed at lower temperatures of 300-400°C preferentially absorb OH⁻ ions. Carbons used for gold recovery usually exhibit both acidic and basic properties.

The carbon-oxygen and other functional groups on the surface of the carbon can undergo electrochemical reactions and thus impart a reduction potential on the active carbon. Different carbons have different reduction potentials which can effect the reduction of gold complexes to gold metal ions.

2.4.2 Adsorption of gold on Activated Carbon

Various researchers have investigated the chemistry of the interaction of gold with carbon during adsorption. Several possible mechanisms have been suggested, and each can fall under one of the following main classifications: (i) adsorption of gold as an $\text{Au}(\text{CN})_2^-$ complex without undergoing any chemical alteration. The aurocyanide complex is believed to be adsorbed by anion exchange mechanisms where the complex is electrostatically held in place by Van der Waals forces. This is known as physical adsorption, (ii) decomposition of $\text{Au}(\text{CN})_2^-$ to $\text{Au}(\text{CN})$ species which then adsorb on the carbon, and (iii) reduction of aurocyanide to metallic gold state (Adams et al., 1987; Jones et al., 1989; McDougall and Hancock, 1981; Wan and Miller, 1990). The last two are classified under chemical adsorption.

The non-conclusivity of gold adsorption on active carbon is due to failure to monitor chemical changes on the carbon surface as carbon is not amenable to procedures such as infra-red spectroscopy and other physical investigation techniques (McDougall and Hancock, 1981; Van Deventer, 1986).

Adams (1990) argued that physical adsorption of the aurocyanide complex is the most favoured adsorption mechanism for carbon-in-pulp conditions. The same author debated against the chemical degradation of aurocyanide to AuCN during adsorption after analysis of gold species adsorbed on the carbon using Mossbauer spectroscopy. This conclusion is supported by Cashion et al. (1988) who after contacting carbons loaded under industrial conditions with potassium dicyanoaurate solution identified $\text{A}(\text{CN})_2^-$ on the loaded carbon. No AuCN or Au was found on the carbon. Adams (1990) concluded that though reduction or decomposition of the aurocyanide complex is not the main adsorption mechanism, it cannot be ruled out. If all the aurocyanide complexes adsorbed as $[\text{Au}(\text{CN})_2]^-$, then the pre-treatment step of the AARL process which uses cyanide to convert gold back to its elutable form $[\text{Au}(\text{CN})_2]^-$ would not be necessary nor would it improve elution rates which has not been found to be the case in practice (Van der Merwe, 1991). It is suspected that the ability of activated carbon to reduce the aurocyanide complex might be a function of the sample of carbon used at the time of study, hence the conflicting conclusions by various authors (Van Deventer and Van der Merwe, 1993).

When visualising the loading pattern of gold cyanide onto carbon using microtomography, Pleysier et al. (2008) found that gold first saturates the external surface of the carbon after which it diffuses to the interior of the carbon. Gold saturation is ascribed to high gold loadings of about $2500 \text{ mg}_{\text{Au}}/\text{kg}_{\text{Carbon}}$ (Pleysier et al., 2008;

Vegter, 1992). During the CIP process however, owing to the long carbon residence times during the process, the gold is expected to be eventually uniformly distributed throughout the carbon.

2.4.3 Factors affecting adsorption onto activated carbon

The design and effective operation of a CIP circuit is governed by process conditions that also have a bearing on adsorption equilibria and kinetics. Conversely, understanding of these factors also allows us to understand what condition would be preferential for desorption (i.e. during elution).

2.4.3.1 pH

Many authors who studied the effect of pH on gold loading noted that a lower pH results in increased adsorption rate and loading capacity of the activated carbon (Fleming, 1984; McDougall and Hancock, 1981). The zeta potential of the carbon depends on the solution pH thus the affinity of carbon for OH⁻ or H⁺ ions changes with changing pH. Hydroxide ions compete with the aurocyanide ions for active sites on the carbon (Petersen et al., 1993; Yannopoulos, 2012). Equilibrium loading capacity of gold improves when the pH is lowered. At high pH values, the aurocyanide ion is stabilised and adsorption decreased. Lime is used to raise the pH of CIP circuits in industry. The Ca²⁺ cations are known to enhance gold adsorption. CIP circuits operate within a narrow pH range (9-11) to derive any significant benefit from lowering pH or using lime as a pH modifier. The use of the larger monovalent sodium cations favours the reverse process (in comparison to calcium), i.e. relative desorption.

2.4.3.2 Temperature

Gold adsorption onto activated carbon is an exothermic process (Fleming, 1984; McDougall et al., 1980; van Deventer and van der Merwe, 1993b). Increasing the temperature affects the loading rate of the gold and loading capacity of the carbon towards gold. Fleming (1984) investigated the effect of temperature (25, 44 and 62 °C) on the adsorption rate and equilibrium loading capacity of carbon. The gold adsorption rate increased with increasing temperature from 3390 h⁻¹ to 4070 h⁻¹ to 4920 h⁻¹ respectively while the equilibrium loading capacity decreased from 62,000, 47,000 to 29,000 mg/L for 25, 44 and 62 °C respectively. The pH for these experiments was maintained between 10.4 and 10.8 while the free cyanide concentration was 130 mg/L and Au 25 mg/L in solution. McDougall et al. (1980) who conducted similar studies from a solution with a higher Au concentration of 180 mg/L came to the same conclusions that gold loading decreased with increasing temperature. Generally, CIP plants perform best during winter or in cold climates

than in hot summer conditions. Conversely, it shows why high temperatures are chosen for elution.

2.4.3.3 Oxygen

Oxygen has been demonstrated to have a beneficial effect on the adsorption of gold onto activated carbon (Petersen and Van Deventer, 1991; Van der Merwe and Van Deventer, 1988). According to Tsuchida et al. (1984), the oxygen consumed during the adsorption of aurocyanide complex under alkaline conditions is not utilised to change $\text{Au}(\text{CN})_2^-$ to AuCN. Van der Merwe and Van Deventer (1988) suggested that the oxygen is used to oxidise the surface functional groups which are responsible for the adsorption of gold onto carbon.

The concentration of oxygen is an important parameter to consider. For each type of carbon, there exists a maximum oxygen level above which equilibrium gold loadings will be maximized and plateau (Van der Merwe and Van Deventer, 1988).

Woollacott and de Guzman (1993) summarised the role oxygen had on the adsorption of carbon as:

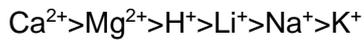
- i) The equilibrium loading increases with increasing oxygen concentration (Adams, 1990; Tsuchida et al., 1984; Van der Merwe and Van Deventer, 1988).
- ii) The beneficial effect is most pronounced in solutions of low ionic strength. In solutions of high ionic strength, the effect of oxygen on gold loading is not significant (Adams, 1990).
- iii) The equilibrium gold loading is highly sensitive to a change in oxygen concentration only at low oxygen concentrations (Van der Merwe and Van Deventer, 1988).

2.4.3.4 Ionic Strength

Davidson (1974) who investigated how different cations enhanced the adsorption of $\text{Au}(\text{CN})_2^-$ showed that the presence of sodium (Na^+) and calcium (Ca^{2+}) ions in the adsorption medium increased the carbon loading capacity. The study showed that calcium ions increased ionic strength to a far greater effect than sodium ions. The findings were corroborated by Fleming and Nicol (1984) who reported that an increase in the ionic strength of solution increased both the gold adsorption kinetics and adsorption capacity of the activated carbon. The ionic strength of a solution depends on the concentration of the dissolved chemical constituents and their charge number thereof. The higher the charge of the ion the higher the ionic strength of the solution.

Divalent ions (Ca^{2+} and Mg^{2+}) therefore produce a higher ionic strength and enhance metal adsorption more than monovalent ions (Na^+ and K^+).

The rate of adsorption and adsorption capacity decreases with changing ionic strength resulting from metal cations as shown below (Davidson, 1974; McDougall and Hancock, 1981):



The effect of ionic strength on the carbon loading capacity is greater than the effect on the loading kinetics (Fleming and Nicol, 1984). An ionic strength of 0.005 M resulted in an adsorption rate constant and equilibrium capacity of $3,150 \text{ h}^{-1}$ and $56,000 \text{ mg}_{\text{Au}}/\text{kg}_{\text{carbon}}$ respectively. When the solution's ionic strength was increased to 1 M, the rate increased by 32% to $4,150 \text{ h}^{-1}$ while the capacity increased by 102% to $113,000 \text{ mg}_{\text{Au}}/\text{kg}_{\text{carbon}}$.

2.4.3.5 Particle Size of Carbon

A smaller carbon particle size exhibits a larger external surface area. However, most of the specific surface area of the carbon particle lies in its internal pore structure. Hence, the size of the carbon particle has little bearing on the total specific area of the carbon. The loading capacity of the carbon is therefore independent of the particle size while the smaller sized carbon granules yield a faster gold adsorption rate. In practice, the choice of particle size is governed by many factors. Finer carbon sized particles are difficult to screen therefore the particle size of the carbon used in CIP plants is a balance between screening efficiency and improved adsorption rates.

Because of its high surface area to mass ratio, fine carbon is more susceptible to attrition than coarser carbon. Carbon attrition causes gold and carbon losses in CIP circuits. According to Marsden and House (1992), in typical CIP operations, 40 – 60 g of carbon per ton of ore is lost to attrition. Since the loading of gold predominantly takes place on the outer surface, fines resulting from abrasion of carbon have a high gold content which is eventually lost (Vandam, 1994). The loss of gold-laden carbon fines has a detrimental effect on the profitability of the operation. Coetzee and Cloete (1989) who studied the effect of different impellers on the attrition rate of activated carbon concluded that the amount of fines produced is related to the energy transferred to the pulp suspension during agitation. Attrition can therefore be lessened by a reduction in the mixing power intensity in the adsorption tanks.

2.4.4 Carbon Fouling

Unwanted species present in the leach solution may adsorb or accumulate on the surface or within the pores of the carbon leading to carbon fouling. The unwanted species may either be organic or inorganic. Inorganic compounds are associated with gold ores and leach alongside gold while organic compounds are usually added to the circuit as part of processing reagents. Since activated carbon is unselective, it adsorbs to varying degrees, dissolved organic and inorganic species found in the leachate (Fisher and Dunn, 2000; McDougall and Fleming, 1987). Carbon fouling has a detrimental effect on the adsorption of gold both kinetically and equilibrium loading capacities. Carbon fouling affects more especially the economics of the process as it significantly reduces the carbon activity resulting in increased carbon inventories, residence time, dissolved gold losses and number of adsorption stages. According to Marsden and House (1992), fouling of carbon may result from any of the following:

- i) adsorption of undesirable organic and inorganic unwanted species on the active sites of the carbon which gold could adsorb on;
- ii) precipitation of inorganic salts on the surface of the carbon leading to blockage of active sites and;
- iii) trapping of solid particles and precipitates in carbon pores occluding active sites and preventing contact with the gold-bearing solution.

2.4.4.1 Inorganic Compounds

Inorganic foulants consist mainly of calcium, magnesium and sodium salts, silica and complex silicates and base metals. Calcium is usually added to the circuit through the addition of lime, which is used as a pH controller in CIP circuits. Calcium and calcium products can result in the formation of calcium scale (CaCO_3) on the carbon's outer surface. The calcium scale occludes the macro and meso pores and prevents gold from being adsorbed onto the carbon. The extent of the detrimental effect that the calcium scale has on gold adsorption is unique to each CIP plant. For some plants, 1.5% calcium on carbon has an effect while other plants can perform satisfactorily with carbon loaded with up to 3% calcium (Marsden and House, 1992).

Metal ions, which are associated with gold deposits, leach alongside gold. They can also originate from process stages such as milling during attrition. The leached metal ions compete with the gold complex for active sites on the carbon thus significantly reducing adsorption efficiencies. Fleming and Nicol (1984) reported that owing to their high concentration in the majority of gold ore deposits, copper and iron have the highest influence compared to other metal ions. Base metal ions, though usually

present in concentrations well above those of gold, do not depress the adsorption of gold as significantly as organic foulants do. Inorganic foulants are therefore not much of a nuisance since, with the exception of copper, they can easily be removed by acid washing during carbon regeneration. A cold caustic cyanide pre-elution wash is often employed for copper removal. Generally, compared to organic foulants, inorganic foulants play a small role in the deactivation of carbon towards gold complexes (La Brooy et al., 1986; Marsden and House, 1992)

2.4.4.2 Organic Compounds

The hydrophobic and non-polar nature of the surface of activated carbon makes it susceptible to adsorb organic compounds readily. Organic fouling agents compete directly with gold for active sites on the carbon and to some extent inhibit the rate of gold uptake (Fleming and Nicol, 1984; Petersen and Van Deventer, 1991). Most CIP leach slurries contain organics such as flotation reagents from upstream processing, machine oils and degreasers from equipment maintenance, dewatering agents and humic acids from vegetation (La Brooy et al., 1986; Petersen and Van Deventer, 1991). The ore and process water also often contain organic products (La Brooy, 1988; La Brooy and Bax, 1985; La Brooy et al., 1986).

According to Fleming and Nicol (1984), one mechanism by which organics can foul the carbon is by absorbing as a thin film on the surface of the carbon granule without penetrating the pores of the carbon particle. This mechanism, which is most likely for organic compounds that are insoluble in water, would affect the rate of loading but not the loading capacity. Petersen and Van Deventer (1991) further confirmed the pore blocking mechanism which inhibits the diffusion of gold into the pore network.

La Brooy et al. (1986) studied the effects of various organic foulants on the kinetics of gold adsorption onto activated carbon. The experimental work included ageing activated carbon in a solution containing: (a) 10-100 ppm of various fouling agents, (b) 200 ppm NaCN, and (c) 10 ppm Au as $\text{Au}(\text{CN})_2^-$ for 24 hours. They reported that flotation reagents like frothers and xanthates caused the most deactivation of carbon. Their findings were later confirmed by Fisher and Dunn (2000), who used thermal analysis techniques to identify xanthates and frothing agents as the main cause for carbon fouling on two commercial CIP plants. The longer alkyl chained xanthates had a more serious effect on the adsorption rate than the shorter chained xanthates. For example, ethyl which is longer had a 280 h^{-1} adsorption rate compared to 40 h^{-1} for amyl which is shorter. The results agreed with Traube's Rule which states that every extra CH_2 group in a surfactant molecule more than triples the adsorption strength.

Because of their hydrophobic nature, xanthates are suspected to inhibit adsorption by competing with the aurocyanide complex for active carbon sites as opposed to forming a thin film on the carbon surface. The k (adsorption rate) values of various organic solvents are presented in Table 2.1 (La Brooy et al., 1986).

Table 2.1 Rate constants for carbon fouled with organic compounds

| Fouling agent (10-100 ppm) | k (h^{-1}) |
|-----------------------------------|---|
| <u>Control</u> | |
| • no ageing | 1200 |
| • distilled water | 640 |
| <u>Collectors</u> | |
| • Sodium ethyl xanthate | 280 |
| • Sodium isobutyl xanthate | 140 |
| • Potassium amyl xanthate | 40 |
| • Aerofloat 208 | 270 |
| <u>Frothing Agents</u> | |
| • Teric 401 | 110 |
| • Teric 402 | 140 |
| • Dowfroth 200 | 130 |
| • MIBC | 270 |
| <u>Oils</u> | |
| • Mobil ALMO 527 | 200 |
| • Diesel | 190 |
| • Multigrade | 390 |
| <u>Vegetation Products</u> | |
| • Swamp water | 120 |

Frothers are suggested to impede the access of gold cyanide by rendering the carbon surface hydrophobic while oils possibly clog the pores.

Other fouling agents studied whose k values are not listed in Table 2.1 included flocculants and viscosity modifiers which had little to no effect on the activity of the carbon. The suspicion was that, their large sized molecules prevents them from accessing the micropores of activated carbon. As a result, they do not impede access of the aurocyanide complex to the active sites of the carbon particle.

2.4.4.3 Assessing the effectiveness of Activated Carbon

To test for the adsorption efficiency, active carbons can be analysed for properties shown in Table 2.2 using any of the numerous available tests (Fisher and Dunn, 2000).

Table 2.2 Analyses for activated carbon characterisation

| Physical Properties | Fouling |
|---|--|
| <ul style="list-style-type: none">• kinetic activity• K-value• total gold• gas adsorption• apparent density• wet attrition• abrasion index• particle size distribution | <ul style="list-style-type: none">• ash content• extractable calcium• total silica• apparent density• lab scale regeneration• thermogravimetric analysis (TG) |

The kinetic activity is indicative of plant efficiency (La Brooy et al., 1986). The K-value used to determine the carbon's activity is calculated from equilibrium loading experimental results fitted to the Freundlich isotherm equation. The carbon's pore structure can be studied and monitored using gas adsorption tests. The apparent density of the carbon is useful when determining the optimum carbon concentration in (g/L dry carbon) for a tank vessel. Also, an increase in the density of the carbon may be a quick indicator that fouling has occurred. The total gold adsorbed gives insights on the efficiency and profitability of the plant.

Similar to the abrasion index, wet attrition tests are utilised to measure the physical degradation of the carbon. The physical condition of the carbon can also be inspected visually by comparison of virgin and used carbon. Physical degradation of the carbon is an important factor to monitor to enable timely carbon replacements in order to maintain the correct carbon quantity to ensure good adsorption efficiencies in the circuit at all times.

Thermal analysis techniques like thermogravimetry (TG) are used to directly determine the extent of fouling on the carbon. Other techniques that can be employed are the ash content and extractable calcium tests. Determination of fouling is important as it can be used to assess how effective employed carbon regeneration techniques are. Total silica tests measure the percentage blockage of the carbon pores.

2.5 Elution

Elution permits the repeated use of granulated activated carbon thereby enhancing the economic feasibility of CIP circuits. Three elution methods mainly used in industry include (Adams, 1990; Banini and Stange, 1994; Van der Merwe, 1991; van Deventer and van der Merwe, 1993b):

- (1) the Zadra Process (also known as the Homestake method) in which a warm cyanide solution (90°C – 95°C) with a typical composition of 0.5% NaCN and 1-2% NaOH, is circulated for several hours through the elution column and electrowinning cells connected in series at atmospheric pressure. The process generally takes about 48 to 72 hours. The gold content of the carbon can be reduced from 4000 g_{Au}/ton_{carbon} to <100 g_{Au}/ton_{carbon} within this time frame. The main disadvantage of the Zadra Process is its slower desorption rate when compared to other alternatives.
- (2) the Anglo American Research Laboratory (AARL) method which involves a series of procedures starting with an acid wash followed by a cyanide pre-treatment step. In the pre-treatment step, the carbon is soaked for about 30 minutes in a solution containing about 0 to 5% NaCN and 2% NaOH. Finally, hot deionised water is used at high pressures (200 - 300 kPa) to elute the loaded carbon. The pregnant eluate is then circulated to the electrowinning cells. The main advantage of the AARL process is the faster elution kinetics and shorter elution cycles of roughly 6 – 8 hours.
- (3) elution with organic solvents which involves variations of the above processes. Large quantities of organic solvents such as methanol, ethanol, isopropanol and ethyl alcohol are added to the eluate to improve the elution efficiency of the process. The main disadvantage with the usage of alcohols in gold processing plants is the potential for fires since alcohols are highly flammable. Several plants utilising alcohol stripping have experienced fires, more especially in the electrowinning sections where a lot of sparks are generated (Heinen et al., 1976).

According to Muir et al. (1985) and Davidson and Schmidt (1986) the AARL method has an economic advantage over the Zadra elution process and elution with organic solvents. The advantage emanates from the operating costs, which are lower for the AARL process. Paterson and Suddaby (1987) however reported that the capital and operating costs of the AARL and Zadra processes were not significantly different and that the AARL process was preferred for its shorter elution times. The AARL method is of more interest to this work.

2.5.1 AARL Elution

The basic AARL elution flow diagram is shown in Figure 2.7 (Stange, 1991).

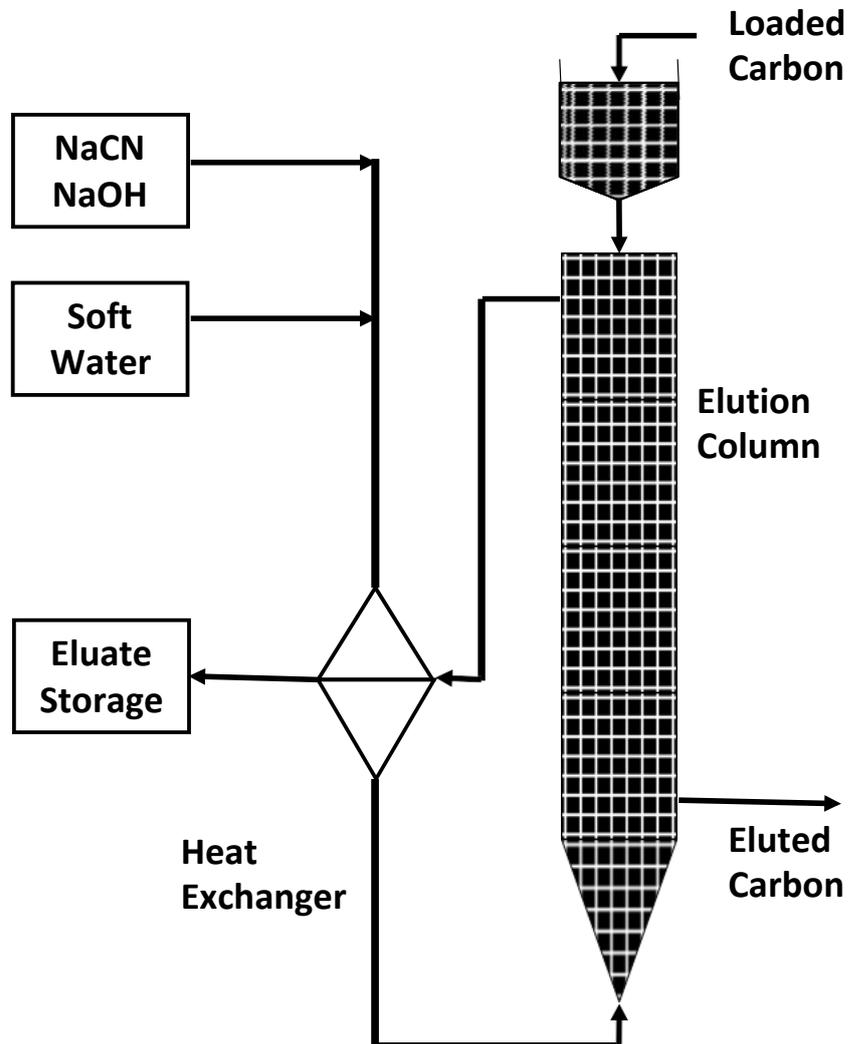


Figure 2.7: Flowsheet of AARL process

A description of the elution process as shown in Figure 2.7 follows. The column is loaded via gravity with gold-laden carbon. This is followed by washing the carbon with 1 bed volume of dilute (3% v/v) hydrochloric acid followed by 2 to 4 bed volumes of water. The acid wash, whose requirements depends on the calcium carbonate content is performed to remove entrapped foulants, including calcium from the surface and pores of the carbon (Davidson and Schmidt, 1986). Cold acid removes calcium and zinc whereas hot acid (90°C) will in addition remove nickel, iron and silica. The acid does not elute gold, silver or copper.

Davidson and Schmidt (1986) summarised the benefits of a hot acid wash as follows:

- (a) Removal of calcium carbonate which clogs the carbon pores thus hindering effective adsorption and elution.
- (b) A hot acid wash brings the elution system close to its ultimate operational temperature.
- (c) Acid washed carbon is less sensitive to the purity of the water used in the subsequent elution step.
- (d) It can be considered as the first step towards regeneration of the carbon.
- (e) Fewer impurities are transferred to the electrowinning circuit.

After the acid wash and water rinse, the acid washed carbon is pre-treated by soaking in one bed volume of caustic cyanide solution for 30 minutes. The cyanide concentration of the caustic cyanide solution depends mainly on the calcium carbonate content and is insensitive to gold loading of the carbon (Briggs, 1983). Finally, the gold is then eluted with 5 to 8 bed volumes of deionised water at 130°C. A plug flow of the eluant is preferred as this type of flow ensures maximum contact of the eluant with the carbon at each cross section of the column thus maximising desorption. The upward flow is usually used in industry to help minimise trapped carbon-dioxide gas produced during acid washing. The column is cooled at the end by using the final bed volume of the eluant at ambient temperature.

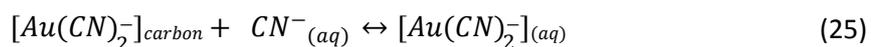
2.5.2 Zadra Elution

In the Zadra elution process, there is no cyanide pre-treatment step. The caustic cyanide eluant, first preheated to 120°C, is fed to the column containing non pre-treated gold loaded carbon. Upon leaving the column, the eluate is cooled to below ambient temperature in the heat exchangers. The cooled solution then gravitates to the electrowinning cells where gold is recovered from solution. The electrowinning cells are in series with the elution column. The solution from electrowinning is circulated back to the elution column.

2.5.3 Elution Mechanism

According to Van Deventer and Van der Merwe (1994), gold adsorption on carbon is thermodynamically reversible. Therefore, factors inhibiting adsorption will enhance elution.

Adams and Nicol (1986) suggested an elution mechanism that is based on the competitive adsorption of CN⁻ ions. According to their theory, free CN⁻ ions in solution compete with and eventually displace the Au(CN)₂⁻ from the carbon. Elution was proposed to occur according to the following equations (Tsuchida et al., 1984);



The mechanism was however dismissed by Van Deventer and Van der Merwe (1994) who proved that, the pre-treatment of the loaded carbon with a caustic cyanide solution, did not result in the presence of gold in the solution used for pre-treating the carbon. The authors hinted an elution mechanism based on the passivation of carbon particle as the more probable elution mechanism. Experimental work done by the authors using fresh and caustic cyanide pre-treated activated carbon, showed that fresh virgin activated carbon adsorbed gold better than treated carbon. It was suggested that, the lower absorptivity of the treated carbon was due to CN⁻ degradation which resulted in a passivating product on the surface of the carbon. The passivation layer in turn made the carbon less susceptible to adsorption thereby promoting gold elution (Van Deventer and Van der Merwe, 1994).

The most widely accepted elution mechanism is based on the modification of the functional groups found on the surface of the carbon. The mechanism as suggested by Adams and Fleming (1989), involves ionisation of the phenol group on the surface of the carbon by OH⁻ ions. This reaction results in a negative net charge of the carbon's surface which does not adsorb the aurocyanide ion pair. Additionally, the positively polarised carbonyl functional groups on the surface of the carbon react with CN⁻ ions increasing the negative charge on the surface of the carbon. The carbonyl functional group is one of the dominant groups found on the surface of the carbon.

Spectator cations (Mⁿ⁺) in solution modify the surface of the carbon by forming neutral Mⁿ⁺{Au(CN)₂⁻}_n rendering the carbon surface neutral (Van Deventer and Van der Merwe, 1994). The removal of these cations (Mⁿ⁺) is therefore important on the elution process.

2.5.4 Factors affecting elution of activated carbon

2.5.4.1 Temperature

Temperature is an important parameter in the effective elution of metals from activated carbon (Adams and Nicol, 1986; van Deventer and van der Merwe, 1993b). As mentioned previously, activated carbon adsorption of gold is an exothermic process. Therefore, an increase in the temperature of the eluant will significantly increase the desorption rate (Davidson and Duncanson, 1977; Van Deventer and Van der Merwe,

1993a). For the AARL elution process, the temperature of the caustic-cyanide pre-treatment step was also reported to have an effect on the elution efficiency (Davidson and Duncanson, 1977; Van Deventer and Van der Merwe, 1993a). The higher the temperature during the pre-treatment step, the faster the gold will desorb from the activated carbon.

It is postulated that the high temperatures used during elution alter the carbon surface making it less susceptible to adsorption. McDougall et al. (1980b) subscribed the beneficial effect of elevated temperature on the high solubility of the $\text{KAu}(\text{CN})_2$ complex in water at high temperatures (79°C) compared to low temperatures (22°C).

2.5.4.2 Pressure

Pressure in elution circuits should always be maintained above the vapour pressure of the eluant for satisfactory elution rates (Jeffrey et al., 2009). A high pressure when utilised has the advantage of shortening the elution duration required.

2.5.4.3 Cyanide (CN^-) and Hydroxide (OH^-) ions Concentration

A higher cyanide concentration enhances elution up to a maximum value beyond which any further increase will lead to a reduction in the elution rate. Adams and Nicol (1986) reported that the corresponding cyanide concentration where elution is at its maximum is 0.2 M. The ionic strength of the system has an effect on how the cyanide concentration affects the elution of gold from activated carbon. Sodium chloride salt (NaCl) is used to maintain a constant ionic strength in CIP circuits. At a constant ionic strength, an increase in cyanide and hydroxide concentration will increase the desorption kinetics (Van Deventer and Van der Merwe, 1994). Van Deventer and Van der Merwe (1994) dismissed displacement of the adsorbed $[\text{Au}(\text{CN})_2]^-$ by CN^- as the reason why cyanide enhances elution. The highest gold elutions were noted when most of the cyanide had been washed out of the system. The effect of cyanide far exceeded that of NaOH (about 10 times more) on the elution of gold from activated carbon (Adams, 1990; Van Deventer and Van der Merwe, 1994).

2.5.4.4 Ionic Strength

Increasing the ionic strength of the system results in a higher gold loading capacity of activated carbon (Adams, 1990). As mentioned earlier, divalent cations (Ca^{2+} and Mg^{2+}) enhances the loading capacity more significantly than monovalent cations (Na^+ and K^+) (Van Deventer and Van der Merwe, 1994). Therefore, elution, being the opposite of adsorption, is favoured by conditions of low ionic strength. This is the main

reason deionised water, which is void of dissolved salts, is effectively utilised to desorb gold from activated carbon in the AARL process.

2.5.4.5 Flow Rate

According to Adams (1990) and Van Deventer and Van der Merwe (1994), under strong pretreatment conditions coupled with high elution temperatures, the elution efficiency becomes independent of the flow rate of the eluant through the column. In investigating the effect of flowrate on the elution of carbon pre-treated with 3% potassium carbonate (K_2CO_3) and 1% potassium hydroxide (KOH), Davidson (1974) showed that, the elution peak decreased with increasing flow rate from 0.5 to 1.5 BV/h suggesting elution to be diffusion controlled under these conditions. A change in the flow rate of the eluate within a range of 1-5 BV/h after pre-treating the carbon with a caustic cyanide solution of 2% NaCN and 2% NaOH had insignificant differences on the effect on the desorption rate of gold (Davidson and Schmidt, 1986). Similar findings were reported by Van Deventer and Van der Merwe (1994) who investigated elution efficiency at flow rates of 2.9, 5.9 and 37 BV/h. Under these conditions, elution was suggested not to be diffusion controlled. Davidson and Schmidt (1986) suggested a 2 BV/h flow rate was suitable for an elution period of 8 hours.

2.5.4.6 Gold Concentration on Carbon

Various authors reported conflicting findings on the effect of carbon loading on elution. The higher the gold loading on the activated carbon, the faster the desorption kinetics according to Davidson and Duncanson (1977). Boshoff (1994) reported elution to be independent of carbon loading. Van Deventer and Liebenberg (2003) stated that, an increase in the gold concentration on the carbon increases formation of gold clusters which adsorb more strongly to the carbon, thus lowering elution efficiency.

2.5.4.7 Elution Column Design

The height to diameter ratio of the column is a crucial design factor of the elution column. The ratio affects the eluant flow pattern in the column and by default the solution distribution within the column. A high column height to diameter ratio is preferred as it yields higher elution efficiencies (Mular et al., 2002). When the height to diameter ratio is low, the distribution of fluid flow within the column becomes uneven. The most desired value in gold plants is a height to diameter ratio of 8:1, which corresponds to column dimensions of 1 meter diameter and 6-8 metres height. Upward rather than downward flow of solution through the column is ideal as it expands the carbon bed instead of compacting it. Carbon compaction hinders ideal fluid flow thus lowering elution efficiencies.

2.6 Conclusions and Significance of Literature Review

Chapter 2 considered glycine systems as viable alternatives in the processing of copper-gold ores. The systems offer potential technical and environmental advantages. The leaching of copper and gold with glycine has been proposed and progress into understanding the leaching mechanism has been made. A broad view of glycine, cyanide and a hybrid of glycine-cyanide leach systems is given. A review of activated carbon adsorption, which is suggested as a feasible metals recovery method from glycine solutions, then follows. Furthermore, the CIP process and its various components is described in detail. Factors affecting CIP plant performance and gold adsorption efficiencies are discussed. As activated carbon is the principal material of the CIP process, it was imperative to understand how it is manufactured, its structure and mechanisms with which it adsorbs gold as it is deemed all these have a bearing on its ultimate performance. The chapter concludes by giving an overview of the elution process, which is very critical for the development of an effective activated carbon adsorption plant for gold recovery.

The literature review has revealed that adsorption of metal complexes onto activated carbon is a thermodynamically reversible process which can occur via reduction, electrostatic attraction or decomposition of the gold cyanide complex. It has been established from literature that, factors that enhance gold adsorption will inhibit its desorption. Reviewed factors include temperature, oxygen concentration, ionic strength of solution, carbon particle size, fouling and presence of organic and inorganic compounds. Activated carbon has a highly porous structure both internally and externally. When in solution, carbon particles are surrounded by a hydrodynamic boundary layer through which gold diffuses from the solution to the external surface of the carbon. Adsorption of gold starts by saturation of the external surface of the carbon then diffusion into the inner pores once outer saturation is reached. Saturation was found to occur at high gold loadings of $25000 \text{ mg}_{\text{Au}}/\text{kg}_{\text{carbon}}$ and above. Fundamental research regarding adsorption process for glycine systems is lacking.

A discussion on the elution process revealed that the AARL elution was preferred over other elution techniques mainly due to its fast desorption kinetics. Gold desorption was suggested to possibly occur via two mechanisms; (i) modification of functional groups and (ii) displacement of the adsorbed gold by CN^- ions, with the former being more widely accepted among researchers. In AARL elution circuits, cyanide is introduced during the pre-treatment step while in the Zadra elution it constitutes part of the eluant. The discussed factors that affect elution of gold from activated carbon include, temperature, pressure, cyanide and hydroxide concentrations, ionic strength, column

design and flow rate of the eluant through the column. The presence of cyanide in the pre-treatment step of the AARL was found to aid elution of gold significantly. The feasibility of eluting gold loaded from pure glycine systems will be discussed in chapter 8 of this thesis. The studies are only preliminary and do not provide an in-depth investigation of how various factors, save for temperature of eluant, affect the process.

Sections 2.3-2.5 have reviewed literature on activated carbon adsorption and elution of gold. The discussions were based on the well-known and well researched cyanide process. Since a similar CIP and elution process are proposed for glycine systems, the literature review provided a fundamental understanding of the processes that will aid in a similar study for glycine based plants.

2.7 References

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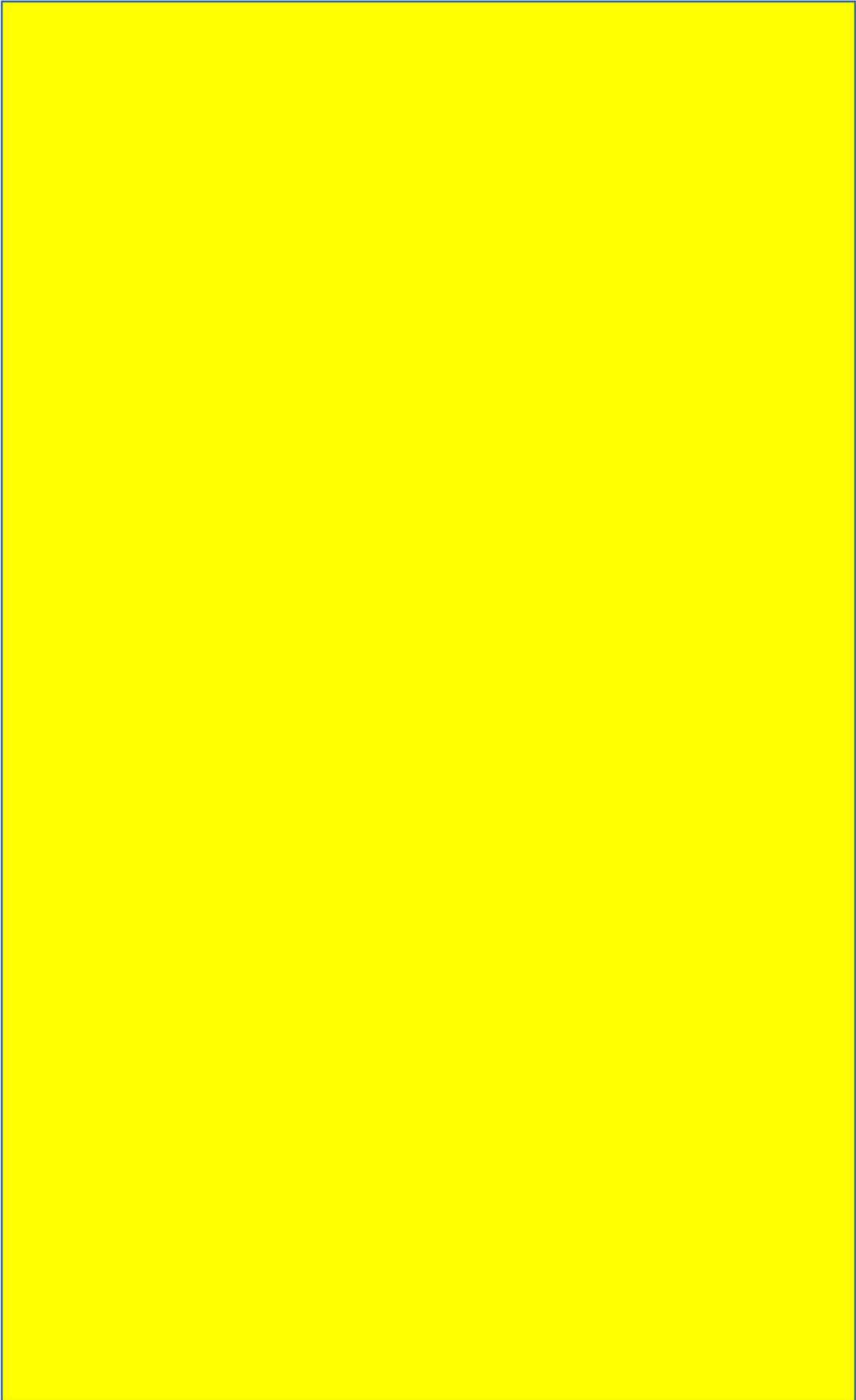
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3 Industrial Application of Glycine Leach Systems

Submitted for publication as:

Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores.

Eksteen, J.J., Oraby, E.A., Tanda, B.C., Tauetsile, P.J., Bezuidenhout, G.A., Newton, T., Trask, F. and Bryan, I., 2018.

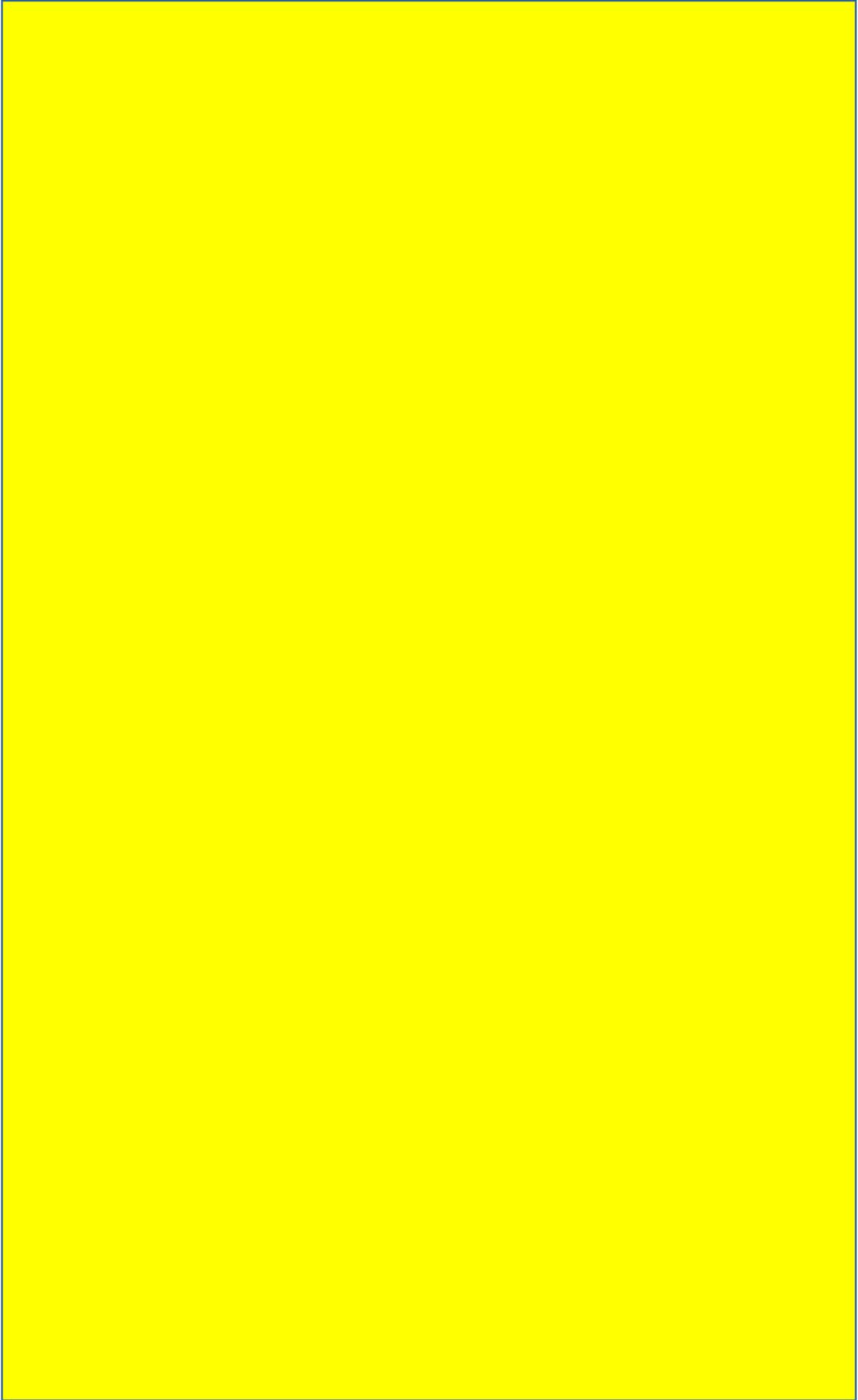
Canadian Metallurgical Quarterly, 57(4), pp.390-398.

Accepted for publication on 02nd Oct 2017.

Taylor & Francis Online.

Removed due to copyright restrictions.

DOI: <https://www.tandfonline.com/doi/full/10.1080/00084433.2017.1391736>



4 Adsorption Isotherms of Au from Alkaline Glycine Solutions containing Cu

Submitted for publication as:

Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 1: Isotherms

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2018.
Hydrometallurgy, 178, pp.202-208.

Accepted for publication on 21st April 2018.

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DOI: <https://www.sciencedirect.com/science/article/pii/S0304386X18301749>



Adsorption behaviour of copper and gold glycinate complexes in alkaline media onto activated carbon. Part 1: Isotherms



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ARTICLE INFO

Keywords:

Gold
Adsorption
Activated carbon
Glycine solutions

ABSTRACT

Alkaline glycine/glycinate solutions have been shown to have significant potential in the leaching of gold and copper from ores, concentrates, and wastes bearing these metals. An attempt was made to understand the adsorption behaviour of the gold glycinate complex onto activated carbon in the presence of copper for a pure alkaline glycine/glycinate system, after the gold has been dissolved using hydrogen peroxide as an oxidant and caustic soda as pH modifier. The adsorptive behaviour under various process conditions was evaluated using equilibrium loading isotherms. The linear regression (R^2) values for the Freundlich isotherm for all tested parameters are close to unity, suggesting the model to be well suited for gold glycinate adsorption onto activated carbon. The maximum adsorption capacity of the gold complex on the activated carbon was determined as a function of free glycine concentration, solution pH, initial gold and copper concentration and calcium chloride salt concentration using synthetic solutions. The adsorption capacity increased with increasing free glycine, copper and calcium chloride concentrations, but decreased with increasing solution pH and initial gold concentration. This information can be used (with adsorption kinetics) to design and evaluate Carbon-in-Pulp (CIP), Carbon-in-Leach (CIL) and Carbon-in-Column (CIC) circuits for gold when copper may be present.

1. Introduction

The increased interest in non-cyanide technology for gold ore processing can be attributed to a number of reasons. From an environmental perspective, cyanide is toxic, and the adverse environmental impacts resulting from its discharge have led to stringent jurisdiction regarding its usage (Eisler et al., 1999; Jeffrey et al., 2002). In some parts of the world, the use of cyanide for gold mining is prohibited while in other places approval for any gold cyanidation project is proving to be extremely difficult (Mudder and Botz, 2004). Geologically, due to the growing demand for gold, exploitation is shifting from cyanide-amenable ores to increasingly refractory or polymetallic ores, increasing the need for alternative processing routes (Hiskey and Atluri, 1988; La Brooy et al., 1994; Breuer et al., 2005; Dai et al., 2012; Jeffrey et al., 2002). Ammonia, thiocyanate, thiourea and thiosulfate are some of the alternative lixivants studied thus far (Pyper, 1981; Aylmore and Muir, 2001; Grosse et al., 2003; Molleman and Dreisinger, 2002; Rezai and Peikary, 2002; Muir and Aylmore, 2004). More recently, the ability of glycine to leach gold and gold-copper ores was shown by a number of researchers (Perea and Restrepo, 2018; Eksteen and Oraby, 2015;

Oraby and Eksteen, 2014; Eksteen et al., 2017a,b; Tanda et al., 2017; Barton et al., 2018). As a leaching agent, glycine has environmental, technical and economic advantages over cyanide. It is environmentally benign and stable, yet easily biologically destructible under neutral and mild acidic conditions, but quite stable compared to sodium cyanide under alkaline conditions. From an economic perspective, apart from it being cheaper than cyanide (the bulk cost of glycine and NaCN respectively is around USD 1000–1800 per tonne (FOB, Feed Grade glycine) versus USD 2000 - USD2500 per tonne (FOB, Industrial grade sodium cyanide, 98%)) at the time of writing and compared to many other alternative plausible lixivants, glycine can easily be recovered, regenerated and reused. Cyanide tends to convert to cyanate, thiocyanate, volatile HCN, and ferrocyanide, making recovery and reuse uneconomical in many cases. To reduce cyanide consumption of oxide gold-copper ores, these ores are conventionally first acid leached prior to neutralisation and cyanidation. However, being an alkaline leach, glycine leaching of gold ores is less susceptible to acid consuming gangue and co-leaching of Fe, Mn, Mg and Al (Eksteen and Oraby, 2015; Tanda et al., 2017). Glycine therefore allows the leaching of copper and gold at the same pH.

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<https://doi.org/10.1016/j.hydromet.2018.04.015>

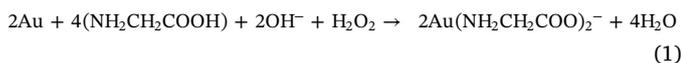
Received 25 February 2018; Received in revised form 12 April 2018; Accepted 21 April 2018

Available online 23 April 2018

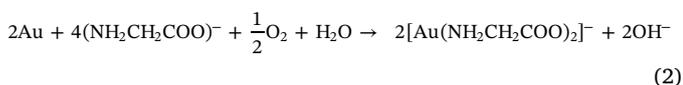
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The alkaline glycine system is characterised by simple chemistry (i.e. not prone to the side reactions as cyanide). Glycine, also known as aminoethanoic/aminoacetic acid, is the simplest neutral amino acid made up of one amine (–NH) and one carboxyl (COOH[–]) functional groups. It can, depending on solution pH, exist as either a glycinium cation (⁺H₃NCH₂COOH), a glycinate anion (H₂NCH₂COO[–]) or zwitterion (⁺H₃NCH₂COO[–]). In the glycine leach system, owing to the alkaline nature of the leach, at pH 10.5–11, the most predominant specie is the glycinate anion (Rega et al., 1998). The leaching process involves metal dissolution in a neutral to alkaline heated (23–60 °C) glycine solution in the presence of a soluble oxidant (Eksteen and Oraby, 2015). The oxidants successfully employed in previous studies include dilute hydrogen peroxide (Eq. (1)) and dissolved oxygen (Eq. (2)). The possible mechanism of gold dissolution in glycine has been proposed as:

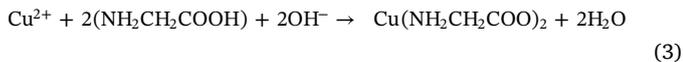
a) Using hydrogen peroxide as oxidant



b) Using oxygen as oxidant



The leaching behaviour of various copper oxide minerals in alkaline glycine systems has also been studied and is reasonably well understood. Results from studies indicate that, at optimum conditions (pH 11, glycine to copper molar ratio of 8:1), the copper extraction was over 80.0% for azurite, malachite and cuprite and < 20.0% for chrysocolla in 24 h. The copper complexing mechanism is shown in Eq. (3) (Tanda et al., 2017):



Methods for gold recovery from resultant polymetallic leachates include precipitation, ion exchange, solvent extraction and adsorption. Preliminary studies have confirmed that activated carbon adsorb gold glycinate complexes extremely well, possibly better compared to gold cyanide (Oraby and Eksteen, 2015). NaSH precipitation and solvent extraction were exploited for copper glycinate recovery and it was found out that it was possible to selectively recover over 99% copper using either method (Eksteen et al., 2016). Based on these results, activated carbon adsorption, currently being the main technique applied in cyanide systems for recovery of gold from cyanide leach liquors, is the starting point of our consideration for the newly developed glycine system. Industrially, it is preferred over other methods since it is cost effective, simple and has a high removal capacity owing to the large surface area of the carbon (Wan and Miller, 1990; Tu et al., 2011). Metals recovery from glycine leachates is still at an early stage and to date, fundamental understanding concerning the adsorption behaviour of metal glycinate complexes on activated carbon under different process conditions is lacking.

The interaction between an adsorbate and an adsorbent for any new system is best understood through the use of adsorption equilibrium information. Adsorption isotherms, their proper understanding and interpretation, are critical in the effective design and optimisation of any adsorption system. The Freundlich and Langmuir adsorption isotherms have been used to describe gold cyanide adsorption onto activated carbon from synthetic solutions with the former giving a much more accurate description of the equilibrium gold adsorption behaviour (Davidson, 1974; Cho et al., 1979). Previous studies have shown that these isotherms are well-suited for low concentration systems (Dixon

et al., 1976; Van Deventer, 1986; Woollacott, 1990) as encountered in most gold leaching operations from its ores. This is usually the case in the carbon-in-pulp (CIP) and the carbon-in-leach (CIL) processes, the two most dominant downstream processes used for gold extraction after cyanide leaching.

The main objective of the current study was to model the adsorption behaviour of metals onto activated carbon from a pure glycine system by generating isotherm parameters. The effects of pH, glycine concentration, ionic strength, initial gold and copper concentrations on the competitive loading of gold and copper glycinate complexes onto activated carbon are evaluated below.

2. Material and methods

2.1. Sorbent characterisation

The adsorbent used in this work was fresh activated carbon: PICA-GOLD® 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, mechanically sieved to –45 µm, 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 N₂BET method was 840.6881 ± 46.5496 m²/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/m²). The activated carbon is pulverised to reduce kinetic effects and allow the carbon to reach equilibrium as quickly as possible. The resultant isotherm results can then be used to calculate the theoretical amount of granular activated carbon needed to meet the treatment objectives industrially.

2.2. Adsorbates

All experiments were carried out using synthetic solutions prepared from Millipore water and analytical grade reagents. The gold glycinate solution was prepared by leaching a 24 ct (99.99%) gold sheet (10 cm × 2.5 cm × 0.03 cm) supplied by A&E Metals in an alkaline glycine solution. Gold dissolution was done in a glass beaker which contained 15 mL hydrogen peroxide (30% w/v, Rowe Scientific), 15 g/L glycine (> 99%, Sigma-Aldrich) dissolved in 500 mL of distilled water and buffered to a pH of 11 by adding NaOH (ThermoFisher Scientific). The alkaline solution was heated to 60 °C and stirred at 400 rpm using Teflon coated magnetic stirrer bars. The beaker was covered to prevent evaporation. Copper was added to the prepared gold glycinate solution as CuSO₄·5H₂O (Asia Pacific Specialty Chemicals).

2.3. Adsorption experiments

The traditional bottle-on-rolls method was employed for the metal glycine 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 (approx. 23 °C). The development of equilibrium isotherms was effected by contacting weighted samples of 0.040, 0.128, 0.256, 0.404 and 0.640 g/L powdered activated carbon with 250 mL of gold and copper synthetic solution. The initial pH of the solutions was adjusted to 11 and controlled during the experiments by using NaOH or H₂SO₄. The mixture was bottle rolled for 24 h at 105 rpm. Preliminary tests indicated that 24 h was sufficient to reach equilibrium conditions. When equilibrium 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 metal concentration in solution was determined by atomic adsorption spectrophotometry by using an Agilent 55B AAS.

3. Results and discussion

3.1. Freundlich isotherm

The experimental adsorption data on activated carbon for gold at temperature range from 22 °C to 25 °C and equilibrium pH 11 was fitted to the Freundlich model which is defined by Eq. (4) below:

$$Q_e = kC_e^n \tag{4}$$

where Q_e (mg g⁻¹) and C_e (mg L⁻¹) represent quantity of adsorbate per unit mass of the adsorbent and concentration of adsorbate in solution respectively at equilibrium (Juarez and Oliveira, 1993). Empirical constants k and n , derived from the intercept and slope of the linear plot of $\log Q_e$ vs $\log C_e$, are reflective of adsorption equilibrium gold loading capacity and adsorption intensity or surface heterogeneity respectively (Cermakova et al., 2017). A value of $1/n$ below unity is indicative of chemisorption while above one indicates cooperative adsorption (Haghseresht and Lu, 1998).

3.2. Effect of glycine concentration

The carbon adsorption capacity of the gold glycinate complex at different free glycine concentrations but otherwise identical conditions was explored and the resultant isotherms are shown in Fig. 1. The corresponding Freundlich constants were computed and are given in Table 1. Generally, the loading capacity of gold on carbon increases with increasing glycine concentration. As reflected by the k values in Table 1, an increase in glycine concentration from 5 g/L to 10 g/L increased the adsorption capacity significantly. However, outside this concentration bracket, the glycine concentration sensitivity is lost as the gold adsorption capacity is practically the same for concentrations below and above 5 and 10 g/L respectively. This result is an indication that, unlike is the case with cyanide, the free glycine species does not have a deleterious effect as it does not appear to adsorb and compete for adsorption sites on the carbon. This is an added advantage as leaching systems are expected to contain an excess of free glycine.

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 | 24.6 | 2.93×10^{-5} | 0.7304 | 0.8705 |
| 5 | 21.6 | 2.57×10^{-5} | 0.5923 | 0.8737 |
| 10 | 34.2 | 4.06×10^{-5} | 0.8038 | 0.9697 |
| 15 | 33.9 | 4.03×10^{-5} | 0.8244 | 0.9838 |

3.3. Effect of solution pH

The pH range for alkaline glycine leaching which results in practical significance is 9–12 with gold leaching maximised at pH 11 (Oraby and Eksteen, 2015). The effect of pH on the adsorption of gold glycinate onto activated carbon was therefore studied within this range at pHs 9, 10, 11 and 12. pH adjustment was done by addition of sodium hydroxide with other parameters kept constant. The loading isotherms shown in Fig. 2 confirm that the loading capacity of the gold complex in glycine systems is affected by solution pH. Overall, an increase in pH decreases the loading capacity with optimal adsorption observed at pH 10 as shown by k values listed in Table 2. A decrease in the loading capacity of gold by increasing pH can be explained by the reduction of active sites on the carbon due to the increased concentration of hydroxide ions. Hydroxide ions adsorb fairly strongly onto activated carbon (Davidson, 1974). At higher pH values more hydroxide anions and the metal glycinate complexes compete for active sites on the carbon thereby retarding gold adsorption. The solution pH is also known to affect the properties of the adsorbent (Nouri et al., 2002). From the results, it can be inferred that the optimal pH for the adsorption of gold glycinate species is pH 10. The surface groups of the activated carbon can be protonated or not (i.e. positively or negatively charged on average) depending on the equilibrium solution pH. The variation on the net surface charge consequently affects the electrostatic attraction and adsorption of metal species onto activated carbon. In the presence of copper, gold glycinate-carbon surface interaction is favoured and maximised between pH 9 to 10.

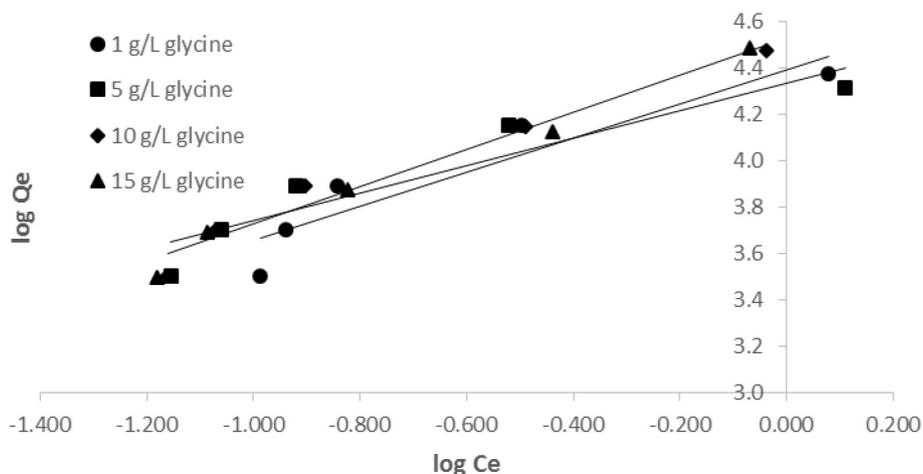


Fig. 1. Adsorption isotherms for gold glycinate complex on carbon as a function of glycine concentration (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 40 ppm, pH 11, 23 °C, 24 h contact time.

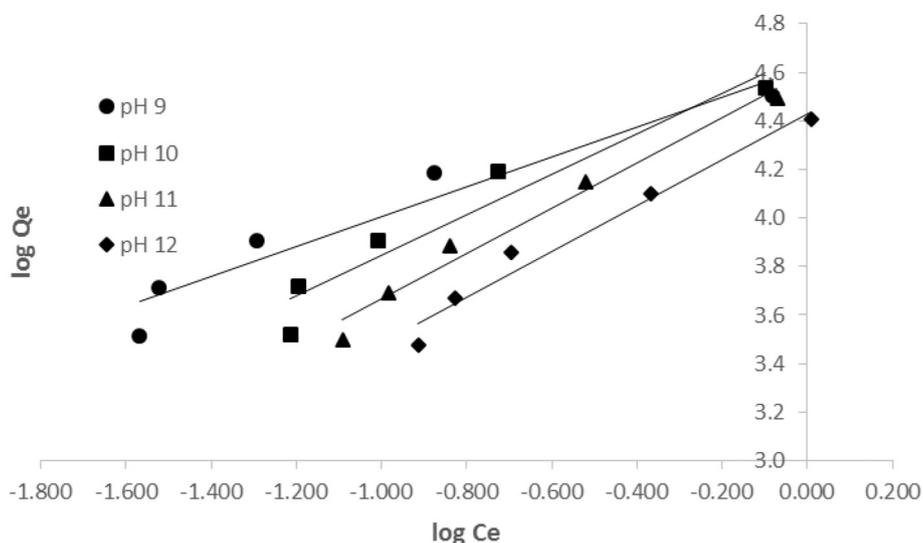


Fig. 2. Adsorption isotherms for gold glycinate complex on carbon as a function of solution pH (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 40 ppm, [Gly] 5 g/L, 23 °C, 24 h contact time.

Table 2
Numerical Freundlich isotherm constants at various solution pHs for gold.

| pH | Freundlich k | | n | R ² |
|----|--------------|-------------------------|--------|----------------|
| | (kg/t) | g/m ² | | |
| 9 | 41.8 | 4.97 × 10 ⁻⁵ | 0.6139 | 0.9297 |
| 10 | 47.8 | 5.68 × 10 ⁻⁵ | 0.8321 | 0.9289 |
| 11 | 39.6 | 4.71 × 10 ⁻⁵ | 0.9342 | 0.9772 |
| 12 | 27.0 | 3.21 × 10 ⁻⁵ | 0.9458 | 0.9685 |

Table 3
Numerical Freundlich isotherm constants for gold adsorption on activated carbon.

| Initial gold conc | Freundlich k | | n | R ² |
|-------------------|--------------|-------------------------|--------|----------------|
| | ppm | (kg/t) | | |
| 2 | 39.6 | 4.71 × 10 ⁻⁵ | 0.9342 | 0.9772 |
| 4 | 20.6 | 2.45 × 10 ⁻⁵ | 0.7190 | 0.9709 |
| 8 | 15.8 | 1.88 × 10 ⁻⁵ | 0.6688 | 0.9475 |
| 16 | 14.0 | 1.67 × 10 ⁻⁵ | 0.5689 | 0.9510 |

3.4. Effect of initial gold concentration

Fig. 3 displays gold adsorption isotherms obtained at various initial gold concentrations. It can be seen that as the initial gold concentration increases from 2 to 16 ppm, the isotherms show progressively lower gold loading capacity. This observation is reflected by the k values as

seen in Table 3. This trend is inconsistent with that of a pure cyanide system. For a pure cyanide system, gold loading capacity was found to increase with increasing gold concentration in solution (Marsden and House, 2006). A similar trend was however observed with the thio-sulphate ammoniacal system where an increase in the initial gold

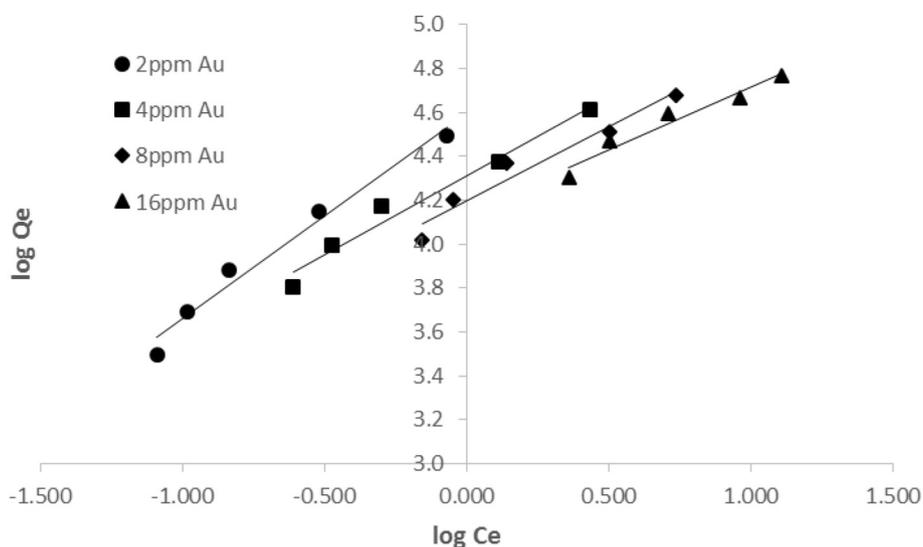


Fig. 3. Adsorption isotherms for gold glycinate complex on carbon as a function of initial gold concentration (Freundlich model). Initial [Cu] 40 ppm, [Gly] 5 g/L, pH 11, 23 °C, 24 h contact time.

concentration decreased the percentage of gold adsorbed onto carbon (Navarro et al., 2006). The authors stated that this behaviour was possibly due to insufficient active sites on carbon that can increase loading proportionately to the increasing gold concentration in solution. Another interesting observation from Fig. 3 is that as the concentration of gold increases, the isotherm is shifted to the right. This is coupled with a significant decrease in the slope. This implies that the adsorption is better suited to leaching from ores rather than concentrates, due to the lower metal concentrations after leaching.

3.5. Effect of initial copper concentration

Cu^{2+} ions were found to significantly enhance gold dissolution in alkaline glycine peroxide systems (Eksteen and Oraby, 2015). Copper is normally present as one of the three major copper-glycine species, $\text{Cu}(\text{H}_2\text{NCH}_2\text{COO})_2$, $\text{Cu}(\text{H}_2\text{NCH}_2\text{COO})_2^-$, $\text{Cu}(\text{H}_2\text{NCH}_2\text{COO})^+$ (Aksu and Doyle, 2001). The influence of copper on gold loading capacity onto activated carbon was determined at various copper concentrations and the loading isotherms are depicted in Fig. 4. There is a notable increase in the gold loading as the copper concentration increases with an intermediate loading maximum observed at a copper concentration of 20 ppm as reflected by the k values in Table 4. This behaviour might be explained by the difference in stability of the gold and copper glycine complexes. The copper glycine complex is significantly stronger ($\log K = 15.6$) and more stable than the gold glycine complex ($\log K = 1.26$) (Aksu and Doyle, 2001; Oraby and Eksteen, 2015). This means that glycine has an affinity for copper over gold. This implies if there is copper adsorbed on carbon and sufficient free glycine in the system, the copper may be eluted back into the bulk of the solution and be replaced by the gold. This contention is further supported by preliminary studies on elution which confirmed that glycine does not elute the gold from carbon but can elute a portion of the copper. Also, the strength of the bond between the gold and carbon is much stronger than that between the copper and carbon making gold detachment from carbon much more difficult.

Table 4
Numerical Freundlich isotherm constants for gold glycinate complex at varying initial Cu concentrations.

| Initial Cu conc | Freundlich k | | n | R^2 |
|-----------------|----------------|-----------------------|--------|--------|
| | ppm | (kg/t) | | |
| 0 | 26.6 | 3.16×10^{-5} | 0.7333 | 0.9361 |
| 20 | 46.5 | 5.53×10^{-5} | 0.941 | 0.951 |
| 40 | 39.6 | 4.71×10^{-5} | 0.9342 | 0.9772 |
| 80 | 39.2 | 4.67×10^{-5} | 1.2019 | 0.9209 |
| 800 | 37.6 | 4.47×10^{-5} | 1.1181 | 0.9577 |

3.6. Effect of Ca^{2+}

Salts of calcium are known to enhance adsorptive capacity of adsorbents, including that of activated carbon (Randtke and Jepsen, 1982). To study the effect of Ca^{2+} on the adsorptive capacity of activated carbon for gold glycine complexes, adsorption was determined at various concentrations of calcium chloride (See Table 5). As can be seen from Fig. 5, the presence of Ca^{2+} in solution as CaCl_2 affects the adsorption capacity of gold onto carbon. The results indicate that the adsorptive capacity is enhanced by increasing concentrations of calcium. Presence of cations in solution are said to improve adsorption in one of the following three ways (Randtke and Jepsen, 1982):

Table 5
Numerical Freundlich isotherm constants for gold adsorption at varying Ca^{2+} concentrations.

| CaCl_2 conc | Freundlich k | | n | R^2 |
|----------------------|----------------|-----------------------|--------|--------|
| | (g/L) | Kg/t | | |
| 0.0 | 39.6 | 4.71×10^{-5} | 0.9342 | 0.9772 |
| 0.5 | 42.2 | 5.02×10^{-5} | 0.8244 | 0.9813 |
| 2.0 | 49.8 | 5.92×10^{-5} | 0.7927 | 0.9905 |

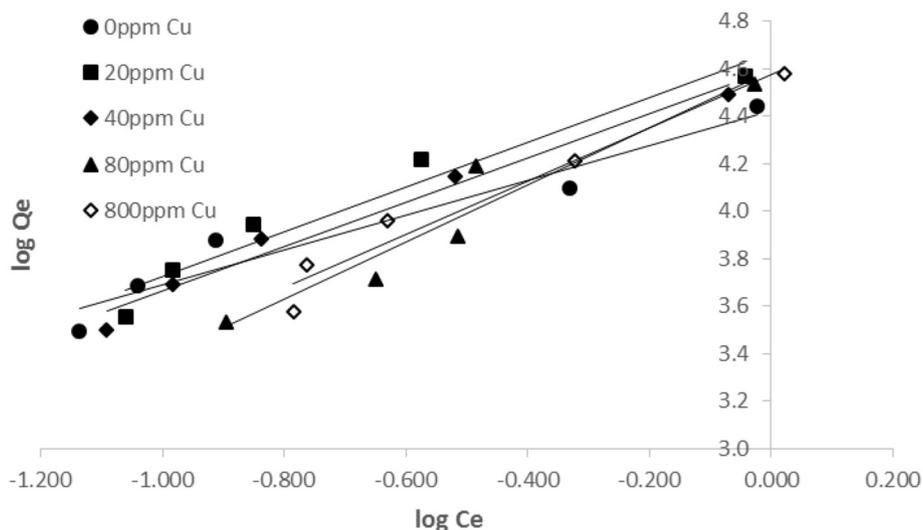


Fig. 4. Adsorption isotherms for gold glycinate complex on carbon as a function of initial copper concentration (Freundlich model). Initial $[\text{Au}]$ 2 ppm, $[\text{Gly}]$ 5 g/L, pH 11, 23 °C, 24 h contact time.

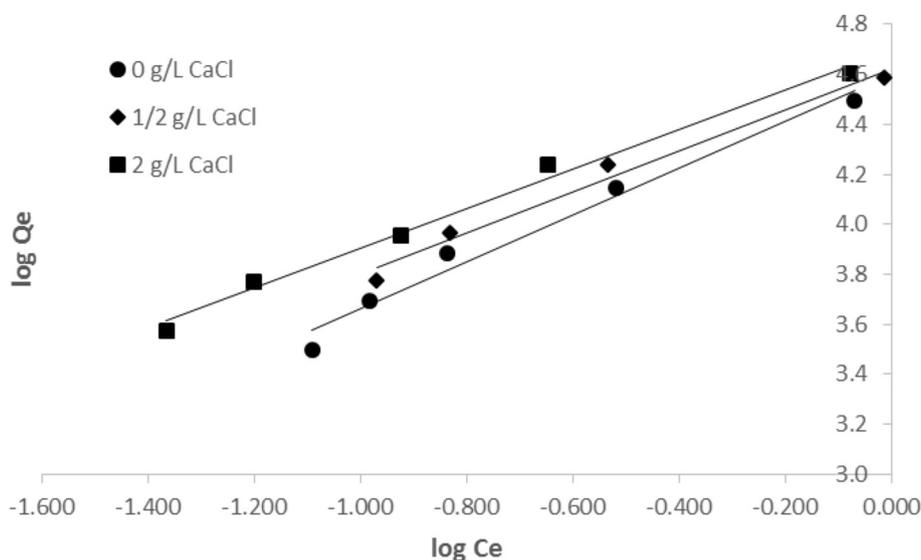


Fig. 5. Adsorption isotherms for gold glycinate complex on carbon as a function of ionic solution strength (Freundlich model). [Gly] 2 g/L, Initial [Au] 2 ppm, Initial [Cu] 40 ppm, [Gly] 5 g/L, pH 11, 23 °C, 24 h contact time.

- Interaction of the cation and functional groups on the adsorbent surface resulting in the neutralisation of repulsive forces between adsorbate and adsorbent and possible creation of new and or favourable active adsorption sites.
- Interaction of the cation with the already adsorbed species possibly resulting in the rearrangement of the packing and alignment of the adsorbed species.
- Interaction of the cation salt with the adsorbate prior to adsorption likely resulting in the alteration of the solubility of the adsorbate.

4. Conclusions

The adsorption isotherms of gold complexes onto activated carbon from alkaline glycine solutions containing copper were studied and modelled using the Freundlich isotherm model. A summary of the results is given below:

- Increasing the glycine concentration up to 10 g/L increases the carbon loading significantly. Above 10 g/L free glycine concentration, the carbon loading capacity is not greatly affected by glycine concentration in solution.
- Increasing the pH from 10 through 11 to 12 decreased the carbon loading capacity due to increased hydroxide ions which compete with gold complexes for active sites on the carbon. pH value that gave the highest gold loading is 10.
- High initial gold concentration lowered the carbon's adsorption capacity. Increasing the initial gold concentration from 2 to 16 ppm reduced the adsorption capacity of the carbon by over 50%.
- Surprisingly, the gold loading capacity of the carbon increased with increasing copper concentration in solution, up to a maximum after which a small decrease was noted. Instead of copper competing for adsorption sites with gold on the carbon, it somehow enhances gold adsorption.
- A higher ionic strength increased the carbons loading capacity for gold glycinate complexes.

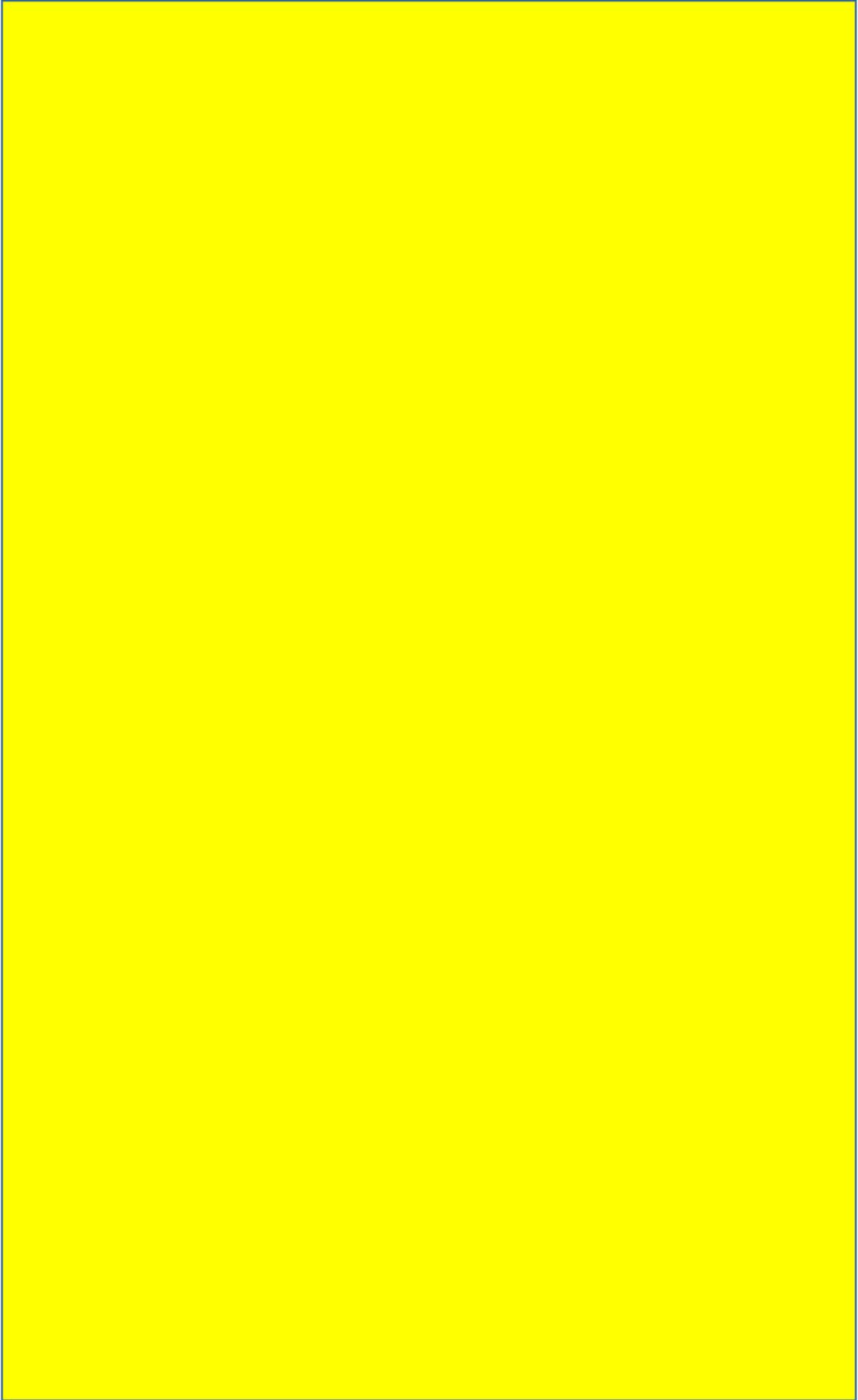
Acknowledgements

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

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5 Adsorption Kinetics of Au and Cu from Alkaline Glycine Solutions

Submitted for publication as:

Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 2: Kinetics

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2018.
Hydrometallurgy, 178, pp.195-201.

Accepted for publication on 21st April 2018.

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DOI: <https://www.sciencedirect.com/science/article/pii/S0304386X18301750>



Adsorption behaviour of copper and gold Glycinates in alkaline media onto activated carbon. Part 2: Kinetics



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ARTICLE INFO

Keywords:

Gold
Copper
Activated carbon
Adsorption
Kinetics
Glycine solutions

ABSTRACT

The kinetics for the competitive adsorption of gold and copper onto activated carbon from synthetic alkaline glycine solutions was studied. The adsorption rate for both gold and copper at the initial stage was modelled using the Fleming k_n adsorption kinetic model. The coefficient of variation (R^2) of the model were close to unity for both gold and copper adsorption data. The effects of pH, free glycine, ionic strength, initial gold and copper concentrations and carbon concentration were assessed on the adsorption kinetics of these two metals. The results showed that > 98% of gold was adsorbed onto activated carbon in 6 h or less under all studied conditions. According to the adsorption tests results, carbon concentration is the only parameter that significantly affected the initial gold adsorption rate. For all other studied parameters, the initial adsorption rate is quite robust, with a few variations in process conditions only affecting it slightly. Activated carbon was found to be very selective for gold glycinate complexes over copper glycinates, with over 99.0% gold adsorbed in 24 h and < 15% copper adsorbed in the same duration under optimum conditions from a solution containing 2 ppm gold and 40 ppm copper.

1. Introduction

The two main technologies used for the concentration and purification of alkaline cyanide leach liquors are the carbon-in-pulp (CIP) and carbon-in-leach (CIL) processes. These processes have been described in detail by several authors (Dahya and King, 1983; Laxen, 1984; Nicol, 1984; Stange, 1999). Both these technologies use activated carbon, a highly porous carbonaceous adsorbent with a large internal surface area and consequently high adsorption capacity. The CIP process, the most commonly used process, accounts for 80% of the world's total gold production. Commercially it is suited for processes requiring removal of small amounts of gold (2 ppm) (McDougall et al., 1980). One of the main advantages of the recently developed alkaline glycine system for gold ore leaching is the ability of the gold glycinate complex to effectively adsorb onto activated carbon (Tauetsile et al., 2018; Oraby and Eksteen, 2015). This renders the existing well established CIP and CIL processes useful for the new alkaline glycine system. The impetus for developing the glycine alkaline leach system, as is the case with other studied cyanide alternative lixiviants, is the increasing practical difficulties and environmental concerns arising from usage of cyanide for gold extraction from copper gold ores. The adsorption isotherms for gold-copper glycinate systems have been recently studied

(Tauetsile et al., 2018), but an investigation of the adsorption kinetics of these systems has not been presented to date.

The reaction rate of an adsorption process is one of the most critical evaluation element used during process operation design of an adsorption circuit. This parameter can be enumerated from kinetic experiments analysis. Activated carbon is known to have a complex structure including a surface with heterogeneous properties and pores with a wide variety of size ranges. The rate of reaction is dependent on both the chemical properties of the carbon surface and the pore distribution of the carbon structure. The surface of the carbon is made up of different functional groups formed from heteroatoms such as nitrogen, oxygen, hydrogen and sulphur (Shafeeyan et al., 2010). Oxygen containing groups like carboxylic acid groups and hydroxyl groups make up most of the outer surface also known as the basal plane of the activated carbon (Boehm, 1994; Mattson and Mark, 1971; Puri, 1970). Adsorptive behaviour of activated carbons is to a great extent influenced by the nature of the complexes present on the surface (Otake and Jenkins, 1993). The porous and large internal surface area of the carbon is ascribable to the presence of pores whose size and shape differs substantially. The pores are classified into one of the following three groups depending on the size of their diameter; macropores (> 50 nm), mesopores (2–50 nm) and micropores (< 2 nm) (Daud and Ali, 2004).

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<https://doi.org/10.1016/j.hydromet.2018.04.016>

Received 25 February 2018; Received in revised form 12 April 2018; Accepted 21 April 2018

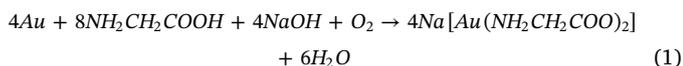
Available online 23 April 2018

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Coconut shell based activated carbon, the most preferred carbon for CIP and CIL circuits, has the majority of its internal structure characterised by fine pores of radius < 1 nm thereby exhibiting a high internal surface area and by default high adsorption capacity (Hashimoto et al., 1979).

The overall rate of gold adsorption onto activated carbon is believed to be controlled by three major mechanisms: 1) film diffusion: mass transport of gold (I) complex from the bulk of the solution through the hydrodynamic boundary layer encircling the carbon particle. This is a very rapid process; 2) pore diffusion: mass transport of the dissolved gold complex from the solution filling the pores onto the active sites of the carbon; and 3) surface diffusion; migration of the already adsorbed gold complex along the internal walls from the macropores into the micropores (Demopoulos and Cheng, 2004; Jones et al., 1989; Le Roux et al., 1991; Nicol, 1984).

Adsorption by carbon is the proposed method for gold recovery from glycine leach liquors. In the presence of a soluble oxidant like hydrogen peroxide, at moderate to slightly elevated temperatures (23–60 °C), gold can be leached by glycine at neutral to alkaline pHs to form a gold glycinate complex. Using caustic as a pH modifier, the stoichiometry of gold dissolution in alkaline glycine solution is as shown in Eq. (1) (Eksteen and Oraby, 2015):



In addition to containing gold glycinate complexes, leach liquors of pure glycine system are envisaged to contain high concentrations of glycine copper complexes as Cu^{2+} ions play a strong catalytic role during the leaching process (Eksteen and Oraby, 2015). Moreover, copper is often present as a nuisance element or a metal of economic value and can be therefore also leached (Eksteen et al., 2017a; Eksteen et al., 2017b; Tanda et al., 2017; Oraby and Eksteen, 2014). A sound knowledge of the mechanisms governing the adsorption of these metal complexes on carbon is of outmost importance as it will allow optimum usage of the carbon during solution purification. However a study is still needed to improve knowledge on the adsorption of the gold glycinate complex. The objective of this paper is to investigate the competitive adsorption kinetics of gold and copper in a pure alkaline glycine system under different experimental conditions. Factors whose influence was studied on the adsorption kinetics of these two metals include pH, free glycine concentration, initial gold and copper concentrations and ionic strength of the solution. A kinetic model was also used to fit the experimental data and the corresponding constants evaluated.

2. Materials and methods

2.1. Sorbent characteristics

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 894.1286 ± 46.6926 m²/g.

2.2. Adsorbates

Gold glycinate solutions were prepared by leaching a 24ct (99.99%) gold sheet (10 cm × 2.5 cm × 0.03 cm) supplied by A&E Metals in an alkaline glycine solution. The leaching solution was prepared by adding 15 mL hydrogen peroxide (30% w/v, Rowe Scientific) and 15 g/L glycine (> 99%, Sigma-Aldrich) to 500 mL of millipore water. The solution was then buffered to pH 11 using NaOH (ThermoFisher Scientific). In a beaker, the solution containing the gold sheet was then heated to

60 °C and stirred at 400 rpm using teflon coated magnetic stirrer bars. The temperature was maintained at 60 °C throughout the leach process. The beaker was covered to prevent evaporation. Copper was added to the gold glycinate solution as $CuSO_4 \cdot 5H_2O$ (Asia Pacific Specialty Chemicals). All used reagents were of analytical grade.

2.3. Adsorption experiments

Loading tests were performed with the sized fresh carbon to provide a carbon concentration of 2 g/L (0.4 g carbon in 200 ml of solution). The solution contained an initial gold and copper concentration of 2 mg l⁻¹ and 40 mg l⁻¹, respectively unless otherwise stated. The traditional bottle-on-rolls method was used for the experiments. The experimental runs were carried in sealed 2.5 L 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 0.22 μm 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 Agilent 55B AAS model atomic adsorption spectrometer.

3. Results and discussion

3.1. Adsorption kinetic model

The adsorption results for both copper and gold were modelled using the Fleming M, (1984) k,n method. The Fleming k,n method is the first carbon adsorption model published for gold adsorption. It is defined as:

$$\Delta Auc = k \times Aus \times t^n \quad (2)$$

where k and n are model parameters. k is the kinetic or rate constant (h^{-1}), n is a model parameter representing the adsorption strength, t is the adsorption time (h), Aus is gold (or metal) in solution (ppm) at time t , ΔAuc is gold metal (ppm) adsorbed on carbon from $t = 0$ up to a certain time t (ppm). The linearized form of the equation is:

$$\ln\left(\frac{\Delta Auc}{Aus}\right) = \ln k + n \ln t \quad (3)$$

In the following sections, the adsorption kinetics of gold and copper were conducted in an alkaline glycine solution containing 2 ppm Au and 40 ppm Cu at pH 11. The effects of glycine concentration, pH, initial gold and copper concentration, carbon concentrations and ionic strength are evaluated below.

3.2. Effect of free glycine concentration

Adsorption kinetic tests for the competitive loading of Au and Cu from a alkaline glycine solutions at glycine concentrations of 1, 5, 10 and 15 g/L were performed. The results are presented in Fig. 1. According to Fig. 1(a), overall Au adsorption recoveries are insensitive to free glycine concentration, with over 99% recovered in the first six hours at various glycine concentrations. For copper, as can be seen from Fig. 1(b), the higher glycine concentration suppresses copper adsorption. However, the dependence of copper adsorption on free glycine concentration is significant between glycine concentrations of 1 and 5 g/L. Beyond 5 g/L glycine concentration, the copper adsorption suppression though observed is not remarkable. This result may be because at high glycine concentration, $Cu(Gly)_3^-$ which has a less affinity for carbon than $Cu(Gly)_2$ is formed. At concentrations of 5 g/L glycine and beyond, copper may be present as $Cu(Gly)_3^-$ hence no effect of glycine beyond 5 g/L glycine concentration. According to Table 1, the model parameter k is slightly higher at 5 g/L glycine for gold. Generally, the adsorption rate is quite insensitive and doesn't depend much on

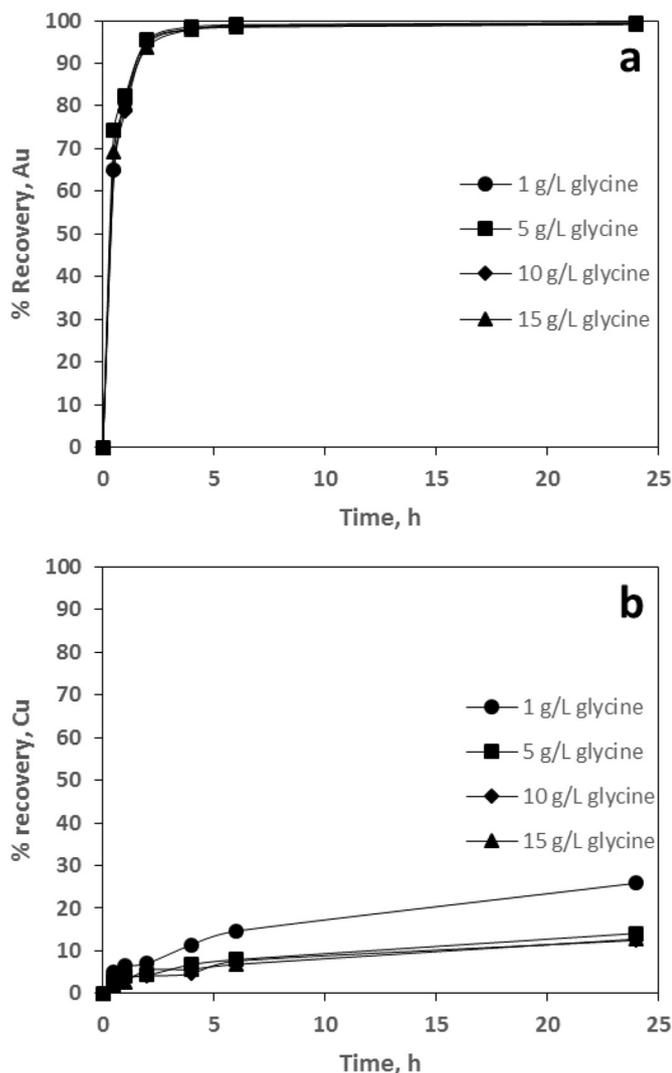


Fig. 1. Adsorption of Au (a) and Cu (b) in glycine solutions at different glycine concentrations ([Au] 2 ppm, [Cu] 40 ppm, pH 11, [Carbon] 2 g/L, 23 °C, 24 h contact time).

Table 1
Fleming Kinetic model constants for Au and Cu at different free glycine concentration.

| Glycine Conc (g/L) | k (h^{-1}) | | n | | R^2 | |
|--------------------|------------------|------|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 1 | 2696.8 | 34.5 | 1.7 | 0.4 | 0.99 | 0.92 |
| 5 | 3491.1 | 20.4 | 1.6 | 0.4 | 0.97 | 0.92 |
| 10 | 2509.9 | 18.3 | 1.6 | 0.2 | 0.98 | 0.94 |
| 15 | 2756.3 | 16.0 | 1.5 | 0.6 | 0.98 | 0.91 |

solution concentration of glycine for gold. For copper, increased glycine concentration decreases the adsorption rate. Another reason why there is less copper recovered at high glycine concentrations.

3.3. Effect of solution pH

Adsorption kinetic curves of gold and copper are shown in Fig. 2(a) and (b). The adsorption kinetics were studied at pH 9, 10, 11 and 12. As can be seen, almost 100% of the gold and < 10% of the copper was adsorbed (recovered) in 6 h for all pH values. Extending the adsorption time increases copper adsorption but does nothing to gold adsorption.

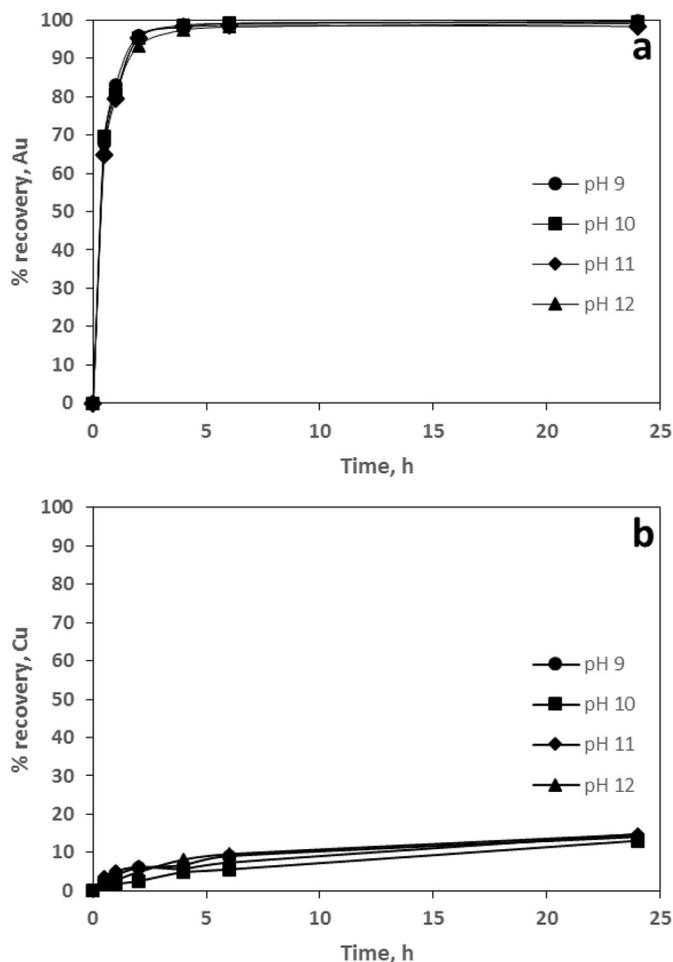


Fig. 2. Adsorption of Au (a) and Cu (b) in glycine solutions at different pH levels ([Au] 2 ppm, [Cu] 40 ppm, [Glycine] 5 g/L, [Carbon] 2 g/L, 23 °C, 24 h contact time).

Table 2
Fleming Kinetic model constants for Au and Cu at different solution pHs.

| pH | k (h^{-1}) | | n | | R^2 | |
|----|------------------|------|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 9 | 3111.2 | 21.5 | 1.6 | 0.4 | 0.98 | 0.96 |
| 10 | 3078.6 | 10.9 | 1.7 | 0.5 | 0.97 | 0.91 |
| 11 | 2657.5 | 25.4 | 1.7 | 0.2 | 0.98 | 0.75 |
| 12 | 2494.0 | 16.5 | 1.4 | 0.7 | 0.99 | 0.98 |

This suggests focus should be on short adsorption times, which is ideal for carbon-in-pulp systems which run with big leach tanks reactors but small adsorption times. As can be inferred from Table 2, the initial rate constant k for gold decreases with increasing pH. This is to be expected as an increase in pH means an increase in hydroxide ions and hence increased competition for active adsorption sites which are known to strongly adsorb onto activated carbons (Davidson, 1974). The pH for all experiments was adjusted by addition of sodium hydroxide.

3.4. Effect of initial gold concentration

Fig. 3 shows the effect of initial gold concentration on the competitive adsorption of gold and copper glycines onto activated carbon. From Fig. 3(a), it is apparent that, in all cases, after 4 h, the rate of gold loading slowed down considerably. Almost 100% gold was recovered within 6 h for 2, 4 and 8 ppm initial gold concentrations implying gold

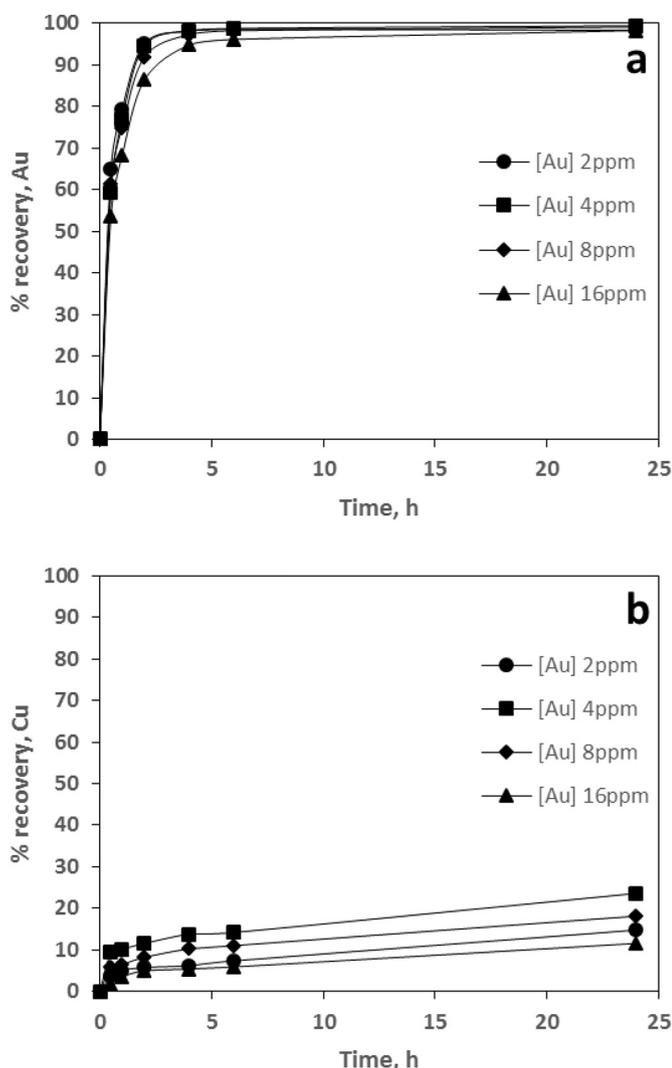


Fig. 3. Adsorption of Au (a) and Cu (b) in glycine solutions at various initial gold concentrations ([Cu] 40 ppm, [Glycine] 5 g/L, [Carbon] 2 g/L, pH 11, 23 °C, 24 h contact time).

Table 3
Fleming Kinetic model constants for Au and Cu for different initial gold concentrations.

| Initial Au Conc (ppm) | k (h^{-1}) | | n | | R^2 | |
|-----------------------|------------------|------|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 2 | 2657.5 | 25.2 | 1.7 | 0.3 | 0.98 | 0.90 |
| 4 | 2281.0 | 59.7 | 1.8 | 0.2 | 0.99 | 0.97 |
| 8 | 2000.8 | 37.6 | 1.6 | 0.3 | 0.98 | 0.98 |
| 16 | 1324.2 | 15.9 | 1.4 | 0.6 | 0.99 | 0.89 |

recovery is independent of initial gold concentration at gold concentrations of 8 ppm and below. There is no obvious trend with copper adsorption as seen in Fig. 3(b). At 2 ppm gold, the copper adsorption is low. Highest copper is recovered at an initial gold concentration of 4 ppm. At 16 ppm, the copper recovery is lowest. This may be explained by increased competition between copper and gold at high gold concentrations. Since activated carbon has a higher affinity for gold than copper glycinate complexes, increasing the gold concentration increases the rate of ion exchange mechanism between copper glycinate and gold glycinate. Copper glycinate is adsorbed and then replaced by

gold glycinate which activated carbon has a high affinity for. As can be seen from Table 3, the initial rate of adsorption for gold decreases with increasing gold concentration. This is counter intuitive as normally for cyanide systems, it has been observed that the initial adsorption rate is bigger at higher gold concentrations (Marsden and House, 2006).

3.5. Effect of initial copper concentration

Different copper concentrations of 0, 20, 40, 80 and 800 ppm with 2 ppm Au were used for adsorption tests. According to the results, presented in Fig. 4(a) gold adsorption, in terms of overall recovery is independent of copper concentration. Increased copper concentration increases the initial rate of adsorption, k , for gold with a maximum rate observed at a copper concentration of 40 ppm which was taken as the optimum concentration for all experiments (Table 4). A high copper system does not necessarily increase overall copper recovery as can be seen from Fig. 4(b). It is however interesting to see that the copper adsorption at 800 ppm Cu is lower than at 20, 40 and 80 ppm Cu. This is an added advantage of the glycine system from a selectivity point of view. Increased copper concentration increases the initial rate of adsorption for copper glycinate complexes.

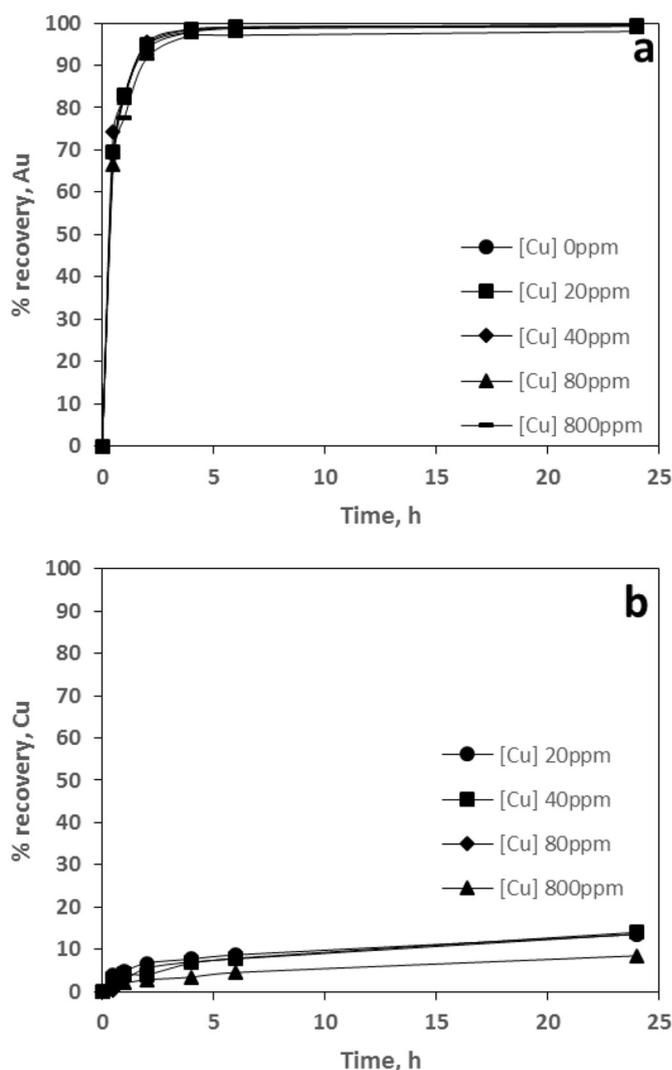


Fig. 4. Adsorption of Au (a) and Cu (b) in glycine solutions at various initial copper concentrations ([Au] 2 ppm, [Glycine] 5 g/L, [Carbon] 2 g/L, pH 11, 23 °C, 24 h contact time).

Table 4
Fleming Kinetic model constants for Au and Cu at different initial copper concentrations.

| Initial Cu Conc (ppm) | k (h^{-1}) | | n | | R^2 | |
|-----------------------|-------------------------|------|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 0 | 2985.5 | – | 1.5 | – | 0.99 | – |
| 20 | 3145.9 | 26.9 | 1.7 | 0.4 | 0.99 | 0.98 |
| 40 | 3491.1 | 20.5 | 1.6 | 0.4 | 0.97 | 0.85 |
| 80 | 2731.4 | 9.1 | 1.5 | 1.3 | 0.99 | 0.88 |
| 800 | 2351.3 | 11.7 | 1.3 | 0.3 | 0.97 | 0.98 |

3.6. Effect of carbon concentration

The rate of loading and overall metals recovery was measured at various carbon concentrations between 2 and 12 g/L (See Table 5). The results shown in Fig. 5(a) indicate that, overall gold recovery is independent of the carbon concentration in solution. The carbon concentration however has a marked effect of the initial gold adsorption rate. Increasing the carbon concentration increases the surface area of the carbon making more active sites available to adsorb metal complexes thereby increasing the rate of adsorption significantly as can be seen from k values in Table 5. An interesting result is observed at 12 g/L carbon, where the initial gold adsorption rate is exponentially higher than for lower carbon concentrations studied. Notably, the corresponding R^2 for this carbon concentration is quite low (0.6). This might be an indication of the limitation of the model used, suggesting that 12 g/L carbon concentration is probably in the range outside what the Fleming k,n model can fit. A more complex model structure might be suitable for high carbon concentrations. Since the gold glycine complex is strongly adsorbed onto carbon, preg-robbing ores, which naturally contain carbonaceous material, are not suited for the glycine leach system. The carbon found in preg-robbing ores tends to be very fine resulting in increased surface area and re-adsorption of the gold complex from solution and hence reduction in the overall gold recovery. For copper glycinates, the reverse is true. The initial copper adsorption rate constant decreases as you increase the carbon concentration. However the overall adsorption increases with increasing carbon concentration. This implies a shorter residence time is appropriate for glycine adsorption system. For a residence time of 3 h for example, as shown by the data in Fig. 5(a) and (b), over 99% gold is recovered while < 8% copper was adsorbed.

Table 5
Fleming Kinetic model constants for Au and Cu at different carbon concentrations.

| Carbon concentration (g/L) | k (h^{-1}) | | n | | R^2 | |
|----------------------------|-------------------------|------|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 2 | 2657.5 | 25.2 | 1.7 | 0.3 | 0.98 | 0.90 |
| 4 | 4749.8 | 17.2 | 1.8 | 0.6 | 0.99 | 0.95 |
| 8 | 72,614.1 | 14.3 | 3.1 | 0.7 | 0.87 | 0.98 |
| 12 | 374,069.4 | 19.0 | 1.7 | 0.6 | 0.60 | 0.99 |

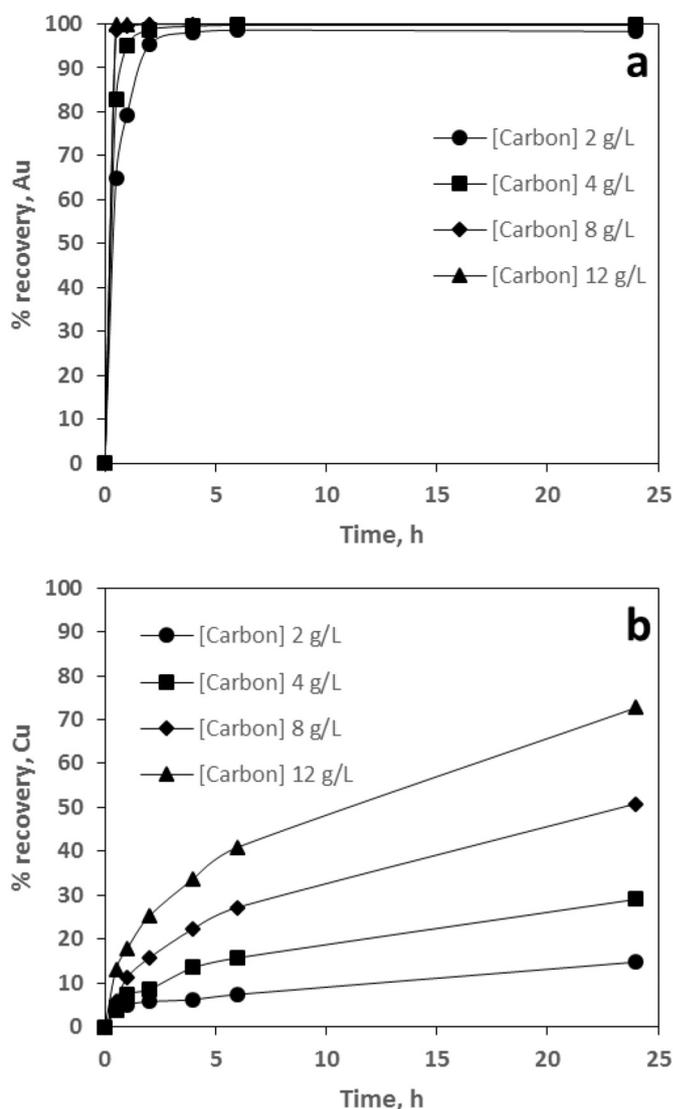


Fig. 5. Adsorption of Au (a) and Cu (b) in glycine solutions at different carbon concentrations ([Au] 2 ppm, [Cu] 40 ppm, [Glycine] 5 g/L, pH 11, 23 °C, 24 h contact time).

3.7. Effect of Ca^{2+}

The initial rate of metals extraction and overall recovery were determined from solutions of varying ionic strength by addition of the Ca^{2+} ion as CaCl_2 . The results are given in Fig. 6 and Table 6. Table 6 shows that a higher ionic strength neither affects the adsorption rate nor the overall gold recovery in alkaline glycine significantly. The effect on the loading capacity is more pronounced than for the loading rate. When the calcium concentration is increased to a certain level, it causes carbon fouling which reduces metal adsorption.

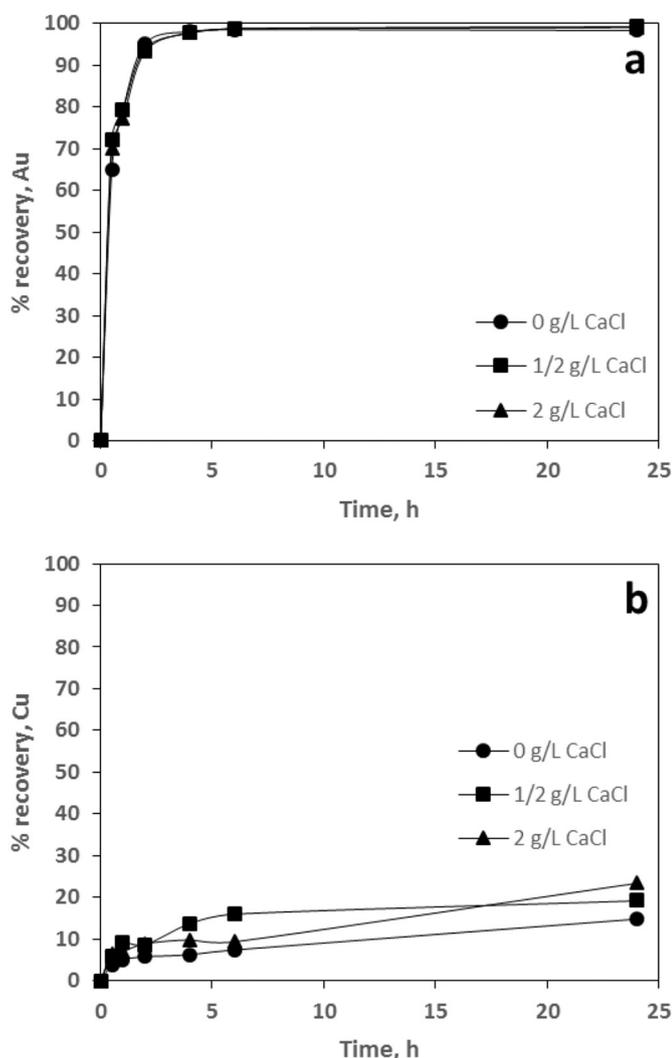


Fig. 6. Adsorption of Au (a) and Cu (b) in glycine solutions at different concentrations of calcium chloride ([Au] 2 ppm, [Cu] 40 ppm, [Glycine] 5 g/L, [Carbon] 2 g/L, pH 11, 23 °C, 24 h contact time).

Table 6

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

| CaCl ₂ Conc (g/L) | <i>k</i> (h ⁻¹) | | <i>n</i> | | <i>R</i> ² | |
|------------------------------|-----------------------------|------|----------|-----|-----------------------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 0.0 | 2845.7 | 25.2 | 1.4 | 0.3 | 0.9616 | 0.90 |
| 0.5 | 2594.5 | 44.2 | 1.5 | 0.4 | 0.9549 | 0.86 |
| 2.0 | 2657.5 | 40.9 | 1.7 | 0.2 | 0.9799 | 0.96 |

4. Conclusions

The data of Au and Cu adsorption recoveries for 24 h adsorption time were modelled by the Fleming *k_n* adsorption kinetic model. The model was applicable for all cases except the high carbon concentration of 12 g/L. It was shown that the overall gold recovery was insensitive to variation of solution pH, free glycine concentration, carbon concentration, initial Au and Cu concentrations as well as ionic strength of the solution. Over 99% gold was recovered in 24 h for all studied parameters. Copper recoveries increased with increasing carbon concentration with 14.8%, 29.1%, 50.7% and 72.7% copper recovered at carbon concentrations of 2, 4, 8 and 12 g/L respectively. This

observation would seem to indicate that in a gold-copper glycinate system, low carbon concentrations with residence times up to 6 h should be used to ensure that gold adsorption is maximised while copper co-adsorption is minimised. Other studied parameters did not have a marked effect on the percentage copper recovery. The effect of studied parameters on the initial rate of adsorption *k*, are summarised below:

- Increasing pH decreases the initial adsorption rate of gold glycinate complexes. The highest adsorption rate for copper (25.4 h⁻¹) occurred at pH 11.
- The highest initial gold adsorption rate of 3491.1 h⁻¹ was observed at 5 g/L glycine. Increasing free glycine concentration decreased the initial rate of adsorption for copper complexes.
- The initial rate constant for gold is independent of the ionic strength of the solution. However for copper, an increase in the ionic strength of the solution almost doubled the initial adsorption rate. The copper rate constants were 25.2 h⁻¹ and 44.2 h⁻¹ for solutions containing 0 g/L and 0.5 g/L CaCl₂ respectively.
- The increasing initial gold concentration in solution decreased the initial gold adsorption rate. The rate value at a gold concentration of 16 ppm was 1324 h⁻¹ which is half the rate at 2 ppm gold concentration which is 2658 h⁻¹. For copper, a maximum adsorption rate (59.7 h⁻¹) was noted an initial gold concentration of 4 ppm.
- Increasing the carbon concentration increases the initial gold adsorption rate but decreases the initial adsorption rate for copper.
- Low copper concentrations of 20 and 40 ppm increases the gold adsorption rate. When copper is present in concentrations above 80 ppm, the initial gold adsorption rate is lower than that of a free copper system.
- Based on the results, the suggested operating parameters for gold adsorption from an alkaline glycine media containing 2 ppm Au and 40 ppm copper are 5 g/L glycine concentration, pH of around 10, with 2 to 4 g/L carbon.

Acknowledgements

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

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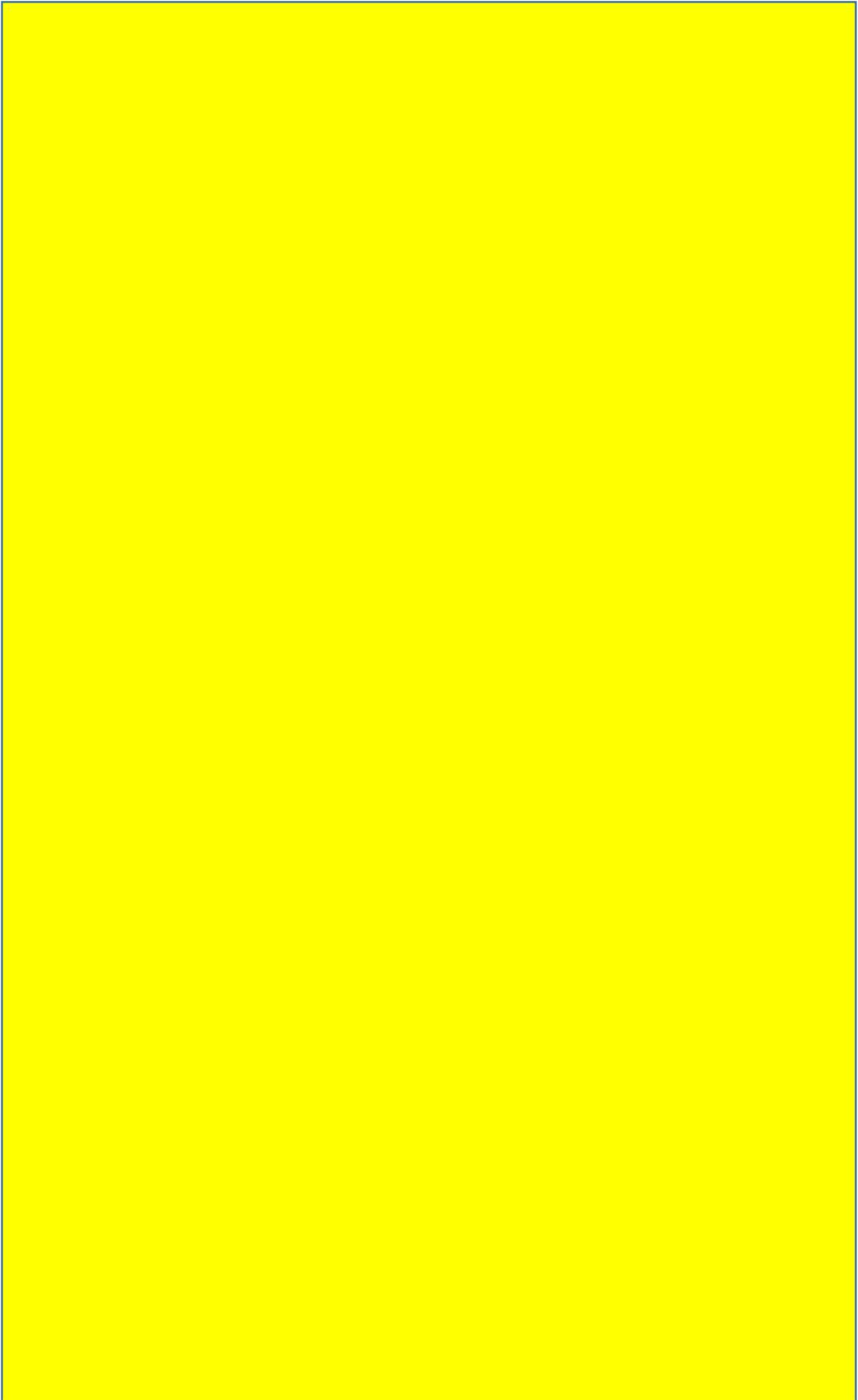
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6 Adsorption Isotherms of Au from Cyanide-Starved Glycine Solutions

Submitted for publication as:

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

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2019.
Separation and Purification Technology, 211, pp.594-601.

Accepted for publication on 9th September 2018.

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DOI: <https://www.sciencedirect.com/science/article/pii/S1383586618323062>



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

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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 ubiquitous 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 of 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 reducing reagent consumption. Copper

minerals 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.



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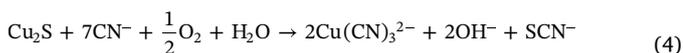
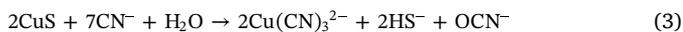
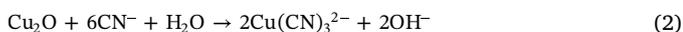
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<https://doi.org/10.1016/j.seppur.2018.09.024>

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

Available online 11 September 2018

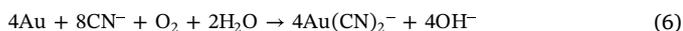
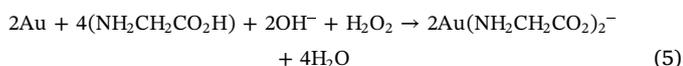
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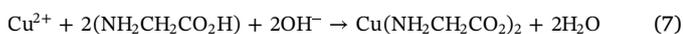
In this regard, the glycine cyanide mixture can be used as an alternative lixiviant, or a synergistic lixiviant with catalytic amounts of cyanide, for the treatment of copper-rich gold ores. On its own, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), the simplest amino acid, in an alkaline environment 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, lixiviant 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 measureable 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 $\text{Cu}(\text{CN})_2^-$.

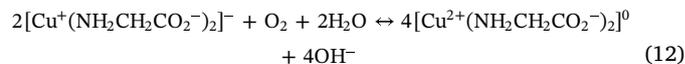
Gold complexes



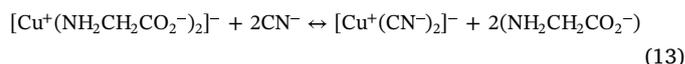
(b) Copper complexes



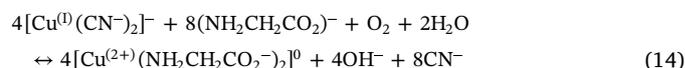
The ratio of WAD cyanide versus Cu glycinate in the system depends on the redox cycling between cuprous (Cu(I)) copper and cupric (Cu(II)) copper (Eqs. (12)–(15)).



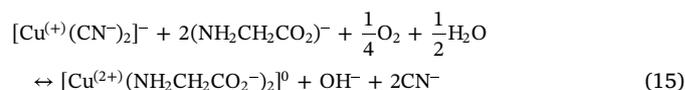
Interchange reaction:



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_2BET (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.

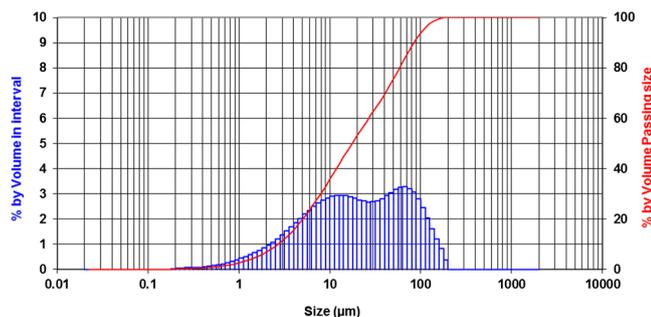


Fig. 1. Particle size distribution of pulverised carbon.

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 be 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.

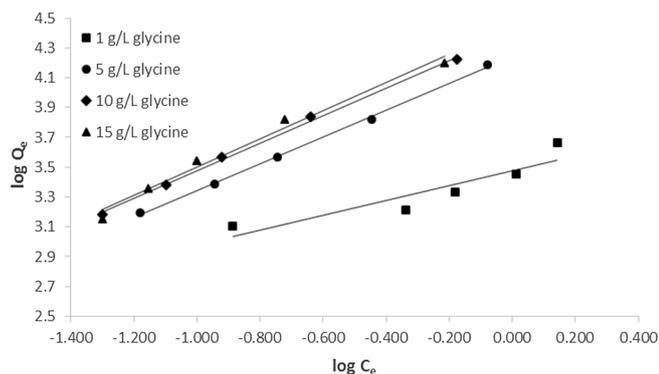


Fig. 2. Gold loading isotherms as a function of glycine concentration (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

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 |

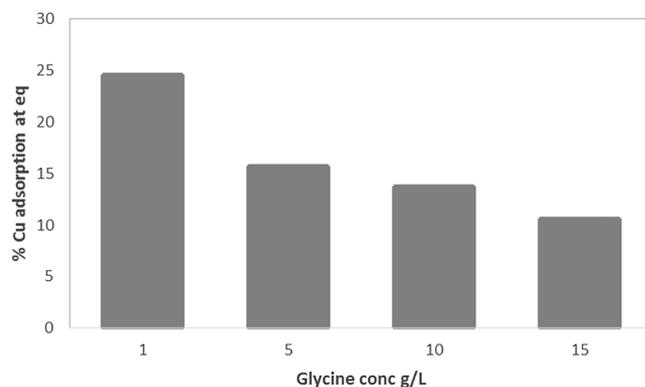


Fig. 3. Effect of glycine concentration on copper adsorption. Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

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.

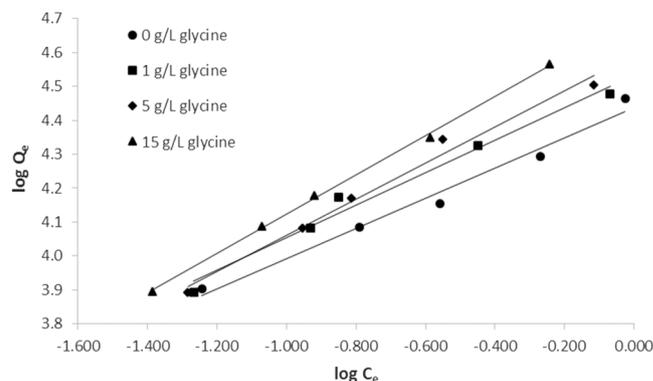


Fig. 4. Gold loading isotherms as a function of glycine concentration (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 0 ppm, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

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].

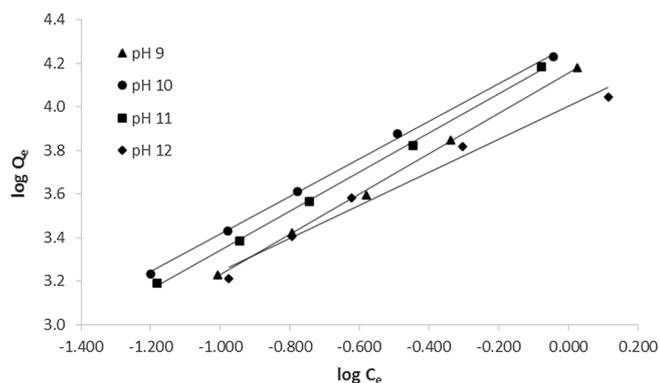


Fig. 5. Gold loading isotherms as a function of solution pH (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [CN] 123 ppm, [Glycine] 5 g/L, 23 °C, 24 h contact time.

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.

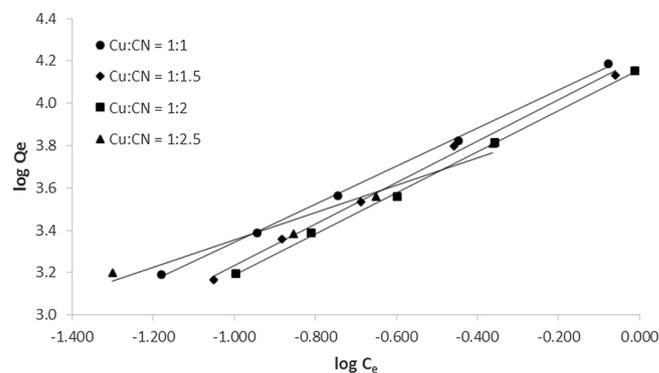


Fig. 6. Gold loading isotherms as a function of cyanide concentration (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [Glycine] 5 g/L, pH 11, 23 °C, 24 h contact time.

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.

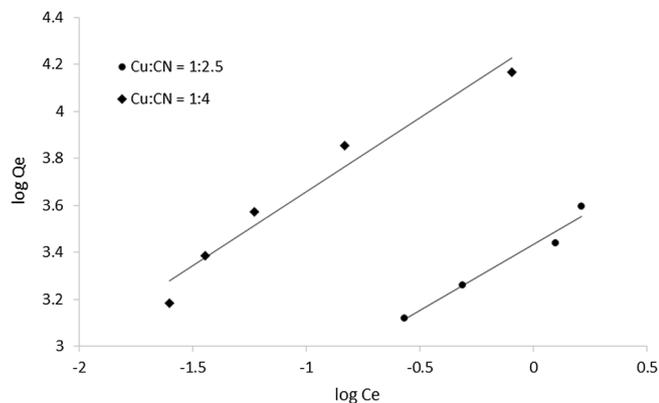


Fig. 7. Gold loading isotherms as a function of cyanide concentration for a pure cyanide system (Freundlich model). Initial [Au] 2 ppm, Initial [Cu] 300 ppm, [Glycine] 0 g/L, pH 11, 23 °C, 24 h contact time.

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].

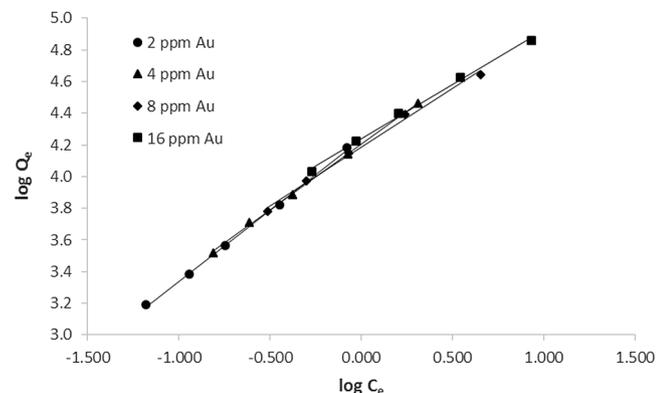


Fig. 8. Gold loading isotherms as a function of initial gold concentration (Freundlich model). Initial [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time.

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.

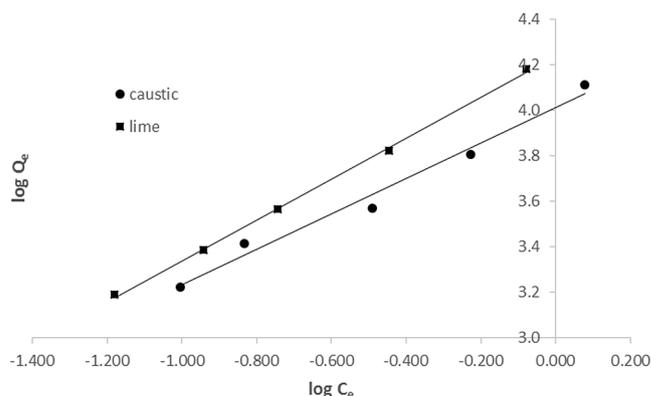


Fig. 9. Gold loading isotherms as a function of ionic strength of the solution (Freundlich model). Initial [Au] 2 ppm, initial [Cu] 300 ppm, [CN] 123 ppm, [Glycine] 5 g/L, pH 11, 23 °C, 24 h contact time.

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:

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

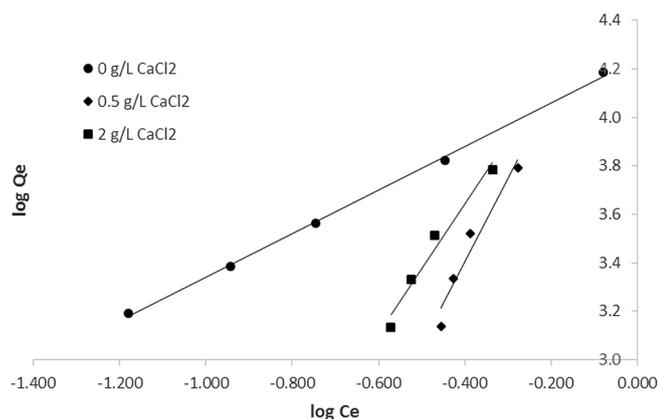


Fig. 10. Gold loading isotherms as a function of ionic CaCl_2 concentration (Freundlich model). Initial $[\text{Au}]$ 2 ppm, initial $[\text{Cu}]$ 300 ppm, $[\text{CN}^-]$ 123 ppm, $[\text{Glycine}]$ 5 g/L, pH 11, 23 °C, 24 h contact time.

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.

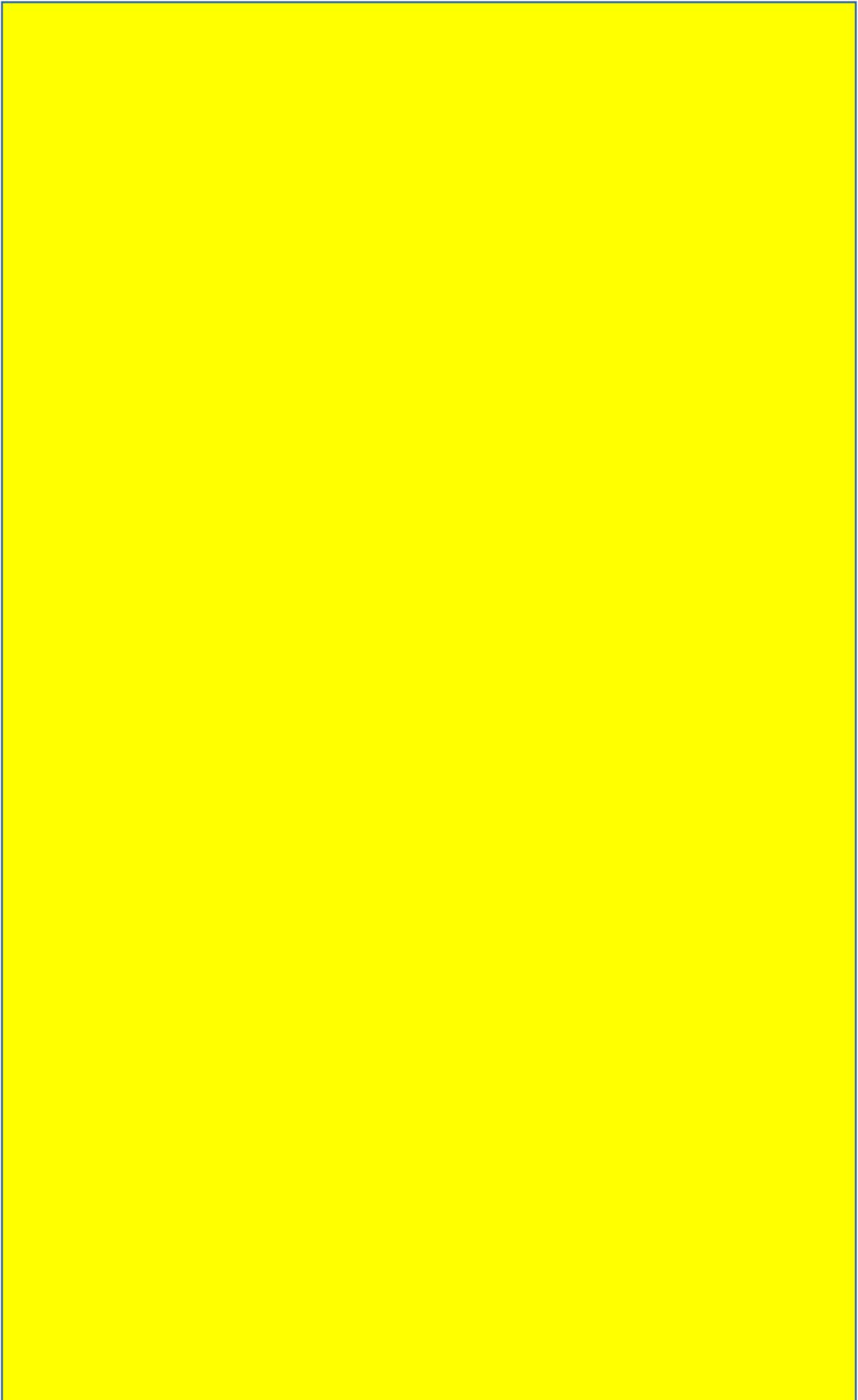
Acknowledgements

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

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7 Adsorption Kinetics of Au and Cu from Cyanide-Starved Glycine Solutions

Submitted for publication as:

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

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2019.
Separation and Purification Technology, 211, pp.290-297.

Accepted for publication on 9th September 2018.

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DOI: <https://www.sciencedirect.com/science/article/pii/S1383586618323074>



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

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ARTICLE INFO

Keywords:

Activated carbon
Gold
Copper
Glycine-cyanide solutions
Adsorption
Kinetics

ABSTRACT

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 6 h) for both gold and copper as evidenced by the regression coefficient (R^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 2 mg/L gold, 300 mg/L copper, pH 11, 5 g/L glycine, Cu:CN of 1:1 (123 mg/L CN) and 8 g/L carbon using lime as a pH modifier reached 99.0% and 52.8% respectively. Most copper and gold was recovered in the first 6 h. The corresponding initial adsorption rates are 1263.8 h^{-1} for gold and 19.0 h^{-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 $\text{Cu}(\text{OH})_2$ 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

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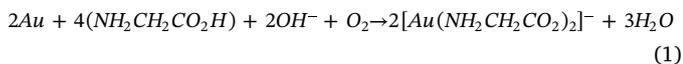
<https://doi.org/10.1016/j.seppur.2018.09.022>

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

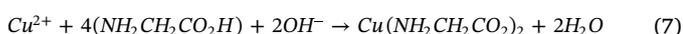
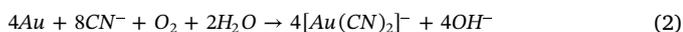
Available online 11 September 2018

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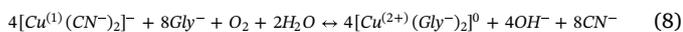
the following reaction:



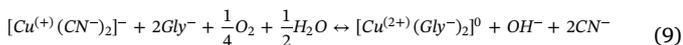
Early research by [24] confirmed that in its pristine form, activated carbon adsorbs the gold glycinate complex. This was further validated during recent studies by [29,30] who showed that the gold glycinate complex adsorbs very strongly onto carbon. However, the solutions resulting from glycine cyanide 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.



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 ($NH_2CH_2CO_2^-$):



Or



The application of activated carbon technique is appropriate for solutions with low content of the metal of interest which is the case with gold in glycine cyanide leachates. Activated carbon has significant advantages over other adsorbents in that it has a high gold selectivity over base metals, high adsorption capacity, is easy to elute and is eco-friendly [4,13,20,27]. Therefore, the use of commercially-available activated carbon is proposed as a means of recovering gold complexes from glycine-cyanide solutions/leachates. From an industrial application perspective, the three carbon based technologies, carbon-in-leach (CIL), carbon-in-pulp (CIP) and carbon-in-column (CIC) processes, widely used in the gold mining industry, may be applicable for use in glycine based systems. However, in order to efficiently utilise the carbon sorbents for metal glycine complexes recovery, the influence of various operating parameters such as initial metal concentration, competitive adsorption, glycine concentration on the adsorption dynamics have to be evaluated and quantified. A study of the kinetic sorption mechanism of metal glycinate from model solutions is therefore necessary to give insights on their adsorption behaviour onto activated carbon.

Both the carbon-in-leach and carbon-in-pulp processes recover gold from slurries of up to 55% solids, with adsorption occurring after leaching in CIP circuits while for CIL plants adsorption and leaching occurs concurrently. The CIC is utilised for gold recovery from solutions. In this research, modelling of activated carbon adsorption of gold and copper glycinate complexes is performed using bench laboratory experimental data. The resulting model parameters would enable design, control and optimisation of the CIP/CIC/CIL adsorption circuits for glycine systems. There are several kinetics equations available for modelling activated carbon adsorption rate [1,2,5,11,12,15–17,28]. These rate models are generally classified into two, empirical or mechanistic rate models [17]. Adsorption kinetics study, used to determine the uptake rate of adsorbate, is important as it can be used to determine the mechanism of adsorption, the efficiency of the adsorbent and control the residual time of the whole adsorption process at industry level.

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 (2 mg L^{-1}) in the presence of 300 mg L^{-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 $-2.36 + 2.00 \text{ mm}$ 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 $894.13 \pm 46.69 \text{ m}^2/\text{g}$.

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 0.45 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 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 mg L^{-1} and 300 mg L^{-1} , respectively unless otherwise stated. The traditional bottle-on-rolls method was used for the experiments. The experimental runs were carried in sealed 2.5 L 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 0.22 μm 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:

$$\Delta Auc = k \times Au_s \times t^n \quad (10)$$

Where k and n are model parameters, k being the rate constant, $1/\text{hours}$, and n a model parameter, t is the adsorption time (h), Au_s is gold concentration in solution (ppm) at time t , ΔAuc 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 lime 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

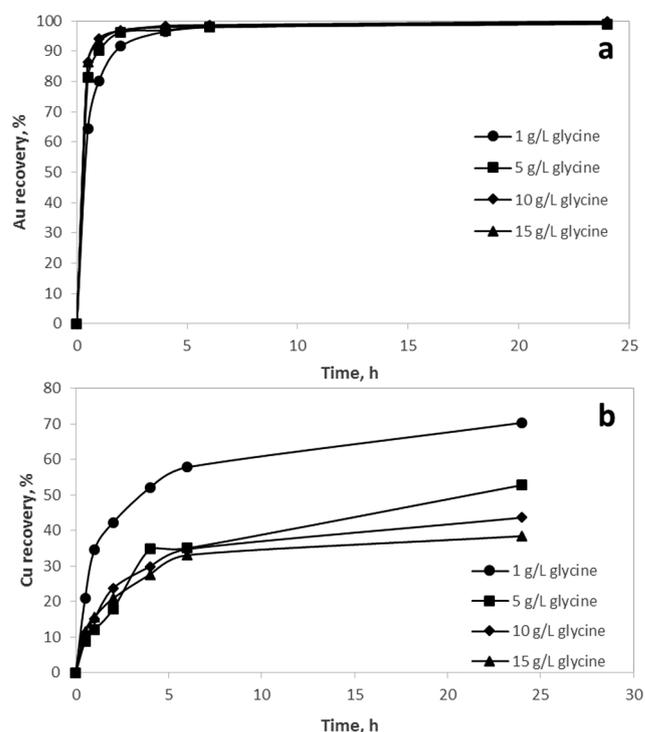


Fig. 1. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different glycine concentrations ([Au] 2 ppm, [Cu] 300 ppm, [CN] 123 ppm, pH 11, [Carbon] 8 g/L, 23 °C, 24 h contact time).

Table 1

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

| Glycine Conc (g/L) | k (h^{-1}) | | n | | R^2 | |
|--------------------|-------------------------|----|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 1 | 557 | 59 | 1.3 | 0.7 | 0.99 | 0.97 |
| 5 | 1264 | 19 | 1.2 | 0.8 | 0.99 | 0.95 |
| 10 | 1842 | 24 | 1.1 | 0.6 | 0.99 | 0.99 |
| 15 | 1758 | 24 | 1.1 | 0.5 | 0.99 | 0.99 |

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 ($(\text{Cu}(\text{H}_2\text{NCH}_2\text{COO}))_2$) which is not readily adsorbed 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 also decreased with increasing free cyanide concentration. Marsden and House [18] ascribed this observation to increased competition of active 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.

Table 2
Fleming Kinetic model constants for Au at different free glycine concentrations in the absence of copper.

| Glycine conc (g/L) | k (h^{-1}) | n | R^2 |
|--------------------|-------------------------|-----|-------|
| 0 | 10,269 | 1.3 | 0.97 |
| 1 | 8320 | 1.2 | 0.96 |
| 5 | 4159 | 0.8 | 0.99 |
| 10 | 4190 | 0.5 | 0.98 |
| 15 | 5190 | 0.8 | 0.98 |

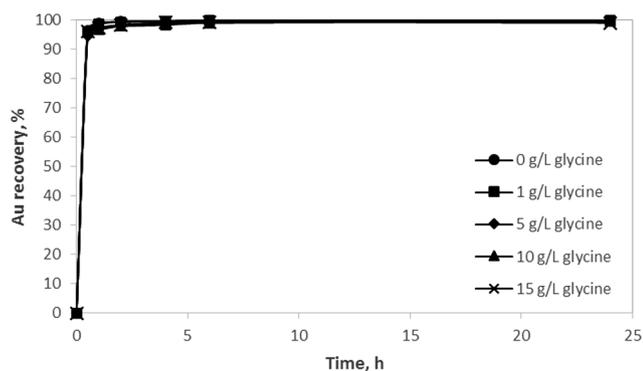


Fig. 2. Adsorption of Au in cyanide starved glycine solutions at different glycine concentrations ([Au] 2 ppm, [Cu] 0 ppm, [CN] 123 ppm, pH 11, [Carbon] 8 g/L, 23 °C, 24 h contact time).

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. As 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

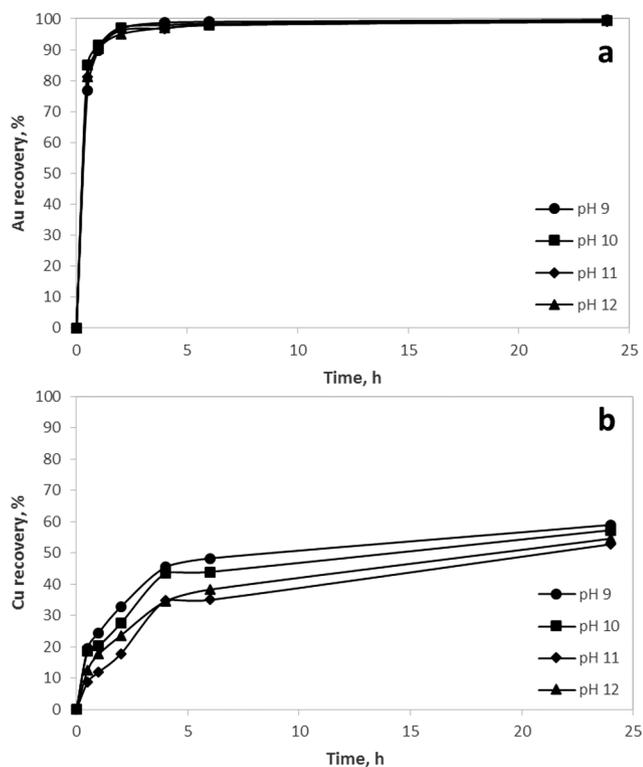


Fig. 3. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different pH levels ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, [Carbon] 8 g/L, 23 °C, 24 h contact time).

Table 3
Fleming Kinetic model constants for Au and Cu at different solution pHs.

| pH | k (h^{-1}) | | n | | R^2 | |
|----|-------------------------|----|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 9 | 1215 | 44 | 1.6 | 0.6 | 0.99 | 0.98 |
| 10 | 1556 | 37 | 1.1 | 0.6 | 0.97 | 0.91 |
| 11 | 1264 | 19 | 1.2 | 0.8 | 0.99 | 0.95 |
| 12 | 1152 | 28 | 1.0 | 0.6 | 0.99 | 0.99 |

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 for which copper recovery was slowest 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 $\text{Cu}(\text{CN})_2^-$ speciation as cyanide concentration is increased [32]. A 1:1 copper-to-cyanide ratio means $\text{Cu}(\text{CN})_2^-$ was dissolved in glycine solution and there was no free cyanide. This means the concentration of the readily

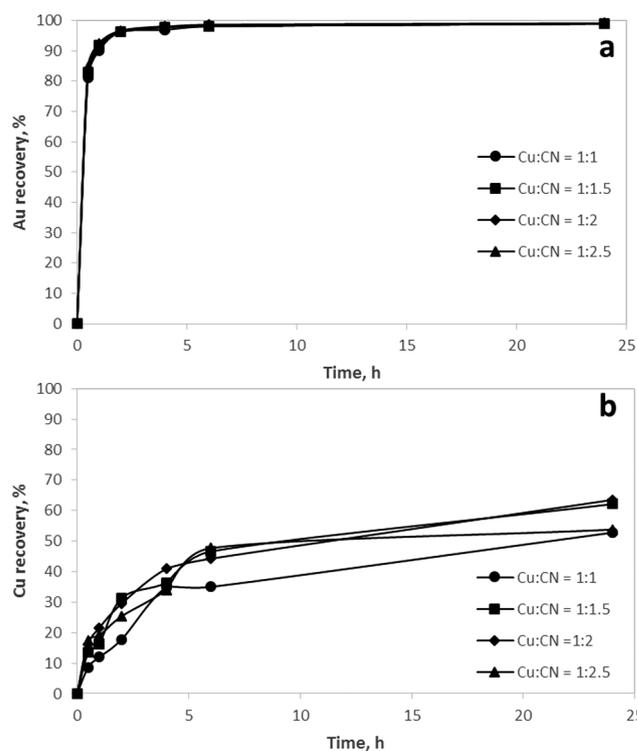


Fig. 4. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions as a function of cyanide concentration ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [Carbon] 8 g/L, pH 11, 23 °C, 24 h contact time).

Table 4
Fleming Kinetic model constants for Au and Cu at different cyanide concentrations (glycine cyanide system).

| Cu:CN | [CN] ppm | k (h ⁻¹) | | n | | R ² | |
|-------|----------|----------------------|----|-----|-----|----------------|------|
| | | Au | Cu | Au | Cu | Au | Cu |
| 1:1 | 123.0 | 1264 | 19 | 1.2 | 0.8 | 0.99 | 0.95 |
| 1:1.5 | 237.1 | 1380 | 30 | 1.1 | 0.7 | 0.99 | 0.93 |
| 1:2 | 352.2 | 1370 | 37 | 1.1 | 0.6 | 0.99 | 0.99 |
| 1:2.5 | 467.3 | 1571 | 34 | 1.1 | 0.4 | 0.99 | 0.95 |

adsorbed Cu(CN)₂⁻ was less than that of Cu²⁺ 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. Cu(CN)₂⁻ adsorbs more than Cu²⁺ 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.

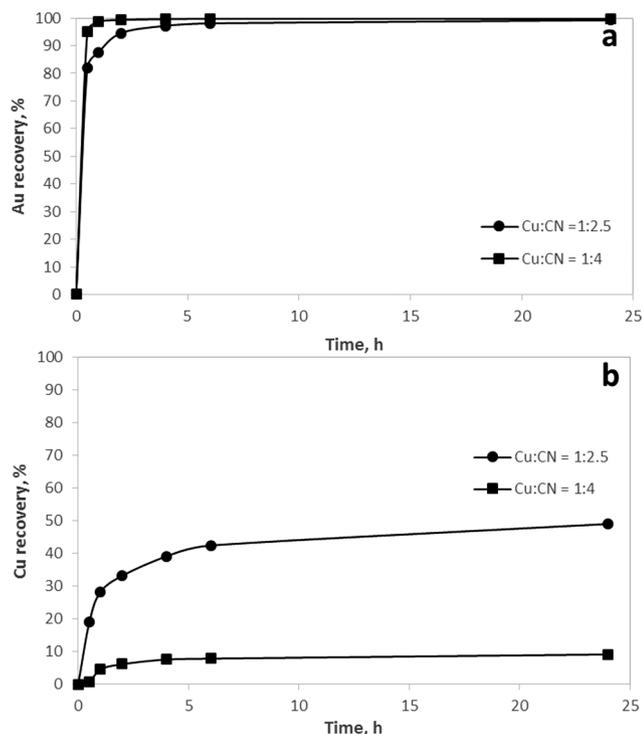


Fig. 5. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions as a function of cyanide concentration ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 0 g/L, [Carbon] 8 g/L, pH 11, 23 °C, 24 h contact time).

Table 5
Fleming Kinetic model constants for Au and Cu at different cyanide concentrations (cyanide only system).

| Cu:CN | [CN] ppm | k (h ⁻¹) | | n | | R ² | |
|-------|----------|----------------------|----|-----|-----|----------------|------|
| | | Au | Cu | Au | Cu | Au | Cu |
| 1:2.5 | 467 | 872 | 45 | 1.2 | 0.5 | 0.99 | 0.96 |
| 1:4 | 814 | 7087 | 3 | 1.3 | 1.2 | 0.96 | 0.77 |

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.

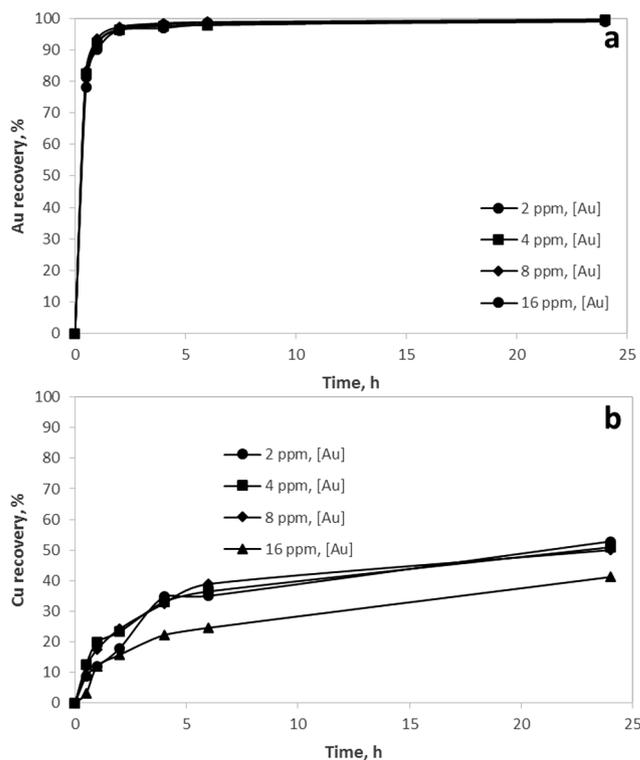


Fig. 6. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at various initial gold concentrations ([Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, [Carbon] 8 g/L, pH 11, 23 °C, 24 h contact time).

Table 6
Fleming Kinetic model constants for Au and Cu at different initial gold concentrations.

| Initial gold conc ppm | k (h ⁻¹) | | n | | R ² | |
|-----------------------|----------------------|----|-----|-----|----------------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 2 | 1215 | 19 | 1.2 | 0.8 | 0.99 | 0.95 |
| 4 | 1404 | 28 | 1.1 | 0.6 | 0.97 | 0.97 |
| 8 | 1688 | 26 | 1.2 | 0.6 | 0.98 | 0.99 |
| 16 | 1295 | 11 | 1.3 | 1.0 | 0.98 | 0.88 |

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 constant but decreased the copper adsorption rate constant as shown by k constant values in Table 7.

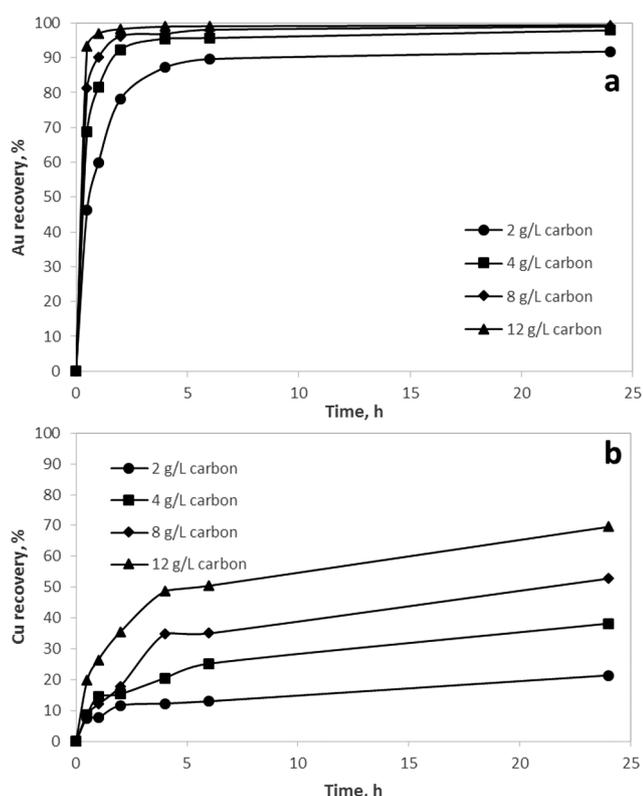


Fig. 7. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different carbon concentrations ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, pH 11, 23 °C, 24 h contact time).

Table 7
Fleming Kinetic model constants for Au and Cu at different carbon concentrations.

| Carbon conc g/L | k (h^{-1}) | | n | | R^2 | |
|-----------------|------------------|----|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 2 | 853 | 49 | 1.0 | 0.3 | 0.99 | 0.86 |
| 4 | 1227 | 36 | 1.1 | 0.4 | 0.99 | 0.91 |
| 8 | 1264 | 19 | 1.2 | 0.8 | 0.99 | 0.95 |
| 12 | 2424 | 32 | 0.9 | 0.6 | 0.99 | 0.99 |

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.

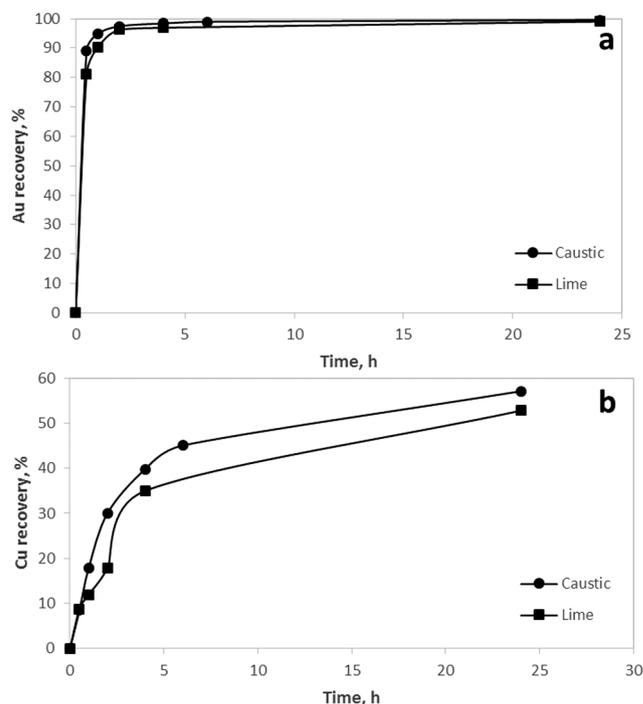


Fig. 8. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions as a function of ionic strength of the solution ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, [Carbon] 8 g/L, pH 11, 23 °C, 24 h contact time).

Table 8
Fleming Kinetic model constants for Au and Cu at different pH modifiers.

| pH modifier | k (h^{-1}) | | n | | R^2 | |
|-------------|------------------|----|-----|-----|-------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| Caustic | 2204 | 25 | 1.0 | 0.9 | 0.99 | 0.98 |
| Lime | 1264 | 19 | 1.2 | 0.8 | 0.99 | 0.95 |

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.

Table 9
Fleming Kinetic model constants for Au and Cu at different free calcium chloride concentrations.

| CaCl ₂ conc g/L | k (h ⁻¹) | | n | | R ² | |
|----------------------------|----------------------|----|-----|-----|----------------|------|
| | Au | Cu | Au | Cu | Au | Cu |
| 0.0 | 1264 | 19 | 1.2 | 0.8 | 0.99 | 0.95 |
| 0.5 | 1275 | 46 | 0.7 | 0.6 | 0.95 | 0.94 |
| 2.0 | 1744 | 36 | 1.0 | 0.5 | 0.98 | 0.99 |

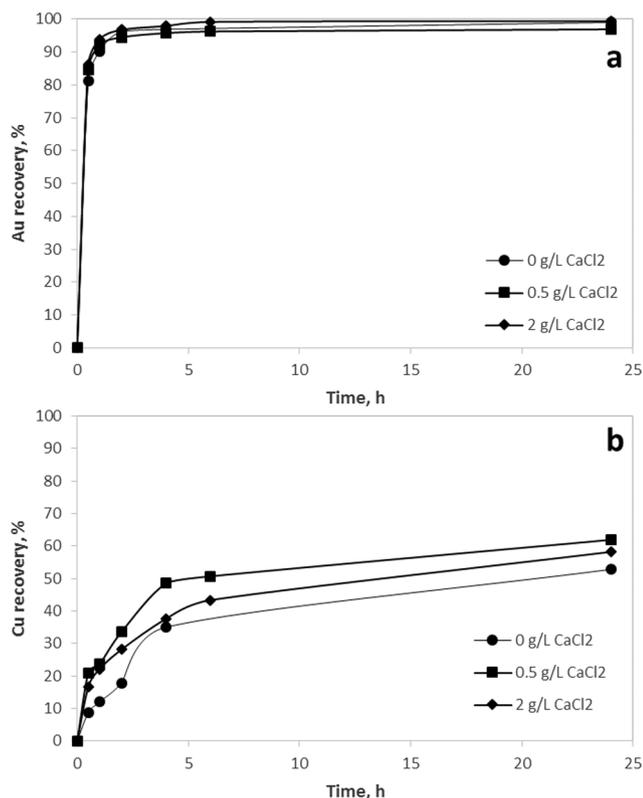


Fig. 9. Adsorption of Au (a) and Cu (b) in cyanide starved glycine solutions at different concentrations of calcium chloride ([Au] 2 ppm, [Cu] 300 ppm, [Glycine] 5 g/L, [CN] 123 ppm, [Carbon] 8 g/L, pH 11, 23 °C, 24 h contact time).

4. Conclusions

The theoretical constants of the Fleming k, n model was used to describe the kinetic adsorption behaviour 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

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

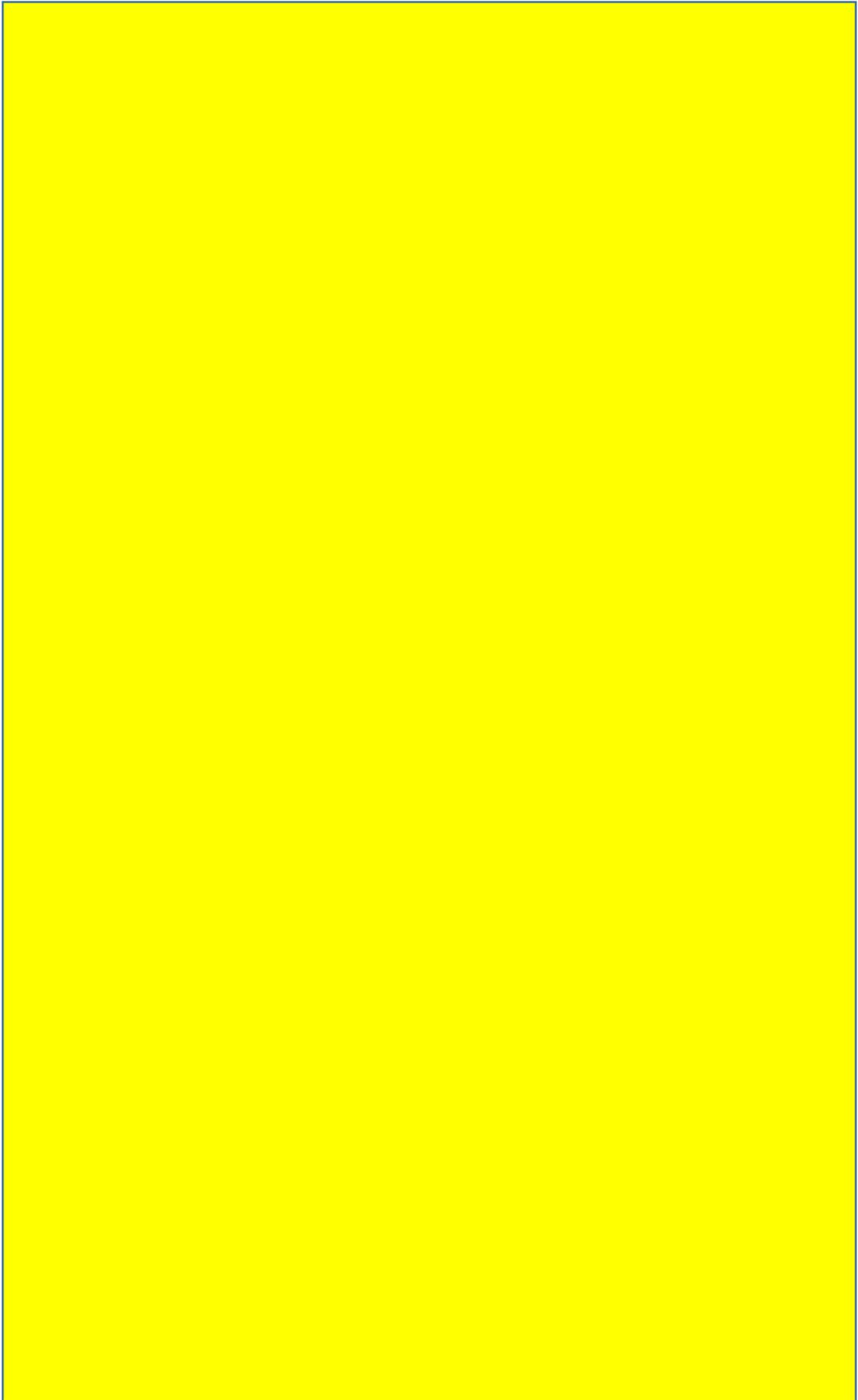
Appendix A. Supplementary material

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

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8 Elution

8.1 Introduction

This chapter is a preliminary investigation into the elution of gold glycinate from activated carbon. The study does not quantify the effects of various variables on the elution of gold, neither does it investigate conditions at which the highest possible elution efficiencies can be realised. The chapter consists of kinetic work for different elution techniques such as AARL elution, elution using deionised water on non-pre-treated carbon and elution using salt (NaCl) water.

8.2 Material and Methods

8.2.1 Activated Carbon

PICAGOLD® G210AS type granulated activated carbon supplied by Jacobi Carbons was used for experimental elution work. The carbon was manufactured from high-grade coconut shell as per specifications from the manufacturer. Prior to use, the carbon was mechanically sized to $-2.36 + 2.00$ mm. The carbon was used as received with no further treatment. Additional specifications from the supplier can be seen in Appendix A.

8.2.2 Adsorbates

All solutions used in these experiments were prepared from analytical grade chemicals. Gold glycinate solutions were prepared by leaching a 24ct (99.99%) gold sheet (10 cm × 2.5 cm × 0.03 cm) supplied by A&E Metals in an alkaline glycine solution. The leaching solution was prepared by dissolving 15 g/L glycine (>99.9%, Sigma-Aldrich) in Millipore water containing 30 mL/L hydrogen peroxide (30% w/v, Rowe Scientific). NaOH (Thermofisher Scientific) was used to adjust and maintain the solution pH at 11. The solution containing the gold sheet was then heated to 60 °C and agitated sufficiently. The temperature of the solution was maintained at 60 °C throughout the leach process.

8.2.3 Loading Carbon for Elution

Loading of the activated carbon was done by contacting the adsorbate synthetic solutions with activated carbon. Loading was done by contacting 18 g activated with 2.25 L of glycine solution whose gold concentration was 20 ppm. Loading of the activated carbon was done in a bottle roll at 105 rpm for 12 hours to achieve the targeted gold loading of $2500 \text{ g}_{\text{Au}}/\text{ton}_{\text{carbon}}$ which is the typical loading in industry.

The loaded carbon was washed with deionised water before being dried in the oven at 70 °C for 8 hours. Equal amounts of gold loading were used for all experiments.

8.2.4 Elution Experimental Set-up

The aim of the study was to investigate the elution behaviour of the adsorbed Au glycinates which were adsorbed from an alkaline glycine leachate and might not reflect the highest possible elution efficiencies. The investigative elution runs were conducted in an elution rig that was specially designed and constructed for this work. The rig consists of a stainless steel elution column, a pump, heating tapes, a cooling coil, pressure gauge and pressure regulator and a sampling port. A conical flask was used to store the solution. The stainless steel column had an internal diameter of 2.2 cm and was 5.1 cm in length. One bed volume of the column was equivalent to 20 cm³ of solution. A bed volume (BV) is the volume of the column occupied by a packed bed of carbon. The carrying capacity (bed volume) of the column was 10 g of packed carbon. The BV was kept constant for all experiments i.e. the solution in all experiments was contacted with 10 g of loaded carbon.

The eluant was circulated through the rig with the aid of a high pressure pump at a flow rate of 3 BV/h. The eluant was first heated by heating tapes wrapped around the coiled section of the rig. The temperature inside the column was monitored by a thermocouple and controlled using an automatic temperature controller. The pressure was monitored by a pressure gauge and controlled manually using a pressure regulator knob. A 50 psi pressure was employed for all runs. Before exiting the rig, the eluate was cooled by the use of a heat exchange mechanism where the cooling coil was inserted in a container filled with cold water. Samples of the cooled eluate were taken at the exit of the rig in 20 minutes intervals. A total of 20 bed volumes were collected for each elution run as indicated by experimental data.

The schematic and laboratory set-up of the elution rig is shown in Figure 8.1 and 8.2 respectively.

8.2.5 Analytical Methods

The gold concentration in solution was determined by an Agilent 55B AAS model atomic adsorption spectrometer. No further analysis was performed on the solution nor on the carbon.

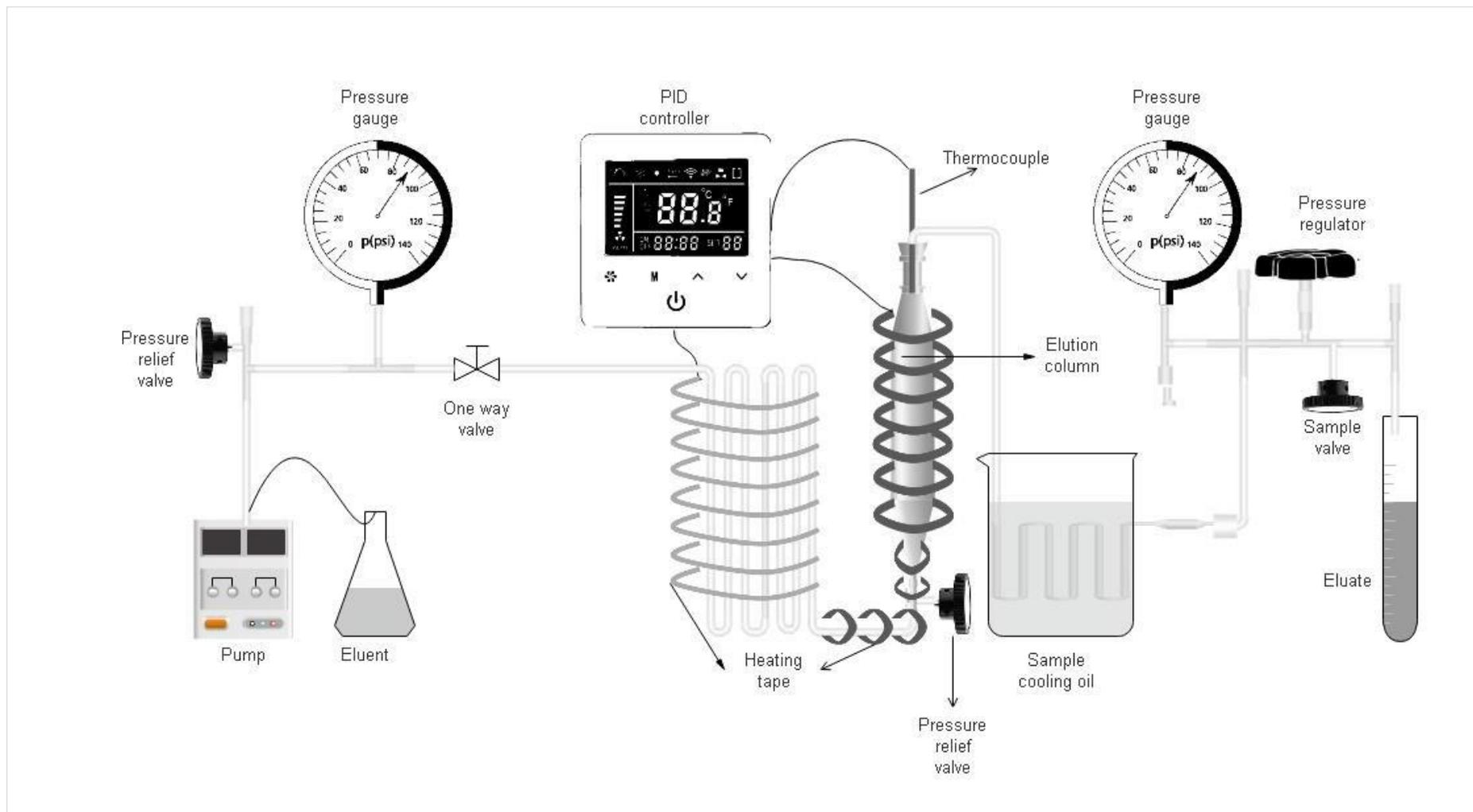


Figure 8.1 Schematic diagram for experimental set-up for elution

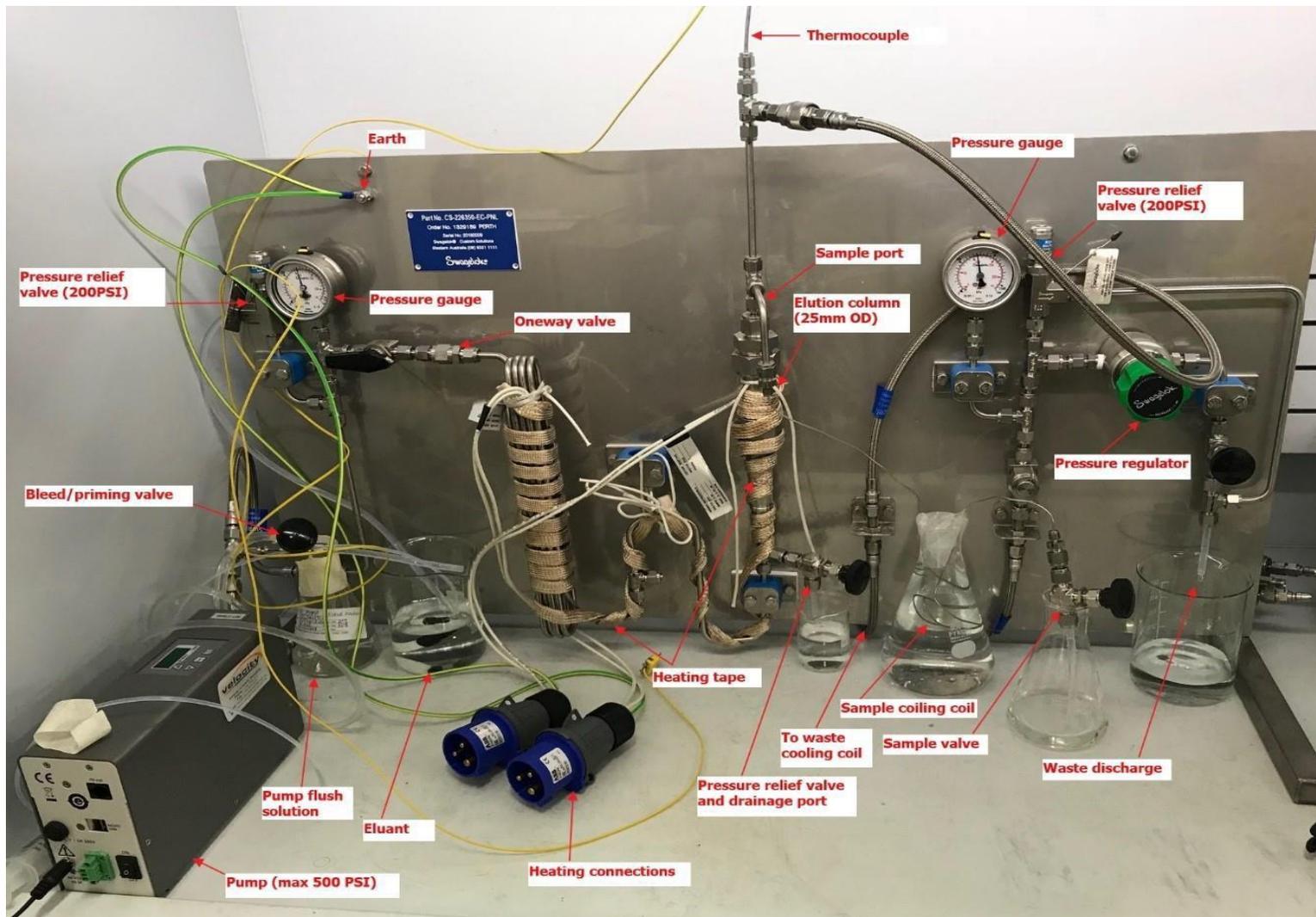


Figure 8.2 Laboratory elution apparatus set-up

8.3 Results and Analysis

The operating conditions of the carbon elution systems studied in this investigation are summarised in Table 8.1.

Table 8.1 also presents gold elution efficiencies after a six-hour elution (20 bed volumes) for various trialled eluants. The results are graphically represented in Figure 8.1. With reference to Table 8.1 and Figure 8.3, the following can be deduced:

- i) Elution efficiency using pure DI water improved from 55.7% to 61.8% when the temperature was increased from 100 to 130°C. Another benefit of increasing the temperature to 130°C is the increase in initial elution kinetics as can be seen by graphs in Figure 8.3. However, it was noted that increasing the temperature beyond 130°C had a detrimental effect as it lowered elution efficiency significantly. The temperature was therefore maintained at 130°C for succeeding trials.
- ii) The AARL elution initially incorporated an acid wash. The loaded carbon was acid washed with one bed volume 3% v/v HCl at 80°C followed by washing with 2BV DI water. The purpose of this step was to remove scale build up on carbon and open up the carbon's micropores and to maximise surface exposure that was believed to improve overall gold elution.

The acid washed carbon was then soaked in 1BV caustic cyanide solution (3% NaCN and 1% NaOH) at a temperature of 110°C for 30 minutes. The sodium cyanide solubilises the adsorbed gold while the caustic maintains a high pH to prevent evolution of HCN gas. It must be noted that there is no gold elution during this stage. Rather the bond between the carbon and gold complexes is weakened making desorption easy in the following step.

Gold was then eluted with DI water at 130°C. The initial kinetics (up to 8 BV) was very fast and most of the gold was eluted within this time frame (3 hours). The acid wash and caustic cyanide pre-treatment were done outside the elution rig.

- iii) A 1M NaCl solution at 130°C resulted in an elution efficiency of 24% on untreated carbon.

Table 8.1 Comparison of elution systems for gold-glycinate loaded carbon

| Elution System | Eluant Composition | Pre-treatment conditions | Temp °C | Elution Rate | Elution Efficiency % |
|---------------------|--------------------------|--|---------|--------------|----------------------|
| DI H ₂ O | Pure DI H ₂ O | No pre-treatment | 100 | M | 55.71 |
| DI H ₂ O | Pure DI H ₂ O | No pre-treatment | 130 | M | 61.85 |
| DI H ₂ O | Pure DI H ₂ O | No pre-treatment | 150 | L | 18.04 |
| Salt water (NaCl) | 1M NaCl solution pH 11 | No pre-treatment | 130 | L | 24.67 |
| AARL | Pure DI H ₂ O | <ul style="list-style-type: none"> • Acid treatment - soak in 3% HCl for 30 mins at 80 °C. • Pre-soak in 1 bed volume of solution (3% NaCN + 1%NaOH) at 110 °C for 30 mins.. | 130 | H | 87.68 |

*L- low; M-medium; H-high NB: elution time was 6-7 hours for all experiments

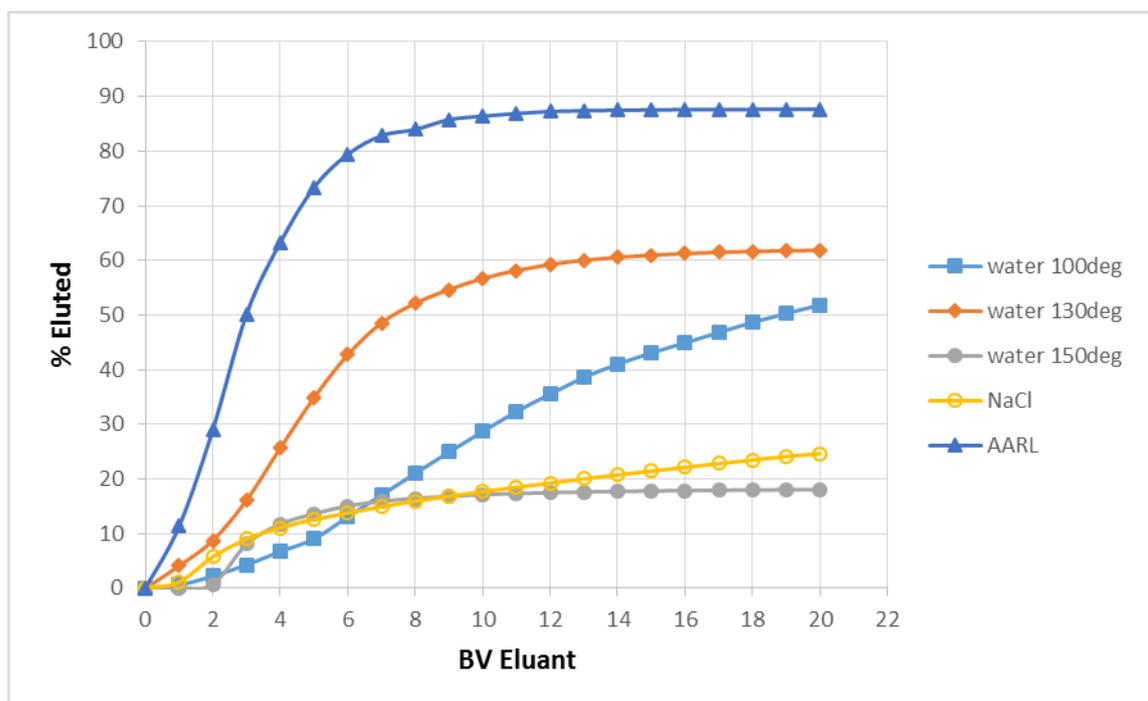


Figure 8.3 Gold elution efficiency curves for gold glycinate loaded carbon

Figure 8.4 illustrates elution profiles of the elution of gold from activated carbon using various elution methods as highlighted previously. The AARL elution profile gave the

highest and more pronounced peak. The peak in concentration occurred around 2 bed volumes. Gold elution then slowed significantly after 4 bed volumes with the concentration of gold in the eluate approaching to zero. A decrease in gold concentration of the eluate with progressing number of bed volumes indicates the gradual reduction of elutable gold species on the carbon. The initial fast elution kinetics could be due to elution of gold on the surface active sites of the carbon which is easier to strip.

The elution using DI water at 100°C exhibited a much less pronounced peak between 8-10 bed volumes signalling that the elution kinetics of gold was significantly slower than for other elution methods. The overall gold recovered after 20 bed volumes was however higher than for NaCl and water at 150°C. Generally, it can be seen that it is possible to elute gold from carbon loaded in pure glycine systems.

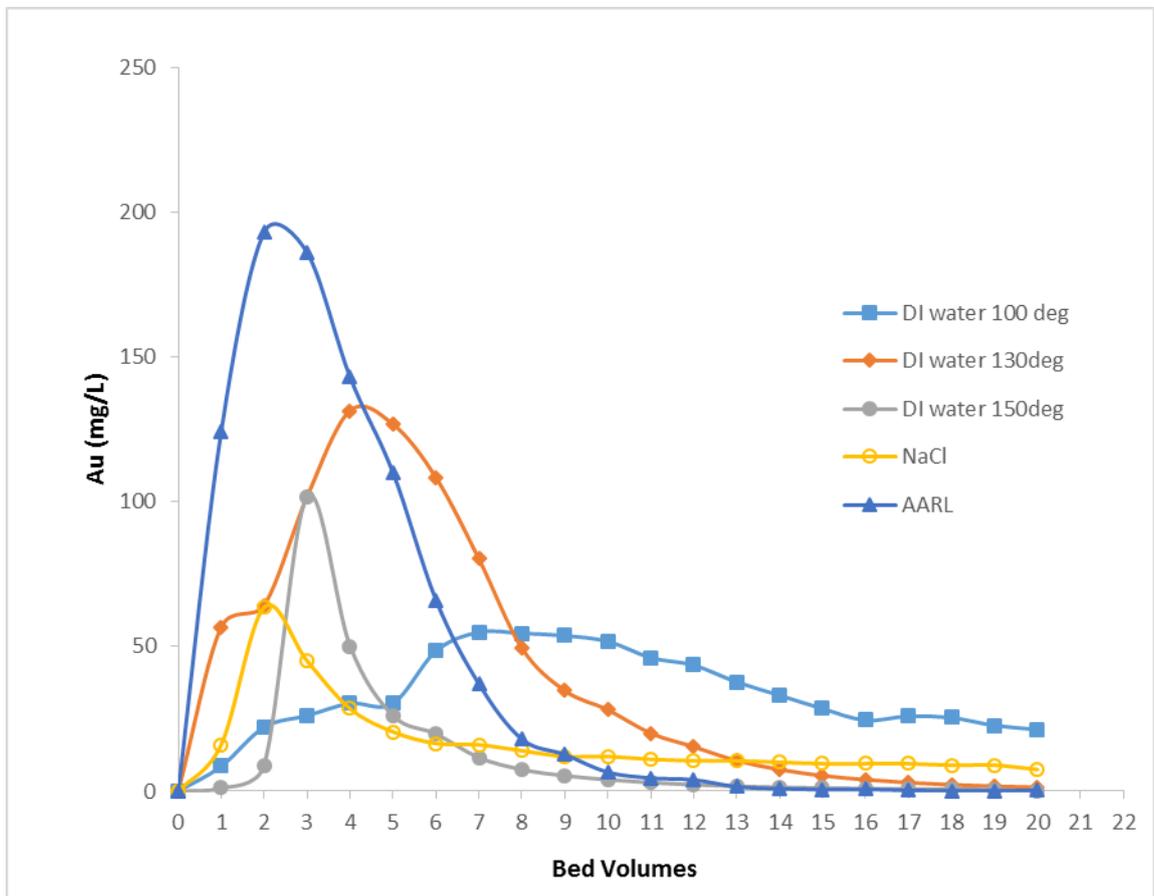


Figure 8.4 Gold elution profiles for the elution of gold glycinate from activated carbon

8.4 Conclusions

It has been shown that gold glycinate can desorb from activated carbon. The elution efficiency will differ under different conditions. The elution of gold glycinate is enhanced by increasing temperatures up to 130°C. The Anglo American Research

Laboratories (AARL) type elution was the most effective with 87.68% gold desorbed after 20-bed volumes at 50 psi. Given the closed circuit nature of the AARL process, it is not seen as problematic as cyanide used to leach ore, where large amounts of effluent (typically more than 1:1 to the mass of ore treated) is pumped to tailings. Cyanide is also destroyed in the gold room during electrowinning due to the decomposition at the electrodes.

9 Conclusions and Recommendations

Leaching of gold-copper ores with glycine has been proposed as a promising alternative to cyanide. Progress into the understanding of glycine leaching of copper and gold containing resources has been made. The principal objective of this research was to investigate the feasibility of activated carbon adsorption processes, similar to the popular gold cyanide CIL/CIP/CIS processes, as a means of the subsequent upgrading and purification of the pregnant glycine leach solutions. Adsorption and elution onto activated carbon for glycine complexes of gold (where copper was also present) were investigated. An investigation in the subsequent purification method of glycine leachates is vital for the implementation of glycine leach systems as an alternative for cyanidation.

It was found that the proposed activated carbon process seems to be a viable option for the recovery of gold in a glycine leach stream. The adsorption of gold from pure glycine and cyanide-starved glycine solutions containing as low as 2 ppm gold has been shown to be possible. The study of adsorption isotherms was used to quantify the capacity of the carbon for gold while the kinetics studies were used to determine the adsorption rate and overall recovery percentage of gold. From the results, it can be concluded that activated carbon is a sufficient substrate for gold in glycine leach systems. Gold adsorption was found to be sensitive to changing process conditions such as solution pH, glycine concentration in solution, ionic strength of the solution, initial gold and copper concentration in solution and copper to cyanide ratio in the case of cyanide-starved glycine leach systems.

Preliminary studies on gold elution from carbon loaded with gold glycinate showed good elution to be possible, in particular when the AARL elution approach is used.

9.1 Enumerated Conclusions

9.1.1 Adsorption

9.1.1.1 Isotherms

The single component equilibrium isotherms for gold complexes onto activated carbon from alkaline glycine solutions containing 40 ppm copper were developed and fitted into the Freundlich isotherm data model. A summary of the results follows:

- The most important parameters affecting the adsorption of gold were identified as glycine concentration, solution pH, solution ionic strength and initial copper and gold concentration in solution.

- Increasing the glycine concentration up to 10 g/L increased the carbon's capacity for gold significantly. Above 10 g/L free glycine, carbon loading was insensitive to a change in the concentration of free glycine. At higher glycine concentrations there was a stronger driving force to keep copper in solution thus reducing copper adsorption onto activated carbon and lessening competition of active sites with gold.
- The optimum pH that correlated with the highest equilibrium gold loading capacity was pH 10. Increasing the pH beyond 10 negatively affected the gold loading capacity. At a high pH (above 10) the concentration of OH⁻ ions is high and the likelihood of copper hydrolysis into Cu(OH)₂ precipitates is increased. The precipitates may then form a physical barrier on the carbon surface thereby fouling the carbon and preventing effective adsorption of gold.
- The lower the initial gold concentration in solution, the higher the equilibrium gold loading capacity of the carbon. Increasing the gold concentration from 2 to 16 ppm reduced the loading capacity of the carbon by over 50%. This implies that adsorption from concentrate leachates which are characterised by high gold concentrations will not be as effective compared to adsorption from low grade ore leaching (low gold concentration) under similar process conditions.
- Increasing the copper concentration from 0 to 20 ppm more than doubled the equilibrium gold loading capacity of the carbon. At copper concentrations 20 ppm and above, a slight decrease in the loading capacity was observed. Increasing the copper concentration to excessive amounts (> 20 ppm) increased the competition for active sites of the carbon between gold and copper.
- Addition of calcium chloride increased the gold loading significantly. The higher the Ca²⁺ concentration in solution the higher the ionic strength of the solution and as a result the electrostatic force between the solution and carbon is increased. Ca²⁺ has a smaller radius but higher corresponding charge and therefore can penetrate between the exfoliated graphene layers of the activated carbon swiftly and form a strong columbic attraction for Au(Gly)₂⁻.

The Freundlich isotherm was similarly used to evaluate equilibrium gold loading capacity of carbon for gold from alkaline cyanide-starved glycine solutions in the presence of 300 ppm copper. A summary of the results follows:

- As was the case with pure glycine only leach systems, the maximum equilibrium gold loading capacity of the carbon was observed at pH 10.
- A Cu:CN molar ratio of 1:1 gave the best equilibrium loading capacity of the carbon. Increasing the free cyanide concentration from 123 ppm (Cu:CN 1:1) to 476.3 ppm (Cu:CN 1:2.5) reduced the gold loading capacity of the carbon by more than half due to increased competition for active sites of the carbon between the gold and cyanide ions.
- Calcium ions through the addition of calcium chloride and calcium hydroxide significantly increased the gold loading capacity of the carbon.

9.1.1.2 Kinetics

The Fleming k,n adsorption kinetic model was used to analyse the adsorption data for alkaline glycine and cyanide-starved glycine solutions. The metal concentrations of the solutions were 2 ppm gold for both solutions and 40 ppm and 300 ppm copper for glycine and cyanide-starved glycine solutions respectively. A general summary of the results for both systems follows:

- Over 99% gold was adsorbed onto activated carbon within 24 hours for both systems under optimum conditions with more than 95% being adsorbed in the first 6 hours.
- Activated carbon was found to be very selective for gold over copper in both glycine and cyanide-starved glycine systems. Though copper was present in very high concentrations compared to gold in both systems, less than 50% copper was recovered in 24 hours compared to 99% gold within the same time frame.
- The gold kinetics of both systems were also significantly higher than the copper kinetics.
- The initial adsorption rate of both copper and gold was dependent on the process conditions.
- A change in the process conditions affected the initial adsorption rate of the gold but not the total gold recovered in 24 hours. For copper, both the rate of adsorption and overall recoveries were affected by a change in the process conditions.

The following is a summary of the kinetic studies for the glycine-only system in particular:

- An increase in pH increased the initial adsorption rate of gold and the highest initial adsorption rate of 25.4 h^{-1} was observed at pH 11.

- The highest initial adsorption rate of gold was observed at 5 g/L glycine for a solution pH of 11.
- Increasing the ionic strength of the solution did not significantly affect the initial gold adsorption rate but almost doubled that of copper when CaCl₂ concentration was increased from 0 to 0.5 g/L.
- Increasing the carbon concentration increased the initial gold adsorption rate but decreased the initial copper adsorption rate.
- Low copper concentrations in solution increased the initial gold adsorption rate. When more than 80 ppm copper was present in solution, the initial gold adsorption rate was lower than that of a copper-free glycine system.

A summary of the kinetic studies specifically for cyanide-starved glycine system follows below:

- Increasing glycine concentration increased the initial gold adsorption rate but decreased copper adsorption rate when copper was present. The opposite was found to be true for copper-free glycine cyanide systems.
- The highest initial gold adsorption rate was observed at pH 10. Increasing the pH beyond 10 decreased the initial gold and copper adsorption rates.
- A high initial gold concentration increased the initial gold and copper adsorption rate.
- At constant copper concentration, increasing the CN:Cu ratio increased the initial rate of adsorption for both gold and copper.

9.1.2 Elution

The experimental elution results showed that effective elution of gold glycinate using the AARL elution method is possible. The gold elution profile for AARL compared to those of pure water (at various elution temperatures) and NaCl water was steeper with the concentration peak appearing earlier, an indication that gold elution kinetics are fastest for AARL process than other evaluated techniques. When deionised water was used as the eluent, 87.7% gold eluted from activated carbon in 20 BV at 130°C after pre-treatment with a caustic cyanide solution (3% NaCN and 1% NaOH) at 80°C.

Still using deionised water as the eluent, non-pre-treated carbon shifted the elution profiles to the right and lowered the gold concentration peak indicating lower elution recoveries of 55.7%, 61.85% and 18.04% at 20 BVs as the elution temperature increased from 100°C to 130 °C and finally 150°C. NaCl water at 130°C exhibited a low elution efficiency desorbing only 24.68% gold from activated carbon.

9.2 Recommendations and Possible Avenues for Future Research

The following were identified as critical research gaps that are worth further investigation to expand on the current research:

(a) No work has yet been published on the co-loading isotherms of gold with other metals, e.g. silver and nickel commonly found in gold-copper ores. How does gold adsorption fare amidst the presence of other constituents (both metallic and non-metallic) in solution that might leach alongside gold?

(b) Very little is known about the purification of a pregnant leach solution that contains a mixture of base and precious metals, e.g. copper, nickel, gold and silver. Can solvent extraction be used to selectively remove the nickel and copper and can the nickel and copper be separated from each other in the solvent extraction circuit using different extractants? What are the kinetics of extraction and phase disengagement and the extraction isotherms as a function of type of extractant, pH and various organic to aqueous ratios in extraction and stripping? To what extent will traces of the organic extractant foul activated carbon if the base metal solvent extraction precedes the adsorption of the precious metals?

(c) A more extensive study on the adsorption mechanism of gold glycinate complex and how it compares with its cyanide counterpart is required. Is the adsorption mechanism similar to that of gold cyanide? Does gold glycinate adsorb as a complex, or is it reduced to its metallic state upon adsorption?

(d) Detailed investigation of how glycine interacts with and alters the carbon surface during adsorption would be insightful. Does it react with any of the functional groups found on the surface of the carbon?

(e) Extensive studies on the elution of gold from carbon loaded in glycine and glycine-cyanide systems needs to be performed. Detailed investigations focusing on optimising and maximising gold elution of these systems is vital. How does various parameters such as temperature, loaded carbon pre-treatment conditions, pressure, pH of eluant, column design, flow rate, affect the elution of gold and to what extent?

(f) The possibility of a cyanide-free elution technique for glycine systems that is as effective as AARL is for cyanidation systems needs to be pursued.

(g) Demonstrate that the eluted carbon can be re-used in a continuous operation.

(h) Applicability of findings to real solutions.

10 Appendices

- **Appendix A:** Signed statements of contribution of co-authors.
- **Appendix B:** Properties of Activated Carbon used for adsorption tests.
- **Appendix C:** Sample calculations for synthetic solution preparation used for adsorption tests.
- **Appendix D:** Tabulation of experimental data.
- **Appendix E:** Examples of carbon loading calculations.

Appendix A

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STATEMENT OF CO-AUTHORS of JOINT PUBLICATIONS - 1

TO WHOM IT MAY CONCERN

I Peo Joanah Tauetsile, the primary author of the following four publications forming part of this thesis, contributed to the conception of the project, design of experimental protocol, data collection, analysis and interpretation and also drafted significant parts of the paper manuscripts.

List of publications:

- **Tauetsile, P. J., Oraby, E. A., & Eksteen, J. J. (2018).** Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 1: Isotherms. *Hydrometallurgy*, 178, 202-208.
- **Tauetsile, P. J., Oraby, E. A., & Eksteen, J. J. (2018).** Adsorption behaviour of copper and gold Glycinates in alkaline media onto activated carbon. Part 2: Kinetics. *Hydrometallurgy*, 178, 195-201.
- **Tauetsile, P. J., Oraby, E. A., & Eksteen, J. J. (2019).** Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 1: Isotherms. *Separation and Purification Technology*, 211, 594-601.
- **Tauetsile, P. J., Oraby, E. A., & Eksteen, J. J. (2019).** Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: Kinetics. *Separation and Purification Technology*, 211, 290-297.

Name of candidate: Peo Joanah Tauetsile

Signature:

Name:

Date:

Title of research thesis: Adsorption of Gold and Copper from Alkaline Glycine-based Leach Solutions using Activated Carbon

Name of first supervisor: Professor Jacques Eksteen

We, the undersigned, co-authors of the above publications, confirm that the above publications have not been submitted as evidence for which a degree or other qualification has already been awarded.

We, the undersigned, further confirm that the candidate's stated contribution to the publications is accurate as detailed above. in our joint statement below.

Signature:

Name:

Date:

Signature:

Name:

Date:

STATEMENT OF CO-AUTHORS of JOINT PUBLICATIONS - 2

TO WHOM IT MAY CONCERN

I Peo Joanah Tauetsile, fourth co-author of the following publication forming part of this thesis, contributed a subsection of the paper. I planned, designed the experimental protocol, performed experiments, collected data, analysed and interpreted data relevant to my part of the publication.

Title of publication:

Eksteen, J.J., Oraby, E.A., Tanda, B.C., **Tauetsile, P.J.**, Bezuidenhout, G.A., Newton, T., Trask, F. and Bryan, I., 2018. Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores. *Canadian Metallurgical Quarterly*, 57(4), pp.390-398.

Name of candidate: Peo Joanah Tauetsile

Signature:

Name:

Date:

Title of research thesis: Adsorption of Gold and Copper from Alkaline Glycine-based Leach Solutions using Activated Carbon

Name of first supervisor: Professor Jacques Eksteen

I, the undersigned, primary co-author of the above publication, confirm that the above publications have not been submitted as evidence for which a degree or other qualification has already been awarded for the PhD candidate in question.

I, the undersigned, further confirm that the candidate's stated contribution to the publications is accurate as detailed above.

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Appendix B

Technical Datasheet: PICAGOLD G210AS

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Source of material: Jacobi Carbons

website: <https://www.jacobi.net/>

APPENDIX B2: Characterisation of Virgin Pulverised Activated Carbon

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Characterization done by: CSIRO Waterford, WA, 6152, Australia

website: <https://www.csiro.au/en/Locations/WA/Waterford>

APPENDIX B3: Particle Size Distribution of Pulverized Carbon

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Characterization done by: CSIRO Waterford, WA, 6152, Australia

website: <https://www.csiro.au/en/Locations/WA/Waterford>

Appendix C

Gyanide-starved Glycine Stock Solution Preparation

For a solution containing 300 ppm Cu, 2ppm Au, Cu : CN =1 : 3, Cu : Gly =1 : 3

Calculations based on **per litre**

CuCN

Molar Mass of CuCN = 89.563 g/mol

Molar Mass of Cu = 63.546 g/mol

Mass of CuCN in grams to add to have 300 ppm Cu in solution

Copper in solution = 300 ppm
= 300 mg/L
= 0.3 g/L

How many grams CuCN to weigh:

$$\begin{array}{l} \text{Cu : CuCN} \\ 63.546 : 89.563 \\ 0.3 : x \\ x = 0.4228 \text{ g CuCN} \end{array}$$

CuCN is 0.95 impure, so to adjust the purity, divide by 0.95 to get 0.445 g/L CuCN.

This amount will provide the Cu concentration needed and plus 1 mole of cyanide.

NaCN

The extra 2 moles of cyanide was sourced from NaCN addition.

$$\begin{array}{l} \# \text{ of moles of Cu} = \text{mass} / \text{MM} \\ = 0.3 / 63.546 \\ = 0.0047 \text{ moles} \end{array}$$

$$\begin{array}{l} \text{Molarity} = \# \text{ of moles} / \text{volume} \\ = 0.0047 / 1\text{L} \\ = 0.0047 \text{ mol/dm}^3 \end{array}$$

Need 2 moles of CN from NaCN

$$\begin{array}{l} \text{Cu : CuCN} \\ 1 : 2 \\ 0.0047 : x \\ x = 0.0094 \end{array}$$

Mass of CN⁻ ions only

$$\begin{aligned}\text{Mass} &= \# \text{ of moles} \times \text{molar mass} \\ &= 0.0094 \times 26.007 \\ &= 0.2444658\end{aligned}$$

Mass of NaCN to weigh

$$\begin{aligned}\text{NaCN} &: \text{CN} \\ 49.0072 &: 26.007 \\ x &: 0.2444658 \\ x &= 0.46066768 \text{ g/L NaCN}\end{aligned}$$

Glycine concentration (for Cu : Gly ratio of 1 : 3)

$$\begin{aligned}\text{Cu} &: \text{Gly} \\ 1 &: 3 \\ 0.0047 &: x \\ x &= 0.0141\end{aligned}$$

$$\begin{aligned}\text{Mass of glycine} &= \# \text{ of moles} \times \text{MM} \\ &= 0.0141 \times 75.07 \\ &= 1.058 \text{ g/L glycine}\end{aligned}$$

Au powder

$$\text{Au molar mass} = 196.966657$$

$$\begin{aligned}\text{Target} &= 2 \text{ mg/L} \\ &= 0.002 \text{ g/L Au powder}\end{aligned}$$

Appendix D

Appendix D1 – GLYCINE ONLY RAW DATA

D.1.1 Isotherms

| Standard experimental run conditions for all tests (unless specified otherwise) | |
|---|-------------------------------|
| Temperature | room temperature (23 – 25 °C) |
| Run time | 24 hours |
| Solution pH | 11 |
| Volume of solution (ml) | 250 ml |
| pH modifier | caustic |
| Glycine concentration | 5 g/L |

Parameter under investigation: Glycine concentration

Stock Solution:

| Metal | mg/L |
|-------|------|
| Au | 2.15 |
| Cu | 43.7 |

| | 1 g/L | | 5 g/L | | 10 g/L | | 15 g/L | |
|--------|-------|--------|-------|--------|--------|--------|--------|------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.010 | 1.200 | 42.300 | 1.290 | 43.500 | 0.918 | 42.800 | 0.853 | 43.6 |
| 0.032 | 0.319 | 41.700 | 0.302 | 43.900 | 0.324 | 43.400 | 0.364 | 42.6 |
| 0.064 | 0.144 | 41.700 | 0.120 | 42.900 | 0.125 | 42.900 | 0.150 | 42.6 |
| 0.101 | 0.115 | 41.300 | 0.087 | 42.500 | 0.085 | 41.900 | 0.082 | 43.3 |
| 0.160 | 0.103 | 40.600 | 0.070 | 42.600 | 0.069 | 41.500 | 0.066 | 42.5 |

Parameter under investigation: pH

Stock Solution:

| Metal | mg/L |
|-------|------|
| Au | 2.11 |
| Cu | 41.8 |

| | pH 9 | | pH 10 | | pH 11 | | pH 12 | |
|--------|-------|--------|-------|--------|-------|--------|-------|--------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.010 | 0.828 | 41.100 | 0.799 | 42.000 | 0.851 | 42.500 | 1.020 | 42.100 |
| 0.032 | 0.133 | 40.900 | 0.188 | 42.900 | 0.302 | 41.100 | 0.428 | 42.500 |
| 0.064 | 0.051 | 40.400 | 0.098 | 42.100 | 0.145 | 42.000 | 0.202 | 41.400 |
| 0.101 | 0.030 | 40.000 | 0.064 | 41.800 | 0.104 | 40.500 | 0.149 | 41.000 |
| 0.160 | 0.027 | 39.200 | 0.061 | 40.700 | 0.081 | 41.800 | 0.122 | 40.600 |

Parameter under investigation: Initial Au concentration

Stock solution:

| Metal | mg/L |
|-------|--------|
| Au | varies |
| Cu | 41.8 |

| | 2 ppm [Au] _i | | 4 ppm [Au] _i | | 8 ppm [Au] _i | | 16 ppm [Au] _i | |
|--------|-------------------------|--------|-------------------------|--------|-------------------------|--------|--------------------------|--------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.010 | 0.828 | 41.100 | 0.799 | 42.000 | 0.851 | 42.500 | 1.020 | 42.100 |
| 0.032 | 0.133 | 40.900 | 0.188 | 42.900 | 0.302 | 41.100 | 0.428 | 42.500 |
| 0.064 | 0.051 | 40.400 | 0.098 | 42.100 | 0.145 | 42.000 | 0.202 | 41.400 |
| 0.101 | 0.030 | 40.000 | 0.064 | 41.800 | 0.104 | 40.500 | 0.149 | 41.000 |
| 0.160 | 0.027 | 39.200 | 0.061 | 40.700 | 0.081 | 41.800 | 0.122 | 40.600 |

i = initial Au conc

Parameter under investigation: Calcium chloride concentration

Stock solution:

| Metal | mg/L |
|-------|------|
| Au | 2.1 |
| Cu | 41.8 |

| | 0 g/L CaCl ₂ | | ½ g/L CaCl ₂ | | 2 g/L CaCl ₂ | |
|--------|-------------------------|--------|-------------------------|--------|-------------------------|--------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.010 | 0.85 | 42.500 | 0.968 | 40.800 | 0.834 | 40.200 |
| 0.032 | 0.30 | 41.100 | 0.292 | 40.200 | 0.225 | 41.200 |
| 0.064 | 0.15 | 42.000 | 0.147 | 40.000 | 0.119 | 40.200 |
| 0.101 | 0.10 | 40.500 | 0.107 | 40.000 | 0.063 | 39.600 |
| 0.160 | 0.08 | 41.800 | 0.099 | 41.200 | 0.043 | 39.600 |

D.1.2 Kinetics

| Standard experimental run conditions for all tests (unless specified otherwise) | |
|--|-------------------------------|
| Temperature | room temperature (23 – 25 °C) |
| Run time | 24 hours |
| Solution pH | 11 |
| Volume of solution (ml) | 200 ml |
| Carbon concentration | 2 g/L |
| pH modifier | caustic |
| Glycine concentration | 5 g/L |

Parameter under investigation: Glycine concentration

| | 1 g/L | | 5 g/L | | 10 g/L | | 15 g/L | |
|------|-------|------|-------|------|--------|------|--------|------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.15 | 40 | 2.14 | 44 | 2.12 | 43.3 | 2.08 | 43.9 |
| 0.5 | 0.752 | 40 | 0.551 | 42.7 | 0.75 | 42.1 | 0.643 | 43 |
| 1 | 0.413 | 39 | 0.377 | 42.2 | 0.452 | 41.7 | 0.401 | 42.7 |
| 2 | 0.108 | 31 | 0.098 | 42.1 | 0.118 | 41.5 | 0.129 | 41.5 |
| 4 | 0.041 | 36 | 0.03 | 41 | 0.042 | 41.3 | 0.042 | 41.4 |
| 6 | 0.029 | 34 | 0.021 | 40.5 | 0.024 | 40 | 0.032 | 40.9 |
| 24 | 0.017 | 30 | 0.01 | 37.8 | 0.014 | 37.9 | 0.018 | 38.3 |

Parameter under investigation: pH

| | pH 9 | | pH 10 | | pH 11 | | pH 12 | |
|------|-------|------|-------|------|-------|------|-------|------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.11 | 41.8 | 2.17 | 42.8 | 2.1 | 43.3 | 2.04 | 42.8 |
| 0.5 | 0.677 | 40.6 | 0.662 | 42.1 | 0.737 | 41.7 | 0.687 | 41.9 |
| 1 | 0.357 | 40.1 | 0.418 | 42 | 0.433 | 41.1 | 0.397 | 41.6 |
| 2 | 0.087 | 39.3 | 0.101 | 41.7 | 0.1 | 40.6 | 0.139 | 40.7 |
| 4 | 0.039 | 39 | 0.029 | 40.7 | 0.039 | 40.8 | 0.053 | 39.3 |
| 6 | 0.018 | 38 | 0.02 | 40.4 | 0.029 | 40.1 | 0.037 | 38.7 |
| 24 | 0.007 | 35.9 | 0.012 | 37.2 | 0.035 | 36.9 | 0.018 | 36.5 |

Parameter under investigation: Initial Au concentration

| | 2 ppm [Au] _i | | 4 ppm [Au] _i | | 8 ppm [Au] _i | | 16 ppm [Au] _i | |
|------|-------------------------|------|-------------------------|-------|-------------------------|-------|--------------------------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.1 | 43.3 | 4.334 | 40.53 | 8.000 | 40.00 | 16.113 | 40.45 |
| 0.5 | 0.737 | 41.7 | 1.764 | 36.72 | 2.836 | 35.94 | 6.993 | 39.55 |
| 1 | 0.433 | 41.1 | 0.994 | 36.4 | 1.84 | 35.69 | 4.81 | 38.66 |
| 2 | 0.1 | 40.8 | 0.231 | 35.84 | 0.594 | 35.03 | 2.052 | 37.95 |
| 4 | 0.039 | 40.6 | 0.075 | 34.94 | 0.195 | 34.26 | 0.779 | 37.7 |
| 6 | 0.029 | 40.1 | 0.052 | 34.77 | 0.128 | 33.95 | 0.583 | 37.46 |
| 24 | 0.035 | 36.9 | 0.024 | 30.96 | 0.062 | 31.25 | 0.259 | 34.61 |

i = initial Au conc

Parameter under investigation: Carbon concentration

| | 2 g/L | | 4 g/L | | 8 g/L | | 12 g/L | |
|------|-------|------|-------|-------|-------|-------|--------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.1 | 43.3 | 2.097 | 38.92 | 2.097 | 38.92 | 2.097 | 38.92 |
| 0.5 | 0.737 | 41.7 | 0.358 | 37.42 | 0.028 | 36.63 | 0.005 | 33.84 |
| 1 | 0.433 | 41.1 | 0.104 | 36.01 | 0.009 | 34.55 | 0 | 32.02 |
| 2 | 0.1 | 40.8 | 0.027 | 35.59 | 0 | 32.81 | 0 | 29.12 |
| 4 | 0.039 | 40.6 | 0.01 | 33.65 | 0 | 30.21 | 0 | 25.79 |
| 6 | 0.029 | 40.1 | 0.005 | 32.8 | 0 | 28.32 | 0 | 23 |
| 24 | 0.035 | 36.9 | 0.005 | 27.61 | 0 | 19.13 | 0 | 10.63 |

Parameter under investigation: Initial Cu concentration

| | 0 ppm [Cu] _i | | 20 ppm [Cu] _i | | 40 ppm [Cu] _i | | 80 ppm [Cu] _i | | 800 ppm [Cu] _i | |
|------|-------------------------|------|--------------------------|------|--------------------------|------|--------------------------|------|---------------------------|------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.42 | 0 | 2.38 | 20.6 | 2.14 | 44 | 2.32 | 82 | 2.57 | 808 |
| 0.5 | 0.748 | 0 | 0.726 | 19.8 | 0.551 | 42.7 | 0.776 | 81.6 | 0.799 | 793 |
| 1 | 0.416 | 0 | 0.404 | 19.6 | 0.377 | 42.1 | 0.406 | 79.8 | 0.574 | 791 |
| 2 | 0.128 | 0 | 0.119 | 19.2 | 0.098 | 42.2 | 0.141 | 77.4 | 0.214 | 785 |
| 4 | 0.047 | 0 | 0.035 | 19 | 0.03 | 41 | 0.048 | 76.2 | 0.074 | 780 |
| 6 | 0.023 | 0 | 0.022 | 18.8 | 0.021 | 40.5 | 0.03 | 75.6 | 0.073 | 771 |
| 24 | 0.011 | 0 | 0.012 | 17.8 | 0.01 | 37.8 | 0.018 | 70.8 | 0.05 | 739 |

i = initial Cu conc

Parameter under investigation: Calcium chloride concentration

| | 0 g/L CaCl ₂ | | ½ g/L CaCl ₂ | | 2 g/L CaCl ₂ | |
|------|-------------------------|------|-------------------------|------|-------------------------|------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.1 | 43.3 | 2.41 | 43.8 | 2.44 | 42.8 |
| 0.5 | 0.737 | 41.7 | 0.696 | 41.2 | 0.728 | 40 |
| 1 | 0.433 | 41.1 | 0.516 | 39.8 | 0.555 | 39.8 |
| 2 | 0.1 | 40.8 | 0.151 | 40 | 0.162 | 39 |
| 4 | 0.039 | 40.6 | 0.057 | 37.8 | 0.051 | 38.6 |
| 6 | 0.029 | 40.1 | 0.029 | 36.8 | 0.03 | 38.8 |
| 24 | 0.035 | 36.9 | 0.018 | 35.4 | 0.022 | 32.8 |

Appendix D2 – GLYCINE CYANIDE RAW DATA

D.2.1 Isotherms

| Standard experimental run conditions for all tests (unless specified otherwise) | |
|--|-------------------------------|
| Temperature | room temperature (23 – 25 °C) |
| Run time | 24 hours |
| Solution pH | 11 |
| Volume of solution (ml) | 250 ml |
| pH modifier | lime |
| Glycine concentration | 5 g/L |
| Cu:CN | 1 : 1 |

Parameter under investigation: Glycine concentration

Stock Solution:

| Metal | mg/L |
|--------------|-------------|
| Au | 2.00 |
| Cu | 300 |

| | 1 g/L | | 5 g/L | | 10 g/L | | 15 g/L | |
|---------------|--------------|-------------|--------------|-------------|---------------|-------------|---------------|-------------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.020 | 1.52 | 256.2 | 0.835 | 309.1 | 0.70 | 307.3 | 0.61 | 309 |
| 0.064 | 0.97 | 238.6 | 0.358 | 305.4 | 0.29 | 295.6 | 0.19 | 307 |
| 0.128 | 0.74 | 222.9 | 0.180 | 284.5 | 0.17 | 291.5 | 0.10 | 295 |
| 0.200 | 0.42 | 211.5 | 0.114 | 292 | 0.14 | 278.4 | 0.07 | 293.7 |
| 0.320 | 0.14 | 193.3 | 0.066 | 265.8 | 0.01 | 266.7 | 0.05 | 283.7 |

Parameter under investigation: pH

Stock Solution:

| Metal | mg/L |
|--------------|-------------|
| Au | 2.00 |
| Cu | 329 |

| | pH 9 | | pH 10 | | pH 11 | | pH 12 | |
|--------|------|-------|-------|------|-------|------|-------|------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.020 | 0.92 | 287.9 | 0.904 | 320 | 0.982 | 313 | 1.300 | 286 |
| 0.064 | 0.44 | 285.5 | 0.323 | 325 | 0.367 | 303 | 0.498 | 279 |
| 0.128 | 0.24 | 273.5 | 0.167 | 300 | 0.193 | 289 | 0.238 | 269 |
| 0.200 | 0.12 | 252.4 | 0.105 | 290 | 0.131 | 286 | 0.161 | 259 |
| 0.320 | 0.06 | 239.4 | 0.063 | 273 | 0.080 | 276 | 0.106 | 223 |

Parameter under investigation: Cyanide concentration

Stock Solution:

| Metal | mg/L |
|-------|------|
| Au | 2.00 |
| Cu | 315 |

| | Cu:CN = 1:1 | | Cu:CN = 1:1.5 | | Cu:CN = 1:2 | | Cu:CN = 1:2.5 | |
|--------|-------------|-------|---------------|-------|-------------|-------|---------------|-------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.020 | 0.835 | 309.1 | 0.873 | 301.3 | 0.97 | 300.5 | 1.007 | 311.7 |
| 0.064 | 0.358 | 305.4 | 0.348 | 292.5 | 0.44 | 278.8 | 0.434 | 305.7 |
| 0.128 | 0.180 | 284.5 | 0.205 | 279.6 | 0.25 | 275.1 | 0.223 | 287.2 |
| 0.200 | 0.114 | 292 | 0.131 | 270.4 | 0.16 | 275.3 | 0.140 | 276.7 |
| 0.320 | 0.066 | 265.8 | 0.089 | 248.7 | 0.10 | 257.2 | 0.050 | 288 |

Parameter under investigation: Initial Au concentration

Stock Solution:

| Metal | mg/L |
|-------|--------|
| Au | varies |
| Cu | 318 |

| | 2 ppm [Au] _i | | 4 ppm [Au] _i | | 8 ppm [Au] _i | | 16 ppm [Au] _i | |
|--------|-------------------------|-------|-------------------------|-------|-------------------------|-------|--------------------------|-------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0.020 | 0.835 | 309.1 | 2.052 | 291.9 | 4.493 | 317.2 | 8.566 | 310.4 |
| 0.064 | 0.358 | 305.4 | 0.840 | 288.9 | 1.737 | 307.3 | 3.490 | 310 |
| 0.128 | 0.180 | 284.5 | 0.418 | 287.9 | 0.856 | 301.2 | 1.608 | 294.8 |
| 0.200 | 0.114 | 292 | 0.244 | 278.8 | 0.497 | 292.6 | 0.934 | 267 |
| 0.320 | 0.066 | 265.8 | 0.155 | 260.5 | 0.308 | 262.6 | 0.535 | 267.8 |

i = initial Au conc

Parameter under investigation: Glycine free cyanide only system adsorption behaviour

Stock Solution:

| Metal | mg/L |
|-------|------|
| Au | 2.00 |
| Cu | 300 |

| | Cu:CN = 1:2.5 | | Cu:CN = 1:4 | |
|--------|---------------|-------|-------------|-------|
| Carbon | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L |
| 0.020 | 1.635 | 192.8 | 0.806 | 231.7 |
| 0.064 | 1.248 | 192.5 | 0.147 | 232.7 |
| 0.128 | 1.074 | 166.8 | 0.059 | 229.8 |
| 0.200 | 0.490 | 158.3 | 0.036 | 231.6 |
| 0.320 | 0.271 | 158.1 | 0.025 | 223.7 |

Parameter under investigation: Ionic Strength [Ca^{2+}] vs [Na^+]

Stock Solution:

| Metal | mg/L |
|-------|------|
| Au | 2.00 |
| Cu | 310 |

| | NaOH* | | Ca(OH) ₂ * | |
|--------|-------|-------|-----------------------|-------|
| | [Au] | [Cu] | [Au] | [Cu] |
| Carbon | [Au] | [Cu] | [Au] | [Cu] |
| g | mg/L | mg/L | mg/L | mg/L |
| 0.020 | 1.198 | 290.5 | 0.835 | 309.1 |
| 0.064 | 0.591 | 284.6 | 0.358 | 305.4 |
| 0.128 | 0.324 | 275.1 | 0.180 | 284.5 |
| 0.200 | 0.147 | 270.9 | 0.114 | 292 |
| 0.320 | 0.099 | 255.1 | 0.066 | 265.8 |

* pH modifier used

Parameter under investigation: Glycine concentration (Cu free Au only glycine-cyanide system)

Stock Solution:

| Metal | mg/L |
|-------|------|
| Au | 2.00 |

| | 0 g/L | 1 g/L | 5 g/L | 15 g/L |
|--------|-------|-------|-------|--------|
| Carbon | [Au] | [Au] | [Au] | [Au] |
| g | mg/L | mg/L | mg/L | mg/L |
| 0.020 | 0.943 | 0.854 | 0.77 | 0.57 |
| 0.064 | 0.538 | 0.356 | 0.28 | 0.26 |
| 0.128 | 0.276 | 0.141 | 0.15 | 0.12 |
| 0.200 | 0.162 | 0.117 | 0.11 | 0.09 |
| 0.320 | 0.057 | 0.054 | 0.05 | 0.04 |

Parameter under investigation: Calcium chloride concentration

Stock solution:

| Metal | mg/L |
|-------|------|
| Au | 2.1 |

| | 0 g/L CaCl ₂ | ½ g/L CaCl ₂ | 2 g/L CaCl ₂ |
|---------------|----------------------------|----------------------------|----------------------------|
| Carbon | [Au] | [Au] | [Au] |
| g | mg/L | mg/L | mg/L |
| 0.020 | 0.835 | 1.061 | 0.939 |
| 0.064 | 0.358 | 0.528 | 0.462 |
| 0.128 | 0.180 | 0.409 | 0.339 |
| 0.200 | 0.114 | 0.374 | 0.299 |
| 0.320 | 0.066 | 0.351 | 0.268 |

D.2.2 Kinetics

| Standard experimental run conditions for all tests (unless specified otherwise) | |
|--|-------------------------------|
| Temperature | room temperature (23 – 25 °C) |
| Run time | 24 hours |
| Solution pH | 11 |
| Volume of solution (ml) | 200 ml |
| Carbon concentration | 8 g/L |
| pH modifier | lime |
| Glycine concentration | 5 g/L |
| Cu:CN | 1 : 1 |

Parameter under investigation: Glycine concentration

| | 1 g/L | | 5 g/L | | 10 g/L | | 15 g/L | |
|------|-------|-------|-------|-------|--------|-------|--------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.272 | 237.6 | 2.066 | 286.5 | 2.239 | 310.7 | 2.147 | 312.5 |
| 0.5 | 0.81 | 187.9 | 0.388 | 261.7 | 0.306 | 276.4 | 0.29 | 276.3 |
| 1 | 0.45 | 155.5 | 0.204 | 252.2 | 0.131 | 263.4 | 0.146 | 263.7 |
| 2 | 0.191 | 137.2 | 0.078 | 235.4 | 0.071 | 237 | 0.067 | 247.3 |
| 4 | 0.079 | 113.8 | 0.064 | 186.8 | 0.036 | 217.8 | 0.044 | 226.1 |
| 6 | 0.048 | 100.2 | 0.04 | 186.2 | 0.031 | 202.7 | 0.037 | 209.1 |
| 24 | 0.017 | 70.4 | 0.021 | 135.2 | 0.003 | 175.1 | 0.006 | 192.4 |

Parameter under investigation: pH

| | pH 9 | | pH 10 | | pH 11 | | pH 12 | |
|------|-------|-------|-------|-------|-------|-------|-------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L |
| 0 | 2.111 | 302.5 | 2.077 | 312 | 2.066 | 286.5 | 2.055 | 306 |
| 0.5 | 0.49 | 243.8 | 0.31 | 254.2 | 0.388 | 261.7 | 0.384 | 267.9 |
| 1 | 0.217 | 228.2 | 0.178 | 248.5 | 0.204 | 252.2 | 0.199 | 252 |
| 2 | 0.067 | 203.2 | 0.06 | 225.9 | 0.078 | 235.4 | 0.103 | 233.5 |
| 4 | 0.026 | 164.8 | 0.042 | 176.2 | 0.064 | 186.8 | 0.06 | 200.1 |
| 6 | 0.021 | 156.4 | 0.034 | 174.8 | 0.04 | 186.2 | 0.043 | 188.7 |
| 24 | 0.007 | 124 | 0.014 | 133.2 | 0.021 | 135.2 | 0.014 | 138.9 |

Parameter under investigation: Cyanide concentration

| | Cu:CN = 1:1 | | Cu:CN = 1:1.5 | | Cu:CN = 1:2 | | Cu:CN = 1:2.5 | |
|------|-------------|-------|---------------|-------|-------------|-------|---------------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.066 | 286.5 | 2.125 | 311.3 | 2.083 | 305.5 | 2.132 | 297 |
| 0.5 | 0.388 | 261.7 | 0.365 | 269 | 0.365 | 256 | 0.325 | 245.6 |
| 1 | 0.204 | 252.2 | 0.175 | 260.4 | 0.18 | 239.5 | 0.16 | 240.3 |
| 2 | 0.078 | 235.4 | 0.081 | 213.7 | 0.076 | 215.2 | 0.071 | 221.6 |
| 4 | 0.064 | 186.8 | 0.047 | 198 | 0.042 | 180.5 | 0.041 | 195.9 |
| 6 | 0.04 | 186.2 | 0.038 | 166.2 | 0.029 | 170.3 | 0.038 | 155.3 |
| 24 | 0.021 | 135.2 | 0.022 | 117.8 | 0.018 | 111.4 | 0.021 | 137.3 |

Parameter under investigation: Initial Au concentration

| | 2 ppm [Au] _i | | 4 ppm [Au] _i | | 8 ppm [Au] _i | | 16 ppm [Au] _i | |
|------|-------------------------|-------|-------------------------|-------|-------------------------|-------|--------------------------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.066 | 286.5 | 4.164 | 347.7 | 8.624 | 349.9 | 13.54 | 312.3 |
| 0.5 | 0.388 | 261.7 | 0.727 | 304.5 | 1.435 | 309.5 | 2.943 | 302.5 |
| 1 | 0.204 | 252.2 | 0.326 | 278.6 | 0.557 | 288.6 | 1.078 | 275.2 |
| 2 | 0.078 | 235.4 | 0.147 | 266.9 | 0.233 | 265.4 | 0.461 | 263.3 |
| 4 | 0.064 | 186.8 | 0.099 | 232.6 | 0.133 | 236.2 | 0.248 | 243 |
| 6 | 0.04 | 186.2 | 0.088 | 220.9 | 0.101 | 213.8 | 0.193 | 235.6 |
| 24 | 0.021 | 135.2 | 0.017 | 170.6 | 0.033 | 174.9 | 0.078 | 183.7 |

i = initial Au conc

Parameter under investigation: Glycine free cyanide only system adsorption behaviour

| | Cu:CN = 1:2.5 | | Cu:CN = 1:4 | |
|------|---------------|-------|-------------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L |
| 0 | 1.979 | 209.8 | 1.894 | 236.1 |
| 0.5 | 0.356 | 170.1 | 0.095 | 234.7 |
| 1 | 0.246 | 150.7 | 0.026 | 225.4 |
| 2 | 0.108 | 140.1 | 0.013 | 221.6 |
| 4 | 0.055 | 127.7 | 0.007 | 218.2 |
| 6 | 0.038 | 120.7 | 0.005 | 217.6 |
| 24 | 0.015 | 106.9 | 0.005 | 214.6 |

Parameter under investigation: Ionic Strength [Ca²⁺] vs [Na⁺]

| | NaOH* | | Ca(OH) ₂ * | |
|------|-------|-------|-----------------------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.077 | 264.8 | 2.066 | 286.5 |
| 0.5 | 0.225 | 242.4 | 0.388 | 261.7 |
| 1 | 0.109 | 217.3 | 0.204 | 252.2 |
| 2 | 0.054 | 185.2 | 0.078 | 235.4 |
| 4 | 0.034 | 159.4 | 0.064 | 186.2 |
| 6 | 0.022 | 145.4 | 0.021 | 135.2 |
| 24 | 0.01 | 113.5 | 2.066 | 286.5 |

* pH modifier used

Parameter under investigation: Glycine concentration (Cu free Au only glycine-cyanide system)

| | 0 g/L | 1 g/L | 5 g/L | 10 g/L | 15 g/L |
|------|-------|-------|-------|--------|--------|
| Time | [Au] | [Au] | [Au] | [Au] | [Au] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.054 | 2.013 | 1.979 | 2.232 | 2.204 |
| 0.5 | 0.071 | 0.083 | 0.105 | 0.089 | 0.084 |
| 1 | 0.02 | 0.027 | 0.061 | 0.071 | 0.054 |
| 2 | 0.01 | 0.01 | 0.03 | 0.045 | 0.036 |
| 4 | 0.005 | 0.007 | 0.02 | 0.035 | 0.017 |
| 6 | 0.001 | 0.003 | 0.011 | 0.019 | 0.011 |
| 24 | 0 | 0 | 0.003 | 0.008 | 0.018 |

Parameter under investigation: Calcium chloride concentration

| | 0 g/L CaCl ₂ | | ½ g/L CaCl ₂ | | 2 g/L CaCl ₂ | |
|------|-------------------------|-------|-------------------------|-------|-------------------------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| 0 | 2.077 | 264.8 | 2.112 | 306.2 | 2.013 | 301.2 |
| 0.5 | 0.225 | 242.4 | 0.324 | 242 | 0.278 | 251.1 |
| 1 | 0.109 | 217.3 | 0.167 | 233.9 | 0.124 | 234.8 |
| 2 | 0.054 | 185.2 | 0.117 | 203.3 | 0.066 | 216.4 |
| 4 | 0.034 | 159.4 | 0.09 | 157.6 | 0.042 | 188 |
| 6 | 0.022 | 145.4 | 0.08 | 151 | 0.017 | 170.6 |
| 24 | 0.01 | 113.5 | 0.066 | 116.6 | 0.013 | 125.9 |

Parameter under investigation: Carbon concentration

| | 2 g/L | | 4 g/L | | 8 g/L | | 12 g/L | |
|------|-------|-------|-------|-------|-------|-------|--------|-------|
| Time | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] | [Au] | [Cu] |
| hrs | mg/L | mg/L |
| 0 | 2.143 | 330.5 | 2.143 | 330.5 | 2.066 | 286.5 | 2.143 | 330.5 |
| 0.5 | 1.149 | 305.7 | 0.668 | 302 | 0.388 | 261.7 | 0.146 | 265.3 |
| 1 | 0.862 | 305.3 | 0.397 | 282.8 | 0.204 | 252.2 | 0.066 | 243.3 |
| 2 | 0.466 | 292.2 | 0.163 | 279.8 | 0.078 | 235.4 | 0.037 | 213.2 |
| 4 | 0.273 | 290.1 | 0.096 | 262.9 | 0.064 | 186.8 | 0.022 | 169.7 |
| 6 | 0.222 | 287.6 | 0.092 | 247.2 | 0.04 | 186.2 | 0.02 | 163.7 |
| 24 | 0.175 | 259.8 | 0.045 | 204.2 | 0.021 | 135.2 | 0.012 | 100.5 |

Appendix E

E.1 Gold loading capacity of activated carbon

Calculation method:

To determine the gold loading on the carbon:

$$\text{Gold Loading on Carbon} = \frac{(B - A) \times 0.25}{\text{Mass of Dry Carbon}} = C, \text{ kg/t}$$

where B is the concentration of gold (in mg/L) in the stock gold solution and A is the concentration of gold (in mg/L) in the final solution.

Plot the adsorption isotherm for the carbon sample, with $\log(A)$ values on the x-axis and the $\log(C)$ values on the y-axis. The y-intercept represents the equilibrium gold loading of the carbon at an equilibrium solution gold concentration of 1 mg/L.

0.25 is volume of solution used in litres.

E2 Example of Fleming k constant calculation

CARBON ACTIVITY CONSTANT, k, DETERMINATION

The rate equation for the determination of the carbon activity constant is given by the expression

$$\log (\Delta [\text{Au}]_c / [\text{Au}]_s) = n \log t + \log k$$

Where: $\Delta [\text{Au}]_c$ = change in [Au] on carbon from $t=0$ to $t=t$ hrs
 $[\text{Au}]_s$ = [Au] in solution at $t=t$ hrs
 n =an experimentally derived constant for the slope of the above equation
 k = an empirical rate constant at $t= 1$ hr

r^2 = the correlation coefficient of the above equation

Test ID: glycine only system. Effect of initial Cu concentration on Au adsorption.

| Sample # Sample ID | 1 0 ppm Cu | 2 20 ppm Cu | 3 40 ppm Cu | 4 80 ppm Cu | 5 800 ppm Cu | 6 |
|-----------------------|---------------------------|----------------|----------------|----------------|-----------------|---------|
| Carbon wt g | 0.4000 | 0.4000 | 0.4000 | 0.4000 | 0.4000 | |
| % moisture | 2.40 | 2.40 | 2.40 | 2.40 | 2.40 | |
| Soln Vol mL | 200 | 200 | 200 | 200 | 200 | 490 |
| Time Hrs | Au solution assays ppm Au | | | | | |
| 0 | 2.4200 | 2.3800 | 2.1400 | 2.3200 | 2.5700 | |
| 0.5 | 0.7480 | 0.7260 | 0.5510 | 0.7760 | 0.7990 | |
| 1 | 0.4160 | 0.4040 | 0.3770 | 0.4060 | 0.5740 | |
| 2 | 0.1280 | 0.1190 | 0.0980 | 0.1410 | 0.2140 | |
| 4 | 0.0470 | 0.0350 | 0.0300 | 0.0480 | 0.0740 | |
| calc k | 2985.5 | 3145.9 | 3491.1 | 2731.4 | 2351.3 | 1.0 |
| n | 1.5 | 1.7 | 1.6 | 1.5 | 1.3 | 0.0 |
| r ² | 0.9910 | 0.9873 | 0.9658 | 0.9958 | 0.9690 | #DIV/0! |
| %Activity | 100.0 | 100.0 | 104.6 | 97.3 | 92.6 | #DIV/0! |
| Average %Activity | 100.0 | | 101.0 | | #DIV/0! | |

CALCULATED DATA

| 1 | 2 | 3 | 4 | 5 | 6 |
|----------------------|--------|--------|--------|--------|--------|
| Dry weight of carbon | | | | | |
| 0.3904 | 0.3904 | 0.3904 | 0.3904 | 0.3904 | 0.0000 |

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