EFFECT OF TEMPERATURE, CONTACT TIME AND AGITATION SPEED DURING PRE-TREATMENT ON ELUTION OF GOLD

by

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Declaration

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Abstract

The pronounced effect of the caustic cyanide (NaOH-NaCN) pre-treatment step of the Anglo American Research Laboratory (AARL) gold (Au) elution process has been widely investigated. However, research into the reaction kinetics of this step is lacking and a set industry standard is yet to be determined, i.e., pre-treatment temperature, contact time and reactor conditions (reactor design and agitation). Among these reactor conditions, the effect of agitation that significantly improves mass transfer processes has not been investigated in the presence of NaOH-NaCN on Au elution recovery. This present study investigates the role of cyanide (CN^-) during pre-treatment as well as the effect of temperature, contact time and agitation speed on the Au elution recovery. A suitable elution mechanism was proposed from the results obtained.

Experiments were statistically designed using a Box Behnken experimental design. The agitation (stirring speed) was correlated by Power number and Reynolds number.

It was shown that Au elution recovery increased by approximately 15% after 6 Bed volumes (BVs) as the pre-treatment temperature increased from 25°C to 80°C which is in agreement with findings by previous researchers. The effect of contact time on Au elution recovery was found to be statistically insignificant between 15 and 45 min. At 25^{o}C, an increase in the recovery of Au of about 4% was seen from 15 to 45 min. Based on the trends of the experimental result and the validity of the statistically determined model to predict the effect of pre-treatment parameters on Au elution recovery, the effect at < 15 min or > 45 min can also be estimated from the result. An increase in the pre-treatment time had an insignificant effect on the subsequent elution recovery at 53^{o}C and 80^{o}C. It was suggested that an increase in the temperature minimises the effect of contact time on the overall Au elution recovery. The effect of agitation showed a decrease of about 10% in Au elution recovery when the agitation speed was increased from 0 to 1200 rev/min. The effect of agitation speed was more significant at 80^{o}C. Further evaluation of solid-liquid mass transfer coefficient (k_{SL}) of CN^- in the pre-treatment medium showed no significant change in the value of k_{SL} from 0 to 1200 rev/min. The results obtained confirmed that the elution process was not limited by diffusion.

Several researchers have proposed different elution mechanisms with regards to the functional role of CN^-. These mechanisms were evaluated based on the results of the current study. It was found that the mechanism where the CN^- is involved in a specific chemical reaction at the carbon surface which increases the negative charge density and renders the surface less receptive for adsorption, was suggested to be more plausible than the oxidation and hydrolysis of CN^-. Further investigation on loaded activated carbon that was thermally regenerated showed that CN^- is required to convert solid Au particle to soluble $Au(CN)_2^-$ which will require longer pre-treatment times and higher concentrations of CN^-. Finally, the relevance of this study was shown to be applicable in gold processing plants where a significant amount of Au remains on carbon after elution, particularly where CN^- free elution is being practised in order to minimise Au loss with the tailings dam.

Opsomming

Die beduidende effek van die bytende sianiedvoorbehandeling stap vir die Anglo Amerikaanse Navorsing Laboratorium (AARL) goud eluering proses is al deeglik bestudeer. Nietemin is navorsing oor die reaksie kinetika gebrekkig en 'n industriestandaard moet nog bepaal word m.b.t. voorbehandelingstemperatuur, tyd en reaktor toestande (reaktorontwerp en menging). Die effek van menging op Au herwinning in die teenwoordigheid van NaOH-NaCN is nog nie ondersoek nie. Die huidige werk bestudeer die rol van CN^- gedurende die voorbehandelingstap sowel as die effek van temperatuur, kontaktydperk en roerderspoed op die herwinning van goud deur eluering. 'n Gepaste eluerings-meganisme is voorgestel gebaseer op die resultate wat verkry is.

Eksperimente is statisties ontwerp deur gebruik te maak van 'n Box Behnken eksperimentele ontwerp met drie faktore en drie vlakke. Veranderlikes soos reaktorontwerp, stuwerdeursnee asook die vorm van die stuwer is saamgegooi met roerderspoed en is gekorreleer deur 'n mag-nommer en 'n Reynolds getal.

Daar is gesien dat verhoging in voorbehandelingtemperatuur vanaf 25°C tot 80°C die herwinning van goud deur eluering verhoog het met nagenoeg 15% na afloop van 6 bedvolumes. Hierdie waarneming het ooreengestem met bevindings van ander navorsers. Daar is bevind dat die effek van kontaktydperk statisties onbeduidend was tussen 15 tot 45 min. 'n Verlenging van voorbehandelingtydperk het 'n onbeduidende uitwerking op herwinning deur eluering by 53°C en 80°C gehad. Dit is voorgestel dat die verhoging in temperatuur die effek van kontaktydperk minimeer op algehele goud herwinning deur eluering. 'n Verhoging in roerderspoed vanaf 0 tot 1200 rpm het 'n afname van nagenoeg 10% goud herwinning van eluering tot gevolg gehad. Die effek van roerderspoed was meer beduidend by 80°C. 'n Ondersoek van die vloeistof-vastestof massa-oordrag koëffisiënt (k_{SL}) van CN^- in die voorbehandelingmedium het geen beduidende verandering getoon met verhoging in roerderspoed vanaf 0 tot 1200 rpm nie. Resultate het daarop gedui dat die elueringsproses nie beperk was deur diffusie nie.

Verskeie navorsers het verskillende eluerings-meganismes voorgestel m.b.t. die funksionele rol van CN^-. Die voorgestelde meganismes is ondersoek deur vergelyking met resultate wat verkry was tydens eksperimentele ondersoek van voorbehandelings

veranderlikes. Die meganisme waar CN^- betrokke is by 'n spesifieke chemiese reaksie op die koolstof oppervlak wat die negatiewe ladingsdigtheid verhoog en sodoende die oppervlak minder vatbaar maak vir adsorpsie, is voorgestel as meer waarskynlik as die oksidasie en hidrolise van CN^-. Ondersoek van termiesgeregenereerde geaktiveerdekoolstof het gewys dat CN^- nodig is om soliede Au te omskep na oplosbare $Au(CN)_2^-$ wat 'n langer voorbehandelingstydperk en hoër CN^- konsentrasies benodig. Ten slotte, die toepaslikheid van hierdie studie is beduidend waar goud in goudverfyningsaanlegte agterbly op koolstof na eluering en veral waar sianied-eluering toegepas word met die oog op vermindering van goudverliese op geëlueerde koolstof.

Acknowledgements

First and foremost, I want to give all the glory to God and my saviour for the gift of life and strength granted onto me in the course of this research and for making it possible “With God all things are possible Mark 10:27 b”.

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Nomenclature

Symbol	Description	Unit
A	Loading capacity	mg/g
C	Concentration of CN^- in the bulk solution at time t	g/L
C*	Concentration of CN^- at the carbon surface	g/L
C_{CA}	Concentration of calcium	g/L
C_f	Final concentration of CN^-	g/L
C_i	Initial concentration of CN^-	g/L
C_K	Concentration of Potassium	g/L
C_o	Concentration at time zero	g/L
C_w	Concentration of solids by weight in slurry	%
D	Impeller Diameter	m
ε	Experimental error	
N	Rotational speed of impeller	rev/min
N_p	Power number	
P	Power consumption	Watts
R	Reynolds number	
V_f	Final volume of water	mL
V_i	Initial volume of water	mL
Y	Percentage Recovery	%
μ_L	Viscosity of Liquid	$N.s/m^2$
μ_m	Viscosity of mixture	$N.s/m^2$
ρ_L	Density of Liquid	kg/m^3
ρ_m	Density of mixture	kg/m^3
ρ_s	Density of solid	kg/m^3
a_s	Interfacial area	m^2/m^3
ϕ	Volume fraction	
θ	Activated carbon loading in solution	g/L
ρ_c	Density of the activated carbon	kg/m^3
d_c	Diameter of the activated carbon	m
k_{SL}	Solid-liquid mass transfer coefficient	$cm\ min^{-1}$
x_1	Temperature	^oC

x_2	Contact Time	minutes
x_3	Agitation speed	rev/min

Abbreviations

Abbreviation	Description
AARL	Anglo American Research Laboratory
AC	Activated carbon
AC-Au	Activated carbon loaded with gold
ANOVA	Analysis of Variance
AV	Average value
BB	Box Behnken
BV	Bed volumes
CIL	Carbon in leach
CIP	Carbon-in-pulp
CV	Coefficient of variation
FTIR	Fourier transform infrared spectroscopy
ICP_MS	Inductively Coupled Plasma-Mass Spectrometry
L	Linear
Min	Minutes
PGM	Platinum group metals
Q	Quadratic
SD	Standard Deviation
SEM	Scanning Electron Microscopy
TPD	Temperature programmed desorption
UAC	Unloaded activated carbon
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron spectroscopy

Subscript	
CA	Calcium
C	Carbon
F	Final
I	Initial
K	Potassium
L	Liquid
M	Mixture
O	Zero
P	Power
S	Solid
sL	Solid-Liquid
W	Weight
Superscript	
*	Carbon surface

1 Introduction

1.1 Background

Two major elution techniques have been widely used for gold (Au) elution recovery from activated carbon using caustic cyanide (NaOH-NaCN) solution (Davidson and Bailey, 1991). These are the Anglo American Research Laboratory (AARL) elution and the Zadra elution techniques. The AARL involves pre-treatment of the granular activated carbon adsorbed with gold-cyanide [[1] $Au(CN)_2^-$] in NaOH-NaCN solution, followed by elution with hot (110^oC–130^oC) deionised water (Davidson and Schmidt, 1986). Zadra elution involves recirculation of hot (≈95°C) eluant containing NaOH-NaCN solution through electrowinning cells connected in series (Zadra et al., 1950). Of these two elution techniques, the AARL is the most widely used due to its numerous advantages; the major one being its short elution time and improved Au elution recovery with high "barrenness" of eluted carbon (Marsden and House, 2006).

Pre-treatment of Au loaded activated carbon with NaOH-NaCN solution and high elution temperature have been investigated to have a significant effect on Au elution recovery in AARL technique (Davidson, 1993). However, no set standard regarding the pre-treatment conditions i.e., pre-treatment temperature (which is the measured temperature of NaOH-NaCN solution in a vessel containing Au loaded carbon before the introduction of eluant) and contact time exists in the industry. According to Van Deventer and Van Der Merwe (1994), high pre-treatment temperature yields improved Au elution recovery than low temperature. The researchers suggested that this was attributed to improved decomposition of cyanide (CN^-), but the conclusion was not proven.

Van Deventer and Van der Merwe (1995) observed an improved decomposition of CN^- by increasing the agitation speed after 70 hours. However, the subsequent effect of agitation speed on elution recovery of Au was not investigated. In this vein, little is

[1] $Au(CN)_2^-$ is a specie of Au formed after leaching that is adsorbed onto activated carbon.

known about the combined effect of temperature and agitation speed for a set time, on the behaviour and decomposition of CN^- during pre-treatment and the elution process that follows.

Clear understanding of the role and behaviour of NaOH-NaCN during pre-treatment in the presence and absence of activated carbon will provide insight into the possible elution mechanisms involved. Following this, the effects of time, temperature, agitation and their interactions were investigated in order to determine how it affects the subsequent elution process. Results obtained on laboratory scale were therefore, related to plant conditions.

1.2 Problem statement

Over the years in gold industries, variability exists among the pre-treatment factors, particularly the pre-treatment temperature and contact time (Davidson and Bailey, 1991). Au elution recovery, with regards to these factors has not received much attention. The effect of pre-treatment temperature on CN^- decomposition that consequently improves Au elution recovery has been suggested (Van Deventer and Van der Merwe, 1993). Similarly, the effect of agitation speed on the decomposition of CN^- for a set contact time has been investigated (Van Deventer and Van der Merwe, 1995). However, the effect of agitation speed on Au elution recovery and its effect on the mass transfer of CN^- during pre-treatment have not been reported. Due to lack of understanding of the effect of temperature, contact time and agitation speed on the Au elution recovery and the associated CN^- mass transfer, it is difficult to carry out optimisation of gold elution process. It was thus the primary objective of this study to investigate the effect of these pre-treatment process parameters on Au elution recovery.

1.3 Research questions

- What are the roles and behaviour of NaOH-NaCN on Au loaded activated carbon during pre-treatment?
- Is there any significant effect of pre-treatment temperature, contact time and agitation speed on Au elution recovery?

- What are all the various proposed elution mechanisms available?
- Which elution mechanism will suitably explain the elution mechanism based on the outcome of the second research question?
- What is the significance of this research to the gold industry?

1.4 Research objectives

In order to gain better understanding of the pre-treatment parameters affecting Au elution recovery, the following were the objectives of this project:

- To investigate the effects of pre-treatment temperature, contact time, agitation speed and their combined effect on Au elution recovery.
- To review the existing theories on elution mechanisms and explain the fitting elution mechanism based on the results obtained.

1.5 Project scope

This work focused on the AARL elution process with the pre-treatment operation conducted at a fixed concentration of NaOH-NaCN. The effects of time, temperature, agitation speed and their interactions on Au elution recovery were investigated. The behaviour of CN^- under these parameters was monitored on activated carbon and in solution, to provide insight into the rate controlling process.

1.6 Significance of the project

This work will provide an understanding of the effects of pre-treatment temperature, contact time and agitation speed on Au elution recovery. Based on this insight and the outcome from the effect of these parameters on Au elution recovery, a better explanation on the appropriate elution mechanism from the already proposed mechanisms by other researchers will be provided. Furthermore, this study will also provide recommendations for South African gold industries on possible ways of improving Au elution recovery.

1.7 Structure of thesis

This study is presented as follows:

Chapter 1

This chapter gives a broad view of what this research is about. It also states the problem statement, objectives and scope of the project.

Chapter 2

This chapter is a review chapter which starts with the broad view of gold processing. It comprises a review of the application and properties of activated carbon in gold processing. The previous findings of Au adsorption and the factors that affect adsorption and elution of Au from activated carbon were also reported in this chapter. Furthermore, the behaviour of CN^- was reviewed. The various pre-treatment operations of Au with NaOH-NaCN solution and the adopted parameters during pre-treatment by different industries were reported.

Chapter 3

The chapter describes the materials used, the methods and analytical techniques adopted in the experimental work. The approach to the design of experiments, choice of factor levels and analytical techniques were also discussed.

Chapter 4

The mechanisms of CN^- loss from pre-treatment solution were discussed and the recovery due to elution at different combinations of pre-treatment parameters were presented and discussed. A result of the investigated parameters applied to Au loaded carbon that has been eluted and regenerated from gold plant was also reported. Based on the results, a possible elution mechanism was suggested.

Chapter 5

Results obtained were statistically analysed. Possible errors that might be associated with the experiment were estimated and discussed.

Chapter 6

The main conclusions drawn from the elution results at different pre-treatment parameters as well as the possible mechanism of pre-treatment were presented in this chapter. Recommendations on the practical implication were also presented and future works to further improve on it.

2 Literature review: Gold process, activated carbon, adsorption and elution

2.1 Overview of gold process

A simplified flow diagram of a typical gold processing operation plant from the ore to the final smelting stage is shown in Figure 2.1. The processes involved are divided into six major steps for this overview study (Table 2.1). These steps include crushing and milling, thickening and oxidation of the ore, leaching, adsorption, elution and electro-winning. The table also shows a brief description of each stage, equipment used as well as the typical operating conditions.

From Figure 2.1, after comminution, the ore is transferred to the leaching tanks. The process of Au leaching with cyanide solution, also known as cyanidation, involves dissolution of finely crushed Au ore in a cyanide solution to form Au complex $[Au(CN)_2^-]$ (La Brooy et al., 1994). The process of cyanidation is represented by the Elsner's equation given by Equation 2.1 (Gavin and Monhemius, 2006).

$$4Au + 8CN^- + O_2 + 2H_2O \leftrightarrow 4Au(CN)_2^- + 4OH^- \qquad 2.1$$

From Equation 2.1, sufficient oxygen and CN^- is required to favour the reaction to the right (Prasad et al., 1991). However, the CN^- concentration is controlled so as to favour the forwad reaction while preventing environmental pollution by evolution of HCN gas. This also reduces the costs that are associated with excessive usage (Metalliferous mining processing, 2010 a).

The Au in the pregnant leach solution (PLS) from the leaching tanks is adsorbed onto activated carbon in a carbon-in-pulp (CIP) plant (Barnes et al., 2000). The CIP plant is further discussed in Section 2.3.1. The adsorbed $Au(CN)_2^-$ is concentrated by elution using water as an eluant in an elution column. Au elution is further discussed in Section 2.8. The barren carbon that has been stripped of Au is reactivated in a kiln at a temperature range of about 200 – 700^oC to burn off the volatile and non-volatile adsorbates (Baily, 1987). These adsorbates exist either as organic (machinery oil from mining equipment, decomposed products of vegetation accompanied during mining) and inorganic substances (calcium from lime in the leaching stage, sodium salts, as

well as fine ore minerals which includes aluminate, complex silicates, silica and base metal precipitates) (Marsden and House, 2006; Fleming, 1992). Volatile adsorbate are vaporised and decomposed between the temperature range of 200 – 500^{o}C while non-volatile adsorbate are pyrolysed at higher temperature of about 500 – 700^{o}C (Baily, 1987). The concentrated Au solution by elution is passed through the electrowinning cell to produce loaded cathodes (Marsden and House, 2006). The 'electrowon' products are smelted into Au bars and transported to a gold refinery for further refining.

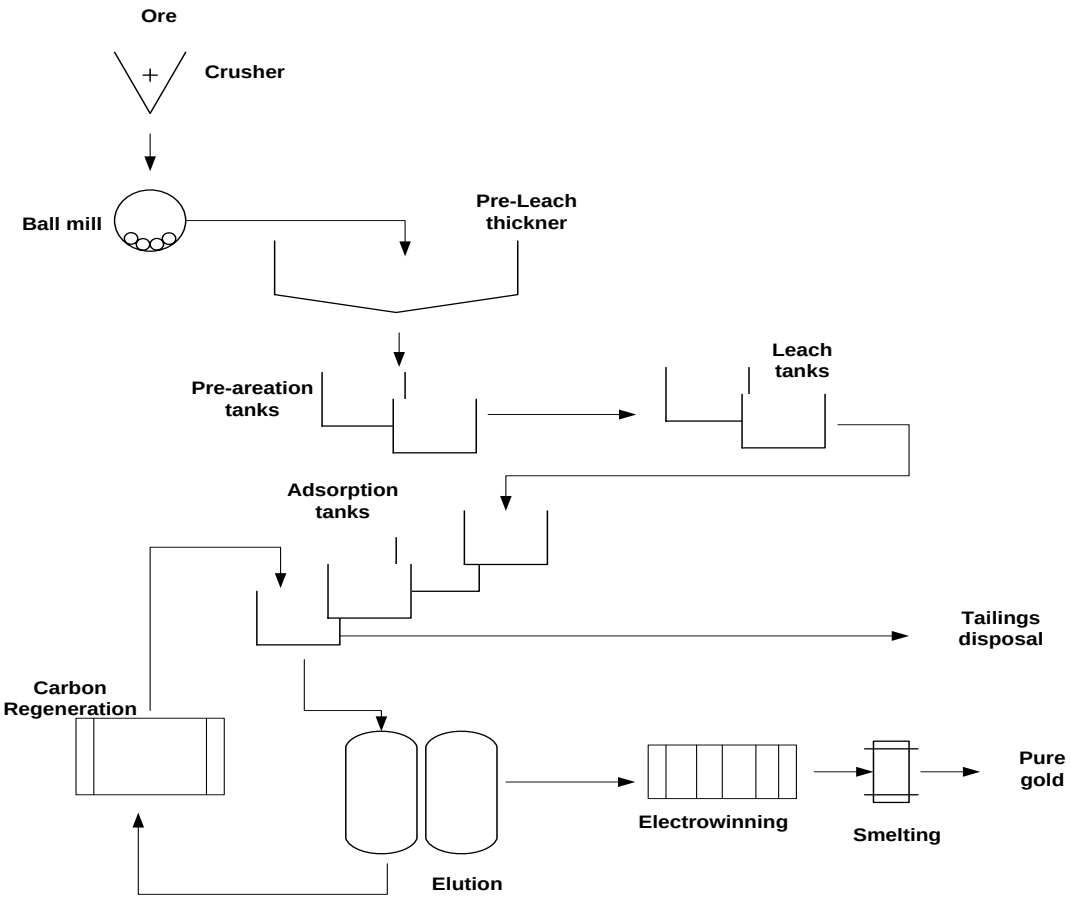


Figure 2.1: Simplified flow-sheet of a gold processing plant. Modified from Mt Todd (2013)

Table 2.1: Description of gold process

STEPS	OPERATION	PURPOSE(S)	EQUIPMENT/REAGENTS	OPERATING CONDITION(S)	REFERENCES
STEP1	Crushing and Milling	Size reduction (<75 µm) for liberation of valuable metals from host rocks Finer grinding (<38 µm) is suitable for refractory ore	Crushers and Ball mills	Depends on the nature of the ore	La Brooy et al., 1994; Fleming, 1992.
STEP2(a)	Thickening (auxiliary operation)	To achieve high pulp density	Pre-leached thickener	Small solid density and high slurry fluid could reduce residence time of leaching and adsorption	Yannopoulous, 1991; Fleming, 2011
STEP2(b)	Oxidation of ore (auxiliary operation)	For refractory ore to passivate sulphide minerals that would consume cyanide	Pre-aeration tanks	48 to 72 hours of retention time for complete oxidation	Marsden and House, 2006; Fleming, 1992
STEP3	Leaching with cyanide, other reagents include; halides, thiourea, thiosulphate, thiocyanate, ammonia	Dissolution	Agitation tanks, heaps	24 hours for free milling ores 48 hours for refractory ores	Marsden and House, 2006; Aylmore, 2005; Fleming, 1992; Groudev et al., 1996
STEP4	Adsorption	Selective adsorption of precious metals	Carbon-in-pulp plant, Carbon-in-leach, Resin-in-pulp, activated carbon, resins (adsorption tanks)	Room temperature, presence of cations	Goyal, 2010, Stanley, 1987
STEP5	Elution	Removal of adsorbed gold (stripping)	Elution columns	High temperature (110–130^{o}C), pressure of 230 kPa, low ionic strength, high cyanide concentration	Jeffery et al., 2010
STEP 6	Electrowinning	Purification	Electro-winning cells	Applied voltage > reversible electrode potential	Marsden and House, 2006; Conradie et al., 1995; Filmer, 1982

2.2 Properties and application of activated carbon

The application of activated carbon either in powdered or granulated form in gold processing has been widely used since the 1880s (Habashi and Fathi, 2005; Bailey 1987). The unique feature that made it gain acceptance in Au process is its large internal surface area (>400m^2/g) and preferential selectivity for precious metals [Au and silver (Ag)] at low metal concentration (0.2 mg/L or less) in pulp (Yalcin and Arol, 2002; McDougal and Hancock, 1981). Although the powdered form of the activated carbon possesses a larger internal surface area of about 1500 m^2/g (Basal and Goyal, 2010), it is less preferable to granulated carbon due to Au loss that is associated with carbon fines (Stanley, 1987).

Spent activated carbon can be reused after reactivation (Marsden and House, 2006). Reactivation below 600^{o}C burns off the volatile materials while higher temperature (700–1000^{o}C) burns the carbon skeleton thus increasing the pores of carbon (Marsh and Reinoso, 2006; Bailey, 1987). These pores have been further classified into macro pores (60–10000 nm), meso-pores (3–60 nm), micro pores (less than 3 nm) (Mahapatra, 2009). A typical activated carbon is shown in Figure 2.2. Some examples of activated carbons that have been investigated apart from coconut shell are peach stones, apricot stones, hazelnut shells (Yalcin and Arol, 2002), charcoal (McDougall and Hancock, 1981) and macadamia nut shells (Poinern et al., 2011).

Figure 2.2: Activated carbon derived from coconut shell

Several researchers (Ibrado and Fuerstenau, 1995; 1992; Klauber, 1991; Cho et al., 1979) have reported a likely mechanism of Au adsorption onto activated carbon on the basis of functional group characterisation. A mechanism of Au elution from carbon surface was also proposed to be as a result of modification of functional group of activated carbon (Adams and Fleming, 1989). Hence the study of the functional group of activated carbon provided a plausible elution mechanism from the result of the effect of pre-treatment parameters investigated in this study. The review of the structure, properties and functional groups in activated carbon is discussed in the next section.

2.2.1 Structure and functional groups in activated carbon

Fullerene, carbyne, diamond and graphite are the widely known crystalline forms of carbon (Jia, 2000). According to McDougall and Hancock (1981), it was reported that the arrangement of carbon atoms is similar to that of a graphite structure through X-ray analysis (Figure 2.3).

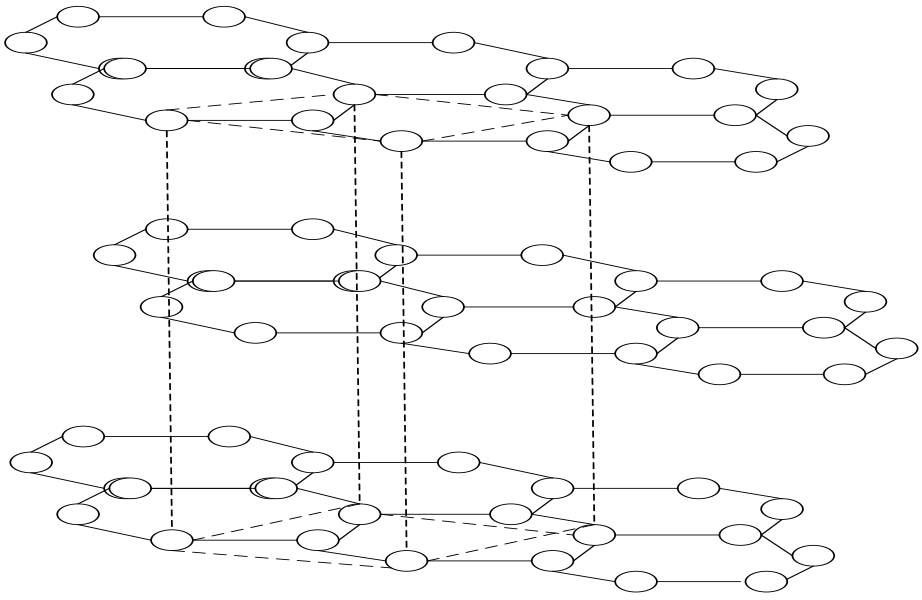


Figure 2.3: Graphitic structure of activated carbon. Redrawn from McDougall (1981).

The activation process in the presence of oxygen results in formation of oxygen contacting functional groups (Bansal and Goyal, 2010). Other elements that can be present during carbonisation apart from carbon and oxygen are sulphur and

hydrogen (Bansal and Goyal, 2010). Jia (2000) reviewed various attempts that have been used to categorise the oxygen functional groups on carbon. These are selective neutralisation, temperature programmed desorption (TPD), Fourier transform infrared spectroscopy (FTIR), specific chemical reaction, potentiometric, polarography, X-ray photoelectron spectroscopy and X-ray absorption near edge structure (XANES). Some of the suggested functional groups due to these investigations are carboxyl, lactones, phenols, anhydrides, ketones, quinones, hydroquinones, aldehydes and ethereal structures (Jia, 2000; McDougal and Hancock, 1981). Jia et al. (1998) suggested that nitrogen functional groups are of less importance to $Au(CN)_2^-$ adsorption in comparison to oxygen functional groups. Some examples of oxygen functional groups are shown in Figure 2.4. However, regarding the significance of oxygen for adsorption, Ibrado and Fuerstenau (1992; 1995) proposed that oxygen functional group was less significant for the adsorption of $Au(CN)_2^-$ after increasing the quantity of oxygen. The authors suggested that the degree of adsorption is strongly dependent on the graphite planes of the activated carbon

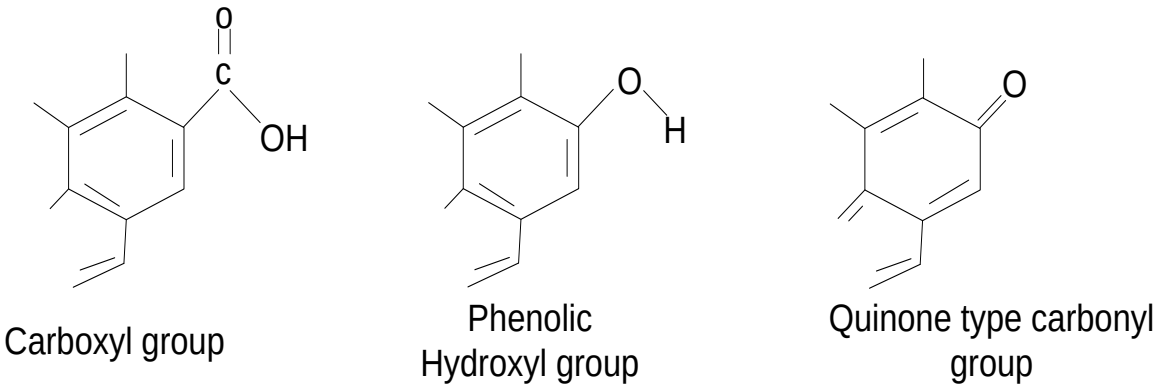


Figure 2.4: Examples of Oxygen functional group. Redrawn from Jia (2000)

2.3 Adsorption

According to Adams and Nicol (1984) and Adams (1983), $Au(CN)_2^-$ adsorption is thermodynamically reversible. Therefore, Au elution recovery is a function of the adsorption stage taking into consideration the factors that influence adsorption (Van der Merwe, 1991). This justifies the need for a detailed discussions on Au adsorption

process. Two major adsorption techniques are typically used. These are CIP and carbon in leach (CIL) technique. These are described in the following sections.

2.3.1 Carbon in pulp process

The CIP circuit is a well-known technology in gold processing. It consists of the adsorption, elution and carbon regeneration stage as shown in Figure 2.5 (La Brooy et al., 1994; Laxen, 1979).

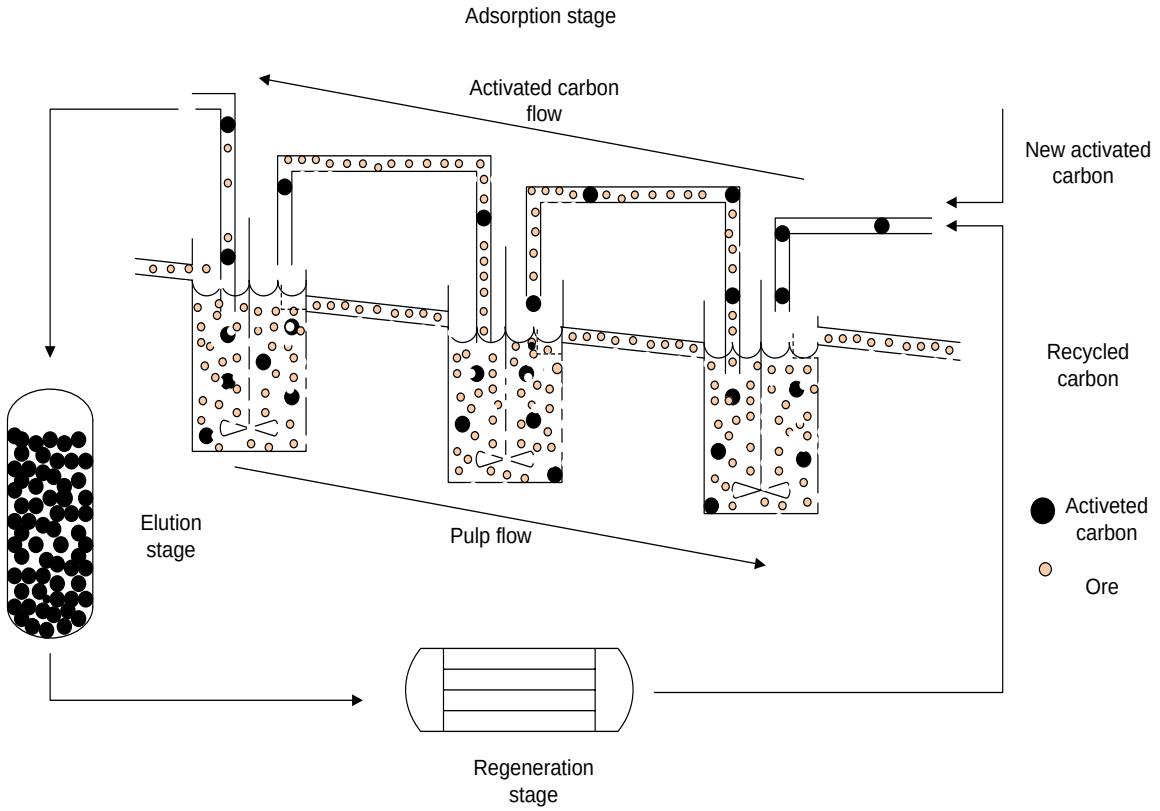


Figure 2.5: CIP circuit modified from Lima (2007)

The leached pulp in the adsorption stage (Figure 2.5) is allowed to flow in a counter-current direction with the activated carbon by means of an airlift in each tank (Laxen, 1979). The average retention time ranges between 20–60 min (Laxen, 1979). However, with the introduction of newer technology such as pump cells, Buson et al. (1999) reported that 15–20 min/stage residence times were obtained and the plant size was reduced thrice compared with a conventional CIP plant. Pump cell offers an advantage of agitation, screening and pumping within the adsorption tank (Dippenaar and Proudfoot, 2005). The agitation provided by the pump cell aids the

mass transport of Au onto activated carbon (Fleming, 2011). The resulting outcome of the counter-current flow is the depletion of Au in the pulp and enrichment of Au on the activated carbon (Davidson et al., 1982; Fleming, 1981). The activated carbon loaded with Au is then transferred to the elution stage.

True equilibrium is rarely achieved during adsorption even after several weeks of adsorption (Fleming and Nicol, 1984). As such, several investigations have been conducted to improve adsorption efficiency. Staunton (2005) summarised a number of factors that are critical in a CIP plant for optimum carbon management and design consideration that can improve adsorption efficiency. These are: agitation with the use of pump cell (discussed above), the number of adsorption tanks, soluble Au loss, carbon residence time, carbon concentration, and target Au loading among other factors. These factors are amplified in the next section.

2.3.1.1 Adsorption tanks and gold loss

According to Stange (1991), increasing the number of adsorption tanks with low amount of carbon in each tank offer the advantages of improving adsorption of Au; reducing Au loss associated with fine carbon particle due to reduced abrasion, shortens retention time and lessens Au lock up. The number of adsorption tanks usually ranges from 4 to 10 but up to 7 adsorption tanks could be beneficial. Insignificant effect in Au adsorption is noticed with further increase in the number of adsorption tanks and loss might be recorded in terms of cost incurred on the tanks (Adams, 2005).

2.3.1.2 Carbon concentration, residence time and target gold loading

Previous reports have shown that most CIP plants operate at carbon concentrations of about 20–25 g/L and retention time of about an hour per stage (Bailey, 1991; Laxen, 1984). These conditions were believed to improve adsorption rate and satisfactory Au adsorption (Laxen et al., 1979). However, plant operation and performance under these conditions have been underutilised (Fleming et al., 2011). Furthermore, through a modelling approach, Fleming et al. (2011) showed that a number of factors can be varied in order to optimise the adsorption process. These are: the number of adsorption tanks, amount of carbon in the adsorption tanks, rate of carbon transfer through the CIP plant, target concentration of Au in solution at the

last adsorption tank and the amount of Au remaining on carbon after elution (Fleming et al., 2011). A high activity for eluted carbon is important to adsorb the trace metals in the last adsorption tank and minimise Au loss into the tailing solution (Snyders et al., 2013; Fleming et al., 2011).

2.3.2 Carbon in leach

Carbon in leach (CIL) is a modification of CIP involving simultaneous leaching and adsorption by the addition of activated carbon in the leaching vessel (Stange, 1999). A major advantage associated with this is cost reduction in terms of replacement of a series of tanks used in CIP plant with a single large vessel (Fleming, 1992). Other advantages of CIL over CIP are in the adsorption of low grade ores that require longer leaching time. Another advantage is the preferential adsorption of $Au(CN)_2^-$ complex onto activated carbon instead of the carbonaceous material (Stange, 1999).

2.4 Adsorption mechanism

Various mechanisms of adsorption of $Au(CN)_2^-$ have been proposed by numerous researchers (Ibrado and Fuerstenau, 1992; Adams and Fleming 1989; Cho et al., 1979) in which the exact mechanism for $Au(CN)_2^-$ adsorption is yet to be established (Free, 2013). Possible reasons for the different proposed mechanisms was suggested to be due to different experimental conditions (high temperature, presence of acid or high alkalinity), types of carbon used and uncertainty of the adsorbed Au species (Van Deventer, 1993). A summary of the proposed mechanisms by various researchers is presented in Table 2.2

Table 2.2: Proposed adsorption mechanisms

Theory	Suggested adsorption mechanisms	Supporting authors
A	reduction mechanism of $Au(CN)_2^-$	Green (1913), Feldtman (1914) Edmands (1917),
B	electrostatic attraction of $Au(CN)_2^-$ on the positively charged surface of the carbon	Garten and Weiss (1957), Cho et al. (1979), Kuzminykh and Tjurin (1968)
C	ion pair mechanism with cation in the form of $M^{n+}[Au(CN)_2^-]_n$	Davidson (1974), McDougall et al.(1980), Gross and Scott (1927), Adams and Fleming (1989), Tsuchida et al. (1984), Cho and Pitt (1979)
D	non- ion pair mechanism on graphite plane in the form of $Au(CN)_2^-$	Jones et al., (1989); Ibrado and Fuerstenau (1992; 1995); Klauber (1991)

Theory A is reduction mechanism, B is electrostatic attraction mechanism, C is ion-pair mechanism and D is non-ion pair mechanism.

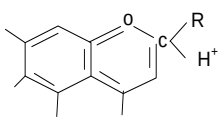
2.4.1 Theory A: Reduction mechanism

The reduction mechanism was based on the explanation that the leached $Au(CN)_2^-$ is reduced to AuCN that was formed as precipitate on the carbon surface (Gross and Scott, 1927 reported by Bailey, 1987). This precipitation was suggested to take place by decomposition reaction given by Equation 2.2.

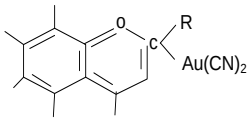
$$Au(CN)_2^- + H^+ \leftrightarrow AuCN_{(s)} + HCN \qquad 2.2$$

2.4.2 Theory B: Electrostatic attraction mechanism

According to this theory, anions $[Au(CN)_2^-]$ are electrostatically adsorbed to the positive carbonium sites of activated carbon given by Equation 2.3 (Garten et al., 1957):



$$+\frac{1}{2}O_2 + K[Au(CN)_2] + CO_2 \rightarrow$$



$$+ KHCO_3 \qquad 2.3$$

Further investigation by Kuzminykh and Tyurin (1968) suggested that the nature of the adsorbed $Au(CN)_2^-$ is not the same in both acidic and alkaline medium. In acidic medium, it exists as $HAu(CN)_2$ on the surface of the carbon through capillary condensation mechanism and in alkaline medium, through electrostatic attraction mechanism, shown by Equation 2.3.

2.4.3 Theory C: Ion pair mechanism

Davidson (1974) supported by McDougall et al. (1980), concluded that $Au(CN)_2^-$ does not get adsorbed without the presence of stabilising cations in alkaline condition. It was further shown that the degree of adsorption depends on the nature of the cations. Divalent alkaline metals such as Ca^{2+} and Mg^{2+} are more strongly adsorbed than monovalent alkaline metals like Na^+ and K^+ (Davidson, 1974) This is generally represented by Equation 2.4 (Adams and Fleming, 1989):

$$M^{n+} + nAu(CN)_2^- \leftrightarrow M^{n+}[Au(CN)_2^-]_n \qquad 2.4$$

where M^{n+} is either of Ca^{2+}, Mg^{2+}, H^+, Li^+, Na^+, K^+

2.4.4 Theory D: Non ion pair mechanism

This theory proposed that Au is adsorbed as $Au(CN)_2^-$ and does not change without undergoing any further chemical reaction after adsorption in alkaline solutions (Klauber, 1991). Ibrado and Fuerstenau (1994) suggested that this is due to fractional contribution of π-electron present on the carbon surface to Au. Jones et al. (1989), proposed that the interaction of the π-electron between $Au(CN)_2^-$ and carbon takes place on the basal planes (parallel to the planes of the graphite structure) of the activated carbon shown in Figure 2.6.

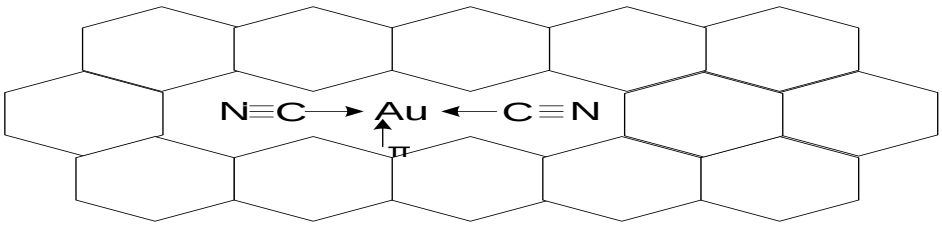


Figure 2.6: Proposed interaction between activated carbon and $Au(CN)_2^-$ Redrawn from Ibrado and Fuerstenau (1994).

2.5 Adsorbed gold species

Understanding the nature of adsorbed Au gives insight into the requirement for reagents needed for the subsequent elution stage. It has been widely suggested that the main probable forms in which Au exists on activated carbon are: $Au_{(s)}$, AuCN, $Au(CN)_2^-$ or $M^{n+}[Au(CN)_2^-]_n$ (Davidson and Bailey, 1991; Adams, 1989; Gross and Scott, 1927). This forms the main disagreement of the adsorption mechanisms proposed by previous authors as discussed in section 2.4. The change in the nature of these species depends on temperature, pH, aging (degradation) and addition of CN^- (McGrath et al., 2002; Van Deventer and Van der Merwe, 1993; Cook et al., 1989). These findings were confirmed by FTIR scans and XPS analysis (Van Deventer and Van der Merwe, 1993). At pH less than 9.3 which is the case in acid washing, reaction shown in Equation 2.5 takes place on the adsorbed $Au(CN)_2^-$ to form AuCN (Adams, 1990c)

$$Au(CN)_2^- + H^+ \rightarrow AuCN + HCN \qquad 2.5$$

2.6 Adsorption factors

2.6.1 Ionic strength

Ionic strength is usually referred to as the concentration of dissolved chemical constituents in solution. Ionic strength is calculated as half the product of the concentration of the chemical constituent and the oxidation number or charge of the chemical constituent (Green, 1996) .This suggest that ionic strength is dependent on the concentration and the charge number of the ion. According to the ion pair

mechanism of adsorption (Theory C), Davidson (1974) investigated the degree of enhanced adsorption of $Au(CN)_2^-$ with different cations. The degree of adsorption decreases as shown in the trend below from calcium ions (Ca^{2+}) to potassium ion (K^+) (Marsden and House, 2006; McDougal et al., 1980; Davidson, 1974):

$Ca^{2+}>Mg^{2+}>H^+>Li^+>Na^+>K^+$.

It was concluded that strong adsorption was more favoured by the presence of divalent ions (Ca^{2+} and Mg^{2+}) than by monovalent ions (Na^+, K^+). An illustration with Mg^{2+} and Na^+ is shown in Figure 2.7. where the ionic strength can be suggested to be higher for Mg^{2+} due to higher oxidation number. The higher magnitude of ionic strength of Mg^{2+} suggest that it will cause better interaction with the of $Au(CN)_2^-$ than Na^+ as shown in Figure 2.7

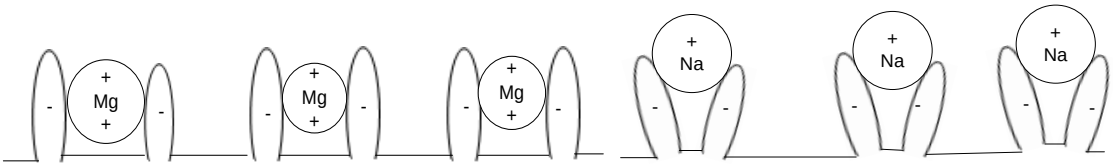


Figure 2.7: Effect of cations: Redrawn from Menńe (1991)

2.6.2 pH

A decrease in pH of the adsorbing medium from 7 to 1 was shown to increase both the loading capacity and adsorption efficiency of $Au(CN)_2^-$. (Marsden and House, 2006). According to Adams (1989), it was suggested that Au is probably loaded as $HAu(CN)_2$. This suggests that the mechanism of ion pair was not supported at this pH range. The presence of high concentration (100 times higher than H^+) of cations used, causes initial adsorption of the ion pair complex at low pH (<7) which later reduced due to the displacement of K^+ and Ca^+ by H^+ (acidic medium) (Adams and Fleming, 1989). This clearly suggests the dominance of pH in equilibrium loading (Fleming and Nicol, 1984). Practically, CIP plants operate at pH above 10. However, the adsorption rate is slower when compared to adsorption at pH below 9 (Marsden and House, 2006). At pH above 10, loss of CN^- through hydrolysis reaction is reduced (Marsden and House, 2006). Further discussions on chemical behaviour of CN^- are discussed in chapter 2.12.

2.6.3 Presence of oxygen

According to Hughes et al. (1984), improved loading of $Au(CN)_2^-$ is as a result of oxygen supply. Van der Merwe (1988) reported that an insignificant amount of oxygen was adsorbed by activated carbon present in water while substantial amount of oxygen was consumed during adsorption of $Au(CN)_2^-$. The benefical effect of oxygen for the adsorption of $Au(CN)_2^-$ was reported to be pronounced under the condition of low ionic strength (Marsden and House, 2006; Adams, 1991). At high ionic strength condition, which is the typical condition in most CIP plant, adsorption in form of ion-pair dominates (Adams, 1991)

2.6.4 Free cyanides

According to Marsden and House (2006), the rate of Au loading and the capacity of activated carbon to adsorbed Au in solution decreases with an increase in concentration of CN^-. These CN^- were suggested to compete with $Au(CN)_2^-$ for adsorption sites. On the other hand, Adams (1990) and Muir et al. (1988) suggested that oxygen aids in the catalytic oxidation of CN^- to form CO_3^{2-} and NH_3. These oxidised products (CO_3^{2-} and NH_3) thereby hinders carbon surface from adsorption of $Au(CN)_2^-$ through competitive adsorption (Van der Merwe, 1991). This suggest that a condition of low CN^- concentration is recommended for Au adsorption.

2.6.5 Temperature

The effect of an increase in temperature on the adsorption of Au has been reported to have a significant effect on the equilibrium loading as well as the loading rate of Au (Adams and Nicol, 1984). This is because Au adsorption is an exothermic process (McDougal, 1980). Fleming and Nicol (1984) investigated the effect of different temperatures (20, 44 and 62^{o}C) on the rate of adsorption and Au loading capacity on activated carbon. It was found that the rate of Au adsorption increased from 3400, 4190 and 4900 h^{-1} while Au loading capacity decreased from 73000, 48000 and 35000 mg/L at these temperatures (20, 44 and 62^{o}C) respectively. Similarly, McDougall et al. (1980) found out that an initial Au concentration of

180 mg/L decreased to about 140 mg/L at 80^{o}C and approximately 70 mg/L at 30^{o}C after 24 hours of adsorption time. It was suggested that the Au metal complex [$KAu(CN)_2$] was highly soluble (14 times) in hot water than in cold water.

2.7 Preliminary summary on adsorption

Gold process was broadly reviewed with more specific discussions on the CIP plant. Furthermore, discussions were made about the application and properties of activated carbon in CIP plant. These are: the structure of the carbon atom arrangement and the functional groups. A detailed literature about the adsorption process was reviewed because $Au(CN)_2^-$ is thermodynamically reversible (Adams, 1983). Therefore, reversing the adsorption conditions for Au loaded activated carbon enhances elution. The factors that were reported to favour adsorption are: high ionic strength, oxygen supply under low ionic strength, low pH, low CN^- concentration, and low temperature. This further led to the reports of various mechanisms proposed by different authors and the adsorption factors. Based on the understood properties of activated carbon, the adsorption mechanism of $Au(CN)_2^-$ and its factors provided a background knowledge to propose a suitable elution mechanism after the investigation of pre-treatment parameters on Au elution recovery. The next sections focus on the elution stage, factors and its mechanisms.

2.8 Elution

The two major types of elution techniques that were earlier introduced in Chapter 1 are Zadra elution and AARL elution techniques. The elution process of either Zadra or AARL elution process takes place in an elution column with a typical industrial elution column shown in Figure 2.8.

The elution columns are made from mild steel with height of about 10 m and a diameter of 1.2 m which also holds pressure of about 350 kPa and accommodates approximately 6 tonnes of activated carbon with a lagged wall to prevent heat loss. These specifications vary for different companies.

Figure 2.8 Typical Elution columns. Sourced from Ur energy (2013)

2.8.1 AARL elution process

The flow sheet of the AARL elution process that is of more interest to this work is shown in Figure 2.9

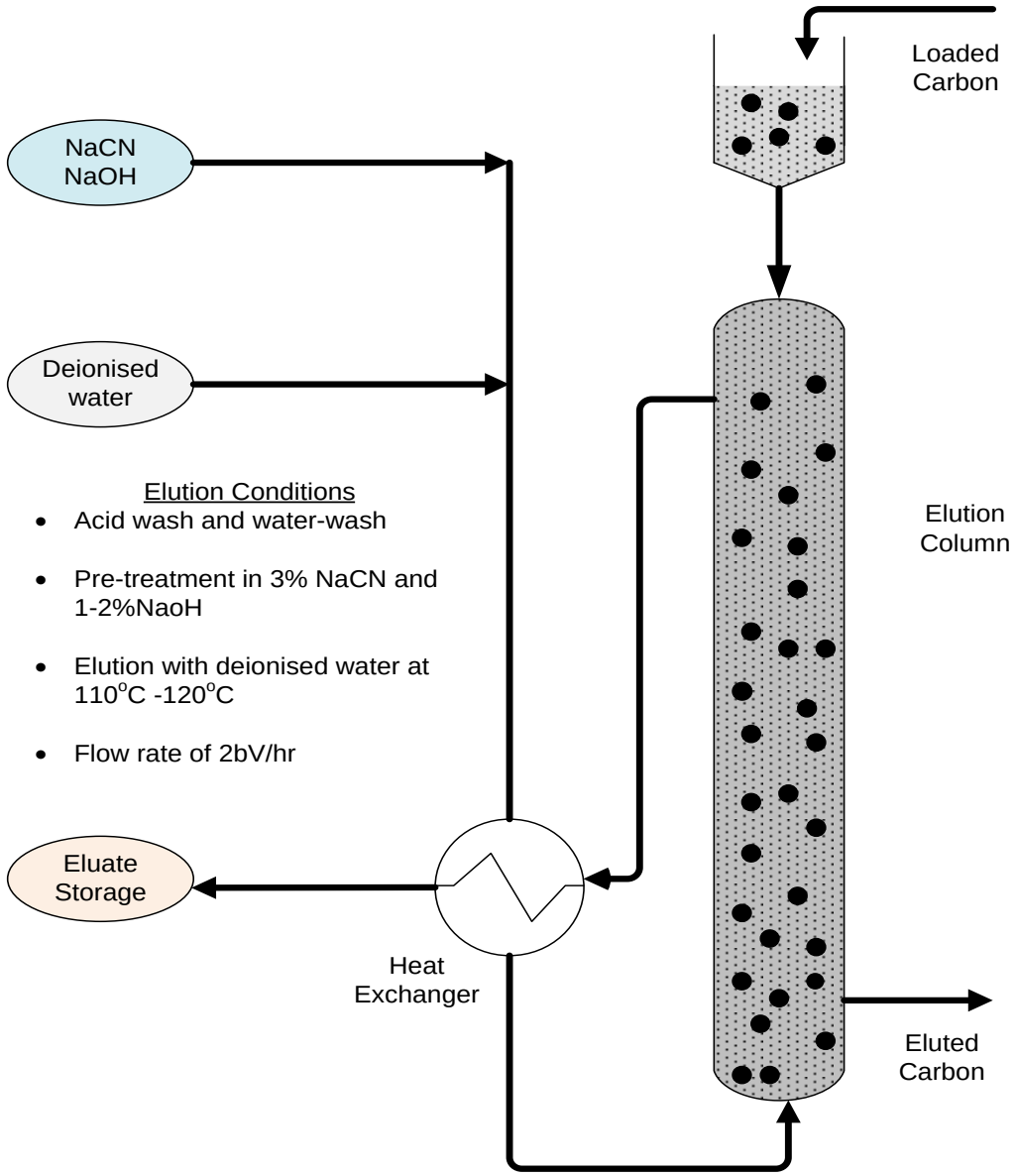


Figure 2.9: Simplified flow sheet of AARL. Modified from Stange (1991).

The AARL elution technique was developed to ensure improved Au elution recovery and reduced operating time to the Zadra elution technique. In the Zadra elution technique, the eluant is recirculated with electrowinning cells connected in series (Zadra et al., 1950). It was believed that some of the desorbed Au gets reabsorbed during the recirculation process. This resulted in high elution time which led to the investigation of AARL with short elution time involving pre-treatment in NaOH-NaCN solution (Davidson and Duncanson, 1977). The elution time is within the range of 32 to 72 hours and 8 to 14 hours for Zadra and AARL elution respectively (Marsden and

house, 2006). AARL elution process typically involves pre-treatment of the Au loaded carbon which has been described in Section 1.1(Davidson, 1986).

The AARL elution process shown in Figure 2.9 is described according to Stanley and Bailey (1987). Carbon loaded with Au is fed into the column through the hopper. This is followed by hot acid washing with 1 bed volume of hydrochloric acid (3%v/v) to remove entrapped contaminants (calcium and foulants), followed by passage of 1 to 2 bed volume of water. Hot acid washing also helps in the removal of calcium that can inhibit adsorption after regeneration (Davidson, 1986). A plug flow of eluant is desirable during elution which can either be upward or downward flow (Davidson and Bailey, 1991). The essence of the plug flow is to ensure desorption of Au at each cross section of the elution column. The upward flow is often used in most industries especially when acid washing occurs prior to elution. In this case, the upward plug flow helps to minimise trapped carbon-dioxide gas produced as a result of the reaction of the carbonate (Davidson and Bailey, 1991). However, in the presence of small wood chips or fibres, neutralisation of the acid washed carbon is carried out prior to elution, in which case downward flow of eluant is preferred (Davidson and Bailey, 1991). According to these authors, there is a tendency of the eluate collector being choked with the wood fibres if upward flow is adopted.

Hereafter, pre-treatment of the acid wash carbon is carried out in about 0.6 bed volumes of NaOH-NaCN solution to soak for about 30 min. Finally, Au is then eluted by pumping de-ionised water through the column at a temperature of 120^{o}C and flow rate of 2 bed volumes per hour for about 8 hours. These values are not fixed and vary for different industries. The inconsistency of the pre-treatment forms part of the objective of this research. The factors that affect the elution process are discussed in the next section.

2.9 Factors affecting elution

2.9.1 Effect of temperature

Elution temperature (measured temperature of the eluant used for washing the Au from loaded carbon after pre-treatment). has been suggested to be the most important factor that influences Au elution recovery (Free, 2013; Adams and Nicol,

1986; Davidson and Duncanson, 1977). An Increase in the elution temperature results in change in equilibrium which favours desorption because adsorption is an exothermic process (Section 2.6.5). According to Adams (1991), adsorbing power of activated carbon to adsorb Au reduces with an increase in temperature which determines the rate of elution. Practically, elution can occur either under atmospheric or pressurised condition in order to control the elution rate (Marsden and House, 2006). Under the atmospheric conditions, elution process takes place in temperature close to the boiling point of water (≈90–95^{o}C) while a pressurised elution process which results in a faster elution rate takes place above 100^{o}C and pressure above 200 kPa depending on the temperature aimed to be achieved (Metalliferous mining processing, 2010 b; Marsden and House, 2006).

Van der Merwe (1991) investigated the effect of temperature in relation to the reaction of CN^- during pre-treatment. The decomposition of CN^- takes place via oxidation at low temperature and hydrolysis at high temperature (Jeffery et al., 2010; Van der Merwe and Van Deventer, 1993, Ver der Merwe, 1991). It was suggested that the decomposed product formed by CN^- inhibits adsorption of Au thereby favouring desorption. The hydrolysis and oxidation reactions that were considered to be relevant in this regards are given by Equations 2.6–2.10 (Nicol, 1986; Van Deventer and Van der Merwe, 1993).

Hydrolysis

$$CN^- + 3H_2O \rightarrow [HCOONH_4] + OH^- \quad (2.6)$$

$$[HCOONH_4] + 0.5O_2 \rightarrow HCO_3^- + NH_4^+ \quad (2.7)$$

$$HCO_3^- + NH_4^- + 2OH^- \xrightarrow{\text{pH } 10.5} NH_3 + CO_3^{2-} + 2H_2O \quad (2.8)$$

Oxidation

$$CN^- + 0.5O_2 \rightarrow [CNO^-] \quad (2.9)$$

$$\left[CNO^-\right] + 2H_2O \rightarrow CO_3^{2-} + NH_4^+ \quad (2.10)$$

2.9.2 Effect of cyanide and hydroxide concentration.

The use of hydroxide (OH^-) alone to achieve an almost complete elution of Au has been reported (Boshoff, 1994; Adams and Fleming, 1989). However, this proceeds at a slower rate when compared with when CN^- is utilised. Adams (1991) reported that the combination of CN^- and OH^- yielded a more effective result than either of OH^- or CN^-. Some theories on the role of CN^- exist. According to Marsden and House (2006), the presence of CN^- during elution causes competition of adsorption site with $Au(CN)_2^-$ which in turn favours elution. Contrary to this, Van Deventer and Van der Merwe, (1992), reported the absence of Au in solution after pre-treatment with NaOH-NaCN. CN^- was therefore, suggested to undergo decomposition reaction that passivated the carbon surface (Van Deventer and Van der Merwe, 1992). According to Adam (1991) and McDougall and Fleming (1987), an increase in concentration of CN^- and OH^- increased Au elution recovery when pre-treated with NaOH-NaCN. However, excessive amounts of NaOH-NaCN resulted in a decrease in elution rate. Optimum concentration of Au elution recovery was suggested to be attained when pre-treated with about 3% concentration of NaOH-NaCN (Davidson and Schmidt, 1986). Elution rate was observed to drop above this suggested concentration of NaOH-NaCN. This opposing effect was suggested to be due to an increase in the ionic strength of the cations (Adams, 1991).

2.9.3 Effect of cations

Accroding to Section 2.6.1 on the level of cations in adsorption, desorption is favoured by the removal of cations. From the trend of the ionic strength presented Section 2.6.1, desorption proceeds easily upon removal of monovalent ions (Na^+, K^+) than the removal of divalent ions (Mg^{2+}, Ca^{2+}) from Au loaded carbon (Van Deventer and Van der Merwe, 1994).

Furthermore, Van Deventer and Van der Merwe (1994), Van der Merwe (1991), showed the influence of cations on Au loading capacity through a model. The model was based on study of previous authors (Van Deventer, 1984; Cho and Pitt, 1979) and adopted a modified Freudlinch isotherm by reducing the number of parameters to Equation 2.11.

$$Q_i = AC_i^{bA+D}, \quad 2.11$$

where Q_i and C_i are the Au loading on activated carbon and in solution respectively, b and D are constants that were measured in a specific carbon in the isotherm equation. A (loading capacity constant) is the only parameter to be determined (Van Deventer and Van der Merwe, 1994). The model showed that there is a strong dependence of loading capacity constant of divalent ions (Ca^{2+}) than monovalent (K^+). This suggests that elution proceeded easily in K^+ than Ca^{2+}. A least square regression model showed that In(A) is a linear function of In(cation concentration) given by Equations 2.12–2.13 at room temperature (Van Deventer and Van der Merwe, 1994) This model indicated that desorption can be explained on this same principle recalling that Au adsorption is thermodynamically reversible.

$$A = 24\ (C_K+1)^{0.069} \quad 2.12$$

$$A = 26\ (C_{Ca}+1)^{0.127} \quad 2.13$$

C_K = concentration of potassium

C_{Ca} = concentration of calcium

2.9.4 Flow rate

The rate of elution has been suggested to be independent on eluant flow rate under strong pre-treatment conditions and high elution temperature (Marsden and House, 2006; Van der Merwe and Van Deventer, 1994; Adams, 1991). Davidson (1974) investigated the effect of elution flow rate on activated carbon loaded with Au and then pre-treated in 3% potassium carbonate (K_2CO_3) and 1% potassium hydroxide (KOH). It was shown that the maximum concentration of Au in the elution profile (Au elution peak on the elution curve shown in Figure 2.10) reduced with an increase in flow rate from about 0.5–1.5 BV/h. Under these conditions, it was suggested that elution is diffusion controlled (Davidson, 1974). Further investigation with pre-treatment concentrations of 2% NaCN and 2% NaOH showed that elution was not affected by flow rate within 1–5 BV/hr (Davidson and Schmidt, 1986). Under this condition, it was suggested that elution was not controlled by diffusion. Van der Merwe and Van Deventer (1994) investigated the effect of different elution flow rates at 2.9, 5.9, and 37 BV/h on Au loaded carbon pre-treated in 2% KCN. The result

showed a similar elution profile with insignificant differences as shown in Figure 2.10. This suggests that a greater volume of water will be used at 37 BV/h with no significant difference in comparison to elution at ≈3 BV/h for the same elution time and the solution becomes less concentrated. Davidson and Schmidt (1986) stated that the choice of elution flow rate depends on the elution time. It was suggested that 2 to 3 BV/h flow rate achieved complete elution for 8 hour of elution time (Davidson and Schmidt, 1986).

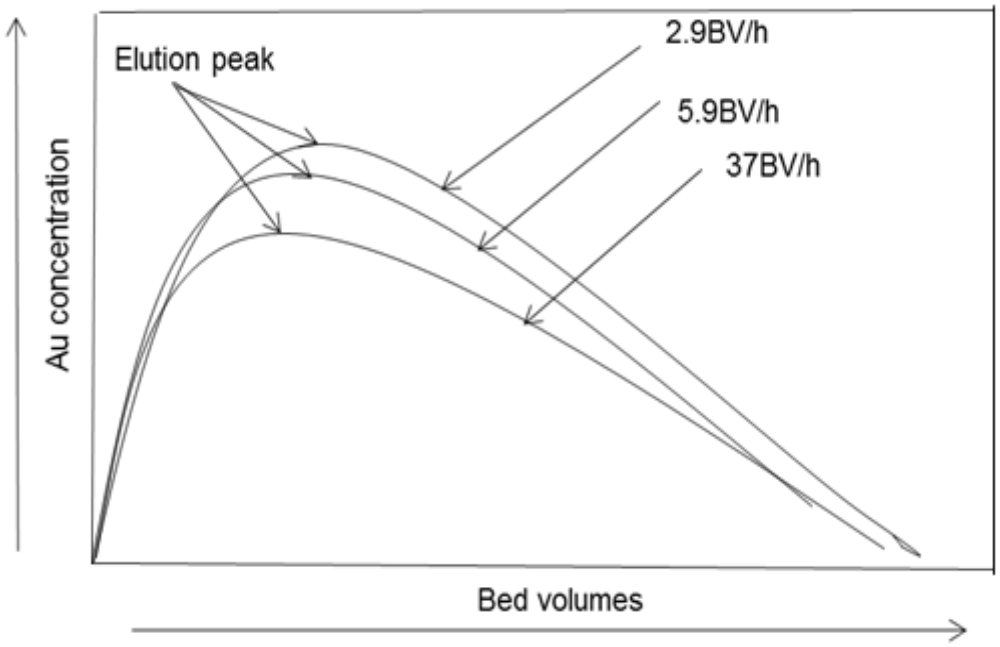


Figure 2.10. Illustration of effect of elution flow rate on the Au elution profile also showing the elution peak of each elution curve. Modified from Van Deventer and Van der Merwe (1994)

2.10 Elution mechanism

Different understanding of the role and requirements for CN^- during pre-treatment and elution has led to different proposed elution mechanisms. These proposed mechanisms by various authors as well as the conditions under which they were proposed are reviewed as follows:

2.10.1 Mechanism based on the nature of the adsorbed gold

According to this mechanism, the nature of the adsorbed Au determines the need for CN^- in the subsequent elution step (Section 2.5). In a typical CIP condition the nature of the adsorbed Au can exist either as AuCN when acid pre-treatment is carried out prior to elution or as $(AuCN)_2^-$ in the absence of acid washing. It was believed that AuCN is strongly adsorbed on carbon while $(AuCN)_2^-$ was more soluble in water and easily desorbed from the carbon surface (Davidson and Bailey, 1991). Therefore, the addition of CN^- will result in the change of the nature of the adsorbed Au according to Equation 2.14 (Adams, 1991).

$$AuCN + CN^- \rightarrow Au(CN)_2^- \qquad 2.14$$

Another form of Au is its existence in the solid state $[Au]_s$ which has been suggested to occur in residual Au on carbon after elution at the regeneration temperature (Vorobev-desyatovskii et al., 2010). In this case, $[Au]_s$ can be suggested to form $Au(CN)_2^-$ through the Elsner's equation (Equation 2.1)

2.10.2 Mechanism based on competitive adsorption of CN^-

According to this theory, the presence of CN^- causes competitive adsorption with $Au(CN)_2^-$ for adsorption site. This results in displacement of $Au(CN)_2^-$ from carbon surface, thereby resulting into elution (Adams and Nicol, 1986). Tsuchida (1984) reported by Van Deventer and Van der Merwe (1994) proposed the following Equations:

$$[AuCN]_{carbon} + CN^- \leftrightarrow [Au(CN)_2^-]_{carbon} \qquad 2.15$$

$$[Au(CN)_2^-]_{carbon} + CN^- \leftrightarrow [CN^-]_{carbon} + [Au(CN)_2^-]_{solution} \qquad 2.16$$

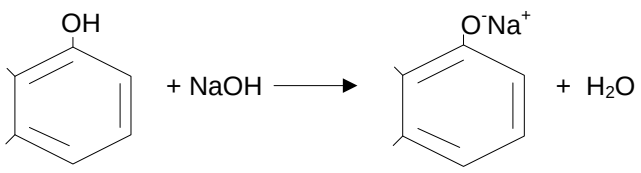
As it appears from Equations 2.15–2.16, the role of CN^- was only seen from the elution point of view even though CN^- from NaOH-NaCN solution was introduced during pre-treatment. This theory was, however, criticised not to be probable due to absence of Au in solution after pre-treatment with NaOH-NaCN (Van Deventer and Van der Merwe, 1994; 1992).

2.10.3 Mechanism based on passivation of the carbon surface

In a quest to gain more insight to the functional role of CN^- after establishing that it is a necessity for the improved elution of Au, Van Deventer and Van der Merwe (1992) showed that CN^- carried over from the pre-treatment step to the elution step had no effect on Au elution. According to these above mentioned authors, it was shown in an experiment that the ability of fresh activated carbon to adsorb Au from an initial concentration of 24.5 mg /L Au is higher than activated carbon pre-treated in 20 g/L KCN and rinsed before being used for adsorption. This lower absorptivity of treated carbon led to the suggestion that CN^- degrades to form a passivating product which becomes deposited on carbon surface during pre-treatment. This renders it less receptive towards adsorption thereby enhancing elution of Au (Van Deventer and Van der Merwe, 1994; 1992). The degree of passivation was further reported to increase with increase in pre-treatment temperature as more elution was obtained at higher pre-treatment temperature of 100^{o}C when compared to 20^{o}C. (Van Deventer and Van der Merwe, 1994).

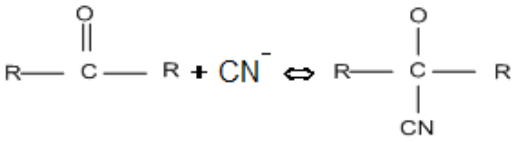
2.10.4 Mechanism based on the modification of functional group of activated carbon

This theory was based on the fundamental chemistry study of nucleophilic-electrophilic reaction. Adams and Fleming (1989) suggested that the presence of OH^- or CN^- causes a specific chemical reaction at the carbon surface. The adsorption of $Au(CN)_2^-$ and Na was investigated on three different types of resins (S-761, S-862 and XAD-8) in both sodium chloride (NaCl) and NaOH solution (Adams and Fleming, 1989). The result of Na extraction analysed when G210 activated carbon was contacted with NaOH solution was shown to be a similar mechanism as S-761 resin which consists of phenol group. This reaction is shown in Equation 2.17 (Adams and Fleming, 1989).

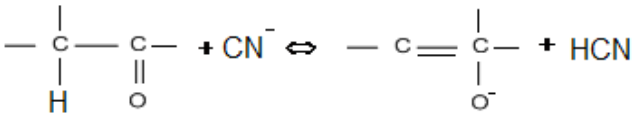


2.17

It was also suggested that CN^- was involved in a specific reaction on the surface of carbon. With CN^- being a strong nucleophile, the appropriate functional group which this nucleophile will react with, to have β acid-base reaction, will be carbonyl group. Equations 2.18 and 2.19 were suggested to be the possible reaction mechanisms (Adams and Fleming, 1989).



2.18



2.19

2.11 Nucleophilic-electrophilic reaction mechanism

The relevance of nucleophilic-electrophilic reaction mechanism is seen when dealing with the reaction of negatively charged ions with positively charged surface functional groups of organic compound such as activated carbon. This will also provide possible insight to a possible reaction mechanism for Au elution mechanism. A brief review of this theory is summarised in this section.

One of the major concepts through which chemical reaction mechanisms are well understood is through the concept of nucleophilic-electrophilic reaction mechanism. According to this theory, a positively polarised site gets attacked by a negatively polarised charge. According to McMurry (1998), carbonyl functional group is one of the main functional groups present in organic compounds. Carbonyl carbon is positively polarised ($C^{\delta+}$) (electrophile) and therefore, shows more tendencies to react with nucleophile and base. A carbonyl oxygen ($O^{\delta-}$) that is negatively polarised readily reacts with electrophiles and acids. Dissolution of NaOH-NaCN on the other hand will ionise to Na^+, OH^- and CN^- in solution. It can be deduced that CN^- and OH^- will react with $C^{\delta+}$.

2.12 Behaviour of cyanide and pre-treatment operation.

2.12.1 Chemical behaviour of cyanide

The reaction of cyanide salt in water takes place through dissociation into ions of the metal cation (M^+) and free cyanide (CN^-). An illustration with NaCN is shown in Equation 3.1.

$$NaCN \rightarrow Na^+ + CN^- \qquad 2.20$$

The main reaction of CN^- with water or oxygen (Equations 2.6–2.10) that has been identified in Au processing plant is decomposition reaction which takes place via oxidation or hydrolysis (Adams 1990b). Some of the factors that influnces the loss of CN^- from solution are a presence of oxygen, a presence of catalyst (activated carbon catalysis reaction by oxidation), constituents of the solution, temperature, pH, agitation speed, presence of metals and ionic strength (Skodra et al., 2015; Moreno-Castilla, 2004; Van Deventer, 1995; Adams, 1994; Adams, 1990b).

Figure 2.11 shows the behaviour of CN^- under the influence of pH at standard temperature and pressure. When CN^- is present in water and the pH is below 9.3, the predominant specie is hydrogen cyanide (HCN) as shown in Figure 2.11. The reaction through which this takes place is a hydrolysis reaction given by Equation 2.21 (Adams, 1990). At pH range between 9.3–9.5, HCN stays in equilibrium with CN^- with HCN (José et al. 2013). CN^- becomes a predominant specie above a pH of 9.5.

$$CN^- + H_2O \rightarrow HCN + OH^- \qquad 2.21$$

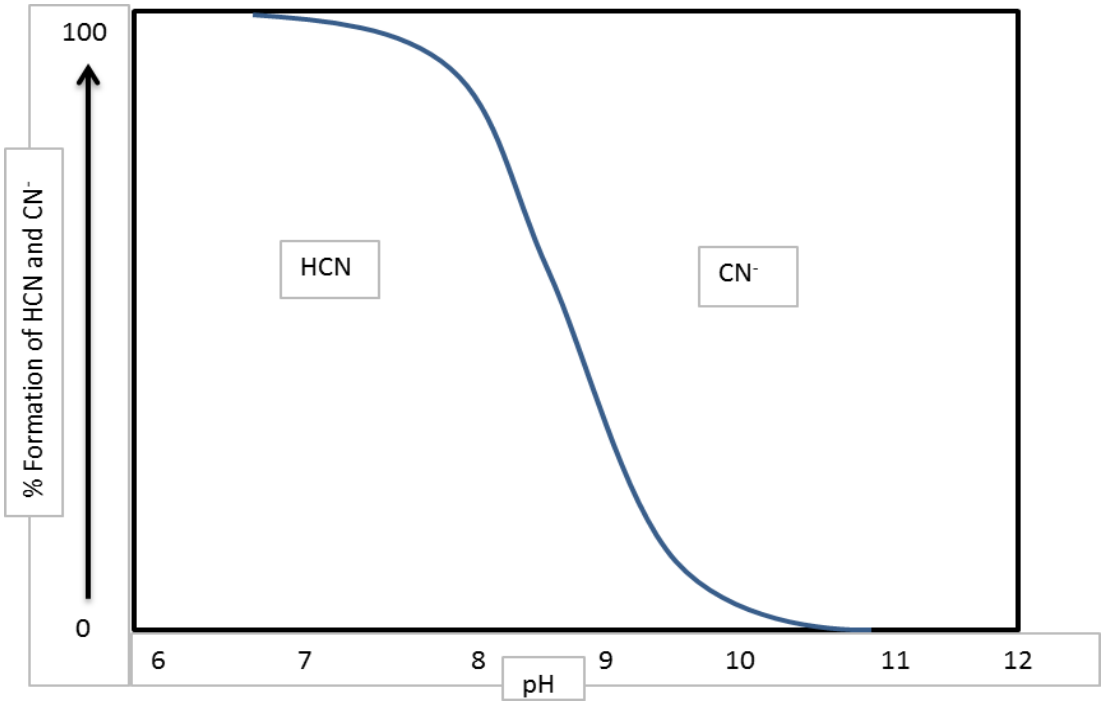


Figure 2.11: Formation of HCN and CN^- with change in pH. Redrawn from José et al. (2013)

In CIP plant, CN^- is utilised during adsorption, elution and electrowinning (Adams 1990a). It was stated that during pre-treatment in AARL elution process, significant amount (about 80–90%) of CN^- is lost via thermal decomposition at temperature above 130^oC. The CN^- loss became evident after 30 min of pretreatment especially at higher temperatures of more than 130^oC (Adams, 1990a; b) Equation 2.22 was suggested as a possible reaction (Mudder et al., 2001; Huiati et al., 1983 cited by Adams 1990)

$$CN^- + H_2O \rightarrow NH_3 + HCO_3^{2-} \qquad 2.22$$

2.12.1.1 Eh-ph of cyanide-water system

Figure 2.12 shows the Eh-pH diagram for CN-H_2O system at 25^oC and the various equilibrium species formed by cyanide in water. It can be seen that HCN is formed from CN^- in water as the pH reduces below 9.3 (Equation 2.21). The formation of HCNO is rarely encountered in Au operation as most processes that involves CN^- use are carried out in alkaline medium. CN^- is oxidized to cyanate CNO at pH above 9.5 given by Equation 2.23 (Adams 1990a; b; Bard, 1973)

$$2(OH)^- + CN^- \leftrightarrow CNO^- + H_2O + 2e^- \quad 2.23$$

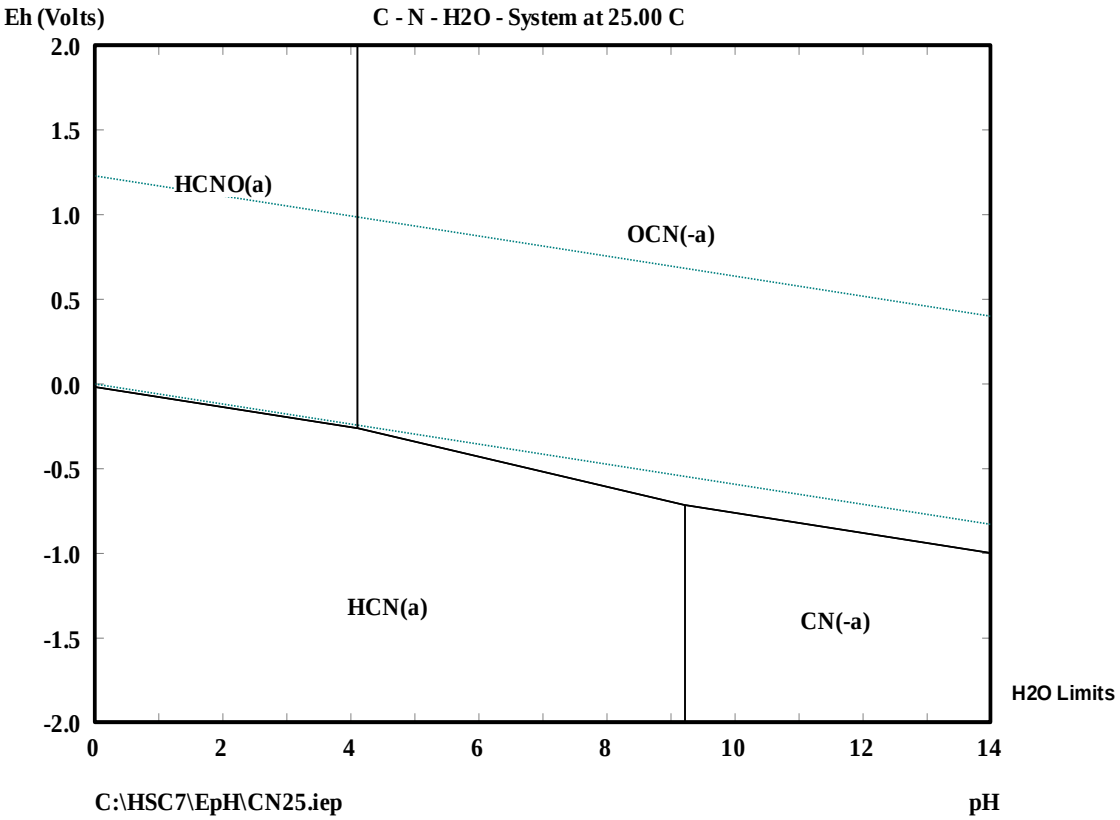


Figure 2.12: Eh-pH diagram of CN-H_2O system at 25°C. Drawn with HSC chemistry 7.31.

2.12.1.2 Cyanide decomposition

Decomposition of CN^- in the presence of activated carbon has been suggested to take place via oxidation with oxygen groups of activated carbon (Adams 1990b). However, there has been no clear distinction between oxidation of CN^- by activated carbon and adsorption on activated carbon. As such, the determination of the amount of CN^- that gets decomposed has been quite difficult to quantify in order to establish a firm mechanism during Au elution.

Van Deventer and Van der Merwe (1995) attempted to formulate a kinetic model for the decomposition of CN^- during elution in a batch stirred vessel under the influence of different parameters. These parameters include different mixing speed (700, 1350 and 1500 rev/min), carbon particle sizes [powdered and granular (mean particle

diameter of about 1.42mm)], constant temperature and initial concentration of CN^-. These authors reported that CN^- decomposition is independent of the particle size, but increased with an increase in agitation speed. Based on these results, it was suggested that the rate limiting process is the mass transfer between the solution and the activated carbon but has nothing to do with pore diffusion (intraparticle diffusion) (Van Deventer and Van der Merwe, 1995).

2.13 Mass transfer theory

One of the main aims of including agitation in chemical and metallurgical processes is to improve rate of mass transfer between the solid and liquid phase (Paul et al., 2004; Cooper et al., 1973). In a solid-liquid system that is mechanically agitated, rate controlling process could either be by (Paul et al., 2004; Forgler, 1999; Doraiswamy and Sharma, 1984):

- External diffusion of specie (film diffusion) of interest (CN^-) from the bulk fluid through the boundary film to the surface of the activated carbon. In this case, agitation and particle size have significant effect.
- Internal or intra-particle diffusion which is influenced by particle size and temperature.
- Surface reaction. This is independent on agitation and particle size but dependent on changes in temperature (Fogler, 1999).

Investigation of any of the above processes will give insight to the rate controlling process and its connection to elution process. Several authors have reported the use of boundary model (rate of mass diffusional transfer) to estimate solid-liquid mass transfer coefficient (k_{SL}) assuming a spherical particle (Atiemo-Obeng et al., 2004; Sağ and Aktay, 2000; Findon et al., 1993; McKay and Poots, 1980; Weber and Mathews, 1976). This model is given by Equation 2.24 was also adopted in this study to estimate the effect of agitation speed on k_{SL}.

$$\frac{dC}{dt} = -k_{SL}a_s(C-C^*) \qquad 2.24$$

Where: C^* = is the concentration of CN^- at the carbon surface

C = concentration of CN^- in the bulk solution at time t

a_s = specific surface area per unit volume

$$a_s = \frac{6\theta}{\rho_c d_c} \quad 2.25$$

Where: θ = activated carbon concentration in solution

ρ_c = density of the activated carbon

d_c = diameter of the activated carbon

In the boundary model, the following assumptions were made:

- Intraparticle diffusion is insignificant and therefore, assumed to be negligible.
- Concentration of CN^- at the carbon surface at time zero (t=0) is negligible.
- At t=0, C becomes C_o.

Based on these assumptions, Equation 2.24 was simplified to Equation 2.26 (Sağ and Aktay, 2000)

$$\left[\frac{d(\frac{C}{C_o})}{dt}\right] = - k_{SL} a_s \quad 2.26$$

Therefore, the gradient of a plot of $\frac{C}{C_o}$ vs t gives $- k_{SL} a_s$ from which k_{SL} can be calculated.

2.14 Pre-treatment operation

Several pre-treatment options with regards to the pre-treatment reagents have been tested over the years. These include; a mixture of potassium carbonate (K_2CO_3) and potassium hydroxide (KOH), KOH, NaOH, lithium hydroxide(LiOH), and a mixture of NaOH and NaCN (Davidson and Duncanson, 1977). Among these reagents, a mixture of K_2CO_3 and KOH and a mixture of NaOH and NaCN were reported to yield more than 99% of Au elution recovery.

NaOH-NaCN solution was suggested as the most suitable reagent because it efficiently eluted both Au and other metals such as silver (Ag), copper (Cu) and nickel (Ni) compared to other pre-treatment reagents (Davidson and Duncanson, 1977). While CN^- helps in the stability of metal cyanide complexes, the hydroxide maintains the alkalinity condition for the stability of CN^- to prevent evolution of HCN gas during pre-treatment (Davidson and Schmidt, 1986)

Two types of pre-treatment techniques are used in industry according to the AARL elution plant design (Riley, 1991). These are batch AARL and continuous AARL elution, which are being used in some plants like Genmin's Grootvlei gold mine (Riley, 1991). In terms of pre-treatment operation, batch AARL uses the same elution column for pre-treatment while the continuous process uses a separated pre-treatment column (Riley, 1991). The adsorbed AC is soaked (usually 30 min) in approximately 1 bed volume of NaOH-NaCN solution (Davidson, 1986). Although it has been suggested that a long pre-treatment time will be necessary for a low (<110^{o}C) pre-treatment temperature (Davidson and Bailey, 1991), many Gold plants operate at different pre-treatment times with no record of a justifiable reason. Results compiled by Davidson and Baily (1991) showing the effect of different pre-treatment time and temperature on elution efficiency is shown in Table 2.3. The average NaOH-NaCN adopted was around 5% NaCN and about 3% NaOH. It could possibly be that the operators of these Gold plants were satisfied with the elution result obtained at these pre-treatment conditions because it has been yielding an acceptable Au elution recovery right from its usage. However, this has led to limited attention given to the optimisation of the pre-treatment parameters.

Table 2.3: Reported AARL conditions at different Gold plants (Davidson and Bailey, 1991)

Gold plant	Pre-treatement condition		Elution condition		Efficiency (%)
	Temp. (^{o}C)	Time (min)	Flow rate (BV/h)	Temp. (^{o}C)	
Ergo	120	60	1.8	120	84.3
Daggafontein	120-140	60	0.8	120-140	95.9
Simmergo	80	<10	1.8	120	90.1
New Brand	120	30	2	120	96.5
Western Deep No 1	125	60	1.8	120	96.8
Western Deep No 3	90	30	2-3	120	97
Afr Lease	70	45	1.6	110	94.2
City Deep	115-110	120	2.7	110	93.6
Crown sands	110-100	120	2.7	110	94.4
Western Areas	110	90	1.8	110	99.6
Doornkop	95	30	1.1	110	96

It can be seen from Table 2.3 that variability exists in the pre-treatment parameters adopted at different Gold plant and no set standard can be suggested to be existing in the industry.

2.15 Summary on literature review

Chapter 2 considered the literature review of gold processing, more specifically the adsorption and elution of Au in CIP plant. This chapter started with a broad view of gold processing operation followed by the review of the application and properties of activated carbon for Au adsorption in CIP plant. Furthermore, the various components of the CIP plant was described. The factors suggested by different authors for optimum performance of the plant.and improved Au adsorption was also reported. According to Adams (1983), $Au(CN)_2^-$ adsorption is thermodynamically reversible. This justified the elaborate discussions on adsorption mechanism and its factors. The suggested mechanisms are reduction mechanism, electrostatic attraction mechanism, ion pair mechanism and non-ion pair mechanism. The factors that were reviewed to enhance Au adsorption are: high ionic strength, oxygen supply under low ionic strength, low pH, low CN^- concentration, and low temperature. This implies that reversing these factors will enhance elution. This led to a discussion of the elution process with more emphasis on AARL elution process that is of more interest to this work. The role of CN^- during pre-treatment in the AARL elution process for improved elution of Au demonstrated by different authors was also reported. However, there still seems to be less agreement on the exact mechanism of how CN^- aids in this efficient elution. This resulted into the review of previously proposed elution mechanisms and elution factors. The theories on which the elution mechanisms were based are: nature of the adsorbed Au, competition of adsorption site by CN^- with $Au(CN)_2^-$, passivation mechanism by the formation of decomposed product formed from the reaction CN^- with carbon surface and the modification of functional group. Furthermore, an overview of the theory of nucleophilic-electrophilic reaction which was considered an important aspect for suggesting a reaction mechanism for organic compounds such as activated carbon was presented.

More emphasis was placed on the various possible reactions of CN^- in CIP plant and pre-treatment stage in AARL elution which will form a sound framework for this study. The inconsistency of the pre-treatment variables i.e., pre-treatment temperature and contact time adopted in different industries which forms one of the main objectives of this work was also reported in this chapter. Agitation speed on the other hand has not been reported as a pre-treatment parameter. However, in relation to decomposition mechanism, improved decomposition of CN^- with an increase in agiation speed for a set time has been suggested but the effect on Au elution recovery has not been investigated.

Significant understanding of the literature about Au process, role of CN^- under the influence of different factors, uncertainity of the exact elution mechanism and the variabilities that exist in the industry with regards to pre-treatment parameter helped to provide reasonable explanations of the effect of pre-treatment parameters. The result obtained further helped to suggest the most suitable elution mechanism with relevant recommendations made to the industry.

The next chapter focuses on the materials and methods used to investigate the effect of the pre-treatment parameters. This gives an understanding of the role of CN^- on Au loaded on activated carbon and noting the effect on elution

.

3 Materials and methodology

3.1 Materials

The following are some of the materials that were used in this study:

- Granular activated carbon.
- Alkaline buffer solution
- Synthetic Au solution
- Water dispensing bottles
- Electrical powered mechanical roller
- Temperature controlled water-bath, beaker, stirrer and impeller
- NaOH, NaCN and sulphuric acid (H_2SO_4)
- Water jakected glass column, peristaltic pump, sample tubes
- Reverse osmosis (RO) water
- 100% Oxygen

3.1.1 Preparation of activated carbon

The activated carbon used was obtained from Marlyn chemicals in South Africa. This is commercially available and used on Gold plants. The properties of activated carbon used for this study are summarised in Table 3.1 below.

Table 3.1: Properties of the activated carbon used in the study

Property	Specification
BET surface area	1200 m^2/g
Iodine number	1075 mg/g
Particle density	0.82 g/cm^3
Bulk density	0.43 g/cm^3
Pore volume	0.62 cm^3/cm^3
Ash content	1.77%

A 900 g of fresh activated carbon was weighed, screened. Thereafter, a geometric mean size of 2537 µm was determined. This was followed by rinsing in RO water for 30 min to remove any contaminants and then oven dried at 90^{o}C for 48 hours. From the prepared 900 g, 840 g was taken and divided into two equal parts (420 g each). Each 420 g of the oven-dried fresh activated carbon was poured into a 10 L bucket each containing de-ionised water and agitated for 30 min to restore the activity of the activated carbon (Lorenzen et al., 1995) after which adsorption of Au was carried out.

3.1.2 Preparation of alkaline buffer solution

Buffer solution was prepared according to the description by Mpinga (2012). Alkaline buffer solution was used to stabilise the pH of the adsorbing medium (sodium salt and weak base). Sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) weighed at 8.4g and 1.91g respectively were poured into a 1000mL beaker followed by the addition of water to two-third of the beaker. This mixture was allowed to dissolved and then acid (H_2SO_4) and base (NaOH) was added to monitor the pH to around 10. Additional water was added to volume of 35 litres.

3.1.3 Preparation of synthetic gold solution

Potassium gold-cyanide $KAu(CN)_2$ salt was mixed in the 9.5 pH prepared buffer solution and diluted to a volume of 30 litres to produce a 200 mg/L Au solution. The pH of the solution was adjusted by adding NaOH and H_2SO_4 to control and maintain a pH of 10. The alkaline medium served to prevent the formation of HCN gas that could evolve at pH below 9.3 (Marsden and House, 2006). The aim of this work was not to obtain an optimum Au adsorption; therefore, a low Au concentration of about 11 mg/L was used. After preparation, a 5 mL solution was taken for ICP_OES analysis for confirmation of the Au uptake by activated carbon.

3.2 Methodology

3.2.1 Phase 1: Adsorption stage

The procedure for the loading of activated carbon is similar to the work of Mpinga (2012). The prepared 420 g activated carbon described in Section 3.1.1 was transferred into an 18.9 litres of water dispensing bottles, which contained 15 litres of the synthetic Au solution. This procedure was carried out for an additional bottle. These two bottles were transferred onto a mechanical roller powered by electricity rotated at a constant speed of 450 rev/min measured with a MT952 tachometer for 72 hours as shown in Figure 3.1. Almost a complete equilibrium would have been achieved at 72 hours of adsorption time which have been demonstrated in a similar adsorption process (Mpinga, 2012; Van Deventer, 1984). The mechanical roller has been demonstrated to give an analogous loading rate in comparison to the conventional CIP plant (Fleming, 2011). A sample of the solution was taken after 72 hours for ICP_MS analysis to determine the Au uptake by the activated carbon. The loaded carbon was filtered with a 800 µm screen, oven dried at 80^{o}Cfor 48 hours and divided into 12 g each using a rotary divider. Each of the 12 g loaded carbon was placed inside a zip-lock and stored in a dry, cool place for the next phase of the experiment. Details of the experimental steps, risk analysis as well as precautions taken during this stage are provided in Appendix A.

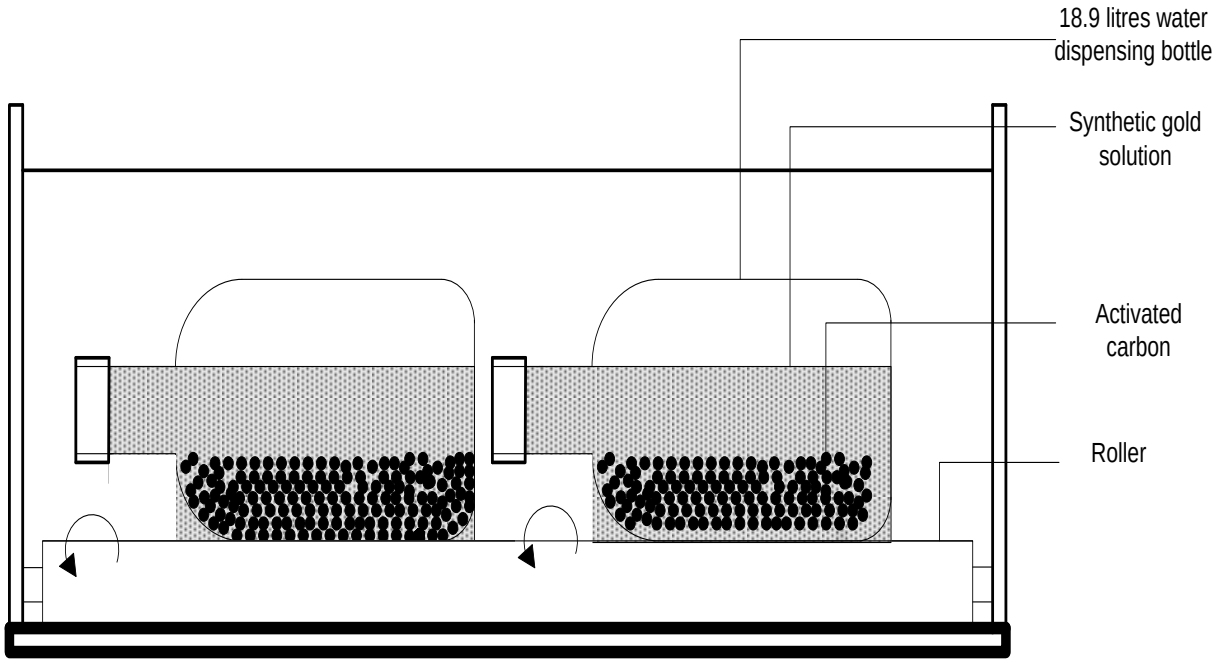


Figure 3.1: Schematic diagram of adsorption setup.

3.2.2 .Phase 2: Pre-treatment stage

The demonstration of the pre-treatment stage by various researchers on a laboratory scale was conducted in a separate reactor (cylindrical beaker) from the elution column (Snyders et al., 2013; Van Deventer and Liebenberg, 2003; Van Deventer, 1994). The pre-treatment operation adopted in this work was also performed in a beaker batch wise, separate from the elution column.The beaker contained NaOH-NaCN solution and the Au loaded activated carbon. The NaOH-NaCN solution was maintained at the required temperature for a set time, after which the pre-treated carbon was passed into a glass column for elution. The concentration of NaOH-NaCN adopted by various researchers vary from one study to another.

3.2.2.1 Reactor design for pre-treatment

This work eliminates the use of baffles (Figure 3.2) in the set up in order to avoid the Au loss that might be associated with carbon breakage during intense agitation. Carbon breakage during adsorption in the gold plant results in Au loss (Staunton, 2005). This setup conveniently fitted a 250 mL beaker and a polytetrafloroethylene (PTFE) lid was fabricated and used.

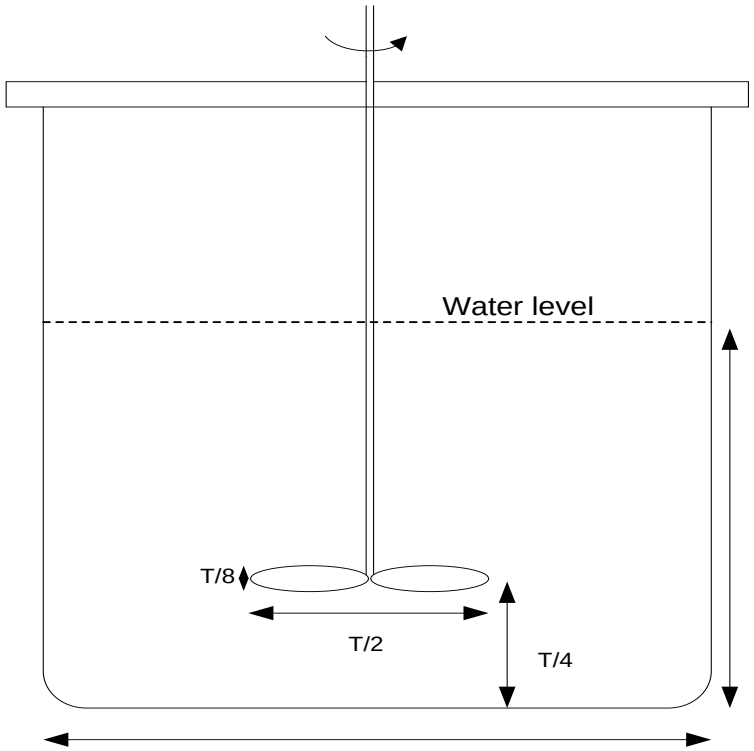


Figure 3.2: Unbaffled reactor used in the study.

3.2.2.2 Pre-treatment procedure

Pre-treatment of the loaded Au on activated carbon was carried out in a fume-hood. The experimental set-up for the pre-treatment step consists of a water-bath with a temperature controlled heating system. The opening of the water bath was designed to accommodate a 250 mL beaker. The PTFE lid used for the beaker was perforated to accommodate the stirrer, temperature probe, Eh probe and pH probe shown in Figure 3.3. For each run, 3% NaCN and 1% NaOH per volume of water was used. It is suggested that the effect of CN^- is evident at this concentration for rapid elution while the concentration of NaOH will maintain an alkaline medium. This corresponds to 2.4 g NaCN and 0.8 g NaOH in 80 mL of water. Before the addition of the NaOH-NaCN reagent, 80 mL of water poured into the beaker was heated to the required temperature according to the experimental design. The temperature, pH and potentials were measured using its respective probes. After attaining the set temperature, the NaOH-NaCN reagent was poured into the solution while the impeller was gently lowered into the solution through the PTFE lid. The pH and potentials were measured and recorded before pouring the activated carbon. The stirrer, set at the required speed was switched on immediately the activated carbon

was poured into the solution. The pH and potentials at 5 min intervals was measured and recorded.

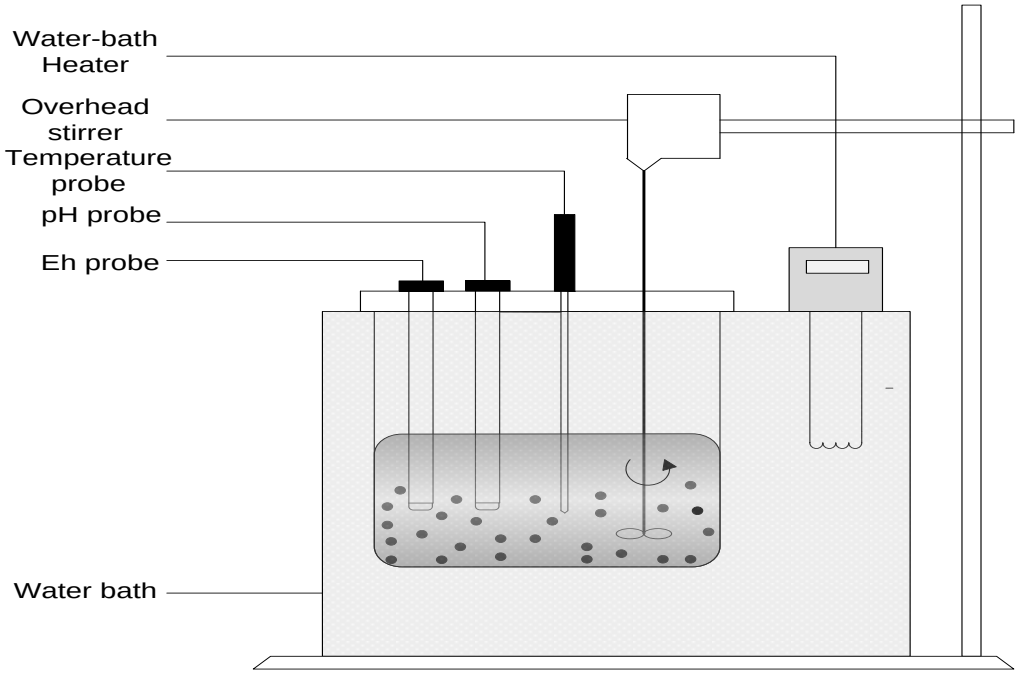


Figure 3.3: Experimental set-up of pre-treatment process.

3.2.2.3 Rinsing of pre-treatment reagent

Some additional experiments were devised to investigate the effect of rinsing the pre-treatment reagent (NaOH-NaCN solution) on the elution process. Rinsing was conducted on the pre-treated activated carbon after decanting the pre-treated solution. RO water with a volume of 5 mL was poured into the pre-treated activated carbon and gently shaken for about 2 min. This procedure was repeated 5 times, which resulted in 300 mL of rinsed solution corresponding to 6 bed volumes of the present elution study. The Au in the pre-treatment solution was analysed. During the rinsing process, the HCN gas detector was placed close to the beaker lid and the observed HCN gas read on the Dragger cyanide detector was recorded.

3.2.3 Phase 3: Elution stage

A simplified flow sheet of the elution set-up is presented in Figure 3.4. This is similar to the experimental set-up adopted by Snyders et al. (2014). Before the start of the elution, RO water was heated to 90^{o}C with water bath pump and the water jacketed

elution column connected to the water bath pump was also maintained at 90^{o}C. The column was filled with RO water up to half bed with the aid of 0.8 mm diameter marprene continuous tube connected to the water-bath through a peristaltic pump. (1 bed volume here is 25 mL which accommodated 12 g of activated carbon). The pre-treated activated carbon loaded with Au was carefully transferred with a spatula into the column from the top of the glass column and RO water was allowed to flow at a flow rate maintained between 2 to 3 bed volumes per hour. The exit of the eluate at the bottom of the column was manually controlled to maintain water level above the carbon bed at that flow-rate. 5 mL of eluate samples were taken at the bed volumes shown in Table 3.2 for each elution process. The aim of this work is to investigate the pre-treatment parameters and not the elution factors therefore, the elution parameters were kept constant throughout the whole elution process. These parameters are shown in Table 3.3.

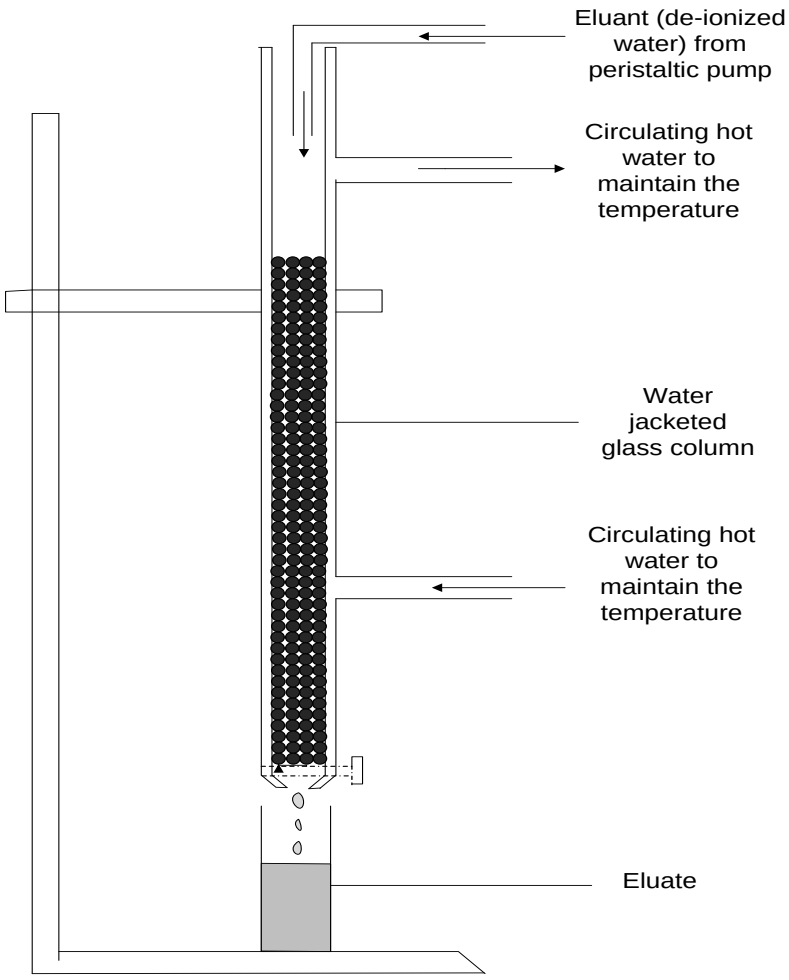


Figure 3.4: Schematic diagram of the step-up for elution process. (Ratio of column length to column diameter (L/d) = 5.2, porosity ≈ 0.4)

Table 3.2: Elution sampling points

Bed volumes													
0.20	0.60	1.0	1.4	2.0	2.4	3.0	3.6	4.0	4.6	6.0	9.0	11	15	20

Table 3.3: Conditions used during the elution process.

Temperature	90^{o}C
Flow rate	3BV/h
Eluant	Reverse osmosis water (0 mg Na/L)

3.2.4 Chosen point of analysis

The plots and comparisons of recovery curves for all pre-treated carbon showed a common trend from 0 to around 4 bed volumes after which it curves and gradually flattens. This is schematically shown in Figure 3.5 below. For the majority of the plots, trends **a** and **b** were observed while trend **c** was observed in a few cases, but with the same endpoint as **a** or **b**. Analysing the results of Au elution curve at 20 BVs (end point of the recovery curve) or the first 4 BVs will provided limited information about what happens in-between the curves.Due to this, common point was chosen where a discrepancy in recovery could be noticed. This corresponds to approximately 6 bed volumes. In this study, 6 bed volumes is a significant point which corresponds to point just after the elution peak in the elution profile where the bulk of Au has been recovered was chosen unless otherwise stated.

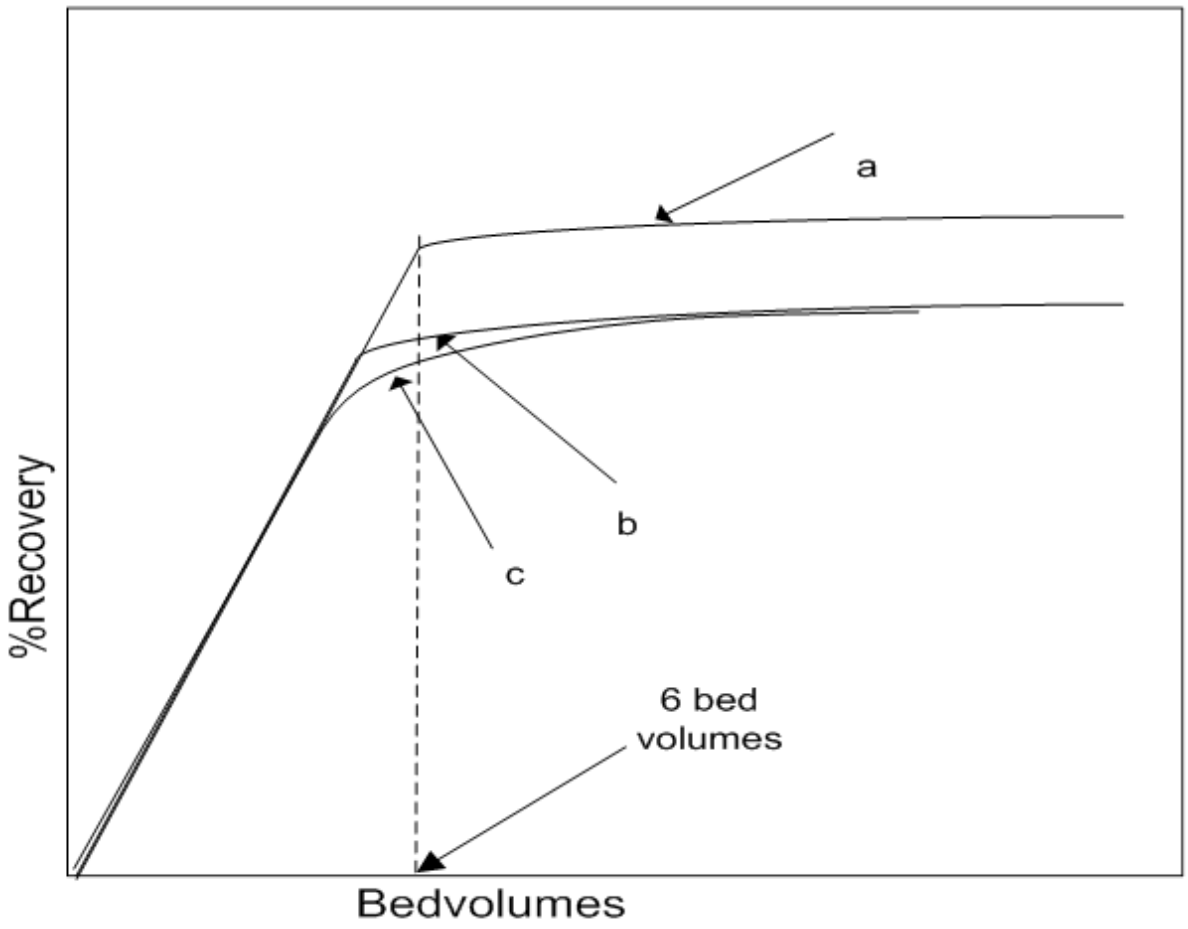


Figure 3.5: Illustration of the different recovery curves detected from the experimental work also showing the point of analysis at 6 bed volumes.

3.3 Experimental design

Based on the three levels and three factors that was investigated, experiments were statistically designed adopting a Box-Behnken design (BB) using Statistical 12 software. BB design offers advantages of fewer runs than three-level full factorial design than the Central composite design (CCD) and it is also suitable for optimisation through the response surface plot (Montgomery, 2013). If a three level full factorial with three replicates were to be adopted, eighty-one runs would have been required. However, with BB design, forty-five efficient runs are required with replications included. The experimental design without replicating is presented in Table 3.4 and the random design with the replicated is shown in Table 3.5. Experiments were replicated three times to minimise errors and improve accuracy of the regression model used for the predictions of points that were not included in the

experiment. Another advantage of BB is that it is rotatable or very nearly rotatable providing equal variances (Montgomery, 2013). This will also reduce the cost and time by approximately 50% when compared with a three level full factorial design.

Table 3.4: Box-Behnken Experimental design in standard order

Run	Temperature (°C)	Time (min)	Speed (rev/min)
1	25	15	600
2	80	15	600
3	25	45	600
4	80	45	600
5	25	30	0
6	80	30	0
7	25	30	1200
8	80	30	1200
9	53	15	0
10	53	45	0
11	53	15	1200
12	53	45	1200
13	53	30	600
14	53	30	600
15	53	30	600

Table 3.5: Box-Behnken Experimental design in random order

Run nr	Replicate	Temperature (°C)	Time (min)	Speed (rev/min)
18	2	25	45	600
29	2	53	30	600
45	3	53	30	600
4	1	80	45	600
16	2	25	15	600
17	2	80	15	600

23	2	80	30	1200
33	3	25	45	600
28	2	53	30	600
19	2	80	45	600
1	1	25	15	600
9	1	53	15	0
8	1	80	30	1200
26	2	53	15	1200
42	3	53	45	1200
31	3	25	15	600
24	2	53	15	0
22	2	25	30	1200
38	3	80	30	1200
43	3	53	30	600
2	1	80	14	600
40	3	53	45	0
35	3	25	30	0
15	1	53	30	600
5	1	25	30	0
11	1	53	14	1200
3	1	25	45	600
25	2	53	45	0
37	3	25	30	1200
44	3	53	30	600
36	3	80	30	0
12	1	53	45	1200
21	2	80	30	0

14	1	53	30	600
41	3	53	15	1200
39	3	53	15	0
6	1	80	30	0
32	3	80	15	600
27	2	53	45	1200
20	2	25	30	0
10	1	53	45	0
30	2	53	30	600
7	1	25	30	1200
34	3	80	45	600
13	1	53	30	600

3.3.1 Choice of levels

The variables that were investigated during the pre-treatment stage and the three levels chosen are:

- Pre-treatment temperature (25, 53, 80) ^{o}C
- Pre-treatment time (15, 30, 45) min
- Stirring during the pre-treatment operation.(0, 600, 1200) rev/min

Three levels of each variable investigated were chosen according to the Box-Behnken experimental design for suitable optimisation (Montgomery, 2013). Incase optimisation will be required.

3.3.2 Pre-treatment temperature

Temperature has been discussed as one of the main factors that favours desorption (Section 2.9.1). Van der Merwe and Van Deventer (1993) investigated the effect of pre-treatment temperature at 20^{o}C and 100^{o}C. Likewise Jeffery et al. (2010) adopted

a pre-treatment temperature of 130^{o}C. In these cases, it was concluded that more elution occurs during pre-treatment at high temperature. 80^{o}C was chosen for the high level pre-treatment temperature in this research. At this temperature, it was a convenient temperature at atmospheric pressure and the aim was to investigate the effect rather than finding an optimum solution. Low level pre-treatment temperature of 25^{o}C was chosen and the mid-point corresponding to approximately 53^{o}C was used as the mid-point level.

3.3.3 Pre-treatment time

According to Laxen et al. (1982), reduction in pre-treatment time from 8 hours to about 2 hours does not have a detrimental effect on elution efficiency. Pre-treatment time of 30 min is commonly used by various researchers on a laboratory scale and variabilities of pre-treatment time exist in the industry (Marsden and House, 2006; Van Deventer and Van der Merwe, 1993; Davidson and Bailey, 1991; Davidson and Schmidt, 1986). 30 min was chosen as the reference and midpoint to investigate the effect above and below the reference point. As such, 15 min and 45 min were chosen for the low and high level respectively.

3.3.4 Agitation speed

Several researchers have shown that no stirring for 30 min was adopted in the pre-treatment condition (Jeffery et al., 2009, Van Deventer 1993; Van Deventer 1992; Davidson 1986; Davidson and Veronese, 1979; Davidson 1977). However, in the investigation of the feasibility of using activated carbon for PGM [Platinum (Pt), Palladium (Pd) and Au] recovery from low grade ore, Snyders (2014) adopted a stirring time of 30 min at a constant speed. Van Deventer and Van der Merwe (1995) investigated the effect of different stirring speeds on the decomposition of CN^{-} for about 70 hours. The result showed that more CN^{-} decomposes with increasing agitation speed, however, the effect on elution was also not provided.

This work adopted a low level of no agitation (0 rev/min) which can be seen as a region of laminar regime and a high level of intense turbulent condition (1200 rev/min) which corresponds to speed of just the suspension (N_{js}) of carbon particles. The Njs was determined based on visual inspection of the carbon particles

at 1200 rev/min (Paul et el., 2004; Gray, 1999). N_{js} is suggested to increase maximum exposure of the particles for uniform mixing (Paul et al., 2004). The midpoint of 600 rev/min was calculated from the range of chosen speeds.

The appropriate dimensionless parameters (Power numbers and Reynolds numbers) used to quantify the agitation speeds were calculated according to Equations 3.1 and 3.2 respectively (Wong et al., 2014; Hemrajani and Tatterson, 2004).

$$N_p = \frac{P}{\rho_m N^3 D^5} \quad 3.1$$

$$R = \frac{D^2 N \rho_m}{\mu_m} \quad 3.2$$

Where: N_p = Power number

P = Power consumption of slurry (W)

N = Rotational speed of the impeller (rps)

D = Impeller Diameter (m)

R = Reynolds number

ρ_m = Density of mixture (kg/m^3)

μ_m = Viscosity of the mixture (N.s/m^2)

[2]The density of the mixture and viscosity of the mixture was calculated using Equations 3.3 and 3.4 respectively (Menon, 2004)

$$\rho_m = \frac{100}{\left[\frac{C_w}{\rho_s} + \frac{[100-C_w]}{\rho_L}\right]} \quad 3.3$$

$$\mu_m = \mu_L * [1 + 2.5*\phi + 10.5*\phi^2 + 0.00237*\exp(16.6*\phi)] \quad 3.4$$

Where: C_w = concentration of solids by weight in slurry (%)

ρ_s = density of solids (kg/m^3)

ρ_L = density of liquid (kg/m^3)

[2] Mixture is a combination of solids (carbon + NaOH-NaCN) and liquids(RO water)

μ_L = viscosity of liquid

ϕ = volume fraction

3.4 Method of analysis

3.4.1 ICP_OS

Au and Na concentrations in solution were analysed using an i-cap 6000 series ICP spectrometer. A standard stock of Au and Na solution was prepared in which the intensities of the wavelength were known. This corresponds to the concentration of the standard solution. The concentration of the wavelengths and intensity of the aqueous samples to be determined are converted to aerosols through a nebulizer at high temperatures between 8000^{o}C to 10000^{o}C. The comparisons of these wavelengths against the standard solution were finally used to correlate the actual concentration.

3.4.2 Silver nitrate titration

Free cyanide (CN^-) was measured by titrating 1 mL volume of solution containing CN^- against a 0.1 M concentration of silver nitrate ($AgNO_3$) with an automatic titrating machine (TIM856 titration manager), using a silver electrode as the indicator. Mille-Q water was added to the 1 mL solution containing CN^- to have contact with the indicator. The potentiometric end-points were detected from the derivated plot (indicated on the screen of the titrating machine) of the potential of the solution against the volume of $AgNO_3$ used. This was signified by the maximum peak in the plot while the corresponding volume was used to calculate the concentration of CN^-. See Appendix B for supporting calculation.

3.4.3 Scanning electron microscopic analysis

The Image of Au loaded activated carbon was investigated using a Zeiss EVO® MA15 Scanning Electron Microscope at the Geology department of Stellenbosch University. Firstly, before the imaging was carried out, the samples were mounted on a stub carbon tape with double side in order to make the sample surface electrically

conducting. The Scanning electron (SE) images show the surface structure of the material. The spot size of the beam was 550 and the conditions of the surface were 20 kV.

3.4.4 Measurement of natural or dissolved oxygen

Dissolved oxygen (DO) in solution was measured using a cyber-scan 300 dissolved oxygen meter connected to a dissolved oxygen probe.

3.5 Chapter summary

The materials and methodology used in the conduction of this research were outlined and described in this chapter. These materials and approaches include the synthetic Au solution, properties of activated carbon, how the loading of Au on activated carbon was performed, pre-treatment and the elution process. In addition, choice of experimental design and the selection of pre-treatment parameters were also discussed. The last section of this chapter discussed the various analytical techniques adopted. These include ICP_OES analysis, titration technique for the measurement of CN^-, SEM and the dissolved oxygen measurement.

The results of these experiments that investigated the role of NaOH-NaCN and effect of temperature, contact time and agiation speed on Au elution are discussed in the next chapter.

4 Results and discussion

The results obtained from the experiments and its interpretations are presented in this charpter in order to answer the research questions. These include a brief summary of the loading on activated carbon and results obtained in the pre-treatment stage where the role of NaOH-NaCN and the effect of pre-treatment parameters on Au elutions were investigated. Adequate understanding of these effects significantly assisted in the explanation of the most suitable elution mechanism. Furthermore, the industrial application on Au loaded activated carbon supplied from Au processing plant was presented.

4.1 Adsorption result

The adsorption experiment was conducted at atmospheric conditions in an electrical powered mechanical roller rotating at a speed of 450 rev/min. ICP analysis of the barren solution after adsorption revealed a concentration of 0.03 mg/L from an initial concentration of 10.6 mg/L of the prepared synthetic Au solution. This showed that more than 99% of the Au was adsorbed. The concentration of carbon used in comparison to the amount of Au adsorbed resulted in large amount of surface area for sufficient adsorption (Van Nguyen et al., 2010). It was assumed that the loading was uniform through the thorough mixing that was carried out using a rotary divider. As such, each 12 g of AC that were subsequently used during pre-treatment and elution were assumed to have 0.38 mg/g of Au. The remaining adsorbed Au on carbon after elution was not estimated. Therefore, It was assumed that the maximum (100%) recovery of Au elution recovery was obtained at the optimum pre-treatment condition at 20 BV

4.2 Elution results

Table 4.1 shows an overview of the Au elution results after pre-treatment and at 6 bed volumes (just after the elution peak). The elution results presented are the average values after three replicates of each run. Using the mean after three replicates minimises the error that might be associated with the experiment, it also improves the accuracy of the regression model used to predict other data points that

are not conducted experimentally. Statistical analysis of results and the errors associated with the experiment are further discussed in chapter 6

Table 4.1: Overview of experimental result of Au elution at different pre-treatment conditions.

Run	Temperature (^{o}C)	Time (min)	Speed (rev/min)	Au (mg/L) after pre-treatment	%Recovery after pre-treatment	%Recovery at 6BV	Na (mg/L) after pre-treatment
1	25	15	600	0.06	0.03	54.6	17156
2	80	15	600	0.61	0.27	61.2	18415
3	25	45	600	0.04	0.02	59.5	17641
4	80	45	600	0.47	0.21	61.7	18942
5	25	30	0	0.06	0.03	59.9	16658
6	80	30	0	0.97	0.44	70.9	18132
7	25	30	1200	0.10	0.04	58.3	16593
8	80	30	1200	0.13	0.06	56.5	18448
9	53	15	0	0.11	0.05	59.9	18283
10	53	45	0	0.17	0.08	60.3	17276
11	53	15	1200	0.06	0.03	56.7	17540
12	53	45	1200	0.04	0.02	56.8	18706
13	53	30	600	0.08	0.04	55.5	18050
14	53	30	600	0.11	0.05	57.3	16958
15	53	30	600	0.05	0.02	55.1	16001

4.2.1 Gold elution after pre-treatment

It can also be seen from Table 4.1 that the percentage of Au eluted after pre-treatment did not exceed 0.44% even at high levels of any of the pre-treatment parameter (80^{o}C or 45 min or 1200 rev/min). This suggested that insignificant amount of Au was eluted during pre-treatment when compared with Au eluted at 6BVs. Therefore, it was assumed that amount of Au eluted after pre-treatment will not influence results found at 6 BVs. The results of elution performed at pre-treatment condition of 80^{o}C, 30 min and no agitation is shown in Figure 4.1. This curve was used as an example for all the elution curves obtained and is used to explain the elution behaviour of Au.

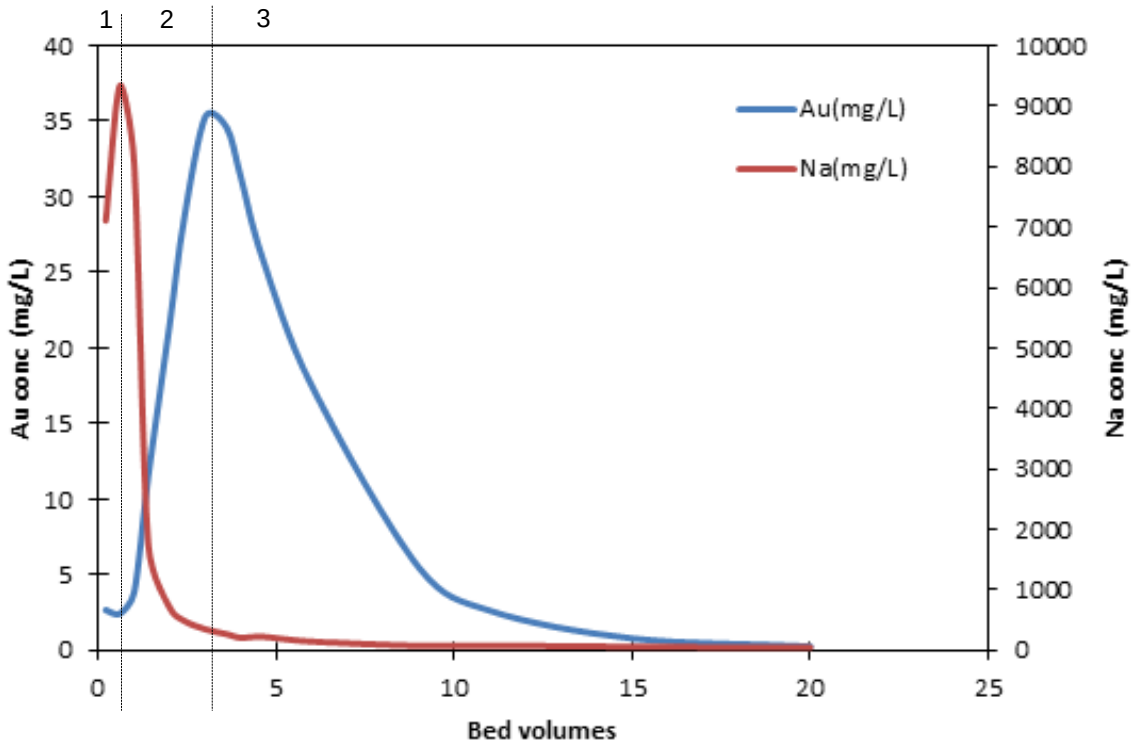


Figure 4.1: Description of Au elution curve. (Pre-treatment with 1% NaOH and 3% NaCN, 80^{o}C, 30 min and no agitation , elution at 90°C)

For clarity, the elution profile was divided into 3 sections. The description for each of this section is shown in Table 4.2 which is similar to the description by Snyders et al. (2015).

Table 4.2: Description of the divided sections of elution curve

Section	Observation and description	Suggestion or possible reason
1	The amount of Na eluted increases while Au is yet to be eluting.	Excessive amount of Na carried over from pre-treatment supressed Au elution.
2	The concentration of Na drops while the concentration of Au increases to a maximum point in solution	Removal of Na favours Au elution recovery
3	The amount of Au eluted from the column decreases while Na remains depleted at low concentration throughout this stage.	Depletion of Au on carbon surface resulting in decrease in concentration of Au in solution

From this description, it can be suggested that the presence of Na in the pre-treatment solution supresses the elution of Au. According to the ion pair mechanism and the effect of cations on adsorption and elution as discussed in Sections 2.6.1 and 2.9.3, the presence of such a high concentration of Na in the pre-treatment solution favours the formation of ($Na^+[Au(CN)_2^-]$) ion pair on the carbon surface thereby inhibiting desorption (Adams and Fleming,1989; McDougall et al.,1980; Davidson,1974; Gross and Scott, 1927). With regards to the role of CN^- during elution, insufficient information is available at this point to prove the exact mechanism through which it aids elution.

In view of this, the effect of Au eluted during pre-treatment are regarded to be negligible for further analysis during elution in subsequent sections and are assumed not to have an effect on the elution analysis.

4.3 Effect and role of caustic-cyanide during pre-treatment.

The behaviour of NaOH-NaCN during pre-treatment can be summarised to take place in two stages. These stages are:

- Dissociation of chemical compounds into its ionic state. NaOH and NaCN will dissociate to Na^+, OH^- and CN^-
- It is proposed that there could be some interactions of these dissociated ions from solution either by adsorption onto the activated carbon (occlusion of any of these ions in carbon pores or just sitting on the carbon surface), or formation of the Au metal complex ($Na^+[Au(CN)_2^-]$) as an ion pair as discussed in Section 4.2.1 for Na^+. This interaction could also either be as a result of catalytic oxidation in the presence of activated carbon or via hydrolysis in the case of CN^- as earlier discussed in Section 2.12.1. Another possible interaction of these ions in the solution could be as a result of specific reaction with functional groups of activated carbon (Adams and Fleming, 1989). At this juncture, the exact form of interaction during pre-treatment was not firmly established especially for CN^-. Na^+ is proposed to form Au metal complex ($Na^+[Au(CN)_2^-]$) through the interaction with adsorbed $Au(CN)_2^-$ on carbon surface according to the ion pair mechanism (Section 4.2.1). Understanding these interactions will enhance the suggestion of a suitable elution mechanism.

In addition, from the first case (dissociation of chemical compounds), depending on the pH of the medium, CN^- can either form HCN or exist as CN^- (Figure 2.11). The presence of OH^- and the stability of CN^- were confirmed with the measured pH of the solution within the range of 11 and 12.9 throughout the whole experiment. CN^- becomes more stable when pH > pKa of HCN. This is in agreement with the work of Van der Merwe (1992) where it was stated that the OH^- ion stabilises the CN^- to prevent evolution of HCN. Although all experiments were conducted in alkaline medium (pH≥11). However, it was observed that HCN gas was evolved at 25^{o}C which fluctuated between 0.1 and 0.6 mg/L as seen in the Drägger HCN gas detector for about a minute. The set of combinations of parameters where this observation occurred were repeated to confirm the evolution of HCN gas. However, observations of the exact concentration of the HCN gas evolved were inconsistent after three repetitions and the HCN gas was considered to be insignificant.

The high amount of Na^+ (>16000 mg/L) present after pre-treatment can be attributed to the contributions from NaOH and NaCN. Further investigation of the effect of Na^+ on the adsorption with carbon surface and $Au(CN)_2^-$ showed that the majority of Na^+ that adsorbed on the carbon surface loaded with $Au(CN)_2^-$ were strongly bonded through ion-pair mechanism (Section 2.4.4). This was confirmed with two sets of pre-treatment experiments. In the first set, the pre-treated Au loaded AC at 80^{o}C, 30 min and 0 rev/min was rinsed with 300 mL of RO water at 25^{o}C to wash off the excess Na^+ on the carbon surface before elution while the other set was eluted immediately after pre-treatment. The result of the two cases, as shown in Figure 4.2, suggested that the Au elution peak was attained after the elution of the majority of Na^+.

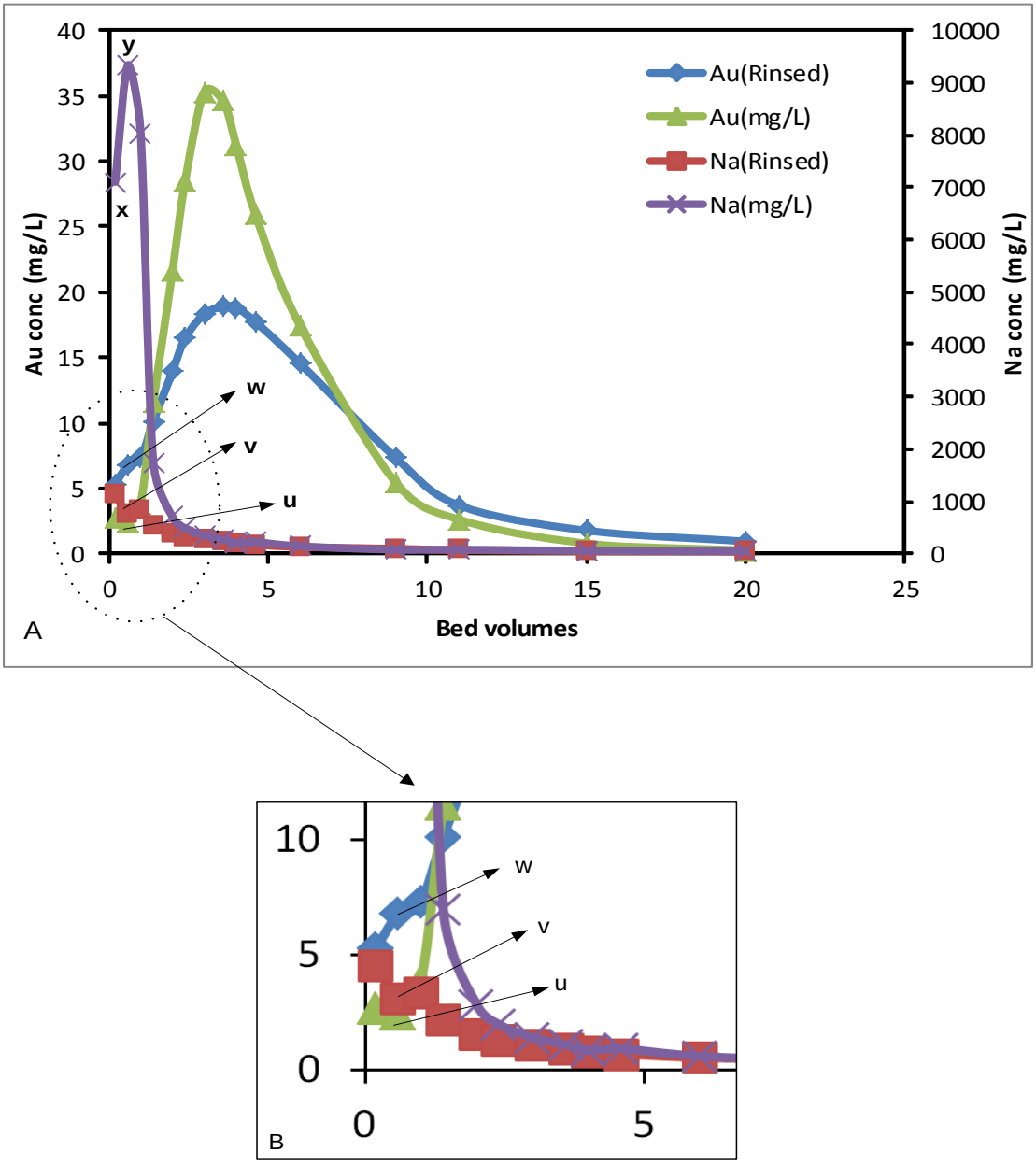


Figure 4.2: Effect of rinsing of excessive Na from the surface of pre-treated carbon. The pre-treatment condition for both rinsed and unrinsed conditions are 80^{o}C, 30mins and 0 rev/min. Point u represent the amount of Au eluted at 0.6 BV at unrinsed pre-treatment condition in the presence of excessive Na carried over from the pre-treatment stage (x-y). Points v and w respectively corresponds to the amount of Au and Na eluted at rinsed conditions at 0.6 BV.

Comparison of Au eluted during this exercise with Au eluted at 6 bed volume equivalent of 300 mL that was used to rinse off the excessive Na^{+} is reported as follows;

In the rinsed solution (6 bed volume), the amount of Au present in the solution was about 0.1%. At 6 bed volumes of the rinsed and unrinsed elution recovery, amount of Au was about 50 and 70% respectively as shown in Figure 4.3. These results correspond to the observed depletion of Na^+ in both cases as shown in Figure 4.2.

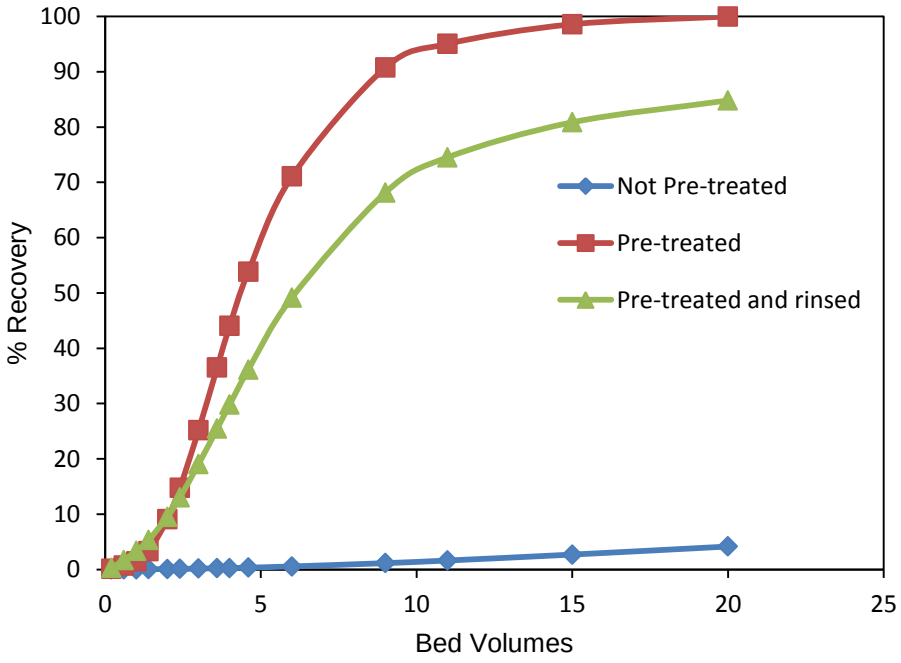


Figure 4.3: Effect of rinsing of excessive free cyanide from the surface of pretreated carbon Pre-treatment condition for both rinsed and unrinsed conditions are 80^{o}C, 30mins and 0rev/min.

This explanation can be supported by the work of Van der Merwe (1994) stating that Au elution is strongly dependent on cation removal. From Figure 4.2 , the effect of excessive sodium carried over from the pre-treatment stage to elution stage was seen to suppress Au elution recovery. This is seen with about 10000 mg/L Na at point y and eluted Au of about 1.6 mg/L (point u) at unrinsed pre-treatment condition. When this is compared with the rinsed condition of excessive Na at the same point of evaluation, It was seen that Au eluted (point w) was high (approximately 7 mg/L) at an approximate concentration of 800 mg/L Na (point v).

Another noticeable observation that can be seen in Figure 4.2 is the discrepancy in the Au elution curves of the rinsed and unrinsed conditions. This discrepancy of the amount of Au eluted in mg was done by calculating the difference in the amount of Au eluted for the two elution recovery curves.

Calculated difference of about 77 mg of Au implies that it remained uneluted on the activated carbon. Possible reasons for this retained Au on carbon can be suggested to be confined into two factors which are the deficit of Na and reduction to AuCN according to Equation 4.1 (Section 2.5)

$$Au(CN)_2^- + H^+ \rightarrow AuCN + HCN \qquad 4.1$$

From these two suggestions, reduction process (Equation 4.1) seems to be a more reasonable explanation due to the drop in pH from 12 to around 8.5 during the rinsing process. In addition the measured HCN gas with the HCN gas detector that remained stable between 0.6-0.8 mg/L suggested that Equation 4.1 occurred. Under severe acidic condition of about 4, greater occurrence of Equation 4.1 would be expected (Adams, 1990c). This implies that some Au may remain strongly adsorbed as AuCN (Van Deventer and Van der Merwe, 1993; Davidson and Schmidt, 1986) which accounts for the residual Au remained on activated carbon in a rinsed pre-treatment condition.

4.4 Cyanide loss during pre-treatment condition

Little is known about the loss of CN^- during pre-treatment of Au. This study will help to better understand the mechanism of CN^- depletion from solution. In this study, similar approach adopted by Nafaâ and Lotfi (2002) and Adams (1990) in the kinetic and equilibrium study of CIL and water containing cyanide was adopted. The concentration of CN^- in solution was measured at 15 min interval for a pre-treatment time of 60 min. This was carried out for NaOH-NaCN solution in the absence of activated carbon, in the presence of unloaded activated carbon (UAC) and carbon loaded with Au (AC-Au). For cases involving activated carbon, 12 g of activated carbon was used and 3% NaCN and 1% NaOH by volume of 80 mL of water as earlier adopted for the elution experiment were used in all cases.

A comparison plot of CN^- concentration against four consecutive contact times at 25^{o}C, 53^{o}C and 80^{o}C in the absence, presence of UAC and AC-Au is shown in Figures 4.4–4.6.

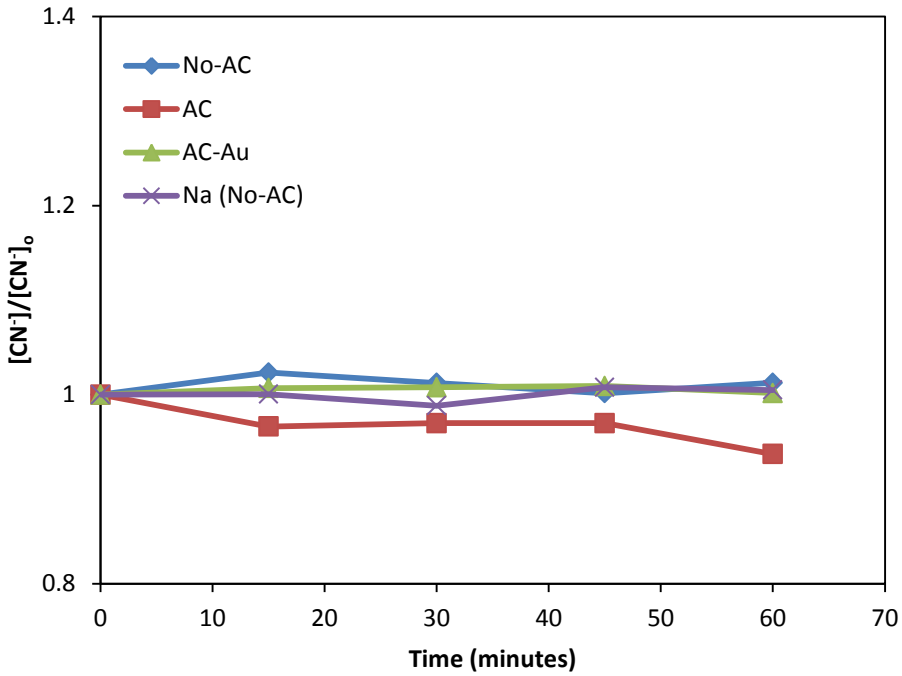


Figure 4.4: Cyanide behaviour in solution at 25°C, 0 rev/min, and 60 min.

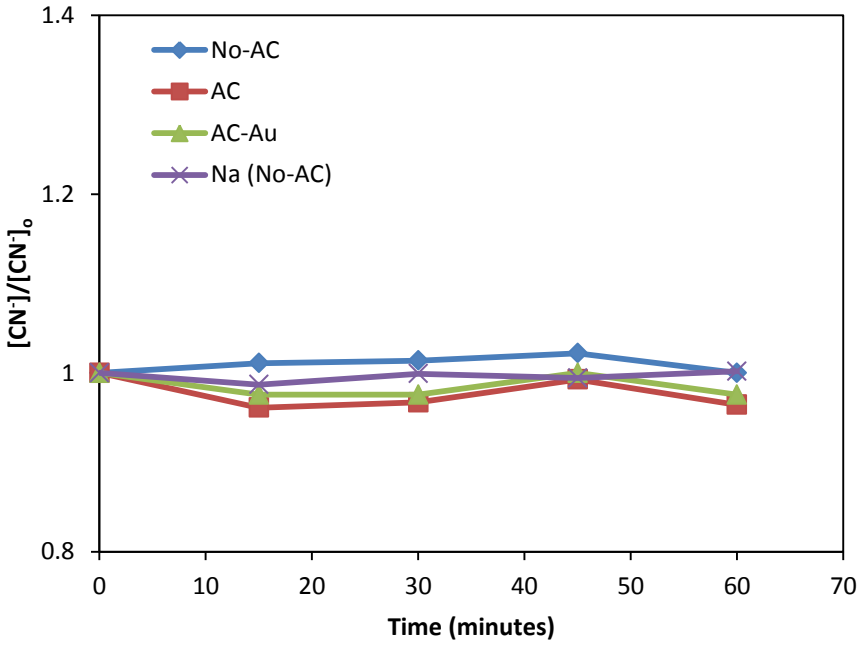


Figure 4.5: Cyanide behaviour in solution at 53°C, 0 rev/min, and 60 min.

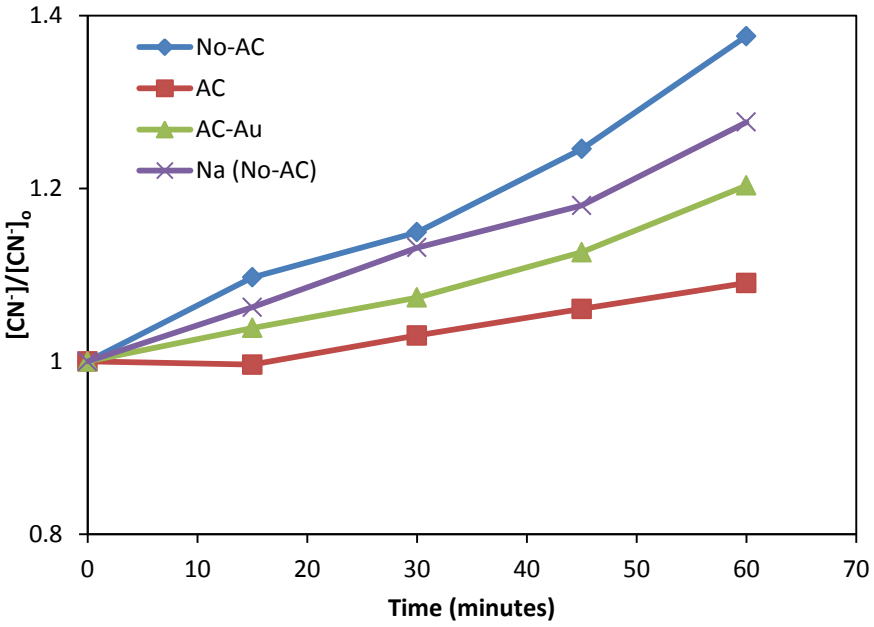


Figure 4.6: Cyanide behaviour in solution at 80°C, 0 rev/min, 60 min

Before the discussion on specific behaviour of CN^-, it is important to consider the behaviour of the overall compound (NaCN). From Figures 4.4 and 4.5, it is seen that there is no significant change in the concentration of CN^- throughout the pre-treatment period at both 25°C and 53°C when compared to Figure 4.6 where the pre-treatment temperature is 80°C. However, at 80°C, the concentration of the measured species in solution was found to increase with contact time. It was found that about 17 mL of water was lost as water vapour at 80°C while around 3.5 mL and 0.4 mL were lost as water vapour at 53°C and 25°C respectively. This accounted for increased concentration of CN^- and Na^+ observed in Figure 4.6. Further investigation after elimination of the evaporation at 80°C showed no significant change in concentration of CN^- occured during this period as shown in Table 4.3. This suggests that there is a low probability of CN^- loss either by adsorption of decomposition occurring during pre-treatment of Au

Table 4.3: Concentration (M) of CN^- at 15-min interval after elimination of vapourisation

Temperature (°C)	Speed (rev/min)	t_0	t_{15}	t_{30}	t_{45}	t_{60}
80	0	0.48	0.56	0.56	0.55	0.56

Eh-ph of the system

In a quest to further gain more insight into the behaviour of cyanide during the pre-treatment process, the phase stability (Eh–pH) of CN–H_2O system was investigated. This is a useful tool for predicting dominant specie (stable or meta-stable) in a region at equilibrium (Free, 2013). Figure 4.7 shows the Eh–pH diagram of CN–H_2O combined for temperatures at 25^{o}C, 53^{o}C and 80^{o}C for ease of comparison with the aid of HSC chemistry 7.31 software. From Figure 4.7, there is no significant change in the equilibrium lines between species at HCNO/HCN, HCN/OCN, HCNO/OCN and CN/OCN species except between CN^- and HCN species at the selected temperatures (25^{o}C, 53^{o}C and 80^{o}C). The equilibrium lines between CN^- and HCN for all temperatures varied between pH of 8 and 9.5. However, the measured pH in the present study prepared at 3% NaOH-NaCN solution was around 12.5. The range of pH maintained, suggests that CN^- present in this pH region can either exist in the form of OCN^- or CN^- depending on the potential of the solution. Bard et al. (1985) reported that CN^- in alkaline medium moderately oxidises to cyanate (OCN^- or CNO^-) and cyanogen gas given by Equations 4.2 and 4.3 respectively.

$$2OH^- + CN^- \rightleftharpoons CNO^- + H_2O + 2e^- \qquad E^o = -0.97v \qquad 4.2$$

$$2CN^- \rightleftharpoons (CN)_{2(g)} + 2e^- \qquad E^o = -0.182v \qquad 4.3$$

An increase in the concentration of CN^- with decreasing volume as earlier discussed and Eh-pH diagram suggested that there is a lower chance of oxidation of CN^- to CNO^- or probably insignificant if there is any. The measured Eh with an ORP electrode dropped from about 0.03 v to around -0.2 v for the pre-treatment time. This drop was observed to continue after the pre-treatment time which did not remain stable at -0.2 v. This suggest that the stable values of the potential has not been reached during this pre-treatment time and more drop in the potiential would be expected to confirm a predominate phase of CN^- as shown in Figure 4.7 .These evidences were used to suggest the possible reactions of cyanide in solution. Similar trend was also noticed with the behaviour of sodium, which suggested dissociation of NaCN to Na^+ and CN^- significantly occurred and that little or no CN^- is being oxidised to CNO^-.

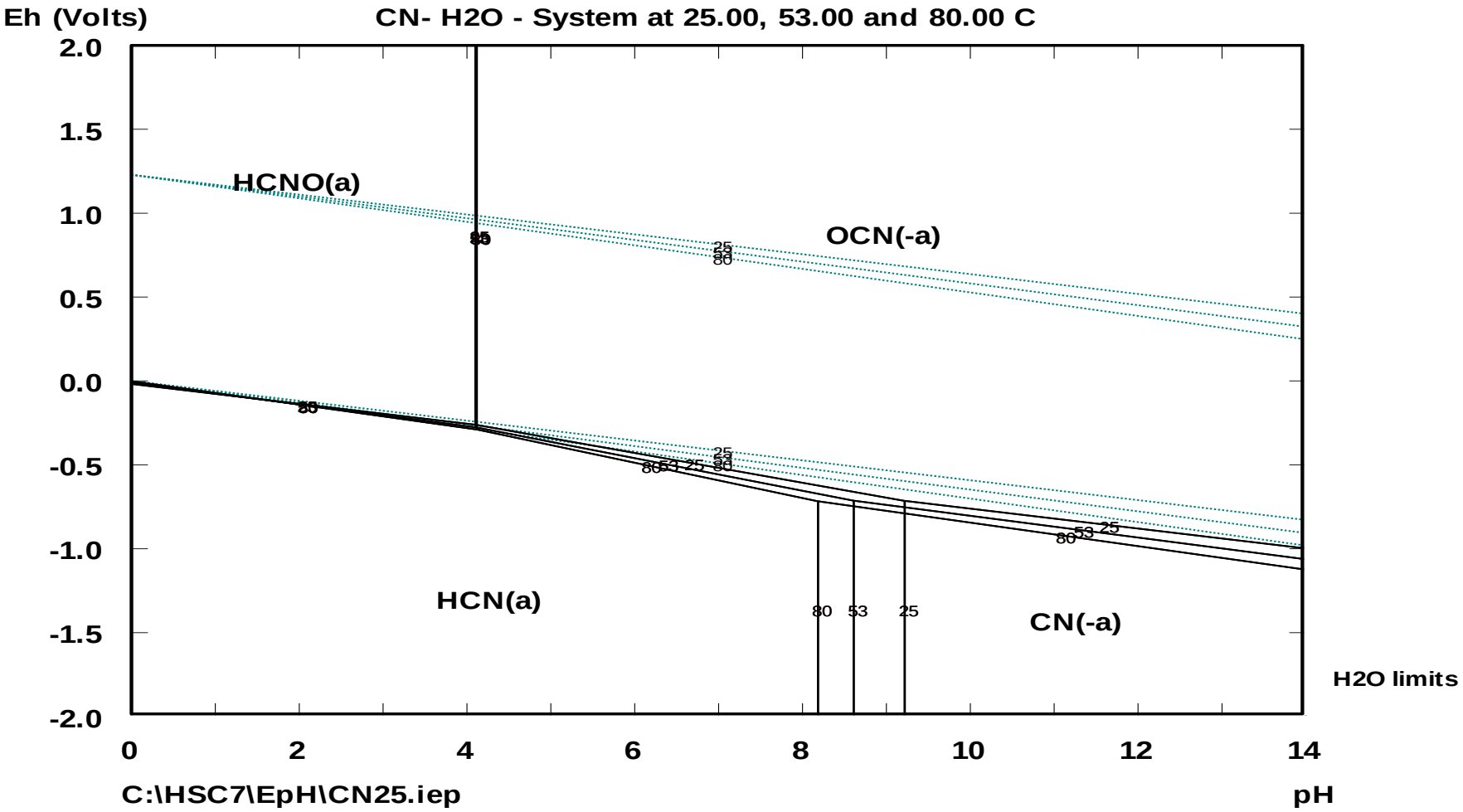


Figure 4.7: Combined Eh-pH diagram of CN-H_2O at 25^oC, 53^oC and 80^oC

4.5 Effect of selected parameters on the elution of gold.

The effect of temperature, contact time and agitation speed is discussed in the following section. The trend of each pre-treatment parameter was defined with at least three data points rather than two. This ensures minimisation of random error that might be associated in the adoption of two data points (ISU, 2014). In addition, the choice of experimental design (Box-behken design) that requires three factors and three levels justified the three chosen points than four or more points. The error bars in the plots indicate the standard deviation. Elaborate discussions with regards to error and the confidence level at ± 95% interval are further discussed in the statistical analysis of results.

4.5.1 Effect of temperature

According to Adams (1991), elution temperature, among other elution factors such as concentration of NaOH-NaCN, ionic strength and organic solvent, significantly affects elution rates. Usually in industry, the same pre-treatment temperature as the elution temperature (110–120^{o}C) is deployed (Davidson et al., 1990). The effect of pre-treatment temperature at 25^{o}C, 53^{o}C and 80^{o}C on Au elution recovery is shown in Figure 4.8. while the surface response plot showing the interaction of pre-treatment temperature with contact time is shown in Figure 4.9. It can be seen that an increase in pre-treatment temperature from 25^{o}C to 53^{o}C resulted in an increase of less than 5% in Au recovery (Figure 4.8). Further increase in temperature from 53^{o}C to 80^{o}C resulted in about 12% increase in Au recovery. The positive effect of pre-treatment temperature on Au elution recovery can also be seen in Figure 4.9. These are in agreement with the study by Van Deventer and Van der Merwe (1994) where it was shown that significant elution recovery was obtained at pre-treatment temperature of 100^{o}C than at 25^{o}C.

According to Figure 4.6, an increase in concentration of CN^{-} observed at 80^{o}C due to vapourisation suggest that more CN^{-} is available for interaction with carbon surface, thereby promoting Au elution recovery than at 25^{o}C and 53^{o}C.(Figures 4.4 and 4.5). However in the industry, the vessels are pressurised and it is expected that the

evaporation will remain minimal and the CN^- concentration will remain constant that still results in increased elution results. It should be noted that the exact interaction of CN^- with carbon surface is not yet fully ascertained. The most likely form of interaction is discussed under the reaction mechanism in Section 4.6.3.

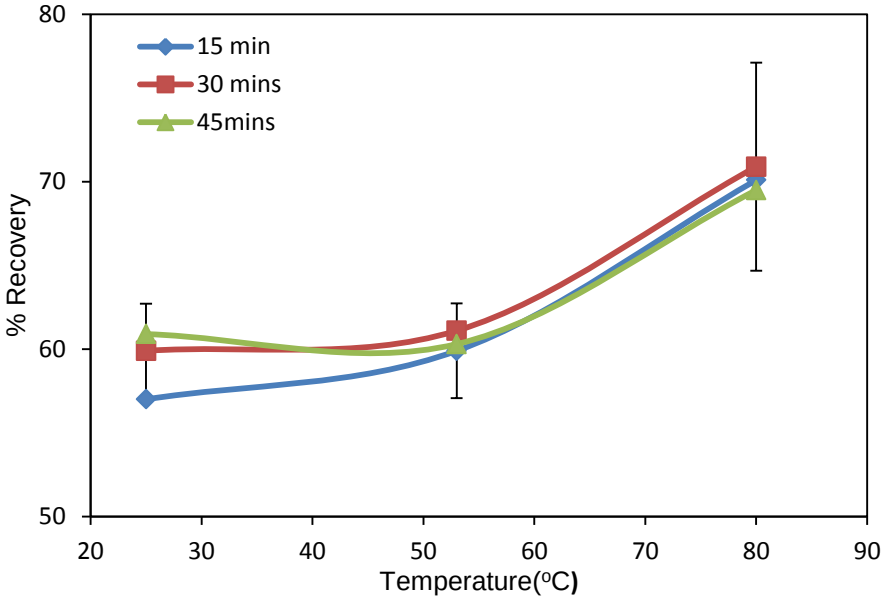


Figure 4.8 The effect of pre-treatment temperature on the elution recovery of Au. (Pre-treatment with 1% NaOH and 3% NaCN and no agitation, elution at 90°C)

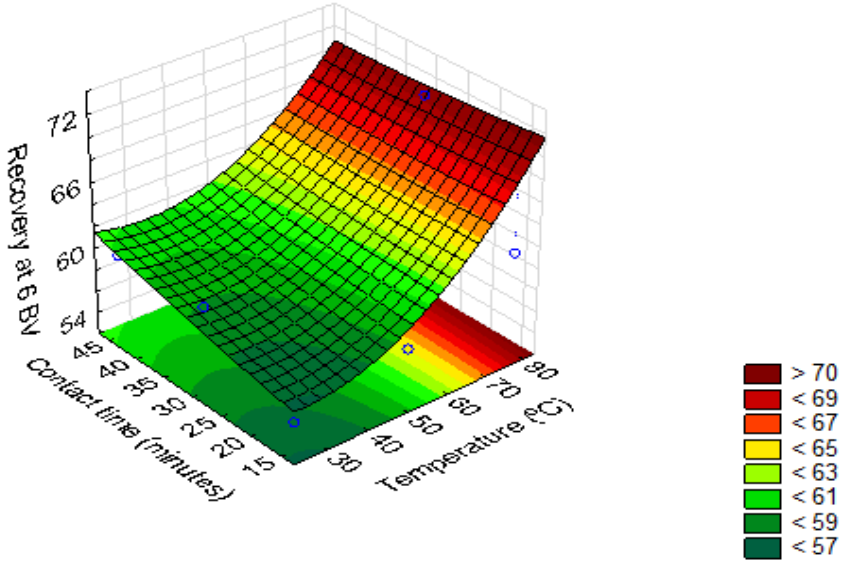


Figure 4.9: Surface response plot of interaction of effect of contact time and temperature at 0 rev/min.

4.5.2 Effect of contact time

The effect of contact time during pre-treatment was investigated at 15, 30 and 45 min. Figures 4.10–4.12 show the plot of the effect of contact time at 25^{o}C, 53^{o}C and 80^{o}C, respectively.Figures 4.13–4.15 present the trends of contact time during the interaction of pre-treatment temperature with agitation speed on Au recovery. At a temperature of 25^{o}C, an increase in recovery of about 4% is seen from 15 to 45 min (Figure 4.10). At temperatures of 53^{o}C and 80^{o}C, increase in the pre-treatment time is statistically insignificant on the subsequent elution recovery (Figures 4.11 and 4.12), indicating that pre-treating for only 15 min will result in similar elution recoveries for other contact times. The insignificant effect of contact time on Au elution recovery is further shown in Figures 4.13–4.15 where there is no significant change in the trends and shapes of the surface response plot. Davidson and Baily (1991) reported the interaction of contact time with pre-treatment temperature. It was stated a long pre-treatment time will be required at lower pre-treatment temperature (<110^{o}C). However, insignificant effect of this can only be seen at 25^{o}C which is an attribute of a chemical reaction controlled process. According to Bruce and Patricia (2007), virtually all rates of chemical reaction increases with an increase in temperature and vice-versa. It is therefore, suggested that increase in temperature minimises the effect of contact time on the overall recovery. This is clearly seen in Figures 4.10–4.12 where recovery line tilts with increase in temperature until an almost horizontal position is reached.

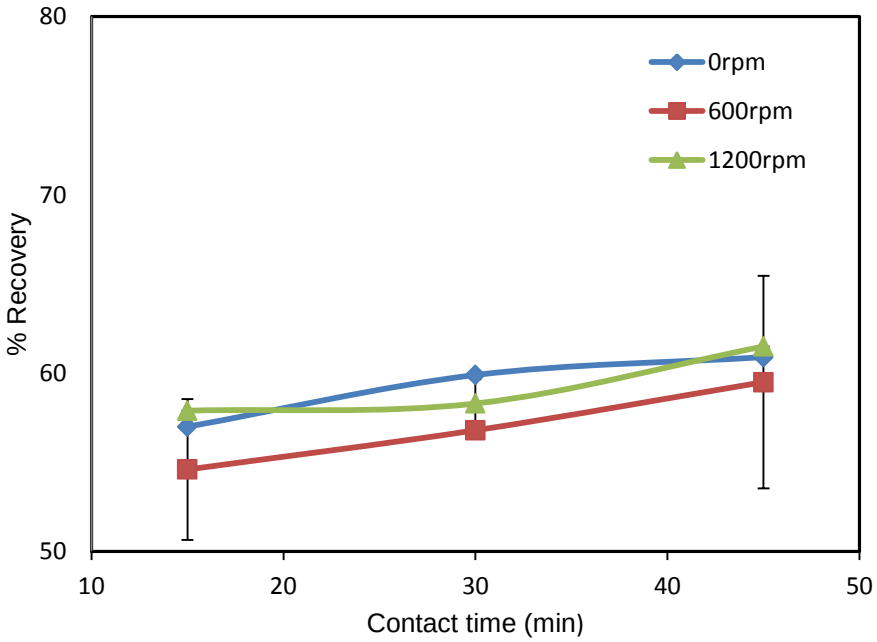


Figure 4.10: The effect of pre-treatment time on the elution recovery of Au for different agitation speeds. (Pre-treatment with 1% NaOH and 3% at 25°C, elution at 90°C).

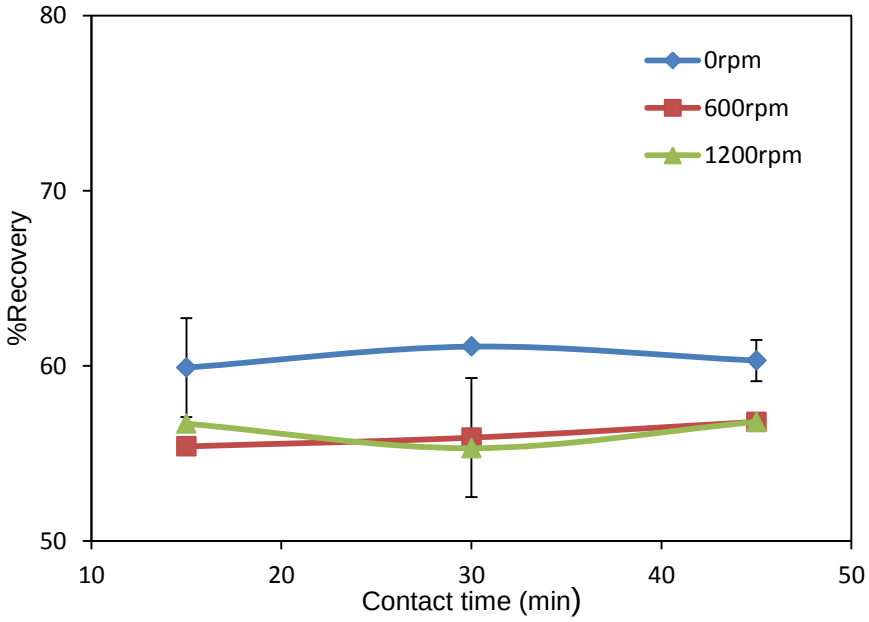


Figure 4.11: The effect of pre-treatment time on the elution recovery of Au for different agitation speeds. (Pre-treatment with 1% NaOH and 3% at 53°C, elution at 90°C).

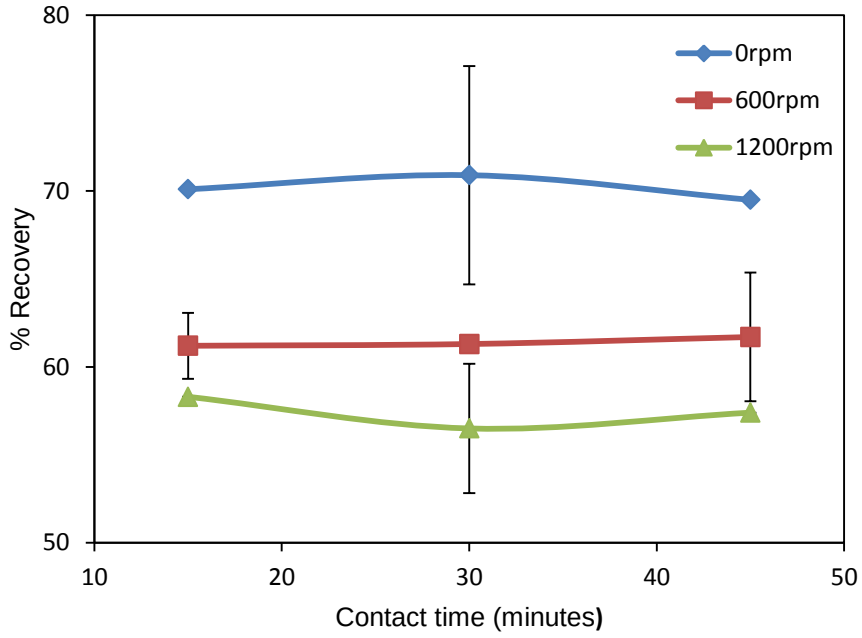


Figure 4.12: The effect of pre-treatment time on the elution recovery of Au for different agitation speeds. (Pre-treatment with 1% NaOH and 3% at 80°C, elution at 90°C).

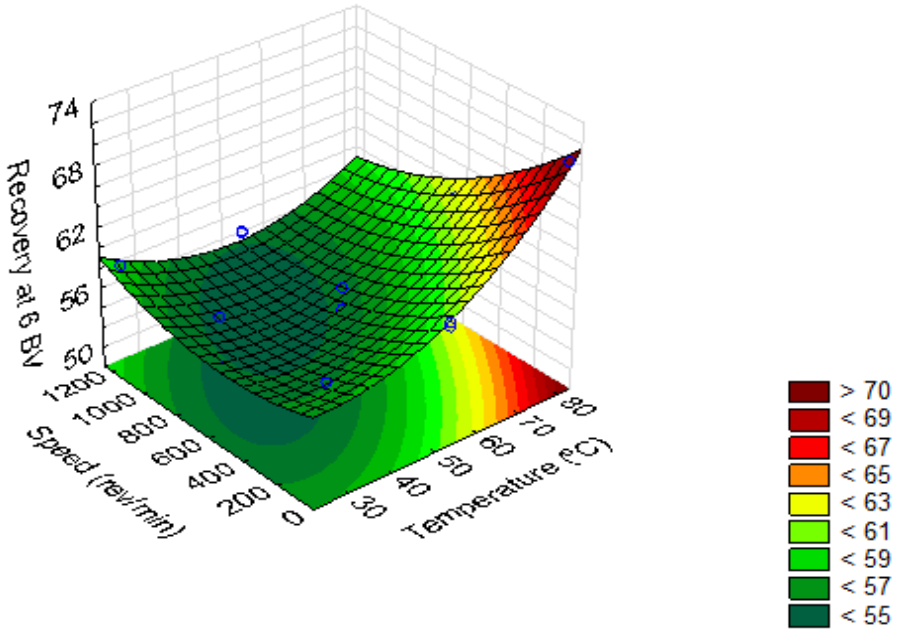


Figure 4.13: Surface response plot of interaction of effect of agitation speed and temperature at 15 min

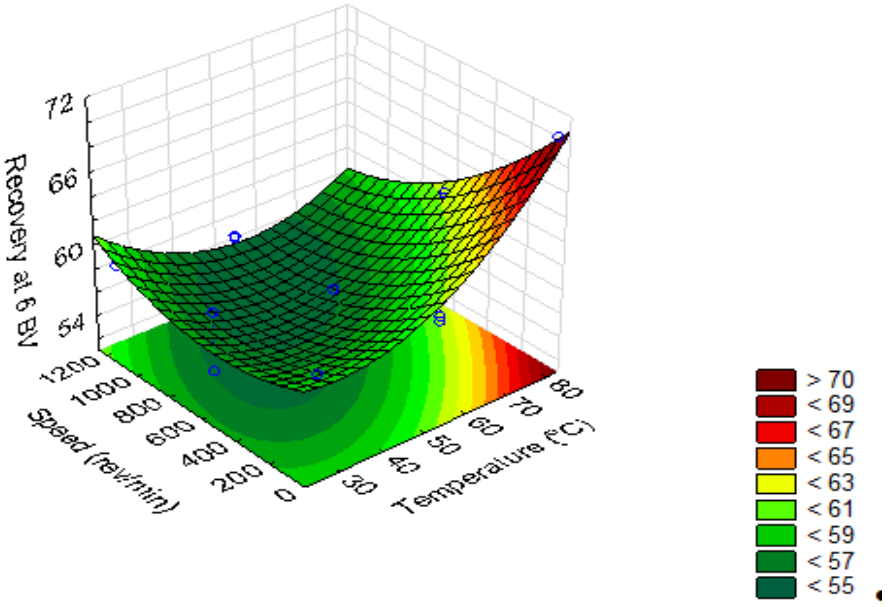


Figure 4.14: Surface response plot of interaction of effect of agitation speed and temperature at 30 min

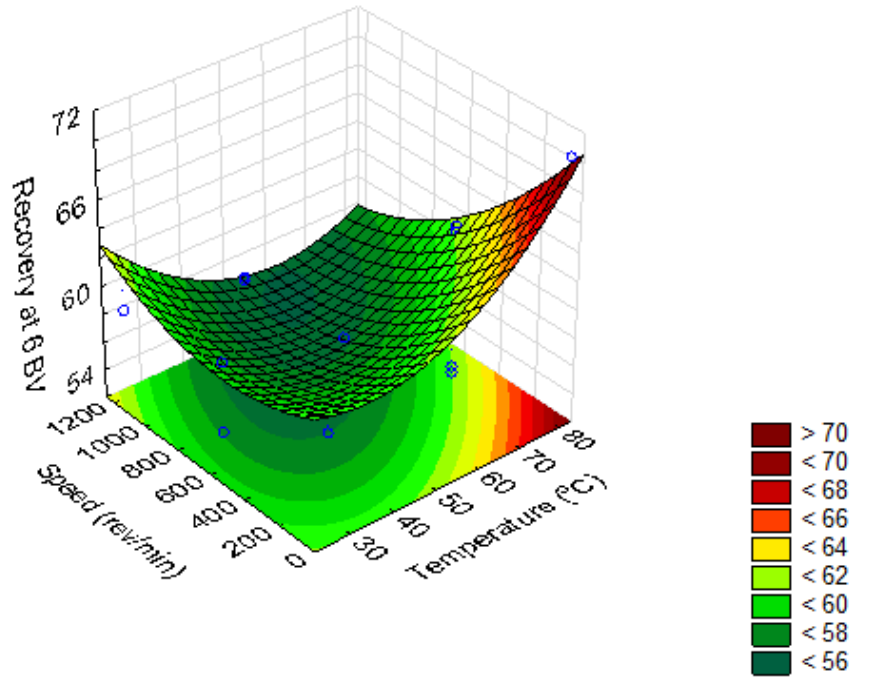


Figure 4.15: Surface response plot of interaction of effect of agitation speed and temperature at 45 min.

4.5.3 Effect of agitation speed

The effects of agitation speed at 0, 600 and 1200 rev/min on Au recovery at different temperatures are shown in Figures 4.16 –4.18. Increasing the agitation speed from 0 to 1200 rev/min at 25^{o}C of pre-treatment temperature did not result in any significant change in Au elution recovery as seen in Figure 4.16. At 53^{o}C, the effect of agitation speed becomes more visible towards a negative side with a decrease in Au elution recovery (Figure 4.17). This is seen with about 6% decrease in elution recovery from 0 to 1200 rev/min. This effect becomes more severe at a higher temperature (80^{o}C) with approximately 10% decrease from 0 to 600 rev/min and additional 7% decrease in Au elution recovery from 600 to 1200 rev/min as shown in Figure 4.18. Likewise the opposing effect of increasing agitation speed on Au elution recovery is also seen with lowering the surface plot especially around the region of high temperature as shown in Figures 4.19–4.21

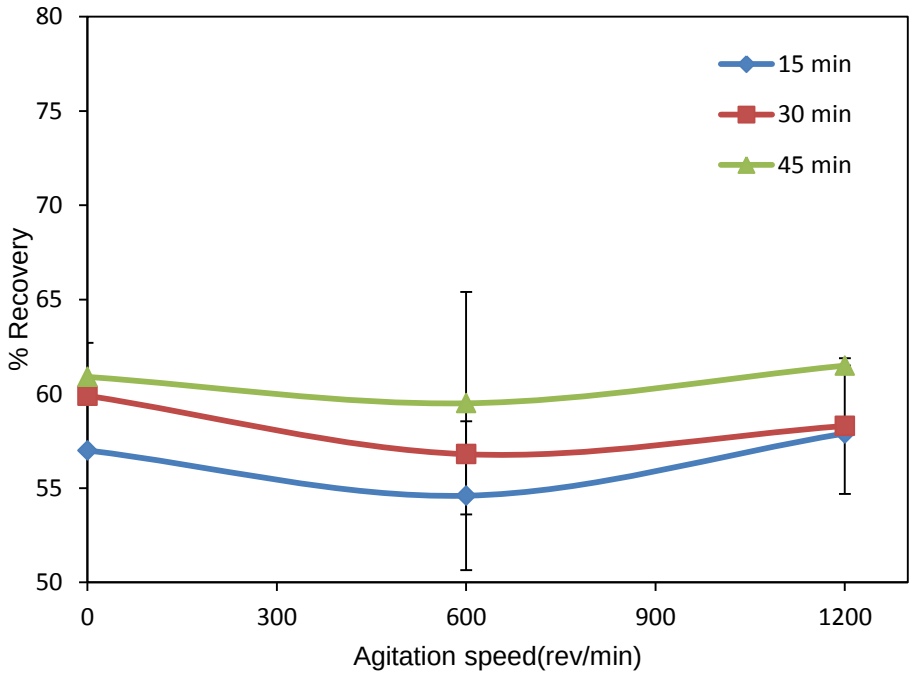


Figure 4.16: The effect of pre-treatment agitation on the elution recovery of Au. (Pre-treatment with 1% NaOH and 3% NaCN at 25°C, elution at 90°C)

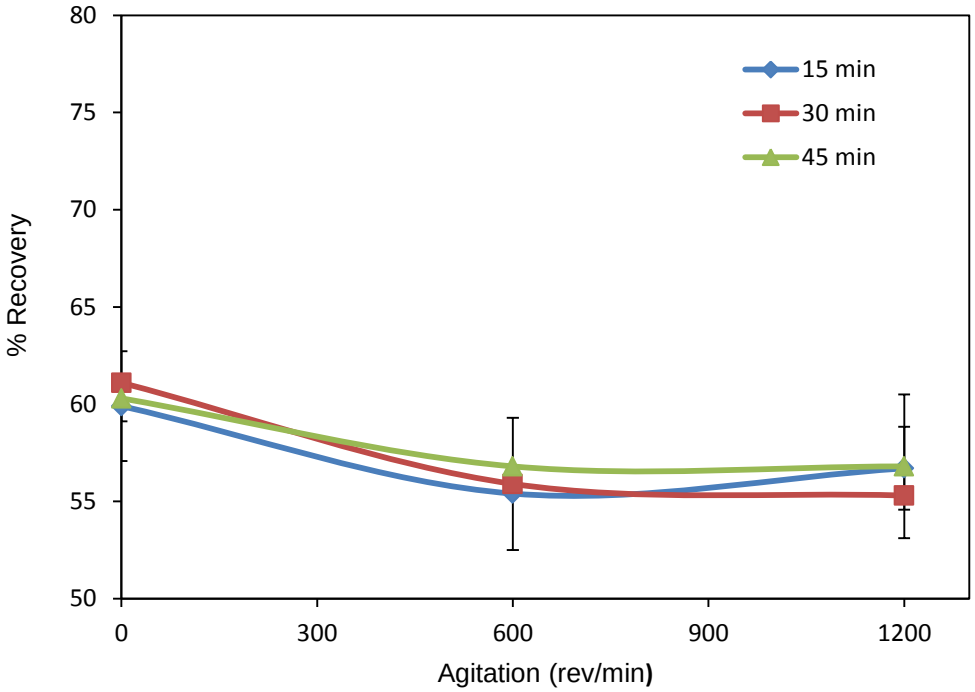


Figure 4.17: The effect of pre-treatment agitation on the elution recovery of Au. (Pre-treatment with 1% NaOH and 3% NaCN at 53°C, elution at 90°C)

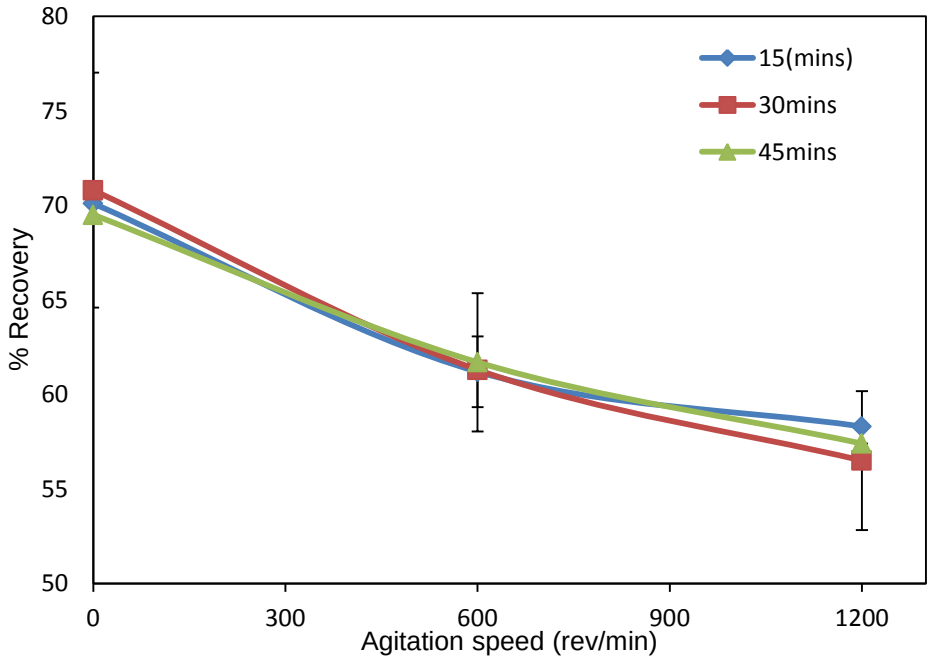


Figure 4.18: The effect of pre-treatment agitation on the elution recovery of Au. (Pre-treatment with 1% NaOH and 3% NaCN at 80°C, elution at 90°C)

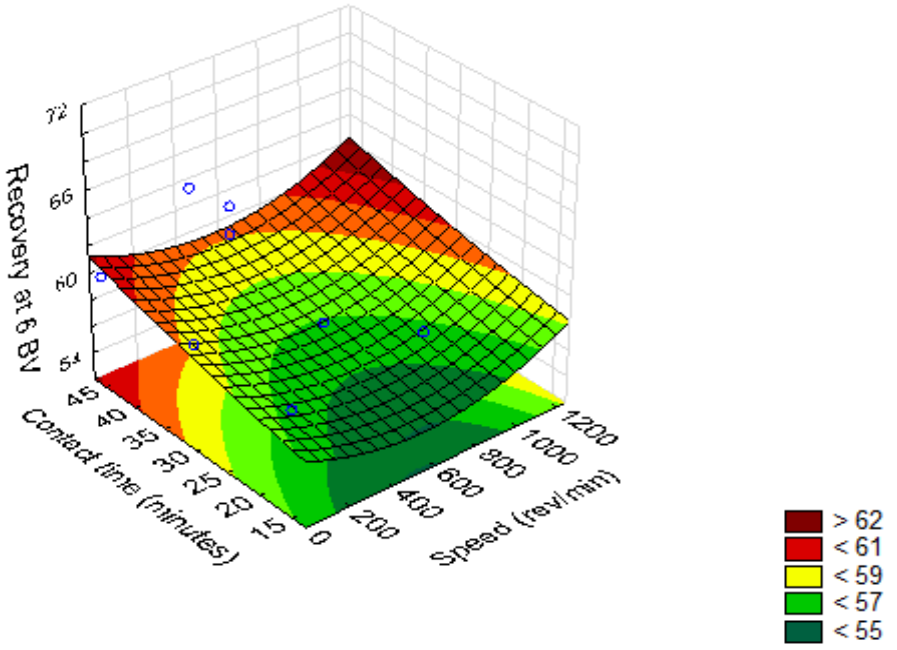


Figure 4.19: Surface response plot of interaction of effect of agitation speed and contact time at 25°C

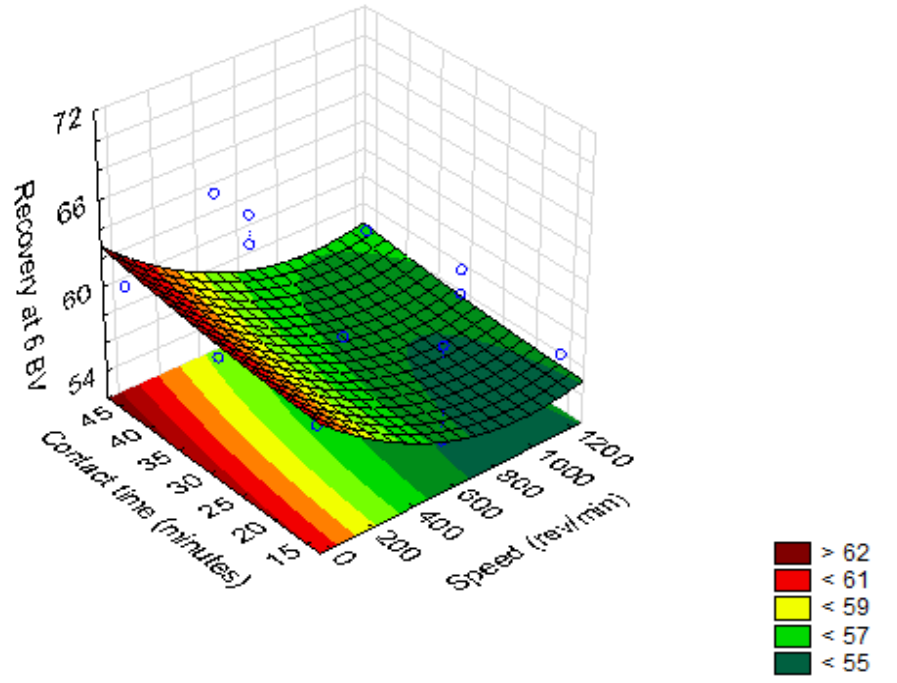


Figure 4.20: Surface response plot of interaction of effect of agitation speed and contact time at 53°C

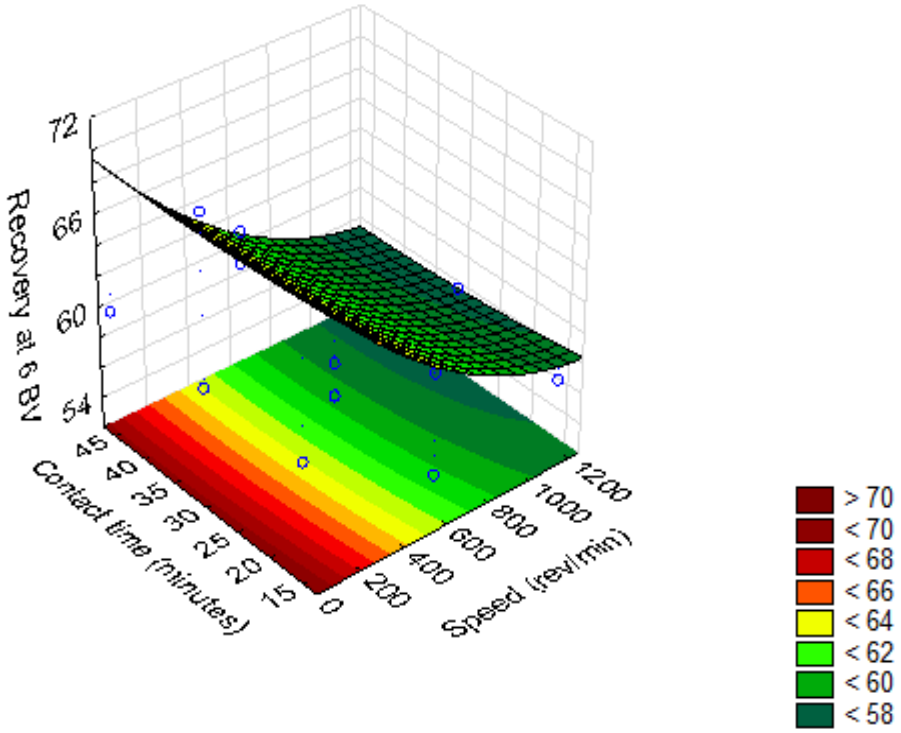


Figure 4.21: Surface response plot of interaction of effect of agitation speed and contact time at 80°C.

Van Deventer and Van der Merwe (1994) reported an improved Au elution recovery at high pre-treatment temperature (100°C). Furthermore Van Deventer and Van der Merwe (1995) reported a higher decomposition of CN^- at higher agitation speed. It is expected that these two factors (temperature and agitation) will contribute to Au elution recovery significantly, based on the mechanism that decomposition of CN^- causes a passivating product to be formed on the carbon surface (Section 2.10). However, the opposite effect seems to be the case. This opposing effect was suggested to be due to two possible reasons that were further investigated:

1) It may be that less CN^- is available for reactions with the carbon surface groups which ultimately results in lower Au elution recoveries.

2) It could possibly be the breakage of carbon granules in fine particles by the impeller which resulted to increase in surface area and a higher loss of Au through the carbon fines. The indication of this effect after separating the fine particles from the

granules are shown in Figures 4.22 and 4.23 at the agitation speeds of 600 and 1200 rev/min respectively.

Figure 4.22: The effect of agitation speed on carbon loaded with Au. Dark portions indicate the amount of carbon fines obtained from carbon granules at the agitation speed of 600rev/min (Pre-treatment conditions: 600 rev/min, 80^{o}C and 30 min)

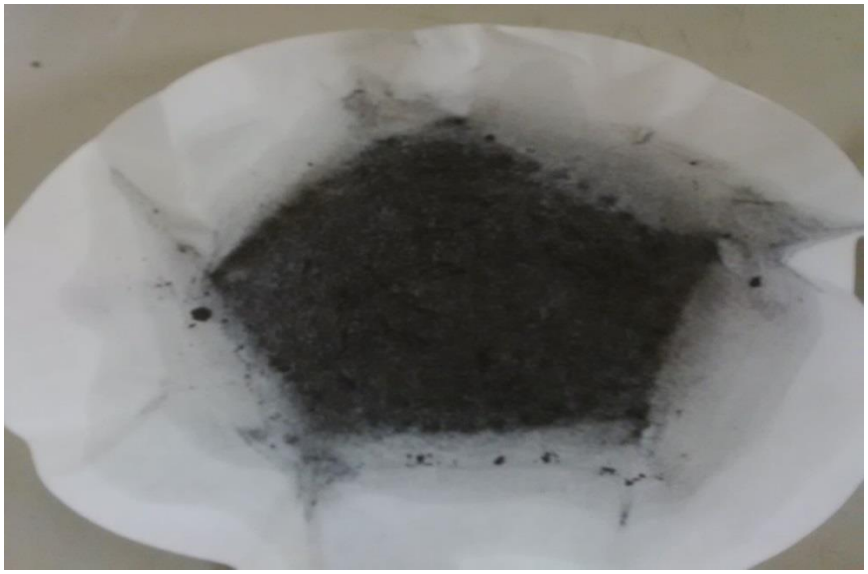


Figure 4.23: The effect of agitation speed on carbon loaded with Au. Dark portions indicate the amount of carbon fines obtained from carbon granules at the agitation speed of 1200rev/min (Pre-treatment conditions: 1200 rev/min, 80^{o}C and 30 min)

As shown in these two Figures, more carbon fines are obtained at 1200 rev/min than at 600 rev/min. The weights of these carbon fines and the Au loss that are possibly associated with the carbon fines at different temperatures and agitation speed are shown in Table 4.4. This is based on the assumption that the loading on each 12 g of activated carbon pre-treated is uniformly loaded with of 0.38 mg/g. An upgrade ratio of about 8 was estimated at 6BV. Upgrade ratio is ratio of the mass of Au in solution to the mass of Au on activated carbon (Rogans and McArthur, 2002). The mass of Au estimated with this upgrade ratio and the estimated gold loss after elution are shown in Table 4.4.

Table 4.4: Effect of agitation speed at different temperatures on carbon fines

Temperature ^{o}C	Agitation speed (rev/min)	carbon fines (g)	Au (mg) on AC	Au (mg) in solution	Estimated loss during elution (%)
25	600	0.05	0.02	0.16	0.5
25	1200	0.16	0.06	0.48	1.4
80	600	0.03	0.01	0.08	0.2
80	1200	0.12	0.05	0.4	1.2

It is seen from Table 4.4 that the estimated percentage loss with carbon fines after elution is insignificant when compared to the loss that was obtained during high agitation speed as earlier discussed in section 4.5.3. This implies that a separate mechanism is responsible for Au loss during agitation which is not well understood at the moment.

A similar indication of carbon fines was also obtained at 600 and 1200 rev/min at 25^{o}C. However, no significant change in the Au elution recovery was seen with increase in agitation speed (Figure 4.16). The exact reason for this behaviour is not fully known, but it is suggested that at this operating temperature (25^{o}C), less CN^{-} will be available for interaction with the carbon surface than at 80^{o}C (Figure 4.4 andFigure 4.6) while agitation still play its “counter intuitive” role to increase surface area.

Further proof to the opposing effect of agitation was further investigated by measuring the concentration of CN^- during different pre-treatment conditions at 15 min interval. These results are presented in Table 4.5. From these results, the evaporation was eliminated and it can be seen that there is no significant change in concentration of CN^-. The results obtained in Table 4.5 were further used to calculate the solid-liquid mass transfer coefficient (k_{SL}) of CN^- using the pre-treatment medium at different agitation speeds using Equation 2.26. 60 min contact time was used to allow sufficient data points.

$$\left[\frac{d(\frac{C}{C_o})}{dt}\right] = - k_{SL} a_s \qquad 2.26$$

Table 4.5: Results of CN^- (M) measured at different pre-treatment conditions at 15 min time intervals

Conditions		Concentration (M) of CN^- at 15 min time interval				
Temperature (^oC)	**Speed (rev/min)**	**t_0**	**t_{15}**	**t_{30}**	**t_{45}**	**t_{60}**
25	0	0.52	0.52	0.56	0.56	0.56
25	600	0.56	0.56	0.56	0.56	0.56
25	1200	0.56	0.56	0.56	0.52	0.56
53	0	0.55	0.55	0.56	0.56	0.56
53	600	0.52	0.56	0.52	0.55	0.56
53	1200	0.56	0.56	0.56	0.55	0.56
80	0	0.48	0.56	0.56	0.55	0.56
80	600	0.56	0.56	0.56	0.56	0.56
80	1200	0.60	0.56	0.52	0.56	0.56

The plot of the effects of increasing agitation speed on k_{SL} is shown in Figure 4.24. It is seen that there is no significant change in k_{SL} from 0 to 1200 rev/min at different temperatures. This result suggests that pre-treatment in the presence or absence of agitation is less likely to be controlled by diffusion process than reaction mechanism.

This rules out the suggestion on the less availability of CN^- for reaction with surface group. It is therefore, concluded that agitating the Au loaded activated carbon in pre-treatment solution of NaOH-NaCN does not improve Au elution recovery.

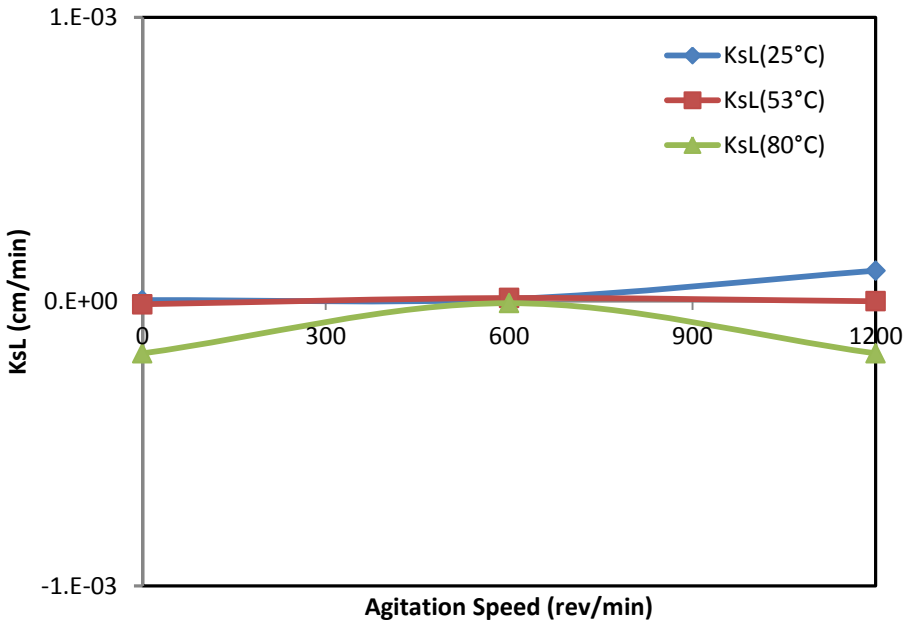


Figure 4.24: Effect of increasing agitation speed from 0 to 1200rev/min on k_{SL} at 25°C, 53°C and 80°C. (Solution condition: 1% NaOH and 3% NaCN)

4.6 Proposed mechanism

4.6.1 Evaluating the previous mechanisms

Various elution mechanisms proposed by different researchers have been reviewed (Section 2.10). A suitable explanation to one of the proposed mechanisms can be suggested based on the results found from the role of NaOH-NaCN and the effect of pre-treatment parameters on Au elution that were investigated .The explanation for this linkage is discussed as follows:

Going by elimination of the previous mechanisms and correlating it with present findings, mechanism of CN^- reacting with AuCN to form a soluble species as given by

Equation 2.14 can be ignored due to no acid washing. As such, the gold is assumed to remain chemically adsorbed as an ion pair ($M^{n+}[Au(CN)_2^-]$).

$$AuCN + CN^- \rightarrow Au(CN)_2^- \qquad 2.14$$

As discussed in Section 4.2.1, an insignificant amount of Au measured just after pre-treatment resulted in the rejection of proposed competitive adsorption of CN^- with adsorbed Au to favour elution. This agrees with previous studies, where no Au was reported to be present after pre-treatment (Van Deventer and Van der Merwe, 1994).

According to decomposition mechanism proposed by Van Deventer and Van der Merwe (1994; 1992), it was suggested that adsorbed CN^- decomposes to form a passivating product to make the surface of carbon less receptive for Au. This also seems unlikely to be the case. It has been reported that an increase in pre-treatment temperature and agitation results in increased decomposition of cyanide (Van Deventer and Van der Merwe, 1995; Van Deventer et al., 1992). This is expected to increase the Au elution recovery which was not the case as shown in Section 4.5.3.

However, the reaction mechanism of CN^- with surface functional groups suggested by Adams and Fleming (1989) seems to be a possible mechanism given by Equations 2.18 and 2.19. Discussions on the role of CN^- in Section 4.3 reasonably support the suggestion that CN^- reacts with the carbon surface to improve Au elution recovery as shown in Figure 4.3.

4.6.2 Possible site(s) of reaction mechansim

There have been some controversies on the adsorption mechanisms of Au, which has led to different proposed theories to describe the mechanism (Section 2.4). Among these theories, the ion-pair mechanism seems to have received significant scientific evidence to be the most plausible mechanism. Despite this, the exact functional group or planes on the activated carbon where this mechanism occurs has not been firmly identified. From the main functional groups identified (Nitrogen and oxygen functional groups), Jia et al. (1998) showed that nitrogen functional groups are of insignificant importance in Au adsorption while oxygen functional groups participate in Au adsorption

(Adams, 1989). From the list of oxygen functional group in Section 2.2.1, Adams (1991) and Adams and Fleming (1989) suggested the possibility of CN^- reacting with ketones and aldehyde functional groups given by Equations 2.18 and 2.19, respectively. CN^- has been identified to be a strong nucleophile (Solomon, 1992). Aldehydes and ketone readily go through nucleophilic attack due to the presence of the highly polar carbonyl group (carbon-oxygen bond: $C^{\delta+}=O^{\delta-}$) (Brown, 2000-2014). According to McMurry (1998), carbonyl groups which are one of important groups in organic chemistry are broadly classified into aldehydes, ketones group, carboxylic acid and their derivative group. It is not unlikely that carboxylic acid groups also undergo reaction with CN^- or OH^- or both. However, the degree and hierarchy of these nucleophilic reactions was not substantiated. These reaction mechanisms with regards to the carbonyl groups are described in the next section.

4.6.3 Reaction mechanisms

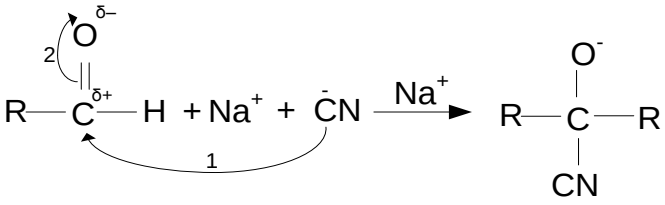
In order to suggest a suitable elution mechanism regarding reaction with or modification of the functional group by CN^-, it is important to understand the properties and behaviour of the carbonyl functional group and the composition of the solvent. Going by this theory and adopting the concept of nucleophilic reaction earlier described in Section 2.11, the mechanism (Equations 2.18 and 2.19) suggested by Adams (1991) are satisfied. In addition, by the adoption of the principle of the steps involved in nucleophilic reaction, the suggested reaction steps for this mechanism as shown in Equations 4.4–4.9 for both NaCN and NaOH are:

1) the nucleophiles (CN^- and OH^-) attacks the substrate at $C^{\delta+}= O^{\delta-}$
2) the substrate gives out one of the double bonds

Additional reactions with carboxylic acid that are being suggested as the elution mechanisms are further elaborated and shown as follows:

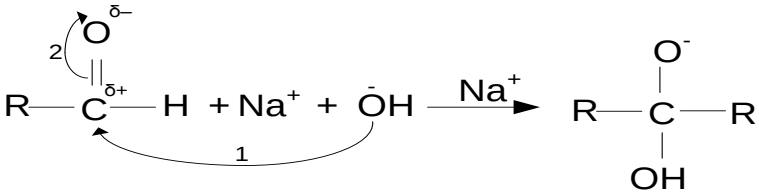
For aldehydes

With NaCN



4.4

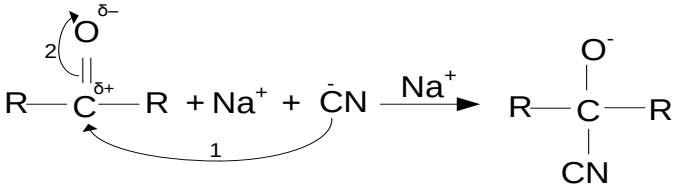
With NaOH



4.5

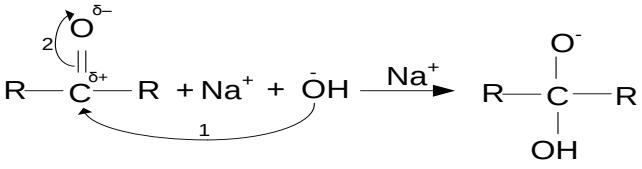
For Ketones

With NaCN



4.6

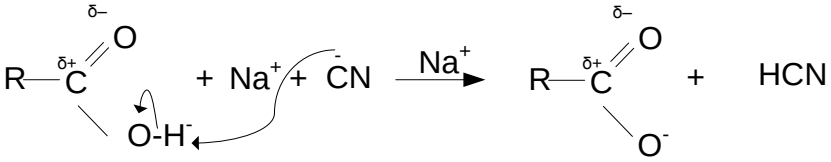
With NaOH



4.7

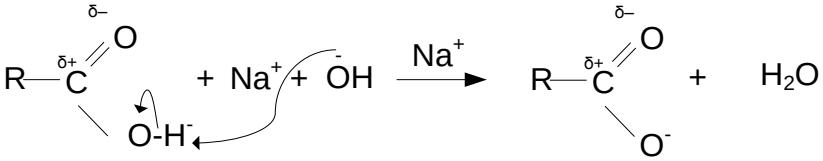
For Carboxylic acid

With NaCN



4.8

With NaOH



4.9

Na^+ only acts as a spectator and does not participate in a specific reaction with the surface group (functional group modification) but exist as $Na^+\{Au(CN)_2^-\}$. However, in the case of carboxylic acid, it undergoes neutralisation reaction to form HCN gas and water upon reaction with CN^- and OH^- respectively. According to Francis (2000), CN^- and OH^- are both good and strong nucleophiles, however, CN^- and OH^- are weak and strong bases respectively. Equation 4.8 could be the possible reason for the insignificant (fluctuation between 0.1 and 0.6 mg/L) amount HCN gas that was observed as earlier discussed in Section 4.3 but was suppressed by the pH of the medium.

If this concept of nucleophilic reaction with CN^- and OH^- are the elution mechanism, a question of why CN^- results in better Au elution recovery than OH^- as shown by previous authors (Van Deventer and Van der Merwe, 1994; Adams and Nicol, 1986; Davidson and Duncanson, 1977) also needs to be answered based on this mechanism.

On a basis of molecular orbital theory, a molecule is formed by the bonding of the frontal orbital to form a new bond which is made up of elections of individual elements (Locke, 1996–1997) A simple case with hydrogen molecule is shown in Figure 4.25. The bonding orbital where the molecule is formed is the highest occupied molecular

orbital (HOMO) while the orbital where no bond is formed is the lowest unoccupied molecular orbital (LUMO). The formation of the new bond results in reduction of the energy level as shown in Figure 4.25.

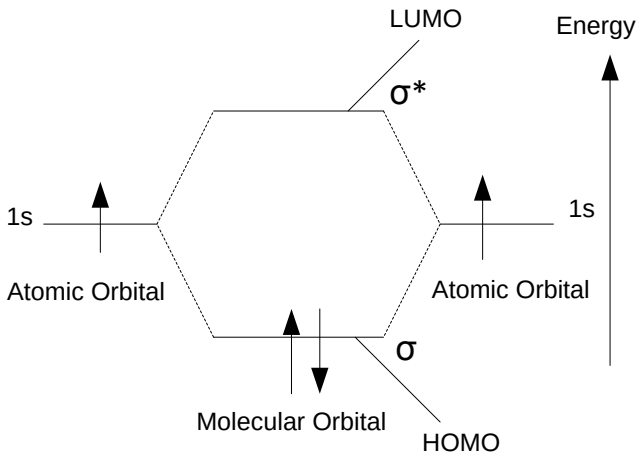


Figure 4.25: Molecular orbital diagram of hydrogen molecule. Redrawn from Locke (1996–1997)

For ions or molecules formed from different atoms such as carbon monoxide, cyanide, hydroxide, the energy level of the new bond varies depending on the number or electrons in the outermost orbital that participate in the bonding (Locke, 1996–1997). In case of OH^- and CN^-, the energy level of OH^- is lower than CN^-. CN^- and OH^- are typical examples of species with HOMO, while the carbonyl groups which is an electrophile represents LUMO species. Furthermore, according to Koopmans's theory (NIST, 2013a; Brown, 2000-2004), the ionisation energy of a molecule or atom can be regarded as the HOMO energy. The ionisation energy of OH^- and CN^- is given as 13.017eV and ≈13.6 eV respectively (NIST, 2013b) This indicate that CN^- and OH^- have different HOMO energy levels against a fixed LUMO energy level of the carbonyl functional group. The difference in the ionisation energy (≈0.6) of these ions seems insignificant compared to the significant Au elution recovery obtained in the presence of CN^- than OH^-. The level of significance of this difference (≈0.6) that could have considerably supported this suggestion was not reported in the publication (NIST, 2013b). However, it is suggested that higher ionisation energy of CN^- compared to OH^- possibly accounts for the improved Au elution recovery. This illustration shown in

Figure 4.26 suggests CN^- will react faster than OH^- due to this high HOMO energy level in order to attain stability. Furthermore, Adams (1989) observed that when CN^- is added to a NaOH solution, the uptake of Na ions by carbon increases.

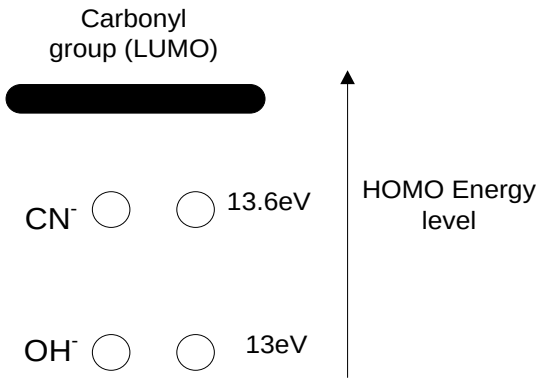


Figure 4.26: Illustration of LUMO-HOMO interaction of carbonyl vs CN^- and OH^-

4.7 Industrial application

Further experimentation were conducted on Au loaded carbon supplied from Goldplat Recovery (PTY) Limited in South Africa. This Au loaded activated carbon has gone through an elution and regeneration step, but significant amounts of Au still remained loaded on it.

Regeneration after elution aims to burn off organics and restore the activity of activated carbon carried out in a steam atmosphere at a temperature below 750^oC (Grimsley, 1991). Effect of such a high temperature on adsorbed Au suggests decomposition of cyanide associated with Au. As a result of this, the Au present on the surface of the carbon surface could be suggested to be present as solid gold $[Au]_s$. According to Vorobev-desyatovskii et al. (2010), at typical regeneration temperatures, thermal decomposition to solid Au occurs on the carbon surface according to Equation 4.10.

$$2\,Na[Au(CN)_2] \rightarrow 2Au_s + (CN)_2 + 2NaCN \qquad 4.10$$

This was confirmed by the SEM analysis of the loaded carbon as shown in Figure 4.27 with the detection spectra shown in Figure 4.28. With this confirmed state of adsorbed Au present on carbon surface, the reaction of CN^- together with the mechanism

proposed by Adams (1991) and the ones suggested in this present study, becomes more important for effective elution to take place. This is being suggested to likely take place according to Equation 2.8.

$$AuCN + CN^- \rightarrow Au(CN)_2^- \qquad 2.8$$

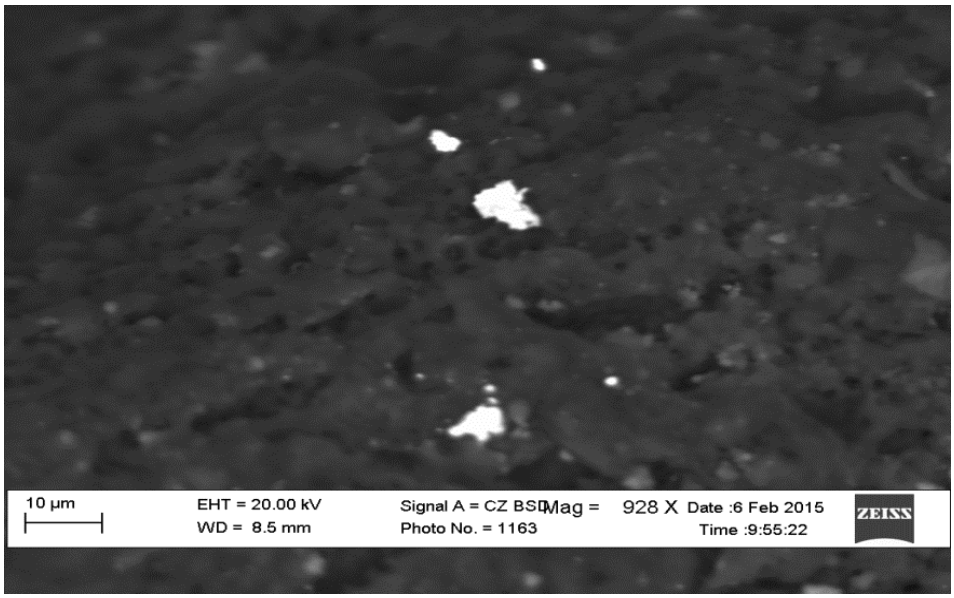


Figure 4.27: SEM analysis of Goldplat loaded carbon after regeneration in kiln.

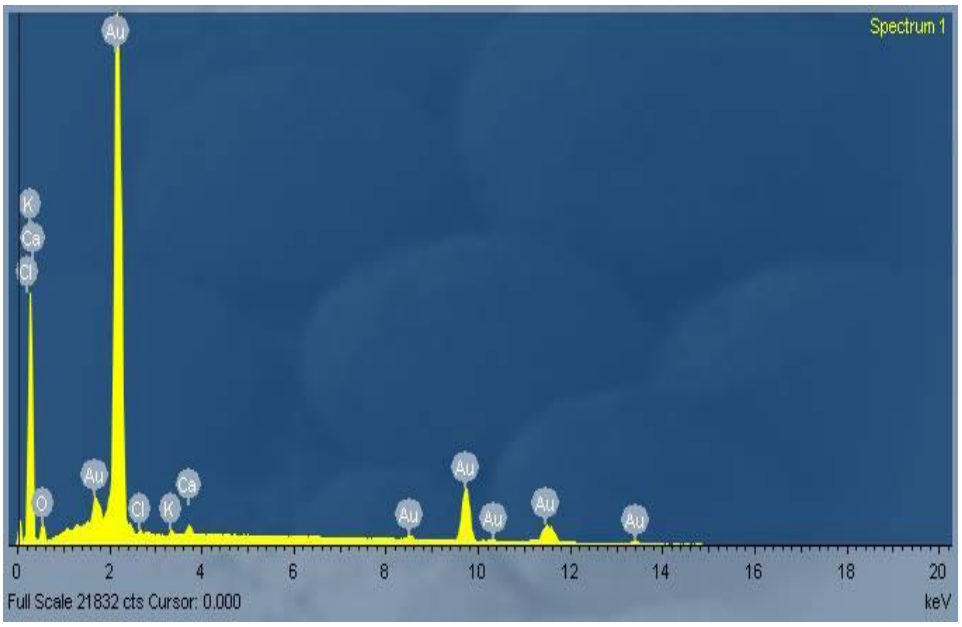


Figure 4.28: Visual Spectra of Au detection on carbon surface

It would also be expected that cyanidation of Au will take place as with the case of leaching of solid Au as given by Equation 2.1

$$4Au + 8CN^- + O_2 + 2H_2O \rightleftharpoons 4Au(CN)_2^- + 4OH^- \quad 2.1$$

The result of changes in dissolved (natural) oxygen of the pre-treatment solution measured at different time interval during the pre-treatment with the aid of cyber-scan 300 dissolved oxygen meter is shown in Table 4.6. This suggests that Equation 2.1 is occurring.

Table 4.6. Dissolved (natural) oxygen (mg/L) measured at different time intervals during pre-treatment with loaded activated carbon sourced from Goldplat Recovery (PTY) at different temperature without stirring. (3%NaCN, 1% NaOH)

Temperature (^oC)	Time (min)				
	0	**5**	**10**	**20**	**30**
25	5	3.8	2.9	2.54	2.1
80	3.2	2.3	1.11	1.1	1.02

4.7.1 Effect of oxygen supply during pre-treatment

A number of authors have reported the the effect of oxygen on the improved adsorption of metal cyanide complex. According to Petersen and Van Deventer (1991), equilibrium loading of metal cyanide complex increased with an increase in oxygen supply however, the kinetics of the adsorption was unchanged. When the ionic strength of the solution is low, Adams (1990d) Woollacott and Nino de Guzman (1993) reported a more improved effect of oxygen than a solution with high ionic strength. In addition, Woollacott and Nino de Guzman (1993) reported an improved effect of oxygen at a CN^- concentration above 100 mg/L

Further experimentation on the effect of oxygen supply during pre-treatment on regenerated Goldplat activated carbon was carried out at no-oxygen supply (0 mL/min), mild oxygen supply (10 mL/min) and an high oxygen supply of 100 mL/min at both 25^{o}C

and 80^{o}C. The effect of this oxygen supply was observed on Au elution recovery as shown in Table 4.7.

Table 4.7: Effect of oxygen supply during pre-treatment on elution at 6 BV. Conditions 3% NaCN, 1% NaOH, no agitation, 30 min

Temperature (^{o}C)	Oxygen supply (mL/min)	% Recovery at 6bv
25	0	63.80
25	10	60.13
25	100	61.37
80	0	78.80
80	10	60.61
80	100	63.91

From the result shown in Table 4.7 it can be seen that oxygen supply into the pre-treatment system does not improve the Au elution recovery at both 25^{o}C and 80^{o}C. This is seen when comparing recovery at no-oxygen (0 mL/min) (≈64 and 80% at 25 and 80^{o}C respectively) with about 60% and 62% at 10 mL/min and 100 mL/min oxygen supply respectively. Reduced recovery with oxygen supply obtained in Table 4.7 suggest that it supports adsorption of some of metal-cyanide complex on carbon surface as earlier discussed.

4.7.2 Effect of pre-treatment parameters on goldplat regenerated carbon

Table 4.8 shows the result of recovery of Au at 20 bed volumes of elution at the selected conditions. The result agrees with findings in Section 4.5.3 regarding decrease in recovery with increasing agitation speed at high temperature as previously shown in Figure 4.18. However, contrary to the previous findings in Section 4.5.2, time also now becomes a factor and when the pre-treatment time is increased from 15 to 45 min, a significant improvement in recovery was obtained especially at the lower cyanide concentration of 2% with about 15% increase in Au recovery both in the presence and absence of agitation.

Table 4.8: Elution recovery at 20 bed volumes, 80^{o}C, different concentration of cyanide, agitation speed and contact time.

	Conditions at 80^{o}C			
NaCN conc.	**0 rev/min, 15 mins**	**0 rev/min, 45 mins**	**1200 rev/min, 15 mins**	**1200 rev/min, 45 mins**
2%	83	97.6	84.9	97.1
4%	92.5	93.1	84.1	95.9
6%	97.8	100	95.9	85.2

The results shown in Table 4.8 becomes increasingly important for industrial plants where inefficient elution occurs on a regular basis with some plants struggling to elute their carbon to less than 100 g/t (Fleming et al., 2011). The Au not eluted from the activated carbon will decompose to solid Au in the regeneration kiln and a longer and more intense cyanidation pre-treatment step will be required to prevent further build-up of the Au on the carbon. This will be specifically applicable to industrial plants where cyanide free elution is practised. In addition to the Au build-up on the carbon, the reduced carbon activity will also directly lead to lower adsorption and Au losses to the tailings dam. Fleming et al (2011) stresses this point and showed through modelling that by increasing the amount of Au on the eluted carbon that is recycled to the last adsorption tank from 0 to 50 g/t, soluble Au losses increased from 0.003 mg/L to 0.011 mg/L.

4.8 Chapter summary

The ICP result of barren $KAu(CN)_2$ solution after adsorption onto activated carbon from an initial concentration of 10.6 mg/L showed that more than 99% of Au was adsorbed. Elution results of the Au loaded activated carbon after pre-treatment in NaOH-NaCN solution at different pre-treatment conditions was found to show similar elution profiles. It was shown from the profiles that removal of Na favoured the elution of Au.

Furthermore, the effect of the pre-treatment parameters i.e., pre-treatment temperature, contact time and agitation speed were discussed. Pre-treatment temperature from 25^{o}C to 80^{o}C was found to increase Au elution recovery by approximately 12 % which is in

agreement with previous studies (Van Deventer and Van der Merwe,1994). Contact time from 15 to 45 min showed insignificant changes in Au elution recovery while an increase in agitation speed from 0 to 1200 rev/min decreased Au elution recovery by approximately 15% at 80^{o}C.

The most suitable elution mechanism was suggested from the proposed mechanisms of previous authors. The mechanism where the CN^- is involved in a specific chemical reaction at the carbon surface to increase the negative charge density and rendering the surface less receptive for adsorption (Adams and Fleming, 1989), is more plausible than the oxidation and hydrolysis of CN^- to form a decomposed product that improves elution.

In addition the application of the results found was extended to Goldplat activated carbon that has gone through regeneration, but with a significant amount of Au on it. Effect of oxygen supply during pre-treatment on regenerated carbon was found not to show any significant effect on Au elution recovery at both 10 mL/min and 100 mL/min. It was also shown that with loaded activated carbon that was thermally regenerated, CN^- is required to convert solid Au particle to soluble Au for effective elution which will require longer pre-treatment times and higher concentrations of CN^-.

The next chapter presents further discussion on the statistical analysis of the results and the analysis of possible errors associated with the experiments.

5 Statistical analysis of results

Analysing results statistically is one of the modern methods through which interpretations are easily made together with the performance of optimisation. This is however based on sound understanding of the process and the functions of the operating variables. Table 5.1 shows the analysis of variance (ANOVA) table after statistically analysing the three-level Box-Behnken experimental design chosen for experimental design.

Table 5.1: ANOVA table showing the effect of factors in terms of Au elution recovery at 6BV; R-square = 0.92413; Adjusted R-square = 0.78757; Derived from Statistical

Factors	Effect	P-Value
Mean/Intercept	59.68	0
(1)Temperature(^{o}C)(L)	4.49	0.02
Temperature(^{o}C)(Q)	-3.21	0.02
(2)Time (min)(L)	1.50	0.30
Time (min)(Q)	-0.21	0.83
(3)Speed (rev/min)(L)	-5.58	0.01
Speed (rev/min)(Q)	-2.33	0.06
1L by 2L	-2.27	0.27
1L by 3L	-6.32	0.02
2L by 3L	-0.13	0.95

where L = Linear effect; Q = Quadratic effect

Table 5.1 shows the effect estimates, the P-values of each factor and interaction at 95% confidence interval were ascertained through ANOVA. The P-values of temperature (0.02), agitation (0.01) for both linear and quadratic effects, and its interaction (1L by 3L= 0.02) shows that they are statistically significant (P-values <0.05) on the recovery at 6 bed volumes. The quadratic effect shows the curvilinear nature or the square of the effect of pre-treatment parameters on Au elution recovery within the extremes of the chosen experimental conditions in the plot. An illustration is shown in Figure 5.1

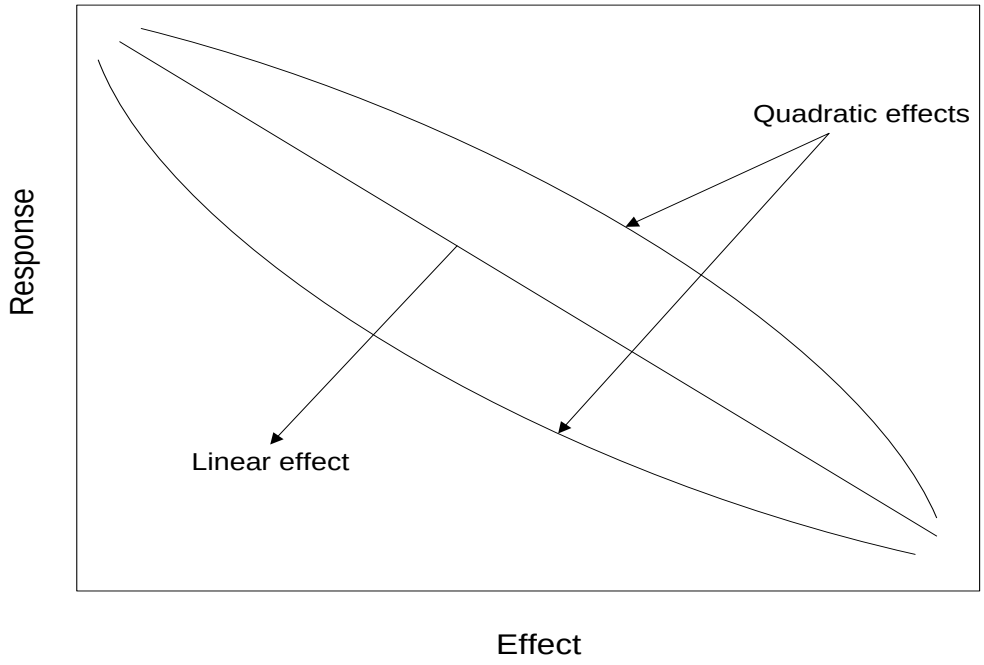


Figure 5.1: Illustration of quadratic effect and linear effect on a response

The positive effect of temperature on the recovery can be seen with the positive value of 4.49 in the linear effect, which shows that temperature plays a synergistic role during pre-treatment as earlier explained in Section 4.5.1 on Au recovery. Conversely, the opposing effect of agitation speed during pre-treatment on Au recovery with a value of -5.58 can be seen from Table 5.1. This agrees with the discussion in Section 4.5.3, where it was shown that Au elution recovery decreases with an increase in agitation speed. Interaction effect of agitation speed and temperature with a value of -6.32 suggests the dominant effect of agitation speed over temperature during pre-treatment on Au recovery. This resulted in decrease in Au elution recovery (Section 4.5.3). Likewise the effect of contact time with a low positive value of 1.5 compared to the effect temperature (4.6) also suggests that it has a beneficial effect on Au recovery. However, P-value of 0.3 suggests that it is not statistically significant on the process. This concurs with the discussion in Section 4.5.2, where it was shown that Au recovery increases with about 2% from 15 min to 30 min and further 5% increase at 45 min at both 0 and 600 rev/min agitation speed at 25^{o}C. At 80^{o}C, recovery stays fairly constant at all contact time (Figure 4.12).

5.1 Pareto chart

Pareto chart is often used to show the frequency of occurrence of a variable on a response at a certain confidence level and standardised reference point (Alessandro, 2014). The Pareto chart showing the recovery at 6 BV from the effect of temperature, contact time, agitation and their interaction at 95% confidence level is shown in Figure 5.2. The values that were used to plot the Pareto chart were statistically derived from the ANOVA analysis previously shown in Table 5.1 using Staistica 12.0 software.The relative magnitude of each parameter against standardised reference line indicates the confidence level (Montgomery, 2013). All effects to the right of the standardised effect (red-line) as shown in Figure 5.2 are statistically significant and should therefore, be included in the regression model. These effects are temperature, agitation and its interactions. Effects that are below the P-value are statistically insignificant and might not be included in the model.

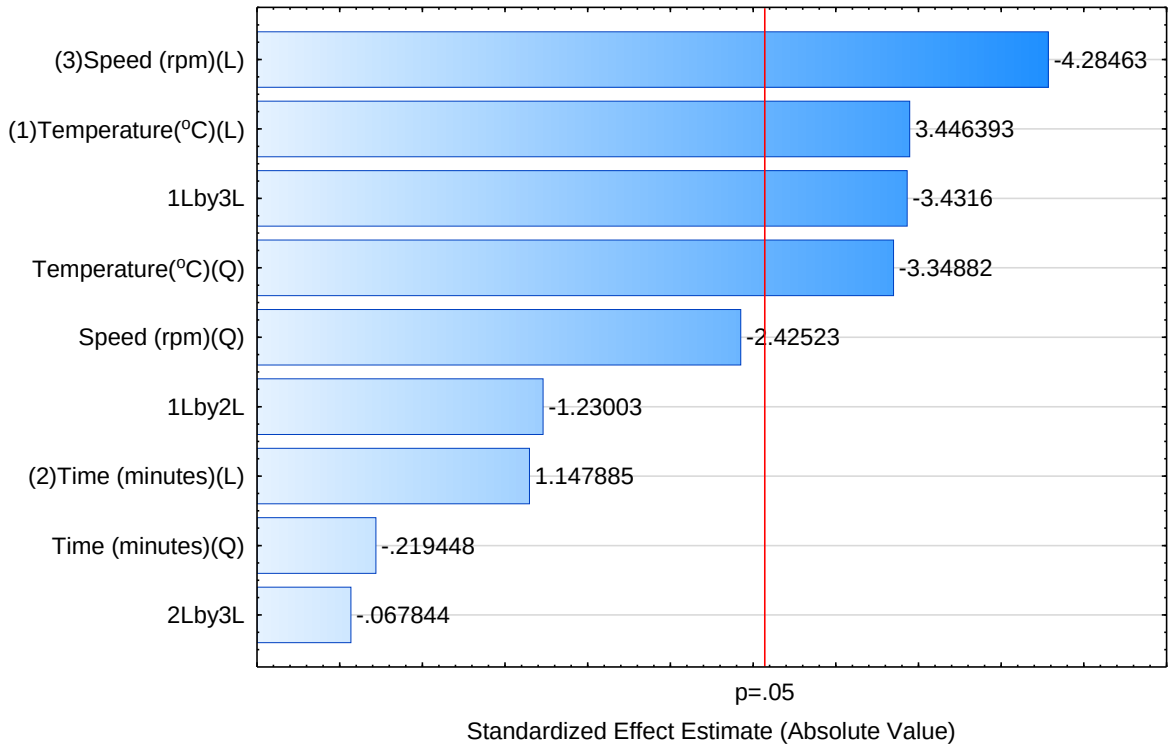


Figure 5.2:Pareto plot for standardised effect of pre-treatment temperature, speed contact time and its intrraction on Au elution recovery

5.2 Regression model

Statistical experimental designs are carried out to enhance the development of a predictive model that will assist in predicting other points of interest and optimisation if required. Second order interaction linear model was derived to predict Au elution recovery at 6 bed volumes as a function of temperature, agitation speed and contact time by fitting the experimental data shown in Table 4.1. The effect of statistically insignificant parameters were ignored to further simplify the model (Equation 5.1) and reduce noise.

The model given by Equation 5.1 below satisfies data points at 6 bed volumes. A similar approach can be used to formulate the model for a desired point estimate for other points of interest.

$$Y = 62.42 - 0.247x_1 + 0.004x_1^2 - 0.002x_3 + 0.00001x_3^2 - 0.0002x_1x_3 + \varepsilon \qquad 5.1$$

Where: Y = % Recovery

x_1 = Temperature (^oC)

x_3 = Agitation speed (rev/min)

ε = Experimental error

5.3 Model adequacy test

The adequacy of the regression model to predict observed value was assessed through the scatter plot of predicted vs observed response. This is shown in Figure 5.3. Other options that can also be used are predicted vs residual, observed vs residual, residual vs deleted residual and residual vs case numbers. According to Manual (2004), these terms are defined as follows:

- Residual = $\frac{\text{Observed-predicted}}{\sqrt{\text{residual mean square}}}$
- Deleted residual are outliers that significantly affects the residual
- Case number are the run numbers

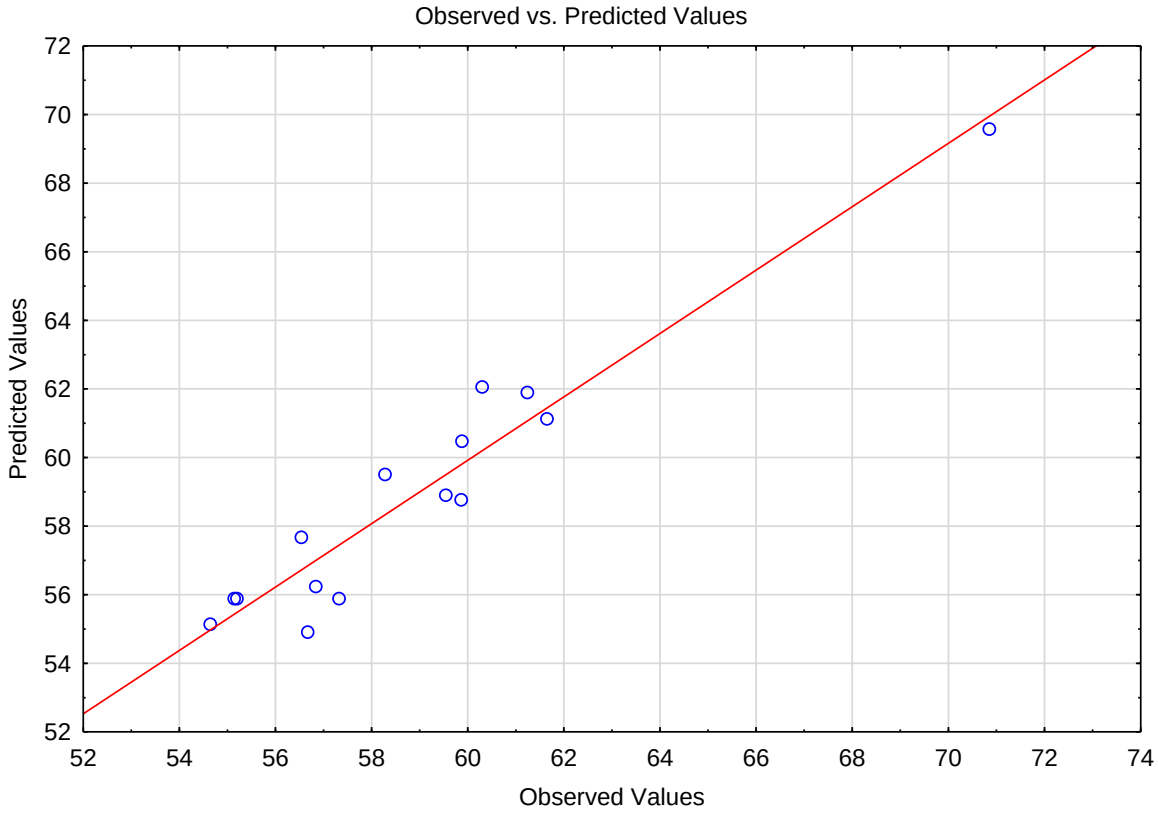


Figure 5.3: Plot of Observed vs predicted values of Au elution recovery at 6 bedvolumes

From Figure 5.3, it can be observed that the scatter plots lie close to the straight line indicating minor deviation from the standardised line, therefore, the model is acceptable according to Pavan et al (2007).

5.4 Model validation

Apart from the correlation coefficient R^2 (0.924) that determines how fit a model is with the experimental data of Au elution recovery at 6 bed volumes. An adjusted R^2 value of 0.788 also suggest a goodness of fit of the model. Validity of the model for predicting experimental data can also be confirmed with the normal probability plot versus the residual plot (Sheridan et al., 2002) as shown in Figure 5.4. According to Pavan et al. (2007), data points on the plot should close to the straight line in order to justify the validity of the model.

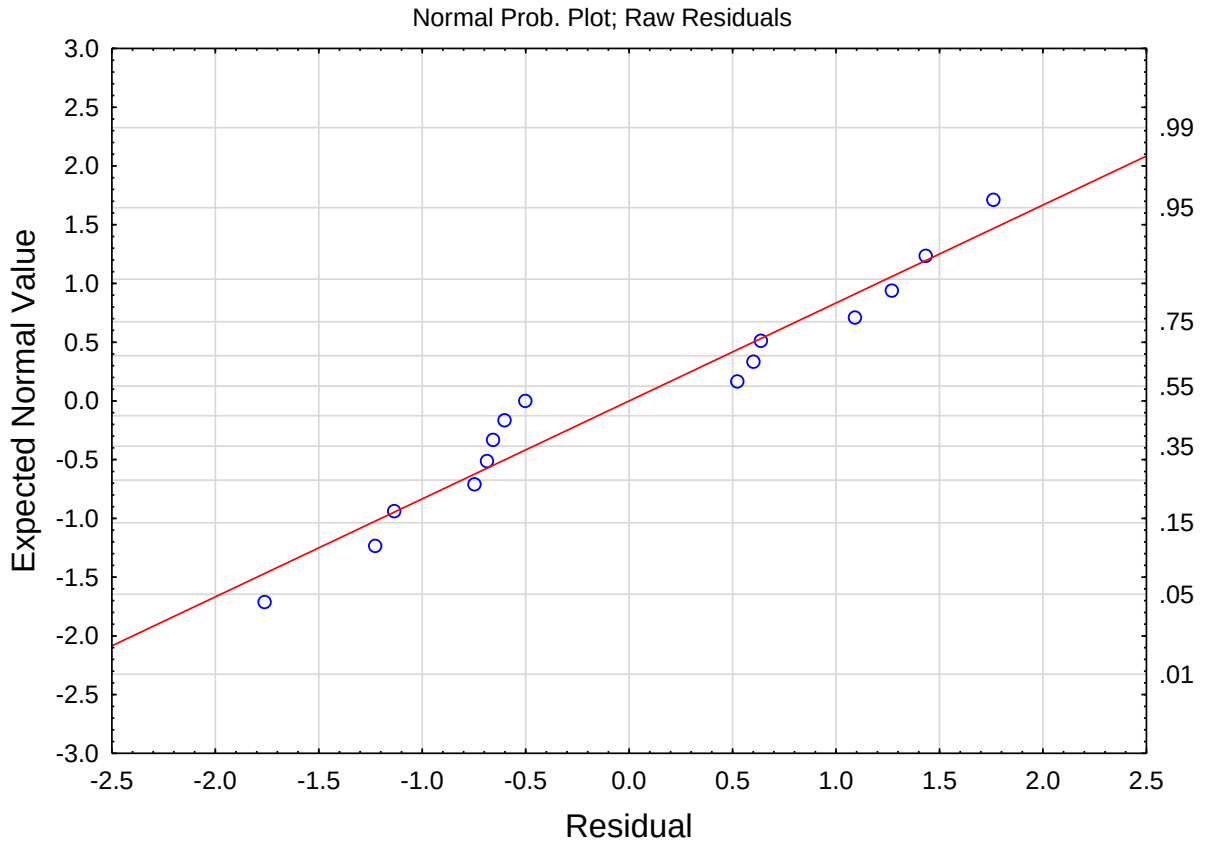


Figure 5.4: Probability plot vs Residuals of Au recovery at 6 bed volumes.

5.5 Pre-treatment parameters within the confidence interval

Further analysis were carried out to show the variation of the pre-treatment parameters within ±95% confidence interval at each condition plotted in Section 4.5. Each condition at which the pre-treatment parameters was evaluated was plotted separately to ensure clarity. The effect of pre-treatment temperature, contact time and agitation speed analysed at each condition are within the ±95% confidence interval. This suggest that the experimental and predicted points are valid. These are shown in Figures 5.4–5.6.

5.5.1 Pre-treatment temperature within ±95% confidence level

The effect of pre-treatment temperature within ±95% confidence level at 0 rev/min different contact time (15, 30 and 45 min) are shown in Figure 5.5 a, b and c respectively. It can be seen that non of the trend lines exceed the ±95% confidence

level indicated with the dotted red lines. This suggest that the adopted Box Behnken model is valid within this confidence limit

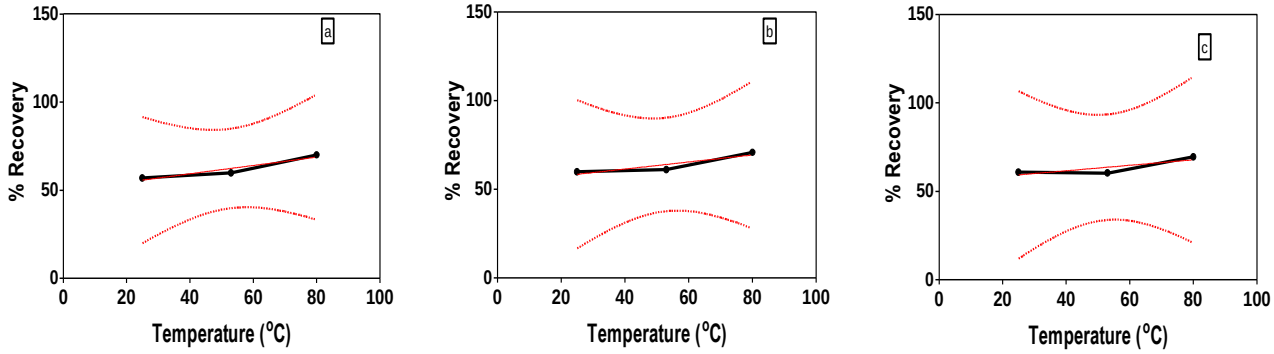


Figure 5.5: Effect of temperature within ±95% confidence level. (a= condition at 15min and 0 rev/min; b= condition at 30 min and 0 rev/min; c= condition at 45 min and 0 rev/min). Dotted red lines represent ±95%; red thin lines represents trend line and the black line represents data point of pre-treatment temperature.

5.5.2 Contact time within ±95% confidence level

Similarly, the effect of contact time at different conditions are shown in Figures 5.6 a–i. None of these effect exceeds the ±95% confidence level (red dotted lines). This suggests the validity of the model to predict the effect of contact time at 15, 30 and 45 min unders these experimental conditions within the ±95% confidence level.

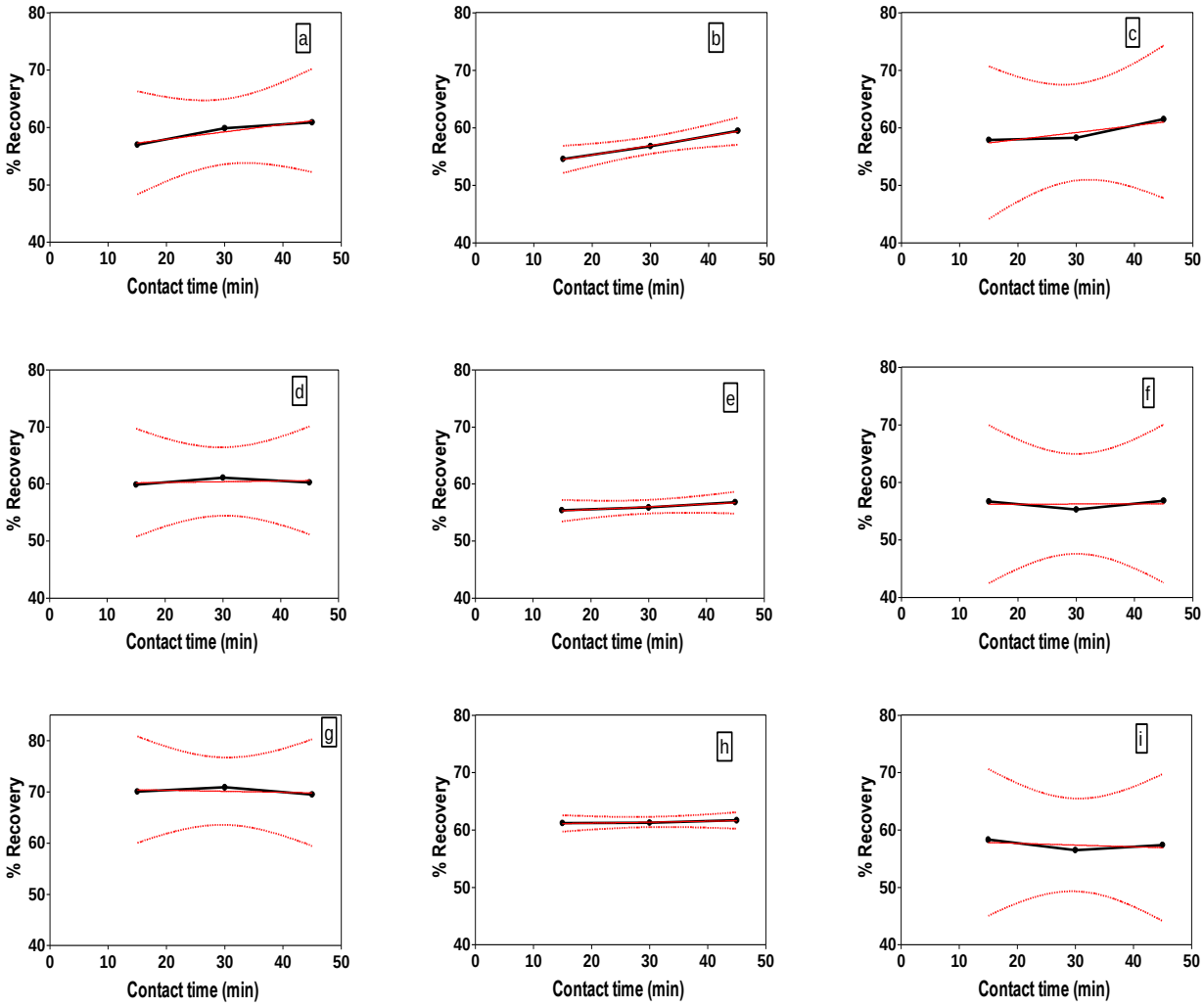


Figure 5.6: Effect of contact time within ±95% confidence level. (a= condition at 0 rev/min and 25°C; b= condition at 600 rev/min and 25°C; c= condition at 1200 rev/min and 25°C; d = condition at 0 rev/min and 53°C; e = condition at 600 rev/min and 53°C; f= condition at 1200 rev/min and 53°C;g = condition at 0 rev/min and 80°C; h = condition at 600 rev/min and 80°C and i= condition at 1200 rev/min and 80°C) Dotted red lines represent ±95%; red thin line represents trend line and the black line represents data point of contact time.

5.5.3 Agitation speed within ±95% confidence level

In the same vein, Figures 5.7 a–i show the effect of agitation plotted at the selected experimental conditions within the ±95% confidence interval. None of these effects exceeds the ±95% confidence interval also suggesting the validity of the Box Behnken model at the ±95% confidence level.

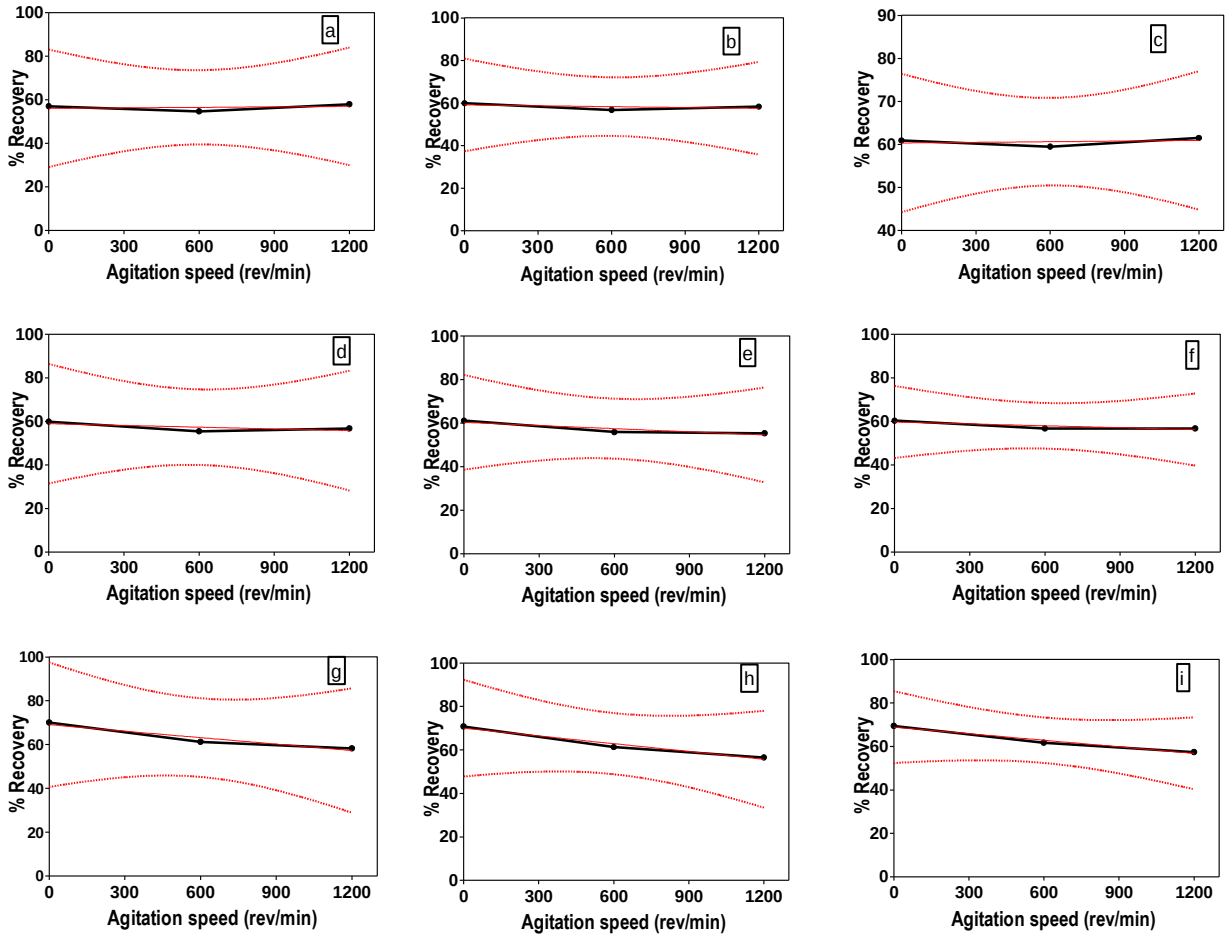


Figure 5.7: Effect of agitation speed within ±95% confidence level. (a= condition at 15 min and 25°C; b= condition at 30 min and 25°C; c= condition at 45 min and 25°C; d = condition at 15 min and 53°C; e = condition at 30 min and 53°C; f= condition at 45 min and 53°C;g = condition at 15 min and 80°C; h = condition at 30 min and 80°C and i= condition at 45 min and 80°C). Dotted red lines represent ±95%; red thin line represents trend line and the black line represents data point of agitation speed

5.6 Optimum condition

A unique advantage of response surface plot is in the determination of the optimum conditions of within the points of the experimental condition (Montgomery, 2013). The optimum condition of the effect of pre-treatment temperature, contact time and agitation speed within the experimental condition from all the surface response plot is shown by point x in Figure 5.8. Point x corresponds to a pre-treatment conditions of 80^{o}C, 30 min and 0 rev/min and the Au elution recovery is approximately 70%. Contact time has been investigated and discussed to be statistically insignificant on Au elution recovery (Section 4.5.2). Au elution recovery that were statiscally determined at this temperature and agitation speed (80^{o}C and 0 rev/min) but at different contact times showed insignificant changes on the surface response plot. It can be further suggested that recovery will improve beyond this optimum condition if the temperature is further increased above 80^{o}C as seen from the trend. The validation of the statistically determined optimum point (point x) with the experimental data conducted at pre-treatment condition of 80^{o}C, 30 min and 0 rev/min showed Au elution recovery of about 71% as shown in Figure 5.9

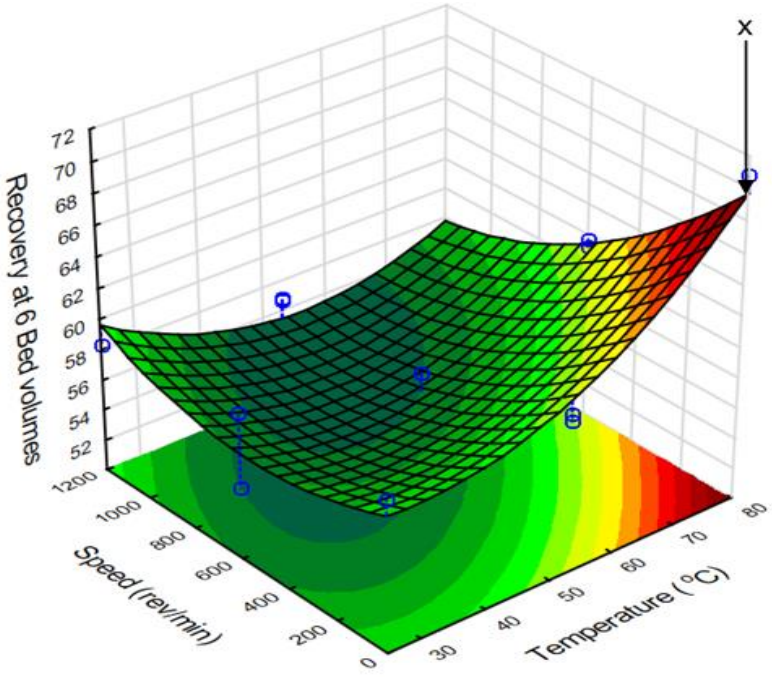


Figure 5.8: Surface response plot showing the optimum recovery at point x. Point x represents the optimum pre-treatment condition (80^{o}C, 30 min, 0 rev/min)

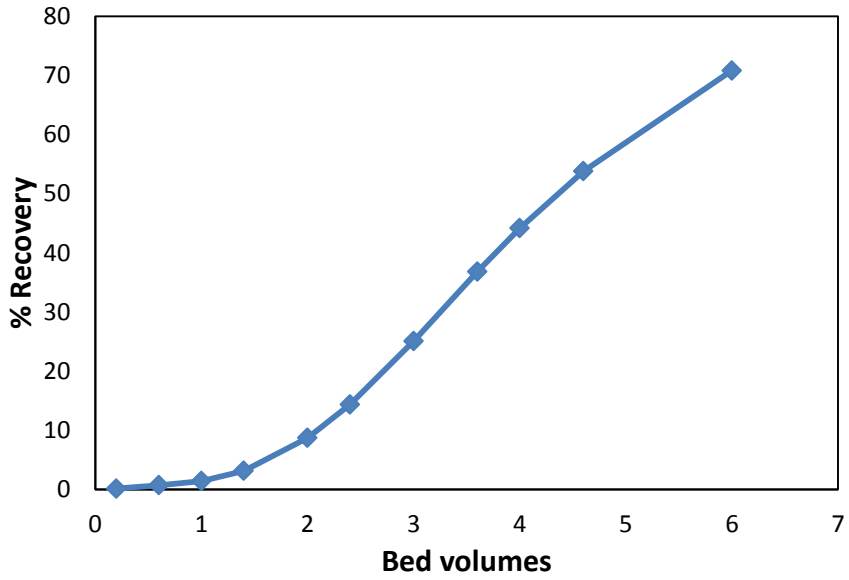


Figure 5.9: Optimum condition for validation of statistically determined optimum condition. pre-treatment condition (80^{o}C, 30 min, 0 rev/min)

5.7 Experimental error and reproducibility

A unique advantage of Box-Behnken experimental design is the efficiency in the number of runs required compared to a full factorial and composite design (Montgomery, 2013). This allows the formation of appropriate regression model to estimate the combined effects of the parameters that are not experimentally conducted (Section 5.2). In order to minimise the error and ensure reproducibility of the experiments, each run of the experiments was replicated three times, giving a total of 45 runs for the elution experiment. The reproducibility is expressed as percentage coefficient of variation (CR) given by Equation 5.2. The significance of the error with respect to the mean value was further statistically analysed using Descriptive Duncan analysis, Statistical 12 software. The error bar for each run indicates the standard error.

$$CR = \frac{SD}{AV} * 100\% \qquad 5.2$$

Where: CR = Coefficient of variation

SD = Standard deviation

AV= Average value of concentration of three trials

According to Chowdhury et al (2012), and as a general rule, an experiment can be regarded to be reproducible, if the CR is less than 10 percent. The experimental error, statistical significance and reproducibility were carried out for both CN^- study and elution experiments.

5.7.1 Cyanide loss study

Figures 5.10–5.12 show the column plot of the CN^- study of average concentration of CN^- and Na^+ at each sampling time both in the presence and absence of activated carbon. The value of the percentage of CR at each sampling point is shown on each bar after three trials which are less than 10% confirms the behaviour at 25°C and 80°C previously discussed in Section 4.4 where no significant changes occurred at 25°C when compared to 80°C. The calculated CR according to Equation 5.2 after three trials are shown in Tables 5.2–5.5 for studies in the absence of activated carbon.

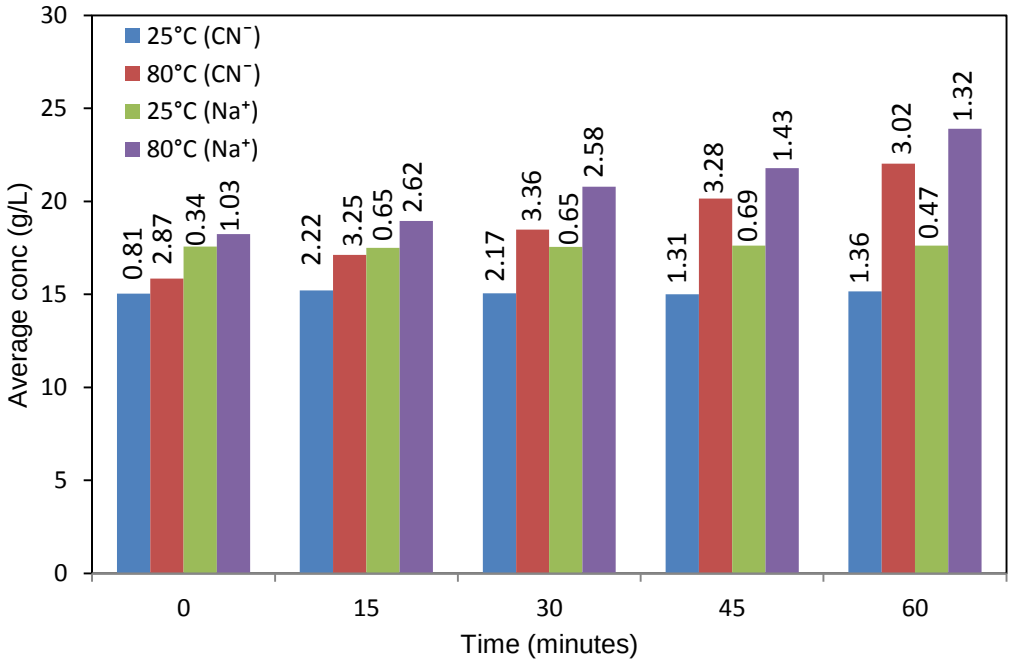


Figure 5.10: Reproducibility of CN^- and Na^+ in the absence of AC. Values shows coefficient of variation

Table 5.2: Average concentration, SD and CR. Condition (25°C, 0 rev/min, No-AC)

Time (minutes)	Trial 1 CN^- (g/L)	Trial 2 CN^- (g/L)	Trial 3 CN^- (g/L)	Average Conc (g/L)	SD	CR
0	15.17	14.93	15.01	15.04	0.12	0.81
15	15.52	15.24	14.85	15.21	0.34	2.22
30	15.36	14.71	15.12	15.06	0.33	2.17
45	15.20	14.81	15.04	15.01	0.20	1.31
60	15.36	14.95	15.17	15.16	0.21	1.36

Table 5.3: Average concentration, SD and CR. Condition (80°C, 0 rev/min, No-AC)

Time (minutes)	Trial 1 CN^- (g/L)	Trial 2 CN^- (g/L)	Trial 3 CN^- (g/L)	Average Conc (g/L)	SD	CR
0	16.12	15.33	16.11	15.85	0.45	2.87
15	17.69	16.58	17.10	17.12	0.56	3.25
30	18.53	17.84	19.08	18.48	0.62	3.36
45	20.08	19.53	20.85	20.15	0.66	3.28
60	22.19	21.30	22.60	22.03	0.67	3.02

Table 5.4: Average concentration, SD and CR. Condition (25°C, 0 rev/min, No-AC)

Time (minutes)	Trial 1 Na^+ (g/L)	Trial 2 Na^+ (g/L)	Trial 3 Na^+ (g/L)	Average Conc (g/L)	SD	CR
0	17.65	17.50	17.55	17.57	0.06	0.34
15	17.66	17.45	17.39	17.50	0.11	0.65
30	17.44	17.71	17.49	17.55	0.11	0.65
45	17.78	17.54	17.51	17.61	0.12	0.69
60	17.73	17.61	17.53	17.63	0.08	0.47

Table 5.5: Average concentration, SD and CR. Condition (80°C, 0 rev/min, No-AC)

Time (minutes)	Trial 1 Na^+ (g/L)	Trial 2 Na^+ (g/L)	Trial 3 Na^+ (g/L)	Average Conc (g/L)	SD	CR
0	18.48	18.21	18.03	18.24	0.19	1.03
15	19.64	18.56	18.61	18.94	0.50	2.62
30	20.92	20.07	21.36	20.78	0.54	2.58
45	21.82	21.38	22.14	21.78	0.31	1.43
60	23.60	24.34	23.78	23.91	0.32	1.32

Similary, Figure 5.11 shows the column plot of CN^- study of average concentration of CN^- and Na^+ at each sampling time in the presence of activated carbon. As indicated on the columns in Figure 5.11 and as it has been calculated from Tables 5.6–5.9. The value of the percentage of CR at each sampling point shown on each bar after three trials that are less than 10% confirms the behaviour at 25°C and 80°C

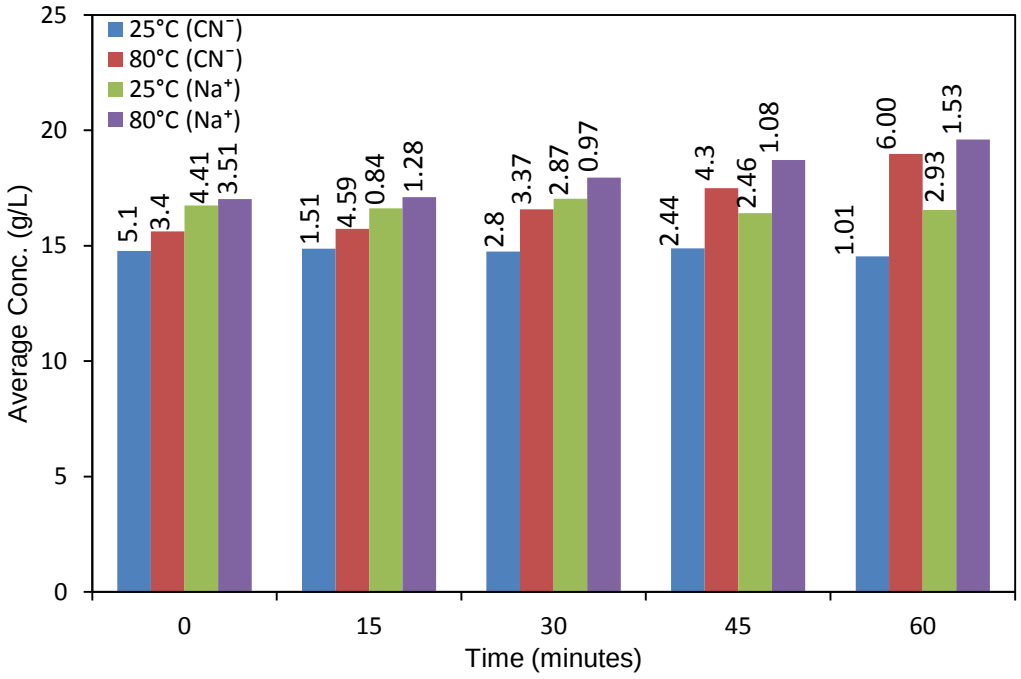


Figure 5.11: Reproducibility of CN^- and Na^+ in the presence of AC Values shows coefficient of variation

Table 5.6: Average concentration, SD and CR. Condition (25°C, 0rpm, AC)

Time (minutes)	Trial 1 CN^- (g/L)	Trial 2 CN^- (g/L)	Trial 3 CN^- (g/L)	Average Conc (g/L)	SD	CR
0	15.65	14.30	14.36	14.77	0.76	5.17
15	15.12	14.82	14.69	14.88	0.22	1.51
30	15.18	14.36	14.70	14.74	0.41	2.81
45	15.18	14.48	14.99	14.88	0.36	2.44
60	14.67	14.56	14.38	14.54	0.15	1.01

Table 5.7: Average concentration, SD and CR. Condition (80°C, 0rpm, AC)

Time (minutes)	Trial 1 CN^- (g/L)	Trial 2 CN^- (g/L)	Trial 3 CN^- (g/L)	Average Conc (g/L)	SD	CR
0	15.90	15.10	14.90	15.30	0.53	3.45
15	16.30	14.96	15.20	15.49	0.71	4.59
30	16.12	15.43	16.50	16.02	0.54	3.37
45	16.60	15.77	17.21	16.53	0.73	4.39
60	17.07	16.25	18.30	17.21	1.03	6.00

Table 5.8: Average concentration, SD and CR . Condition (25°C, 0rpm, AC)

Time (minutes)	Trial 1 Na^+ (g/L)	Trial 2 Na^+ (g/L)	Trial 3 Na^+ (g/L)	Average Conc (g/L)	SD	CR
0	17.59	16.20	16.45	16.75	0.74	4.41
15	16.53	16.54	16.78	16.62	0.14	0.84
30	17.49	17.10	16.52	17.04	0.49	2.87
45	16.81	16.00	16.42	16.41	0.40	2.46
60	17.10	16.30	16.23	16.54	0.48	2.93

Table 5.9: Average concentration, SD and CR . Condition (80°C, 0rpm, AC)

Time (minutes)	Trial 1 Na^+ (g/L)	Trial 2 Na^+ (g/L)	Trial 3 Na^+ (g/L)	Average Conc (g/L)	SD	CR
0	17.96	16.91	16.91	17.26	0.61	3.51
15	16.85	17.23	17.23	17.10	0.22	1.28
30	17.76	18.00	18.10	17.95	0.17	0.97
45	18.74	18.90	18.50	18.71	0.20	1.08
60	19.59	19.90	19.30	19.60	0.30	1.53

5.7.2 Elution

In the same vein, the estimated CR for elution process which are less than 10 percent for each run are shown in the column plot in Figure 5.12. Duncan analysis of the error that might be associated with elution shown in Figure 5.13 with the error bar indicating the standard error. The data used for the estimation of these values for each run are shown in Table 5.10

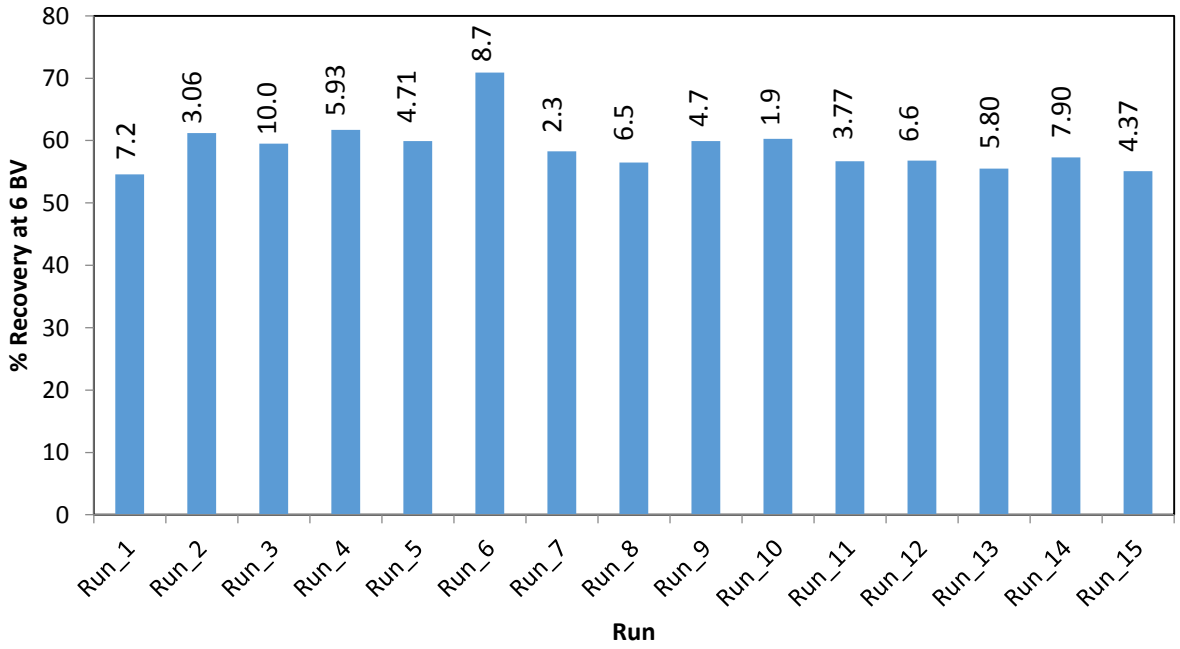


Figure 5.12: Reproducibility plot of elution experiment. Value on each column indicate coefficient of variation.

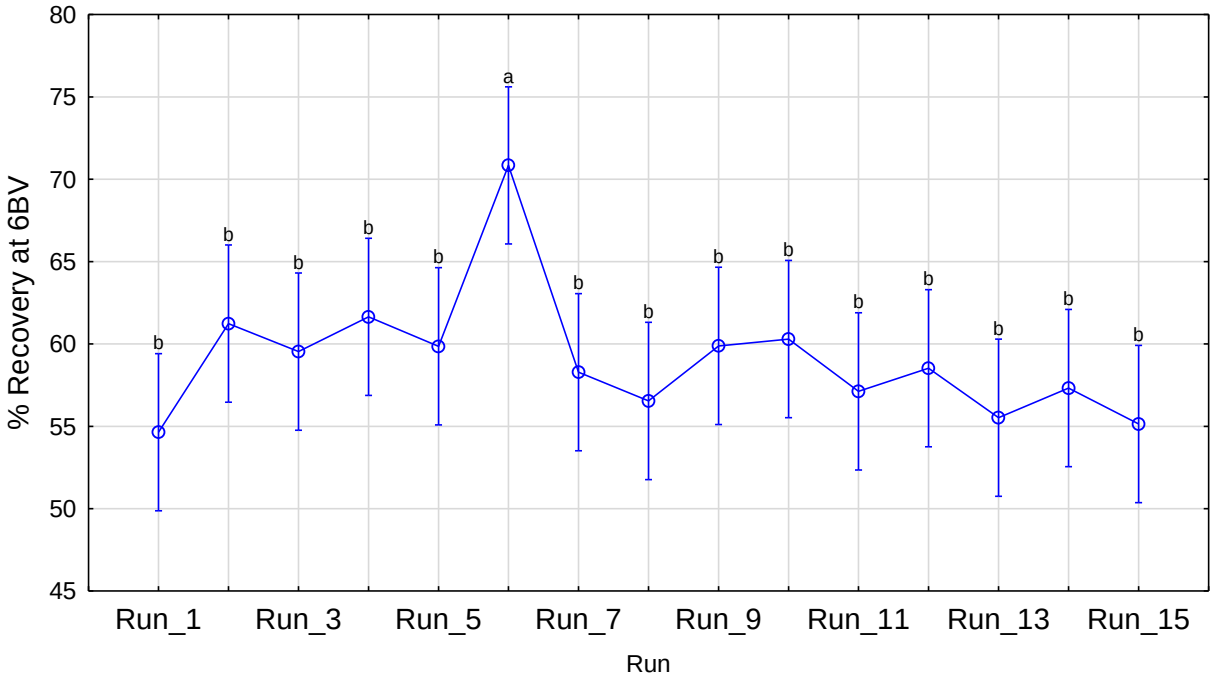


Figure 5.13: Descriptive Duncan analysis of the elution experiment. Error bars indicate standard error

Table 5.10: Average concentration, SD and CR for elution results

Run	Temperature	Time		Mean	SD	CR
Run_1	25	15	600	54.6	3.96	7.24
Run_2	80	15	600	61.2	1.87	3.06
Run_3	25	45	600	59.5	5.96	10.0
Run_4	80	45	600	61.7	3.67	5.93
Run_5	25	30	0	59.9	2.82	4.71
Run_6	80	30	0	70.9	6.21	8.75
Run_7	25	30	1200	58.3	1.36	2.33
Run_8	80	30	1200	56.5	3.67	6.49
Run_9	53	15	0	59.9	2.84	4.73
Run_10	53	45	0	60.3	1.18	1.96
Run_11	53	15	1200	56.7	2.14	3.76
Run_12	53	45	1200	56.8	3.79	6.67
Run_13	53	30	600	55.5	3.22	5.80
Run_14	53	30	600	57.3	4.53	7.91
Run_15	53	30	600	55.1	2.41	4.37

5.8 Chapter Summary

The P-values of 0.02, 0.01,and 0.02 for temperature, agitation speed and their combined effect in the ANOVA result showed these factors are statistically significant on Au elution recovery. The positive and negative effects of temperature and agitation speed was seen with values of 4.49 and -5.58 respectively. Regression model was formulated to enable prediction of points that are not conducted experimentally. The regression model was validated using probability plot vs residuals plot.

Surface response plot of the pre-treatment parameters and its interactions concurred with the metallurgical explanations given in chapter 5.

Reproducibility of CN^- study and elution experiment with CR less than 10% indicate that the experiment is reproducible. The insignificance of the standard error also showed that the error is minimal.

The overvall thesis summary and conclusion is given in the next chapter.

6 Conclusions and Recommendations

6.1 Conclusions

The variabilities and non-standard guidelines of pre-treatment parameters i.e., pre-treatment temperature and contact time that exist in Au elution process has been reported. Several elution mechanisms have been studied. One of such is the decomposition of CN^- on carbon surface which passivates carbon surface and ultimately improved Au elution recovery. Furthermore decomposition of CN^- as a result of agitation at different speeds have been reported. However, the effect on Au elution recovery has not been investigated. Due to this variabily of the pre-treatment paramenets and the lack of understanding of the effect of agitation on elution process, this study investigated the effects of temperature, contact time and agitation speed during pre-treatment on the elution of Au from activated carbon. Furthermore, the study on the role of NaOH-NaCN during the pre-treatment step assisted in the suggestion of suitable pre-treatment mechanism. The results of this investigation is as follows:

- Elution results showed that Au elution recovery increased by approximately 15% after 6 BVs as the pre-treatment temperature increased from 25°C to 80°C. This is in agreement with the work of previous researchers
- At 25^{o}C, an increase in Au elution recovery of about 4% was seen from 15 min to 45 min, while at the 53^{o}C and 80^{o}C increase in the pre-treatment time had insignificant effect on the Au elution recovery. It was suggested that an increase in temperature minimises the effect of contact time on the overall recovery, which agrees with the findings of Bailey (1991).
- Agitation of the pre-treatment solution on the other hand showed no significant change from 0–1200 rev/min at 25^{o}C, 6% decrease at 53^{o}C and about 10% decrease in Au elution recovery was noticed at 80°C indicating an antagonistic effect of agitation. Evaluations of k_{SL} at 0 , 600 and 1200 rev/min showed insignificant change in k_{SL}
- Proposed elution mechanisms were reviewed from several authors and related to the findings from this study. The mechanism where the CN^- is involved in a

specific chemical reaction at the carbon surface to increase the negative charge density and rendering the surface less receptive for adsorption (Adams and Fleming, 1989) best explained the possible elution mechanism.

- In the case where loaded activated carbon was thermally regenerated as in the case of Au loaded carbon supplied from Goldplat Recovery (PTY), CN^- is required to convert solid Au particle to soluble $Au(CN)_2^-$ which will require longer pre-treatment times and higher concentrations of CN^-.
- Finally, the relevance of this research was shown to be applicable to Au plants where a significant amount of Au still remains on carbon after elution, especially where cyanide-free elution is being practised. in order to minimise Au loss with the tailings.

From this study, it is suggested that gold plant continue to operate at high pre-treatment temperature and not adopt agitation into the pre-treatment process. A longer contact time is suggested when Au adsorbed on activated carbon remained adsorbed as solid Au.

6.2 Recommendations

- To use a pilot plant experiment to further investigate regenerated Au loaded activated carbon in order to determine optimum cyanide consumption under the effect of the pre-treatment parameters.
- This present study will provide a solid framework to investigate the possible elution mechanisms of PGMs, following the recent feasibility study by Snyders et al. (2013) on using activated carbon in the adsorption and elution of platinum group metals (PGMs) in a similar approach to Au.

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Appendix A: Experimental steps, risks and precautions

Adsorption

S/N	Step	Risk	Precaution(s)
1	Prepare the fresh activated carbon for use: • Weigh 840g of fresh AC • Pour in 10liter bucket and rinse with deionised water for 20min • Pour the water off through sieve and oven dry at 80^{o}C for 24 hours	Stain, Burn,	Use rubber gloves, safety glass.
2	Measure 34 litres of buffer solution mixed with 1.5 litres of 200ppm gold solution to dilute to approximate concentration of 9ppm and maintained at pH of 9.5	Spillage which might lead to slipping,	Careful pouring of the buffer solution, Clean immediately in any event of spillage, use rubber gloves
3	Pour 420g of the already oven dried AC into the bottle containing 15 litres of the solution prepared in (2) and with the appropriate lid. ensure that there is no leakage	----------	----------
4	Repeat step 2-3 for another water dispensing bottle	Same as above(2 and 3)	Same as above (2 and 3)
5	Place the bottle in the electrical powered roller and switch on the roller for 48hours to achieve pseudo-equilibrium	Electric shock, improper adsorption through mis-alignment on the roller	Avoid naked cables; ensure bottles are well placed on the roller, regular checking of the roller.
6	After 48 hours, switch off the roller and take sample of the liquid with filter-syringe for ICP-MS analysis	electric shock	Avoid naked cables and use rubber gloves
7	Decant close to 5 litres of the liquid in a container to rinse the wetted carbon stocked inside the bottle. Pour the AC through a filter paper and use the liquid for rinsing	Stain	Use rubber gloves
8	Place the AC in the oven set at 80^{o}C for 24hours to dry off the moisture	Burn	Use rubber glove, eye goggle.

9	Use rotary divider (splitter) to thoroughly mix the AC and divide i. Keep each 12g in a small zip-lock for the pre-treatment and elution process.		

Pre-treatment

S/N	Step	Risk	Precaution
1	Prepare NaOH-NaCN solution (3% NaCN and 1%NaOH) at correct temperature	Contamination through splash, inhalation, spillage and death	Put on PPE and cyanide detector. call for emergency in case of excessive spillage, work in the fume cupboard
2	Keep the unused NaOH-NaCN solution in a locked cupboard and the quantity to be used in the fume-hood	Contamination and inhalation	Put on PPE, Respirator, work in the fume cupboard
4	Place the beaker in the water bath and insert the temperature, pH and Eh probes	Contamination Burn ($90^{o}C$)	Careful insertion, PPE
5	Carefully pour 12g of the adsorbed activated into the beaker and gently lower the stirrer into the beaker. Ensure the stirrer is not sitting on any carbon particle to warrant free-stirring	Splash, burn	Safety goggle and rubber gloves in use.
7	Set the over-head stirrer to the required speed as defined by the Reynolds number and switch it on for the required time as per experimental plan. Monitor the temperature, pH and Eh probes. Take values of pH and Eh every 3 minutes to check for any changes.	Dis-organisation of the set up and breakage of beaker possibly leading to splash, spillage and contamination	Ensure that the over-head stirrer is well fastened to the retort stand, avoid contact of the stirring blade with the wall of the beaker. Use safety googles and gloves

8	After the time is reached, switch off the stirrer, remove the probes and clean them with paper tissue, return the pH and Eh probes into its respective buffers.	Contamination of the buffer	Wash and Clean probes after use
9	Carefully remove lid and the stirrer and then take samples of the solution with filter- syringe.	Burn and contamination	Use rubber gloves, safety goggle, and manual single channel volume pipette
10	Carefully pour the pretreated solution into the liquid waste container while the remaining wet carbon is poured in a paper towel to drain the remaining liquid	Burn, contamination, spillage,	Maintaining focus, clean with paper tower, safety goggle and gloves.

Elution

S/N	Steps	Risk	Precaution
1	Clean the glass column with acetone and blow air through. Also wash the water bath thoroughly with water to prevent contamination of the eluant	Spillage in the eye. Contamination of the column with acetone	Use safety goggle. Rinse the column thoroughly with water after washing with acetone
2	Set up the temperature controlled water-bath together with glass column connected to pipes and peristaltic pump	Breakage of column and possibly piercing and injury. spillage	Careful handling of the column while connecting and disconnecting the pipes. Paper towel in place
3	Ensure the water is flowing in and out of the jacket of the glass column till 90^{o}C temperature is reached	Burn	Use rubber gloves

4	Pour the pre-treated carbon into the column using spatula to gently assist in the transfer process	--------	----------
5	Introduce hot water (90^{o}C) into the column through the pipe connected to the peristaltic pump supplying the water at 2bv/h (0.8mL/min). 1 bed volume = 25mL	Burn, splash	Use goggle, rubber gloves and safety shoe.
6	Ensure that the water level maintained at least slightly above the carbon in the column throughout the run	----------	----------
7	Pick samples at 5mL interval. Pick total of 100 samples. 15 of the samples would be analysed based on elution strategy	----------	Use rubber glove and goggle
8	Switch off the water bath and peristaltic pump while the glass column is carefully disconnected.	Burn	Allow to cool

Appendix B: Sample preparation and supporting calculations

1) Carbon Loading Calculation

Total mass set to be prepared for the experiment = 840g (420g for each 18.9litres bottle)

$$GL = \frac{(C_i - C_f)\,v}{w}$$

GL = Gold loading on carbon (mg/g)

C_i = Initial concentration of gold solution = 10.6 mg/L

C_f = Concentration of barren solution after adsorption = 0.03 mg/L

v= volume of gold solution = 30 Litres

w = weight of carbon = 840 g

By substituting these values into the equation above, GL = 0.38 mg/g

2) CN^- analysis by titrating with Silver nitrate ($AgNO_3$)

Equation of reaction: $Ag + 2CN^- \rightarrow Ag(CN)_2$

Mole ratio of Ag:CN is expressed as $\frac{Ag}{CN} = \frac{1}{2}$

Required volume and concentration after calculation can be calculated as:

$2 * C_{Ag} * V_{Ag} = C_{CN} * V_{CN}$

Where: C_{Ag} = prepared $AgNO_3$ solution (0.0964 M)

V_{Ag} = Volume of $AgNO_3$ used (determined from reading)

V_{CN} = Volume of CN^- used for each titration (0.5 mL)

C_{CN} = Concentration of CN^- (calculated)

3) Recovery calculation (elution efficiency)

Elution efficiency is usually reported in the form shown in Equations B0.1 or B0.2 (Boshoff, 1993; Laxen et al., 1982).

$$\frac{\text{Gold eluted from carbon}}{\text{Gold loaded from carbon}} \text{ X } 100\% \qquad \text{B0.1}$$

$$\frac{\text{Total gold eluted}}{\text{Total gold eluted+residual gold on carbon}} \text{ X } 100\% \qquad \text{B0.2}$$

It is being suggested that these equations will be easily applicable when the history (amount) of loading of gold on AC is known while an unkown parameter can be calculated through gold mass balance. In a case where the amount of gold remained on carbon is not fully acertain as in Section 5.7, the elution efficieny was calculated based on the maximum gold assay eluted of different elution results of the same set of carbon originating from the same loading conditions. For instance if carbon A originating from the same loading condition is pre-treated and eluted at different conditions resulting in different elution results, the elution efficiency was calculated using B0.3.

$$\frac{\text{Cummlative gold eluted from carbon}}{\text{Maximum cummlative gold eluted}} \times 100\% \qquad \text{B0.3}$$

This study adopts Equation 4.7 for the calculation of elution efficiency.

The steps taken to calculate the cumulative gold eluted are shown below. A simple illustration of these steps are shown at pre-treatment conditions of 25^{o}C, 45 mins and 600 rev/min. Maximum cumulative gold eluted was found at 80^{o}C, 0 rev/min and 30 mins with total mass of 178.51 mg.

Step1

Gold and sodium analysis received from ICP analysis were tabulated on excel sheet as shown below.

	A	B	C	D
1				
2				
3	Conditions: 25oc,600rpm,45mins			
4	Bed volur	Au (mg/L)	Na (mg/L)	
5	0	0		
6	0.2	1.50	6393.06	
7	0.6	1.71	8332.50	
8	1	5.14	2765.70	
9	1.4	10.69	1159.19	
10	2	17.57	640.16	
11	2.4	20.77	491.05	
12	3	24.26	395.39	
13	3.6	27.20	285.01	
14	4	26.60	262.08	
15	4.6	25.26	234.24	
16	6	16.10	159.23	
17	9	7.14	109.01	
18	11	4.59	88.08	
19	15	1.89	66.34	
20	20	0.72	51.50	
21		191.15		

Figure B 1: Step 1. Excel tabulation of ICP analysis of Au and Na

Step 2

Mass of gold eluted at each bed volume was calculated by finding the area under curve. This was done by calculating the average concentration and multiplying it by the volume (BV). For instance, the mass of gold eluted at 0.2 and 0.6 bed volume were calculated as follows:

At 0.2 BV, mass eluted (mg) = (B6+B5)/2*(A6-A5)

At 0.6 BV, mass eluted (mg) = (B7+B6)/2*(A7-A6)

This is done up to 20 BVs. Results obtained are shown in the figure below.

	A	B	C	D	E
1					
2					
3	Conditions: 25oc,600rpm,45mins				
4	Bed volur	Au (mg/L)	Na (mg/L)		Area (mg)
5	0	0			
6	0.2	1.50	6393.06		0.15
7	0.6	1.71	8332.50		0.64
8	1	5.14	2765.70		1.37
9	1.4	10.69	1159.19		3.17
10	2	17.57	640.16		8.48
11	2.4	20.77	491.05		7.67
12	3	24.26	395.39		13.51
13	3.6	27.20	285.01		15.44
14	4	26.60	262.08		10.76
15	4.6	25.26	234.24		15.56
16	6	16.10	159.23		28.95
17	9	7.14	109.01		34.87
18	11	4.59	88.08		11.74
19	15	1.89	66.34		12.96
20	20	0.72	51.50		6.51
21		191.15			171.78

Figure B 2: Step 2. Calcualtion of mass of Au in mg

Step 3

The cummulatve mass was calculated and the percentage of gold elution recovery at each bed volume was calculated using Equation B0.3. The results generated are shown below

	A	B	C	D	E	F	G
1							
2							
3	Conditions: 25oc,600rpm,45mins						
4	Bed volur	Au (mg/L)	Na (mg/L)		Area (mg)	cumm	% Recovery
5	0	0					
6	0.2	1.50	6393.06		0.15	0.15	0.08
7	0.6	1.71	8332.50		0.64	0.79	0.44
8	1	5.14	2765.70		1.37	2.16	1.21
9	1.4	10.69	1159.19		3.17	5.33	2.99
10	2	17.57	640.16		8.48	13.81	7.73
11	2.4	20.77	491.05		7.67	21.47	12.03
12	3	24.26	395.39		13.51	34.98	19.60
13	3.6	27.20	285.01		15.44	50.42	28.25
14	4	26.60	262.08		10.76	61.18	34.27
15	4.6	25.26	234.24		15.56	76.74	42.99
16	6	16.10	159.23		28.95	105.70	59.21
17	9	7.14	109.01		34.87	140.57	78.74
18	11	4.59	88.08		11.74	152.30	85.32
19	15	1.89	66.34		12.96	165.27	92.58
20	20	0.72	51.50		6.51	171.78	96.23
21		191.15			171.78		

Figure B 3: Step 3. Au recovery calculation

Appendix C: Results of experimental anaysis

Results presented here are the raw data from ICP_MS analysis of Au and Sodium concentration for the elution result. The replicate of each condition are presented together in the same table as shown below. Concentration of free cyanide used for the kinetic study that was generated through titration is also presented.

Table C. 1. ICP result for pre-treatment condition at 25^{o}C, 600rpm, 45 minutes

Bed volumes	Run 33		Run 18		Run3	
	Au (mg/L)	**Na (mg/L)**	**Au (mg/L)**	**Na (mg/L)**	**Au (mg/L)**	**Na (mg/L)**
0.20	1.501	6393	1.241		1.380	6904
0.60	1.710	8332	1.637		1.830	9843
1.0	5.142	2765	6.413		5.931	3204
1.4	10.72	1159	12.73		14.21	1112
2.0	17.61	640.1	19.71		23.08	547.2
2.4	20.84	491.1	22.34		26.65	382.6
3.0	24.37	395.4	25.90		30.34	295.7
3.6	27.26	285.0	22.79		30.47	235.2
4.0	26.64	262.1	20.65		28.50	211.1
4.6	25.37	234.2	17.38		25.21	190.1
6.0	16.10	159.2	10.45		16.89	136.2
9.	7.140	109.0	3.902		12.15	107.1
11	4.590	88.08	2.083		6.380	97.44
15	1.890	66.34	1.288		2.030	55.13
20	0.7200	51.50	0.2955		0.7200	57.25

Table C. 2. ICP result for pre-treatment condition at 80°C, 600rpm, 15, minutes

Bed volumes	Run 17		Run 2		Run 32	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	2.050	8325	1.850	7398	2.110	6034
0.60	2.100	10090	2.070	7543	1.980	8835
1.0	4.830	4294	5.690	2621	3.420	6018
1.4	11.03	1198	11.42	1061	8.270	1385
2.0	20.08	590.2	19.06	595.1	16.82	681.7
2.4	25.10	431.3	22.35	429.9	20.64	457.2
3.0	26.30	333.7	26.63	326.6	26.64	301.8
3.6	26.98	256.1	27.04	251.7	28.39	261.0
4.0	25.67	214.8	27.2	244.2	27.80	231.6
4.6	21.42	194.4	26.59	189.6	26.22	187.3
6.0	16.21	151.8	18.83	150.8	18.12	150.5
9.0	4.690	76.68	7.370	99.11	7.200	95.68
11	2.810	65.29	4.010	80.17	3.690	80.00
15	1.510	56.12	1.530	76.22	1.210	68.40
20	0.3700	34.92	0.4800	43.05	0.4900	44.73

Table C. 3. ICP result for pre-treatment condition at 80°C, 1200rpm, 30 minutes

Bed volumes	Run 23		Run 8		Run 38	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.450	10390	1.870	6207	1.350	4430
0.60	2.390	9008	1.760	7314	1.600	7922
1.0	7.660	2281	4.870	2316	2.740	5565
1.4	14.47	1002	10.20	994.2	7.300	1581
2.0	23.42	589.1	17.16	536.7	14.74	641.8
2.4	26.08	460.4	20.40	402.4	17.60	517.4
3.0	26.70	376.7	23.40	293.4	20.99	386.4
3.6	26.53	302.3	24.03	242.1	24.61	301.8
4.0	24.28	254.0	23.50	232.7	24.72	243.1
4.6	20.65	240.2	21.35	172.4	24.65	200.4
6.0	14.15	167.1	17.05	125.0	17.61	128.1
9.0	5.290	109.6	8.460	97.85	6.810	110.1
11	3.050	92.00	5.960	87.34	4.230	89.69
15	1.150	67.57	2.370	56.19	1.520	55.70
20	0.4700	51.48	0.3800	32.95	0.5800	67.87

Table C. 4. ICP result for pre-treatment condition at 80^{o}C, 600 rpm, 45 minutes

Bed volumes	Run 19		Run 4		Run 34	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.530	7835	1.920	9851	2.020	6223.23
0.60	1.880	8898	2.150	10560	1.840	7957.13
1.0	5.350	2607	6.120	3017	4.950	2809.72
1.4	10.75	1047	11.39	1343	19.01	488.02
2.0	17.55	592.6	18.91	734.9	21.10	443.77
2.4	23.68	383.2	24.98	494.8	24.94	342.80
3.0	27.01	298.2	27.18	3900	27.56	253.75
3.6	25.26	240.2	28.22	305.2	27.55	201.02
4.0	23.46	218.8	26.26	315.2	26.01	200.72
4.6	22.39	171.2	25.12	195.8	23.02	163.60
6.0	14.58	142.5	19.61	1501.0	16.46	96.50
9.0	7.130	113.3	5.400	112.7	7.020	93.24
11	4.420	102.7	2.600	84.78	3.740	72.19
15	1.390	71.82	0.8900	57.14	1.280	45.72
20	0.5500	53.36	0.3200	38.68	0.3900	36.05

Table C. 5. ICP result for pre-treatment condition at 25^{o}C, 600 rpm, 15 minutes

Bed volumes	Run 16		Run 1		Run 25	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.240	7647	1.070	6977	1.220	6517
0.60	2.260	6289	1.380	7405	1.250	7742
1.0	7.870	1436	5.590	1655	3.970	2668
1.4	13.18	786.6	10.36	749.1	10.09	834.7
2.0	18.06	529.9	15.43	454.5	15.73	466.7
2.4	24.26	370.4	19.11	346.4	19.46	369.4
3.0	26.97	288.6	22.54	249.3	23.63	277.8
3.6	25.61	241.9	22.55	214.4	25.20	190.4
4.0	23.91	338.8	21.44	182.8	23.87	201.6
4.6	21.53	218.9	19.29	152.9	22.13	181.4
6.0	14.42	131.1	14.67	139.7	16.14	109.3
9.0	5.680	95.20	7.070	94.02	7.610	63.61
11	3.350	79.19	4.910	80.29	4.720	65.84
15	1.790	65.20	2.120	43.68	2.210	50.89
20	0.4900	41.34	0.9600	51.32	0.9700	33.81

Table C. 6. ICP result for pre-treatment condition at 53°C, 0rpm, 15 minutes

Bed volumes	Run 9		Run 24		Run 39	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.750	6394	1.510	6389	1.320	7368
0.60	1.620	8526	1.510	9003	1.690	8398
1.0	6.670	1793	3.940	3822	7.720	1536
1.4	12.72	862.2	10.15	1152	13.30	744.4
2.0	18.89	470.3	16.44	546.1	19.15	465.2
2.4	22.57	383.3	21.28	386.3	23.42	389.9
3.0	27.01	263.7	26.45	303.1	25.89	304.1
3.6	27.69	250.1	26.47	231.6	26.37	235.0
4.0	27.25	205.2	24.72	195.6	24.96	191.3
4.6	24.45	180.2	21.34	181.3	23.23	190.1
6.0	17.02	143.0	16.94	139.3	17.07	169.3
9.0	8.280	93.35	7.980	92.14	7.940	118.4
11	5.590	89.94	4.640	66.52	4.510	51.01
15	1.640	50.17	1.750	61.28	1.420	62.38
20	0.6600	43.98	0.5000	30.74	0.4700	33.14

Table C. 7. ICP result for pre-treatment condition at 25°C, 0rpm, 30 minutes

Bed volumes	Run 35		Run 5		Run 20	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.440	5907	1.360	6436	1.210	7389
0.60	1.570	7802	1.630	8174	1.470	8615
1.0	4.260	2996	5.290	2639	5.170	2654
1.4	10.11	1006	8.550	802.7	12.21	913.7
2.0	15.81	455.9	19.35	493.4	19.52	413.6
2.4	21.10	394.0	23.12	376.6	21.20	333.2
3.0	25.72	278.0	27.60	307.1	23.12	288.8
3.6	26.89	244.7	29.45	240.1	24.33	215.5
4.0	25.66	222.1	28.10	203.1	24.67	258.8
4.6	23.98	175.6	26.07	165.0	23.06	141.7
6.0	18.67	152.3	17.80	107.7	17.24	122.9
9.0	8.000	101.6	5.600	50.94	7.620	108.6
11	4.040	86.49	3.980	66.97	4.750	61.03
15	1.610	43.89	1.250	32.46	2.300	59.06
20	0.5700	62.56	0.4900	22.29	1.010	58.63

Table C. 8. ICP result for pre-treatment condition at 80°C, 0rpm, 30 minutes

Bed volumes	Run 36		Run 21		Run 6	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	2.520	7129	3.190	9099	2.310	5089
0.60	2.400	8448	2.500	11110	2.430	8449
1.0	3.940	5415	3.750	11570	3.880	7115
1.4	11.96	1280	10.90	2446	11.85	1499
2.0	21.74	625.8	24.42	862.4	18.71	632.7
2.4	27.29	460.8	33.75	565.9	24.46	450.8
3.0	32.84	333.9	41.71	412.4	31.34	306.2
3.6	33.10	247.2	39.27	342.2	31.37	222.9
4.0	31.74	223.2	33.43	207.7	28.58	197.6
4.6	25.00	272.1	29.49	188.9	23.47	224.0
6.0	17.70	154.0	19.23	156.8	15.43	132.9
9.0	5.050	87.93	6.270	80.95	5.150	63.25
11	2.410	88.32	3.110	96.22	2.360	60.06
15	0.660	54.08	0.8800	69.90	0.8500	60.86
20	0.3200	56.94	0.2600	48.77	0.2300	43.41

Table C. 9. ICP result for pre-treatment condition at 25°C, 1200rpm, 30 minutes

Bed volumes	Run 22		Run 37		Run 7	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.310	7831	1.170	7064	0.9900	5773
0.60	1.790	9776	1.430	9704	1.340	8067
1.0	5.750	2214	2.820	6027	4.490	2560
1.4	13.02	795.2	8.640	1625	9.490	867.4
2.0	20.90	470.3	15.83	604.5	15.18	473.2
2.4	25.52	349.0	20.70	459.0	19.87	311.1
3.0	25.88	244.4	26.96	316.8	24.76	239.6
3.6	24.16	228.9	26.78	234.5	25.53	208.8
4.0	24.10	198.9	27.06	246.5	25.63	158.6
4.6	21.39	169.3	24.79	177.3	23.37	145.6
6.0	16.21	138.0	18.36	164.3	17.89	134.3
9.0	7.450	94.28	8.230	127.2	8.090	73.97
11	4.090	75.32	4.070	75.47	4.010	91.44
15	1.720	63.76	1.690	72.63	1.990	51.42
20	0.5000	24.09	0.9500	30.00	0.7400	36.36

Table C. 10. ICP result for pre-treatment condition at 53°C, 0rpm, 45 minutes

Bed volumes	Run 40		Run 31		Run 10	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.480	3913	1.830	5846	2.020	5446
0.60	1.950	7971	1.770	7757	1.910	9045
1.0	2.710	5887	3.020	5036	5.060	3371
1.4	8.740	1406	9.640	1262	10.62	1217
2.0	16.89	6230	16.38	646.6	17.71	572.3
2.4	20.38	422.8	21.36	442.0	22.10	451.2
3.0	26.13	338.1	26.21	349.1	26.59	301.5
3.6	27.37	287.3	27.94	267.8	27.98	250.5
4.0	25.64	252.5	27.58	244.9	26.62	196.8
4.6	24.87	198.4	26.20	187.9	24.48	179.3
6.0	18.34	157.2	18.53	158.2	17.92	141.7
9.0	7.930	123.9	6.510	100.2	5.460	78.94
11	4.830	104.1	4.040	75.64	3.300	75.19
15	1.502	53.92	1.000	32.04	1.310	73.20
20	0.4400	62.80	0.8000	34.01	0.6600	40.77

Table C. 11. ICP result for pre-treatment condition at 53°C, 1200rpm, 15 minutes

Bed volumes	Run 26		Run 11		Run 41	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.380	6884	1.370	3987	1.090	7640
0.60	1.470	9430	1.550	7732	1.300	9779
1.0	2.970	5094	3.350	3830	4.660	2817
1.4	8.530	1317	8.570	1158	10.12	937.6
2.0	16.63	527.5	15.33	562.5	17.32	511.3
2.4	21.25	443.9	24.64	344.0	21.33	380.2
3.0	23.42	286.1	25.52	290.2	25.49	299.4
3.6	24.57	258.8	28.52	209.3	26.60	227.9
4.0	24.57	193.8	26.75	176.4	26.53	207.0
4.6	22.07	163.7	24.02	160.1	24.75	179.5
6.0	16.41	125.0	14.83	104.7	15.22	113.2
9.0	7.120	87.20	8.930	87.51	7.770	75.75
11	4.490	62.13	5.040	68.66	4.570	79.86
15	1.770	39.84	2.030	61.74	1.570	70.87
20	0.7200	28.62	0.700	32.70	0.7000	40.84

Table C. 12. ICP result for pre-treatment condition at 53°C, 1200rpm, 45minutes

Bed volumes	Run 42		Run 12		Run 27	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.470	5944	1.350	6551	1.400	6095
0.60	1.610	9948	1.360	10240	1.730	9837
1.0	3.280	6321	2.820	6457	2.800	7854
1.4	8.080	1322	8.780	1575	10.85	1538
2.0	15.96	633.7	16.01	639.0	17.18	598.4
2.4	18.28	411.1	21.17	874.9	23.25	512.6
3.0	23.28	297.4	23.99	382.8	25.36	274.8
3.6	23.81	225.8	28.84	323.4	26.14	230.7
4.0	23.72	194.4	32.94	290.3	25.44	214.3
4.6	23.32	178.3	25.78	202.9	23.73	207.5
6.0	17.90	133.5	20.51	130.1	18.84	129.7
9.0	9.010	87.86	9.200	78.78	8.590	106.5
11	5.780	74.70	5.580	65.37	4.900	75.90
15	2.230	43.43	2.130	59.01	1.600	51.58
20	0.9100	36.38	0.6800	28.85	0.6300	46.46

Table C. 13. ICP result for pre-treatment condition at 53°C, 600rpm, 30minutes

	Run 29		Run 45		Run 28	
Bed volumes	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	1.560	5543	1.720	6719	1.350	7194
0.60	1.930	9539	1.820	8427	1.330	9726
1.0	6.710	2432	7.200	1708	3.910	2982
1.4	10.49	916.2	12.86	911.9	8.710	1147
2.0	17.57	511.4	18.60	490.1	16.22	546.8
2.4	23.15	380.2	23.74	395.0	20.18	415.8
3.0	24.45	306.5	27.30	342.4	22.99	322.0
3.6	24.38	209.9	26.46	289.2	23.75	260.0
4.0	23.68	204.0	24.71	252.3	22.48	243.4
4.6	20.01	185.5	20.85	218.0	21.18	219.8
6.0	13.57	125.4	15.55	177.3	15.77	143.0
9.0	5.380	77.55	5.506	103.2	7.660	94.75
11	3.570	74.61	3.120	83.32	4.550	87.19
15	1.610	55.70	1.440	69.55	2.040	65.80
20	0.6700	46.43	0.3700	47.88	0.8000	54.26

Table C. 14. . ICP result for pre-treatment condition at 53°C, 600rpm, 30minutes

	Run 43		Run 15		Run 44	
Bed volumes	**Au (mg/L)**	**Na (mg/L)**	**Au (mg/L)**	**Na (mg/L)**	**Au (mg/L)**	**Na (mg/L)**
0.20	1.230	4509	1.720	5240	1.360	7026
0.60	1.410	7964	1.950	8383	1.470	9758
1.0	2.870	4106	2.450	7512	3.920	3999
1.4	7.950	1115	7.960	1476	9.850	1057
2.0	14.03	602.4	16.33	808.6	17.41	497.9
2.4	19.16	369.0	20.33	595.2	21.59	420.4
3.0	19.29	389.9	24.88	339.1	25.99	295.9
3.6	23.38	271.5	28.84	258.4	27.75	255.2
4.0	24.41	203.1	28.40	237.1	26.46	195.8
4.6	22.60	182.6	26.09	228.6	24.34	165.9
6.0	17.63	159.2	19.60	150.8	17.08	122.7
9.0	9.270	115.1	10.35	121.2	6.800	110.4
11	5.380	90.79	5.370	67.29	3.560	62.54
15	2.050	61.71	1.810	46.72	1.550	55.38
20	0.6900	62.17	0.5400	60.86	0.5900	47.54

Table C. 15. . ICP result for pre-treatment condition at 53°C, 600rpm, 30minutes

	Run 30		Run 13		Run 14	
Bed volumes	**Au (mg/L)**	**Na (mg/L)**	**Au (mg/L)**	**Na (mg/L)**	**Au (mg/L)**	**Na (mg/L)**
0.20	1.050	5182	1.200	8019	1.230	3659
0.60	1.220	7587	1.470	8130	1.320	8185
1.0	1.660	6706	5.380	1817	3.430	4393
1.4	7.180	1424	9.880	816.4	8.270	1195
2.0	15.11	526.0	16.88	435.1	14.71	565.1
2.4	20.11	390.2	22.33	367.6	18.30	417.1
3.0	21.37	349.9	23.42	246.7	22.73	303.2
3.6	24.84	226.5	23.53	233.6	25.67	232.7
4.0	24.05	193.4	23.84	186.1	24.54	217.7
4.6	21.88	171.7	23.88	182.2	25.03	191.3
6.0	16.88	134.8	18.10	118.7	18.65	151.4
9.0	8.400	87.11	8.000	70.51	8.600	76.17
11	4.660	47.76	4.400	61.16	5.080	34.36
15	2.709	38.14	2.010	37.89	2.280	72.44
20	1.000	34.10	0.7600	45.89	0.8900	47.15

Table C. 16. ICP result of oxygen supply experiment. Pre-treatment condition: 3%NaCN, 1%NaOH, 25°C,0 rpm and 30minutes

Bed volumes	0mL/min		10mL/min		100mL/min	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	20.29	8396	17.09	9305	18.08	9201
0.60	29.87	7225	28.90	6327	30.68	5623
1.0	89.76	1628	62.51	2199	56.49	2441
1.4	129.9	691.1	108.1	782.7	97.74	952.2
2.0	113.2	382.2	107.3	408.7	107.9	461.8
2.4	94.53	300.8	90.77	310.7	95.34	341.4
3.0	68.26	216.5	71.00	261.1	74.46	235.4
3.6	50.97	177.5	53.65	211.3	55.60	177.9
4.0	41.62	150.7	46.78	238.8	47.95	146.8
4.6	33.62	122.8	36.17	148.7	39.37	134.5
6.0	21.59	80.98	20.53	79.89	26.43	90.05
9.0	11.92	47.72	10.69	46.37	14.05	40.13
11	9.661	27.58	9.965	28.65	10.46	25.14
15	4.654	15.99	5.964	14.68	5.962	13.88
20	2.365	6.549	1.965	7.747	2.669	7.697

Table C. 17. ICP result of oxygen supply experiment at different flow rates. Pre-treatment condition: 3%NaCN, 1%NaOH, 80°C,0 rpm and 30minutes

Bed volumes	0mL/min		10/mL/min		100mL/min	
	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)	Au (mg/L)	Na (mg/L)
0.20	25.31	11587	19.46	12310	17.46	28980
0.60	50.76	5109	28.21	8212	27.05	17560
1.0	104.5	1734	57.66	2930	83.23	2789
1.4	138.1	932.7	106.5	1019	130.9	1127
2.0	136.9	522.4	117.9	498.3	126.1	620.1
2.4	122.0	409.5	99.27	370.6	110.0	518.7
3.0	90.32	289.3	74.12	281.9	67.72	286.1
3.6	67.19	223.8	54.52	224.5	48.09	213.7
4.0	55.22	192.0	43.57	198.6	39.59	197.8
4.6	42.25	155.7	32.68	169.2	30.24	184.9
6.0	24.74	121.7	17.94	114.8	16.94	128.8
9.0	11.44	50.66	8.058	62.26	6.987	70.08
11	8.239	28.48	5.814	48.62	5.172	59.29
15	5.452	16.32	3.894	29.00	3.452	33.49
20	1.698	8.562	1.862	14.37	2.014	20.15

Table C. 18. ICP result of both no-pre-treated and pre-treated and rinsed at 80°C,0 rpm and 30minutes

Run 47: No Pre-treatment		
Bed volumes	**Au(mg/L)**	**Na(mg/L)**
0.20	0.0526	111.9
0.60	0.0385	160.6
1.0	0.0494	87.21
1.4	0.0674	53.57
2.0	0.1091	31.04
2.4	0.1323	23.92
3.0	0.1587	19.90
3.6	0.1847	17.29
4.0	0.2195	15.18
4.6	0.2356	13.10
6.0	0.2938	10.63
9.0	0.3940	10.65
11	0.4371	7.068
15	0.4896	6.519
20	0.5223	5.607

Run 51:Pre-treated and rinsed		
Bed volumes	**Au(mg/L)**	**Na(mg/L)**
0.20	5.310	1135
0.60	6.810	776.5
1.0	7.320	836.3
1.4	10.14	541.6
2.0	13.94	385.1
2.4	16.48	323.3
3.0	18.32	273.2
3.6	18.90	226.7
4.0	18.81	197.0
4.6	17.74	170.9
6.0	14.56	131.4
9.0	7.370	97.67
11	3.700	70.51
15	1.790	52.95
20	0.9600	43.84

Table C. 19: ICP result for validation of statistical model.

Run 48: 53°C, 0rpm and 30mins				Run49: 25°C, 600rpm, 30mins				Run 50: 80°C, 600rpm and 30mins		
Bed volumes	Au(mg/L)	Na(mg/L)		Bed volumes	Au(mg/L)	Na(mg/L)		Bed volumes	Au(mg/L)	Na(mg/L)
0.20	4.660	64.17		0.20	0.990	6057		0.20	2.530	7120
0.60	4.150	6494		0.60	1.230	7646		0.60	1.950	8618
1.0	1.630	8967		1.0	4.740	2162		1.0	4.000	3974
1.4	3.160	4601		1.4	10.23	858.8		1.4	10.23	1343
2.0	8.770	1399		2.0	17.11	474.5		2.0	18.04	670.7
2.4	16.39	631.9		2.4	19.50	377.5		2.4	22.18	515.9
3.0	20.32	498.8		3.0	21.72	298.9		3.0	25.50	383.4
3.6	26.45	286.8		3.6	22.96	247.7		3.6	27.10	310.7
4.0	25.97	250.7		4.0	23.20	219.5		4.0	26.05	264.8
4.6	23.00	196.3		4.6	21.51	183.1		4.6	22.66	227.5
6.0	18.66	160.1		6.0	15.92	123.0		6.0	16.52	157.1

Titration analysis for CN^-

Table C. 20. Titration result at 25°C, 0rpm, No-AC

R1 (25°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	8.752	0.5830
15mins	S2	8.956	0.5970
30mins	S3	8.860	0.5910
45mins	S4	8.766	0.5840
60mins	S5	8.862	0.5910

Table C. 21. Titration result 25°C,600 rpm, No-AC

R2 (25°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	8.788	0.5860
15mins	S2	8.838	0.5890
30mins	S3	8.647	0.5760
45mins	S4	8.550	0.5700
60mins	S5	8.599	0.5730

Table C. 22. Titration result at 25°C, 1200 rpm, No-AC

R3 (25°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	8.576	0.5720
15mins	S2	8.550	0.5700
30mins	S3	8.555	0.5700
45mins	S4	8.589	0.5730
60mins	S5	8.550	0.5700

Table C. 23. Titration result at 53°C, 0 rpm, No-AC

R4 (53°C, 0rpm)		Vol ($AgNO_3$)(ml)	CN-(Molar)
Initial conc	S1	8.742	0.5830
15mins	S2	8.838	0.5890
30mins	S3	8.862	0.5910
45mins	S4	8.935	0.5960
60mins	S5	8.742	0.5830

Table C. 24. Titration result at 53°C, 600 rpm, No-AC

R5 (53°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	8.732	0.5820
15mins	S2	8.951	0.5970
30mins	S3	8.550	0.5700
45mins	S4	9.170	0.6110
60mins	S5	9.201	0.6130

Table C. 25. Titration result at 53°C, 1200 rpm, No-AC

R6 (53°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.000	0.5840
15mins	S2	3.093	0.6020
30mins	S3	3.079	0.5990
45mins	S4	3.197	0.6220
60mins	S5	3.181	0.6190

Table C. 26. Titration result at 80°C, 0 rpm, No-AC

R7 (80°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.186	0.6200
15mins	S2	3.496	0.6800
30mins	S3	3.662	0.7130
45mins	S4	3.969	0.7720
60mins	S5	4.385	0.85300

Table C. 27. Titration result at 80°C, 600 rpm, No-AC

R8 (80°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.183	0.6190
15mins	S2	3.380	0.6580
30mins	S3	3.770	0.7340
45mins	S4	4.274	0.8320
60mins	S5	4.981	0.9690

Table C. 28. Titration result at 80°C, 1200 rpm, No-AC

R9 (80°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.093	0.6020
15mins	S2	3.187	0.6200
30mins	S3	3.592	0.6990
45mins	S4	3.881	0.7550
60mins	S5	4.097	0.7970

Table C. 29. Titration result at 25°C, 0 rpm, in the presence of AC

R1 (25°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.093	0.6020
15mins	S2	2.989	0.5820
30mins	S3	3.000	0.5840
45mins	S4	3.000	0.5840
60mins	S5	2.899	0.5640

Table C. 30. Titration result at 25°C,600 rpm, in the presence of AC

R2 (25°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.989	0.5820
15mins	S2	3.000	0.5840
30mins	S3	3.000	0.5840
45mins	S4	2.885	0.5610
60mins	S5	2.899	0.5640

Table C. 31. Titration result at 25°C,1200 rpm, in the presence of AC

R3 (25°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.971	0.5780
15mins	S2	2.885	0.5610
30mins	S3	2.788	0.5430
45mins	S4	2.881	0.5610
60mins	S5	2.897	0.5640

Table C. 32. Titration result at 53°C, 0 rpm, in the presence of AC

R4 (53°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.999	0.5840
15mins	S2	2.881	0.5610
30mins	S3	2.899	0.5640
45mins	S4	2.977	0.5790
60mins	S5	2.892	0.5630

Table C. 33. Titration result at 53°C, 600 rpm, in the presence of AC

R5 (53°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.979	0.5790
15mins	S2	2.895	0.5630
30mins	S3	2.999	0.5840
45mins	S4	2.993	0.5820
60mins	S5	2.989	0.5820

Table C. 34. Titration result at 53°C, 1200 rpm, in the presence of AC

R6 (53°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.979	0.5790
15mins	S2	2.881	0.5600
30mins	S3	2.979	0.5790
45mins	S4	2.977	0.5790
60mins	S5	2.898	0.5640

Table C. 35. Titration result at 80°C, 0 rpm, in the presence of AC

R7 (80°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.093	0.6020
15mins	S2	3.075	0.5980
30mins	S3	3.186	0.6200
45mins	S4	3.281	0.6380
60mins	S5	3.374	0.6570

Table C. 36. Titration result at 80°C, 600 rpm, in the presence of AC

R8 (80°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.186	0.6200
15mins	S2	3.289	0.6400
30mins	S3	3.594	0.6990
45mins	S4	3.972	0.7730
60mins	S5	4.669	0.9090

Table C. 37. Titration result at 80°C, 1200 rpm, in the presence of AC

R9 (80°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3	0.5840
15mins	S2	3.083	0.6000
30mins	S3	3.382	0.6580
45mins	S4	3.584	0.6970
60mins	S5	3.771	0.7340

Table C. 38. Titration result at 25°C, 0 rpm, in the presence of AC-Au

R1 (25°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.972	0.5780
15mins	S2	2.993	0.5820
30mins	S3	2.995	0.5830
45mins	S4	2.999	0.5840
60mins	S5	2.977	0.5790

Table C. 39. Titration result at 25°C, 600 rpm, in the presence of AC-Au

R2 (25°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.977	0.5790
15mins	S2	2.999	0.5840
30mins	S3	3.075	0.5980
45mins	S4	2.978	0.5800
60mins	S5	3.000	0.5840

Table C. 40. Titration result at 25°C, 1200 rpm, in the presence of AC-Au

R3 (25°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.000	0.5840
15mins	S2	2.989	0.5820
30mins	S3	2.977	0.5790
45mins	S4	2.881	0.5610
60mins	S5	2.978	0.5800

Table C. 41. Titration result at 53°C, 0 rpm, in the presence of AC-Au

R4 (53°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.075	0.598
15mins	S2	3.000	0.584
30mins	S3	3.000	0.584
45mins	S4	3.075	0.598
60mins	S5	3.000	0.584

Table C. 42. Titration result at 53°C, 600 rpm, in the presence of AC-Au.

R5 (53°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.075	0.5980
15mins	S2	3.000	0.5840
30mins	S3	3.000	0.5840
45mins	S4	3.000	0.5840
60mins	S5	3.090	0.6010

Table C. 43. Titration result at 53°C, 1200 rpm, in the presence of AC-Au

R6 (53°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	3.075	0.5980
15mins	S2	2.998	0.5830
30mins	S3	2.899	0.5640
45mins	S4	2.987	0.5810
60mins	S5	3.000	0.5840

Table C. 44. Titration result at 80°C, 0 rpm, in the presence of AC-Au

R7 (80°C, 0rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.978	0.5800
15mins	S2	3.093	0.6020
30mins	S3	3.198	0.6220
45mins	S4	3.354	0.6530
60mins	S5	3.584	0.6970

Table C. 45. Titration result at 80°C, 600 rpm, in the presence of AC-Au

R8 (80°C, 600rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.977	0.5790
15mins	S2	3.079	0.5990
30mins	S3	3.487	0.6790
45mins	S4	3.686	0.7170
60mins	S5	4.089	0.7960

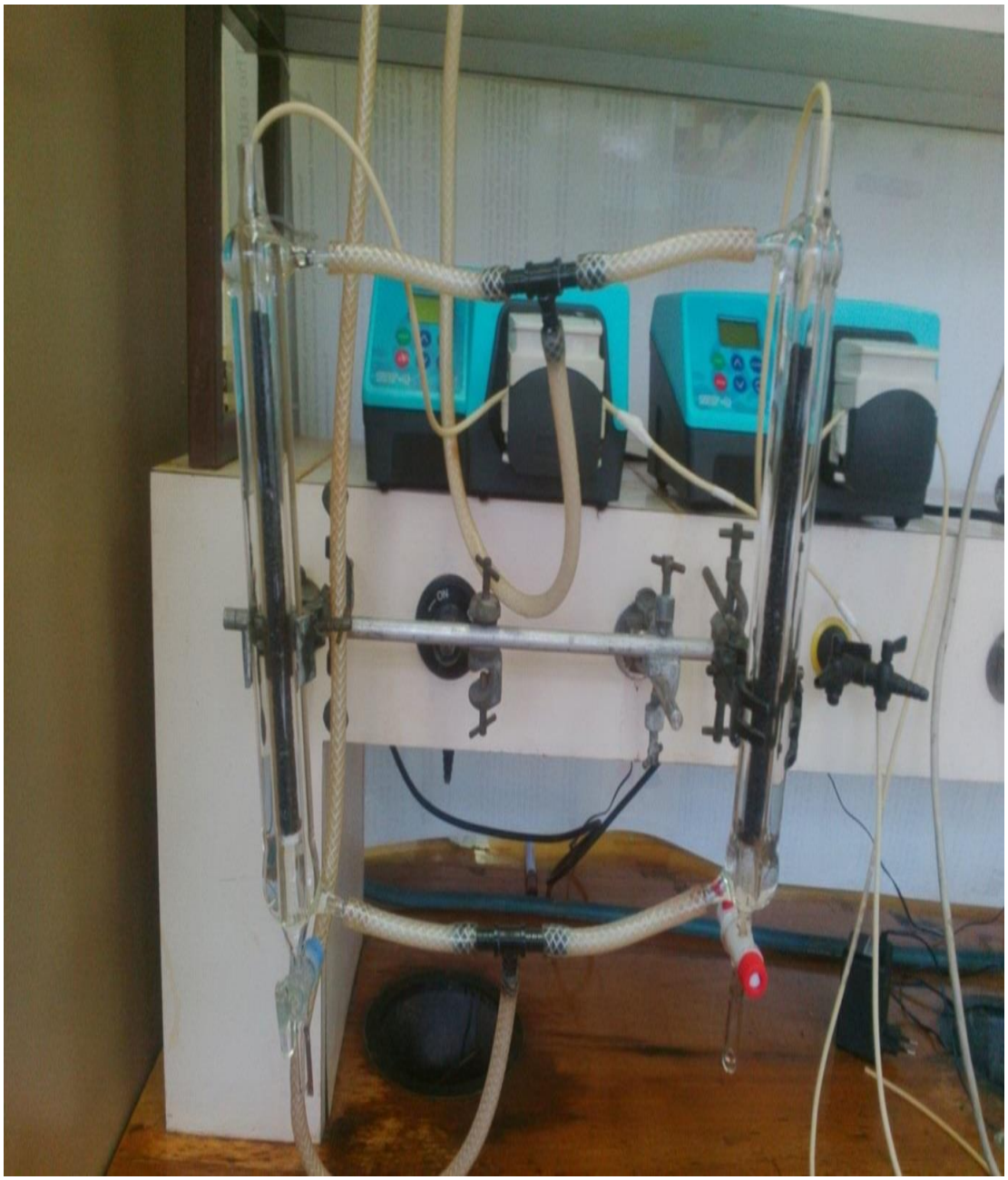
Table C. 46. Titration result at 80°C, 1200 rpm, in the presence of AC-Au

R9 (80°C, 1200rpm)		Vol ($AgNO_3$)(mL)	CN-(Molar)
Initial conc	S1	2.989	0.5820
15mins	S2	3.176	0.6180
30mins	S3	3.374	0.6570
45mins	S4	3.778	0.7350
60mins	S5	3.969	0.7720

Appendix D: Pictures of experimental setup

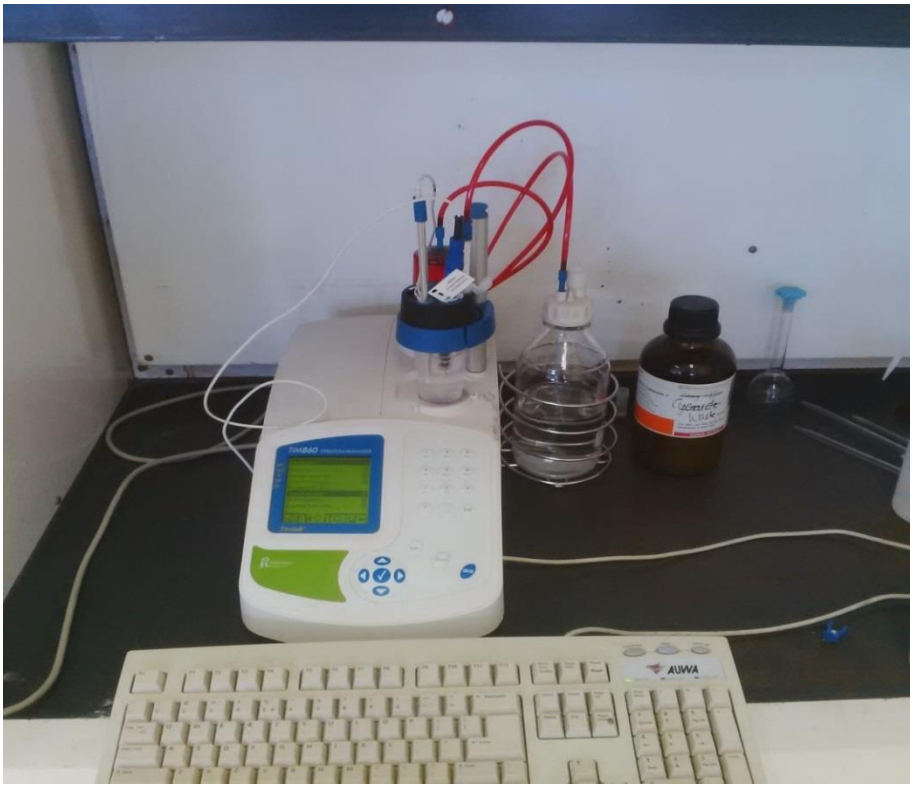
Adsorption

Pre-treatment



Elution set-up

Dissolved oxygen meter and probe



Automatic titrating machime

Pre-treatment setup connected to oxygen supply

Appendix E: Publication based on this thesis

Non-refereed paper presented at international conference.

- Oladele, T.P., Snyders, C.A., Bradshaw, S.M., 2015. Effect of temperature, contact time and agitation speed during pre-treatment on elution. *Precious Metals'15*, Falmouth, UK, 11-12 May 2015.

Refereed full length paper presented at world gold conference and accepted for publication SAIMM World gold conference proceedings.

- Oladele, T.P., Snyders, C.A., Bradshaw, S.M., 2015. Effect of temperature, contact time and agitation speed during pre-treatment on gold elution. *World Gold conference 2015*, Johanesburg, South Africa, 28th September-1 October 2015.