

The extraction of precious metals from an alkaline cyanided medium by granular activated carbon

by

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DECLARATION

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SYNOPSIS

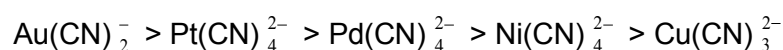
A 2 stage heap leach process to extract base and precious metals from the Platreef ore is currently being investigated industrially. A first stage bioleach is used to extract the base metals. In the 2nd stage, cyanide is used as the lixiviant at high pH to extract the platinum group metals and gold. By analogy with current gold recovery practices, the present study investigates the preferential and quantitative adsorption of precious metals (Pt, Pd, Rh and Au) over base metals (Cu, Ni and Fe) from an alkaline cyanide medium, by means of granular activated carbon.

Experiments were designed statistically to optimise the process parameters using synthetic alkaline cyanide solutions close in composition to those expected from plant leach solutions. The statistical approach allowed the development of a reliable quantitative approach to express adsorption as a response variable on the basis of a number of experiments. A $2_{IV}^{(7-2)}$ fractional factorial design approach was carried out in a batch adsorption study to identify significant experimental variables along with their combined effects for the simultaneous adsorption of Pt(II), Pd(II), Rh(III) and Au(I). The adsorbent was characterized using SEM-EDX, and XRF. Precious metals adsorption efficiency was studied in terms of process recovery as a function of different adsorption parameters such as solution pH, copper, nickel, free cyanide ion, thiocyanate, initial precious metal (Pt, Pd, Rh and Au) ion and activated carbon concentrations.

It was shown that adsorption rates within the first 60 minutes were very high (giving more than 90% extraction of precious metals) and thereafter the adsorption proceeds at a slower rate until pseudo-equilibrium was reached. Among the different adsorption parameters, at 95% confidence interval, nickel concentration had the most influential effect on the adsorption process followed by the adsorbent concentration. Adsorption of Ni was found to proceed at approximately the same rate and with the same recovery as the precious metals, showing a recovery of approximately 90% in two hours. The kinetics of Cu adsorption were slower, with less than 30% being recovered at the 120 minute period. This suggests that the co-adsorption of Cu can be minimised by shortening the residence time.

Adsorption of Fe was found to be less than 5%, while the recovery of Rh was negligibly small. The effect of thiocyanate ion concentration was not as important as the effect of free cyanide ion concentration but still had some influence. The correlation among different adsorption parameters was studied using multivariate analysis.

The optimum experimental conditions resulted in a solution with pH of 9.5, [Cu(I)] of 10 ppm, [Ni(II)] of 10 ppm, [CN⁻] of 132.44 ppm, [SCN⁻] of 98.95 ppm, [PMs] of 2.03 ppm and [AC] of 10 g/L. Under these conditions, predicted adsorption percentages of Pt, Pd and Au were approximately 98, 92 and 100%, at the level of 95% probability within two hours as an effective loading time. The negative values of ΔG° for all ions under optimum conditions indicate the feasibility and spontaneous nature of the adsorption process. Chemisorption was found to be the predominant mechanism in the adsorption process of Pt(II), Pd(II) and Au(I). Based on their distribution coefficients, the affinity of activated carbon for metal ions follows the selectivity sequence expressed below.



Finally, it is important that additional research and development activities in the future should prove the economic viability of the process. Future work is also needed to investigate the adsorption of precious metals (PMs) by comparing the efficiencies and kinetics of adsorption when using sodium hydroxide (in this study) or lime, respectively, in order to control the pH.

OPSOMMING

'n Tweefasige hooploogproses vir die ontginning van basis- en edelmetale van die Platirf-erts word tans industrieel ondersoek. 'n Eerstefase-bioloog word gebruik om die basismetale te ontgin. In die 2^{de} fase word sianied gebruik as die uitloog by hoë pH om die platinum-groepmetale en goud te ontgin. Na analogie van hedendaagse goudherwinningspraktyke het die huidige studie die voorkeur- en kwantitatiewe adsorpsie van edelmetale (Pt, Pd, Rh en Au) bo basismetale (Cu, Ni en Fe) vanuit 'n alkaliese sianiedmedium met behulp van korrelrige geaktiveerde koolstof ondersoek.

Eksperimente is op statistiese wyse ontwerp om die parameters van die proses te optimaliseer deur van sintetiese alkaliese sianiedoplossings wat in hulle samestelling nou ooreenstem met dié wat van oplossings van plant-loog verwag word, gebruik te maak. Die statistiese benadering het die ontwikkeling van 'n betroubare kwantitatiewe benadering om adsorpsie as 'n responsveranderlike op grond van 'n aantal eksperimente uit te druk, moontlik gemaak. 'n $2_{IV}^{(7-2)}$ -Fraksionele faktorale ontwerp-benadering is tydens 'n lot-adsorpsiestudie gevolg om beduidende eksperimentele veranderlikes tesame met hulle gekombineerde uitwerkings vir die gelyktydige adsorpsie van Pt(II), Pd(II), Rh(III) en Au(I) te identifiseer. Die adsorbeermiddel is met behulp van SEM-EDX en XRF gekenmerk. Adsorpsiedoeltreffendheid van edelmetale is bestudeer ten opsigte van proseskinetika en herwinning as 'n funksie van verskillende adsorpsieparameters soos oplossing-pH, koper, nikkel, vry sianiedioon, tiosianaat, aanvanklike edelmetaal (Pt, Pd, Rh en Au)-ioon en geaktiveerde koolstofkonsentrasies.

Daar is aangetoon dat adsorpsietempo's binne die eerste 60 minute baie hoog was (het meer as 90% ekstraksie van edelmetale opgelewer) en daarna het die adsorpsie teen 'n stadiger tempo voortgegaan totdat pseudo-ekwilibrium bereik is. Onder die verskillende adsorpsieparameters, by 95%-vertroubaarheidsinterval, het nikkel-konsentrasie die grootste invloed op die adsorpsieproses gehad, gevolg deur konsentrasie van die adsorbeermiddel. Daar is bevind dat die adsorpsie van Ni teen nagenoeg dieselfde tempo en met dieselfde herwinning as die edelmetale voortgegaan het, wat ná twee uur 'n herwinning van nagenoeg 90% getoon het. Die kinetika van Cu-adsorpsie was stadiger, met minder as 30% wat teen die 120-minute-tydperk herwin is. Dit dui daarop dat die ko-adsorpsie van Cu tot die minimum beperk kan word deur verkorting van die verblyftyd.

Daar is bevind dat die adsorpsie van Fe minder as 5% is, terwyl die herwinning van Rh onbeduidend klein was. Die uitwerking van die konsentrasie van die tiosianaatone was nie



so belangrik as die uitwerking van die konsentrasie van vry sianiedione nie maar het steeds 'n mate van invloed gehad. Die korrelasie tussen verskillende adsorpsieparameters is met behulp van meerveranderlike analise bestudeer.

Die optimale eksperimentele toestande het gelei tot 'n oplossing met 'n pH van 9.5, [Cu(I)] van 10 dpm, [Ni(II)] van 10 dpm, [CN⁻] van 132.44 dpm, [SCN⁻] van 98.95 dpm, [EM'e] van 2.03 dpm en [AC] van 10 g/L. Onder hierdie toestande was die voorspelde adsorpsiepersentasies van Pt, Pd en Au nagenoeg 98, 92 en 100%, op die vlak van 95%-waarskynlikheid binne twee uur as 'n doeltreffende laaityd. Die negatiewe waardes van ΔG° vir alle ione onder optimale toestande dui op die uitvoerbaarheid en spontane aard van die adsorpsieproses. Daar is bevind dat chemisorpsie die deurslaggewende meganisme by die adsorpsieproses van Pt(II), Pd(II) en Au(I) is. Gebaseer op hulle distribusiekoëffisiënte volg die affiniteit van geaktiveerde koolstof vir metaalione die selektiwiteitsvolgorde soos hieronder voorgestel.



Laastens, dit is belangrik dat addisionele navorsing en ontwikkelingsaktiwiteite in die toekoms die ekonomiese haalbaarheid van die proses bewys. Werk in die toekoms is nodig om die adsorpsie van edelmetale (EM'e) te ondersoek deur vergelyking van die doeltreffendhede en kinetika van adsorpsie wanneer natriumhidroksied (in hierdie studie) of kalk, onderskeidelik, gebruik word ten einde die pH te beheer.

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DEDICATION

To my dear wife Francine, my kids Celine, Herman, Adonai and Benita for your tolerance, patience, understanding and support.



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NOMENCLATURE

SYMBOLS	DESCRIPTION	UNITS
[AC]	Activated carbon concentration	g/L
a_{ij}	Competition coefficients describing the inhibition to the adsorption of component i by component j	-
C_0 or $[C]$	Initial analytical concentration of metal Pt(II), Pd(II), Rh(III) or Au(I)	mg/L
C_e	Equilibrium concentration	mg/L
$[C]_c^e$	Analytical concentration of metal on the carbon at equilibrium (interface)	mg/kg
$[C]_s^e$	Analytical concentration of metal in the solution at equilibrium (interface)	mg/L
k	Rate constant	h^{-1}
k_2	Pseudo-second-order rate constant for the adsorption process	$g \cdot mg^{-1} \cdot min^{-1}$
K_a	Ionisation constant of acid	-
K_D	Distribution coefficient	L/kg
K_{sp}	Solubility product	-
m	Mass of dry activated carbon	g
N	Number of points in data set	-
q	Amount of metal adsorbed (adsorption capacity) by the activated carbon	mg/g
q_t	Amount of metal adsorbed on the surface of the adsorbent at any time t	mg/g
q_e	Amount of metal adsorbed at equilibrium	mg/g
R	Universal gas constant (8.314)	J/mol·K
R^2	Correlation coefficient between experimental and modelled data	-
t	Time	min
T	Absolute temperature	K
V	Volume of the solution	L
Δ°	Standard Gibbs free energy	kJ/mol
% R	Adsorption percentage	%
%w/v	Weight/volume percentage: 1 gram of activated carbon in 100 mL of solution equals 1 %w/v	-
%v/v	Percentage by volume = [(volume of solute)/(volume of solution)] × 100%	-

LIST OF ABBREVIATIONS

ABBREVIATIONS	DESCRIPTIONS
Δ	Electrode potential difference
E_{Me}	Redox potential of the metal
E_c	Potential of the coal surface
AES	Atomic Emission Spectrophotometer
BMs	Base Metals
BIC	Bushveld Igneous Complex
AC	Activated Carbon
CIL	Carbon-In-Leach
CIP	Carbon-In-Pulp
CIS	Carbon-In-Solution
EDX	Energy-Dispersive X-ray spectroscope
2E	Two elements: Pt and Pd
GAC	Granular Activated Carbons
n	Valence
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
Lm	Ligand
M_e	Metal
min	Minute
SHE	Standard Hydrogen Electrode
PGMs	Platinum Group Metals
PLS	Pregnant leach solution
PMs	Precious metals
ppm	Parts Per Million (mg/L)
ppb	Parts Per Billion ($\mu\text{g/L}$)
rpm	Revolutions per minute
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy

WAD cyanide	Weak Acid Dissociable cyanide
XPS	X-ray Photoelectron Spectroscopy
XRF	X-ray Fluorescence

SUPERSCRIPTS		SUBSCRIPTS	
s	Interface	aq	Aqueous
		e	Equilibrium
		$0 \text{ or } i$	Initial state
GREEK LETTERS		t	Time
β	Stability constant	c	Activated carbon
β	Stability constant	s	Solution
$\eta_{...}$	Separation factor	cal	Calculated
		exp	Experimental

CHAPTER 1 : INTRODUCTION

This chapter provides an introduction to the research work presented in this thesis. It describes the research background and explains the motivation for pursuing this work.

The major portion of platinum and palladium produced today originate from the Bushveld Igneous Complex in South Africa. The most important reefs mined are the Merensky, Upper Group Two (UG2) and Platreef. Ore grades range from 3 to 8 g PGM/t, with associated nickel and copper in the 0.1 to 0.2% range present mainly as sulphides (Kyriakakis, 2005). The platinum group metals were initially recovered from high grade concentrate by the traditional matte-smelting technique. The smelting has serious environmental impacts – large carbon footprint due to huge quantities of FeS per PGM-unit which has to be converted to Fe-bearing slag and SO₂ gas – and the lengthy overall flowsheet resulting in unavoidable losses of PGMs (Chen and Huang, 2006).

However high-grade precious metal reserves have been diminished and the remaining reserves contain low-grade ores associated with high chromite grades (in the case of UG2) or high pyrrhotite content (in the case of Platreef), which invariably leads to high smelting costs (low-grade) and smelter integrity risks (due to the chromite). In this regard a low-cost hydrometallurgical process, alternative to the smelting, consisting of a heap bioleach process to first extract the base metals (BMs); followed by a caustic rinse of the residue material and a heap cyanidation process to subsequently extract the PGMs, has been suggested for treating low-grade ore concentrate (Mwase, 2009). Lonmin Plc has developed and patented a novel integrated hydrometallurgical method, suitable to treat low-grade PGM sulphide ores efficiently and economically (Bax *et al.*, 2009).

Unlike the gold industry, where carbon adsorption has found widespread use in extracting value from low-grade solutions, no such methods have been widely applied at an industrial level in the PGM industry. Therefore the recovery of platinum, palladium and eventually other noble metals from their alkaline cyanide solutions by adsorption onto carbonized supports, is complex and requires extensive fundamental studies of the mechanism by which activated carbon adsorbs; with particular regard to possible impurities in the ore body and leach solution which may interfere. A literature survey of the above requirements revealed very little relevant information. This work was aimed to fill this gap.

1.1 PROBLEM STATEMENT

The present research formed part of a concomitant program of work at the University of Cape Town on heap bioleaching and cyanide leaching, exploring the practicability of a two stage heap leach process for the extraction and recovery of PGMs and Au from the Platreef ore body, with the specific task of investigating the technical feasibility of using granular activated carbons (GAC) to adsorb Pt(II), Pd(II), Rh(III) and associated Au(I) from the pregnant leach solution (PLS). Its purpose was to examine the role that some selected parameters play in understanding and optimizing the conditions favouring the simultaneous adsorption of Pt(II), Pd(II), Au(I) and Rh(III) on activated carbon. The recent papers by Mwase *et al.* (2012) provide further general background to the process development.

Following their analogous behaviour to cyanidation (PGMs and Au), the application of carbon adsorption for extracting PGMs is much more time saving for comparing results than the use of underdeveloped and/or costly techniques such as: chemical precipitation, solvent extraction, Merrill-Crowe process and resin exchange. PGM extraction is susceptible to large number of influences of which the feed composition is the main control parameter; thereby carbon adsorption was regarded as an invaluable asset for adsorbing PGMs that could lead to potential optimization. Previous PGM-carbon adsorption of various complexities has been attempted but still fall short of providing a complete picture of simultaneous extraction of Pt, Pd and Au in the presence of large amount of base metals, and then several scenarios such as high thiocyanate and nickel concentrations are yet to be addressed.

1.2 OVERVIEW OF TREATMENT METHODS FOR PRECIOUS METALS RECOVERY FROM LEACH SOLUTIONS

Various techniques for recovering precious metals from pregnant solutions after cyanide leaching, including solvent extraction, resin ion-exchange, Merrill-Crowe zinc precipitation technology and adsorption onto activated carbon, have been used (Kyriakakis, 2005; Cortina *et al.*, 1998; Kordosky *et al.*, 1992). Each method has its own advantages and disadvantages, and may be effective in recovery of precious metals from the common concentration of clear solutions, but may become less efficient or even inadequate when trace precious metal ions are to be recovered from cyanided pulp (e.g. solvent extraction).

However, the adsorption of precious metal cyanide ions onto activated carbon is probably the most suitable as large volumes of very dilute solutions can be treated economically. The adsorption method is widely used for aurocyanide treatment because of its convenient operation, effectiveness and relatively low cost. Activated carbon is the main adsorbent material used in the adsorption process due to its high specific surface area, which is

normally in the range of 800 to 1500 m²/g (Hu *et al.*, 2000; Hassler, 1963). Hence in this study, the analogous route to Au extraction was used for extracting PGMs.

1.2.1 Solvent extraction route

Efforts have been made to investigate the use of liquid extractants for various separations and purification processes involving base and precious metal ions. Recently, Mintek has developed a gold (from chloride media) refining process based on solvent extraction (Feather *et al.*, 1997). Mooiman and Miller (1991) have used tributyl phosphate (TBP) and dibutyl butyl phosphate (DBBP) as carriers for quantitative extraction of Au(I) from cyanide alkaline medium. They demonstrated that the adsorptive behaviour of Au(CN)₂⁻ in presence of solvating extractants is analogous to that observed onto activated carbon. Riveros (1990) studied the recovery of gold from real cyanide solutions using commercial quaternary amines and aromatic diluent, found that quaternary amines exhibited fast kinetics, high loading capacity, low water solubility and good selectivity for gold over base metals.

However according to Kargari *et al.* (2004), solvent extraction is very difficult for the separation of trace amounts of metal ions (\approx 0.1 ppm in this work) because of low driving force, and then a large amount of solvent is required. These make the extraction and stripping of desired species very expensive. Niu and Volesky (1999) stressed that solvent extraction is restricted to treatment of clarified solutions and liquid extractants have some solubility in water, which results in solvent and gold losses to the aqueous phase as well as a pollution issue.

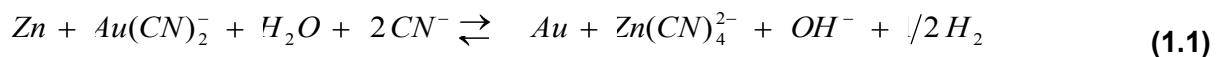
1.2.2 Resin ion-exchange process

Like solvent extraction, adsorption by ion-exchange resins often offers higher selectivity (Niu and Volesky, 1999). The uptake of gold and silver cyano complexes from dilute cyanide solutions can be accomplished with both strong and weak-base resins. Strong-base resins have the advantage of fast loading rates and high loading capacity, but with the drawback of poor selectivity with respect to base metals and more difficult elution than weak-base resins (Ciminelli, 2002). According to Grosse *et al.* (2003), the use of resin adsorbents for the recovery of precious metals is relatively underdeveloped area of hydrometallurgy. The principal reason behind this is the abundance and efficacy of cheap activated carbon adsorbents. Wan and Miller quoted by Flett (1992) caution that additional contributions in the area of resin synthesis are still required, and that elution procedures for strong base resins are still not satisfactory despite the demonstrated ability to elute gold from strong base resins with alkaline zinc cyanide.

1.2.3 Merrill – Crowe zinc precipitation technology

The Merrill-Crowe process is a classic cementation reaction involving oxidation and reduction. Normally it is applied to solutions generated either from a solid-liquid separation step downstream of a grinding and leaching operation, or from solutions originating from heap-leaching, if the concentration of gold in solution is not below a nominal of 1.42 ppm (Heinen *et al.*, 1978). It has also been used on eluates from carbon stripping and solutions from intensive cyanidation (Walton, 2005). The process was first used to treat hot, high-grade solutions produced by carbon elution in 1981 in the United States and South Africa, and have subsequently been applied widely around the world as an alternative to electrowinning (Marsden and House, 2006).

The Merrill-Crowe procedure, in which gold is precipitated with zinc dust in accordance with the reaction shown in Equation 1.1, is the traditional technology (Laxen *et al.*, 1979). The precipitant, carefully chosen for redox potential, stoichiometrically reduces the precious metals in solution. The more common precipitants are copper and zinc, although iron or aluminium are sometimes employed (Grosse *et al.*, 2003).



The drawback with the Merrill-Crowe process is the separation stage prior to cementation. The solution is clarified and degassed to remove the remaining solids and oxygen, respectively. Such a process is costly and usually results in a loss of approximately 1% of the gold in solution (Fleming, 1992).

From the previously published literature, the results are sometimes conflicting and often the conditions used are not described in much detail. Miller *et al.* (1990) stated that the Merrill-Crowe process is generally used for gold precipitation from dilute aurocyanide solutions. According to Parga *et al.* (2007), the process is preferred for a very rich pregnant solution. Paul *et al.* (1983) have defined a concentrated aurocyanide solution as having gold concentrations ranging from 50 to 2000 ppm, while dilute aurocyanide solutions from heaps are defined as those having gold concentrations in the range of 1 to 10 ppm Au.

McDougall and Hancock (1981) have demonstrated that activated carbon is an excellent scavenger for small concentrations of dissolved gold (0.2 mg/L or less), while the Merrill-Crowe process as currently practised in South Africa requires very careful control in order to yield barren solutions analysing less than 0.01 ppm of gold. Thus it is sometimes difficult to interpret the results found from this literature, given their inconsistencies.

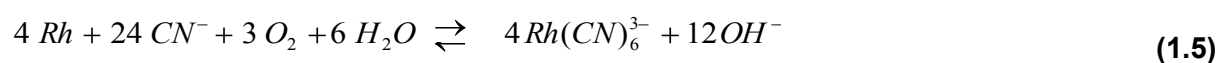
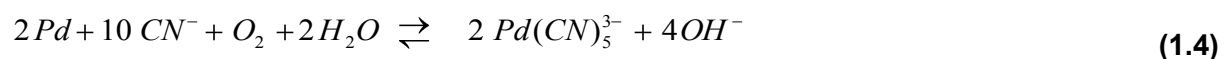
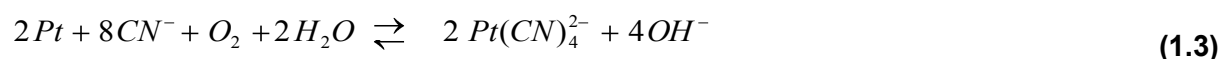
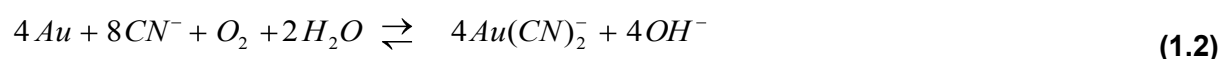
Furthermore, many of the more common constituents of gold-cyanidation solutions such as sodium sulphide, cyanide complexes of copper, arsenic and antimony significantly decrease the cementation recovery of gold when they are present in concentrations of more than 10^{-7} M (Davidson *et al.*, 1979). Fleming (1992) argued that the only species that have a marked deleterious effect on cementation process – effect observed even at very low concentrations of 1 ppm and lower – appear to be sulphide ions, soluble compounds of arsenic and antimony.

Finally, the Merrill-Crowe process is preferred over carbon adsorption for the treatment of high-grade gold solutions, or for solutions which contain a large amount of silver; typically a recoverable silver content of more than 10 g/t (0.3 oz/ton) of ore (Kappes, 2005; Walton, 2005; Kongolo and Mwema, 1998).

1.2.4 Cyanidation and possible extraction methods from the PLS, analogous to those used for Au

Mwase *et al.* (2012) and Baghalha *et al.* (2009) observed that at room temperature and pressure, the reaction between sodium cyanide and platinum group metals proceeds slowly due to poor kinetics. Cortina *et al.* (1998) studied speciation in leaching process of platinum group metals (PGMs) and revealed that at room temperature (25°C) $Pt(CN)_4^{2-}$, $Pd(CN)_5^{3-}$ and $Rh(CN)_6^{3-}$ are the predominant species present in solution over the pH working range of 9 to 12.5. Other metal-cyanide complexes in typical mine leaching solutions such as $Ag(CN)_2^-$, $Fe(CN)_6^{4-}$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$ have been also reported by Nguyen *et al.* (1997a).

As in the case of gold, the reactions for PGMs dissolution (Equations 1.3 to 1.5) reported follow kinetics described by the Elsner Equation 1.2 (Chen and Huang, 2006; Aguilar *et al.*, 1997; Trexler *et al.*, 1990).



The recovery of gold by adsorption of aurocyanide complexes onto activated carbon is a well-established commercial metallurgical process. The carbon-in-pulp (CIP) process, which

eliminates the necessity of filtrating and thickening, is a complex technique involving treatment with cyanide under aerobic conditions at high pH (9.5 to 11), to give $\text{Au}(\text{CN})_2^-$ ions according to the generally accepted Elsner Equation 1.2 (Heinen *et al.*, 1978). The ions are then recovered by adsorption on activated carbon, followed by elution process in cyanide caustic solution and electrowinning of the gold (Acton, 1982). A similar approach may be envisaged for PGMs extraction.

1.2.5 Comparison of aforementioned approaches

As can be seen, both solvent extraction and Merrill-Crowe require solid-liquid separation to produce clear solutions before their application, while resin ion-exchange is more costly than adsorption onto activated carbon (Aktas and Morcali, 2011). Thus, complication and additional expenses render the carbon adsorption process more attractive (Sun and Yen, 1993). Heinen *et al.* (1978) stressed that the preferred method for recovering precious metal values from heap-leach effluents when the concentration of the metal ion in solution is below a nominal of 1.42 ppm is by adsorption on activated carbon. According to Mwase *et al.* (2012) the expected concentration of PGMs in the solution under investigation is most likely to be in the ppm range.

This makes adsorption on GAC potentially appropriate for the current study, because of the expected PGM and Au concentrations ranging between 0.5 to 1 ppm each. Barnes *et al.* (2000) indicated that the process is repeated in several stages, or tanks, called cascades. The barren effluent, which is discarded, contains less than 0.04 ppm of gold. By replacing the Merrill-Crowe zinc cementation step, carbon-in-pulp (CIP) recovery provides a process that allows the treatment of lower grade and problematic ores (e.g. high-clay ores), at lower capital, operating costs and higher metal recoveries (Staunton, 2005). Although the CIP process is generally used to treat low grade gold ore feed, it can also be used for concentrated feed (Acton, 1982).

1.2.6 Gold cyano complex adsorption mechanisms proposed in the literature

Despite the extensive industrial application of this technology (carbon adsorption) and numerous studies made on the subject, the mechanism of the adsorption of metal cyano complexes, including gold, silver etc., onto activated carbons still remains assumptive (Jia *et al.*, 1998). However, it transpires from the examination of the literature, a common consensus among most authors with regard to the occurrence of two distinct and successive (or overlapping) mechanisms of metal cyanides adsorption on activated carbon. These incorporate both the external film and intraparticle diffusion. This assumption is made by most authors when modelling the adsorption of gold on activated carbon (e.g. Fleming and Nicol, 1984; Westermarck, 1975).

1.2.7 Platinum group metal (PGM) complexes uptake

Literature for adsorption of PGMs in cyanide medium using activated carbon is scarce. Ageeva *et al.* (2001) had examined the adsorption behaviour of platinum, palladium and gold from chloride solutions using activated carbon. With regard to Pt, Pd and Au adsorption, optimal conditions were found to be pH of 1 to 3. Chand *et al.* (2009) studied the adsorption process in a hydrochloric acid medium to evaluate the extraction of precious metals from other divalent base metals like Fe, Ni, Cu. They used porous carbon prepared by carbonisation from agro-waste. Preferential quantitative adsorption of Au, Pd and Pt was achieved over various base metals. Cox *et al.* (2005) reported that activated carbon prepared from flax shive can be used for gold, silver, palladium and platinum adsorption in hydrochloric acid medium. Adsorption efficiency decreased in the order $\text{Au(III)} > \text{Pd(II)} > \text{Ag(I)} > \text{Pt(II)} \approx \text{Pt(IV)}$. This behaviour could be associated with their respective redox potentials (Simanova *et al.*, 2008).

Fu *et al.* (1995) reported on the reducing action of activated carbon fibers. Depending on the reaction conditions (acidic or alkaline), they observed that metallic platinum precipitated on the activated carbon fiber surface either as elemental platinum or PtO. Chen *et al.* (2007) similarly studied, in hydrochloric acid medium, the reduction-adsorption behaviour of platinum ions on activated carbon fibers. They indicated that most of the adsorbed platinum ions were reduced into metallic platinum and about 25% of platinum atoms remained as Pt(II) or Pt(IV). According to Simanova *et al.* (2008), activated coals and activated carbon fibers either usual or modified (for example with coordinating compounds) are capable of quantitatively and selectively adsorbing trace amounts of the platinum metals from solution.

Although these studies were carried out in clarified synthetic solutions, they present one common point that activated carbon exhibits not only pronounced ability to ion-exchange, but also significant reducing ability. Acton (1982) revealed that the oxidation treatment of the activated carbon not only can be used to selectively erode its surface, create porosity and thereby increase the surface area; but it gives a variety of oxygen-containing functional groups on the surface which can play an important role in the adsorption process. Therefore, knowledge of all aspects taking place at the activated carbon – liquid interface will channel to a better understanding of the entire PGMs adsorption process. Consequently, this will in turn lead to an efficient process and increased adsorption efficiency.

1.3 OBJECTIVES OF THE RESEARCH

From the literature review, it was apparent that much research has been and is still being devoted to the performance of gold adsorption and how to improve such performance. There were no reliable data available in open literature on PGM adsorption behaviour using

activated carbon in an alkaline cyanided medium. Thereby, the problem of precious metals recovery from their cyanided solution by adsorption onto carbonised supports may be complex and requires extensive fundamental studies of the mechanism.

The present work deals with the evaluation of granular activated carbon as a carrier, for the adsorption of PGMs (Pt, Pd, Rh) and Au from cyanided leach solution obtained from Platreef ore after biooxidation and cyanidation processes as depicted in Figure 1.1. This study investigated – using activated carbon for adsorbing precious metals – the important factors which impact the reaction kinetics and to optimize the process. The effect of various factors, viz., solution pH, copper, nickel, free cyanide ion, thiocyanate, adsorbate and adsorbent concentrations, on the metal anions adsorption were scrutinized. An attempt was made to elucidate the mechanism of precious metals adsorption.

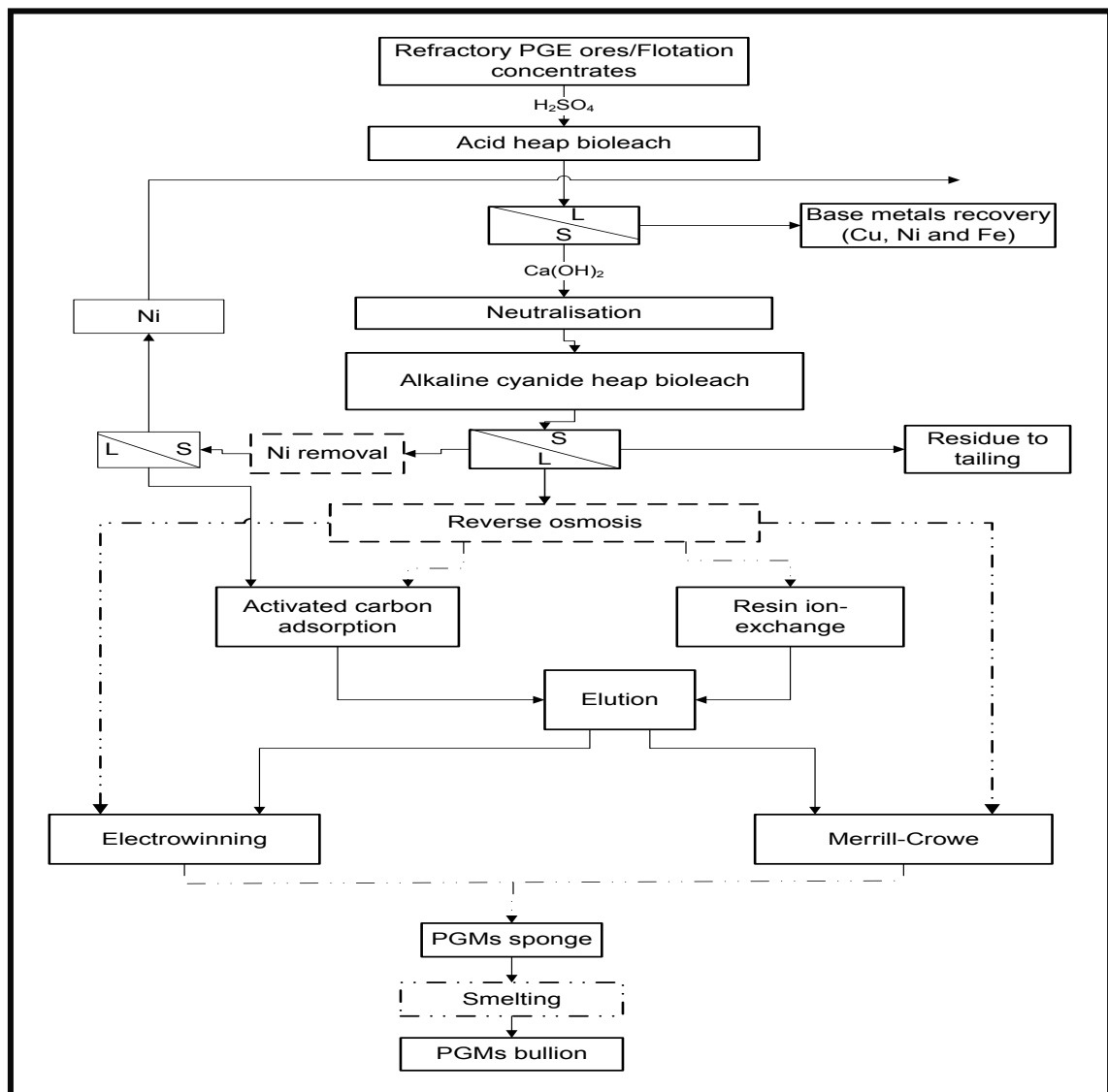


Figure 1.1: Conceptual flowsheet for precious and base metals recovery

In order to complete the abovementioned aim, the following tasks have been identified for the research, namely:

- To investigate possible factors influencing the adsorption process, emphasizing the effect of the selected parameters. Furthermore, the test program should provide the opportunity to elucidate the possible transport mechanism.
- To investigate and develop a simple empirical model that can predict the extent to which activated carbon extraction methods can be used to adsorb PM ions from a cyanided leachate.

1.4 IMPORTANCE AND BENEFITS OF THE RESEARCH

This study will be of significance in developing efficient, cost effective procedure of PMs recovery from cyanided solution using activated carbon adsorption route. Moreover, this research project will provide the researcher with experimental values, which will be useful for a test on a pilot scale, as well as contribute to the academic discourse and debate within this discipline.

The objectives of the current study are encompassed in the following research questions:

- Can activated carbon be used to adsorb PGMs?
- What are the effects of key operating parameters?
- What is the loading capacity of the carbon?
- When the activated carbon exhibits its dual features (physical and chemical), which one is predominant over another?

1.5 RESEARCH DESIGN AND METHODOLOGY

Even though the traditional approach “one-factor-at-a-time” experimentation can be useful in finding predominant factors in a given situation, it is a time and energy consuming method (Diamond, 1989). Furthermore, since the results are valid only under fixed experimental conditions, prediction based on them for other conditions is uncertain (Robinson, 2000). Design of experiments is a process of testing using a structured plan in which the input factors are varied in an organized manner to optimize efficiently output responses of interest with minimal variability (Frey *et al.*, 2003).

Thus in order to achieve significant information with the smallest number of experiments, reducing overall working costs, fractional factorial design and scrutiny of tests were used in an attempt to not only predict adsorption rate accurately but also to incorporate selected operating parameters namely: solution pH, copper, nickel, free cyanide ion, thiocyanate, adsorbent and initial metal ion (Pt, Pd, Rh and Au) concentrations.

1.6 THESIS OVERVIEW

The first chapter of this thesis presents the overall objectives for the study. Currently used techniques for extracting PMs are also discussed. Chapter 2 is a review of the literature, providing background information on the extraction processes and a review of the methods employed in the recovery of gold and PGMs from cyanide solutions. Major references related to this study are cited. Several factors that influence the adsorption process performance are reviewed. This chapter provides a comprehensive overview of recent research and illuminates on-going investigations and open issues to provide a foundation for further study.

In Chapter 3, the experimental methodologies to address the problem are outlined. This chapter provides also the experimental procedure used to achieve the objectives expressed in section 1.3. Chapter 4 presents the findings of the preliminary adsorption tests, outlining the effects of iron, copper, nickel and thiocyanate on the adsorption of Pt(II), Pd(II) and Au(I). Chapter 5 provides a discussion of the results of the investigation. Quantitative data were analysed and the emergent findings of the investigation are presented in this chapter. The chapter also explores approaches involving formal statistical analysis to support the arguments on effects of process parameters.

Chapter 6 summarizes major findings of the entire research study. Recommendations for future research are also listed in this chapter. Appendix A gives the tabulation of experimental data derived from the screening and actual tests, whilst Appendix B provides figures. The tabulation of statistical data is displayed in Appendix C, while Appendix D provides the supporting calculations derived from synthetic stock solution preparation and mean particle size of activated carbon. Appendix E gives an overview of the risk management plan of the Akanani platinum project and Appendix F provides publications from this thesis.

CHAPTER 2 : LITERATURE REVIEW

This chapter provides an overview of relevant academic studies on the topic under discussion, as well as an evaluation of theory related to the subject. In addition it provides an overview of the approach taken as well as of the results obtained.

The most important parts in activated carbon-based recovery processes are the leaching and the adsorption sections, because the efficiency of these operations determines the amount of soluble metals lost in the residues from a plant. The need to treat increasingly low grade and/or refractory PGM ores and the continuing search for improvements in the economics of existing operations has led to several developments and innovations in PGM extraction metallurgy during the last two decades (Liddell and Adams, 2012; Prasad *et al.*, 1991). A comprehensive review exploring test-work on sulphide PGMs leaching, in which a variety of lixiviants were evaluated, has been presented by Green *et al.* (2004). However, more recent works by Mwase *et al.*, 2012; Chen and Huang (2006); Huang *et al.* (2006) have focused attention upon a direct hydrometallurgical processing of sulphide flotation concentrates.

2.1 MINERALOGY OF PLATREEF ORES

Three broad ore types are found within the Bushveld Igneous Complex (BIC) and exploited for their PGM values: the Merensky reef, Upper-Group-Two (UG2) reef and Platreef (Cramer, 2001). Numerous studies have been carried out on the mineralogy of the main PGM-bearing horizons in the Eastern and Western limbs of the Bushveld Complex (i.e. the Merensky and UG2 reefs), but new information is only just beginning to emerge on the mineralogy of the PGM-bearing lithologies of the Northern Limb (Hutchinson and McDonald, 2008).

Generally PGM ores are grouped into three primary classes based on the combination of PGMs content and the mode of geological occurrence (Xiao and Laplante, 2004): 1) PGM dominant ores, 2) Ni-Cu dominant ores, 3) Miscellaneous ores. The Platreef in the northern limb of the Bushveld Igneous Complex (BIC) area, near Potgietersrus can be classified in the second category. Grades are low on average, at 2 to 5 g/t, but with high nickel and copper grades of 0.2 to 0.3% and 0.15 to 0.20%, respectively (Cramer, 2001).

From their studies, Schouwstra and Kinloch (2000) found that the Platreef mineralogy consists of a complex assemblage of pyroxenites, serpentinites and calc-silicates. Both PGM and BM populations display large mineralogical variability in value as well as in distribution. The PGMs occurrence of the Platreef has been also described by Newell (2008). He

revealed a PGM assemblage dominated by different phases including: Pt-Pd tellurides, followed by the arsenides, alloys and sulphides. Newell (2008) argued that PGMs are coarser than those in the Merensky reef ores, PGM tellurides and arsenides are encapsulated in the silicate gangue. The following PGM minerals have been identified: Moncheite [(Pt,Pd)(Bi,Te)₂ – PtTe₂] + Merenskyite [(Pd,Pt)(Bi,Te)₂ – PdTe₂] >> Sperrylite (PtAs₂) > Isoferroplatinum (Pt₃Fe) > Braggite (Pt,Pd,Ni)S.

Cramer (2001) has indicated that PGM mineralogy in the Platreef is more complex and erratic. Tellurides and arsenides are more common minerals. Sperrylite (PtAs₂) is the most common PGM mineral, and the platinum-palladium ratios are typically 1:1 within the Platreef (Lee, 1996). Schouwstra and Kinloch (2000) found that common base metal sulphides include pyrrhotite (Fe_(1-x)S, 0 < x < 0.2), pentlandite (Ni,Fe)₉S₈ and chalcopyrite (CuFeS₂). PGM minerals frequently occur enclosed in or on grain boundaries of these base metal sulphides. Table 2.1 outlines the characteristics of Platreef PGM ore types, while the mineralisation of a typical Platreef flotation concentrate is displayed in Table 2.2.

**Table 2.1: Characteristics of Platreef PGM ore types
(Newell, 2008)**

Grade	PGMs (g/t)	3 to 4
	Ni (%)	0.36
	Cu (%)	0.18
PGMs grain size	40 to 200 µm	
Gangue minerals (%)	Pyroxene	80 to 90
	Plagioclase	10 to 20
	Chromite	3 to 5
	Talc	0.5 to 3

Recent work by Adams *et al.* (2010), identified the main sulphides in a sample of a composite concentrate as being pyrrhotite, chalcopyrite and pentlandite with minor pyrite. Fine grained PGM particles varied between 2 and 35 µm in size along the longitudinal axis were mainly locked in silicates and feldspars as well as in sulphide particles such as pentlandite and chalcopyrite. Table 2.2 displays the chemical composition of the concentrate.

Table 2.2: Ni/PGM Platreef concentrate (Adams *et al.*, 2010)

Elemental composition	Pt (g/t)	Pd (g/t)	Au (g/t)	Rh (ppb)	Ru (ppb)	Ni (%)	Cu (%)	Co (%)	S (%)
Content	1.8	2.8	0.5	128	153	1.5	1.2	0.07	8.5

2.2 EFFECT OF MINERALOGY ON CYANIDE LEACHING AND ADSORPTION ONTO ACTIVATED CARBON

While this study is mainly concerned with the adsorption processes, equally important is the knowledge of how the biohydrometallurgical process (upstream stage) could impact on the PM recovery step (e.g. CIP, CIL or CIS: downstream stage).

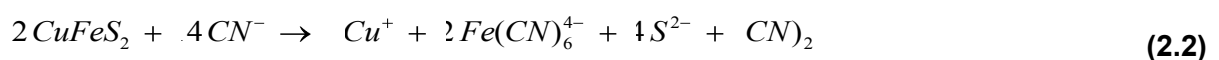
2.2.1 Pyrite – Pyrrhotite – Arsenopyrite

Pyrite (FeS_2) and arsenopyrite (FeAsS) are the major, common sulphide minerals in base and precious metal ores and concentrates. Swash (1988) has argued that the more arsenic-rich varieties of sulphide are likely to break down at a faster rate than the low-arsenic pyrite and arsenopyrite. However, pyrrhotite is the most reactive, the highest cyanide and oxygen consuming iron sulphide mineral due to the formation of $\text{Fe}(\text{OH})_3$ and SCN^- (Ellis and Senanayake, 2004). Lorenzen and van Deventer (1992) have demonstrated that minerals such as pyrrhotite and pyrite cause a significant decrease in the rate of gold dissolution, mainly as a result of complexes of iron cyanide and thiocyanate, respectively. Deschenes (2005) found that the negative effect on gold-leaching was manifested in the order expressed in Equation 2.1.



2.2.2 Copper

In cyanide solution, except for chrysocolla $(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ and chalcopyrite (CuFeS_2), the majority of copper minerals are readily leachable. Coderre and Dixon (1999) showed that in the presence of significant chalcopyrite, high consumption of cyanide could be expected owing to the irreversible formation of the hexacyanoferrate (II) complex as expressed in Equation 2.2.



Swash (1988) found that pyrrhotite and base-metal sulphides such as chalcopyrite (CuFeS_2), covellite (CuS) are cyanicides, and can consume both oxygen and cyanide during

cyanidation; thereby giving rise to problems in the extraction of precious metals. According to Deschenes (2005), copper sulphides usually show higher cyanide consumptions than iron sulphides.

A. Behaviour of copper on carbon adsorption processes

As stated earlier, copper dissolves readily in alkaline cyanide solution to give the di-, tri- and tetracyanocuprate (I) complexes, of which $\text{Cu}(\text{CN})_3^{2-}$ is the predominant complex ion; while $\text{Cu}(\text{CN})_2^-$ is the least stable complex and tends to disproportionate to $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_{\text{solid}}$ (Coderre and Dixon, 1999). On acidification or lowering of the cyanide level, $\text{Cu}(\text{CN})_2^-$ is formed, which is strongly adsorbed onto activated carbon, resulting in an increase in the rate of free cyanide (CN^-) destruction (van Deventer and Ross, 1991). The adsorption of copper species onto activated carbon increases in the following order expressed in Equation 2.3 (Marsden and House, 2006). This order could be related to their respective ionic solvation energy (charge density).

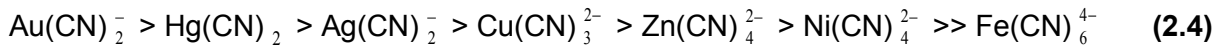


Marsden and House (2006) stated that copper concentration as low as 100 mg/L can interfere severely with gold adsorption processes. The molar ratio of cyanide to copper should be maintained at or above 4:1 in leach solutions prior to feeding the carbon adsorption processes. According to Nguyen *et al.* (1997b), under normal leaching conditions, the presence of copper, whether in synthetic or native form, causes the cementation of gold, which is strongly dependent on the cyanide concentration and temperature. In the presence of copper, polysulfides precipitate with copper to form CuS whose solubility product, K_{sp} , equals 6×10^{-16} at 25°C; with solubility of 2.34 ppb (Aylmore, 2005). The low value for the solubility product indicates that the salt is not very soluble and the concentration of ions in a saturated solution is very low.

However, in the presence of oxygen and sufficient free cyanide, the cemented gold can be redissolved into the solution (see Equation 1.2). Marsden and House (2006) stressed that, processes that treat materials containing high concentrations of cyanide-soluble copper, that is, yielding more than 200 mg/L Cu in solution; may be unsuitable for treatment by carbon adsorption because they require very careful control of pH and cyanide to allow satisfactory treatment.

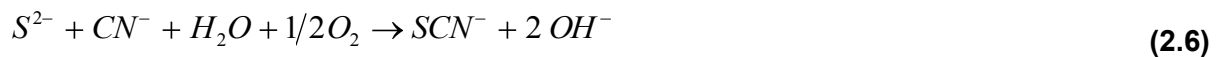
B. Behaviour of other metals

McDougall and Hancock (1981) have observed that, with the exception of copper and to a lesser extent nickel, metal-cyanide complexes have little effect on gold adsorption efficiency if they are present in very low concentrations. It can be seen (Equation 2.4) that activated carbon is highly selective for gold and silver over most other metal species. However Marsden and House (2006) have postulated that high loadings of nonprecious metals could be achieved onto activated carbon in the absence of significant precious metal values.



2.2.3 Sulphide mineral chemistry – Thiocyanate and Thiosulphate formation

It is generally believed that thiocyanate (SCN^-) is formed during cyanidation as a result of reactions between CN^- and sulphur species (solid or dissolved sulphur). Some of these reactions are listed in Equations 2.5 to 2.7 below (Botz *et al.*, 2001).



According to Coderre and Dixon (1999), thiosulphate is the primary product of sulphide oxidation above pH of 8.5, regardless of the S^{2-}/O_2 mole ratio, in accordance with the reaction shown in Equation 2.8.



Lan *et al.* (1994) found that the amount of elemental sulphur existing in the residue from bacterial leaching increased with the biooxidation time. Coderre and Dixon (1999) suggested the dominant reaction pathways for the formation of thiocyanate from the oxidation products of sulphide to be reaction with either polysulphides or thiosulphate as expressed in Equations 2.9 and 2.10, respectively.



Lorenzen and van Deventer (1992) indicated that pyrrhotite varying in chemical composition from Fe_5S_6 to $Fe_{16}S_{17}$, readily reacts with cyanide to form thiocyanate. According to Lizima *et al.* (2005) in heap bioleaching, several chemical reactions occur simultaneously, individual metal extractions cannot be studied separately; sulphur may be formed by the reaction between pyrrhotite and ferric iron as in Equation 2.11. Holtum and Murray (1994) have shown that sulphur may also be formed by the reaction between pyrite and ferric iron in Equation 2.12. Jones and Hackl (1999) argued that thiocyanate results from the reaction of cyanide with incompletely oxidized, meta-stable sulphur compounds that form during biooxidation.



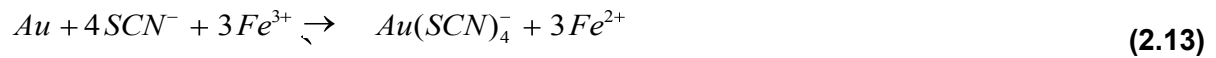
Iglesias and Carranza (1996) have concluded that any elemental sulphur formed during the ferric pre-treatment, can cause serious difficulties in the further cyanide leaching stage, because it produces thiocyanate ions; these may reduce gold dissolution, increasing the consumption of cyanide. Jeffrey and Breuer (2000) argued that at the typical pH of gold processing, ten or more, any S^{2-} present in solution is converted to HS^- . It was found that sulphide species decreased the dissolution rate of gold and also counteracted the accelerating effect of lead species within the potential range typically encountered in conventional gold leaching, i.e. from - 600 to 0 mV (SCE) (Tshilombo and Sandenbergh, 2001).

Bacteria can oxidize elemental sulphur to sulphate. The oxidation involves several intermediates (e.g. thiosulphate, tetrathionate, sulphite) in the oxidative pathway to sulphate formation. According to Bevilaqua *et al.* (2002), the oxidation rate appears to be slower than the rate of elemental sulphur formation, because elemental sulphur is often found in solid residues from bacterial leaching systems. As can be seen, the analysis for all individual sulphur components of such mixture (solution) is desirable since the measurement of total sulphur content does not usually provide sufficient information.

2.2.4 Effect of thiocyanate – Complex stability

Depending on the solution potential, acidified thiocyanate in aqueous solutions can dissolve gold to form both Au(I) and Au(III) complexes (Kuzugüdenli and Kantar, 1999). Aylmore (2005) found that gold can be leached by thiocyanate at potentials of around 0.4 to 0.45 V and pH of 1 to 3 in the presence of either ferric ions or peroxide as oxidant. Therefore, it is imperative that an oxidizer and complexing agent are present in solution to extract gold.

Higher redox potentials and relatively acidic conditions are required as compared with cyanide solutions (Iglesias and Carranza, 1996). The simplified reaction can be written as in Equation 2.13.



Thiocyanate anions were shown to have a very detrimental effect on the rates and capacity constants of gold adsorption, when added individually to a synthetic solution at the approximate concentration levels of 100 ppm as found in the plant solutions (Davidson *et al.*, 1979). Whereas Cortina *et al.* (1998) have observed a very high concentration of SCN^- , about 150 ppm, due to the dissolution of pyrrhotite that was present at only 1.5% level in the treated minerals.

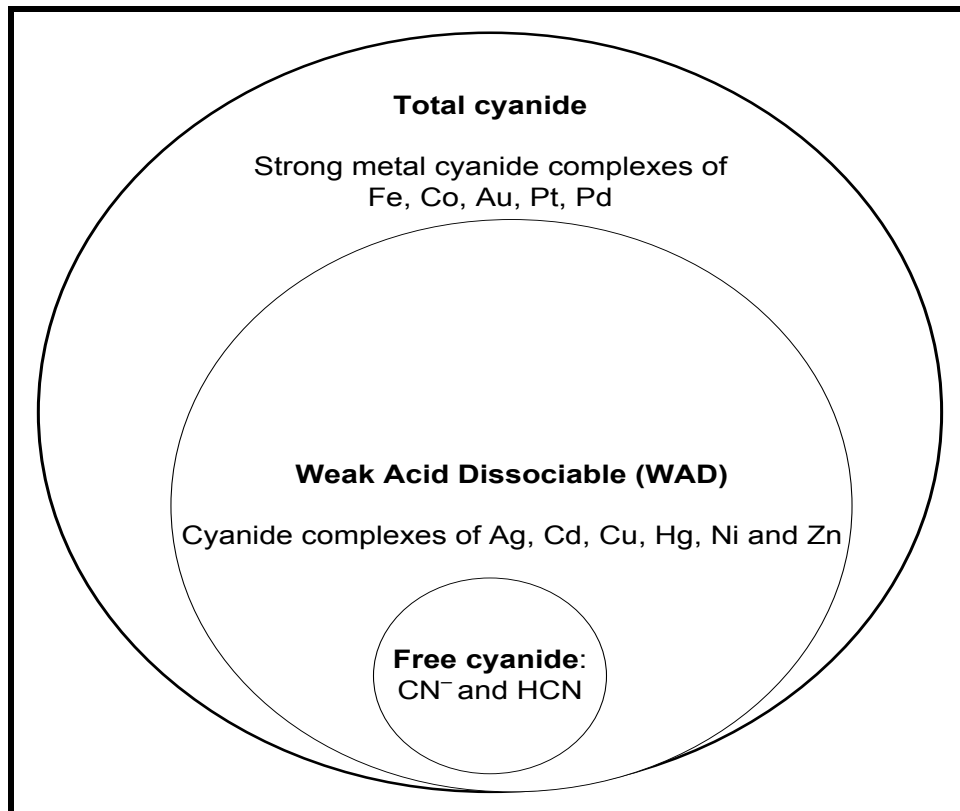
SCN^- being a strong complexing agent can further react with metals to form thiocyanate complexes such as $Au(SCN)_2^-$ and $Au(SCN)_4^-$ (Iglesias and Carranza, 1996). Furthermore, the same authors have argued that silver, like gold, can form a series of thiocyanate complexes: $AgSCN$ has both solid and soluble forms. The solid $AgSCN$ is a very stable compound under the cyanide leaching conditions [K_{sp} at $25^\circ C = 1.03 \times 10^{-12}$, with solubility of 168.4 ppb. For $Pd(SCN)_2$, $K_{sp} = 4.39 \times 10^{-23}$, with solubility of 4.95 ppb]. Thiocyanate is also known to form complexes with several metal cations. For instance, a precipitate, probably $Cu(CNS)_2$, is formed with copper (Aylmore, 2005).

Gallagher *et al.* (1990) have established the effectiveness of activated carbon in removing complexed gold from aqueous solutions, as decreasing in the following ligand order: $SCN^- > SC(NH_2)_2 > CN^- > S_2O_3^{2-}$. The capacity of activated carbon for the gold (I) complexes also follows this order. The same authors investigated gold adsorption properties of activated carbon through scanning electron microscopy, and concluded that dithiocyanatoaurate (I), $Au(SCN)_2^-$, adsorbed onto carbon as metallic gold with no evidence that the Au(I) complex was present. It bears noting that the dicyanoaurate (I) eluted more readily with deionized water, while the thiocyanato complex was only removed through a chemisorption process.

2.3 SIMULTANEOUS DETERMINATION OF $[CN^-]$ AND $[SCN^-]$ IN AQUEOUS SOLUTIONS

Young *et al.* (2008) stated that the analysis of cyanide is frequently a source of concern and confusion for industry; especially in the understanding of the methods, limitations as well as the cyanide chemistry. In its document, AngloGold Ashanti Limited (Maree, 2008) stressed

that cyanide analyses must be conducted according to accredited and internationally approved procedures. The term 'cyanide' generally refers to one of the three classifications highlighted in Figure 2.1 and, each of these forms of cyanide has a specific analytical methodology for its measurement.



**Figure 2.1: General classification of cyanide compounds
(Adapted from U.S. Environmental Protection Agency, 1994)**

Methods used to detect free cyanide should be clear of interferences due to the presence of high concentrations of more stable cyanide complexes or other cyanide forms, hence should not alter the stability of weaker cyanide complexes. Literature shows the existence of a number of methods for the analysis of cyanide directly in the matrix or following a pretreatment. These methods include among others titrimetric, spectrophotometric, potentiometric, ion-selective electrode, ion chromatography-high performance liquid chromatography (IC-HPLC), polarographic, indirect atomic-absorption spectrophotometry, gas chromatographic and infrared spectrometric (Sun and Noller, 1998).

In the gold industry, the traditional method for free cyanide determination is the titration with silver nitrate using rhodanine as the indicator (Dai *et al.*, 2005). Pohlandt *et al.* (1983) argued that titrimetric procedures are generally employed for the determination of larger quantities of cyanide in the absence of weakly complexed metal cyanides and other interferences.

However, in addition to the free cyanide and solubilized PMs, typical leach liquor also contains numerous other species produced by reaction of cyanide with components of the ore. These species include other metal cyanide complexes (especially those of iron and copper) and thiocyanate (Fagan and Haddad, 1991).

Breuer *et al.* (2011) clearly demonstrated that the use of rhodanine as indicator in the determination of free cyanide in cyanidation leach solutions containing copper and/or thiosulfate, over-estimated free cyanide concentration and could not be compared directly against an online cyanide analyser using a potentiometric determination. Fagan and Haddad (1991) pointed out that the presence of copper cyanide caused interference during titration with silver nitrate because $\text{Cu}(\text{CN})_4^{3-}$ is a dissociable complex and the loss of CN^- from the copper/cyanide complex increases the value for free cyanide according to Equations 2.14 and 2.15.



Rhodanine titrations performed on solutions containing sulphide ions are masked by silver sulphide precipitate. Young *et al.* (2008) have shown that the most serious interferences during silver nitrate titration are caused by copper, sulphide and thiosulphate. Samples containing high sulphide and thiosulphate levels will impart a positive interference in the silver nitrate titration method through its reaction to yield silver sulphide during titration (Ag_2S , K_{sp} at 25°C equals 6×10^{-50} , with solubility of 6.11×10^{-9} ppb). Moreover, SCN^- reacts with Ag^+ according to the Volhard titration illustrated in Equation 2.16 (Law and Gabriel, 1986).



Pohlandt *et al.* (1983) reported that sulphide and thiocyanate complexes are responsible for the most serious interferences in cyanide determination. Barnes *et al.* (2000) observed that sulphide and thiocyanate usually distil with the cyanide and interfere with most analytical methods. Young *et al.* (2008) have argued that in the presence of nitrate, thiocyanate decomposes to form CN^- , resulting in a positive bias during cyanide distillations; as both thiocyanate and nitrate are common by-products of cyanidation practice in gold industry.

Thus routine titration procedures applied to copper-containing ores can yield erroneously high results for free cyanide. Failure to make this correction can lead to a decrease in the rate of PGMs dissolution in the leaching process and ultimately, a reduction in precious metals recovery at both stages: leaching and adsorption (Fagan and Haddad, 1991).

Pohlandt *et al.* (1983) have shown that potentially accurate methods for the simultaneous determination of ionic cyanide and its accompanying interferent, i.e. thiocyanate, include ion chromatography and indirect atomic-absorption spectrophotometry. According to Gumus *et al.* (2000), Fagan and Haddad (1991); thiocyanate is the common interferent in almost all spectrophotometric determinations of cyanide. When comparing assay techniques for cyanide and related species, Breuer *et al.* (2009) and Adams (2001) have mentioned ion chromatography method as an approach to the simultaneous determination of free cyanide, cyanate complexes and thiocyanate in cyanidation leach liquor samples.

2.4 ADSORPTION OF PRECIOUS METALS

According to Bailey quoted by Stange (1999), the successful operation of a carbon-in-pulp plant is centred on the adsorption section, which is expected to extract more than 99.6% of the gold present in solution. Adsorption processes may be classified as chemical (chemisorption) and physical adsorption (physisorption), depending on the nature of the interactive forces. The former, generally irreversible, refers to processes involving homopolar forces (ionic or covalent bonds), while in the latter (physisorption) interactive forces are relatively weak: van der Waals forces also dipole-dipole interactions and hydrogen bonding (McDougall, 1991).

2.4.1 Speciation of aqueous PGM cyano complexes

Knowledge of chemical speciation of the target metals in the leaching solutions to be treated and the nature and structure of the metal complex to be extracted is very important in understanding the metal-extraction reactions and selectivity factors (Cortina *et al.*, 1998). As stated earlier in section 1.2.4, speciation studies by Roijals *et al.* (1996); Cortina *et al.* (1998), revealed $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pd}(\text{CN})_5^{3-}$ ions at room temperature, while $\text{Pd}(\text{CN})_4^{2-}$ is formed at 140°C. Chen and Huang (2006) pointed out that $\text{Pd}(\text{CN})_4^{2-}$ is not stable at high temperature and is easily decomposed to Pd metal when the reaction temperature was higher than 160°C, whilst the Pt and Rh cyanide complexes remained relatively stable in solution at 180°C. However, McInnes *et al.* (1994) have mentioned $\text{Pd}(\text{CN})_4^{2-}$ complexes formed at ambient temperature. Considering their divergence, all are assumed doubtful until additional supporting data are forthcoming.

There are not sufficient equilibrium data of Rh cyanide complex formation, but several references point to the formation of $\text{Rh}(\text{CN})_6^{3-}$ in excess CN^- at 25°C (Aguilar *et al.*, 1997; Roijals *et al.*, 1996). The most stable oxidation state in Cu, Ag and gold cyano compounds is one (Sharpe, 1976). The dissolution of gold in an aqueous cyanide solution gives just one anionic complex (Equation 1.2). Silver dissolves readily in alkaline cyanide solution to give the di-, tri- and tetracyanosilverate (I) complexes with almost similar formation constants (Gomes *et al.*, 2001).

2.4.2 Adsorption mechanisms

2.4.2.1 Dicyanoaurate (I) complex

A number of adsorption mechanisms of dicyanoaurate (I) complex on activated carbons have been proposed over the years (Woollacott *et al.*, 1990; McDougall *et al.*, 1980; Davidson, 1974). Despite years of research and development with activated carbon related to its commercial importance, there is still not a complete agreement of the gold adsorption mechanism. The main reason for this is the fact that activated carbon cannot be investigated by direct physical procedures such as infrared spectroscopy or X-ray diffraction, so that very little is known about the adsorbent itself (McDougall *et al.*, 1980). The mechanisms proposed over the years can be simplified into one of the following four different approaches (McDougall and Hancock, 1981):

- $\text{Au}(\text{CN})_2^-$ ion is adsorbed without undergoing chemical change and held by electrostatic or van der Waals forces,
- adsorption of $\text{Au}(\text{CN})_2^-$ accompanied by the reduction of the group to metallic gold $\text{Au}(0)$,
- adsorption of the aurocyanide ion group in the form of a metal complex $M^{n+}[\text{Au}(\text{CN})_2]_n^-$,
- $\text{Au}(\text{CN})_2^-$ decomposition to AuCN and adsorbed as such.

According to Lagerge *et al.* (1997), the two most widely accepted theories reduce to:

- adsorption involving ion pairs, $M^{n+}[\text{Au}(\text{CN})_2]_n^-$ and
- adsorption of unpaired $\text{Au}(\text{CN})_2^-$ ions onto activated carbons.

McDougall and Hancock (1981) have argued that the nature of the mechanism depends on several parameters such as solution pH, adsorbent and metal ion properties. According to Yin *et al.* (2007), activated carbon as an inert porous carrier material, is capable of distributing chemicals on its large hydrophobic internal surface; thus making them accessible

to reactants. It is also well established that activated carbon has a very low affinity for small, highly hydrated inorganic ions (McDougall and Hancock, 1981).

2.4.2.2 PGM cyano complexes

Although the kinetics of gold adsorption onto activated carbon are well documented, the consensus on the mechanism is only recently being achieved (Poinern *et al.*, 2011). As far as the kinetics of PGM cyano complexes adsorption on activated carbon are concerned, the information available is rather limited.

Aguilar *et al.* (1997) reported their study on adsorption (onto activated carbon) of Fe(II), Cu(I), Ni(II), Pd(II), Pt(II), Rh(III)-cyano complexes and NO_3^- ions from a mixture of leaching solutions. With regard to the adsorption uptake, they found that Pt(II), Pd(II) and Ni(II) cyanides were selectively adsorbed in a short time, while Rh(III) and Fe(II) cyanide showed much slower and lower adsorption. They concluded that the selective uptake could be bound to their chemical structures: square planar for Pd(II), Pt(II) and Ni(II) while octahedral for Fe(II) and Rh(III).

Ionic solvation energy theory has also been used to explain the selective adsorption mechanism onto activated carbon (Jia *et al.*, 1998; McDougall and Hancock, 1981). According to the theory, a large, weakly hydrated anion (with low charge density) will be specifically adsorbed on the adsorbent surface after losing some of its primary-hydration water molecules. Small anions with a large number of strongly bound water molecules in their primary hydration shells (high charge density) will not be specifically adsorbed and will therefore remain in the outer part of the electrical double layer (McDougall *et al.*, 1980).

The aforementioned behaviour is possibly a consequence of densely charged species having larger hydration shells, have lower coulombic interaction with their counterions than those with smaller hydration shells (Bernardis *et al.*, 2005). The larger cations, however, are less well hydrated resulting in an enhanced extractability into the hydrophobic carbon phase (Adams *et al.*, 1987). According to the charge density principle, $\text{Pt}(\text{CN})_4^{2-}$ (2 electric charges are carried out by 9 atoms) can be expected to be more strongly extracted than the highly hydrated $\text{Rh}(\text{CN})_6^{3-}$ complex (Cortina *et al.*, 1998). It is also generally known that if two species in a loading solution are competing for adsorption onto carbon, the latter will prefer the least soluble (McDougall and Hancock, 1981). Walter and Weber (1974) stressed that the more hydrophilic a substance, the less likely it is to be adsorbed. Conversely, a hydrophobic substance will more likely be adsorbed.

By analogy to what is observed in gold complex coordination compounds which incorporate cyanide as a ligand, these considerations give rise to the statement that the dissolved PGM cyanide is adsorbed as the cation PGM cyanide ion pair. Thus, it is reasonable to assume that the mechanism of PGMs recovery from cyanide solutions could occur as proposed in Equation 2.17.



where X denotes Pt, Pd or Rh, M^{n+} is an appropriate metal ion such as Na^+ , K^+ , Ca^{2+} or H^+ ; $m = 1, 2$ or 3 .

Moreover, a simple approach to the problem of whether platinum and palladium are present as $Pt(CN)_4^{2-}$ and $Pd(CN)_5^{3-}$, would involve the analysis of loaded carbons for their PGM and nitrogen contents, which would indicate how many cyanide ions are associated with the PGMs on the carbon. Surface analysis studies of the barren and loaded carbon will contribute to a better understanding of the mechanisms involved in the PGMs adsorption process. Furthermore, an additional evidence of the proposed mechanism will come through the magnitude of standard Gibbs free energy (see section 2.6.2).

2.4.3 Activated carbon – Electrochemical reduction

Although the adsorption capacity of activated carbons is determined mainly by their porous structure, it is also influenced by the chemical structure of their inner surface (Swiatkowski, 1999). Due to its structural imperfections, there are many opportunities for reactions with carbon atoms forming the edges of the planar layers. These reactions result in the formation of oxygen containing functional groups on the surface of the carbon (McDougall, 1991). A large number of these groups have been identified and it has been suggested though that they may belong to the following groups: carboxyl, phenolic hydroxyl, quinone-type carbonyl, normal lactones, fluorescein-type lactones, carboxylic acid anhydrides and cyclic peroxides (Yin *et al.*, 2007; McDougall and Hancock, 1981). However, carbon is not readily amenable to physical investigation by techniques such as infrared spectroscopy, therefore; very little information is available about the surface functional groups present on it (McDougall *et al.*, 1980).

The important role of these groups is to impart a hydrophilic character to the predominantly hydrophobic skeleton of the carbon (McDougall and Hancock, 1981). The chemical nature of activated carbon depends on conditions during and after manufacture (McDougall, 1991). Depending on the presence of surface functional groups, it is an established fact that the activated carbon surface can display acidic, basic and/or neutral characteristics (Yin *et al.*,

2007). In fact some carbons, especially those prepared by high temperature steam activation route, exhibit at a pH of 6 a reduction potential E_c of about -0.14 V against the saturated calomel electrode (SCE) (McDougall and Hancock, 1981). McDougall *et al.* (1980) found for typical activated carbons a E° value of about 0.24 V.

Therefore, direct electrochemical reduction of noble metal ions is thermodynamically possible if the electrode potential ΔE of the $AC/[M_eLm]^{n-}$ system is greater than zero, where M_e is the metal, Lm is the ligand and n is the valence. This condition is met when the equilibrium potential E_{Me} of the $[M_eLm]^{n-}/M_e^0$ pair is more positive than the working potential of the coal surface E_c as expressed in Equation 2.18 (Simanova *et al.*, 2008).

$$\Delta E = E_{cathode} - E_{anode} = E_{Me} - E_c > 0 \quad (2.18)$$

Thus the suggestion that the thiocyno – PGM ions could be reduced to metal on the surface of the activated carbon, can also be accounted (in acidic medium) as a mechanism of adsorption by considering the reduction potential measurements recorded in Table 2.3. However, Adams *et al.* (1992) suggested a physical adsorption mechanism onto activated carbon of $Au(CN)_4^-$ species, which is normally not present in gold plant liquors.

Table 2.3: Stability constants and standard reduction potentials for a selection of complexes of gold (I and III) at 25°C (Aylmore, 2005)

Ligand	Au(I or III) complex	$\log \beta$ or β	E° Au(I or III)/Au (V vs. SHE ^a)	pH range
CN ⁻	$Au(CN)_2^-$	38.3	- 0.57	> 9
	$Au(CN)_4^-$	56	- 1.81	-
SCN ⁻	$Au(SCN)_2^-$	17.1	0.66	< 3
	$Au(SCN)_4^-$	43.9	0.66	-

^aStandard hydrogen electrode

2.4.4 Adsorption loading capacity

The volume of the pores in activated carbons is generally defined as being greater than 0.2 mL/g, and the internal surface area is generally larger than 400 m²/g as measured by the nitrogen BET method (McDougall, 1991). The loading capacity of an activated carbon is often determined from an adsorption isotherm and is defined as the equilibrium loading on carbon in contact with a residual PM solution concentration of 1 mg/L (Marsden and House,

2006). Most laboratories such as The Parker Centre, Mintek, Norit and Anglo American Research Laboratories have developed methods involving contacting varying masses of pulverized carbon with a volume of gold cyanide solution for 20 hours or more (Staunton, 2005; Davidson *et al.*, 1982). The development of equilibrium adsorption isotherms from these data also allows fitting of isotherm models, such as the Langmuir or Freundlich models, which may yield insight into the nature of the adsorption.

However in the Pica procedure, a sample of carbon is contacted for 1 hour with 1 L of 10 mg/L gold solution. The carbon is recovered and put into a new fresh batch solution for a further hour. This is repeated 11 times or more if the carbon has high gold-loading capacity. The cumulative gold loading after each contact is calculated and the data points are plotted to show the increase in the gold loading on the carbon with increasing number of solution contacts (Staunton, 2005). Although this method does not appear to include a means of calculating a definitive value of the loading capacity of the carbon, the time required for multiple contacts; including the extraction per stage, would be of some interest in the development of industrial processes.

In practice only a small fraction of the total adsorption capacity of carbon for gold is utilized (Yalcin and Arol, 2002). Syna and Valix (2003) have observed the adsorption capacities exhibited by physically activated bagasse ranged between 11 and 229 mg Au/g of carbon. It has been shown in the laboratory that gold loading levels as high as 45 mg Au/g of carbon can be achieved, whereas the loading of gold on carbon in the first stage of a carbon-in-pulp plant seldom exceeds 10 mg Au/g of carbon (Yalcin and Arol, 2002). According to Heinen *et al.* (1978), typical loadings obtained commercially range from 5.670 to 22.680 mg of gold, or combination of gold and silver, per gram of carbon. More recently Marsden and House (2006) have demonstrated that the rate of gold adsorption and the equilibrium loading capacity both increase with increasing gold concentration in solution. In practice at CIP gold plants, gold-loading rates of 0.01 to 0.1 mg Au/hr/g of carbon and loadings of 5 to 10 mg Au/g of carbon are achieved.

It can be seen that a consistent correlation between the adsorption capacity of each individual carbon is often difficult to obtain. All the characteristics of the carbon change simultaneously as a function of burnoff. Changes in burnoff result in the total surface area to increase accompanied by changes in the pore diameter, carbon pH and other surface chemical properties (Yalcin and Arol, 2002). Heinen *et al.* (1978) pointed out some factors that influence the loading such as (1) the concentration of gold and silver in cyanide leach solutions, (2) the ratio of gold to silver, (3) the pH of leach solution, (4) the concentration of impurities, (5) the flow rate, (6) the type and particle size of granular carbon employed.

Loaded carbon is stripped in hot caustic cyanide solution to produce a concentrated solution in the range of 50 to 1000 ppm Au from which the gold is electrowon (Brandon *et al.*, 1987). The same authors have suggested that heap leaching procedures could be simplified by electrowinning gold directly from the dilute heap leach liquor, in order to eliminate the activated carbon adsorption, stripping and regeneration steps. However they concluded that direct electrowinning was more expensive than a conventional carbon system for treating heap leach liquors because of large volumes of liquor held within the process coupled with the very low outlet gold concentration demanded.

Finally reverse osmosis has also been investigated as a means to concentrate the dilute gold solutions. Williams (2003) postulated that reverse osmosis systems could replace or be used in conjunction with other treatment processes such as oxidation, adsorption, stripping, or biological treatment (as well as many others) to produce a high quality product water that can be reused or discharged.

2.4.5 Activated carbon fouling – Carbon retention time

Carbon adsorbs organic and inorganic species such as silica, alumina, iron oxide, flotation reagents and calcium from the pulp in the adsorption plant. These species are poisons in that they tend to reduce the carbon's capacity for gold adsorption (Stange, 1999). The fouling of the adsorbent results both in higher soluble losses and lower loadings on the activated carbon (van Der Walt and van Deventer, 1992). The longer the carbon remains in contact with pulp, the more poisons are adsorbed. Thus, lengthy contact between the pulp and the carbon will invariably result in more poisoning and poorer adsorption of gold (Stange, 1999). An acid washing with HCl is able to remove most of these precipitates and thus improve adsorption performance (Stange, 1999; Laxen, 1984).

Researchers have reported that equilibrium between gold cyanide and activated carbon had not been achieved after three months and, in another case, after six months (Le Roux *et al.*, 1991). Conventional practice is to have a mean pulp residence time of about an hour in each tank (Stange, 1999). According to Laxen *et al.* (1979), contact times of between 20 and 60 minutes are reported, and then contact times of 30 minutes are used frequently. Another similar investigation by Nicol *et al.* (1984) demonstrated that the residence time of carbon seldom exceeds 48 hours per stage in an operating plant, so that true equilibrium is never achieved. Hence any rational approach to the modelling of the adsorption process should therefore be based on the kinetics of the adsorption reaction.

2.4.6 Carbon transfer

Although the transfer of carbon is an important operational parameter, Stange (1991) has observed that most attempts at modelling CIP adsorption have ignored the manner in which carbon may be transferred on a real plant. Carbon transfer is dependent mainly on the dissolved gold fed to the circuit and its loading onto carbon (Laxen *et al.*, 1979). Carbon is transferred in many ways, and operating practices vary widely. The countercurrent transfer of carbon can be carried out continuously or intermittently (Stange *et al.*, 1990). Transfer of carbon between stages is generally achieved by recessed-impeller-type pumps (in replacement of airlifts), suspended in the top of the tanks (Hartman, 1992). The amount of carbon transferred daily is not constant and carbon transfer is not an instantaneous process. As a result of these variations, steady-state is never reached (Schubert *et al.*, 1993). A detailed block-flow diagram of a typical CIP plant for a non-refractory gold ore is shown in Figure 2.2. It is envisaged that a process for recovering PGMs from a PLS could be developed using analogous blocks except for blocks 3 and 14.

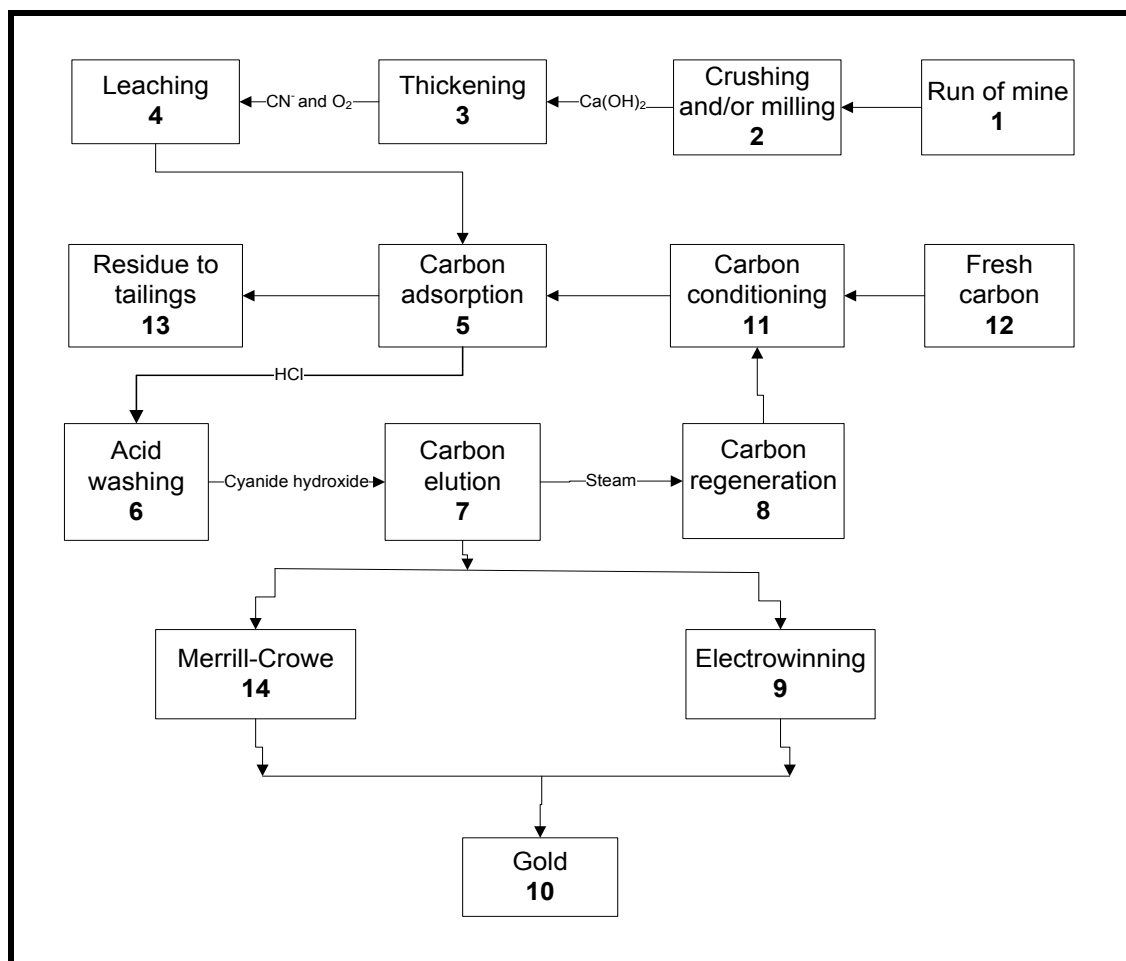


Figure 2.2: Carbon-in-pulp process schematic flowsheet (Adapted from Stange, 1999)

2.5 CHOICE OF ACTIVATED CARBON

The pore structure and pore size distribution are largely predetermined by the nature of the starting material, while the chemical nature of the surface oxides and surface area of the activated carbon are developed during the carbonisation and activation processes (McDougall and Hancock, 1981). Pore structure and pore size distribution are more important factors in controlling gold adsorption capacity (Jia *et al.*, 1998). The size of pores developed during activation has an important influence on adsorption behaviour because pores act as a screen, preventing the adsorption of large molecules, while promoting the adsorption of adsorbates that fit snugly into the pores (McDougall, 1991). The suitability of an activated carbon for a particular application depends on the ratio in which pores of different sizes are present (Swiatkowski, 1999). A good activated carbon must have a combination of the micro and macropore ranges (Duong, 1998).

Hardness, surface area and iodine number are the most critical properties of the activated carbon. While hardness is required to withstand abrasion (hence precious metal losses), surface area and iodine number are related to the adsorption characteristics (pore structure) of the carbon. Iodine numbers are a measure of the amount of micropores in carbons (Yalcin and Arol, 2002). Finally according to Ibragimova *et al.* (2007), in a real industrial adsorption process performed in the counter-current mode, the value of the pseudokinetic adsorption rate constant at 25°C is within the range of 80 to 100 h⁻¹ and should remain approximately constant in all tanks of the cascade, irrespective of the concentration of Au(CN)₂⁻ anion in the liquid phase in each vessel.

2.6 THERMODYNAMICS OF ADSORPTION – TEMPERATURE EFFECT

2.6.1 Cyanide complex solubility

Temperature is the most complex factor affecting the equilibrium in adsorption processes. McDougall (1991) observed that generally gold adsorption decreases with increasing temperature. In other words, increase in temperature could decrease the adsorption due to the increased solubility of the complex at higher temperatures (McDougall *et al.*, 1980).

2.6.2 Standard Gibbs free energy of adsorption

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. However in actual reactions, the composition of the reaction mixture seldom corresponds to standard-state pressures and concentrations. Free energy change ΔG for a reaction when reactants and products are present at non-standard state is given in Equation 2.19 (McMurry and Fay, 1995).

$$\Delta G = \Delta G^\circ + RT \ln K_D \quad (2.19)$$

At equilibrium $\Delta G = 0$, then 2.19 gives 2.20.

$$\Delta G^\circ = -RT \ln K_D = -2.303RT \log K_D \quad (2.20)$$

Considering corrections from Milonjić (2007), Equation 2.20 gives Equation 2.21.

$$\Delta G^\circ = -2.303RT \log 55.5K_D \quad (2.21)$$

From the thermodynamic point of view, the sign of the standard Gibbs free energy change of adsorption, expressed in Equation 2.21, is the fundamental criterion of spontaneity (probable occurrence). Reaction occurs spontaneously at a given temperature if the value of ΔG° is negative. According to McDougall (1991), surface adsorption, regardless of the energy of the interaction, must always proceed with a negative change in free energy. It may be noted that spontaneous does not imply that it is instantaneous, it could happen over the course of years or decades.

The extent of standard free energy can also give an idea about whether the adsorption process is physical or chemical. Generally, values of ΔG° up to -20 kJ/mol are consistent with electrostatic interaction between adsorbate molecules and the adsorbent surface (physical adsorption), while ΔG° values more negative than -40 kJ/mol involve charge sharing or transfer from the adsorbate molecules to the adsorbent surface to form a coordinate type of bond which indicates chemical adsorption (Horsfall *et al.*, 2006).

2.7 SUMMARY OF LITERATURE REVIEW

This chapter started by giving a brief background to the mineralogy of Platreef ores, their effect on cyanide leaching and adsorption onto activated carbon, as well as the simultaneous determination of $[\text{CN}^-]$ and $[\text{SCN}^-]$ in cyanide solutions. The following chapter (Chapter 3) provides the preparative steps before the experimental tests. These latter include: a) screening tests on the PLS resulting from cyanide extraction of Platreef ore; b) a series of tests constructed through a factorial design matrix, to demonstrate the influence of selected factors and their interactions with each other on the equilibrium isotherm. This is followed by the adsorption mechanism, loading capacity and reproducibility tests.

CHAPTER 3 : MATERIALS AND METHODS

This chapter describes the experimental conditions, procedures and analytical techniques followed in this research study. In order to observe the combined influence of certain factors on adsorption rate, equilibrium tests were carried out batchwise using successively real and synthetic solutions.

In depth evaluation of possible synergic and antagonistic interaction effects involving two or more parameters on the adsorbed quantity of metal complex anions, required a systematic study. For this purpose, various adsorption parameters like solution pH, copper, nickel, free cyanide ion, thiocyanate, adsorbent and initial metal ion concentrations were studied. Coconut shell derived activated carbon known for its resistance to abrasion and selectivity for gold, has been the selected adsorbent for precious metals adsorption from alkaline cyanided solution. The experimental procedure consisted of two distinct sequential steps: screening tests were first undertaken using real heap cyanide solution, and then using synthetic solutions, actual tests were performed based on some identified findings from the former tests.

3.1 MATERIALS

3.1.1 Pregnant leach solution (PLS)

A preliminary test-work programme of adsorption experiments was completed using real heap cyanide solution (Mwase *et al.*, 2012). Table 3.1 details the components identified in the pregnant leach solution and their concentrations. It can be seen that copper concentration is below the limit of 200 ppm set by Marsden and House (2006), which means that adsorption of precious metals by means of activated carbon may be a suitable technique of extraction. The constituent concentrations in the solution were analysed using analytical methods detailed in 3.2.3.

Table 3.1: Elemental composition of heap cyanide pregnant solution as received (35-day leach cycle, pH = 10)

Elemental composition	Concentration (ppm)	Elemental composition	Concentration (ppm)
Pt	0.150	Pb	0.010
Pd	0.380	Ca	18.500
Rh	0.010	Li	0.007
Ru	0.010	Na	6136.610
Ir	0.001	K	23.150
Au	0.100	Mg	1.670
Ag	0.040	NO ₃ ⁻	0.000
Cu	18.840	Cl ⁻	12.600
Co	< 1	CN ⁻	12.500
Ni	18.300	SCN ⁻	3669.789
Fe	47.300	S ²⁻	2.644
Zn	0.060	SO ₄ ²⁻	11229.897

ICP-MS assay detection limit: ≈ 0.1 ppb for most elements

3.1.2 Synthetic solutions

In order to generate precious and base metals for adsorption studies in a shorter period of time than the cyanide heap leach process, synthetic solutions – used in the second phase of the experimental work – that resembled typical cyanide leach liquors were prepared from precious and base metal salts. According to La Brooy *et al.* (1994), typical heap leach recoveries are in the range of 60 to 80%. Therefore, expecting further improvements in value metal recoveries at the acid leach and cyanidation stages, the amount of precious metals in the synthetic mixed solutions (Tables 3.2 and 3.5) was calculated by targeting an average of 80% extraction at cyanidation stage based on actual concentration and percentage recoveries of precious metals in the leachate.

Synthetic mixed solutions simulating the cyanided heap leach solution after BMs removal and containing Pt(II), Pd(II), Au(I) and trace amounts of Ni(II), Cu(I) were made by dissolving the required weighted amount of analytical grade of corresponding metal cyanides: K₂Pt(CN)₄, K₂Pd(CN)₄, KAu(CN)₂, K₂Ni(CN)₄, and CuCN in alkaline NaCN (KSCN) buffered solutions, followed by dilution as required (see Table 3.5 and supporting calculations are given in Appendix D). Unless otherwise stated, in all experiments the pH of solutions was adjusted manually using either NaOH solution (1N) or H₂SO₄ (1N). All other chemicals were of analytical grade and were used without further purification.

The precious metal cyanide concentrations depicted in Table 3.2 is close to that of a typical cyanide heap leach liquor solution which contains 0.5 to 5 mg/L of valuable metals (Brandon *et al.*, 1987).

Table 3.2: Averaged amount of PMs (Pt, Pd and Au) cyanide in mixed synthetic solutions

Elemental composition	Actual amount in leachate (ppm)	Actual extraction %	Averaged 80 % extraction (ppm)
Pt(II)	0.15	13.90	0.86
Pd(II)	0.38	29.91	1.00
Au(I)	0.10	47.92	0.17

3.1.3 Activated carbon

The granular activated carbon, MC 110 displayed in Figure 3.1, was supplied by Marlyn Chemicals (Pty) Ltd-South Africa. The BET surface area was 1200 m²/g and iodine number 1075 mg/g according to the specifications of the supplier. The characterization by selected physical property of the activated carbon used is depicted in Table 3.3. Prior to use, the adsorbent was washed with hydrochloric acid (5%v/v) at 25°C and subsequently dried at 80°C for 48 hours in order to volatilize any organic impurities before being weighed. In practice, acid washing is performed at temperatures ranging from ambient to 90°C (Stange, 1999). After acid washing operation, the water-washing (rinsing) was stopped when the pH value of the suspension remained unchanged at pH ≈ 7. These operations are reported to significantly reduce the amount of superficial mineral impurities and powder (ash) (Lorenzen *et al.*, 1995). The activated carbon was sieved to obtain a particle size fraction between 1180 and 3350 μm for all the experiments, and the size distribution is reported in Table 3.4. The mean grain size was about 2582 μm (supporting calculations are given in Appendix D).

Table 3.3: Physical property of activated carbon used in this study

Physical property	Value
Particle density (g/cm ³)	0.82
Bulk density (g/cm ³)	0.43
Pore volume (cm ³ /cm ³)	0.62
Ash content (%)	1.77

Owing to the adsorptive properties of activated carbon, it was stored afterwards in a desiccator to avoid adsorption of moisture from the atmosphere. XRF analysis of the carbon for impurities was conducted and the results are recorded in Table 4.1. The activity of the adsorbent was restored by stirring in distilled water for 30 minutes at a carbon loading of 10 g/L (Lorenzen *et al.*, 1995).

Table 3.4: Size fraction analysis of granular activated carbon MC 110

Screen size (μm)	Weight retained (g)
+ 3350	76.03
- 3350 + 2800	425.28
- 2800 + 2360	274.70
- 2360 + 2000	102.66
- 2000 + 1700	28.95
- 1700 + 1400	3.51
- 1400 + 1180	0.21
- 1180	0.00
Total	911.34



Figure 3.1: Granular MC 110 coconut shell derived carbon

3.2 METHODS

3.2.1 Factorial design

In order to develop an adsorption process, a good basic understanding of parameters influencing the process is essential. However, the study of each and every factor is quite tedious and time consuming (Diamond, 1989). Such a study can involve a prohibitively large number of experiments and severely limits predictive ability essential to the control of long-term performance (Sheridan *et al.*, 2002). This because most chemical systems are affected by more than one independent variable or factor (multifactor systems), and exhibit interactions between two or more factors.

In the aforementioned approach, if one wants to optimize many variables or parameters that influence a given response [such as the $\text{Pt}(\text{CN})_4^{2-}$ loading onto carbon], each factor is independently varied whilst holding all others constant. Thus, instead of conducting a series of independent studies, fractional factorial design technique minimized the above difficulties by optimizing all the affecting parameters collectively at a time. Factorial design, comprising a greater precision in estimating the overall main factor effects and interactions of different factors, was employed to reduce the total number of experiments in order to achieve the best overall optimization of the process. Design-Expert® software 8.0.2 was used for the regression analysis, statistical and optimization calculations.

3.2.2 Sampling strategy

A common experimental design is one with all input factors set at two levels each. These levels are called 'low' and 'high' or '-1' and '+1', respectively. If there are f factors each at two-levels, a full factorial design has 2^f runs. In the present study, seven-factor, two-level fractional factorial design was used for the modelling of the adsorption process. The Plackett-Burman matrix (Resolution IV) reduced the number of trials to forty, and the experimental layout for these parameters is listed in Appendix A. At each combination of those process settings, the adsorption percentages were recorded. The goal was to maximize the adsorption rate of PMs and also try to find conditions that would allow a reduction in the concentration of copper, nickel, thiocyanate and/or activated carbon; therefore, final PMs adsorption was the higher-the-better performance characteristic.

3.2.2.1 Input factors set at two levels each

The factors involved in the design have been shown to have significant influence on gold adsorption. Hence in light of some previously established optimum values for gold adsorption, the individual levels denoted by (-1) and (+1) for all seven input factors are shown in Table 3.5 below.

Table 3.5: Individual levels of the seven operating factors

OPERATING FACTORS	NOTATION	(-)	(+)
pH	A	9.5	12
[Cu(I)] (ppm)	B	10	100
[Ni(II)] (ppm)	C	10	100
[CN ⁻] (ppm)	D	100	300
[SCN ⁻] (ppm)	E	50	100
[PMs]: 2E + Au(I) (ppm)	F	0.63	2.03
Carbon concentration [AC] (g/L)	G	10	20

3.2.2.2 Choice of the two levels used in the experimental design

A Two level – pH

In the cyanidation process (MacArthur-Forrest process) the solid matter is treated with a diluted solution (about 200 to 250 ppm) of NaCN for a typical residence times ranging from 20 to 40 hours depending on the head grade and nature of the ore (Stange, 1999). However, HCN_(aq) is a weak acid and can dissociate in accordance with the dissociation reaction shown in Equation 3.1 below.



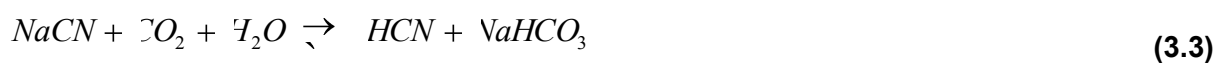
At 25°C, the equilibrium constant pK_a value of the reaction in Equation 3.1 is approximately 9.31 (Marsden and House, 2006). This means that at pH of about 9.31, half of total cyanide exists as hydrogen cyanide and half as free cyanide ions. At a pH lower than 9.31, HCN prevails over CN⁻, while the reverse is observed for a pH over 9.31. However, free cyanide refers to cyanide anion and hydrogen cyanide (see Figure 2.1); their relative amounts present are largely controlled by the solution pH (Adams, 1990). Thus, considering Equation 3.2 at pH of 9.5:

$$\frac{[CN^-]}{[HCN]} = \frac{10^{-pK_a}}{10^{-pH}} = \frac{10^{-9.31}}{10^{-9.5}} = .55 \quad (3.2)$$

This means that there is 1.55 times as much CN⁻ than HCN present at this pH, with roughly 78% of the total cyanide present as CN⁻. This is important because HCN has a relatively high vapor pressure (100 kPa at 26°C) and consequently volatilizes readily at liquid surface under ambient conditions, causing a loss of cyanide from solution (Marsden and House,

2006). However Sheya and Palmer (1989) have reported, in cyanide solutions, maximum gold cyanide adsorption onto activated carbon (96%) below pH of 8.

Although this seems conflicting, it is advantageous to work at pH above the pK_a in order to prevent the build up of and possible release of HCN, to ensure that most of the cyanide is in the ionic form (Fleming, 1992). Therefore a high pH is necessary for both safety and economic reasons. By maintaining the alkalinity of the leach solution at pH of 10 or 11, the possibility of generating hydrogen cyanide gas (HCN) is minimized, and only trace amounts of HCN can be released by interaction of NaCN and CO_2 in the environment according to the 3.3 reaction (Heinen *et al.*, 1978).



Finally the pH can affect the ionicity, chemical nature of species present and their relative concentration, knowing that generally carbon has a low affinity for ions with a high charge-to-surface ratio (McDougall, 1991).

B Two level – free cyanide $[CN^-]$ and $[Cu(I)]$

The loading of copper in the adsorption process of gold is controlled by the pH value and free cyanide ion concentration of the solution. At low pH values, the predominant copper complex present is $Cu(CN)_2^-$ which loads very well onto carbon, while at high free cyanide concentration; the predominant copper complexes are $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$, which do not easily load onto activated carbon (Davidson *et al.*, 1979). In conventional CIP plants, high levels of free cyanide ion are maintained to favour the adsorption of the $Au(CN)_2^-$ anion over $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ anions (Marsden and House, 2006). Deschenes and Wallingford (1995) reported that the usual concentrations of free cyanide are between 150 to 280 ppm to process normal gold ores. Yannopoulos (1991) argued that the concentration of cyanide ion in the leaching process is normally of the order of 200 ppm at the start of the process and falls to 120 ppm at the end because of side reactions with cyanide-consuming agents contained in the ore, reaction with dissolved carbonic acid and hydrolysis of the cyanide.

La Brooy *et al.* (1994) stated that sufficient cyanide is added to leave a concentration of 100 to 250 ppm at about pH of 10 by the end of the leach. Meinhardt *et al.* (1996) found that cyanide concentration changes through the mineral leaching step from values of 1000 ppm (starting point) to 100 – 200 ppm (closing point). According to Kappes (2005), the level of

cyanide in the heap onflow solution ranges from 100 to 600 ppm NaCN and averages 240 ppm, while a heap discharge solution (pregnant solution) averages 110 ppm. Finally Sheya and Palmer (1989) reported that a cyanide concentration above 2 g/L inhibited the loading rate of gold on activated carbon. Thus, the effect of free cyanide concentration on PM-cyanides adsorption was evaluated in the range of 100 to 300 ppm expected from the processing of mineral ores (cyanide leaching). Additional information can be obtained in part A of section 2.2.2.

C Two level – adsorbent and initial metal ion concentrations

Conventionally, gold leached by cyanidation process is recovered by contacting the pulp with 10 to 20 grams of carbon per litre of solution, but on occasions up to 40 grams per litre have been used (Butler, 1993). The effect of initial metal ion concentration on the adsorption equilibrium was studied by varying the initial PM concentrations between its current concentration and a predicted one, as the typical range for any heap leach solutions is between 0.5 and 5 mg/L (Brandon *et al.*, 1987). The initial concentration of both Cu(I) and Ni(II) solutions tested were 10 and 100 ppm in accordance with their minimum average concentrations in the leachate and those (from the literature) believed to be detrimental for PMs adsorption, respectively (Marsden and House, 2006).

3.2.3 Analytical methods

Morphological characteristics and qualitative analyses of both fresh and loaded samples of granulated activated carbon were examined under scanning electron microscope (SEM-EDX) with a detection limit of around 0.1% for most elements. Fresh activated carbon was also subjected to XRF to analyse the chemical compositions of some minerals that are present on its surface. To visualize the size, structure and surface morphology of the solid particles, and hence evaluate the active sites on activated carbon; SEM images were obtained using a Zeiss EVO® MA15 Scanning Electron Microscope at Stellenbosch University.

Quantitative analysis and backscatter images required 15 micrometer thickness (peacock blue colour) of carbon coating, a flat and polished surface. Samples were identified with backscattered electron (BSE) and/or secondary electron images. Phase compositions were quantified by EDX analysis using an Oxford Instruments® X-Max 20 mm² detector and Oxford INCA software. Beam conditions during the quantitative analyses were 20 kV, with a working distance of 8.5 mm and approximately beam current of – 20 nA. The counting time was 10 seconds live-time. Internal Astimex Scientific mineral standards were used for standardization and verification of the analyses. Pure Co was used periodically to correct detector drift.

Metal concentrations in the aqueous phase were measured by ICP-MS and, where necessary, for CN^- , SCN^- , S^{2-} by potentiometric titration, High-Performance Liquid Chromatography (HPLC) and ion chromatography techniques, respectively (refer to section 2.3 for additional information). A gas detector and a tachometer were used to monitor any HCN gas release and for speed measurements, respectively. Special care was taken in the choice of the filter material, to avoid any losses of the test substance on it (Samiullah, 1985).

3.2.4 Experimental set-up and equilibrium tests

Precious metal adsorption tests were performed with the traditional bottle-on-rolls method in 2.5 litre bottles containing 500 mL of the solution (Figure 3.2). According to Fleming *et al.* (2011) this procedure (bottle-on-rolls) gives similar kinetic performance to that achieved in large conventional CIP tanks. Varying amounts of carbon were contacted with 500 mL of the cyanided solution of known precious and base metal concentrations, adjusted at appropriate pH. The effect of alkalinity on the PMs profile was investigated at two different levels, namely pH of 9.5 and 12.

In order to ensure that pseudo-equilibrium was attained, the mixture was rotated for 72 hours. This duration was selected on the basis of gold adsorption experiments (assuming pseudo-equilibrium conditions) reported by van Deventer (1984), who showed that equilibrium was still not achieved between gold cyanide and activated carbon after several weeks of adsorption. Liebenberg and van Deventer (1997) indicated that pseudo-equilibrium isotherms could be used, but carbon/solution contacting times of less than 72 hours could lead to ineffective modelling.

The rate of loading of gold cyanide onto carbon in a rolling bottle test is insensitive to the rate at which the bottle is rolled as long as the inside of the bottle smooth without baffles (Fleming *et al.*, 2011). However, preventing any eventual attrition of the activated carbon (still assuring a good solid/liquid contact), the rotational rate was kept at 105 rpm as this was the maximum speed of the used device.

Solution sampling was done at pre-determined times depending on screening, actual or optimum tests and involved withdrawal of 5 mL of solution using 0.22 μm pore size syringe filters (to remove any carbon fines that might be present in the solution) followed by ICP-MS analysis of the filtrate. The uptake of PMs (Pt, Pd, Au and Rh) with activated carbon was determined from the difference of PM concentrations in the initial and final solutions. Unless stated otherwise, all adsorption experiments were performed at the temperature of 25°C and rotational rate of 105 rpm.

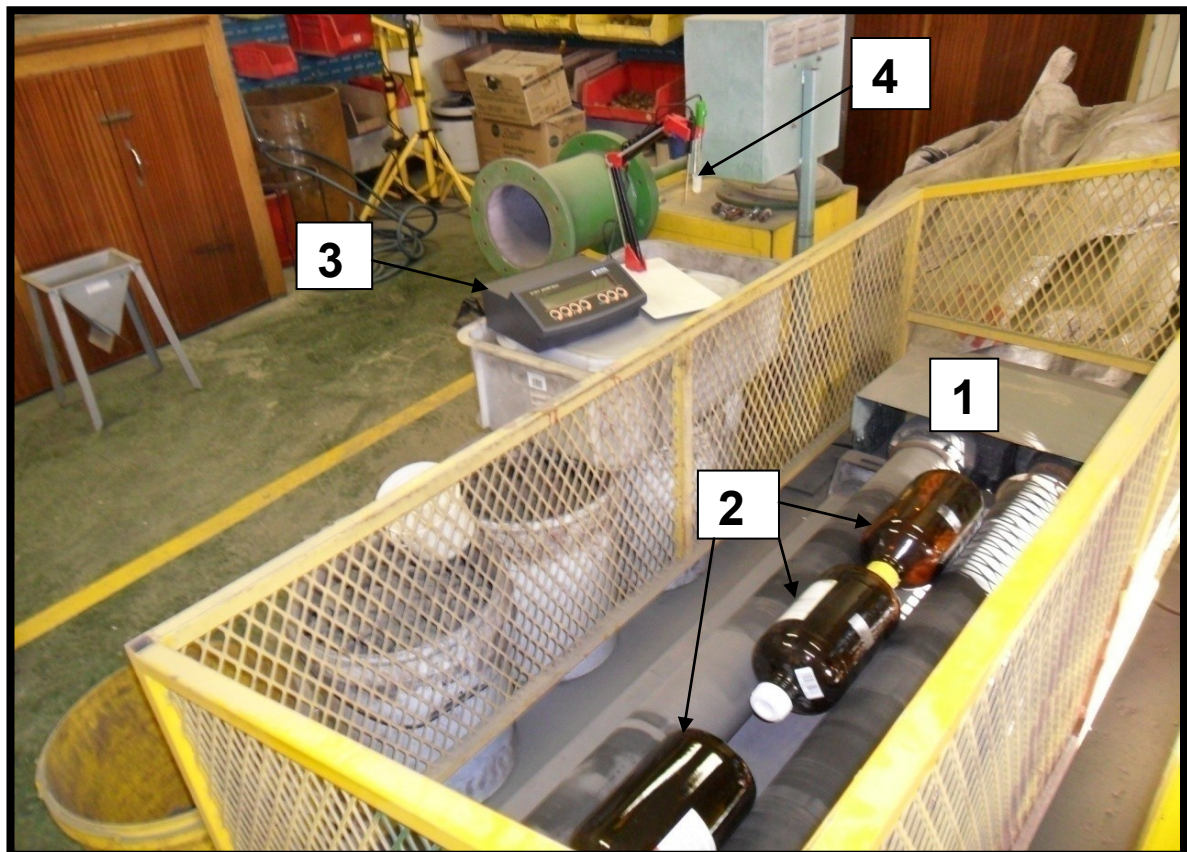


Figure 3.2: Adsorption experimental set-up: (1) Roller (2) 2.5 litre bottles containing 500 mL of the solution (3) pH meter Hanna HI 2211 (4) Probes Hanna HI 1131 and HI 7662-T for pH and temperature measuring, respectively

3.2.5 Data treatment

3.2.5.1 Adsorption mechanism – Rate-limiting step

Generally for design purposes, the prediction of the rate-limiting step is an important factor to be considered in the adsorption process mechanism (Vadivelan and Kumar, 2005). For a solid-liquid adsorption process, the solute transfer (overall rate of adsorption) is usually characterized either by the external mass transfer (boundary layer diffusion), intraparticle diffusion, or both (Acheampong *et al.*, 2011). The adsorption of PMs onto activated carbon may be controlled due to film diffusion at earlier stages and later as the adsorbent particles becomes loaded with metal ions, the adsorption process may be controlled due to intraparticle diffusion. The adsorption dynamics can be described by the following three consecutive steps which are as follows (Qiu *et al.*, 2009):

- (1) mass transfer across the external boundary layer film of liquid surrounding the outside of the adsorbent particles, i.e., external diffusion or film diffusion,
- (2) diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intraparticle diffusion;

- (3) adsorption and desorption between the adsorbate and active sites, i.e., mass action.

The last step is considered to be an equilibrium step. For physical adsorption, mass action is a very rapid process and can be neglected in kinetic studies. Thus, the kinetics of the adsorption process are always controlled by either liquid film diffusion or intraparticle diffusion, i.e., one of the processes will be the rate-limiting step. Walter and Weber (1974) argued that for most operating conditions, transport of adsorbate through the 'surface film' or boundary layer is rate-limiting. If sufficient turbulence is provided, transport of the adsorbate within the porous carbon may control the rate of uptake.

A plot of $\ln(1-q_t/q_e)$ vs. t (Equation 3.4) should be a straight line if the film diffusion is the rate limiting step (Qiu *et al.*, 2009), where k is the overall rate constant, q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (minute), respectively.

$$\ln(1-q_t/q_e) = -kt \quad (3.4)$$

The most commonly used technique for evaluating the mechanism involved in the adsorption process is by fitting an intraparticle diffusion plot described in Equation 3.5 (Vimonses *et al.*, 2009).

$$q_t = k_{id}t^{1/2} + C_{id} \quad (3.5)$$

where values of C_{id} give information on the thickness of the boundary layer (intercept), k_{id} (mg/g.min^{1/2}) is the intraparticle diffusion rate constant (slope).

The intraparticle diffusion is the sole rate-limiting step in determining the kinetics of the process if the plot of q_t against $t^{1/2}$ is linear and the line passes through the origin. Otherwise, some other mechanism such as ion-exchange may also control the rate of adsorption (Wang *et al.*, 2010).

However, adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering these steps mentioned above (Qiu *et al.*, 2009). According to Allard *et al.* quoted by Sutherland and Venkobachar (2010), there are three further pathways by which adsorption may occur onto the surface:

- (1) physical adsorption which is considered rapid, reversible and is due to non-specific forces of attraction (e.g. van der Waals forces);
- (2) electrostatic adsorption due to coulombic forces of attraction between charged solute species and the adsorbing phase - this process is usually rapid and largely reversible;
- (3) specific adsorption due to the action of chemical forces of attraction which leads to surface bonding at a specific site on the solid phase - this process can be slow and partly irreversible.

If the pseudo-second order kinetic model holds true, the rate law for the reaction is expressed as in Equation 3.6 based on adsorption equilibrium capacity (Ho and McKay, 1999).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3.6)$$

3.2.5.2 Equilibrium constant, adsorption percentage, capacity and selectivity

The distribution coefficient K_D is often used to characterise the mobility of metal ions in solutions. It describes the binding ability of the adsorbent surface for an element and measures how well-extracted a species is. Low K_D values imply that most metal remains in solution, and high K_D values indicate that the metal has great affinity for the adsorbent (Echeverria *et al.*, 1998). The distribution coefficient is defined as the ratio of the metal concentration in the solid phase to that in the equilibrium solution after a specified reaction time as expressed in Equation 3.7 below.

$$K_D = \frac{[C]_c^e}{[C]_s^e} = \frac{\text{ng adsorbate} / \text{kg adsorbent}}{\text{mg adsorbate} / \text{L solution}} \quad (3.7)$$

The percentage adsorption for each metal ion was calculated using the following 3.8 Equation:

$$\%R = 100 \times \frac{C_0 - C_e}{C_0} \quad (3.8)$$

The amount of metal adsorbed (adsorption capacity, equilibrium uptake) by the activated carbon, q (mg PMs/g of dry activated carbon) was evaluated using Equation 3.9.

$$q = \frac{(C_0 - C_e)V}{m} \quad (3.9)$$

where C_0 and C_e are the concentrations of PM ions in solution before and after adsorption (mg/L); V is the solution volume (L); m is the weight of activated carbon (g) (Lam *et al.*, 2007).

CHAPTER 4 : PRELIMINARY ADSORPTION TESTS

Preliminary adsorption tests were performed and the emergent findings of the investigation are presented in the present chapter.

This present chapter reports on preliminary adsorption tests performed on a pregnant alkaline leach solution resulting from cyanide extraction of the Platreef ore performed in column leach tests. Two fractions of a low grade sulphide ore originating from the Platreef deposit were leached in two separate columns run in up-flow mode (Mwase, 2009). BM and PM values were recovered from the ore in a two-stage leaching process comprising a first extraction with an aqueous acid solution to remove part of the base metals and a second extraction with cyanide to remove PM values and the residual base metals from the residue. Leachate from column 1 after the second extraction (cyanide), whose chemical composition is displayed in Table 3.1, was used for screening adsorption tests. Tests were conducted for 72 hours and two carbon concentrations were used, viz. 10 and 20 g/L. The granular activated carbon was investigated before and after adsorption by SEM-EDX. X-ray fluorescence (XRF) was used to analyse the chemical compositions of some minerals that are present on the fresh activated carbon surface.

4.1 RESULTS AND DISCUSSION

4.1.1 Characterisation of GAC

4.1.1.1 Scanning electron microscope (SEM) analysis of unloaded GAC

The SEM images of the fresh and acid washed coconut shell MC 110 are shown in Figures 4.1 to 4.4. These illustrate that the granules have a coarse, porous surface with irregular pores, and show the presence of small cavities; cracks, asperities, attached fine particles and many cavernous structures over the activated carbon surface, forming a system of complicated pore networks. The surface character of the GAC is likely to be significant in the loading of PMs. Pleysier *et al.* (2008) report that at gold loadings typical of CIP plants, gold is predominantly adsorbed onto the external surface of the carbon. As similar or lower loadings are expected in the current application, with some similarities in the species being adsorbed, it can be expected that the mechanism might be similar.

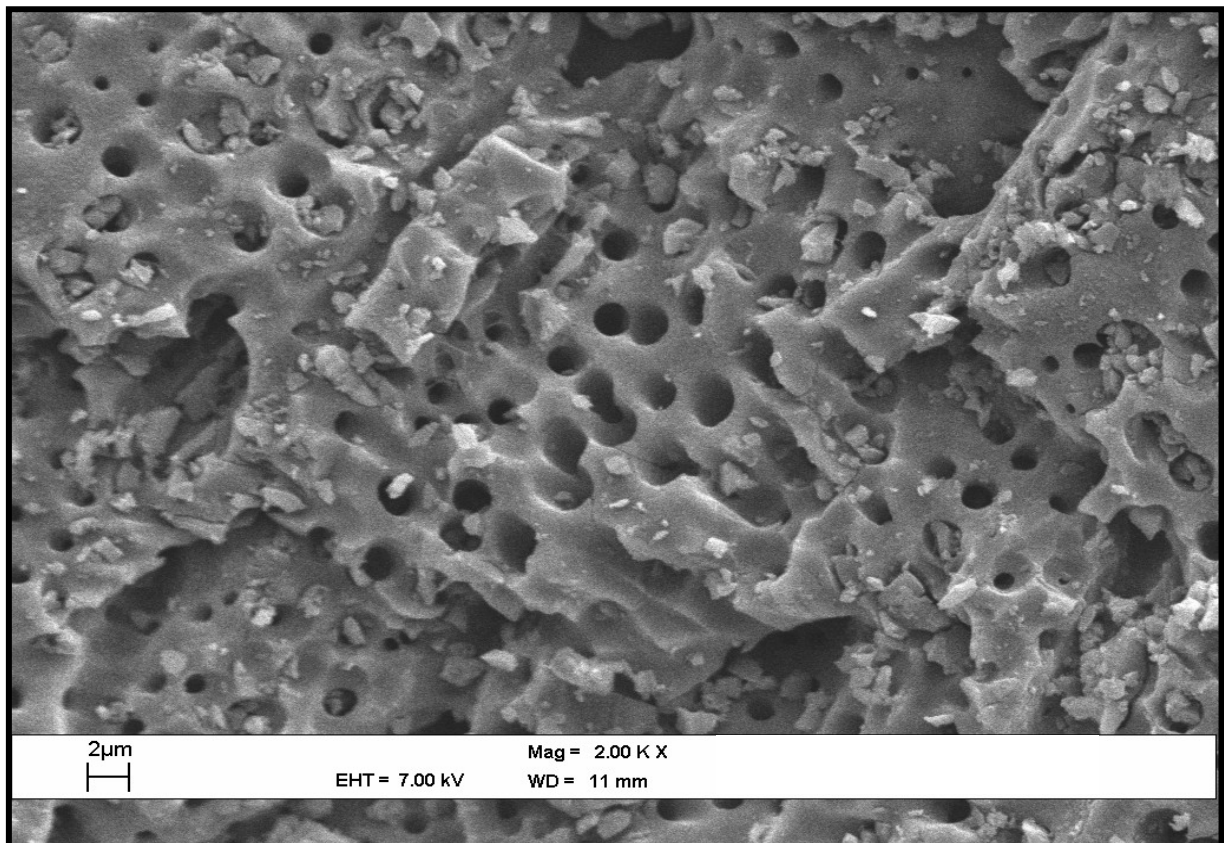


Figure 4.1: Scanning electron micrograph of fresh, unwashed activated carbon particles illustrating the nature of the carbon porosity observed at 2000x magnification

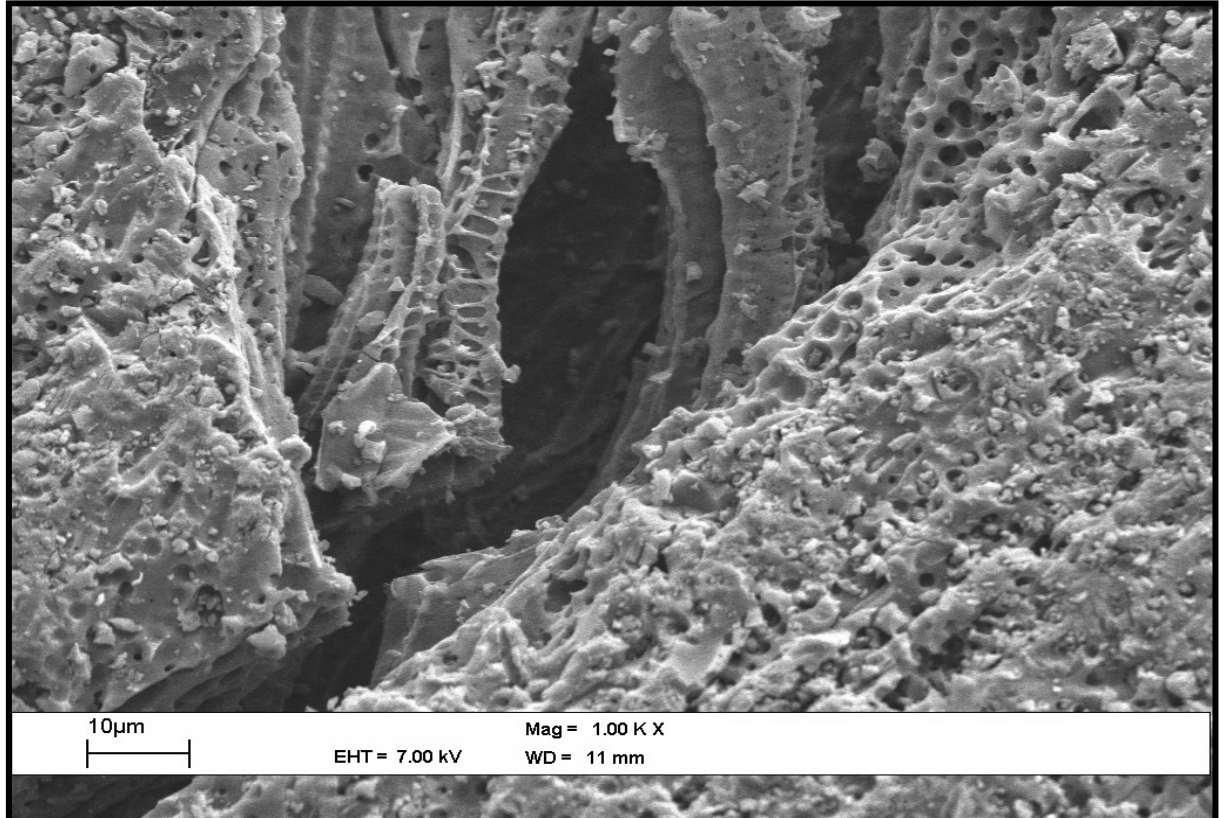


Figure 4.2: Scanning electron micrograph of fresh, unwashed activated carbon particles, showing the inside of the activated carbon (cross-section) observed at 1000x magnification

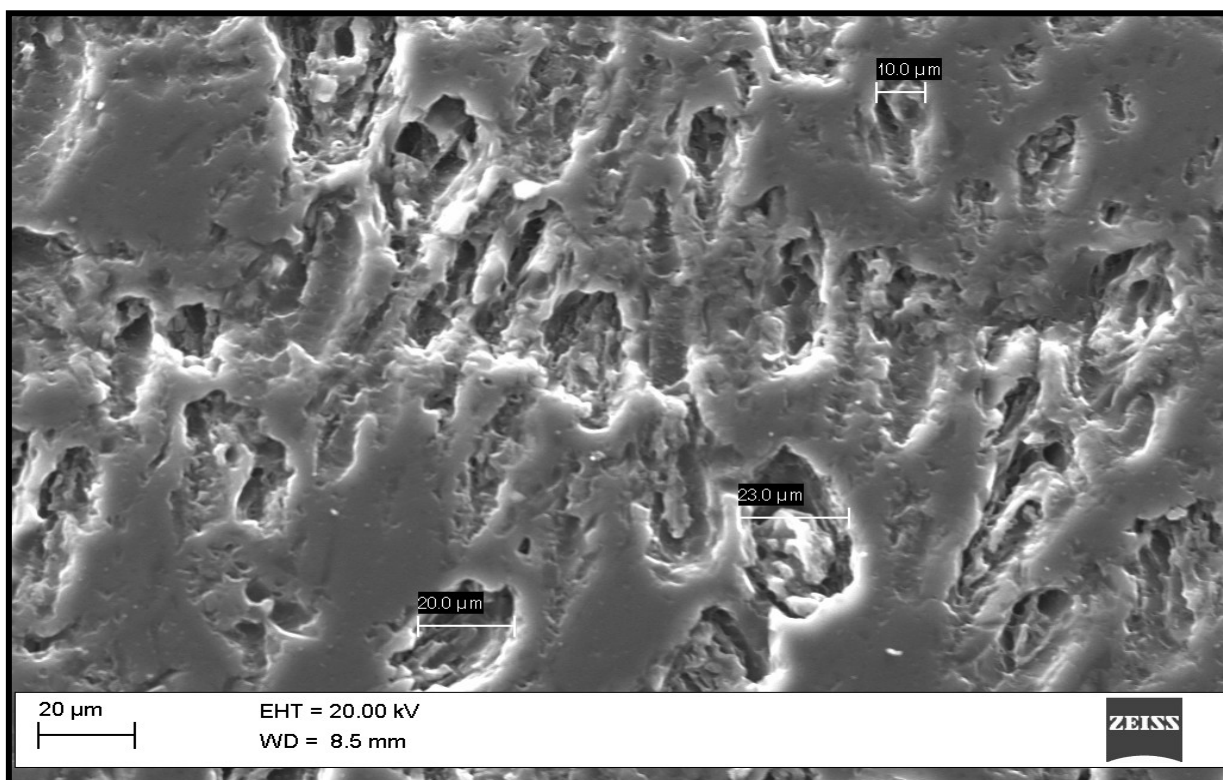


Figure 4.3: Scanning electron micrograph of fresh, unwashed activated carbon particles observed at 2000x magnification

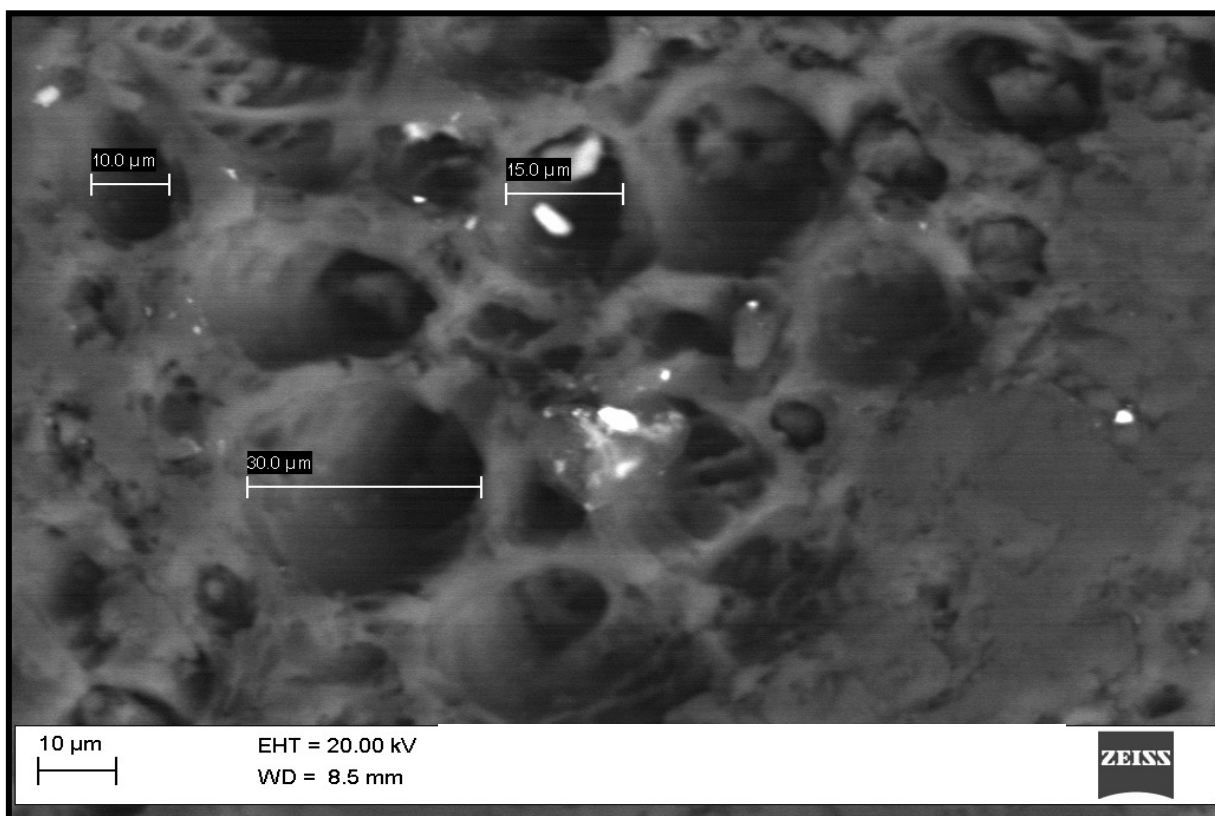


Figure 4.4: Scanning electron micrograph of fresh, acid washed activated carbon particles observed at 2000x magnification

Pore openings of various dimensions were evident on the surface of treated activated carbon (Figure 4.4). External pore openings were observed to be larger in size for larger granules of activated carbon. Further, the pores on the surface of the adsorbent were highly heterogeneous, this combined with surface cavities; provide a large exposed surface area for the adsorption of both precious and base metals.

4.1.1.2 Scanning electron microscope (SEM) analysis of loaded GAC

Figure 4.5 shows a SEM micrograph of activated carbon after adsorption. PMs were not observed in any of the analysed samples. It should be noted that PMs present in low concentrations as sub-micron grains could not be detected by the SEM-EDX analysis. Identification of particles of that size amongst the surface structure on MC 110 is very difficult. Some base metal particles were observed to be adsorbed on the surface of the loaded activated carbon. However these base metal particles were not evenly distributed on the surface.

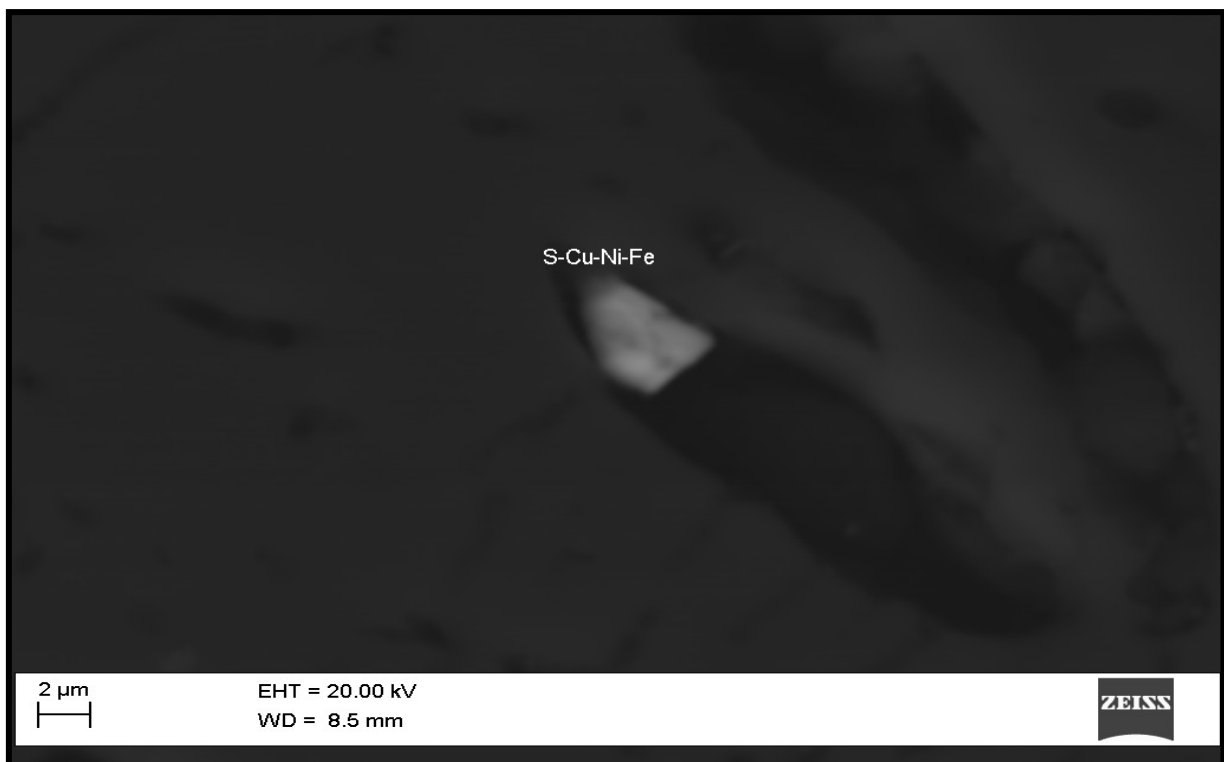


Figure 4.5: Scanning electron microscope image showing mineral assemblage on loaded activated carbon particles after platinum compounds adsorption observed at 2460x magnification

Figure 4.6 shows the EDX spectrum of Figure 4.5 at position S-Cu-Ni-Fe, which indicates effectively the existence of S, Cu, Ni and Fe in the analyzed sample.

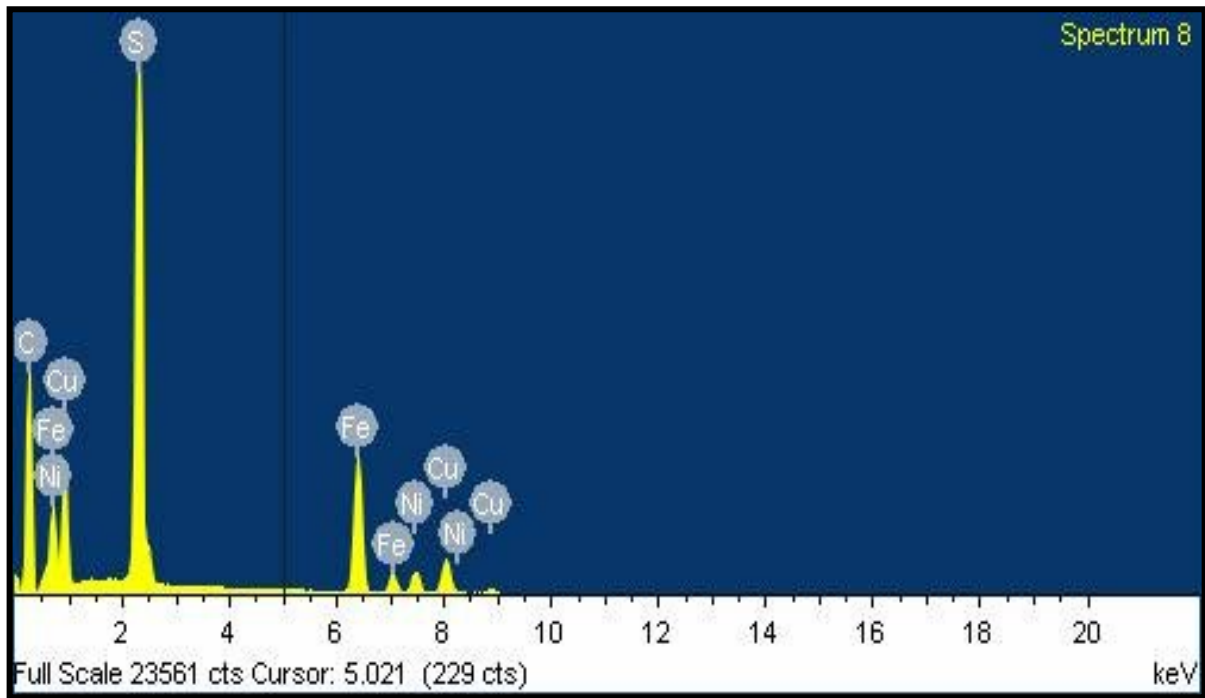


Figure 4.6: EDX spectrum of Figure 4.5 at S-Cu-Ni-Fe position

The SEM-EDX analyses also allowed for the identification of some elements (Pb, Ti and Sn) in minor and trace quantities, which were not identified by XRF.

4.1.1.3 Virgin activated carbon – X-ray fluorescence (XRF) analysis

The composition of inorganic impurities varies widely between carbons of different nature. To determine the metals present in the carbon, XRF was used. Table 4.1 shows some elements identified on the surface of the GAC MC 110 prior to adsorption testing. It can be seen that the amount of transition metal compounds is small, but that potassium compounds are present in significant quantity. The main forms in which metals are present, in the virgin and acid washed activated carbon, were assumed to be the corresponding carbonates, metal oxides, metal chlorides, hydroxides and the unvolatilized elemental metal crystals.

Marsden and House (2006) have shown that under laboratory conditions, gold loading capacity increases with increasing concentration of cations in solution in the following order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{H}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+$. This indicates the possible contribution of metal impurities to the adsorption process. Lagerge *et al.* (1997) pointed out that in industry, sodium aurocyanide (sodium used as counterion) is very often preferred to potassium aurocyanide.

Following acid washing, the presence of residual chloride ions in carbon pores was observed, which are difficult to remove effectively (Table 4.1). According to Marsden and House (2006), despite the washing and neutralizing acid-washed carbon with sequential water and sodium hydroxide washes, 100% removal of chloride species is rarely achieved. The same authors found that Ag, Hg and Cu were not removed from carbon by dilute HCl.

Table 4.1: Activated carbon examined by XRF technique

Elemental composition	Activated carbon content	
	Virgin	Acid washed
Pt	*	*
Pd	*	*
Rh	*	*
Au	*	*
Ni	90.36 ppm	80.27 ppm
Cu	**	**
K	8.20 %	5.64 %
Na	0.13 %	0.07 %
Cl	182.43 ppm	3878.95 ppm

* Below detection limit: 5 ppm

** Below detection limit: 1 ppm

4.1.2 Metal loading

Using the pregnant alkaline leach solution in Table 3.1, the loadings of base and precious metals after 72 hours (one loading cycle) at two different carbon concentrations are displayed in Table 4.2.

Table 4.2: Pseudo-equilibrium uptake of precious and base metals (one loading cycle)

Component Adsorbent concentration	Pt(II)	Pd(II)	Rh(III)	Au(I)		Cu(I)	Ni(II)	Fe(II)
	mg/g	mg/g	mg/g	mg/g		mg/g	mg/g	mg/g
10 g/L	0.0150	0.0370	0.0000	0.0100		1.6500	1.6700	0.1150
20 g/L	0.0075	0.0190	0.0000	0.0050		0.9320	0.8880	0.0000
Total uptake	PMs (mg/g)					BMs (mg/g)		
10 g/L	0.0620					3.4350		
20 g/L	0.0315					1.8200		

From Table 4.2, it can be seen that the pseudo-equilibrium loadings of both precious and base metals are in the range that would be considered 'low'. Typical process loadings in gold operations are higher than those achieved in this work, due to the higher solution concentrations. Heinen *et al.* (1978) have reported that typical loadings obtained commercially range from 5.670 to 22.680 mg of gold, or combination of gold and silver, per gram of carbon; while Fleming (1992) reports loadings of 1 mg/g.

Pleysier *et al.* (2008) noted that in Au adsorption, when the loading is very low, equilibrium is approached rapidly and analytical errors become of greater consequence when determining kinetic parameters. This should be borne in mind when interpreting the loading of Rh, which was present in very low concentration in the leach solution (0.010 ppm), and for which the pseudo-equilibrium loading was not measurable on the basis of solution concentrations. Table 4.2 indicates that Fe was poorly adsorbed compared with the other base metal cyanide complexes.

4.1.3 Effect of activated carbon concentration

The adsorption capacity increased with decreasing activated carbon concentration and the highest PMs uptake (0.0620 mg/g) was achieved when using 10 g/L of solution. Many factors can contribute to this adsorbent concentration effect. The most important factor is that adsorption sites remain unsaturated during the adsorption process whereas the number of available adsorption sites increases by an increase in adsorbent concentration, thereby resulting in an increase in adsorption percentage (Nguyen *et al.*, 2010). Further tests were required to confirm these preliminary conclusions, to determine the kinetics, the optimum adsorbent concentration and saturated metal loading capacity.

4.1.4 Adsorption profiles

The adsorption profiles for both precious and base metals expressed as dimensionless concentrations in the aqueous phase are shown in Figures 4.7 to 4.10, where the ratio $[C]_t/[C]_0$ denotes the fractional amount of the species that remains in solution at time t . It is evident from Figures 4.7 and 4.8 that the adsorption of both Pt(II) and Pd(II) is comparatively fast for the first 120 minutes, and then slows, achieving close to 100% adsorption for Pt, Pd and Au. At these loadings, it is likely that film diffusion is the rate-limiting step and that metals will be adsorbed predominantly on the surface, by analogy with findings for gold adsorption (Pleysier *et al.*, 2008).

As the concentration drops in the bulk solution, the driving force decreases and this might explain the reduction in kinetics. However at much higher activated carbon loading than that observed in this investigation, any reduction in the adsorption kinetics might be explained by the difficulty to occupy the remaining vacant surface sites due to repulsive forces between the solute molecules on the solid and bulk phase. Thereby surface diffusion in the interior of the particles becoming rate-limiting.

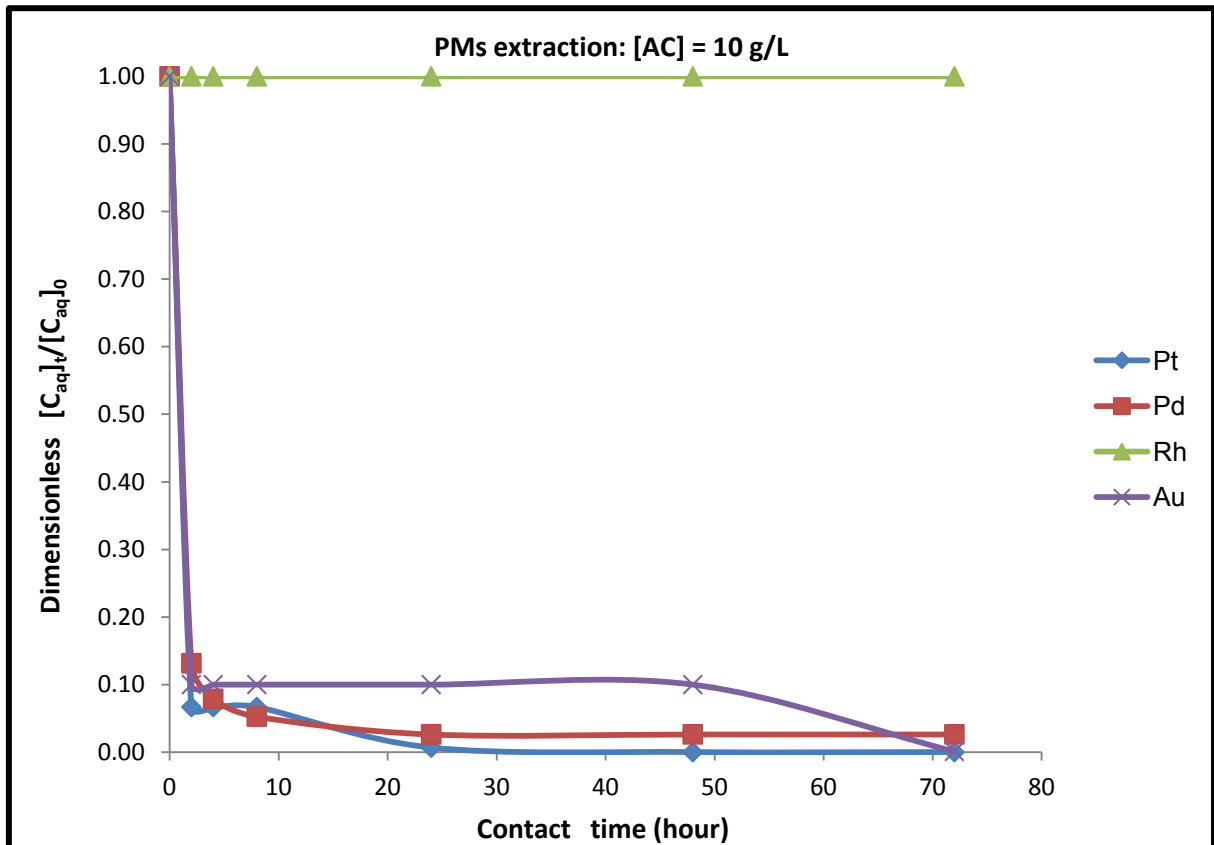


Figure 4.7: Dimensionless time-concentration profiles for precious metal adsorption (Conditions: pH = 10, [CN] = 12.5 ppm, [SCN] = 3670 ppm, [Activated carbon] = 10 g/L and contact time = 72 hours)

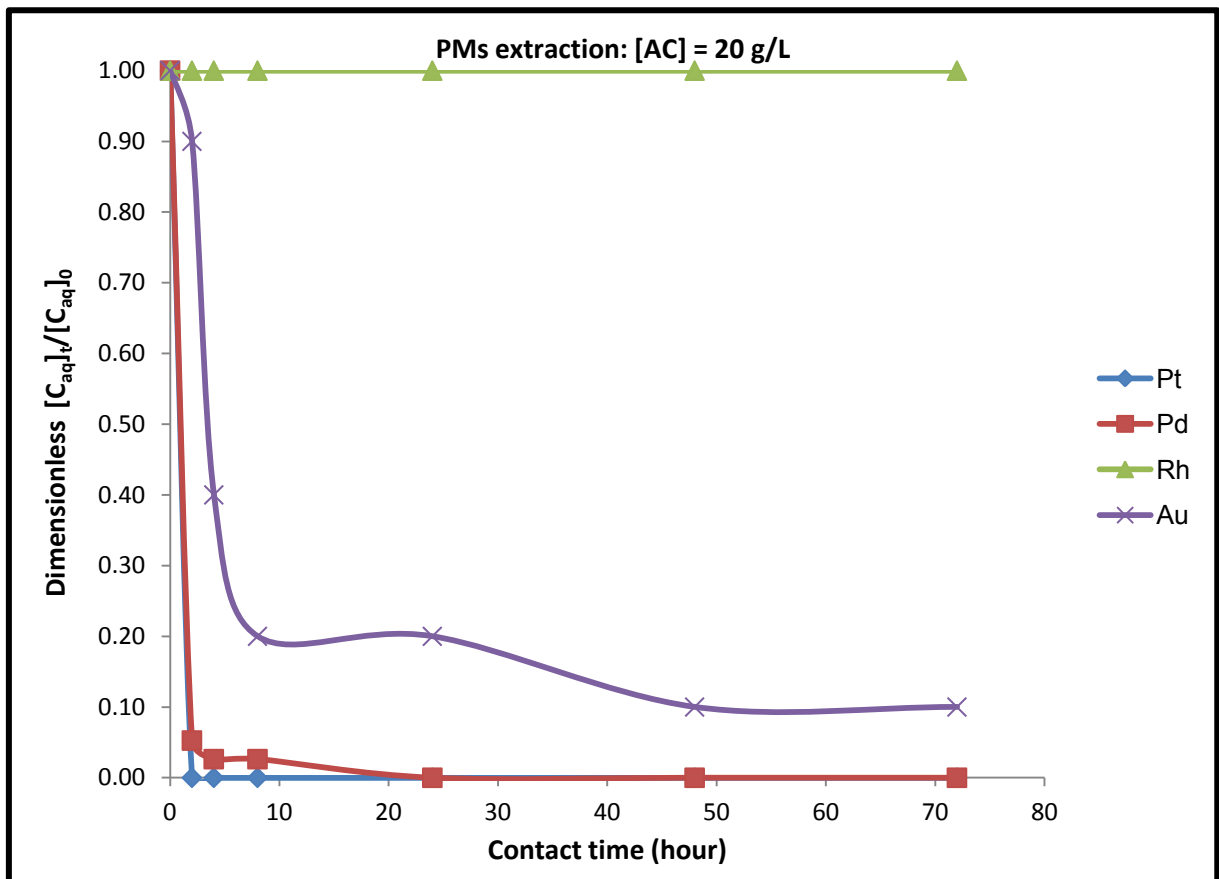


Figure 4.8: Dimensionless time-concentration profiles for precious metal adsorption (Conditions: pH = 10, [CN] = 12.5 ppm, [SCN] = 3670 ppm, [Activated carbon] = 20 g/L and contact time = 72 hours)

Figures 4.9 and 4.10 reveal that after one hour, Cu(I) adsorption was roughly 5% for the two tests whilst Pt(II) extraction was between 95 to 100%. Hence Cu(I) co-adsorption might be avoided by operating with a residence time of less than one hour. Copper adsorption increased considerably over time from 5% after one hour to between 90 and 100% after 72 hours. Ni(II) adsorption exhibits kinetics similar to those of Pt(II), Pd(II) and Au(I) as can be seen in Figures 4.11 and 4.12. The high initial uptake rate of Ni(II) may also be ascribed to the availability of a large number of adsorption sites on the adsorbent surface and film diffusion being rate-limiting. As mentioned previously in section 2.2.2 B, Marsden and House (2006) have observed that despite the highly selectivity of activated carbon for gold and silver over most other metal species, high loadings of nonprecious metals could be achieved onto activated carbon in the absence of significant precious metal values, irrespective of the general order expressed in Equation 2.4.

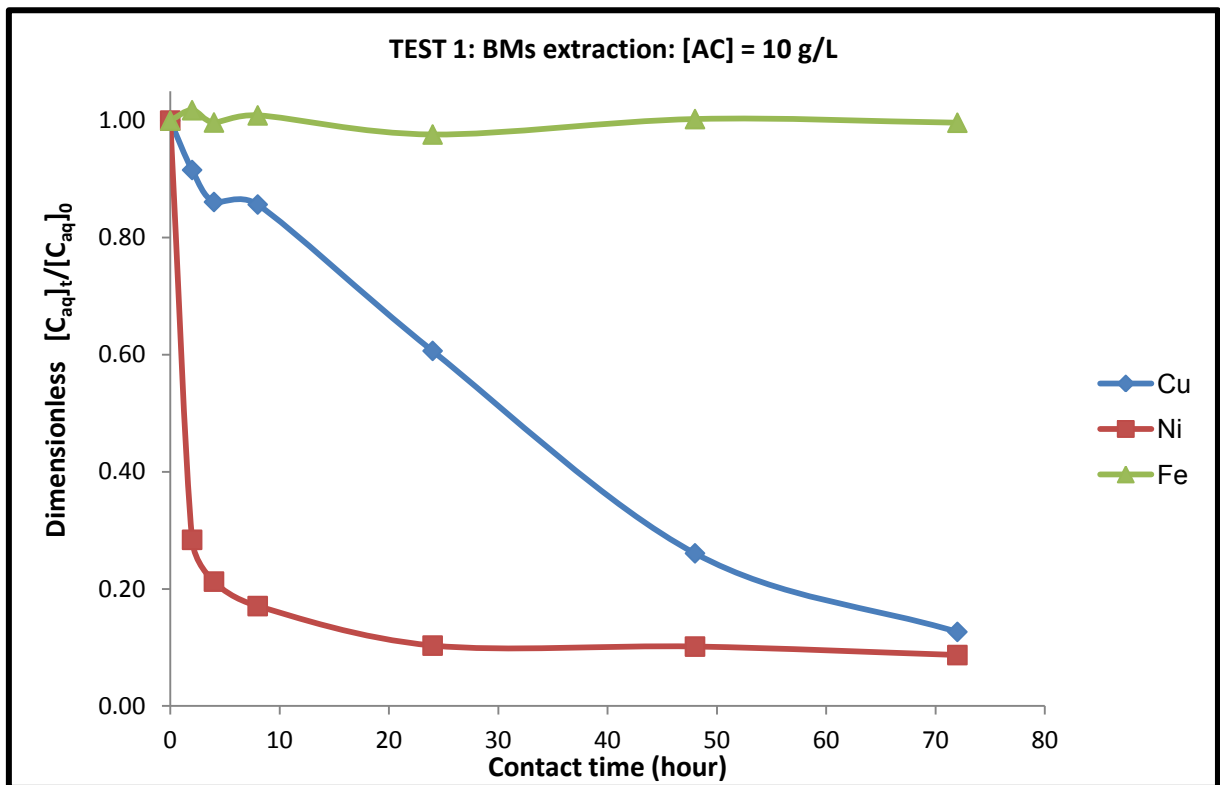


Figure 4.9: Dimensionless time-concentration profiles for base metal adsorption (Conditions: pH = 10, [CN] = 12.5 ppm, [SCN] = 3670 ppm, [Activated carbon] = 10 g/L and contact time = 72 hours)

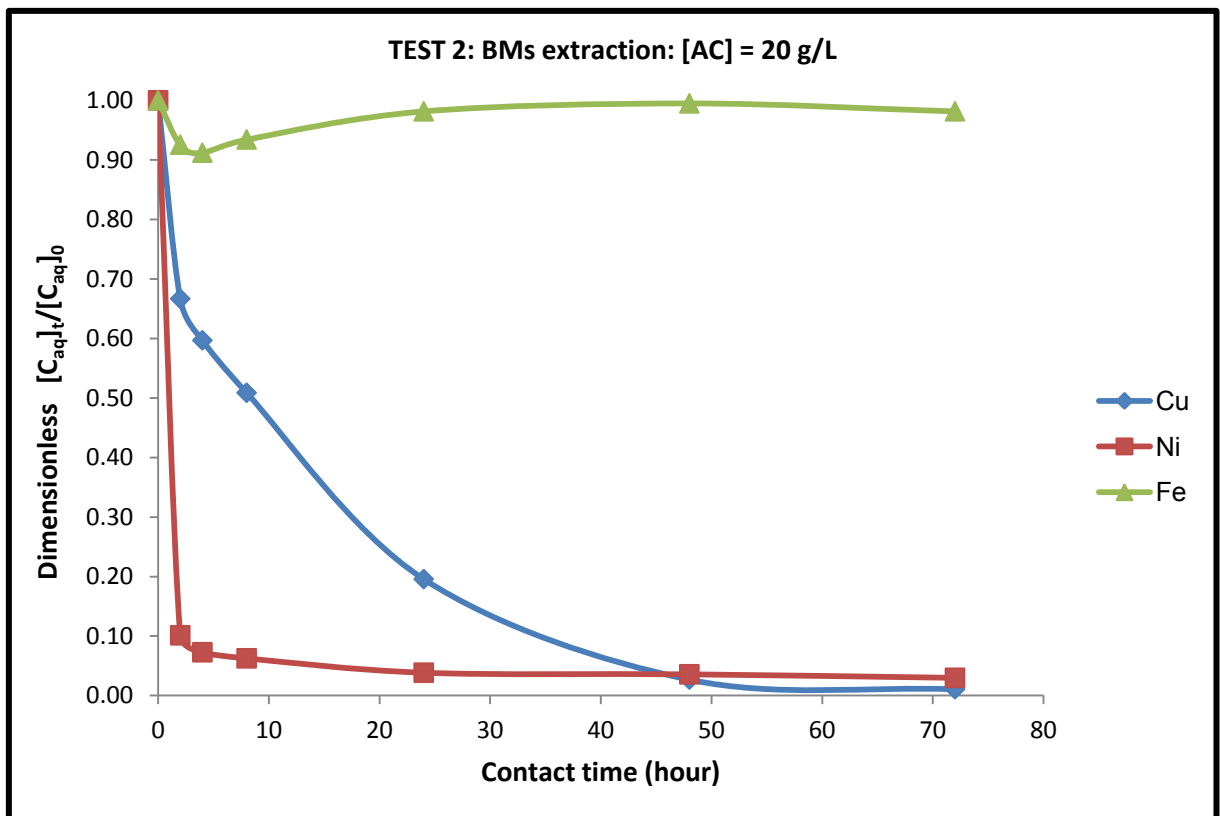
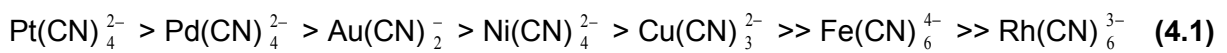


Figure 4.10: Dimensionless time-concentration profiles for base metal adsorption (Conditions: pH = 10, [CN] = 12.5 ppm, [SCN] = 3670 ppm, [Activated carbon] = 20 g/L and contact time = 72 hours)

No significant changes in the solution concentrations of Rh(III) and Fe(II) were observed after 72 hours. At such low solution concentrations (0.010 ppm), it is possible that Rh reaches equilibrium very rapidly at a concentration where analytical errors are significant. It is also expected that Rh is present in the solution as $\text{Rh}(\text{CN})_6^{3-}$ but it has not been established in these tests how this influences the adsorption reaction, which would require three cation molecules for each $\text{Rh}(\text{CN})_6^{3-}$ molecule adsorbed. According to Aguilar *et al.* (1997), the selective adsorption of Pt(II), Pd(II), Rh(III), Fe(II) and Ni(II) cyanides can be linked to their chemical structure (see section 2.4.2.2). The order of adsorption for the screening study was suggested to be as expressed in Equation 4.1. In other words, the selectivity of activated carbon for PGMs and Au in the presence of high base metal concentrations needed to be investigated further.



A brief and comparative summary of processes covering both recoveries of base and precious metal cyanide complexes is summarized in Figures 4.11 and 4.12 below.

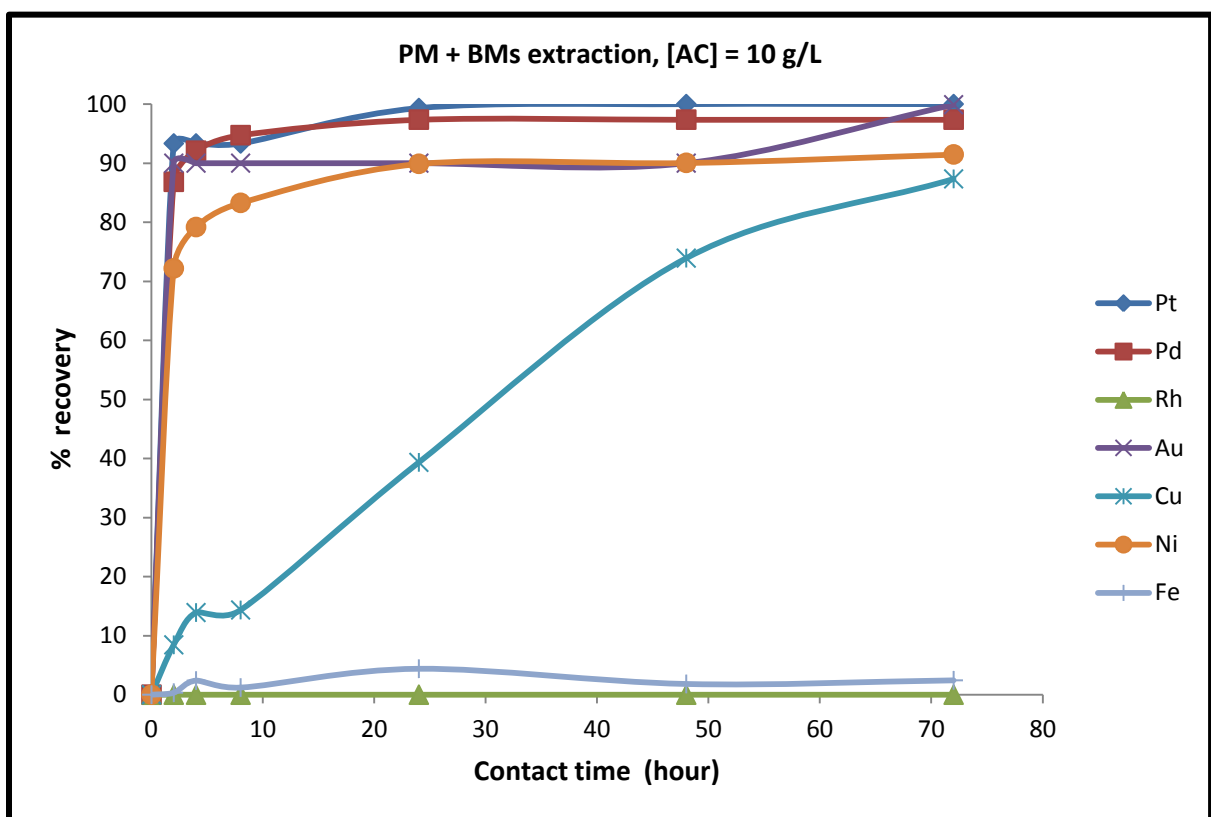


Figure 4.11: Summary of results obtained from studying the kinetics of the activated carbon/PM-BMs adsorption; unless otherwise stated, experimental conditions were: pH = 10, [CN] = 12.5 ppm, [SCN] = 3670 ppm, [Activated carbon] = 10 g/L and contact time = 72 hours

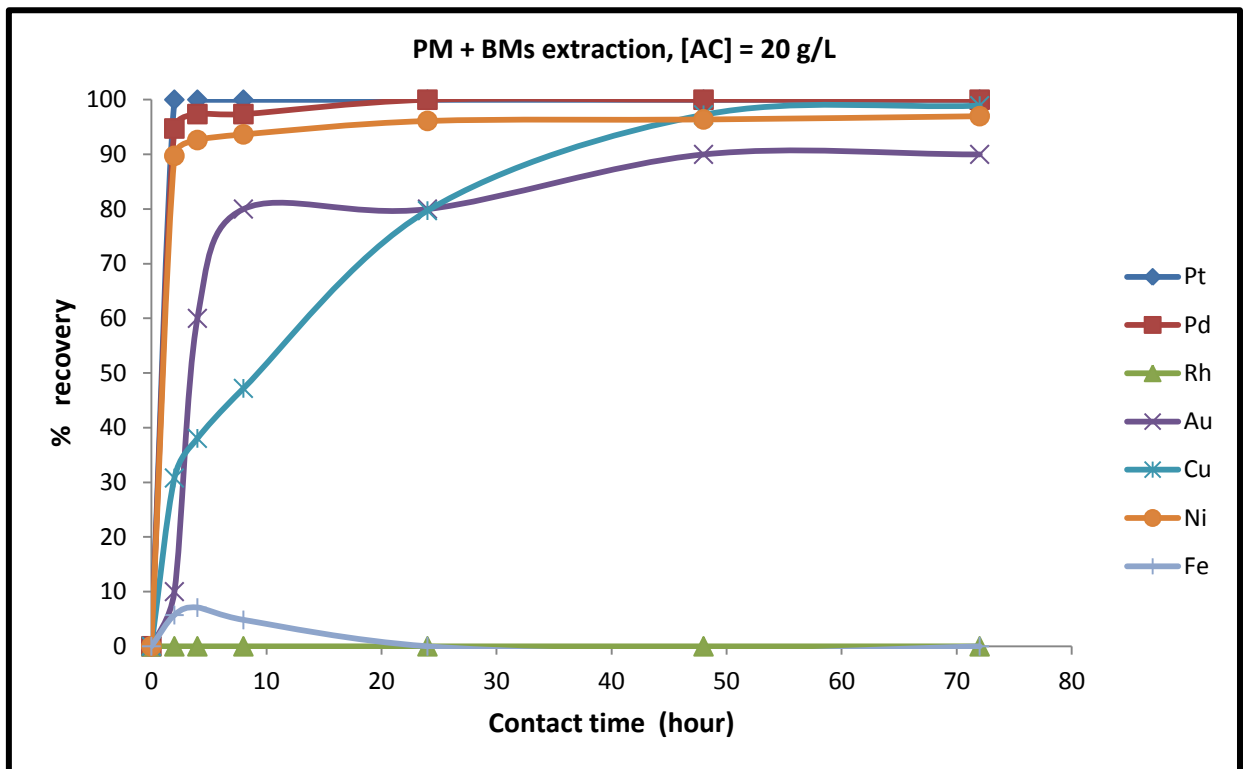


Figure 4.12: Summary of results obtained from studying the kinetics of the activated carbon/PM-BMs adsorption; unless otherwise stated, experimental conditions were: pH = 10, [CN] = 12.5 ppm, [SCN] = 3670 ppm, [Activated carbon] = 20 g/L and contact time = 72 hours

4.1.5 Adsorption mechanism

According to Gardea-Torresday and co-workers as reported by Wankasi *et al.* (2006), a long contact time to reach equilibrium indicates that the predominant mechanism is physical adsorption, while short contact times indicate chemisorption. The relatively short contact times for the carbon-metal ion systems observed in this investigation could indicate that chemisorption is probably the predominant mechanism. A further confirmation on the mechanism of adsorption is discussed in Section 5.6.2.

4.2 CONCLUDING REMARKS

Bottle-roll adsorption tests performed with 10 and 20 g/L of MC 110 granular activated carbon showed that adsorption of Pt(II), Pd(II) and Au(I) from a pregnant alkaline cyanide leach solution gave recoveries of > 90% in 2 hours, suggesting that this is a feasible process option for the recovery of these metals. The recovery of Rh(III) was negligibly small. Adsorption of Ni(II) was found to proceed at approximately the same rate and with the same recovery as the precious metals. Adsorption of Cu(I) proceeded more slowly to recoveries of approximately 90%. The slower kinetics suggest that co-adsorption of Cu(I) might be avoided by contact times of less than 2 hours. Adsorption of Fe(II) was found to be less than 5%.

CHAPTER 5 : EFFECT OF SELECTED OPERATING PARAMETERS ON THE ADSORPTION PROCESS – RESULTS AND DISCUSSION

Findings, discussions and interpretation of results are presented in the present chapter. As mentioned previously in Chapter 3, the general experimental procedure consisted of two distinct sequential steps: screening tests were first undertaken in Chapter 4, and then statistically designed experiments in Chapter 5 were performed based on findings from the former chapter.

The preceding chapter described preliminary studies of the adsorption of precious and base metal cyanides from actual heap leach solutions by activated carbon MC 110. However, in optimizing the performance of any particular carbon-adsorption process, it is necessary to examine in detail the various parameters that influence the adsorption, and to assess their relative importance on the adsorption performance characteristic. In this chapter, results are reported of experiments in which the influence of a number of variables on the rate of adsorption, loading, equilibrium capacity of platinum group metal and gold cyanides was examined.

5.1 SELECTION OF OPERATING VARIABLES

The choice of parameter values can greatly affect the final outcome of a process. Thus care must be taken in their determination. In order to best select operating variables for the test-work, consideration of the behaviour of copper during precious metals leaching and carbon adsorption processes was important. Copper remains one of the most troubling elements in both processes. The variables affecting its adsorption on activated carbon included among others, the solution pH and free cyanide (CN^-) concentration. As stated earlier in Chapter 4, nickel cyanide complexes were fully loaded on activated carbon. Previous studies by Davidson *et al.* (1979) have shown that thiocyanate ion (SCN^-) is generated from cyanide treatment of refractory sulphide ore/concentrate, with its potential negative implication on gold adsorption.

Finally, it is usually acknowledged that increasing adsorbent and initial metal ion concentrations would result in the increase of adsorption rate. Hence, parameters to be investigated in this experimental study were: solution pH, copper, nickel, free cyanide ion, thiocyanate, adsorbent and initial metal ion (Pt, Pd and Au) concentrations. Iron and rhodium adsorptions were omitted from this study as their effective adsorption were found negligibly small in the preceding chapter.

5.2 EXPERIMENTAL PROCEDURE

Two sets of laboratory scale experiments were conducted using synthetic solutions whose chemical composition is displayed in Tables 5.1 and 5.7. The first set consisted of loading tests that were designed to generate the optimum operating conditions of the adsorption process. The second set of experiments consisted of loading capacity studies. From the first set, a screening approach based on factorial design was used to select factors displaying the most effects on the adsorption process. In a multi-response situation the problem is more complex than in the single response case. Having high adsorption efficiency with the least amount of adsorbent usage is more favourable. High loading capacity avoids excess carbon to elution and regeneration stages. Simultaneous optimization of adsorption responses (R) excluding adsorption capacity (q) was carried out for simplification purposes.

Table 5.1: Factors and levels used in factorial design

OPERATING FACTORS	NOTATION	Low level	High level
pH	A	9.5	12
[Cu(I)] (ppm)	B	10	100
[Ni(II)] (ppm)	C	10	100
[CN ⁻] (ppm)	D	100	300
[SCN ⁻] (ppm)	E	50	100
[PMs]: 2E + Au(I) (ppm)	F	0.63	2.03
Carbon concentration [AC] (g/L)	G	10	20

5.3 RESULTS AND DISCUSSION

5.3.1 Adsorption equilibrium time of PMs: Pt, Pd and Au

The effect of contact time on the adsorption of PMs onto activated carbon was studied over mixing times of 0 to 72 hours, using different initial precious and base metal concentrations. Figures in Appendix B showed that the adsorption of PMs increases rapidly in the first contact time of 2 hours and then achieves pseudo-equilibrium in almost 10 hours. The initial rapid stage is probably due to the abundant availability of functional groups at the surface of the adsorbent. The initial concentration of PMs (Pt, Pd and Au) did not have a significant effect on the contact time to achieve equilibrium. On the contrary, the quick adsorption of PMs suggests that chemical adsorption rather than physical adsorption could contribute to their adsorption. However, the longer the residence time of the process, the more copper and nickel are adsorbed. As a result, a contact time of 2 hours was selected as the effective loading time – as depicted for illustration purposes in Figure 5.1 – in order to prevent excessive co-adsorption of those two base metals, particularly copper.

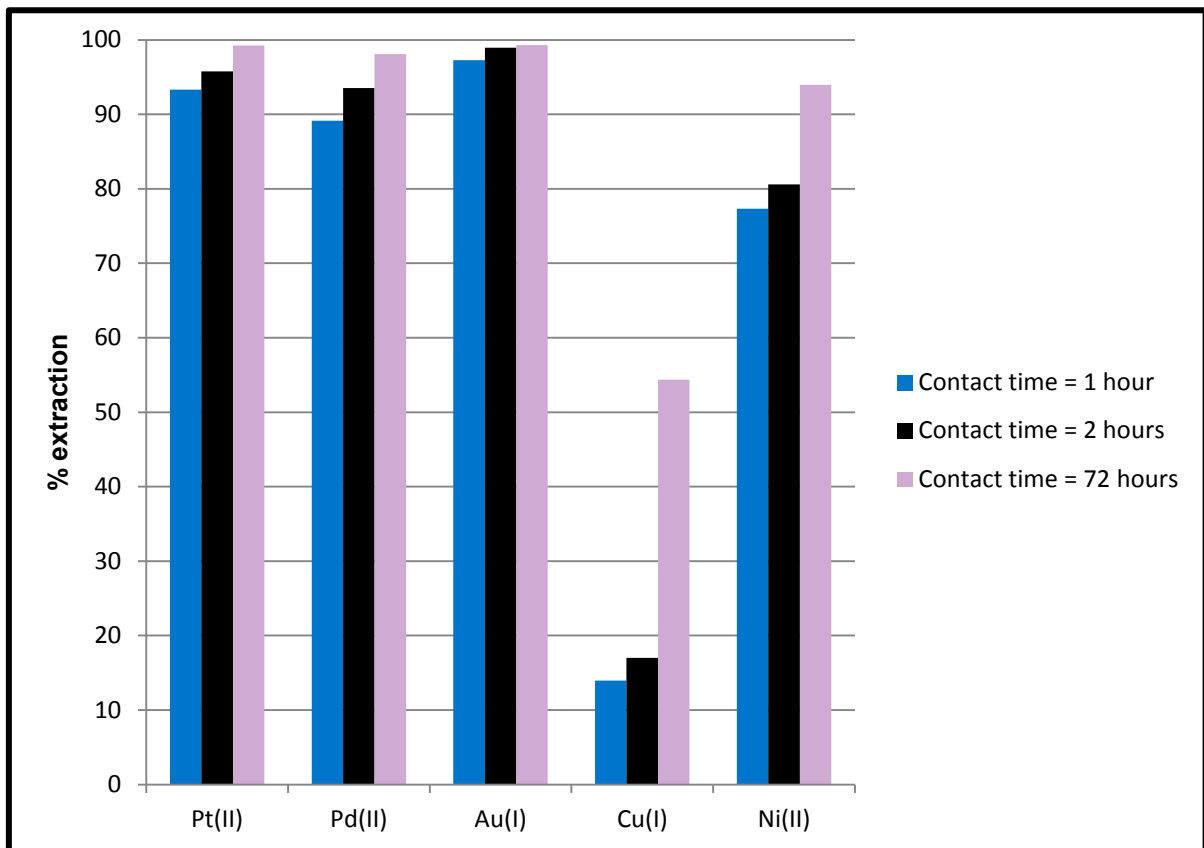


Figure 5.1: Effect of contact time on the adsorption efficiency of precious and base metals under the specified conditions: (Adsorbent concentration: 10 g/L; [Cu(I)]: 10 ppm; [Ni(II)]: 10 ppm; pH: 9.5; [CN]: 300 ppm; [SCN]: 100 ppm; [PMs]: 0.63 ppm)

5.3.2 Screening important factors – Analysis of variance (ANOVA)

In order to identify the factors influencing PMs (Pt, Pd and Au) adsorption onto activated carbon, the results were tested for significance graphically using half-normal plots (Daniel plot) and Pareto charts, as displayed in Figures 5.2 to 5.7.

5.3.2.1 Half-normal plot (Daniel plot)

The half-normal plot leads to a straight line for normally distributed effects; a deviation from this straight line indicates that the corresponding effect has to be considered significant (Hund *et al.*, 2000). The larger the significant effects, the further away they are from the straight line (Gómez and Callao, 2008). In other words, all the effects that lay along the line are negligible.

The half-normal probability plot for the adsorption of Pt(II) appears in Figure 5.2. There are basically four effects which lie away from the straight line, in order of significance: [Ni(II)], [AC], [Cu(I)] concentrations and solution pH. These factors are the most important affecting Pt(II) adsorption.

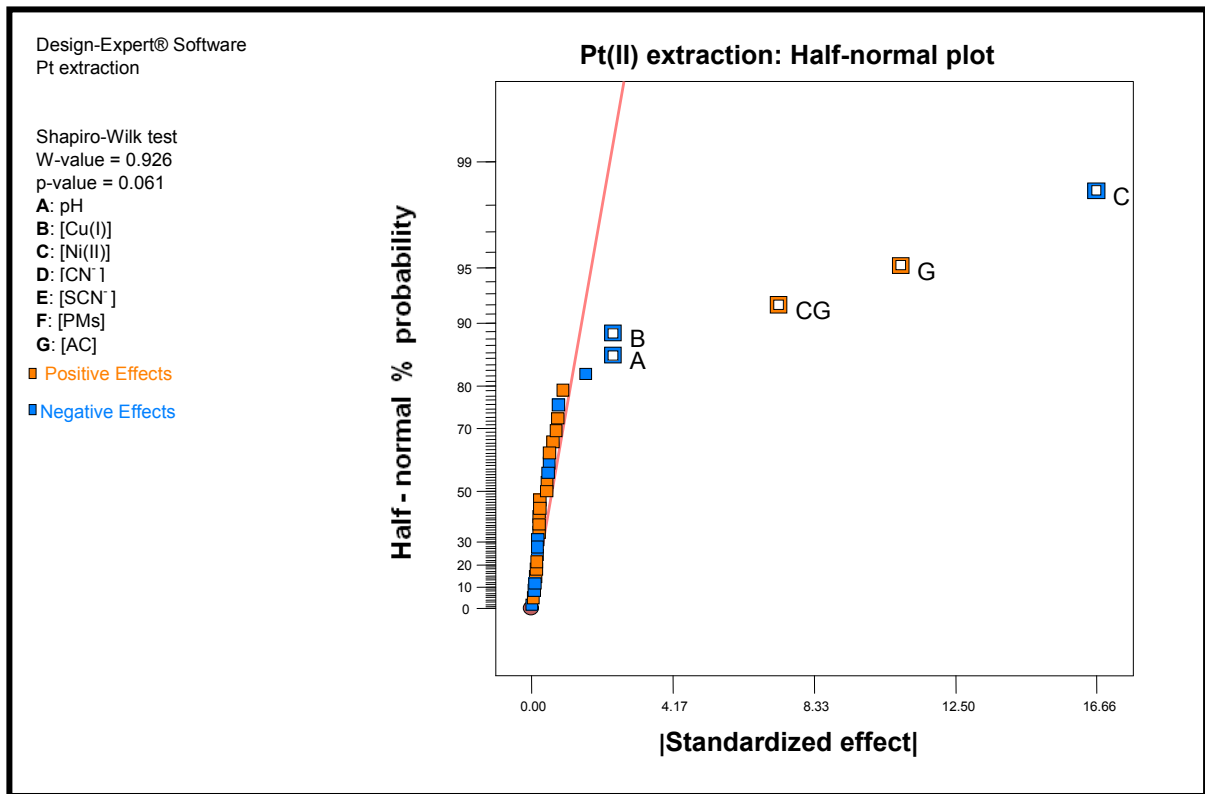


Figure 5.2: Half – normal probability plot of effects on Pt(II) adsorption

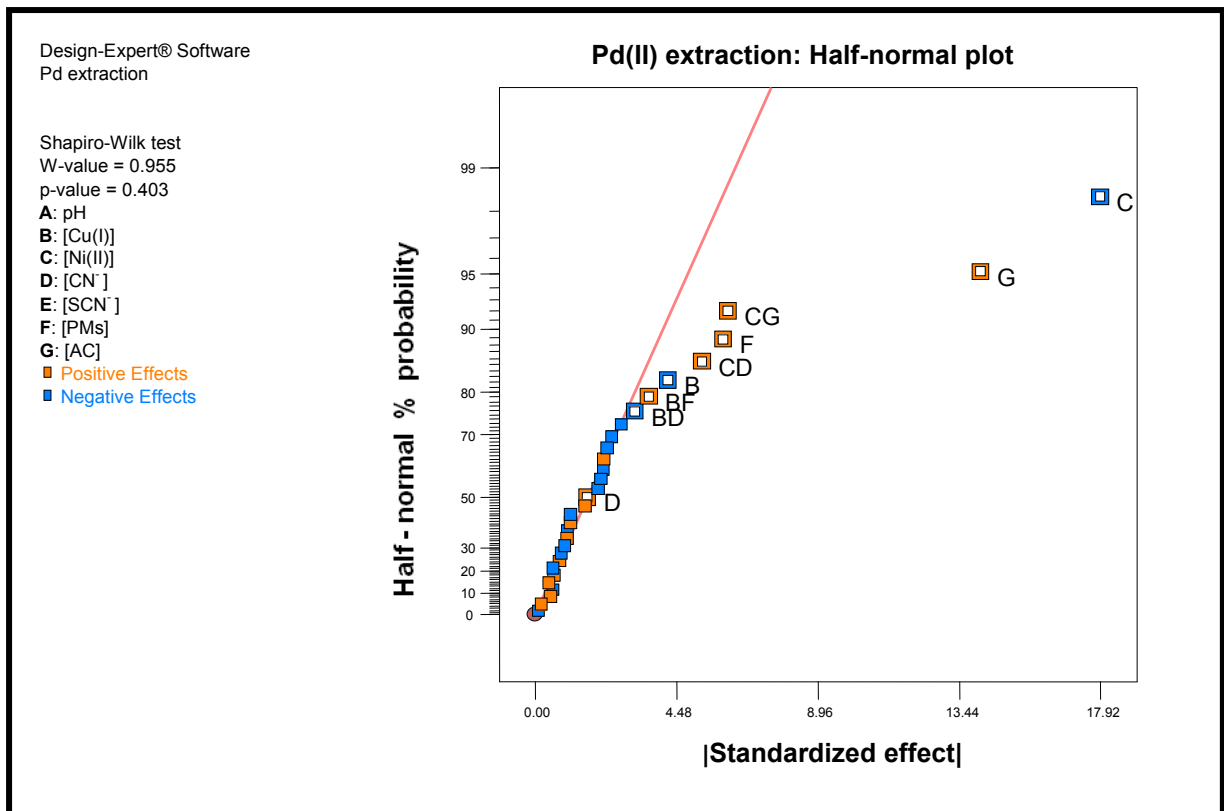


Figure 5.3: Half – normal probability plot of effects on Pd(II) adsorption

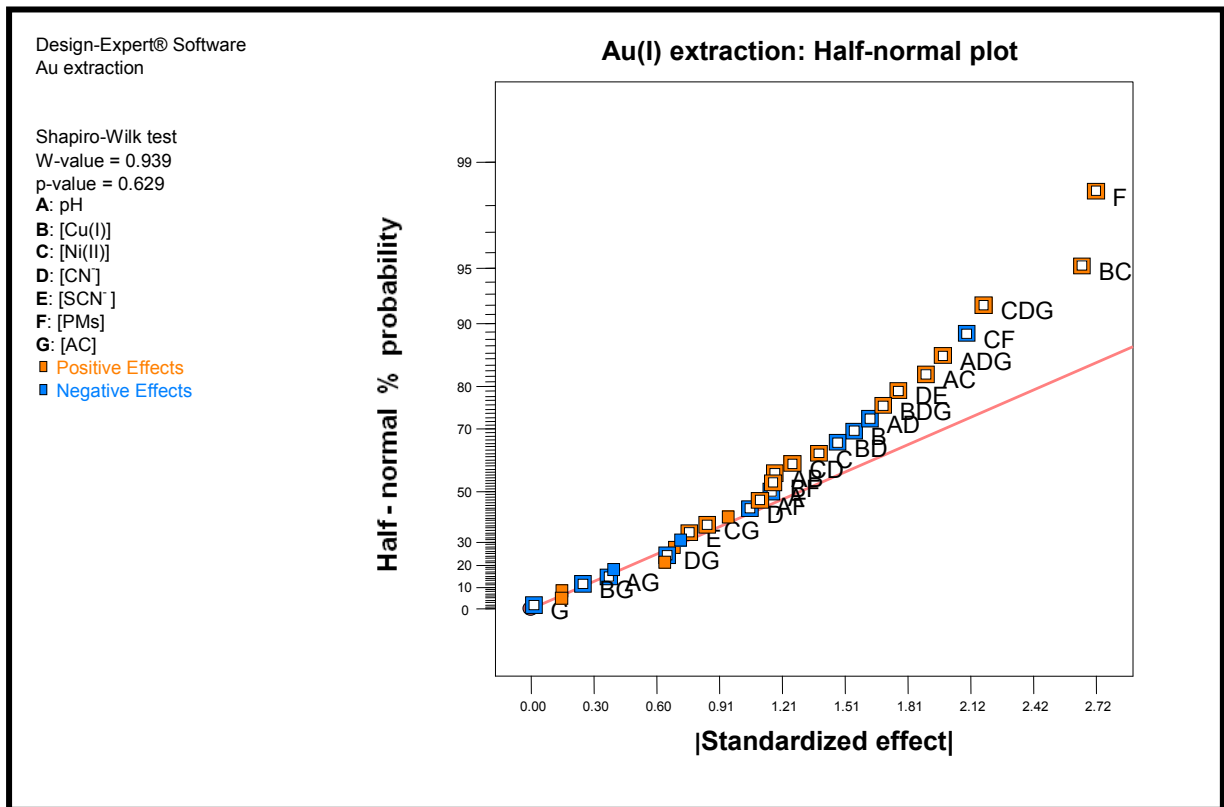


Figure 5.4: Half – normal probability plot of effects on Au(I) adsorption

Regarding the adsorption of Pd(II), the half-normal probability plot of the effects displayed in Figure 5.3 showed that [Ni(II)], [AC], [PMs] and [Cu(I)] were the most important factors affecting its adsorption.

The half-normal probability plot for the adsorption of Au(I) appears in Figure 5.4. There is basically only one effect which lies far away from the straight line: [PMs]. It may be noted that the half-normal plot of effects gives a visual tool to split effects. However as there is no limit distance between effects and the straight line, the use of this tool is qualitative rather than quantitative. [Cu(I)] and [Ni(II)] lie slightly far away from the straight line, but are not statistically significant ($p > 0.05$). Combine this visual tool with both the ANOVA p-values (Pareto chart) will determine which effects to put into the final prediction model.

5.3.2.2 Pareto chart

The importance (magnitude) of the chosen effects from Daniel plot was also visually studied with Pareto charts, which show important factors in the response in the form of a graph (Figures 5.5 to 5.7). The Pareto plot draws two different reference lines that indicate the confidence level. Two different t limits are plotted based on the Bonferroni corrected t and standard t (Moradi and Monhemius, 2011). Effects that are above the Bonferroni limit are almost certainly significant and should be added to the model. Effects that are above the t-

value limit are possibly significant and should be added if they make sense, while effects that are below the t-value limit are considered to be not significant (Antony, 2003).

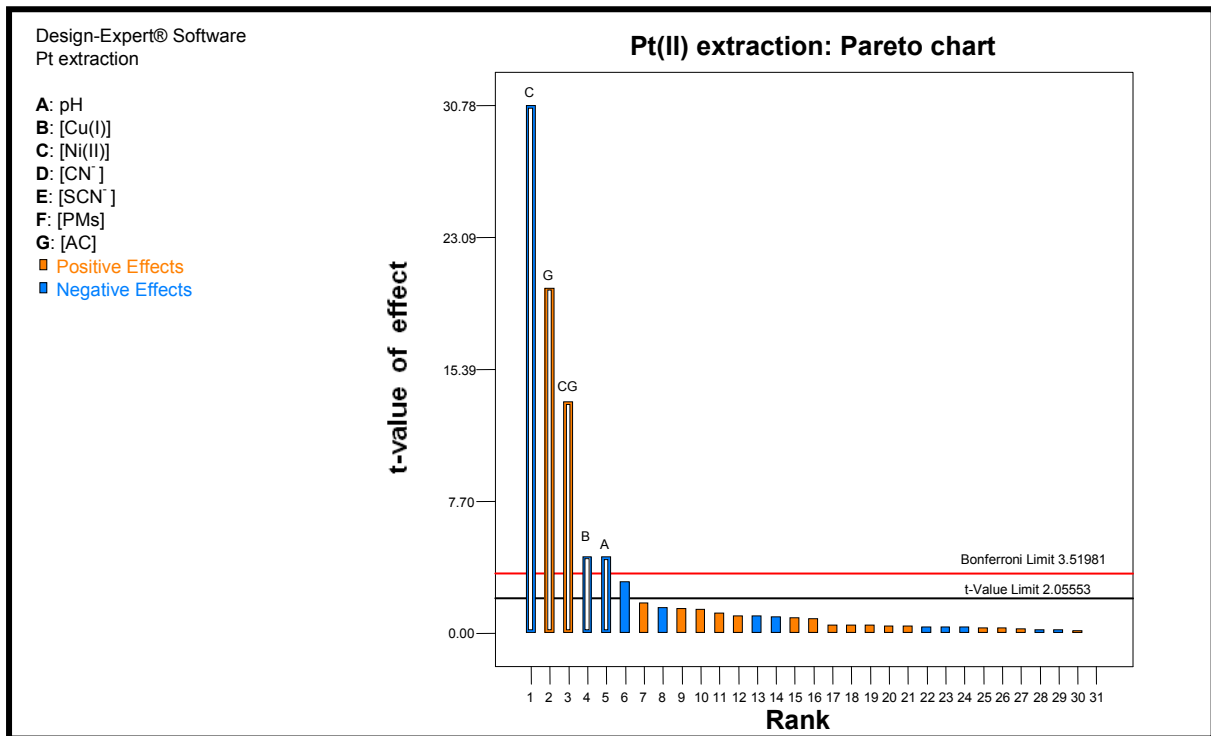


Figure 5.5: Pareto chart of standardized effects for Pt(II) adsorption onto activated carbon

The Pareto chart in Figure 5.5 shows the effect of different factors on Pt(II) adsorption. It was found that t-value of [Ni(II)], [AC], [Cu(I)] and solution pH were higher than the Bonferroni limit, which indicates that their concentrations are critical for Pt(II) adsorption. However the initial concentration of PMs was not important, which indicated that adsorption tests were carried out in experimental conditions in which PMs were mainly adsorbed.

Figure 5.6 shows the Pareto chart which gives the relative importance of the individual and interaction effects with regards to Pd(II) adsorption. Effects that are above the t-limit are significant ([Cu(I)]) and those above the Bonferroni limit are definitely significant and must be included in the model ([Ni(II)], [AC], [PMs]).

Pareto chart bars in Figure 5.7 shows the effect of different factors on Au(I) adsorption. It was found that t-value of [PMs] factor and all interaction effects were lower than Bonferroni limit, which indicates that their concentrations are not critical for Au(I) adsorption. Although [Ni(II)] and [Cu(I)] effects were higher than the t-value limit, they were statistically insignificant ($p = 0.1065$ and 0.0757 , respectively). On the other hand, Figure 5.7 shows that two variables, CN^- and SCN^- concentrations, do not reach the reference line but have an influence on responses because of their interaction with other variables.

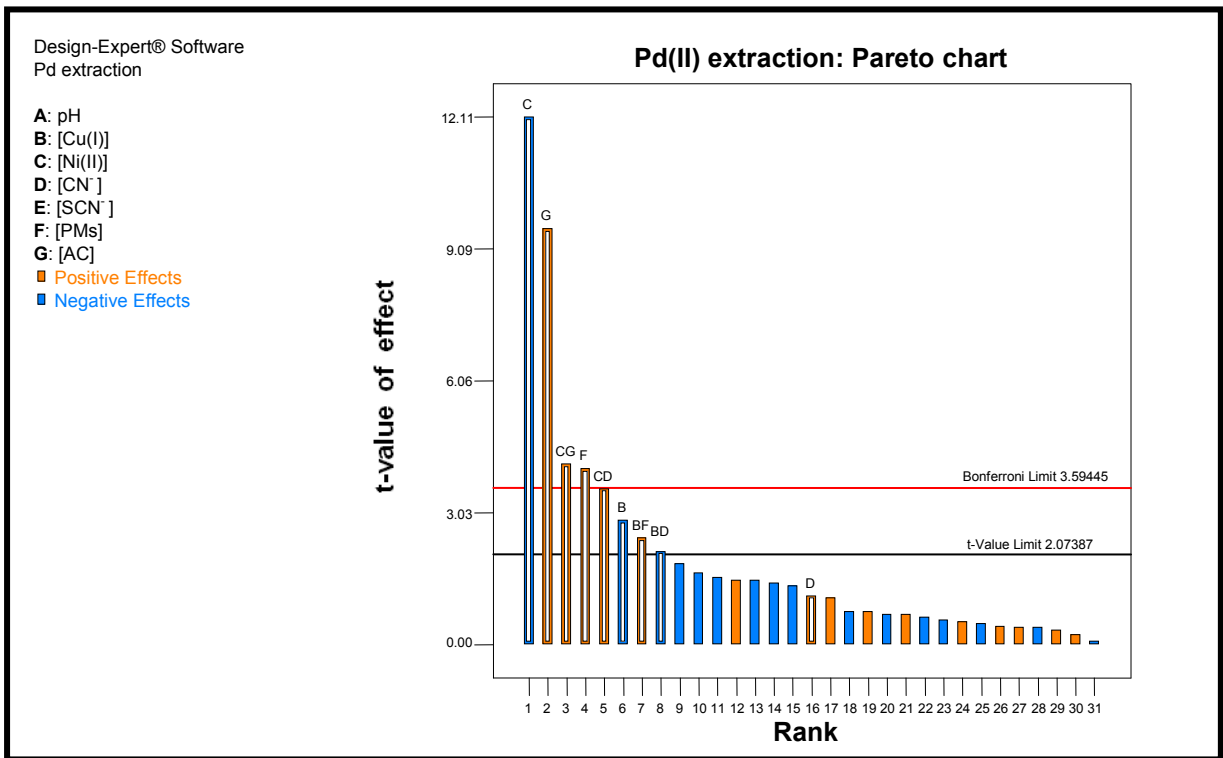


Figure 5.6: Pareto chart of standardized effects for Pd(II) adsorption onto activated carbon

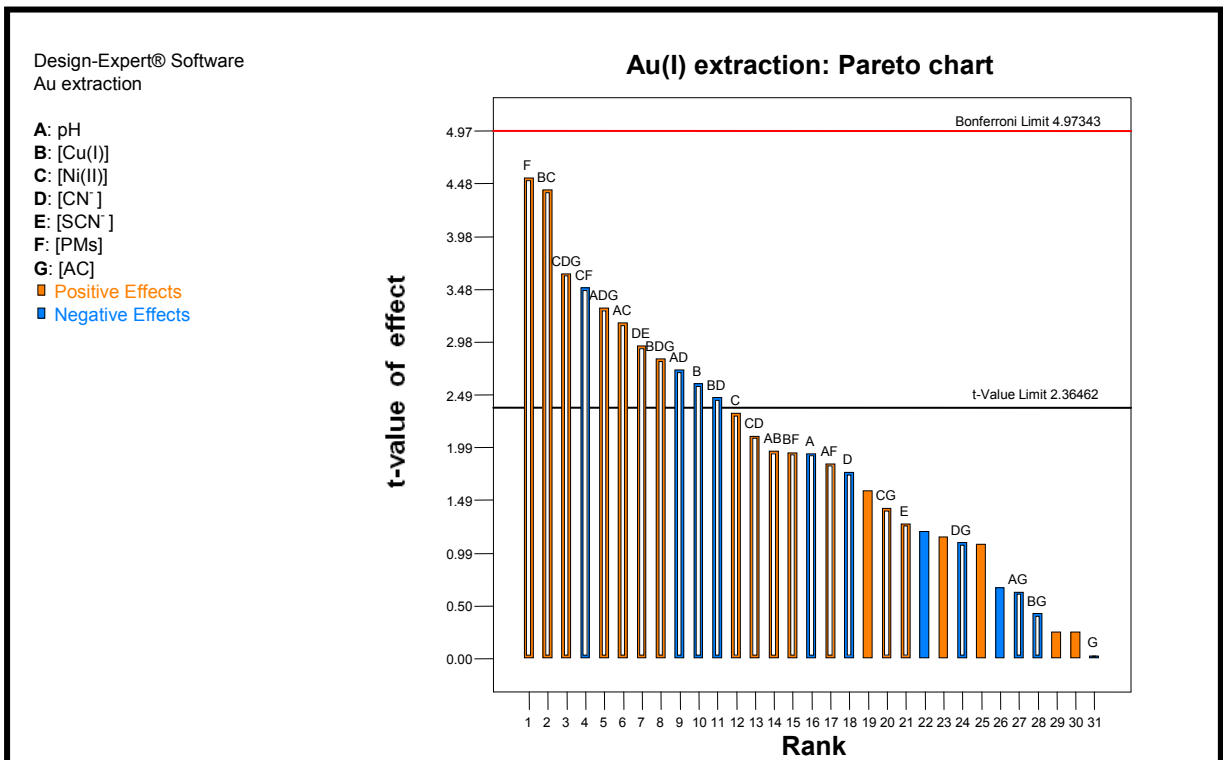


Figure 5.7: Pareto chart of standardized effects for Au(I) adsorption onto activated carbon

Table 5.2: Standardised main effects from the fitted models for the responses Pt(II), Pd(II) and Au(I)

Term	Pt (II) adsorption		Pd(II) adsorption		Au(I) adsorption	
	Standardised effects	% Contribution	Standardised effects	% Contribution	Standardised effects	% Contribution
A = pH	- 2.41	1.20	- 1.04	0.15	- 1.16	2.21
B = [Cu(I)]	- 2.41	1.20	- 4.22	2.38	- 1.56	3.97
C = [Ni(II)]	- 16.67	57.25	- 17.92	42.94	1.39	3.16
D = [CN ⁻]	0.15	0.00	1.67	0.37	- 1.06	1.83
E = [SCN ⁻]	0.48	0.05	1.13	0.17	0.76	0.95
F = [PMs]: Pt, Pd and Au	0.65	0.09	5.96	4.76	2.72	12.14
G = Carbon concentration [AC]	10.90	24.49	14.13	26.71	- 0.02	0.00

The main effects of each factor upon responses were ascertained through ANOVA. The results shown in Table 5.2 indicate that Ni(II) concentration was the most significant adsorption process factor, due to its highest percentage contribution (negative) among the process parameters: 3.16; 42.94 and 57.25% in Au(I), Pd(II) and Pt(II) adsorption responses, respectively.

Table 5.3: Coefficient of Pt(II), Pd(II) and Au(I) model responses in coded form

Response	Intercept	A pH	B [Cu(I)]	C [Ni(II)]	D [CN ⁻]	E [SCN ⁻]	F [PMs]	G [AC]	AB pH-[Cu(I)]	AC pH-[Ni(II)]	AD pH-[CN ⁻]	AF pH-[PMs]
Pt(II)	88.7318	- 1.2066	- 1.2072	- 8.332				5.4491				
p =		0.0156	0.0156	< 0.0001				< 0.0001				
Pd(II)	83.8173		- 2.1091	- 8.9578	0.8309		2.9822	7.0647				
p =			0.0355	< 0.0001	0.3879		0.0044	< 0.0001				
Au(I)	97.3695	- 0.5803	- 0.7784	0.6941	- 0.5278	0.3816	1.3609	- 0.0084	1.314	2.1278	- 0.8178	0.5522
p =		0.1669	0.0757	0.1065	0.2041	0.3467	0.0073	0.9829	0.1622	0.0373	0.0645	0.1860

Table 5.3 (continued)

Response	AG pH-[AC]	BC [Cu(I)]-[Ni(II)]	BD [Cu(I)]-[CN ⁻]	BF [Cu(I)]-[PMs]	BG [Cu(I)]-[AC]	CD [Ni(II)]-[CN ⁻]	CF [Ni(II)]-[PMs]	CG [Ni(II)]-[AC]	DE [CN ⁻]-[SCN ⁻]
Pt(II)								3.6509	
p =								< 0.0001	
Pd(II)			- 1.5822	1.8078		2.6503		3.0628	
p =			0.1073	0.0681		0.0100		0.0036	
Au(I)	- 0.1884	2.9672	- 0.7397	0.5841	- 0.1266	0.6303	- 1.0497	0.4247	1.9791
p =	0.6348	0.0084	0.0886	0.1645	0.7487	0.1372	0.0250	0.2981	0.0490

Table 5.3 (continued and end)

Response	DG [CN ⁻]-[AC]	ADG pH-[CN ⁻]-[AC]	BDG [Cu(I)]-[CN ⁻]-[AC]	CDG [Ni(II)]-[CN ⁻]-[AC]
Pt(II)				
p =				
Pd(II)				
p =				
Au(I)	- 0.3284	<i>2.2191</i>	1.8972	<i>2.4384</i>
p =	0.4145	<i>0.0316</i>	0.0569	<i>0.0212</i>

Legend: In italic are significant factors and interactions ($p \leq 0.05$)

From Table 5.3, p-values of less than 0.05 imply that there is more than 95% chance that the observed change in the response variable is due change in the given model term (Antony, 2003). The small p-values (< 0.05) mean that not all the main effects and interactions are zero at the 5% significance level. In other words, there is reasonably strong evidence that at least some of the main effects and interactions are not equal to zero.

Generally, a term that has a probability value less than or equal to 0.05 would be considered as significant effect at a confidence level $\geq 95\%$, while a probability value greater than 0.10 is generally regarded as not significant. In the latter case, the term should be removed from the model, unless it is needed to satisfy the hierarchy i.e., it is a parent term of a significant interaction. Thus the dominant factors assessed using Daniel plots and Pareto charts were found in order of decreasing ranking of importance to be: [Ni(II)], [AC], [PMs], [Cu(I)] and solution pH.

5.3.3 Examining main effects

5.3.3.1 Influence of pH

It has been reported by Das (2010) that the solution pH is one of the most important variables affecting the surface charge of the activated carbon through dissociation of functional groups on its surface active sites, the speciation of metals in solution through hydrolysis, complexation and redox reactions during metal recovery. Adams *et al.* (1987) indicated that the aurocyanide complex adsorption onto activated carbon decreases with increasing equilibrium pH, possibly due to the carbon deprotonation at higher pH values. Fleming and Nicol (1984) have observed that an increase in the concentration of free cyanide depresses the rate of loading and the equilibrium capacity of gold adsorption. Lu *et*

al. (2002) have indicated that increasing pH is similar to increasing free cyanide ion concentration.

Analyzing values in Tables 5.2 and 5.3, it can be inferred that the solution pH was effectively one of the most important variables for the overall adsorption of the three chosen adsorbates (Pt, Pd and Au). The negative value of its coefficient meant that the adsorbates taken up by the granular activated carbon were favoured at pH of 9.5. In other words, the decrease in pH as displayed in Figure 5.8, leads to an increase of the uptake of Pt(II) ions by the adsorbent. Adams *et al.* (1987) indicated that the enhanced adsorption at low pH is due to the H^+ and $Au(CN)_2^-$ association. However, Pd(II) and Au(I) adsorption rates remained insensitive to the pH variation ($p > 0.05$).

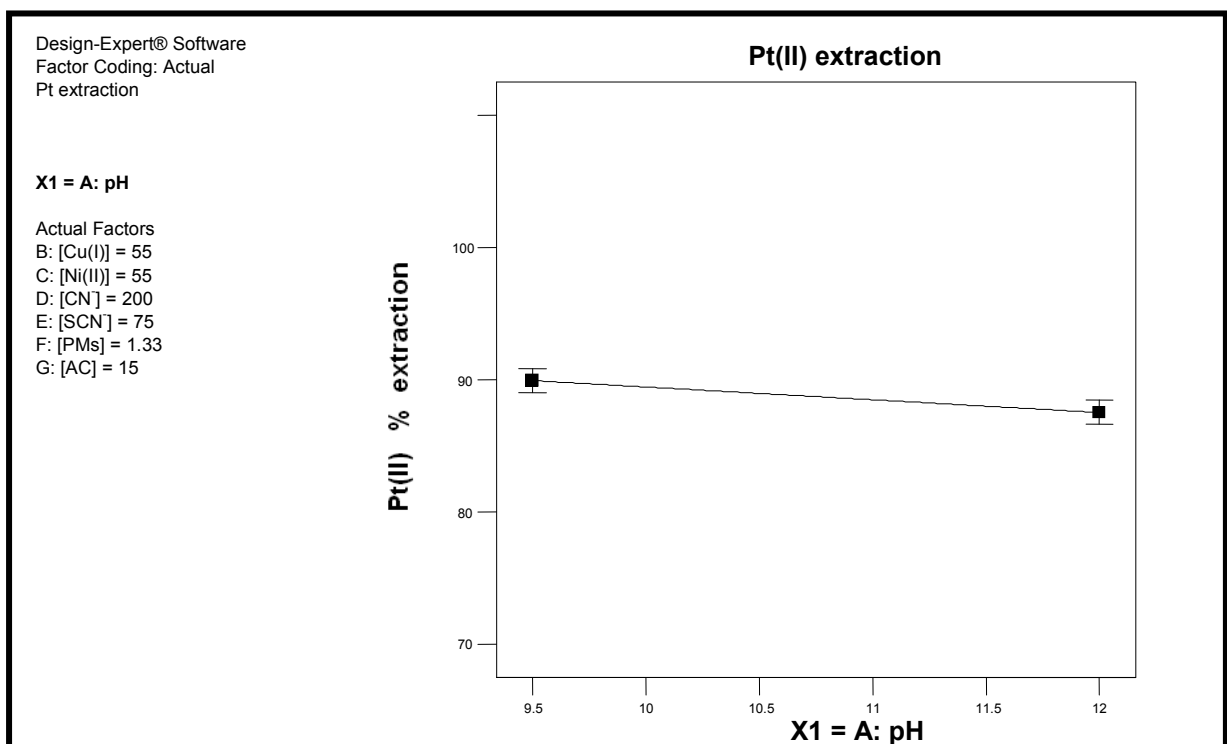


Figure 5.8: Effect of pH on the adsorption efficiency of PMs (Pt, Pd and Au)

5.3.3.2 Influence of copper concentration

It was observed from the experimental data that Cu(I) concentration had significant effects on Pt ($p = 0.0156$) and Pd ($p = 0.0355$) extractions. Although negative, its effect on Au(I) adsorption was found statistically insignificant ($p = 0.0757$). The increase in copper concentration caused a decrease in the adsorption percentage of Pt and Pd as shown in Figure 5.9, indicating that $Cu(CN)_2^-$ complex loaded well, because $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ species do not load appreciably (Fleming and Nicol, 1984). Lu and co-workers (2002) stated

that the increase of $[\text{CN}^-]/[\text{Cu(I)}]$ mole ratio, shifts the distribution of copper cyanide species to the highly coordinated complex $\text{Cu}(\text{CN})_4^{3-}$, which is less loaded onto carbon. This also matches the earlier findings on gold adsorption quoted by other researchers (Marsden and House, 2006).

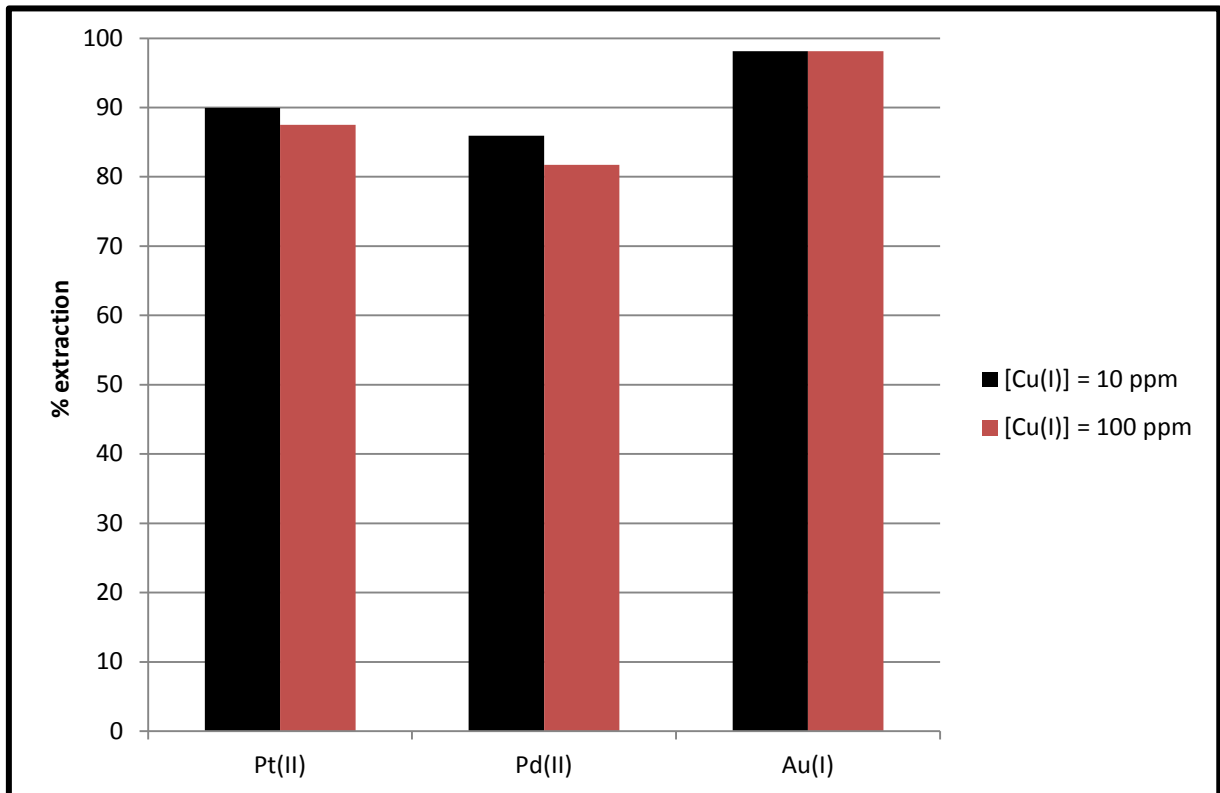


Figure 5.9: Effect of copper on the adsorption efficiency of PMs (Pt, Pd and Au)

Fleming and Nicol (1984) have observed that the effect of pH value on copper loading is in all probability associated with the effect of free cyanide concentration. Coderre and Dixon (1999) pointed out that the $[\text{CN}^-]/[\text{Cu(I)}]$ ratio at any given pH governs the speciation of cyanocuprate(I) complexes. According to Lu *et al.* (2002), the stability of the copper-cyanide solution depends not only on the ratio of total cyanide to copper, but also on the concentrations of total copper, pH and temperature. Therefore, the effects of copper concentration can be explained by the fact that there are a number of exchangeable sites in activated carbon structure at high $[\text{CN}^-]/[\text{Cu(I)}]$ ratio, as this ratio decreases; exchangeable sites are saturated with $\text{Cu}(\text{CN})_2^-$, resulting in a decrease in the adsorption efficiency of PMs.

5.3.3.3 Influence of nickel concentration

Figure 5.10 shows a decrease in percentage adsorption of Pt(II) and Pd(II) with the increase in concentration of Ni(II), while in contrast, the adsorption of Au(I) was found statistically insignificant ($p = 0.1065$) with Ni(II) concentration. Copper and nickel form different complexes at different cyanide concentrations yielding different levels of loading (van Deventer *et al.*, 1995). Laxen *et al.* (1979) reported that silver is adsorbed rapidly but not as strongly as gold, and nickel is more strongly adsorbed than copper. All the ions compete with one another, and the complexes that are adsorbed vary with changes of pH and ionic strength.

It is also worth noting that in such competitive environment, the significant differences in the adsorption behaviour of copper and nickel towards gold ions as compared to platinum and palladium, can adequately be explained in terms of chemical structures and charge densities. It can be seen that in all instances Au(I) ions have to be extracted first leaving behind the competition between Pt(II), Pd(II), Cu(I) and Ni(II) that have either a high charge density or a chemical structure largely different to that of gold (infinite linear chains).

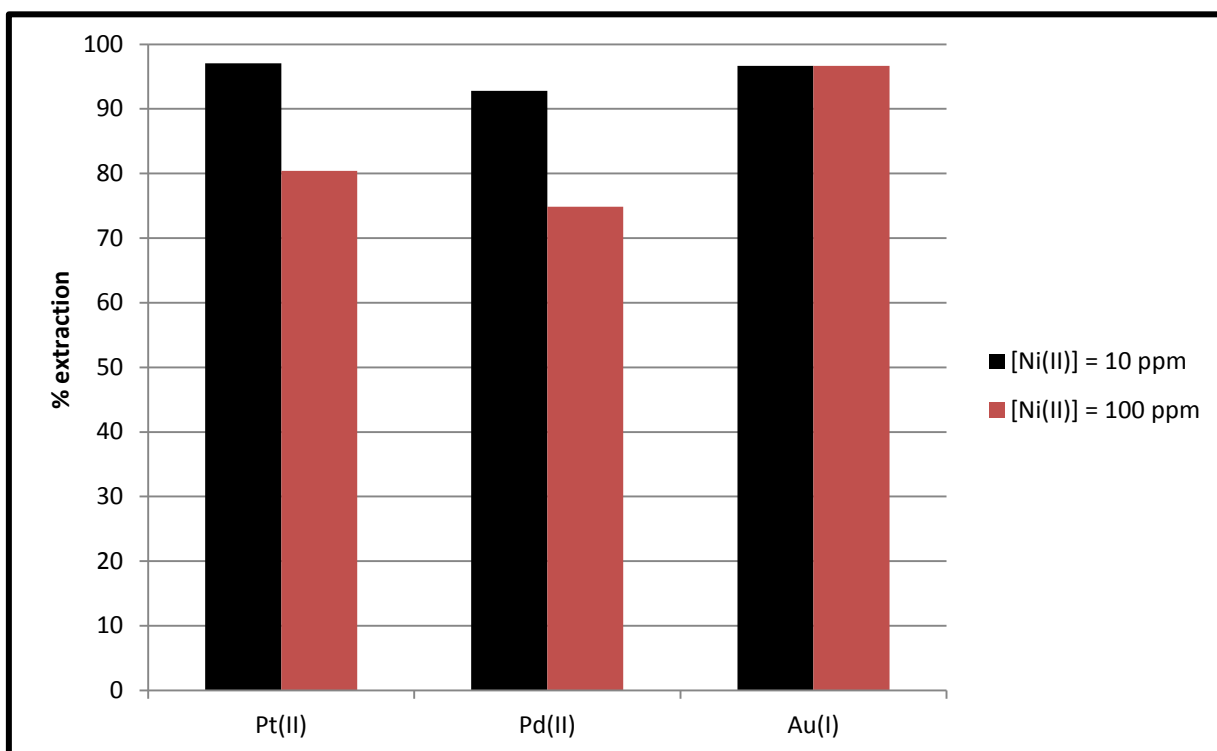


Figure 5.10: Effect of nickel on the adsorption efficiency of PMs (Pt, Pd and Au)

5.3.3.4 Influence of free cyanide $[CN^-]$ concentration

Fleming and Nicol (1984) have suggested that an increase in the concentration of free cyanide ion depresses the rate of loading and the equilibrium capacity of gold onto activated carbons. This feature, also pointed out by Dixon *et al.* (1999) and McDougall *et al.* (1980), is utilized in the elution of gold from activated carbons. The experimental results indicated that there is no change in the adsorption behaviour of the [PMs] system between 100 and 300 ppm $[CN^-]$. From Table 5.3, the effect of $[CN^-]$ concentration was found statistically insignificant within the interval studied.

5.3.3.5 Influence of thiocyanate $[SCN^-]$ concentration

As stated earlier, Davidson *et al.* (1979) argued that thiocyanate anions were shown to have a very detrimental effect on the rates and capacity constants of gold adsorption, when added individually to a synthetic solution at the approximate concentration levels of 100 ppm as found in the plant solution. However, in this work, experimental findings revealed that the presence of 100 ppm SCN^- did not appreciably affect PMs adsorption as displayed in Table 5.3. This observation is supported by the selective and quantitative adsorption of Pt(II), Pd(II) and Au(I) from a real leach liquor containing 3670 ppm SCN^- (see chapter 4 of this work).

The reasons for such a disparity would be at this stage only speculative, and further investigations in this direction would appear to be warranted. The insignificant effects of Cu(I) and Ni(II) at higher concentrations as competing anions on adsorption of Au(I) (earlier noticed in precedent sections of this work), may to some degree explain certain of these observed differences.

5.3.3.6 Influence of initial concentration of precious metal ions

Initial concentration is also one of the significant factors affecting adsorption. Higher initial adsorbate concentration provides higher driving force to overcome mass transfer resistances of the metal ions from the aqueous to the solid phase, resulting in higher probability of collision between metal ions (PMs) and the active sites (Rane *et al.*, 2010). Adsorption experiments resulted in higher uptake of Pd(II) and Au(I) for the given amount of treated activated carbon, while there was no effect of initial PMs concentration on Pt(II) adsorption as presented in Figure 5.11.

A number of properties has been suggested for ordering the affinity rank of precious and base metals towards activated carbon, including ionic radius, ionic strength and chemical structures (Jia *et al.*, 1998; Aguilar *et al.*, 1997; Fleming, 1992; McDougall *et al.*, 1980). These properties may play an important role in the interaction between precious metal ions

and the adsorbent, as multicomponent adsorbate – adsorbent systems generally exhibits three possible types of behaviour: 1) synergism, 2) antagonism and 3) non-interaction. Therefore the results may be explained by an increase in the number of metal ions competing for the available binding sites in the adsorbent – for adsorption of Pt(II) ion – at higher concentration levels and constant amount of adsorbent.

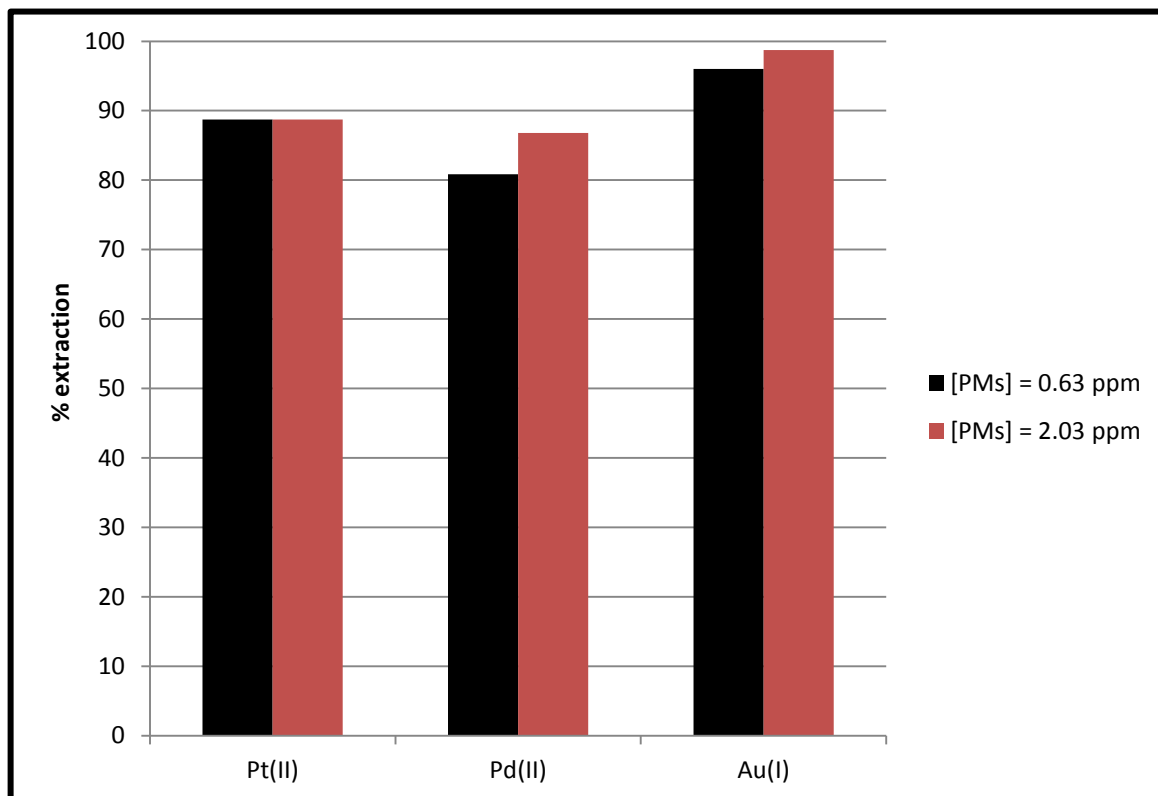


Figure 5.11: Effect of initial [PMs] concentration on their adsorption efficiencies

5.3.3.7 Influence of adsorbent concentration

As expected, the equilibrium concentration increases with increasing adsorbent concentration for a given initial PM concentration (Figure 5.12), because for a fixed initial solute concentration; increasing the adsorbent concentration provides a greater surface area or adsorption sites. Nevertheless, the effect of adsorbent concentration on Au(I) adsorption was found statistically insignificant ($p = 0.9829$). The adsorption remains unchanged above activated carbon concentration of 10 g/L, this is probably because the active sites on the adsorbent become saturated at this concentration and subsequent increase in concentration does not affect the adsorption capacity.

Amarasinghe and Williams (2007) pointed out that, in some cases, the amount of metal ions adsorbed per unit weight of adsorbent (q) decreases with the adsorbent concentration. This is due to the fact that at higher adsorbent concentration, the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of (q), indicating that the adsorption sites remain unsaturated.

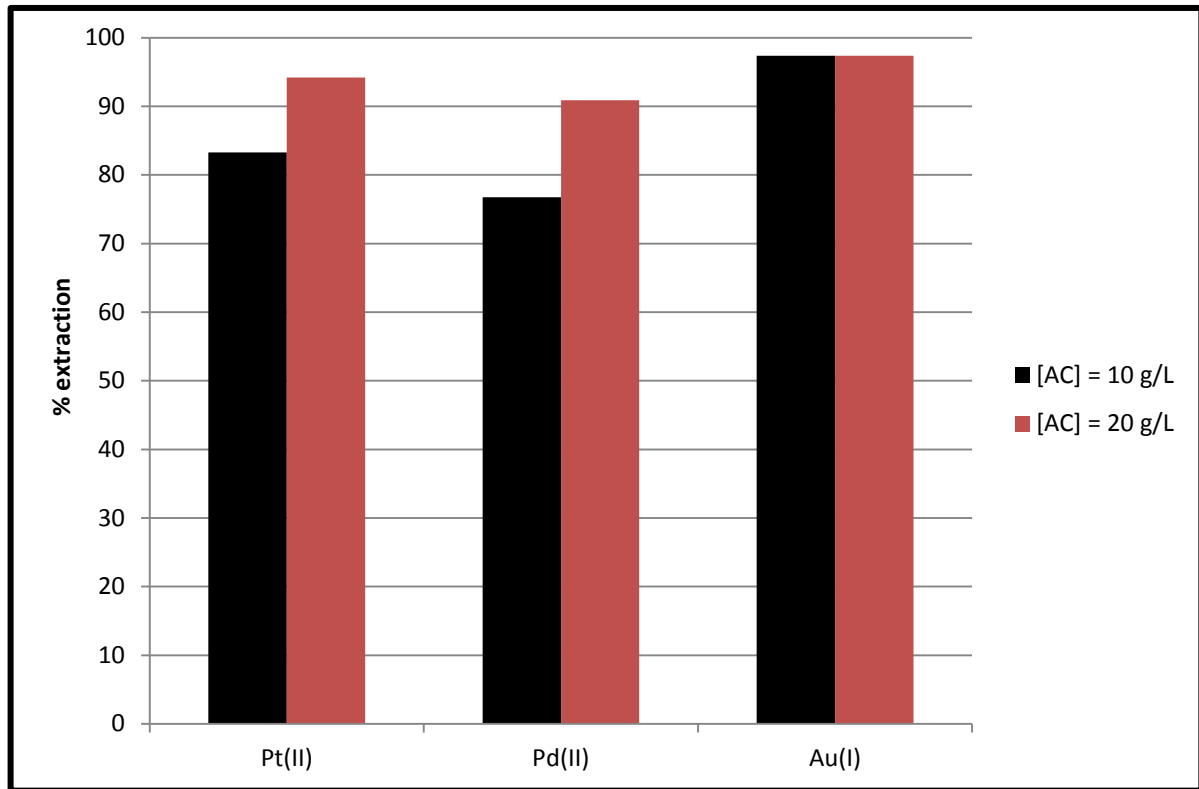


Figure 5.12: Effect of activated carbon concentration on the adsorption efficiency of PMs

5.3.4 Assessment of significant interactions in PMs adsorption process

The main effect plots in Figures 5.8 to 5.12 are helpful in visualizing which factors most affect the responses. If there were no significant interactions between the factors, a main effects plot would adequately describe where it is possible to obtain the biggest payoff for changes to the adsorption process. Because the interactions in this study were found to be significant (Figures 5.13 to 5.21 and Table 5.3), the interaction plots should be examined next.

p-values were used to determine the significance of each of the interactions among the variables. Interactions (factors) with negative influence (coefficient) indicate that these are interactions (factors) that reduce efficacy of the adsorption process (antagonistic effect). Similarly, interactions (factors) with positive influence indicate that these are interactions (factors) that increase efficacy of adsorption (synergistic effect). The ranking of the importance of each interaction and factor in the global processes of adsorption will depend

on the numerical value of the coefficient of each interaction or its factor in absolute value. The experimental results, done in terms of coded factors, from which a number of interesting features emerged, are given in Table 5.3.

An interaction plot details the impact that the act of changing the settings of one factor has on another factor. Therefore in an interaction plot, if the lines of two factors are parallel, there is no interaction. On the contrary, when the lines are far from being parallel, the two factors interact. Interaction plots for the significant interactions of Pt(II), Pd(II) and Au(I) are shown in Figures 5.13 to 5.21. The interaction plots for Pt(II) showed that the interaction of Ni(II) and activated carbon concentrations played a major role and was very significant ($p < 0.0001$), in addition, it was found to be solely responsible for achieving a relatively high Pt(II) ion uptake. In the case of Au(I) adsorption, interactions of Ni(II) and activated carbon concentrations were statistically insignificant ($p = 0.2981$).

5.3.4.1 Interaction involved in Pt(II) adsorption: [Ni(II)] – [Activated carbon]

Analysing the experimental results displayed in Figure 5.13, it can be said that the effect of Ni(II) concentration is less significant at the high level of activated carbon concentration. Therefore, the experiments can be performed at high activated carbon concentration and reduced concentration of Ni(II), while maintaining or even increasing the Pt(II) adsorption rate.

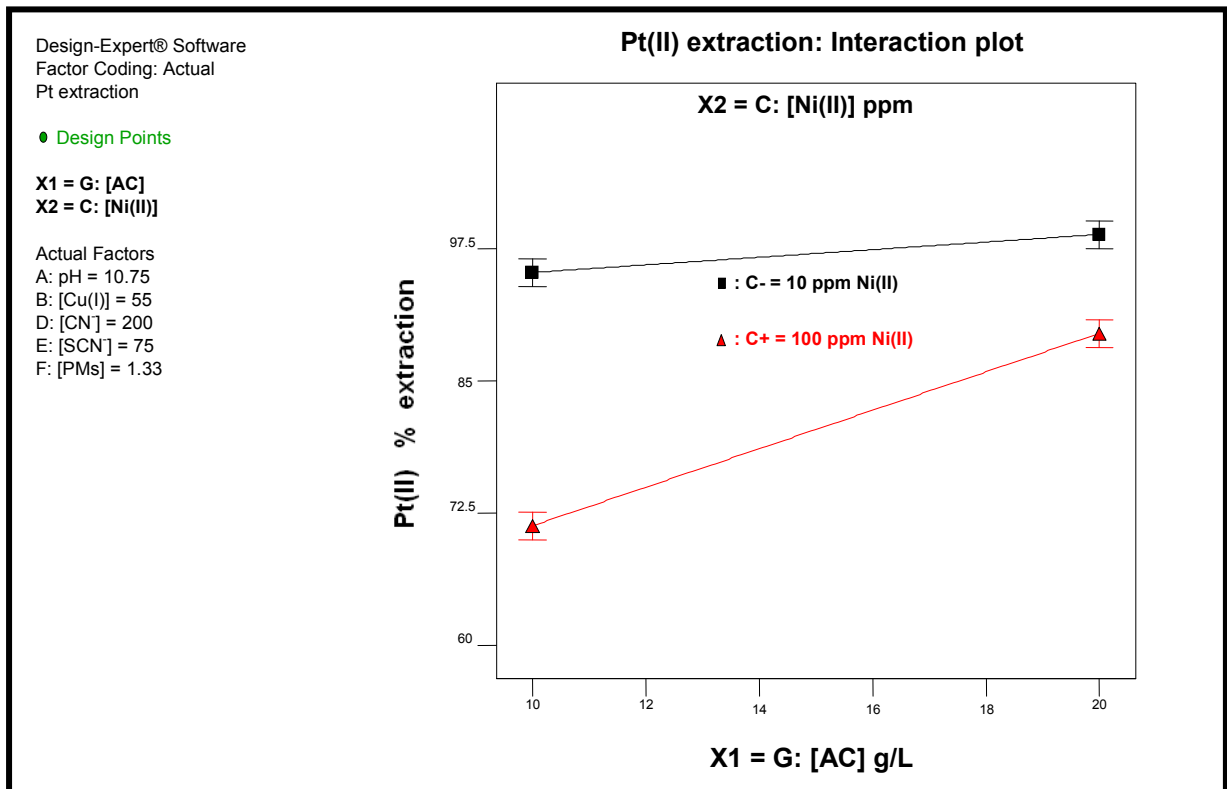


Figure 5.13: Interaction graph for the effects of Ni(II) and [AC] on the adsorption of Pt(II)

5.3.4.2 Interactions involved in Pd(II) adsorption process

A. Influence of [Ni(II)] – [CN⁻] on Pd(II) adsorption

Because of their significance in the hydrometallurgical recovery of gold, the interaction between free cyanide ion and copper has received significant attention in literature. However in this study no interaction takes place between [CN⁻] and [Cu(I)]; data analysis showed that the interaction was statically insignificant in all cases. The results suggest a relatively strong interaction between initial nickel concentration and [CN⁻], which was reflected by the corresponding p-value ($p < 0.0100$). The interaction plot in Figure 5.14 showed that the effect of Ni(II) concentration is less significant at the high level of CN⁻ concentration. Therefore, the experiments can be carried out at high concentration of CN⁻ and reduced concentration of Ni(II), while maintaining or even increasing the Pd(II) adsorption rate.

B. Influence of [Ni(II)] – [Activated carbon] on Pd(II) adsorption

It was also observed that Pd(II) adsorption was affected by the interaction of the adsorbent and initial nickel concentrations ($p = 0.0036$). Analysing the experimental results displayed in Figure 5.15, it can be said that the effect of Ni(II) concentration is less significant at the high level of activated carbon concentration. Therefore, the experiments can be executed at high concentration of activated carbon and reduced concentration of Ni(II), while maintaining or even increasing the Pd(II) adsorption rate.

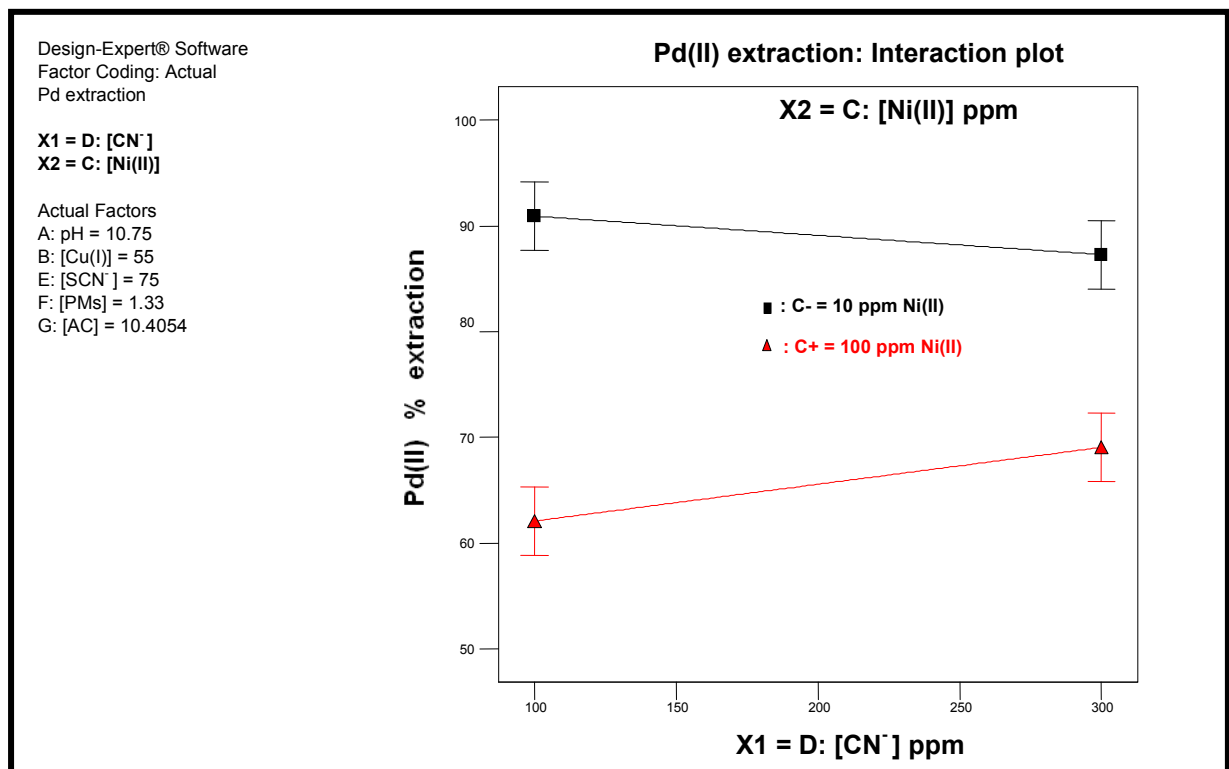


Figure 5.14: Interaction graph for the effects of Ni(II) and [CN⁻] on the adsorption of Pd(II)

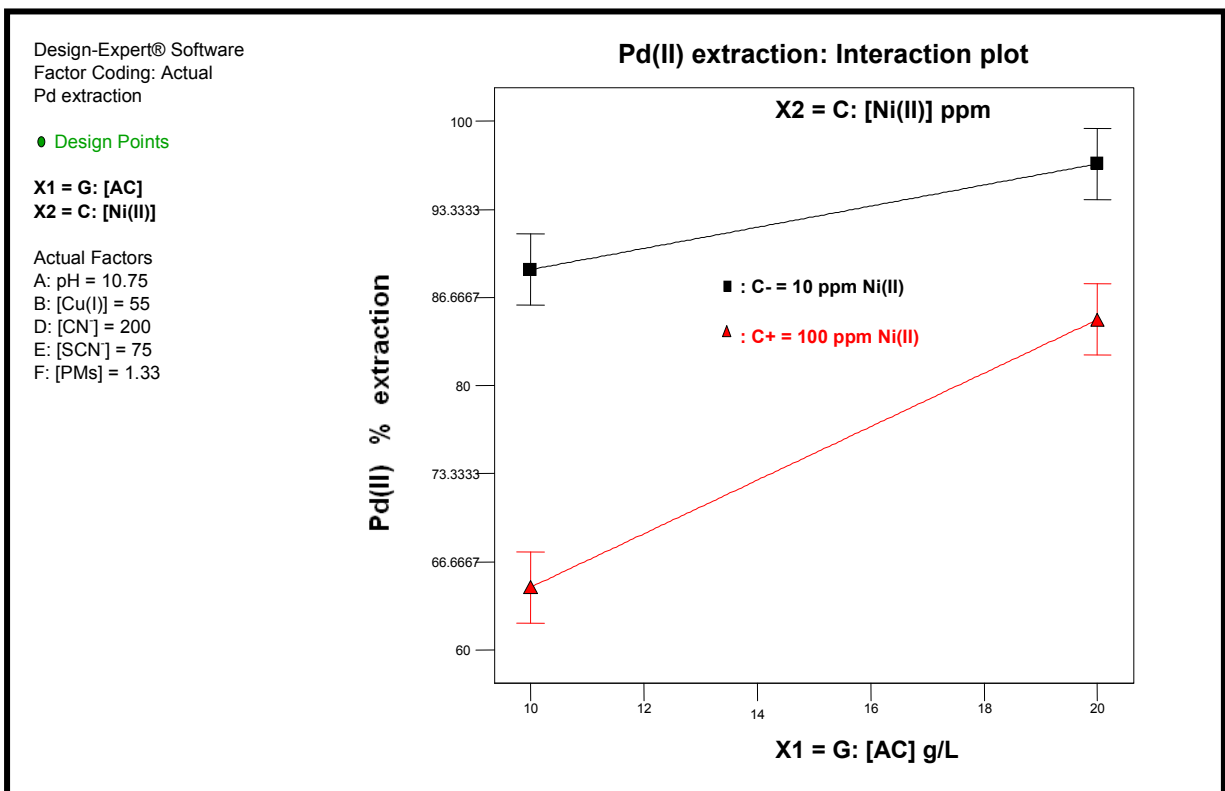


Figure 5.15: Interaction graph for the effects of Ni(II) and [AC] on the adsorption of Pd(II)

5.3.4.3 Interactions involved in Au(I) adsorption process

A. Influence of [Ni(II)] – pH on Au(I) adsorption

Analysis of the results (Table 5.2) showed that the solution pH has a negative effect (- 1.16) on Au(I) recovery with an insignificance in excess of 83% (Table 5.3). The negative effect of this variable, probably due to kinetic causes, is mitigated by the presence of a 96% significant positive interaction between the solution pH and Ni(II) concentration ($p = 0.0373$). In other words, the decrease in the amount of Au(I) recovery resulting from the increase of the solution pH and Ni(II) concentration, is partially limited by the combined effect of the two variables as displayed in Figure 5.16.

B. Influence of [Ni(II)] – [Cu(I)] on Au(I) adsorption

From Table 5.3, Ni(II) – Cu(I) interaction is positive and very high (2.9672), thereby indicating that both variables must be optimized simultaneously. The effect of Cu(I) concentration is less significant at the high level of Ni(II) concentration. Therefore, the experiments can be carried out at high concentration of Ni(II) and reduced concentration of Cu(I), while maintaining or even increasing Au(I) adsorption rate as displayed in Figure 5.17.

C. Influence of [Ni(II)] – [PMs] on Au(I) adsorption

The interaction effect between Ni(II) and PM concentrations was also significant ($p = 0.0250$). Interpreting the interaction shown in Figure 5.18, it can be said that the effect of PM concentration is less significant at the high level of Ni(II) concentration. Therefore, the experiments can be achieved at high concentration of Ni(II) and reduced concentration of PMs, although this would not be an appropriate operating strategy; while maintaining or even increasing the Au(I) adsorption rate. This is only relevant in terms of this particular interaction and its effect on Au(I) adsorption.

D. Influence of [SCN⁻] – [CN⁻] on Au(I) adsorption

The individual contributions of [SCN⁻] (0.76) and [CN⁻] (- 1.06) were positive and negative, respectively (see Table 5.2). However, interaction [SCN⁻] – [CN⁻] showed a positive effect on the experimental response ($p = 0.0490$). It can be said that the effect of CN⁻ concentration is less significant at the high level of SCN⁻ concentration. Therefore, the experiments can be achieved at high SCN⁻ concentration and reduce the concentration of CN⁻, while maintaining or even increasing Au(I) adsorption rate as shown in Figure 5.19.

E. Three factor interactions: pH – [CN⁻] – [AC] and [Ni(II)] – [CN⁻] – [AC]

In addition to the main and two factor interaction of the selected variables, interactions between three variables were found in the Au(I) adsorption response. As shown in Figures 5.20 and 5.21, all treatment combinations are displayed geometrically as cubes. This type of plot is helpful for visualizing interactions between three factors. Each dimension of the cube plot represents one factor. The corners of the cube are the low and high levels selected for that factor.

Figure 5.20 represents the cube plot which depicts the three-factor interaction among solution pH (A), free cyanide ion (D) and activated carbon concentration (G). According to the plot, three combinations can be made in order to maximize the outcome: 1) Low pH – High [CN⁻] and low [AC], 2) Low pH – low [CN⁻] and high [AC], 3) High pH – low [CN⁻] and low [AC].

Figure 5.21 displays the cube plot which depicts the three-factor interaction among Ni(II) (C), free cyanide ion (D) and activated carbon concentration (G). According to the plot, two combinations can be performed for maximizing Au(I) adsorption: 1) Low CN⁻ – low [Ni(II)] and high [AC], 2) High CN⁻ – high [Ni(II)] and high [AC].

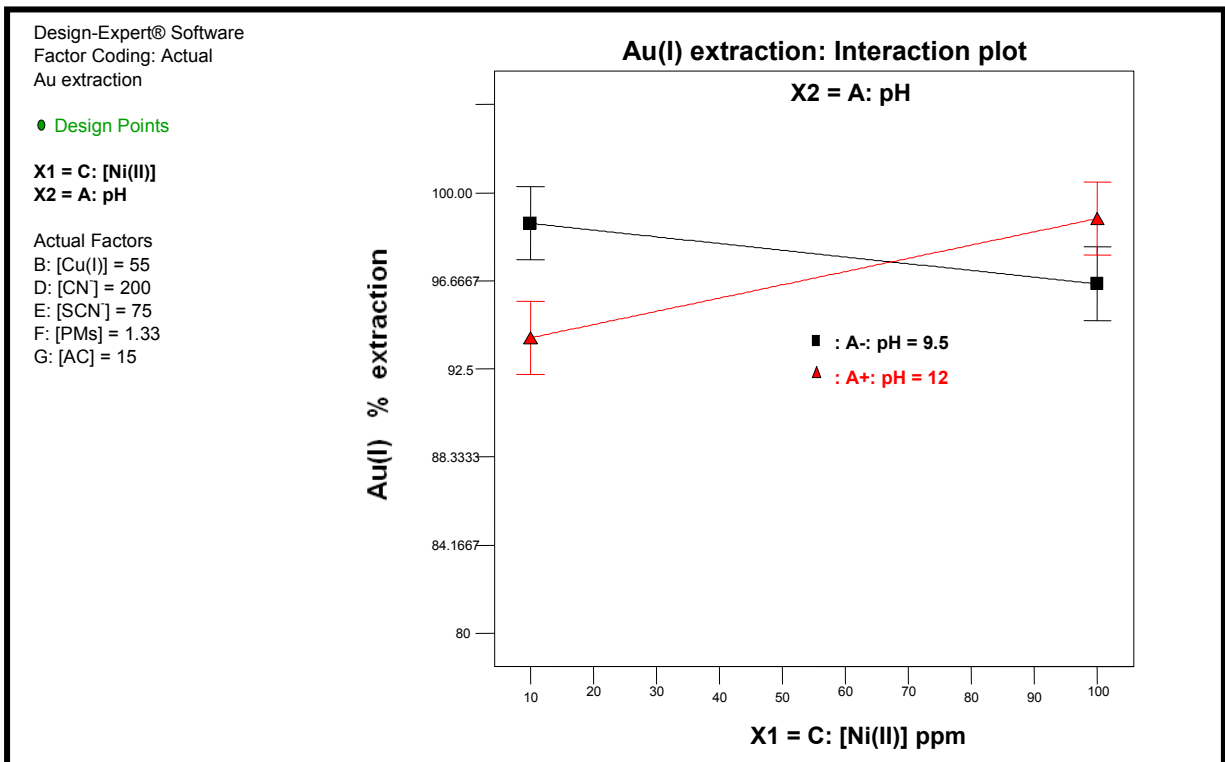


Figure 5.16: Interaction graph for the effects of Ni(II) and pH on the adsorption of Au(I)

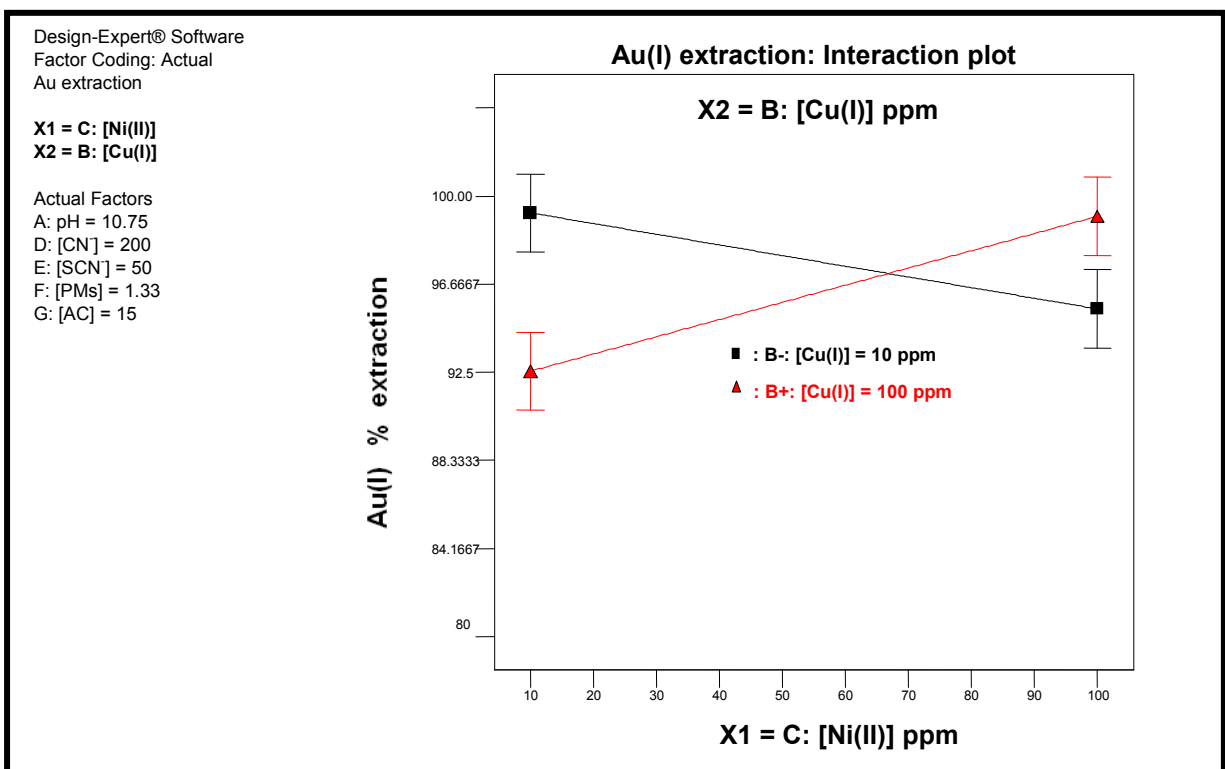


Figure 5.17: Interaction graph for the effects of Ni(II) and Cu(I) on the adsorption of Au(I)

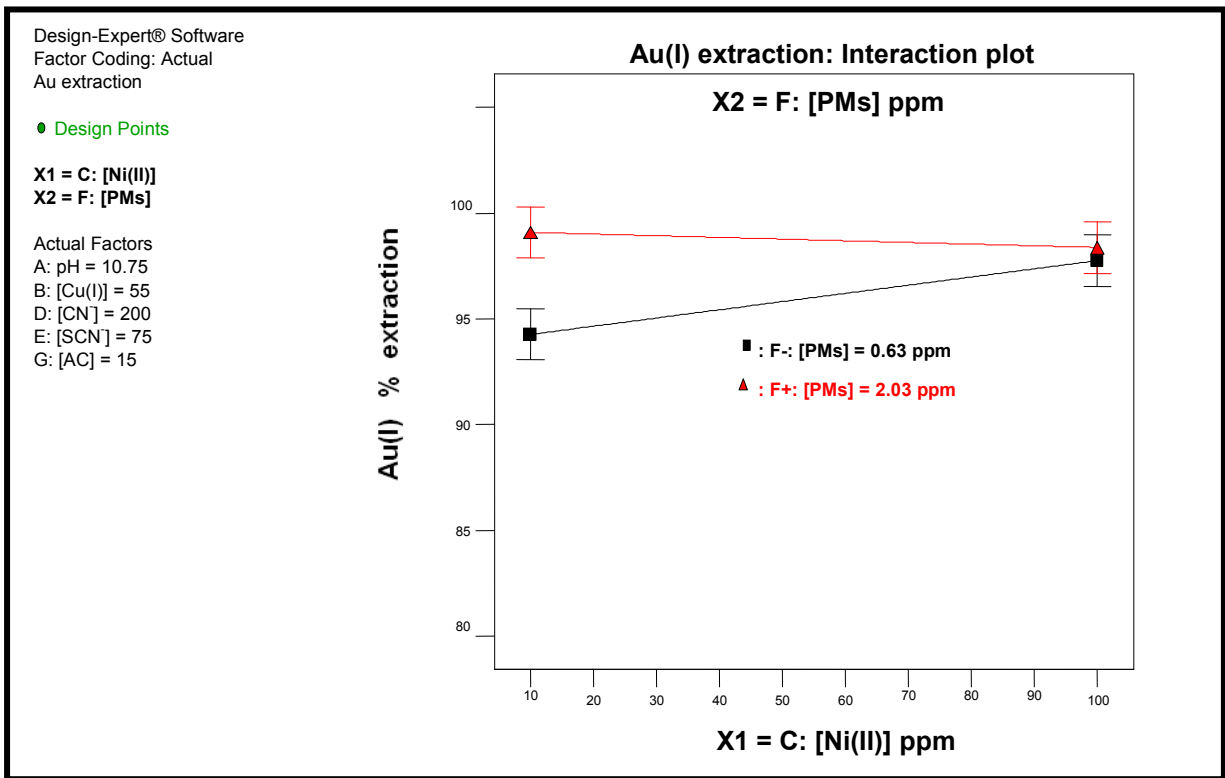


Figure 5.18: Interaction graph for the effects of Ni(II) and PMs on the adsorption of Au(I)

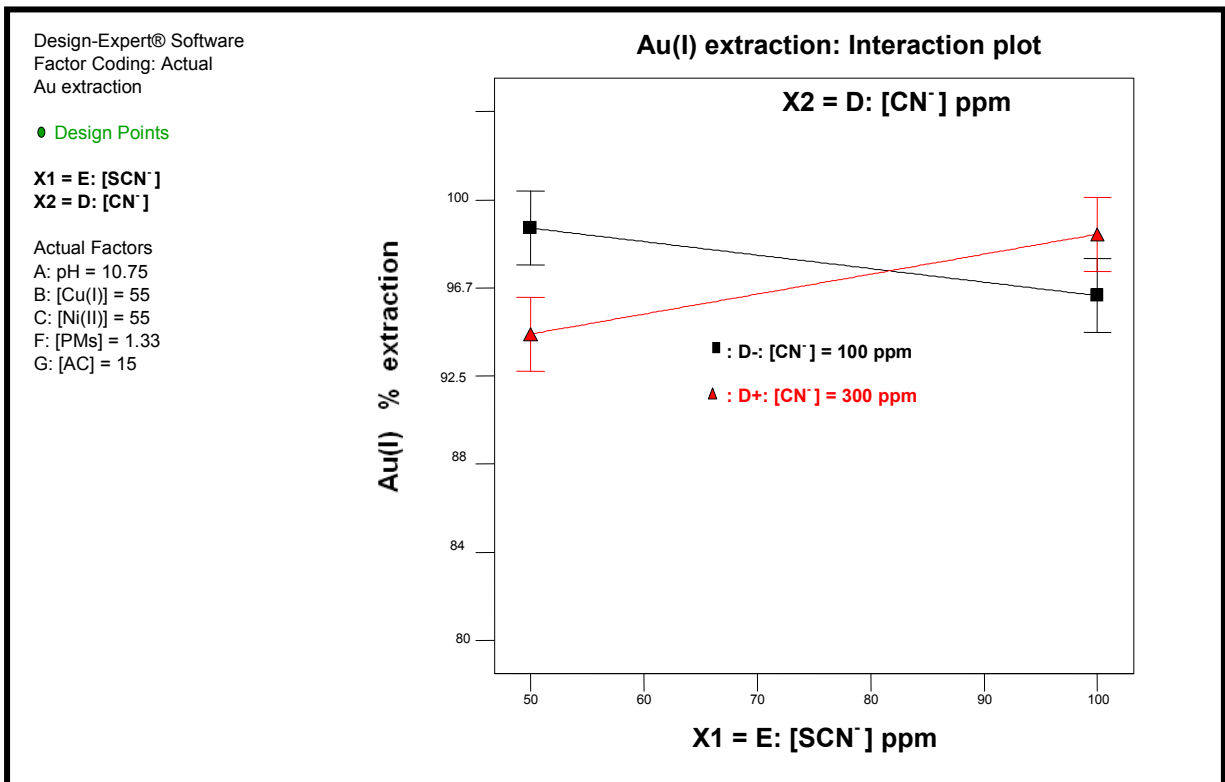


Figure 5.19: Interaction graph for the effects of CN and SCN on the adsorption of Au(I)

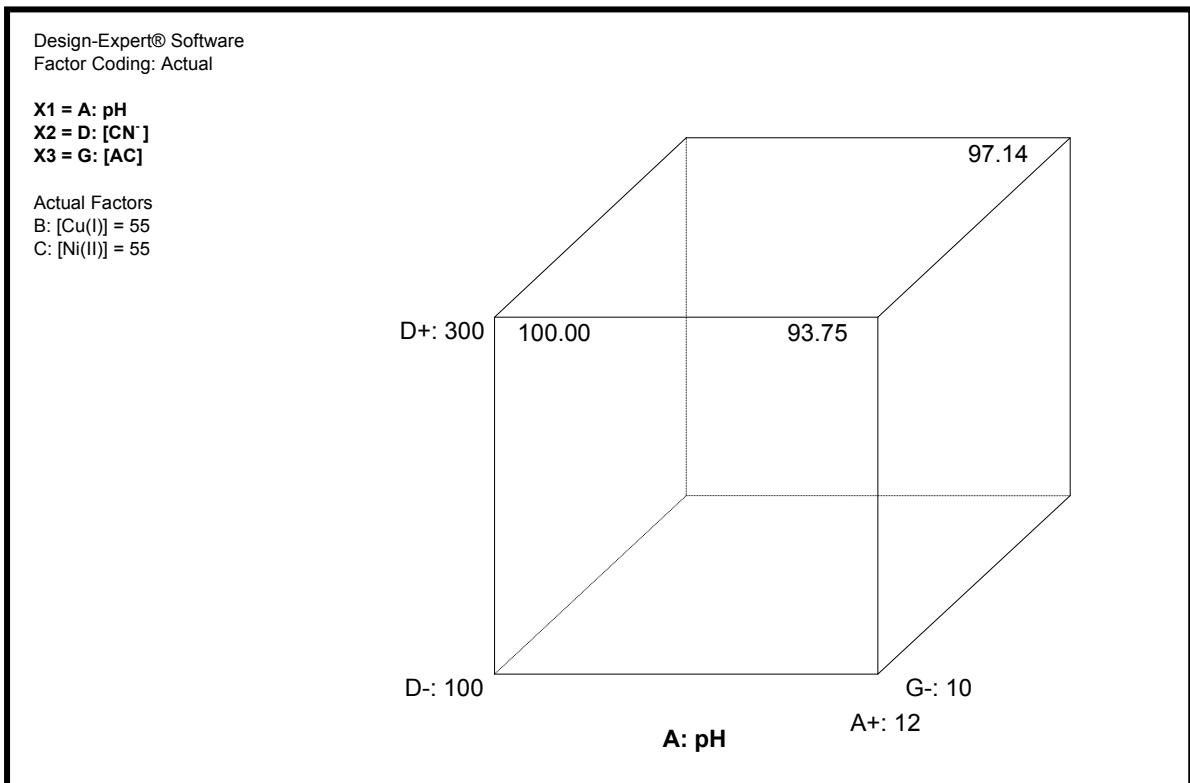


Figure 5.20: Cube plot of the interaction pH – [CN⁻] – [AC] for Au(I) adsorption

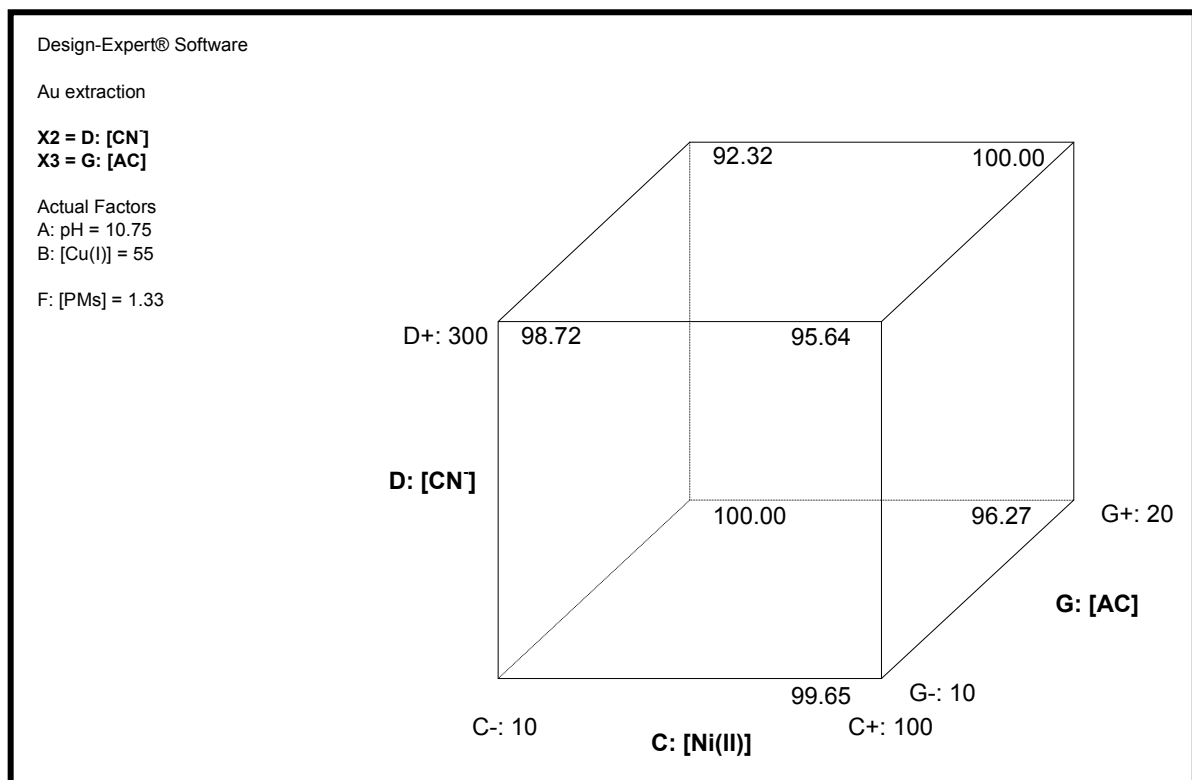


Figure 5.21: Cube plot of the interaction [Ni(II)] – [CN⁻] – [AC] for Au(I) adsorption

As is seen from the plots, there are interactions between factors within the experimental domain. However, it is difficult to optimize these responses under the same conditions, because the interest regions of factors are different; several variables need to be controlled, i.e., reagent concentrations, solution pH, etc. Accordingly, there is a need for a practical optimization of the adsorption process.

5.3.5 Simultaneous optimization strategy

One of the main aims of this study was to determine values of the design parameters at which the response reaches its optimum. The latter could be either a maximum or a minimum of a function of the design parameters (e.g. high PM and less BM adsorption). The conventional “one-variable-at-a-time” approach to optimization will require a great many adsorption experiments, and even this approach may fail to predict such optimum conditions precisely due to lack of interactions among factors (Czitrom, 1999). One of the methodologies for obtaining the optimum results, through a relatively smaller number of systematic experiments that can reduce time, cost and resources (achieving a high quality product), is response surface methodology (RSM). The main objective of RSM is to determine the optimum operational conditions of a process or to determine a region that satisfies the operating specifications. However, it is noteworthy that the response surface methodology does not elucidate the mechanism of the processes studied, but only ascertains the effects of factors upon response and the interactions between factors. The numerical optimization of the software has been chosen in order to find the specific point that either maximizes or minimizes the desirability function.

5.3.5.1 Desirability function approach

The desirability function is a popular and established technique for the simultaneous determination of optimum settings of input variables that can determine optimum performance levels for one or more responses (Azharul *et al.*, 2009). Desirability is an objective function that ranges from zero outside of the limits, to one at the goal. Desirability function approaches are based on the idea that, when one of the quality characteristics of an industrial process or product with many characteristics is not in the desired limits, then the entire quality of the industrial process or the product is not desirable (Pasandideh and Niaki, 2006). The desired goal was selected by adjusting the weight or importance that might alter the characteristics of a goal. The goal fields for response have five options: maximum, minimum, target, within range and none. For simultaneous optimization, each response must have a low and high value assigned to each goal (Table 5.5). The meanings of the goal parameters are as follows:

Maximum:

$d_i = 0$ if response < low value.

$0 \leq d_i \leq 1$ as response varies from low to high.

$d_i = 1$ if response > high value.

Minimum:

$d_i = 1$ if response < low value.

$1 \leq d_i \leq 0$ as response varies from low to high.

$d_i = 0$ if response > high value.

Target:

$d_i = 0$ if response < low value.

$0 \leq d_i \leq 1$ as response varies from low to target.

$1 \geq d_i \geq 0$ as response varies from target to high.

$d_i = 0$ if response > high value.

Within range:

$d_i = 0$ if response < low value.

$d_i = 1$ as response varies from low to high.

$d_i = 0$ if response > high value.

where d_i indicate the desirability of the response.

None:

If the goal is none, the response will not be used for the optimization.

The individual desirability functions d_i – generated based upon the type of each characteristic – are calculated as shown in Equation 5.1.

$$d_i = \begin{cases} 0, & y_i < L \\ \left(\frac{y_i - L}{T - L} \right)^w, & L \leq y_i \leq T \\ 1, & y_i > T \end{cases} \quad (5.1)$$

where L, T stand for lower limit of the response (y_i) and its target value, respectively.

A weight (w) can be assigned to each goal to adjust the shape of its particular desirability function. Weight gives added emphasis to upper (lower) bounds or emphasizes target values. The maximum weight is 10. Selecting $w > 1$ places more emphasis on being close to the target value, and selecting $0 < w < 1$ makes this less important.

The individual desirabilities are then combined using the geometric mean, which gives the overall desirability D expressed in Equation 5.2 below.

$$D = \sqrt[r]{d_1(y_1) \times d_2(y_2) \times \dots \times d_r(y_r)} \quad (5.2)$$

with (r) denoting the number of responses.

5.3.5.2 Setting the optimization criteria

Maximum recovery with acceptable grade is a constant goal for operators and producers. The target criteria were set as maximised values for each PM adsorption response, while values of the variables were set within the ranges being studied.

Kyriakakis (2005) has indicated that a typical final concentrate feed assay to Precious Metals Refinery (PMR) after base metal extraction contains 60 to 80% PM as displayed in Table 5.4. However as stated earlier in section 2.4, the successful operation of a carbon-in-pulp plant is expected to extract more than 99.6% of the gold present in solution. Thereby, optimization criteria for adsorption procedure of the PMs considered were at least 60% – a lower threshold below which the results were not acceptable – and if possible 99.6% (rounded to 100%) recovery for each PM compound (Pt, Pd and Au).

Table 5.4: Typical range of PM in final concentrates after base metal extraction (Kyriakakis, 2005)

Elemental composition	Au	Pt	Pd	Rh	Ru	Ir	Total PM
Level (%)	0.9 – 1.8	36 – 40	17 – 22	4 – 5	7 – 11	1.4 – 2	60 – 80

As shown in Table 5.3, the main effects of Cu(I) and Ni(II) were negatively significant, therefore their goals in the optimization procedure were assigned as ‘minimize’ with corresponding ‘importance’ 3. For safety concerns, pH goal was ‘within range’ with ‘importance’ 3. The goal of $[\text{CN}^-]$, $[\text{SCN}^-]$ and [PMs] was ‘in range’ as this was the expected working interval. Although activated carbon is a relatively low-cost material, but in order to avoid its excess to elution and regeneration stages, the goal for its concentration was ‘minimize’ with medium priority of importance. The adsorption percentage of targeted adsorbates: Pt(II), Pd(II) and Au(I) was assigned as ‘maximize’ for goal with the highest importance ‘5’ as depicted in Table 5.5. ‘Importance’ ranges from 1 to 5, it is a tool for changing relative priorities to achieve established goals for some or all variables.

Table 5.5: Optimization of individual responses (d_i) in order to obtain the overall desirability response (D)

Name	Goal	Lower limit	Upper limit	Importance
pH	In range	9.5	12	3
Cu(I) (ppm)	Minimise	10	100	3
Ni(II) (ppm)	Minimise	10	100	3
[CN ⁻] (ppm)	In range	100	300	3
[SCN ⁻] (ppm)	In range	50	100	3
[PMs] (ppm)	In range	0.63	2.03	3
[AC] (g/L)	Minimise	10	20	3
Pt(II) adsorption (%)	Maximise	60	100	5
Pd(II) adsorption (%)	Maximise	60	100	5
Au(I) adsorption (%)	Maximise	60	100	5

The bar graph depicted in Figure 5.22 shows how well each variable satisfied the criteria and the overall combined desirability: values near one are recommended. A value of one represents the ideal case, while a zero indicates that one or more responses fall outside desirable limits.

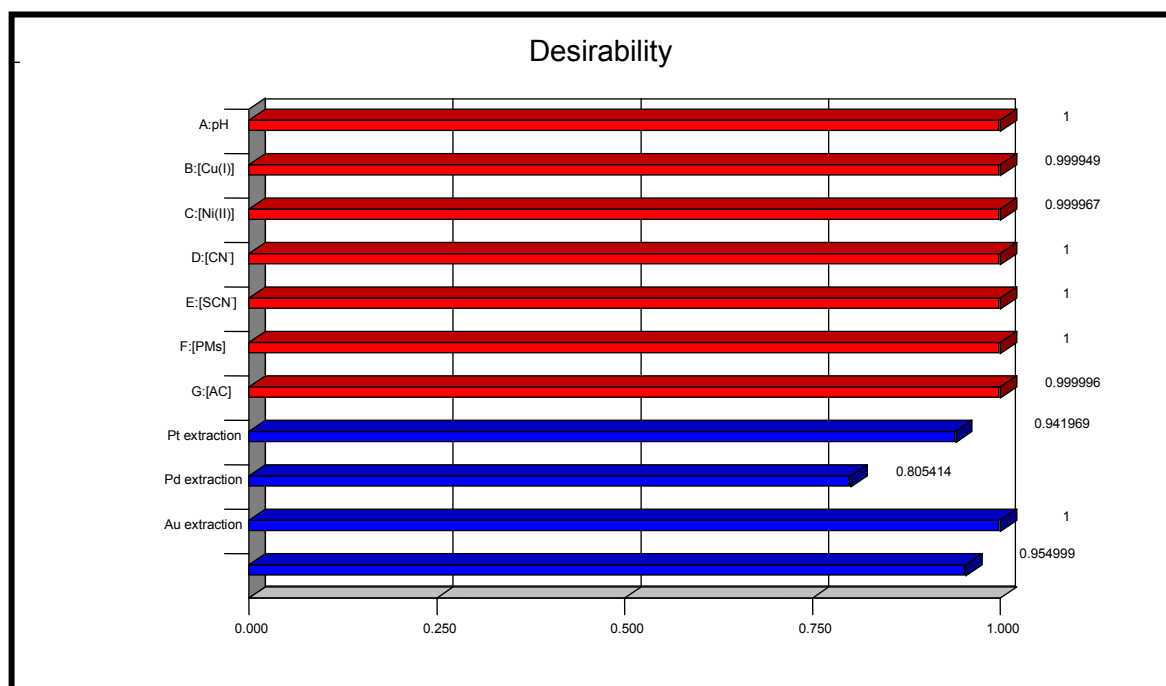


Figure 5.22: Desirability bar graph representing individual desirability of all responses (d_i) in correspondence with combined desirability (D)

Table 5.6: Suitable combination of optimization on PMs (Pt, Pd and Au) adsorption

Number	pH	Cu(I) ppm	Ni(II) ppm	[CN ⁻] ppm	[SCN ⁻] ppm	[PMs] ppm	[AC] g/L	Pt(II) adsorption	Pd(II) adsorption	Au(I) adsorption	Overall desirability
1	9.50	10.00	10.00	132.44	98.95	2.03	10.00	97.68	92.25	100.00	0.95
2	9.50	10.03	10.00	117.81	59.30	2.03	10.00	97.68	92.23	100.00	0.95
3	9.80	10.01	10.00	126.92	59.76	2.03	10.00	97.39	92.23	100.00	0.95
4	9.56	10.00	10.00	231.97	50.06	2.03	10.00	97.62	91.98	100.00	0.95
5	9.50	10.04	10.00	281.95	55.41	2.03	10.00	97.68	91.86	100.00	0.95
6	9.50	10.00	10.00	130.28	61.51	1.65	10.00	97.68	91.58	100.00	0.95
7	10.14	10.00	10.00	214.94	98.32	1.96	10.00	97.07	91.90	100.00	0.95
8	9.58	10.00	10.11	276.89	52.85	2.02	10.01	97.57	91.85	100.00	0.95
9	10.39	10.00	10.00	275.06	98.56	2.02	10.01	96.82	91.88	100.00	0.95
10	9.93	10.00	10.00	186.50	81.86	1.49	10.00	97.27	91.19	100.00	0.95
11	10.21	10.00	10.00	248.01	86.77	1.71	10.00	97.00	91.41	100.00	0.95
12	9.63	10.00	10.00	297.22	65.23	1.38	10.00	97.56	90.74	100.00	0.95
13	10.50	10.00	10.00	215.31	79.08	1.67	10.00	96.71	91.42	100.00	0.95
14	9.64	10.00	10.00	218.59	74.45	1.20	10.00	97.54	90.63	100.00	0.95
15	11.13	10.00	10.00	253.73	73.19	1.86	10.00	96.11	91.65	100.00	0.95

Numerical optimization performed to achieve the optimum solutions of factor combinations, produced 49 optimum solutions with desirability of > 90%. The best 15 solutions are sorted in Table 5.6. The first combination was chosen for loading capacity tests because it has the highest desirability.

5.3.6 Predictive Anova model

The fundamental objective of a factorial design is to develop a predictive model. All experiments were performed according to statistical designs, in order to develop predictive regression models used for optimization. RSM makes it possible to represent independent process parameters in quantitative form as in Equation 5.3.

$$Y = f(X_1, X_2, X_3, \dots, X_n) \pm \varepsilon \quad (5.3)$$

where, Y is the response, f is the response function, ε is the experimental error and $X_1, X_2, X_3, \dots, X_n$, are independent parameters.

The true relationship between Y and X_n may be complicated and, in most cases, it is unknown. A sequential model fitting test was carried out in order to choose suitable models. A two factor interaction model for the analysis of Pt(II) and Pd(II) adsorption and three factor interaction (3FI) model for the analysis of Au(I) have been used to identify all possible interactions of selected factors.

After discarding insignificant terms (i.e. terms having a probability p-value > 0.05), but keeping parent term of significant interactions – in order to satisfy the hierarchy – the resultant models comprising all the explanatory variables (interactive) for describing the value of responses in any particular combination in terms of the compounds tested, can be described in term of actual factors by Equations 5.4 to 5.6 below.

$$R_{Pt(II)} = + 107.81 - 0.97 \cdot \text{pH} - 0.03 \cdot [\text{Cu(I)}] - 0.43 \cdot [\text{Ni(II)}] + 0.20 \cdot [\text{AC}] + 0.02 \cdot [\text{Ni(II)}] \cdot [\text{AC}] \quad (5.4)$$

$$R_{Pd(II)} = + 86.86 - 0.05 \cdot [\text{Cu(I)}] - 0.52 \cdot [\text{Ni(II)}] - 4.75 \times 10^{-3} \cdot [\text{CN}] + 1.10 \cdot [\text{PMs}] + 0.66 \cdot [\text{AC}] - 3.52 \times 10^{-4} \cdot [\text{Cu(I)}] \cdot [\text{CN}] + 0.06 \cdot [\text{Cu(I)}] \cdot [\text{PMs}] + 5.89 \times 10^{-4} \cdot [\text{Ni(II)}] \cdot [\text{CN}] + 0.01 \cdot [\text{Ni(II)}] \cdot [\text{AC}] \quad (5.5)$$

$$R_{Au(I)} = - 6.13 + 7.74 \cdot \text{pH} - 0.08 \cdot [\text{Cu(I)}] - 0.16 \cdot [\text{Ni(II)}] + 0.75 \cdot [\text{CN}] - 0.14 \cdot [\text{SCN}] - 4.03 \cdot [\text{PMs}] + 10.13 \cdot [\text{AC}] + 0.02 \cdot \text{pH} \cdot [\text{Cu(I)}] + 0.04 \cdot \text{pH} \cdot [\text{Ni(II)}] - 0.06 \cdot \text{pH} \cdot [\text{CN}] + 0.63 \cdot \text{pH} \cdot [\text{PMs}] - 0.74 \cdot \text{pH} \cdot [\text{AC}] + 1.47 \times 10^{-3} \cdot [\text{Cu(I)}] \cdot [\text{Ni(II)}] - 1.43 \times 10^{-3} \cdot [\text{Cu(I)}] \cdot [\text{CN}] + 0.02 \cdot [\text{Cu(I)}] \cdot [\text{PMs}] - 0.02 \cdot [\text{Cu(I)}] \cdot [\text{AC}] - 1.49 \times 10^{-3} \cdot [\text{Ni(II)}] \cdot [\text{CN}] - 0.03 \cdot [\text{Ni(II)}] \cdot [\text{PMs}] - 0.02 \cdot [\text{Ni(II)}] \cdot [\text{AC}] + 7.92 \times 10^{-4} \cdot [\text{CN}] \cdot [\text{SCN}] - 0.05 \cdot [\text{CN}] \cdot [\text{AC}] + 3.56 \times 10^{-3} \cdot \text{pH} \cdot [\text{CN}] \cdot [\text{AC}] + 8.43 \times 10^{-5} \cdot [\text{Cu(I)}] \cdot [\text{CN}] \cdot [\text{AC}] + 1.08 \times 10^{-4} \cdot [\text{Ni(II)}] \cdot [\text{CN}] \cdot [\text{AC}] \quad (5.6)$$

where $R_{Pt(II)}$, $R_{Pd(II)}$ and $R_{Au(I)}$ are the predicted values of the percentage of Pt(II), Pd(II) and Au(I) extracted, respectively. Correlation coefficients (R^2) were found to be 0.95, 0.89 and 0.92 (see statistical details given in Appendix C), which means that the models could explain 95, 89 and 92% of the total variations in the system. It was therefore concluded that all models were satisfactory.

However, it should be noted that the model parameters were determined by an ANOVA fitting exercise so that the model is used to predict the remaining data, i.e., the measurement performed within the interval studied. In other words, the model is essentially predictive (empirical), rather than mechanistic.

5.3.7 Model validation

Apart from correlation coefficients (R^2), the closeness of fit to the experimental data could be tested either by normal probability plots of the residual between the response and the prediction or by comparing the experimental data against the data predicted by the models used for the regression analysis (Sheridan *et al.*, 2002).

With normal probability plots shown in Figures 5.23 to 5.25, all the points on the plot should reasonably be close to the straight line, which would determine if the output regression model was reasonable and the assumptions of the analysis were justified (Pavan *et al.*, 2007). Figures 5.26 to 5.28 display the influence plot for the detection of outliers in relation with Pt(II), Pd(II) and Au(I) uptake. None of the points stand out, all data being within the confidence range of 95%.

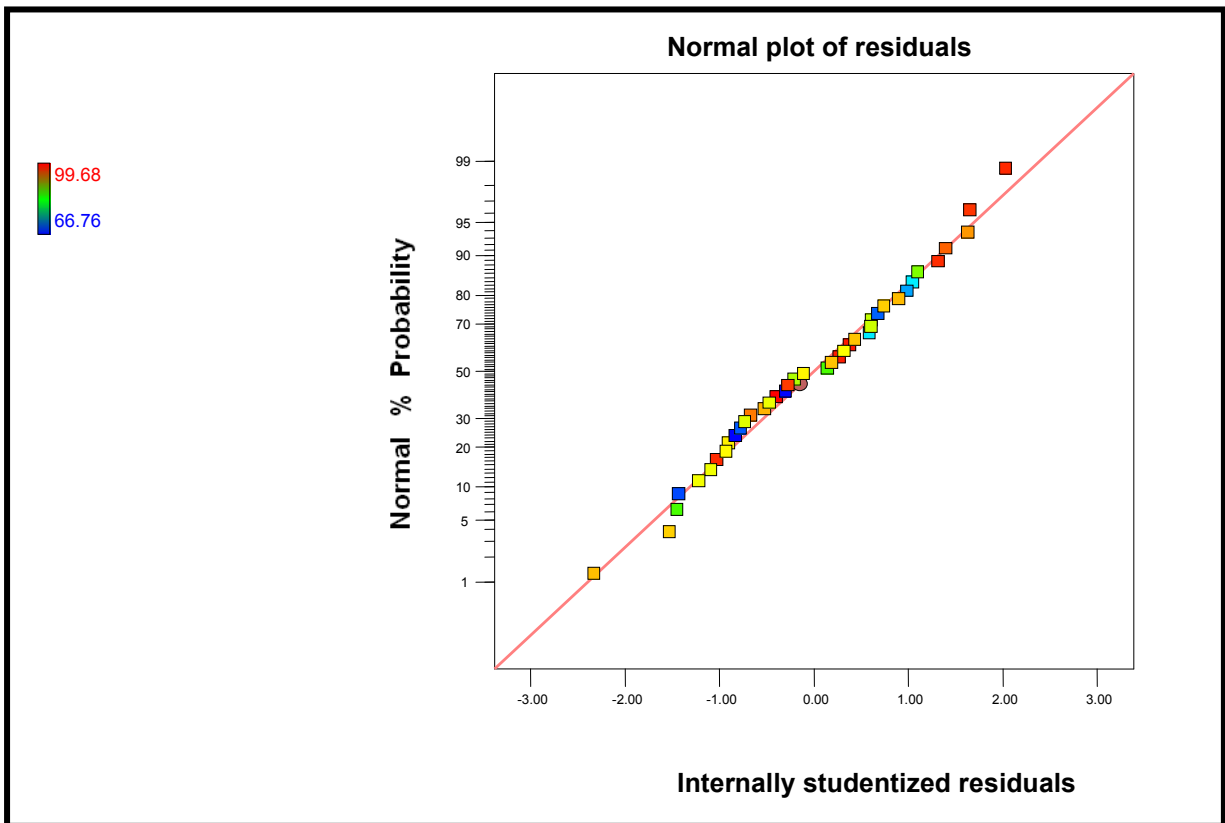


Figure 5.23: Predicted vs. Experimental values for adsorption capacity of the activated carbon for the adsorption of Pt(II) ions

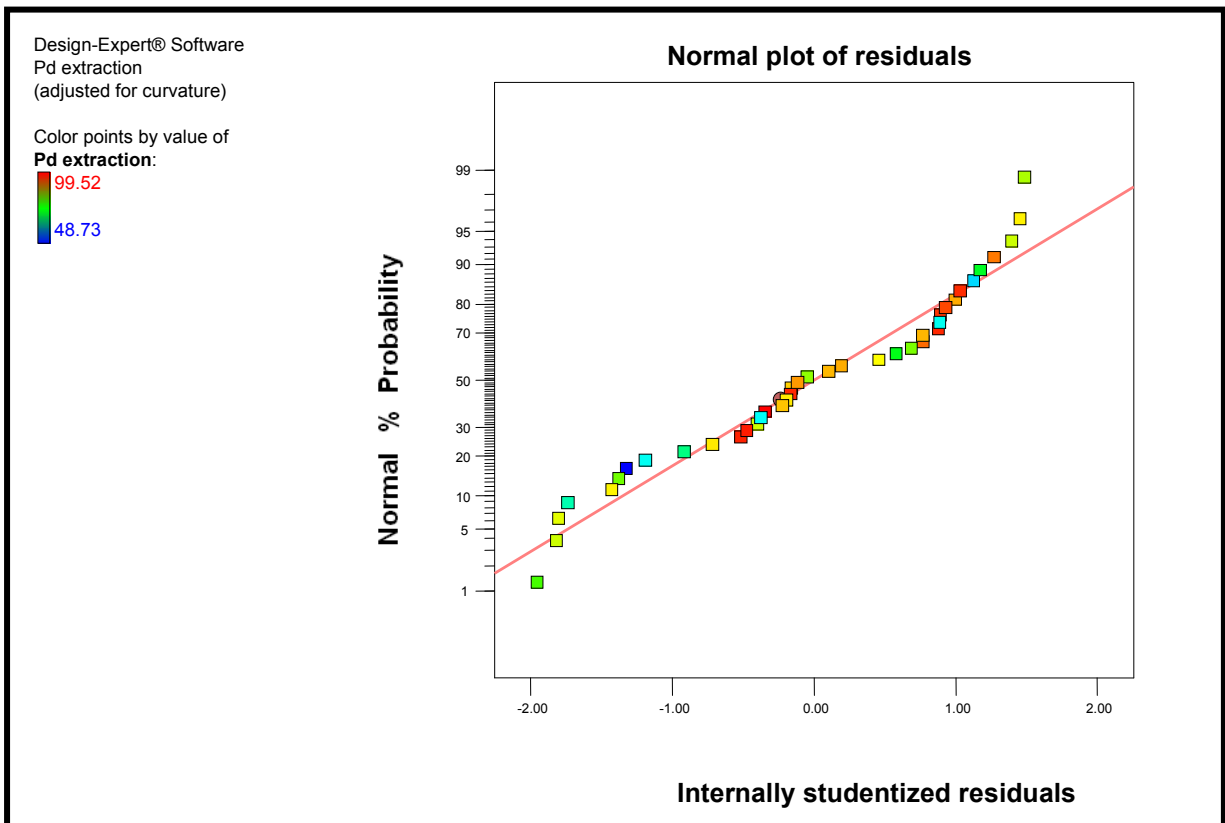


Figure 5.24: Predicted vs. Experimental values for adsorption capacity of the activated carbon for the adsorption of Pd(II) ions

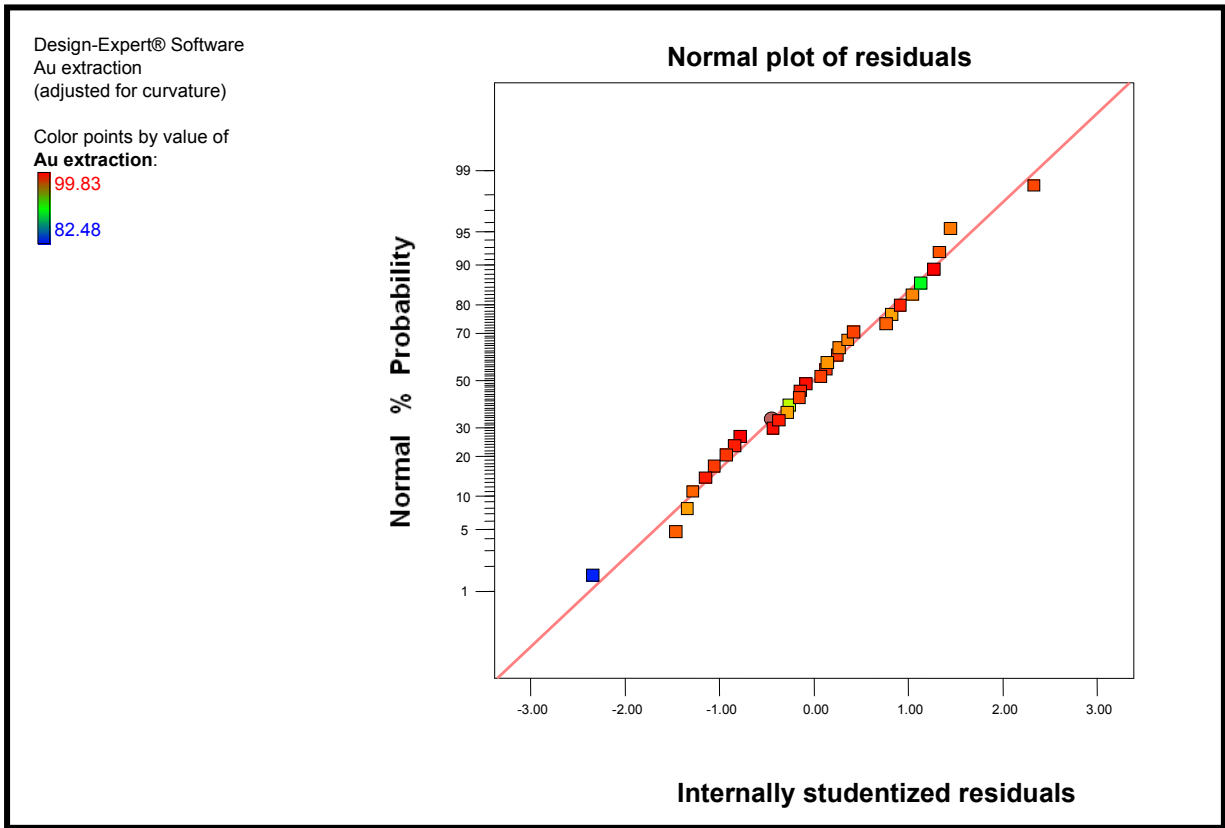


Figure 5.25: Predicted vs. Experimental values for adsorption capacity of the activated carbon for the adsorption of Au(I) ions

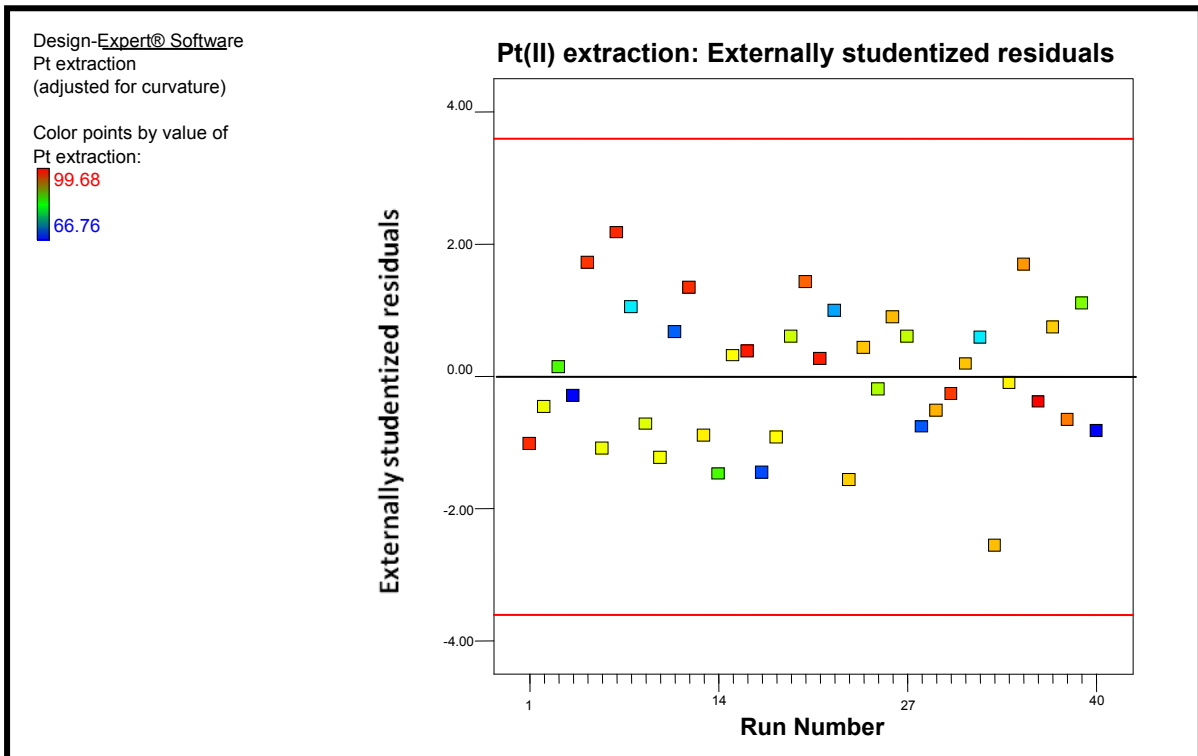


Figure 5.26: Influence plot for detection of outliers in relation with Pt(II) uptake

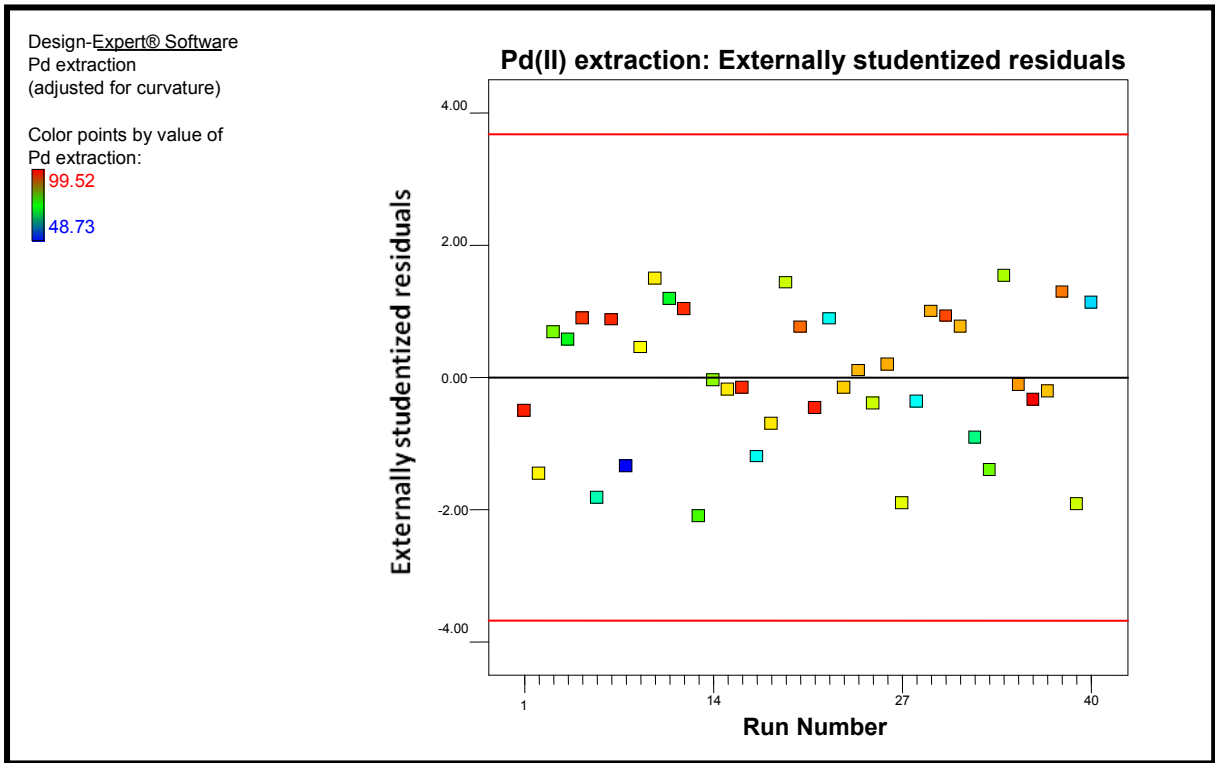


Figure 5.27: Influence plot for detection of outliers in relation with Pd(II) uptake

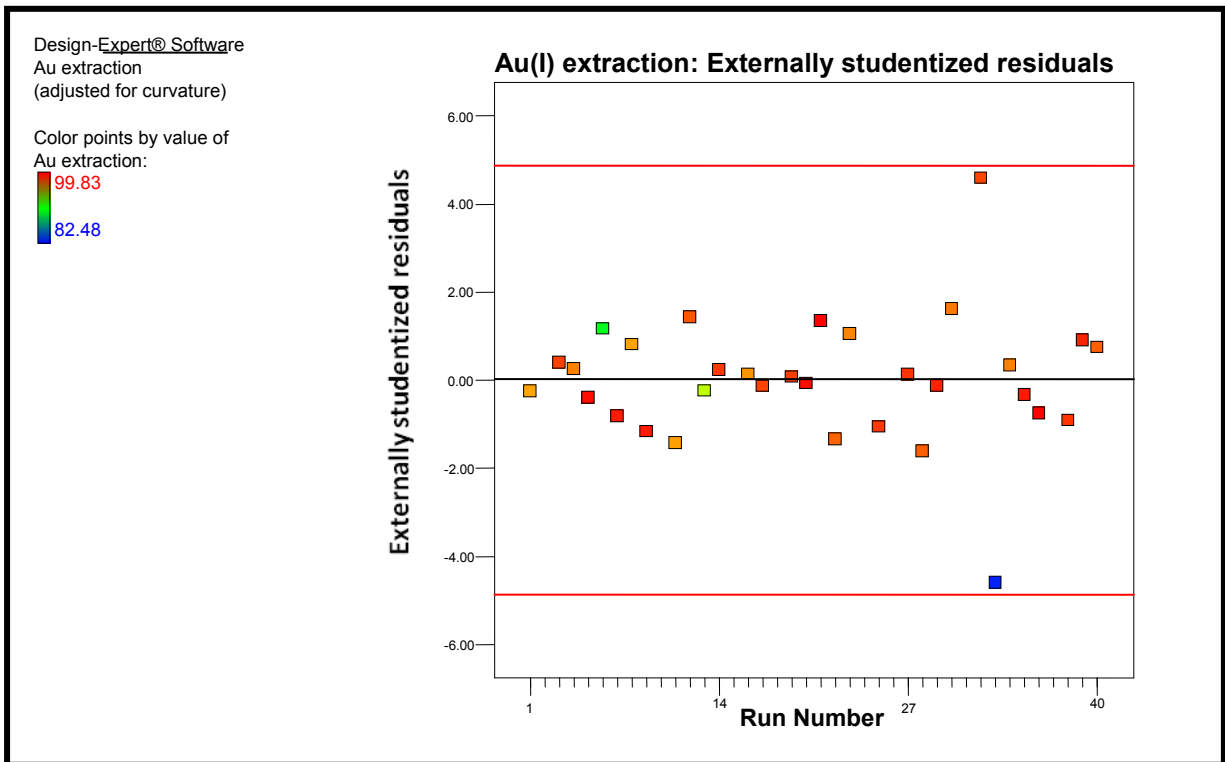


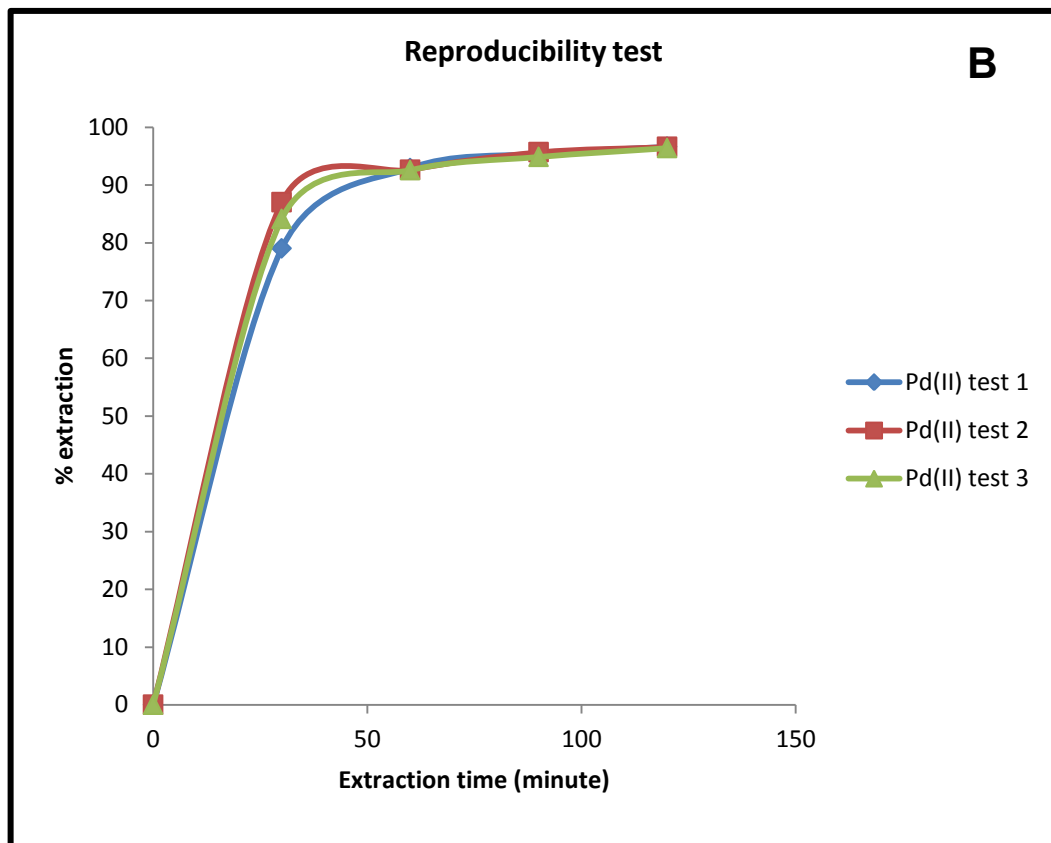
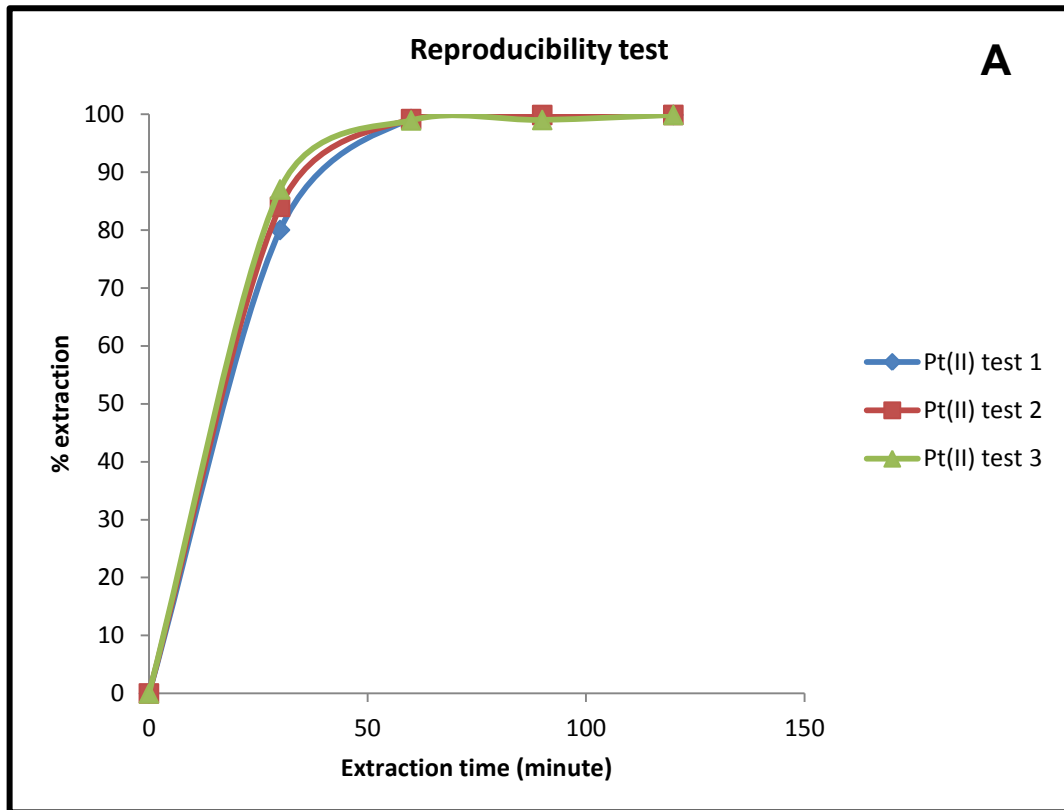
Figure 5.28: Influence plot for detection of outliers in relation with Au(I) uptake

5.3.8 Experimental error – reproducibility of the adsorption process

A $2^{(7-1)}_{IV}$ fractional factorial experimental design, with eight replicates at the centre point leading to a total of 40 experiments, was performed in this study. The centre points were used to determine the experimental error and the reproducibility of the data. Knowing that, the overall error consists of errors associated with assaying process combined with titration, random and operator errors. The centre points were also used to test the curvature. The order of experiments was randomised, to avoid any lurking factors that change with time or any possible memory effect of the analytical apparatus, which could bias the outcomes.

As the results of the eight runs at centre point were consistent, hence only a single replicate experiment (32 runs) was needed for this study. The relative standard deviation was 2.64 for Pt(II), 5.34 for Pd(II), and 2.16 for Au(I) after the 72 hours of adsorption process. Furthermore, relatively lower values of the coefficient of variation (CV): 2.98; 6.37; 2.22% for Pt(II), Pd(II) and Au(I), respectively, indicate a better precision and reliability of the experiments carried out. The coefficient of variation as the ratio of the standard error of estimate to the mean value of the observed response (as a percentage), is a measure of the reproducibility of a model. According to Chowdhury *et al.* (2012), as a general rule, a model can be considered reasonably reproducible if its coefficient of variation is not greater than 10%.

Finally, to assure the validity of the experimental results (optimum conditions and reproducibility), three additional confirmatory tests were conducted using the optimized parameters in Table 5.7. The outcomes displayed in Figures 5.29 (A) to (C) (separately presented for clarity purposes) show that the adsorption efficiency was more than 60% (over a period of 2 hours) in all cases as previously set-up in Table 5.5.



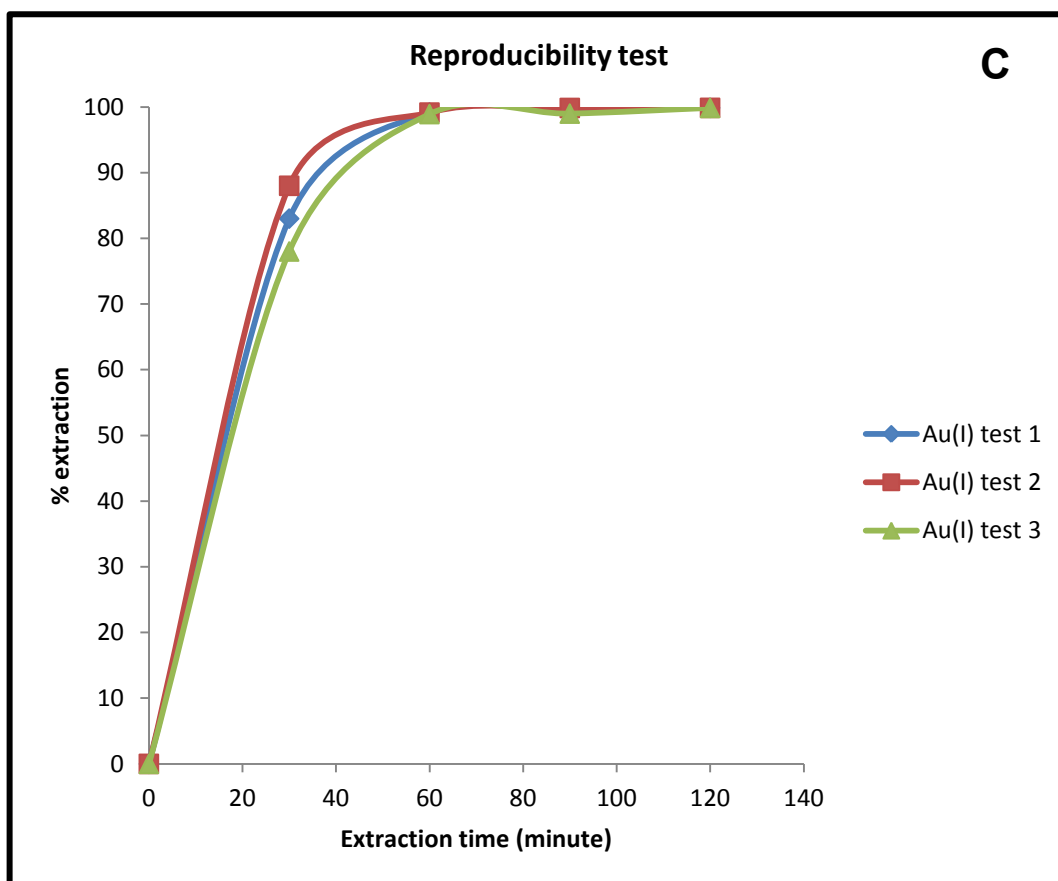


Figure 5.29: Corresponding percentage adsorption profiles for Pt (II), Pd(II) and Au(I) cyanide on carbon under optimum conditions – Reproducibility of the adsorption process

5.4 MEASURING ADSORPTION CAPACITY

Based on the optimum conditions in Table 5.7 and using a modified Pica procedure (refer to section 2.4.4 for additional information), a 10 g sample of activated carbon was contacted ten times with the same volume (1000 mL) of a fresh synthetic BM – PM liquor (pH = 9.5), and allowed to equilibrate at room temperature for 2 hours. Activated carbon loadings were calculated from the changes in solution concentration before and after equilibration according to 3.9 Equation and results are given in Table 5.8.

Table 5.7: Feed solution used in loading capacity tests

Elemental composition	Pt(II)	Pd(II)	Au(I)	Cu(I)	Ni(II)	CN ⁻	SCN ⁻
Content (ppm)	0.86	1.00	0.17	10	10	132.44	98.95

The cumulative adsorption loading capacity at the activated carbon to aqueous phase ratio of 1% w/v in ten discontinuous stages was found to be 0.64, 0.66, 0.17 mg of Pt, Pd and Au/g of carbon; respectively (Figure 5.30 and Table 5.8). Base metal concentrations being relatively higher than the PM, it seemed that competition for activated carbon sites was responsible for depression of PM loading. The Pie chart in Figure 5.31 – calculated using the formula: $100 \times \frac{q_i}{\sum q_i}$, where q stands for adsorption capacity, i is the individual element – indicates the presence of base metals, especially Ni(II); in higher capacities that might result in pore blockage of the adsorbent. Jones *et al.* quoted by Fisher and LaBrooy (1997) have reported that when the pH is reduced, the nickel tetracyano complex, $\text{Ni}(\text{CN})_4^{2-}$, can lose cyanide and precipitate as nickel dicyanide $\text{Ni}(\text{CN})_2$ which may cause pore blockage; while at pH of 12 and above, there is co-precipitation of gold with the nickel hydroxide.

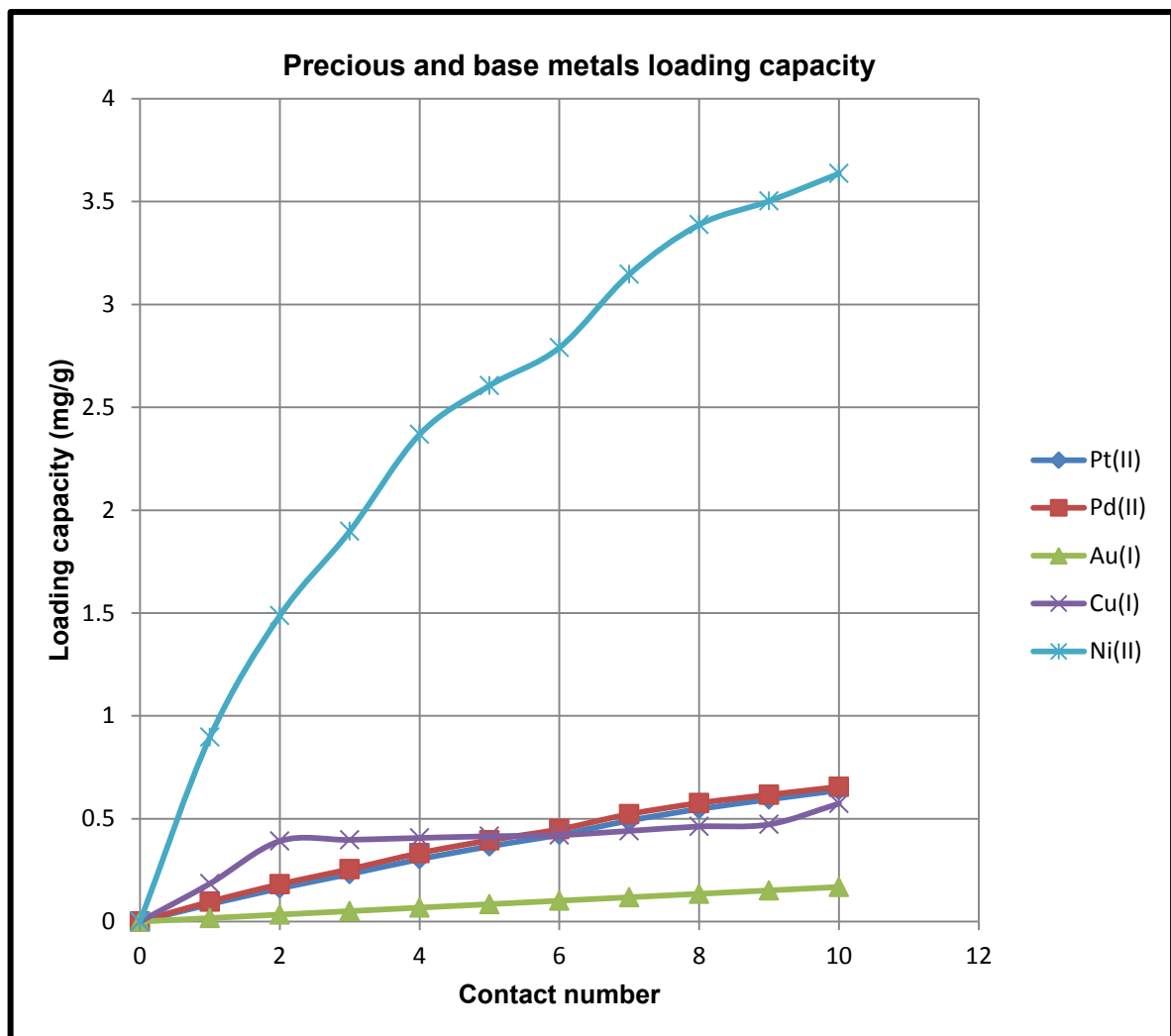


Figure 5.30: Loading of precious and base metals from synthetic solution onto activated carbon; unless otherwise stated, experimental conditions were: pH = 9.5, [CN] = 132.44 ppm, [SCN] = 98.95 ppm and [Activated carbon] = 10 g/L

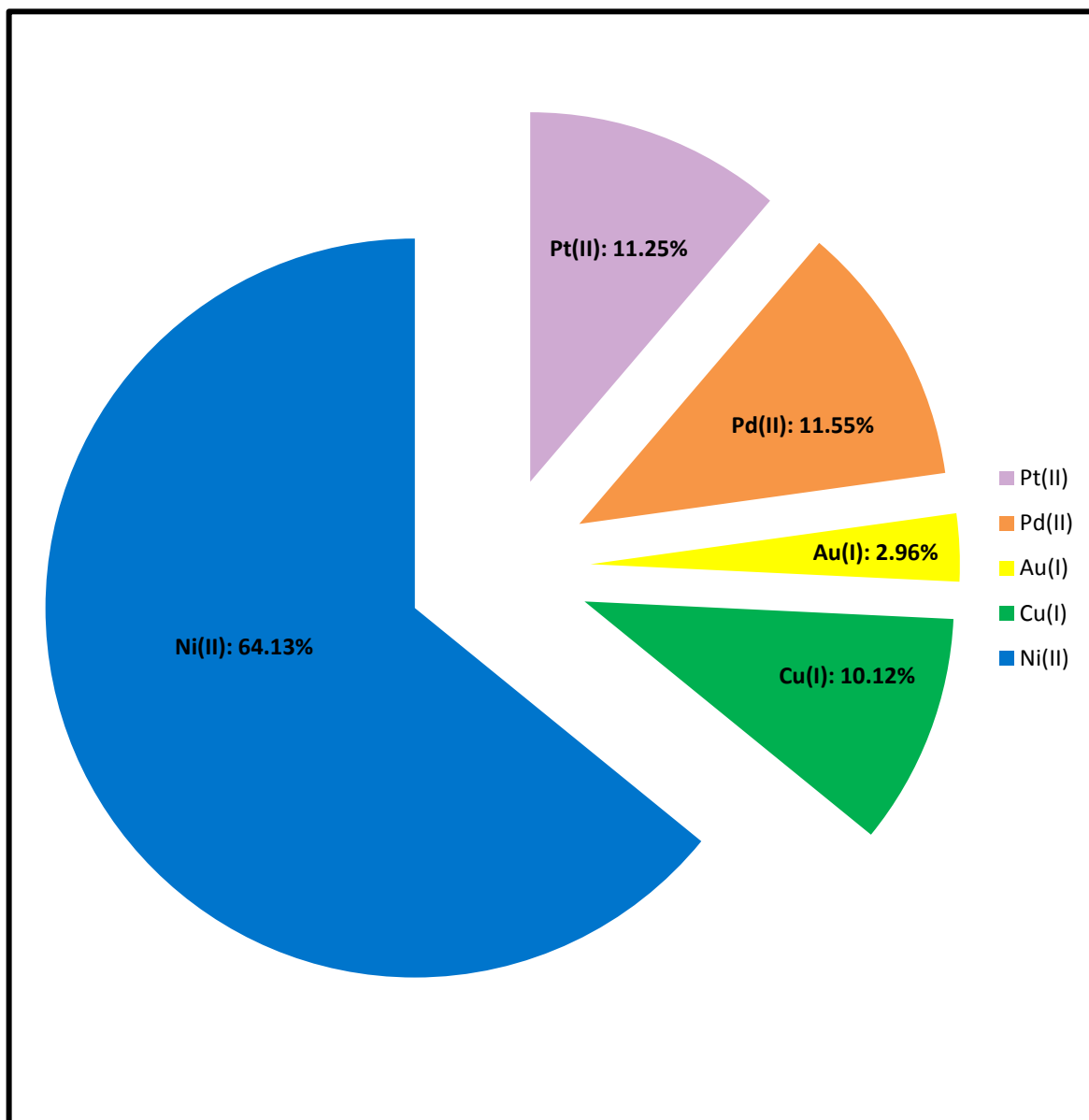


Figure 5.31: Competitive site occupation of precious and base metals loaded onto activated carbon under optimum conditions: pH = 9.5, Pt(II) = 0.86 ppm, Pd(II) = 1 ppm, Au(I) = 0.17 ppm, Cu(I) = 10 ppm, Ni(II) = 10 ppm, [CN] = 132.44 ppm, [SCN] = 98.95 ppm and 10 times contact

Table 5.8: Profiles for precious and base metals in solution, loading capacity of Pt(II), Pd(II) and Au(I) under optimum conditions

Contact	Adsorbate in solution ($\times 10^{-3}$ ppm)					Adsorbate on carbon ($\times 10^{-4}$ mg/g) and percentage adsorption per stage									
	Pt(II)	Pd(II)	Au(I)	Cu(I)	Ni(II)	Pt(II)	%	Pd(II)	%	Au(I)	%	Cu(I)	%	Ni(II)	%
0	860.00	1000.00	170.00	10000.00	10000.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	19.86	33.69	0.22	8154.09	1032.10	840.14	97.69	966.31	96.63	169.78	99.87	1845.91	18.46	8967.94	89.68
2	88.83	152.28	1.10	7932.18	4097.71	1611.31	89.67	1814.03	84.77	338.68	99.35	3913.73	20.68	14870.19	59.02
3	165.58	268.01	1.09	9940.09	5897.52	2305.73	80.75	2546.02	73.20	507.59	99.36	3973.64	0.60	18972.67	41.02
4	135.85	222.08	0.83	9905.83	5288.36	3029.88	84.20	3323.94	77.79	676.76	99.51	4067.81	0.94	23684.31	47.12
5	236.70	376.05	2.06	9920.69	7631.04	3653.18	72.48	3947.89	62.40	844.74	98.79	4147.12	0.79	26053.27	23.69
6	296.53	460.49	1.73	9944.04	8152.44	4216.65	65.52	4487.44	53.95	1012.97	98.98	4203.08	0.56	27900.83	18.48
7	171.67	271.00	2.21	9793.74	6434.34	4904.98	80.04	5216.43	72.90	1180.76	98.70	4409.34	2.06	31466.49	35.66
8	297.02	458.39	2.83	9785.59	7587.85	5467.96	65.46	5758.01	54.16	1347.93	98.34	4623.75	2.14	33878.64	24.12
9	394.46	595.40	3.99	9898.00	8850.56	5933.5	54.13	6162.61	40.46	1513.94	97.65	4725.75	1.02	35028.08	11.49
10	415.27	614.51	4.26	8989.01	8663.35	6378.23	51.71	6548.14	38.55	1679.68	97.49	5736.74	10.11	36364.73	13.37
Loading capacity (mg/g) from modified Pica procedure						0.64		0.66		0.17		0.57		3.64	

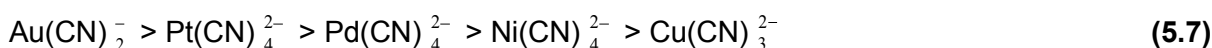
5.5 DISTRIBUTION COEFFICIENT – LOADING SELECTIVITY

The distribution coefficient, defined as the ratio of the metal concentration in the solid phase to that in the equilibrium solution after a specified reaction time, was calculated using Equation 3.7. K_D describes the extent to which adsorbates are adsorbed onto activated carbon. The experiment was carried out with solution of initial concentrations of 0.86, 1, 0.17, 10 and 10 ppm for Pt(II), Pd(II), Au(I), Cu(I) and Ni(II) respectively; at CN^- concentration of 132.44 ppm, SCN^- concentration of 98.95 ppm, solution pH of 9.5, for a contact time of 72 hours.

Table 5.9: Distribution coefficients for adsorption of base and PMs onto activated carbon

Species	Pt(II)	Pd(II)	Au(I)	Cu(I)	Ni(II)
Distribution coefficient K_D (L/kg)	1535.92	1065.58	39429.11	63.82	419.75

The highest K_D values (Table 5.9) were found for Au(I) followed by those of Pt(II) and Pd(II), while those of Ni(II) showed intermediate K_D values. However, low K_D values were pronounced for Cu(I). This implies that under competitive conditions, Au(I) is the most strongly adsorbed metal, whereas Cu(I) is the least adsorbed one. Lower solubility leads to higher distribution coefficients on carbon. No sequence is available in open literature for the order of adsorption of Pt and Pd cyanide complexes onto activated carbon. Based on their distribution coefficients, the affinity of activated carbon for metal ions follows the selectivity sequence expressed in Equation 5.7.



5.6 ADSORPTION MECHANISM APPROACH

5.6.1 Assessment of rate-limiting step

Sarkar *et al.* (2003) observed that external transport is usually the rate-limiting step for a system having (a) poor mixing, (b) dilute solute concentration, (c) small particle size of adsorbent and (d) high affinity of solute for adsorbent. In contrast, intraparticle diffusion usually limits the overall transfer for a system having (a) good mixing, (b) high solute concentration, (c) larger particle size of adsorbent, and (d) low affinity of solute for adsorbent.

According to Fleming and Nicol (1984) the rate of extraction of gold cyanide by resins and activated carbon is controlled by film diffusion in the initial stages (less than 30% of gold loading) and by both film and intraparticle diffusion in the latter stages, as equilibrium is approached.

The assessment of the rate-limiting step was investigated with solution of initial concentrations of 0.86, 1, 0.17, 10 and 10 ppm for Pt(II), Pd(II), Au(I), Cu(I) and Ni(II) respectively; at CN^- concentration of 132.44 ppm, SCN^- concentration of 98.95 ppm, solution pH of 9.5, for a contact time of 2 hours. The correlation coefficients (Figure 5.32) for the linear plots of t/q_t against time from the pseudo-second order rate law are greater than 0.99 for contact time of 120 minutes. This suggests that the adsorption system is not a first order reaction and that it is a pseudo-second order model, based on the assumption that the rate-limiting step may be chemical adsorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate, provides the best correlation of the data.

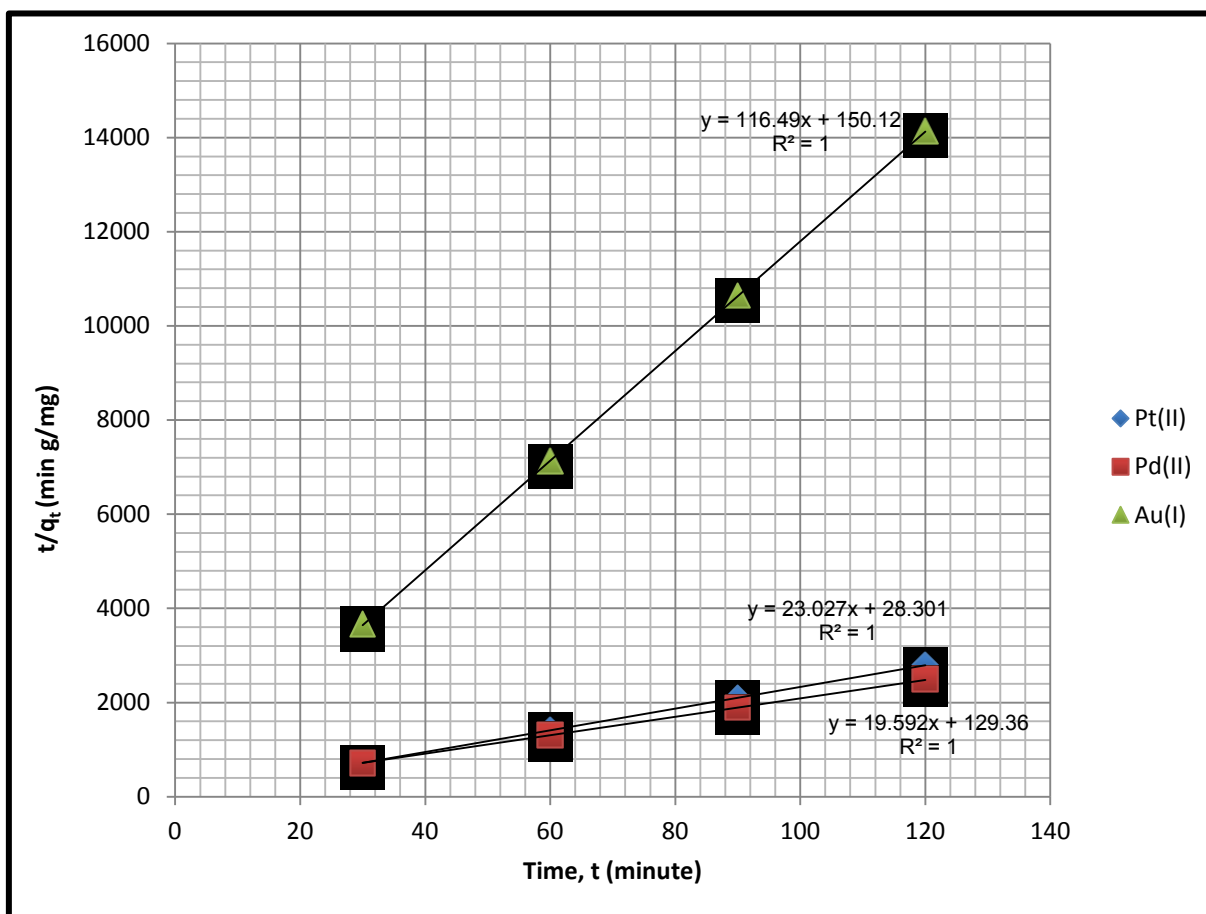


Figure 5.32: Pseudo-second order adsorption kinetics of Pt(II), Pd(II) and Au(I) onto activated carbon as a function of time measured at solution pH of 9.5, adsorbent concentration of 10 g/L, [Pt(II)] of 0.86 ppm, [Pd(II)] of 1 ppm, [Au(I)] of 0.17 ppm, [Cu(I)] of 10 ppm, [Ni(II)] of 10 ppm at 25°C and 2 hours contact time

5.6.2 Thermodynamic evaluation of the process – Standard Gibbs free energy

Gold adsorption by commercial activated carbon has been proposed to occur by both “irreversible” and “reversible” mechanisms (Schmitz *et al.*, 2001; Lagerge *et al.*, 1999). The results from this study suggest the occurrence of PM chemisorption.

The change in Gibbs free energy, ΔG° , of precious metal adsorption was computed at 25°C using Equation 2.21. As presented in Table 5.10, the negative values of ΔG° for all ions under optimum conditions indicate the feasibility and spontaneous nature of the adsorption process (no external energy source is required for the system), then ΔG° values indicate chemisorption as the predominant mechanism in the adsorption process of Pt(II), Pd(II) and Au(I).

Table 5.10: Standard Gibbs free energy for the adsorption of Pt(II), Pd(II) and Au(I) onto activated carbon

Metal	Gibbs free energy ΔG° (kJ/mol) at 25°C
Pt(II)	- 28.13
Pd(II)	- 27.23
Au(I)	- 36.18

5.7 CONCLUDING REMARKS

- The five most influential factors were in order of decreasing ranking of importance: [Ni(II)], [AC], [PMs], [Cu(I)] and solution pH. From the factorial experimental design, the optimum conditions for the best adsorption results were found as: solution pH of 9.5, [Cu(I)] of 10 ppm, [Ni(II)] of 10 ppm, [CN⁻] of 132.44 ppm, [SCN⁻] of 98.95 ppm, [PMs] of 2.03 ppm and [AC] of 10 g/L. At these conditions, Pt, Pd and Au predicted adsorption percentages were approximately 97.68, 92.22, 100%, at the level of 95% probability.
- Under these optimal conditions, for a load cycle time of 2 hours and ten discontinuous loading cycles (Total test loading time: 20 hours), the loading capacity of the activated carbon for PMs was observed to be 0.64, 0.66, 0.17 mg of Pt, Pd and Au/g of carbon, respectively.

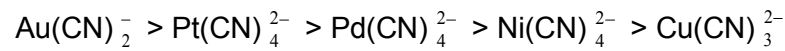
CHAPTER 6 : OVERALL CONCLUSIONS AND RECOMMENDATIONS

This concluding chapter presents conclusions and suggests useful avenues for future research.

The use of a factorial experimental design has allowed the identification of the most important factors influencing Pt(II), Pd(II) and Au(I) ions adsorption from cyanide media employing coconut shell MC 110 as adsorbent. The following conclusions were drawn:

- Adsorption rates of Pt, Pd and Au – within the first 60 minutes – were observed to be very high and thereafter the reaction proceeds at a slower rate until equilibrium was obtained. The saturation loading time was found to be 120 minutes based on the initial metal concentration.
- It was found that $[\text{SCN}^-]$ concentration was not identified as a significant (preventing) factor for PM adsorption, while Ni(II) concentration was the most significant adsorption process parameter due to its highest percentage contribution (negative) among the process parameters.
- The five most influential factors were, in order of decreasing ranking of importance, [Ni(II)], [AC], [PMs], [Cu(I)] and solution pH. From the factorial experimental design, the optimum conditions for the best adsorption results were found to be: solution pH of 9.5, [Cu(I)] of 10 ppm, [Ni(II)] of 10 ppm, $[\text{CN}^-]$ of 132.44 ppm, $[\text{SCN}^-]$ of 98.95 ppm, [PMs] of 2.03 ppm and [AC] of 10 g/L. At these conditions, Pt, Pd and Au predicted adsorption percentages were approximately 98, 92, 100%, at the level of 95% probability.
- Under these optimal conditions, for a load cycle time of 2 hours and ten discontinuous loading cycles (Total test loading time: 20 hours), the loading capacity of the activated carbon for PMs was observed to be 0.64, 0.66, 0.17 mg of Pt, Pd and Au/g of carbon, respectively.
- Base metal concentrations being relatively higher than the PM in the PLS, it seemed that competition for activated carbon sites was responsible for depression of PM loading.

- Thermodynamic data analysis revealed that the adsorption process is spontaneous and chemical in nature.
- Based on their distribution coefficients, the affinity of activated carbon for metal ions follows the selectivity sequence expressed below.



RECOMMENDATIONS AND FUTURE WORK

It is well-known that batch kinetics cannot be scaled-up directly to simulate a large scale CIL/CIP plant in view of differences in hydrodynamics. Nevertheless, a change in batch behaviour gives a relative indication of changes to be expected on a continuous plant. Selective adsorption of specific adsorbates has been indicated. Some of the key parameters important for controlling adsorption have been described in this work, providing the necessary foundation for the next step, which is to establish the economic viability of the technology which is important for its industrial application.

Maximum control of the stability of nickel complexes would be a key factor for success, especially for the heap leach operation. In other words, for PMs (Pt, Pd and Au) to be efficiently extracted from clarified or plant pregnant solution, it is necessary for all the nickel in solution to be extracted first. Although the strategy used in this work has given very promising results, there are a number of areas that need further investigation. These include:

- The need to investigate the adsorption of PMs by comparing the efficiencies and kinetics of adsorption when using sodium hydroxide (in this study) or lime, respectively, in order to control the pH.
- An investigation on separation and preconcentration of PM cyanide ions from dilute and large volume of solutions using reverse osmosis.
- An eventual incorporation of all the experimental data to formulate a computer package which will assist plant operators in the optimization of the carbon-in-pulp circuit.

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APPENDICES



APPENDIX A

TABULATION OF EXPERIMENTAL DATA

DERIVED FROM THE

SCREENING AND ACTUAL TESTS

SCREENING TEST 1 OPERATING CONDITIONS:								
Rotational rate (rpm): 105				Temperature of the solution (°C): 25				
Extraction time (hour): 72				Alkalinity level (pH): 10				
[CN ⁻] = 12.5 ppm				[Cu(I)] = 18.48 ppm				
[SCN ⁻] = 3670 ppm				[AC] = 10 g/L				
Solution volume = 500 mL				Adsorbent mass = 5 g				
[PMs] ppm	Time (h)		2	4	8	24	48	72
	Feed							
	Pt(II)	0.15	0.01	0.01	0.01	0.00	0.00	0.00
	Pd(II)	0.38	0.05	0.03	0.02	0.01	0.01	0.01
	Rh(III)	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Au(I)	0.10	0.01	0.01	0.01	0.01	0.01	0.01	
% Extraction	Pt(II)	0.00	93.33	93.33	93.33	99.33	100.00	100.00
	Pd(II)	0.00	86.84	92.11	94.74	97.37	97.37	97.37
	Rh(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Au(I)	0.00	90.00	90.00	90.00	90.00	90.00	99.90

SCREENING TEST 1 (Continued) OPERATING CONDITIONS:								
Rotational rate (rpm): 105				Temperature of the solution (°C): 25				
Extraction time (hour): 72				Alkalinity level (pH): 10				
[CN ⁻] = 12.5 ppm				[Cu(I)] = 18.84 ppm				
[SCN ⁻] = 3670 ppm				[AC] = 10 g/L				
Solution volume = 500 mL				Adsorbent mass = 5 g				
[BMs] ppm	Time (h)		2	4	8	24	48	72
	Feed							
	Cu	18.84	16.92	15.91	15.83	11.21	4.82	2.34
	Ni	18.30	5.09	3.81	3.06	1.85	1.82	1.56
Fe	47.30	47.14	46.17	46.73	45.22	46.44	46.15	
% Extraction	Cu	0.00	10.19	15.55	15.98	40.50	74.42	87.58
	Ni	0.00	72.19	79.18	83.28	89.89	90.05	91.48
	Fe	0.00	0.34	2.39	1.21	4.40	1.82	2.43

**SCREENING TEST 2
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 12.5 ppm
[SCN⁻] = 3670 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 10
[Cu(I)] = 18.84 ppm
[AC] = 20 g/L
Adsorbent mass = 10 g

[PMs] ppm	Time (h)		2	4	8	24	48	72
	Feed							
Pt(II)	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pd(II)	0.38	0.02	0.01	0.01	0.01	0.00	0.00	0.00
Rh(III)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Au(I)	0.10	0.12	0.04	0.02	0.02	0.02	0.01	0.01
% Extraction	Pt(II)	0.00	100.00	100.00	100.00	100.00	100.00	100.00
	Pd(II)	0.00	94.74	97.37	97.37	100.00	100.00	100.00
	Rh(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Au(I)	0.00	0.00	60.00	80.00	80.00	90.00	90.00

**SCREENING TEST 2 (Continued)
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 12.5 ppm
[SCN⁻] = 3670 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 10
[Cu(I)] = 18.84 ppm
[AC] = 20 g/L
Adsorbent mass = 10 g

[BMs] ppm	Time(h)		2	4	8	24	48	72
	Feed							
Cu	18.84	12.79	11.45	9.76	3.75	0.51	0.20	
Ni	18.30	1.88	1.35	1.16	0.71	0.66	0.55	
Fe	47.30	44.60	43.95	45.02	47.30	47.94	47.30	
% Extraction	Cu	0.00	32.11	39.23	48.20	80.10	97.29	98.94
	Ni	0.00	89.73	92.62	93.66	96.12	96.39	96.99
	Fe	0.00	5.71	7.08	4.82	0.00	-1.35	0.00

**EXPERIMENT 1
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 300 ppm
[SCN⁻] = 50 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 9.5
[Cu(I)] = 10 ppm
[AC] = 20 g/L
Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	2.57	2.48	1.99	1.96	0.638	0.95	0.95
	Pd(II)	380	10.33	7.97	6.57	5.26	1.40	4.78	4.78
	Au(I)	100	3.05	3.01	3.37	0.63	2.711	0.60	0.60
	Cu(I)	10000	7430	7320.2	6856.8	6572.6	3551.48	3428	2142.3
	Ni(II)	10000	745.14	467.26	429.75	341.5	152.43	134.1	113
% Extraction	Pt(II)	0.00	98.29	98.35	98.67	98.69	99.57	99.37	99.37
	Pd(II)	0.00	97.28	97.90	98.27	98.62	99.63	98.74	98.74
	Au(I)	0.00	96.95	96.99	96.63	99.37	97.29	99.40	99.40
	Cu(I)	0.00	25.70	26.80	31.43	34.27	64.49	65.72	78.58
	Ni(II)	0.00	92.55	95.33	95.70	96.59	98.48	98.66	98.87

**EXPERIMENT 2
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 200 ppm
[SCN⁻] = 75 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 10.75
[Cu(I)] = 55 ppm
[AC] = 15 g/L
Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	505	65.15	45.82	38.14	30.15	14.14	9.95	9.39
	Pd(II)	690	120.54	87.53	73.80	58.23	29.16	21.01	19.39
	Au(I)	135	2.17	1.70	1.72	1.27	0.89	0.71	0.71
	Cu(I)	55000	51594	51623	52237	51910	50610.6	49386	48509
	Ni(II)	55000	25984	21443	19300	16482	9530.88	7562	7135.3
% Extraction	Pt(II)	0.00	87.10	90.93	92.45	94.03	97.20	98.03	98.14
	Pd(II)	0.00	82.53	87.31	89.30	91.56	95.77	96.96	97.19
	Au(I)	0.00	98.39	98.74	98.73	99.06	99.34	99.47	99.47
	Cu(I)	0.00	6.19	6.14	5.02	5.62	7.98	10.21	11.80
	Ni(II)	0.00	52.76	61.01	64.91	70.03	82.67	86.25	87.03

**EXPERIMENT 3
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 100$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	27.867	21.613	17.238	14.088	7.5596	5.967	5.292
	Pd(II)	380	93.77	75.18	61.02	49.60	27.56	22.33	20.27
	Au(I)	100	1.88	1.26	1.06	0.81	0.64	0.62	0.68
	Cu(I)	100000	91400	91741	82875	81308	76767	69257	63924
	Ni(II)	100000	49145	45459	39404	34488	23720	20384	18845
% Extraction	Pt(II)	0.00	81.42	85.59	88.51	90.61	94.96	96.02	96.47
	Pd(II)	0.00	75.32	80.22	83.94	86.95	92.75	94.12	94.67
	Au(I)	0.00	98.12	98.74	98.94	99.19	99.36	99.38	99.32
	Cu(I)	0.00	8.60	8.26	17.13	18.69	23.23	30.74	36.08
	Ni(II)	0.00	50.85	54.54	60.60	65.51	76.28	79.62	81.16

**EXPERIMENT 4
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 100$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	428.97	285.10	242.22	208.94	129.75	98.46	103.36
	Pd(II)	1000	388.62	269.75	235.51	209.63	143.71	121.7	129.24
	Au(I)	170	8.2567	4.0122	2.8004	2.2164	1.6451	1.300	1.369
	Cu(I)	100000	76604	64411	56775	61679	58293	51788	57183
	Ni(II)	100000	58902	46969	42891	41697	34178	30468	32513
% Extraction	Pt(II)	0.00	50.12	66.85	71.84	75.70	84.91	88.55	87.98
	Pd(II)	0.00	61.14	73.02	76.45	79.04	85.63	87.83	87.08
	Au(I)	0.00	95.14	97.64	98.35	98.70	99.03	99.24	99.19
	Cu(I)	0.00	23.40	35.59	43.23	38.32	41.71	48.21	42.82
	Ni(II)	0.00	41.10	53.03	57.11	58.30	65.82	69.53	67.49

EXPERIMENT 5 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 10$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
In ppb	Pt(II)	860	33.23	16.94	11.14	7.40	3.68	1.79	0.73
	Pd(II)	1000	58.03	30.58	19.56	14.28	6.58	3.58	1.39
	Au(I)	170	1.52	0.65	0.59	0.38	0.35	0.27	0.10
	Cu(I)	10000	8121.96	7612.75	7421.29	6938.48	5270	2229.8	338.29
	Ni(II)	10000	1491.46	907.85	629.199	473.07	228.32	114.04	42.66
% Extraction	Pt(II)	0.00	96.14	98.03	98.70	99.14	99.57	99.79	99.92
	Pd(II)	0.00	94.20	96.94	98.04	98.57	99.34	99.64	99.86
	Au(I)	0.00	99.11	99.62	99.65	99.78	99.79	99.84	99.94
	Cu(I)	0.00	18.78	23.87	25.79	30.62	47.30	77.70	96.62
	Ni(II)	0.00	85.09	90.92	93.71	95.27	97.72	98.86	99.57

EXPERIMENT 6 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 100$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	20.16	13.53	12.18	8.83	4.22	3.30	3.12
	Pd(II)	380	219.72	131.61	111.94	82.21	41.77	31.43	29.15
	Au(I)	100	15.92	9.33	7.97	6.31	3.89	3.14	2.80
	Cu(I)	100000	88670	90411	88283	86653	81312	80887	78155
	Ni(II)	10000	3821.3	3056.97	2737.30	2242.18	1357.6	1189.6	1170.1
% Extraction	Pt(II)	0.00	86.56	90.98	91.88	94.11	97.19	97.80	97.92
	Pd(II)	0.00	42.18	65.37	70.54	78.37	89.01	91.73	92.33
	Au(I)	0.00	84.08	90.67	92.03	93.69	96.11	96.86	97.20
	Cu(I)	0.00	11.33	9.59	11.72	13.35	18.69	19.11	21.85
	Ni(II)	0.00	61.79	69.43	72.63	77.58	86.42	88.10	88.30

**EXPERIMENT 7
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 100$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	20.64	13.86	9.56	9.11	3.82	2.77	1.85
	Pd(II)	1000	37.36	24.24	18.11	16.03	7.06	5.18	3.62
	Au(I)	170	1.88	1.07	2.711	0.36	0.39	2.711	2.711
	Cu(I)	100000	82930	73234	51713	68686.17	56431.4	33647	25754.4
	Ni(II)	10000	1331.6	909.71	592.49	668.33	331.91	223.64	172.13
% Extraction	Pt(II)	0.00	97.60	98.39	98.89	98.94	99.56	99.68	99.78
	Pd(II)	0.00	96.26	97.58	98.19	98.40	99.29	99.48	99.64
	Au(I)	0.00	98.89	99.37	98.41	99.79	99.77	98.41	98.41
	Cu(I)	0.00	17.07	26.77	48.29	31.31	43.57	66.35	74.25
	Ni(II)	0.00	86.68	90.90	94.08	93.32	96.68	97.76	98.28

**EXPERIMENT 8
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 10$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	48.90	38.32	29.32	23.32	15.12	13.28	11.21
	Pd(II)	380	234.16	194.82	147.59	122.45	83.79	72.59	63.03
	Au(I)	100	4.57	2.94	2.06	1.68	1.41	1.38	1.17
	Cu(I)	10000	9245	9654	8956	9204	8942	9292	8966
	Ni(II)	100000	62878	56190	51199	46261.19	36723.8	33999	32329
% Extraction	Pt(II)	0.00	67.40	74.45	80.45	84.45	89.92	91.15	92.53
	Pd(II)	0.00	38.38	48.73	61.16	67.78	77.95	80.90	83.41
	Au(I)	0.00	95.43	97.06	97.94	98.32	98.59	98.62	98.83
	Cu(I)	0.00	7.55	3.46	10.44	7.96	10.58	7.08	10.34
	Ni(II)	0.00	37.12	43.81	48.80	53.74	63.28	66.00	67.67

EXPERIMENT 9 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 10$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	120.35	81.91	63.88	47.25	25.36	20.98	16.67
	Pd(II)	1000	185.05	132.03	103.78	96.22	43.93	35.62	29.45
	Au(I)	170	1.45	1.04	0.81	9.96	1.60	0.89	0.68
	Cu(I)	10000	9238.9	8956.9	8864.9	8918.684	8889.18	8587.2	8441.4
	Ni(II)	100000	47258	39650	35898	29908.6	21998.6	20197	18247.6
% Extraction	Pt(II)	0.00	86.01	90.48	92.57	94.51	97.05	97.56	98.06
	Pd(II)	0.00	81.50	86.80	89.62	90.38	95.61	96.44	97.06
	Au(I)	0.00	99.15	99.39	99.52	94.14	99.06	99.48	99.60
	Cu(I)	0.00	7.61	10.43	11.35	10.81	11.11	14.13	15.59
	Ni(II)	0.00	52.74	60.35	64.10	70.09	78.00	79.80	81.75

EXPERIMENT 10 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 200$ ppm
 $[SCN^-] = 75$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 10.75
 $[Cu(I)] = 55$ ppm
 $[AC] = 15$ g/L
 Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	505	63.08	44.97	37.01	29.19	13.56	9.64	8.83
	Pd(II)	690	118.41	86.15	70.85	57.45	27.50	19.76	18.02
	Au(I)	135	2.38	2.06	1.81	1.20	0.95	0.92	0.76
	Cu(I)	55000	52675	51615	51713	51722	50836.4	48803	47306.11
	Ni(II)	55000	26130	21401	18883	16305	9311.3	7003	6647.8
% Extraction	Pt(II)	0.00	87.51	91.10	92.67	94.22	97.31	98.09	98.25
	Pd(II)	0.00	82.84	87.51	89.73	91.67	96.01	97.14	97.39
	Au(I)	0.00	98.24	98.47	98.66	99.11	99.30	99.32	99.44
	Cu(I)	0.00	4.23	6.16	5.98	5.96	7.57	11.27	13.99
	Ni(II)	0.00	52.49	61.09	65.67	70.35	83.07	87.27	87.91

**EXPERIMENT 11
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 300 ppm
[SCN⁻] = 100 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 12
[Cu(I)] = 10 ppm
[AC] = 10 g/L
Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	60.99	45.12	44.33	36.57	21.02	18.14	15.75
	Pd(II)	380	134.4	104.8	104.8	89.1	52.1	44.5	40.9
	Au(I)	100	4.78	2.88	1.62	1.253	1.303	1.6	0.75
	Cu(I)	10000	6804.8	6628.3	7321.8	7064.03	6450.82	6644.7	6013.6
	Ni(II)	100000	66763	60384	57876	55137	41354	38948	40028
% Extraction	Pt(II)	0.00	59.34	69.92	70.45	75.62	85.99	87.91	89.50
	Pd(II)	0.00	64.64	72.43	72.41	76.55	86.29	88.30	89.24
	Au(I)	0.00	95.23	97.13	98.38	98.75	98.70	98.40	99.25
	Cu(I)	0.00	31.95	33.72	26.78	29.36	35.49	33.55	39.86
	Ni(II)	0.00	33.24	39.62	42.12	44.86	58.65	61.05	59.97

**EXPERIMENT 12
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 300 ppm
[SCN⁻] = 100 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 9.5
[Cu(I)] = 100 ppm
[AC] = 20 g/L
Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	23.35	14.93	14.18	10.87	7	6.18	5.09
	Pd(II)	1000	41.58	26.66	25.51	19.51	9	11.97	9.87
	Au(I)	170	1.20	2.71	0.56	0.72	7	0.59	0.13
	Cu(I)	100000	87783	58223.62	88263	82586	49348.6	75908	70903.6
	Ni(II)	10000	1381	815.72	923.25	750.64	340.4	476.55	426.08
% Extraction	Pt(II)	0.00	97.28	98.26	98.35	98.74	99.19	99.28	99.41
	Pd(II)	0.00	95.84	97.33	97.45	98.05	99.10	98.80	99.01
	Au(I)	0.00	99.29	98.41	99.67	99.58	95.88	99.65	99.92
	Cu(I)	0.00	12.22	41.78	11.73	17.41	50.65	24.09	29.10
	Ni(II)	0.00	86.19	91.84	90.77	92.49	96.60	95.23	95.74



EXPERIMENT 13 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 100$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	24.79	12.07	7.85	10.25	3.06	1.06	1.67
	Pd(II)	380	156.41	85.07	60.61	58.9	22.92	7.61	15.93
	Au(I)	100	9.44	5.60	4.00	3.39	3.55	2.33	24.36
	Cu(I)	100000	75778	68239	64894	58483	26259	4032	461
	Ni(II)	10000	3306.3	2202.75	1706.5	1163.7	579.37	161.87	22.46
% Extraction	Pt(II)	0.00	83.47	91.95	94.77	93.17	97.96	99.29	98.89
	Pd(II)	0.00	58.84	77.61	84.05	84.50	93.97	98.00	95.81
	Au(I)	0.00	90.56	94.40	96.00	96.61	96.45	97.67	75.64
	Cu(I)	0.00	24.22	31.76	35.11	41.52	73.74	95.97	99.54
	Ni(II)	0.00	66.94	77.97	82.94	88.36	94.21	98.38	99.78

EXPERIMENT 14 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 10$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	161.37	124.49	108.13	89.15	52.71	41.88	35.35
	Pd(II)	1000	237.42	187.50	163.35	135.64	84.05	68.78	58.10
	Au(I)	170	2.68	1.96	1.6	1.34	0.94	0.81	0.72
	Cu(I)	10000	9274.2	9151.6	9384.8	9053.7	9313.17	9213.7	9417.4
	Ni(II)	100000	48997	43168.3	40697	36401	26758.8	23450	21564
% Extraction	Pt(II)	0.00	81.24	85.52	87.43	89.63	93.87	95.13	95.89
	Pd(II)	0.00	76.26	81.25	83.66	86.44	91.59	93.12	94.19
	Au(I)	0.00	98.42	98.85	99.06	99.21	99.45	99.52	99.58
	Cu(I)	0.00	7.26	8.48	6.15	9.46	6.87	7.86	5.83
	Ni(II)	0.00	51.00	56.83	59.30	63.60	73.24	76.55	78.44

**EXPERIMENT 15
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 200$ ppm
 $[SCN^-] = 75$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 10.75
 $[Cu(I)] = 55$ ppm
 $[AC] = 15$ g/L
 Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	505	60.71	43.44	36.26	28.94	13.71	9.94	8.91
	Pd(II)	690	113.42	83.90	70.37	56.37	28.02	20.61	18.61
	Au(I)	135	2.60	2.03	1.60	1.63	1.11	0.72	0.57
	Cu(I)	55000	52214	51370	51288	51096	48824	47620	47625.68
	Ni(II)	55000	25121	21031	18920	16026	9439	7316	6978
% Extraction	Pt(II)	0.00	87.98	91.40	92.82	94.27	97.29	98.03	98.24
	Pd(II)	0.00	83.56	87.84	89.80	91.83	95.94	97.01	97.30
	Au(I)	0.00	98.07	98.50	98.81	98.79	99.18	99.47	99.58
	Cu(I)	0.00	5.07	6.60	6.75	7.10	11.23	13.42	13.41
	Ni(II)	0.00	54.33	61.76	65.60	70.86	82.84	86.70	87.31

**EXPERIMENT 16
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 10$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	4.02	1.66	2.03	2.03	2.03	0.638	0.638
	Pd(II)	380	17.43	9.30	9	7.80	9	1.91	2.11
	Au(I)	100	2.711	2.711	7	0.73	7	2.711	0.61
	Cu(I)	10000	7516.6	6968	7684.53	7499.71	7295.44	5851.7	4753.54
	Ni(II)	10000	1131.1	644.09	656.60	687.29	367.90	235.06	202.17
% Extraction	Pt(II)	0.00	97.32	98.89	98.65	98.65	98.65	99.57	99.57
	Pd(II)	0.00	95.41	97.55	97.63	97.95	97.63	99.50	99.44
	Au(I)	0.00	97.29	97.29	93.00	99.27	93.00	97.29	99.39
	Cu(I)	0.00	24.83	30.32	23.15	25.00	27.05	41.48	52.46
	Ni(II)	0.00	88.69	93.56	93.43	93.13	96.32	97.65	97.98

EXPERIMENT 17 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 100$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	349.34	265.57	219.69	175.92	99.12	86.55	80.07
	Pd(II)	1000	472.44	379.56	327.39	266.83	171.00	154.48	147.99
	Au(I)	170	4.27	2.20	1.78	1.41	0.93	0.83	17.74
	Cu(I)	100000	99815	99789	95921	94199.9	79647.2	69563	53562
	Ni(II)	100000	73200	65175	61692	56644.89	44253.19	42358	40485.6
% Extraction	Pt(II)	0.00	59.38	69.12	74.45	79.54	88.47	89.94	90.69
	Pd(II)	0.00	52.76	62.04	67.26	73.32	82.90	84.55	85.20
	Au(I)	0.00	97.49	98.71	98.95	99.17	99.46	99.51	89.56
	Cu(I)	0.00	0.19	0.21	4.08	5.80	20.35	30.44	46.44
	Ni(II)	0.00	26.80	34.82	38.31	43.36	55.75	57.64	59.51

EXPERIMENT 18 OPERATING CONDITIONS:

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 200$ ppm
 $[SCN^-] = 75$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 10.75
 $[Cu(I)] = 55$ ppm
 $[AC] = 15$ g/L
 Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	505	58.90	42.50	35.15	28.83	13.53	10.03	9.05
	Pd(II)	690	111.82	83.35	68.02	56.45	28.31	20.44	18.69
	Au(I)	135	5.84	3.64	2.72	2.02	1.46	1.06	0.78
	Cu(I)	55000	50997	50966	47667	49783	48696.7	48069	46332.36
	Ni(II)	55000	24538	20761	17447	15958	9214.69	7336	6967.09
% Extraction	Pt(II)	0.00	88.34	91.58	93.04	94.29	97.32	98.01	98.21
	Pd(II)	0.00	83.79	87.92	90.14	91.82	95.90	97.04	97.29
	Au(I)	0.00	95.67	97.30	97.99	98.50	98.92	99.21	99.42
	Cu(I)	0.00	7.28	7.33	13.33	9.49	11.46	12.60	15.76
	Ni(II)	0.00	55.39	62.25	68.28	70.99	83.25	86.66	87.33

**EXPERIMENT 19
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 100$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	21.94	15.29	12.18	9.8	4.63	3.18	2.33
	Pd(II)	380	84.09	59.83	49.02	56.5	19.71	13.51	10.29
	Au(I)	100	2.04	1.24	1.06	1.02	1.95	1.15	0.85
	Cu(I)	100000	90276	93168	89000.1	89338.8	82181	74802	44375.7
	Ni(II)	100000	45532	37650	32319.9	27593.2	16684	12524	9800.77
% Extraction	Pt(II)	0.00	85.37	89.81	91.88	93.47	96.91	97.88	98.45
	Pd(II)	0.00	77.87	84.26	87.10	85.13	94.81	96.44	97.29
	Au(I)	0.00	97.96	98.76	98.94	98.98	98.05	98.85	99.15
	Cu(I)	0.00	9.72	6.83	11.00	10.66	17.82	25.20	55.62
	Ni(II)	0.00	54.47	62.35	67.68	72.41	83.32	87.48	90.20

**EXPERIMENT 20
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 10$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	45.78	29.72	23.89	18.24	9.11	7.72	5.67
	Pd(II)	1000	83.00	57.88	43.96	35.25	17.99	15.29	11.77
	Au(I)	170	1.14	0.65	0.51	0.40	0.17	0.09	0.13
	Cu(I)	10000	9224.0	8865.3	8918.54	8776.1	8667.84	8972.1	8638.23
	Ni(II)	10000	2532.2	1973.2	1552.71	1310.35	785.78	729.41	544.04
% Extraction	Pt(II)	0.00	94.68	96.54	97.22	97.88	98.94	99.10	99.34
	Pd(II)	0.00	91.70	94.21	95.60	96.48	98.20	98.47	98.82
	Au(I)	0.00	99.33	99.62	99.70	99.76	99.90	99.95	99.92
	Cu(I)	0.00	7.76	11.35	10.81	12.24	13.32	10.28	13.62
	Ni(II)	0.00	74.68	80.27	84.47	86.90	92.14	92.71	94.56

**EXPERIMENT 21
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 300 ppm
[SCN⁻] = 100 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 12
[Cu(I)] = 10 ppm
[AC] = 20 g/L
Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	12.19	10.51	8.32	6.50	3.37	3.07	2.13
	Pd(II)	1000	22.34	18.53	15.19	12.59	6.67	5.93	4.24
	Au(I)	170	0.42	0.29	0.18	0.18	0.05	0.07	0.08
	Cu(I)	10000	7629.4	8011.2	7997.71	7617.21	7396.21	7138.2	6931.48
	Ni(II)	10000	798.42	690.82	600	501.88	308.62	276.38	213.82
% Extraction	Pt(II)	0.00	98.58	98.78	99.03	99.24	99.61	99.64	99.75
	Pd(II)	0.00	97.77	98.15	98.48	98.74	99.33	99.41	99.58
	Au(I)	0.00	99.75	99.83	99.89	99.89	99.97	99.96	99.95
	Cu(I)	0.00	23.71	19.89	20.02	23.83	26.04	28.62	30.69
	Ni(II)	0.00	92.02	93.09	94.00	94.98	96.91	97.24	97.86

**EXPERIMENT 22
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 300 ppm
[SCN⁻] = 100 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 9.5
[Cu(I)] = 100 ppm
[AC] = 10 g/L
Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	53.52	41.85	33.91	28.31	17.27	15.21	13.66
	Pd(II)	380	171.93	143.87	119.54	101.55	65.72	58.30	53.59
	Au(I)	100	3.21	1.84	1.37	1.29	0.68	0.54	0.50
	Cu(I)	100000	95120.97	99270	95760	92244.75	93898	94297	95341.8
	Ni(II)	100000	70295.92	65262	60211	56354.4	45028	42787	41173.7
% Extraction	Pt(II)	0.00	64.32	72.10	77.39	81.13	88.49	89.86	90.89
	Pd(II)	0.00	54.76	62.14	68.54	73.28	82.70	84.66	85.90
	Au(I)	0.00	96.79	98.16	98.63	98.71	99.32	99.46	99.50
	Cu(I)	0.00	4.88	0.73	4.24	7.76	6.10	5.70	4.66
	Ni(II)	0.00	29.70	34.74	39.79	43.65	54.97	57.21	58.83



**EXPERIMENT 23
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution (°C): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 10$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	16.42	10.51	9.31	7.36	2.54	3.52	2.64
	Pd(II)	380	70.3	41.01	38.28	28.9	13.37	13.32	12.92
	Au(I)	100	2.711	2.41	4.79	1.17	2.711	0.48	0.82
	Cu(I)	10000	8799.3	7182.3	6781.3	5563	1973.3	1677.3	570.34
	Ni(II)	10000	3382	3104	2889.9	2454.9	1105.4	1245	944.1
% Extraction	Pt(II)	0.00	89.05	92.99	93.79	95.09	98.31	97.65	98.24
	Pd(II)	0.00	81.50	89.21	89.93	92.39	96.48	96.49	96.60
	Au(I)	0.00	97.29	97.59	95.21	98.83	97.29	99.52	99.18
	Cu(I)	0.00	12.01	28.18	32.19	44.37	80.27	83.23	94.30
	Ni(II)	0.00	66.18	68.96	71.10	75.45	88.95	87.55	90.56

**EXPERIMENT 24
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 200$ ppm
 $[SCN^-] = 75$ ppm
 Solution volume = 500 mL

Temperature of the solution (°C): 25
 Alkalinity level (pH): 10.75
 $[Cu(I)] = 55$ ppm
 $[AC] = 15$ g/L
 Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	510	60.43	33.92	29.95	21.46	11.02	6.20	3.91
	Pd(II)	690	110.77	65.95	56.53	40.85	21.70	11.94	7.29
	Au(I)	135	7.36	3.26	2.40	1.83	1.25	1.15	0.93
	Cu(I)	55000	51584	51503	52237	51950	50820.6	49596	48309
	Ni(II)	55000	25984	21443	19300	16482	9530.88	7562	7325.3
% Extraction	Pt(II)	0.00	88.15	93.35	94.13	95.79	97.84	98.78	99.23
	Pd(II)	0.00	83.95	90.44	91.81	94.08	96.86	98.27	98.94
	Au(I)	0.00	94.55	97.59	98.22	98.64	99.07	99.15	99.31
	Cu(I)	0.00	6.21	6.36	5.02	5.55	7.60	9.83	12.17
	Ni(II)	0.00	52.76	61.01	64.91	70.03	82.67	86.25	86.68

**EXPERIMENT 25
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 100$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	147.08	95.96	75.72	54.36	24.66	18.46	13.97
	Pd(II)	1000	231.61	156.85	125.93	93.27	47.48	37.20	29.34
	Au(I)	170	3.22	1.93	1.47	1.17	0.85	0.80	0.55
	Cu(I)	100000	88338	82434	80247	73002	46715	23240	10561
	Ni(II)	100000	46528	37861	32332	26131	15434	12252	10293
% Extraction	Pt(II)	0.00	82.90	88.84	91.20	93.68	97.13	97.85	98.38
	Pd(II)	0.00	76.84	84.32	87.41	90.67	95.25	96.28	97.07
	Au(I)	0.00	98.11	98.86	99.14	99.31	99.50	99.53	99.68
	Cu(I)	0.00	11.66	17.57	19.75	27.00	53.29	76.76	89.44
	Ni(II)	0.00	53.47	62.14	67.67	73.87	84.57	87.75	89.71

**EXPERIMENT 26
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 200$ ppm
 $[SCN^-] = 75$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 10.75
 $[Cu(I)] = 55$ ppm
 $[AC] = 15$ g/L
 Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	510	52.17	32.40	27.14	19.28	10.51	5.63	3.86
	Pd(II)	690	97.12	62.40	51.84	36.95	20.62	11.12	7.07
	Au(I)	135	2.69	2.31	1.84	1.71	1.47	1.25	1.28
	Cu(I)	55000	52605	51600	51203	51722	50836.4	48803	47246.11
	Ni(II)	55000	24130	21391	18883	16315	9210.3	7099	6587.8
% Extraction	Pt(II)	0.00	89.77	93.65	94.68	96.22	97.94	98.90	99.24
	Pd(II)	0.00	85.92	90.96	92.49	94.64	97.01	98.39	98.98
	Au(I)	0.00	98.01	98.29	98.64	98.73	98.91	99.07	99.05
	Cu(I)	0.00	4.35	6.18	6.90	5.96	7.57	11.27	14.10
	Ni(II)	0.00	56.13	61.11	65.67	70.34	83.25	87.09	88.02

**EXPERIMENT 27
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 10$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs] in ppb	Time (h)		1	2	3	6	24	48	72
	Feed								
	Pt(II)	150	22.47	15.70	13.32	10.48	6.46	5.56	4.83
	Pd(II)	380	76.20	54.95	46.79	46.81	22.06	17.27	14.86
	Au(I)	100	1.78	1.06	2.28	7.38	2.01	1.13	1.97
	Cu(I)	10000	5795	5958	6112	3574	4778	5554	3683
	Ni(II)	100000	45284.5	37624.1	34373.4	28853.8	19573.7	17074.1	16240.6
% Extraction	Pt(II)	0.00	85.02	89.54	91.12	93.01	95.69	96.29	96.78
	Pd(II)	0.00	79.95	85.54	87.69	87.68	94.19	95.46	96.09
	Au(I)	0.00	98.22	98.94	97.72	92.62	97.99	98.87	98.03
	Cu(I)	0.00	42.05	40.42	38.88	64.26	52.22	44.46	63.17
	Ni(II)	0.00	54.72	62.38	65.63	71.15	80.43	82.93	83.76

**EXPERIMENT 28
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 10$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs] in ppb	Time (h)		1	2	3	6	24	48	72
	Feed								
	Pt(II)	860	331.61	261.03	226.92	199.91	136.72	117.94	102.85
	Pd(II)	1000	466.46	382.19	340.61	306.37	221.12	192.77	173.04
	Au(I)	170	5.32	2.99	2.49	1.99	1.12	0.95	0.88
	Cu(I)	10000	9730.97	9700.20	9358.58	9605.52	10033.93	9757.79	9263.91
	Ni(II)	100000	75270.52	71294.32	66755.32	64719.72	57305.92	54190.82	50499.92
% Extraction	Pt(II)	0.00	61.44	69.65	73.61	76.75	84.10	86.29	88.04
	Pd(II)	0.00	53.35	61.78	65.94	69.36	77.89	80.72	82.70
	Au(I)	0.00	96.87	98.24	98.54	98.83	99.34	99.44	99.48
	Cu(I)	0.00	2.69	3.00	6.42	3.95	-0.34	2.42	7.36
	Ni(II)	0.00	24.73	28.71	33.24	35.28	42.69	45.81	49.50

**EXPERIMENT 29
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 100$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	83.17	52.29	34.99	29.48	14.87	16.94	14.88
	Pd(II)	1000	140.77	90.10	63.26	52.91	27.96	33.65	28.14
	Au(I)	170	2.36	1.31	0.95	0.67	0.64	0.29	1.18
	Cu(I)	100000	95594	98849	93738	94286	90447.6	94260.6	96647
	Ni(II)	10000	3677.1	2906	1855	1882.4	1091.83	1301.98	1183.46
% Extraction	Pt(II)	0.00	90.33	93.92	95.93	96.57	98.27	98.03	98.27
	Pd(II)	0.00	85.92	90.99	93.67	94.71	97.20	96.64	97.19
	Au(I)	0.00	98.61	99.23	99.44	99.61	99.62	99.83	99.31
	Cu(I)	0.00	4.41	1.15	6.26	5.71	9.55	5.74	3.35
	Ni(II)	0.00	63.23	70.94	81.45	81.18	89.08	86.98	88.17

**EXPERIMENT 30
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 100$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	7.96	3.27	2.13	1.25	0.42	0.16	0.12
	Pd(II)	380	34.61	15.11	10.05	6.24	1.79	0.46	0.15
	Au(I)	100	4.91	2.21	1.50	1.30	26.30	2.67	1.13
	Cu(I)	100000	55287	46757	40226	27089	1016	179	114
	Ni(II)	10000	1039.44	602.38	456.40	277.69	26.13	5.93	3.79
% Extraction	Pt(II)	0.00	94.69	97.82	98.58	99.17	99.72	99.89	99.92
	Pd(II)	0.00	90.89	96.02	97.36	98.36	99.53	99.88	99.96
	Au(I)	0.00	95.09	97.79	98.50	98.70	73.70	97.33	98.87
	Cu(I)	0.00	44.71	53.24	59.77	72.91	98.98	99.82	99.89
	Ni(II)	0.00	89.61	93.98	95.44	97.22	99.74	99.94	99.96

**EXPERIMENT 31
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 200$ ppm
 $[SCN^-] = 75$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 10.75
 $[Cu(I)] = 55$ ppm
 $[AC] = 15$ g/L
 Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	510	56.48	33.63	28.76	20.09	10.20	5.58	3.46
	Pd(II)	690	106.80	66.07	55.55	46.20	21.78	11.78	7.17
	Au(I)	135	5.12	3.86	3.43	3.40	3.34	4.03	3.05
	Cu(I)	55000	52194	51290	51108	51096	48824	47520	47640
	Ni(II)	55000	25121	21031	18920	16026	9499	7350	7415
% Extraction	Pt(II)	0.00	88.93	93.41	94.36	96.06	98.00	98.91	99.32
	Pd(II)	0.00	84.52	90.42	91.95	93.30	96.84	98.29	98.96
	Au(I)	0.00	96.21	97.14	97.46	97.48	97.53	97.01	97.74
	Cu(I)	0.00	5.10	6.75	7.08	7.10	11.23	13.60	13.38
	Ni(II)	0.00	54.33	61.76	65.60	70.86	82.73	86.64	86.52

**EXPERIMENT 32
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 10$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	284.72	220.13	186.85	147.54	95.25	85.47	75.49
	Pd(II)	1000	397.55	322.63	283.27	227.62	154.17	139.43	124.43
	Au(I)	170	4.01	2.29	1.72	1.29	0.86	0.68	0.58
	Cu(I)	10000	9630.30	9060.08	9015.5	9257.3	8897.5	9122	8656.54
	Ni(II)	100000	66694.80	60698.65	57835	52874	42424	41029	38363.3
% Extraction	Pt(II)	0.00	66.89	74.40	78.27	82.84	88.92	90.06	91.22
	Pd(II)	0.00	60.25	67.74	71.67	77.24	84.58	86.06	87.56
	Au(I)	0.00	97.64	98.65	98.99	99.24	99.50	99.60	99.66
	Cu(I)	0.00	3.70	9.40	9.85	7.43	11.03	8.78	13.44
	Ni(II)	0.00	33.31	39.30	42.16	47.13	57.58	58.97	61.64

**EXPERIMENT 33
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 300$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 100$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	21.92	9.64	6.95	5.34	2.88	2.19	1.62
	Pd(II)	380	217.92	76.96	44.50	31.37	16.62	12.80	9.73
	Au(I)	100	76.13	16.94	11.60	15.59	5.07	4.01	3.11
	Cu(I)	100000	70173	67296	62612	63517	56662	52001	48501
	Ni(II)	10000	1447.48	1040.48	904.69	727.04	430.44	360.97	330.29
% Extraction	Pt(II)	0.00	85.39	93.57	95.37	96.44	98.08	98.54	98.92
	Pd(II)	0.00	42.65	79.75	88.29	91.74	95.63	96.63	97.44
	Au(I)	0.00	23.87	83.06	88.40	84.41	94.93	95.99	96.89
	Cu(I)	0.00	29.83	32.70	37.39	36.48	43.34	48.00	51.50
	Ni(II)	0.00	85.53	89.60	90.95	92.73	95.70	96.39	96.70

**EXPERIMENT 34
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 10$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	21.59	12.37	11.73	9.72	4.62	3.55	1.55
	Pd(II)	380	113.97	65.69	59.83	77.50	24.48	14.41	7.79
	Au(I)	100	3.58	2.36	2.33	23.49	4.34	2.64	1.69
	Cu(I)	10000	8746.994	9036.4	9696	8256.6	8522.8	4546.5	831.33
	Ni(II)	100000	42723.19	30969.32	27331	20775	11181	6627.6	4094.8
% Extraction	Pt(II)	0.00	85.61	91.75	92.18	93.52	96.92	97.63	98.97
	Pd(II)	0.00	70.01	82.71	84.26	79.61	93.56	96.21	97.95
	Au(I)	0.00	96.42	97.64	97.67	76.51	95.66	97.36	98.31
	Cu(I)	0.00	12.53	9.64	3.04	17.43	14.77	54.53	91.69
	Ni(II)	0.00	57.28	69.03	72.67	79.23	88.82	93.37	95.91

**EXPERIMENT 35
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 100$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 12
 $[Cu(I)] = 100$ ppm
 $[AC] = 10$ g/L
 Adsorbent mass = 5 g

[PMs] and [BMs] in ppb	Time (h)		1	2	3	6	24	48	72
	Feed								
	Pt(II)	860	77.19	44.60	34.82	24.06	11.87	11.49	9.17
	Pd(II)	1000	130.60	80.91	64.33	44.22	22.58	21.14	16.60
	Au(I)	170	3.13	1.00	1.04	2.711	0.46	0.94	0.98
	Cu(I)	100000	91372	84774	88745	54164	77340	74726	64936
	Ni(II)	10000	3675.81	2748.31	2309.2	1404	1013.7	977.63	769.01
% Extraction	Pt(II)	0.00	91.02	94.81	95.95	97.20	98.62	98.66	98.93
	Pd(II)	0.00	86.94	91.91	93.57	95.58	97.74	97.89	98.34
	Au(I)	0.00	98.16	99.41	99.39	98.41	99.73	99.45	99.42
	Cu(I)	0.00	8.63	15.23	11.26	45.84	22.66	25.27	35.06
	Ni(II)	0.00	63.24	72.52	76.91	85.96	89.86	90.22	92.31

**EXPERIMENT 36
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 72
 $[CN^-] = 100$ ppm
 $[SCN^-] = 50$ ppm
 Solution volume = 500 mL

Temperature of the solution ($^{\circ}C$): 25
 Alkalinity level (pH): 9.5
 $[Cu(I)] = 10$ ppm
 $[AC] = 20$ g/L
 Adsorbent mass = 10 g

[PMs] and [BMs] in ppb	Time (h)		1	2	3	6	24	48	72
	Feed								
	Pt(II)	860	4.20	2.71	1.86	1.55	0.53	0.49	0.27
	Pd(II)	1000	7.55	4.83	3.30	2.49	1.11	0.85	0.73
	Au(I)	170	0.59	0.33	0.35	0.31	0.23	0.32	0.07
	Cu(I)	10000	6689.04	5278.6	4164.98	3310.31	810.92	261.35	172.46
	Ni(II)	10000	232.52	156.91	101.58	74.80	17.40	4.32	3.94
% Extraction	Pt(II)	0.00	99.51	99.68	99.78	99.82	99.94	99.94	99.97
	Pd(II)	0.00	99.25	99.52	99.67	99.75	99.89	99.92	99.93
	Au(I)	0.00	99.65	99.81	99.79	99.82	99.86	99.81	99.96
	Cu(I)	0.00	33.11	47.21	58.35	66.90	91.89	97.39	98.28
	Ni(II)	0.00	97.67	98.43	98.98	99.25	99.83	99.96	99.96

**EXPERIMENT 37
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 200 ppm
[SCN⁻] = 75 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 10.75
[Cu(I)] = 55 ppm
[AC] = 15 g/L
Adsorbent mass = 7.5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	505	54.48	35.17	29.65	21.04	11.53	5.65	3.00
	Pd(II)	690	105.97	70.40	59.27	43.96	24.66	13.06	7.33
	Au(I)	135	30.84	23.65	15.03	12.13	9.58	6.10	6.25
	Cu(I)	55000	50946	50959	47698	49795	48699.7	48086	46398.36
	Ni(II)	55000	24599	20881	17987	15989	9550.69	7585	6995
% Extraction	Pt(II)	0.00	89.21	93.04	94.13	95.83	97.72	98.88	99.41
	Pd(II)	0.00	84.64	89.80	91.41	93.63	96.43	98.11	98.94
	Au(I)	0.00	77.16	82.48	88.87	91.01	92.90	95.48	95.37
	Cu(I)	0.00	7.37	7.35	13.28	9.46	11.46	12.57	15.64
	Ni(II)	0.00	55.27	62.03	67.30	70.93	82.64	86.21	87.28

**EXPERIMENT 38
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 300 ppm
[SCN⁻] = 100 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 9.5
[Cu(I)] = 10 ppm
[AC] = 10 g/L
Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	10.05	6.37	3.74	4.11	1.61	1.4	1.16
	Pd(II)	380	41.28	24.6	18.55	18.2	8.85	7.69	7.33
	Au(I)	100	2.711	1.06	2.711	4.48	2.71	2.71	0.72
	Cu(I)	10000	8602.48	8298.17	5791.67	5483.67	5303.17	5203.67	4564
	Ni(II)	10000	2269	1941	1196	1534	702.6	643.7	602
% Extraction	Pt(II)	0.00	93.30	95.75	97.51	97.26	98.93	99.07	99.23
	Pd(II)	0.00	89.14	93.53	95.12	95.21	97.67	97.98	98.07
	Au(I)	0.00	97.29	98.94	97.29	95.52	97.29	97.29	99.28
	Cu(I)	0.00	13.98	17.02	42.08	45.16	46.97	47.96	54.36
	Ni(II)	0.00	77.31	80.59	88.04	84.66	92.97	93.56	93.98



**EXPERIMENT 39
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 300 ppm
[SCN⁻] = 100 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 12
[Cu(I)] = 100 ppm
[AC] = 20 g/L
Adsorbent mass = 10 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	860	158.76	109.08	82.86	70.84	36.66	29.67	28.35
	Pd(II)	1000	215.20	156.24	128.38	108.88	61.88	50.67	50.77
	Au(I)	170	2.09	1.25	13.04	1.58	0.93	0.73	0.57
	Cu(I)	100000	79065	77056	69130	73058	66308	61764	64554
	Ni(II)	100000	44432	36754	32045	28637	19838	16793	17348
% Extraction	Pt(II)	0.00	81.54	87.32	90.36	91.76	95.74	96.55	96.70
	Pd(II)	0.00	78.48	84.38	87.16	89.11	93.81	94.93	94.92
	Au(I)	0.00	98.77	99.27	92.33	99.07	99.45	99.57	99.67
	Cu(I)	0.00	20.94	22.94	30.87	26.94	33.69	38.24	35.45
	Ni(II)	0.00	55.57	63.25	67.95	71.36	80.16	83.21	82.65

**EXPERIMENT 40
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
Extraction time (hour): 72
[CN⁻] = 100 ppm
[SCN⁻] = 50 ppm
Solution volume = 500 mL

Temperature of the solution (°C): 25
Alkalinity level (pH): 12
[Cu(I)] = 100 ppm
[AC] = 10 g/L
Adsorbent mass = 5 g

[PMs] and [BMs]	Time (h)		1	2	3	6	24	48	72
	Feed								
in ppb	Pt(II)	150	60.25	49.86	42.24	36.99	23.32	19.92	17.83
	Pd(II)	380	179.60	153.68	136.47	119.26	81.99	70.46	64.28
	Au(I)	100	3.01	1.80	1.43	1.10	0.65	0.52	0.49
	Cu(I)	100000	91643.18	92544.96	90020	89647	86787	87289	82222.2
	Ni(II)	100000	73450.42	68396.52	65723	62135	51798	48763	46926.7
% Extraction	Pt(II)	0.00	59.83	66.76	71.84	75.34	84.45	86.72	88.11
	Pd(II)	0.00	52.74	59.56	64.09	68.62	78.42	81.46	83.09
	Au(I)	0.00	96.99	98.20	98.57	98.90	99.35	99.48	99.51
	Cu(I)	0.00	8.36	7.46	9.98	10.35	13.21	12.71	17.78
	Ni(II)	0.00	26.55	31.60	34.28	37.87	48.20	51.24	53.07



PGM and BMs extraction for various bottles-on-roll operating conditions after 72 hours contact

Trial	Block	pH	[Cu(I)] mg/L	[Ni(II)] mg/L	[CN] mg/L	[SCN] mg/L	[PMs] mg/L	[AC] g/L	PM and BMs extraction (%)				
									Pt(II)	Pd(II)	Au(I)	Cu(I)	Ni(II)
1	1	9.5	10	10	300	50	0.63	20	99.37	98.74	99.40	78.58	98.87
2		10.75	55	55	200	75	1.33	15	98.14	97.19	99.47	11.80	87.03
3		12	100	100	100	100	0.63	20	96.47	94.67	99.32	36.08	81.16
4		12	100	100	300	50	2.03	10	87.98	87.08	99.19	42.82	67.49
5		9.5	10	10	100	100	2.03	10	99.92	99.86	99.94	96.62	99.57
6	2	12	100	10	300	100	0.63	10	97.92	92.33	97.20	21.85	88.30
7		12	100	10	100	50	2.03	20	99.78	99.64	98.41	74.25	98.28
8		9.5	10	100	100	50	0.63	10	92.53	83.41	98.83	10.34	67.67
9		9.5	10	100	300	100	2.03	20	98.06	97.06	99.60	15.59	81.75
10		10.75	55	55	200	75	1.33	15	98.25	97.39	99.44	13.99	87.91
11	3	12	10	100	300	100	0.63	10	89.50	89.24	99.25	39.86	59.97
12		9.5	100	10	300	100	2.03	20	99.41	99.01	99.92	29.10	95.74
13		9.5	100	10	100	50	0.63	10	98.89	95.81	75.64	99.54	99.78
14		12	10	100	100	50	2.03	20	95.89	94.19	99.58	5.83	78.44
15		10.75	55	55	200	75	1.33	15	98.24	97.30	99.58	13.41	87.31
16	4	12	10	10	100	100	0.63	20	99.57	99.44	99.39	52.46	97.98
17		9.5	100	100	100	100	2.03	10	90.69	85.20	89.56	46.44	59.51
18		10.75	55	55	200	75	1.33	15	98.21	97.29	99.42	15.76	87.33
19		9.5	100	100	300	50	0.63	20	98.45	97.29	99.15	55.62	90.20
20		12	10	10	300	50	2.03	10	99.34	98.82	99.92	13.62	94.56

PGM and BMs extraction for various bottles-on-roll operating conditions after 72 hours contact time

Trial	Block	pH	[Cu(I)] mg/L	[Ni(II)] mg/L	[CN] mg/L	[SCN] mg/L	[PMs] mg/L	[AC] g/L	PM and BMs extraction (%)				
									Pt(II)	Pd(II)	Au(I)	Cu(I)	Ni(II)
21	5	12	10	10	300	100	2.03	20	99.75	99.58	99.95	30.69	97.86
22		9.5	100	100	300	100	0.63	10	90.89	85.90	99.50	4.66	58.83
23		12	10	10	100	50	0.63	10	98.24	96.60	99.18	83.23	90.56
24		10.75	55	55	200	75	1.33	15	93.35	90.44	97.59	6.36	61.01
25		9.5	100	100	100	50	2.03	20	98.38	97.07	99.68	89.44	89.71
26	6	10.75	55	55	200	75	1.33	15	93.65	90.96	98.29	6.18	61.11
27		12	10	100	300	50	0.63	20	96.78	96.09	98.03	63.17	83.76
28		12	10	100	100	100	2.03	10	88.04	82.70	99.48	7.36	49.50
29		9.5	100	10	300	50	2.03	10	98.27	97.19	99.31	3.35	88.17
30		9.5	100	10	100	100	0.63	20	99.92	99.96	98.87	99.89	99.96
31	7	10.75	55	55	200	75	1.33	15	93.41	90.42	97.14	6.75	61.76
32		9.5	10	100	300	50	2.03	10	91.22	87.56	99.66	13.44	61.64
33		12	100	10	300	50	0.63	20	98.92	97.44	96.89	51.50	96.70
34		9.5	10	100	100	100	0.63	20	98.97	97.95	98.31	91.69	95.91
35		12	100	10	100	100	2.03	10	98.93	98.34	99.42	35.06	92.31
36	8	9.5	10	10	100	50	2.03	20	99.97	99.93	99.96	98.28	99.96
37		10.75	55	55	200	75	1.33	15	98.14	97.19	99.47	11.80	87.03
38		9.5	10	10	300	100	0.63	10	99.23	98.07	99.28	54.36	93.98
39		12	100	100	300	100	2.03	20	96.70	94.92	99.67	35.45	82.65
40		12	100	100	100	50	0.63	10	88.11	83.09	99.51	17.78	53.07

**REPRODUCIBILITY TESTS N^o 1
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 2
 $[\text{CN}^-] = 133 \text{ ppm}$
 $[\text{SCN}^-] = 100 \text{ ppm}$
 Solution volume = 500

Temperature of the solution ($^{\circ}\text{C}$): 25
 Alkalinity level (pH): 9.5
 $[\text{Cu(I)}] = 10 \text{ ppm}$
 $[\text{AC}] = 10 \text{ g/L}$
 Adsorbent mass = 5 g

[PMs] and [BMs] in ppb	Time (min)		30	60	90	120
	Feed					
	Pt(II)	860	102.56	42.59	27.90	19.11
	Pd(II)	1000	149.28	70.03	48.43	34.12
	Au(I)	170	3.98	2.25	2.10	0.30
	Cu(I)	10000	9035.248	8880.073	8295.245	7773.384
	Ni(II)	10000	2777.992	1704.592	1318.486	1026.806
% Extraction	Pt(II)	0.00	88.07	95.05	96.76	97.78
	Pd(II)	0.00	85.07	93.00	95.16	96.59
	Au(I)	0.00	97.66	98.68	98.76	99.82
	Cu(I)	0.00	9.65	11.20	17.05	22.27
	Ni(II)	0.00	72.22	82.95	86.82	89.73

**REPRODUCIBILITY TESTS N^o 2
OPERATING CONDITIONS:**

Rotational rate (rpm): 105
 Extraction time (hour): 2
 $[\text{CN}^-] = 133 \text{ ppm}$
 $[\text{SCN}^-] = 100 \text{ ppm}$
 Solution volume = 500

Temperature of the solution ($^{\circ}\text{C}$): 25
 Alkalinity level (pH): 9.5
 $[\text{Cu(I)}] = 10 \text{ ppm}$
 $[\text{AC}] = 10 \text{ g/L}$
 Adsorbent mass = 5 g

[PMs] and [BMs] in ppb	Time (min)		30	60	90	120
	Feed					
	Pt(II)	860	115.30	42.74	24.02	18.38
	Pd(II)	1000	164.20	68.50	40.22	31.70
	Au(I)	170	4.96	1.74	0.31	0.28
	Cu(I)	10000	6307.03	7163.89	7103.03	7068.48
	Ni(II)	10000	2535.51	1439.38	1040.63	807.52
% Extraction	Pt(II)	0.00	86.59	95.03	97.21	97.86
	Pd(II)	0.00	83.58	93.15	95.98	96.83
	Au(I)	0.00	97.08	98.98	99.82	99.84
	Cu(I)	0.00	36.93	28.36	28.97	29.32
	Ni(II)	0.00	74.64	85.61	89.59	91.92

**REPRODUCIBILITY TESTS N^o 3
OPERATING CONDITIONS:**

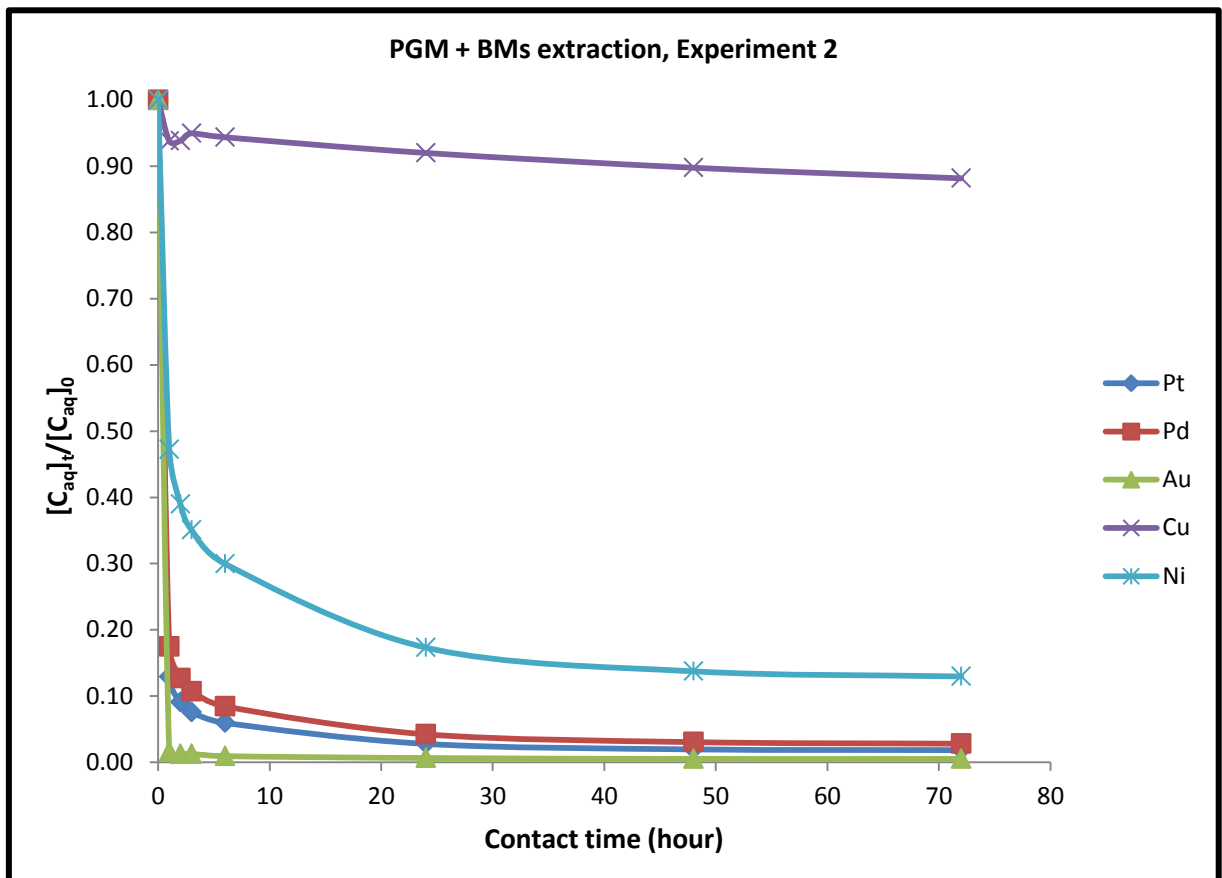
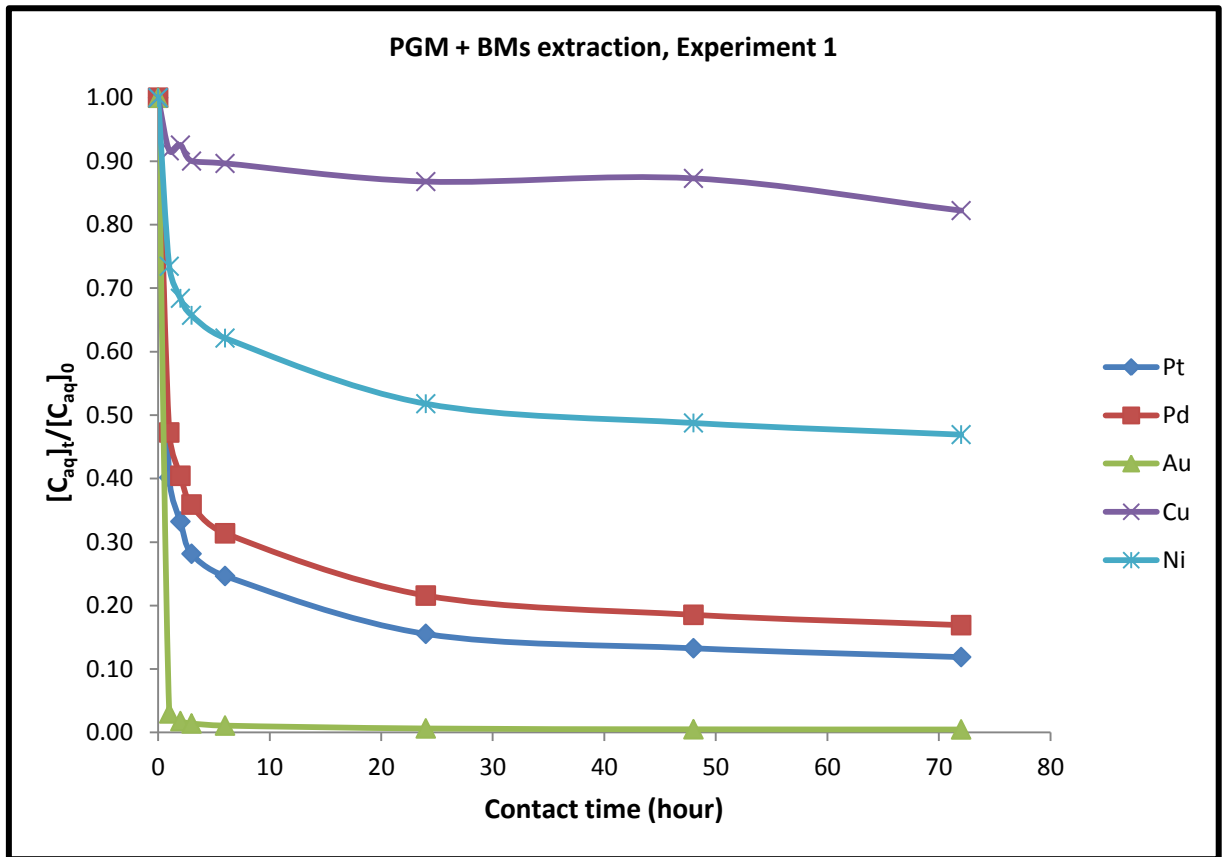
Rotational rate (rpm): 105
Extraction time (hour): 2
[CN⁻] = 133 ppm
[SCN⁻] = 100 ppm
Solution volume = 500

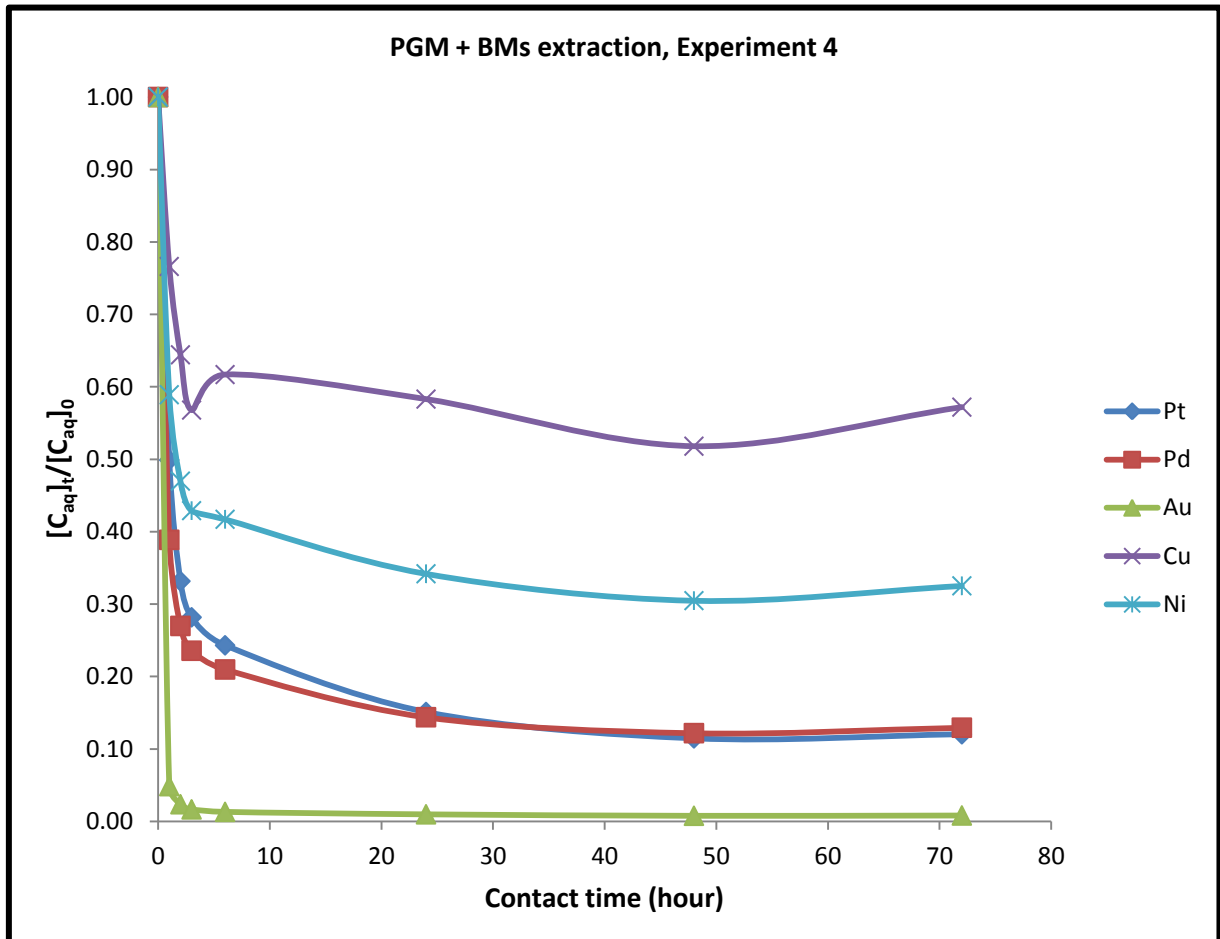
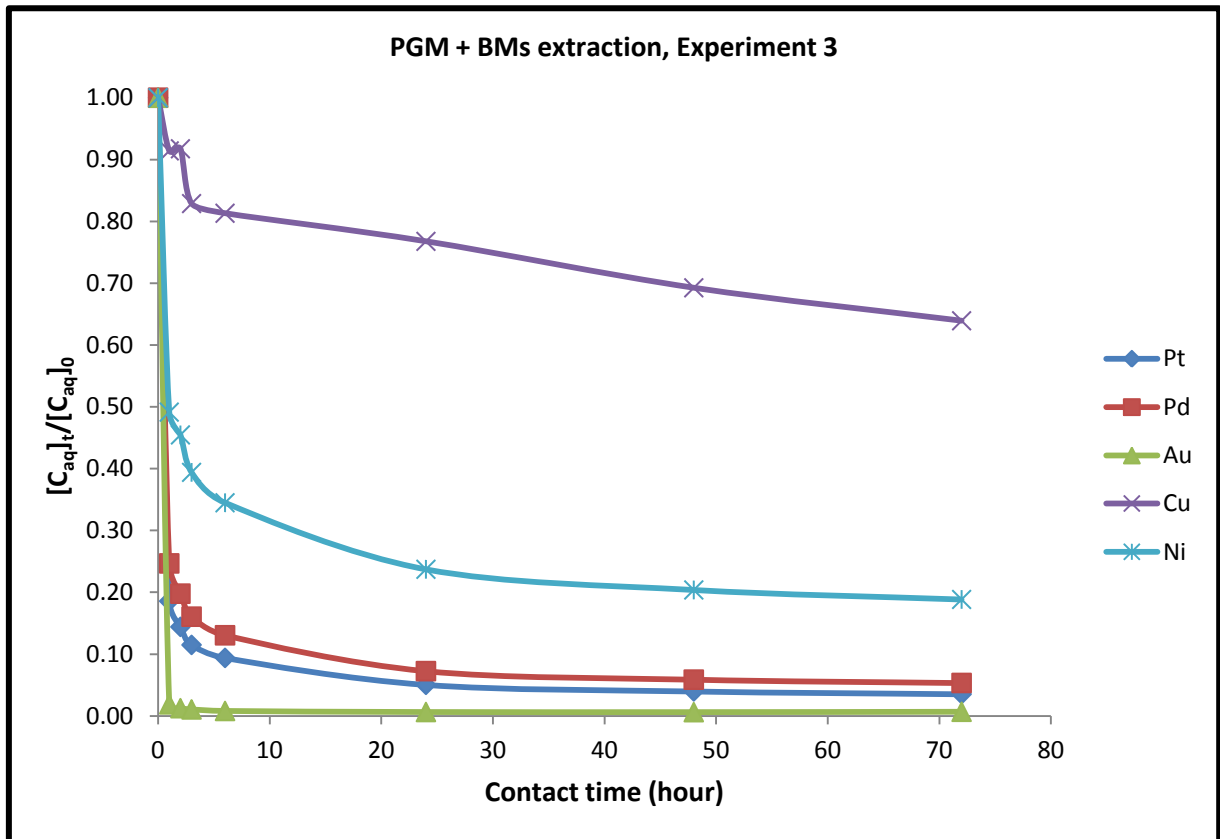
Temperature of the solution (°C): 25
Alkalinity level (pH): 9.5
[Cu(I)] = 10 ppm
[AC] = 10 g/L
Adsorbent mass = 5 g

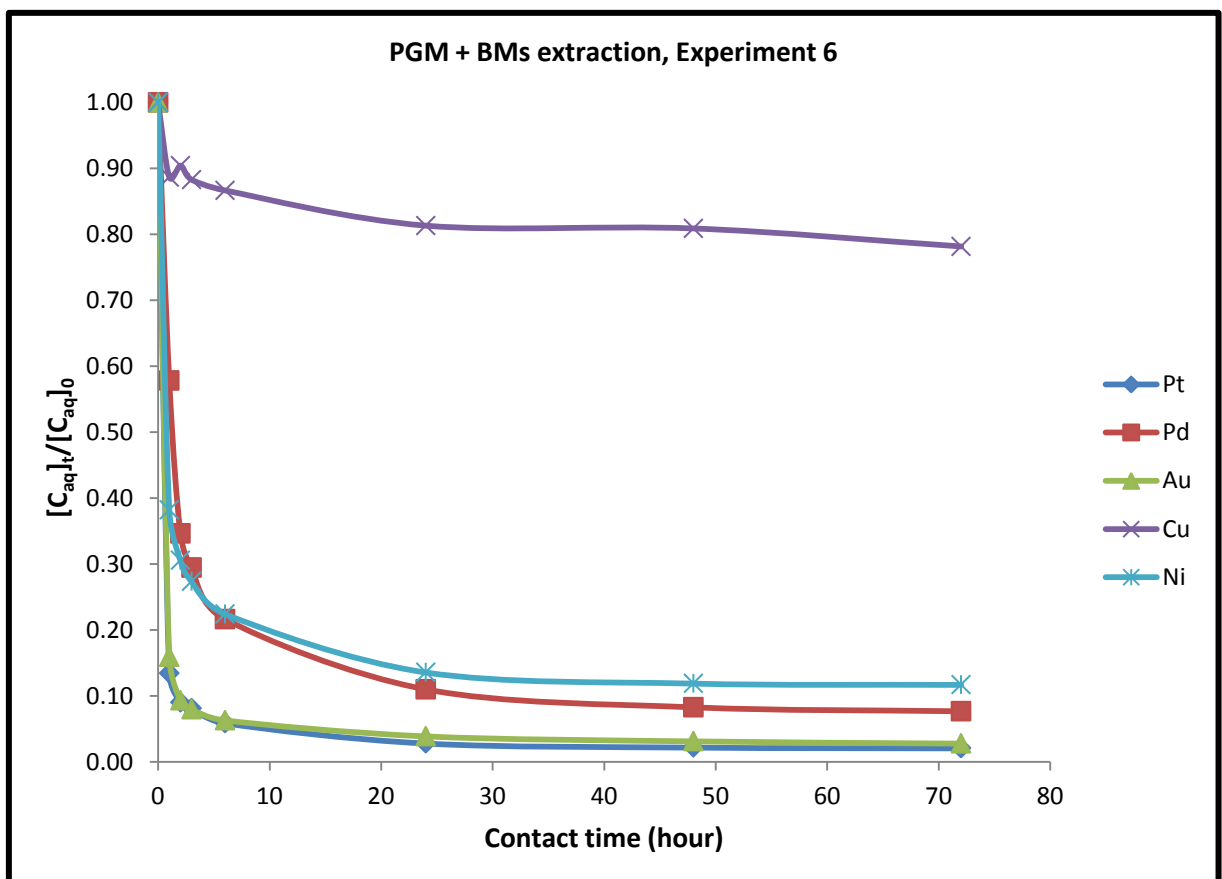
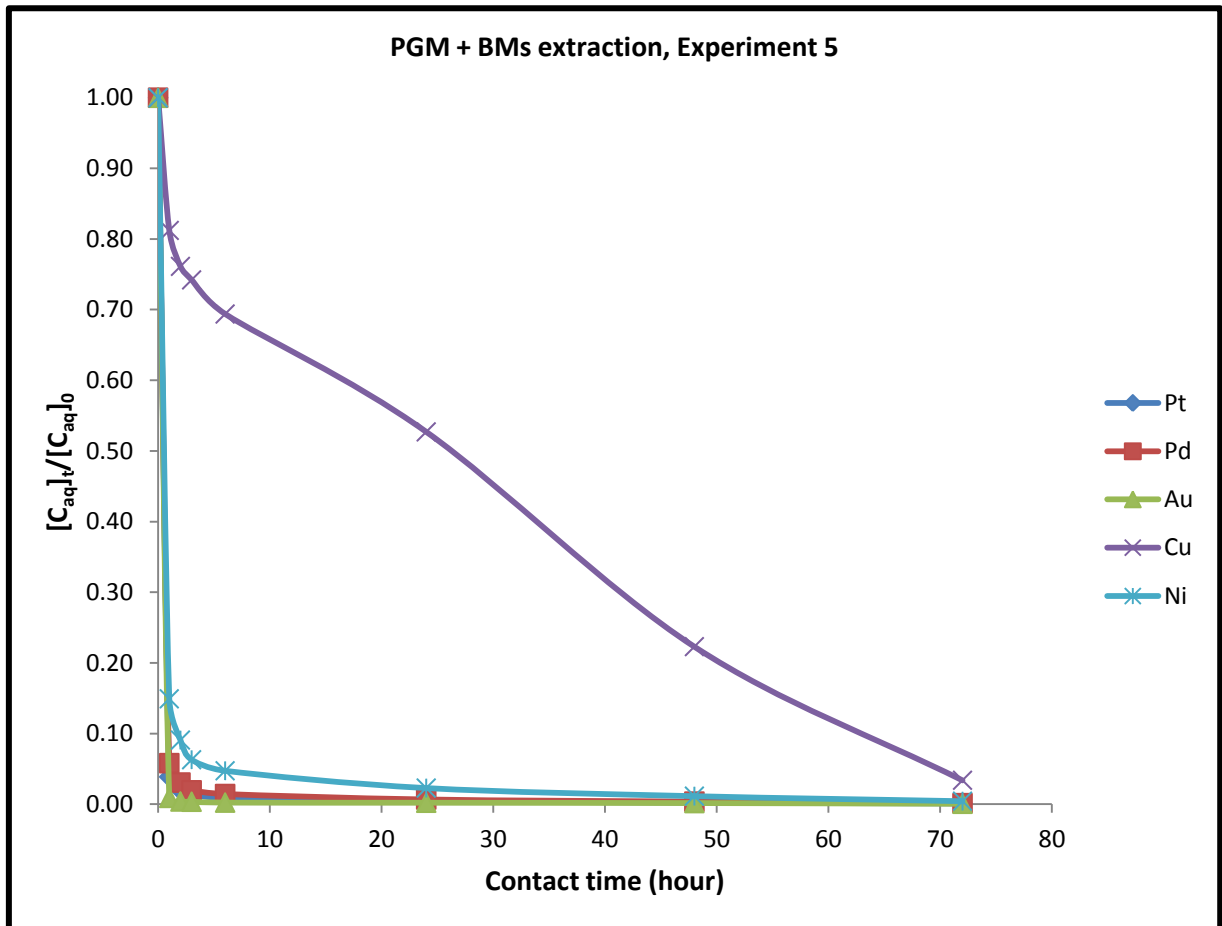
[PMs] and [BMs] in ppb	Time (min)		30	60	90	120
	Feed					
	Pt(II)	860	105.69	40.80	25.06	18.28
	Pd(II)	1000	152.84	65.84	42.33	31.50
	Au(I)	170	8.31	1.72	0.98	0.29
	Cu(I)	10000	8083.76	7982.55	7191.71	7099.13
	Ni(II)	10000	2792.27	1583.07	1053.85	811.85
% Extraction	Pt(II)	0.00	87.71	95.26	97.09	97.87
	Pd(II)	0.00	84.72	93.42	95.77	96.85
	Au(I)	0.00	95.11	98.99	99.42	99.83
	Cu(I)	0.00	19.16	20.17	28.08	29.01
	Ni(II)	0.00	72.08	84.17	89.46	91.88

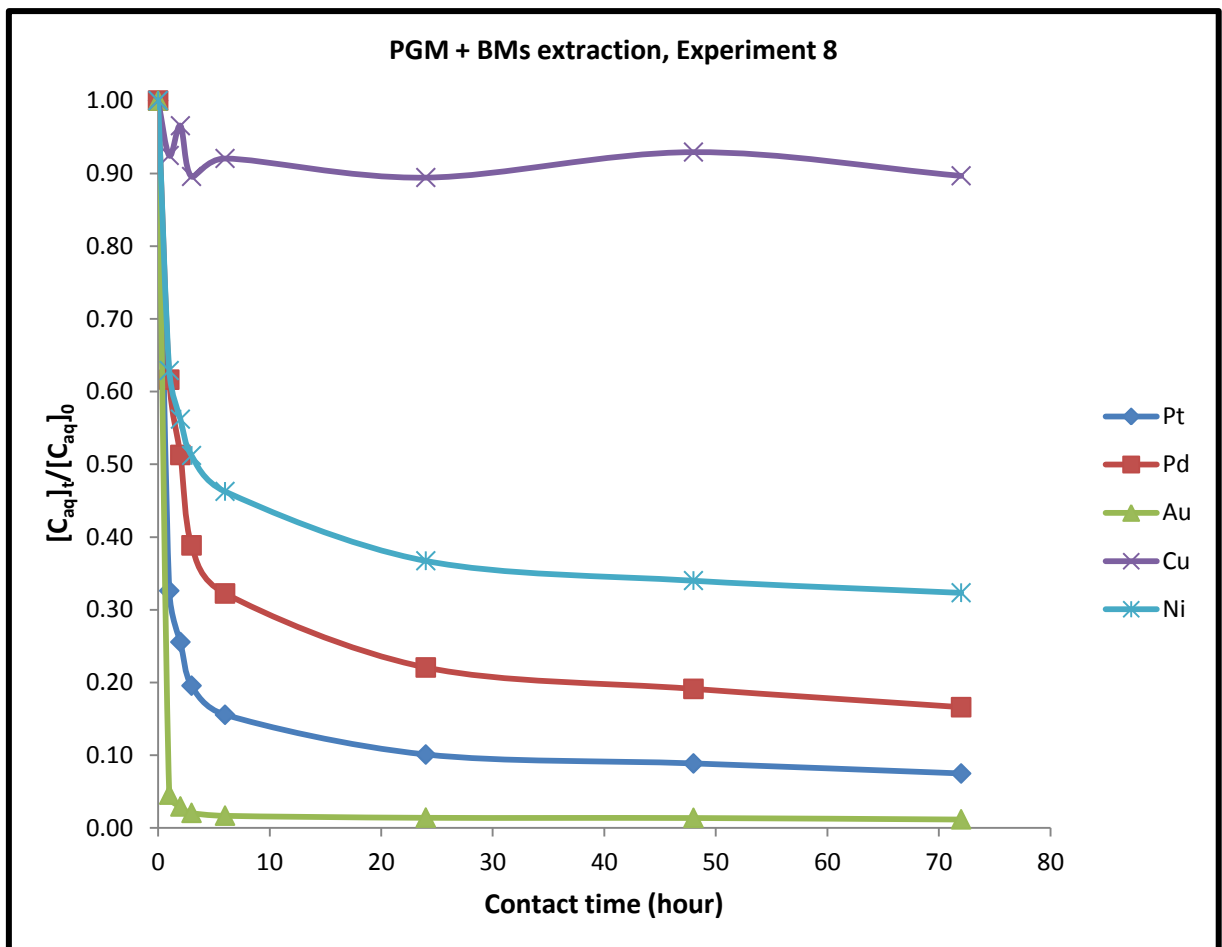
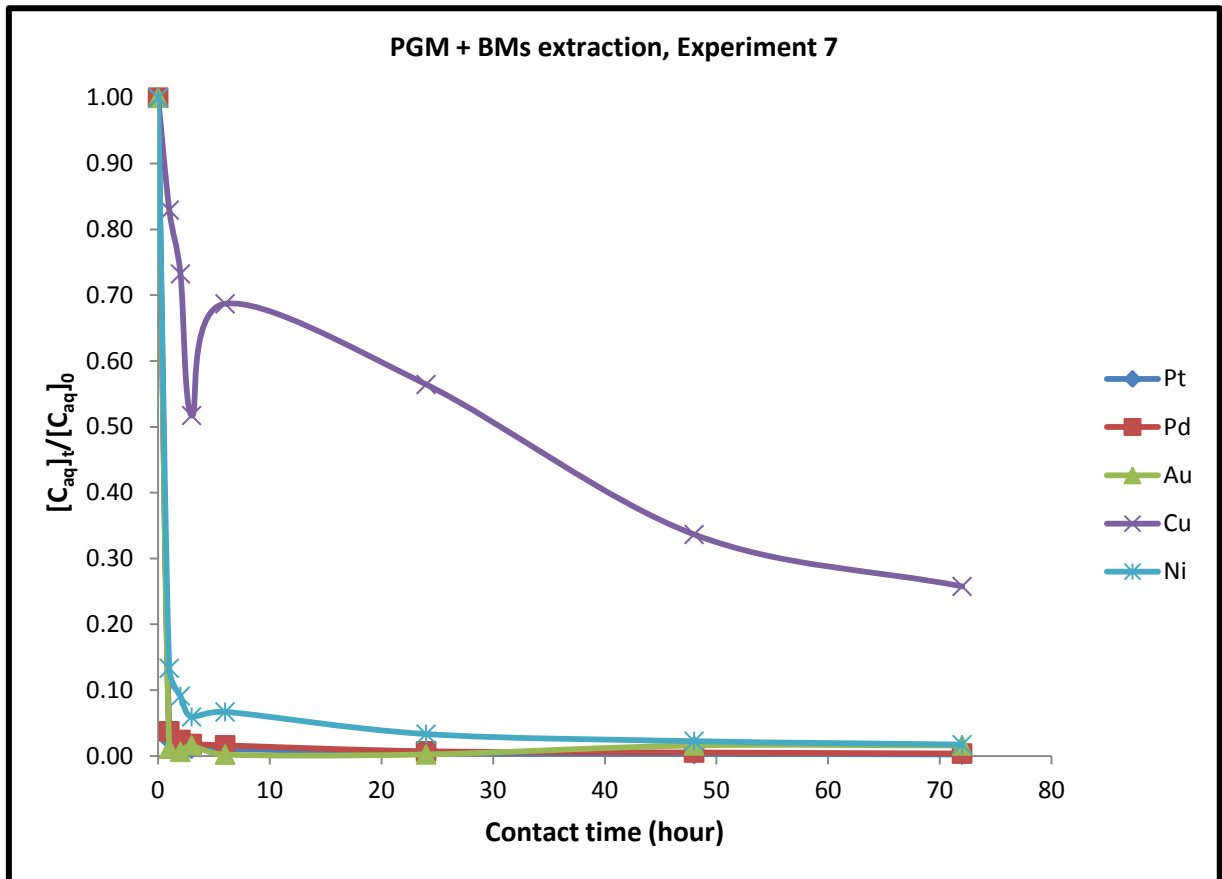
APPENDIX B

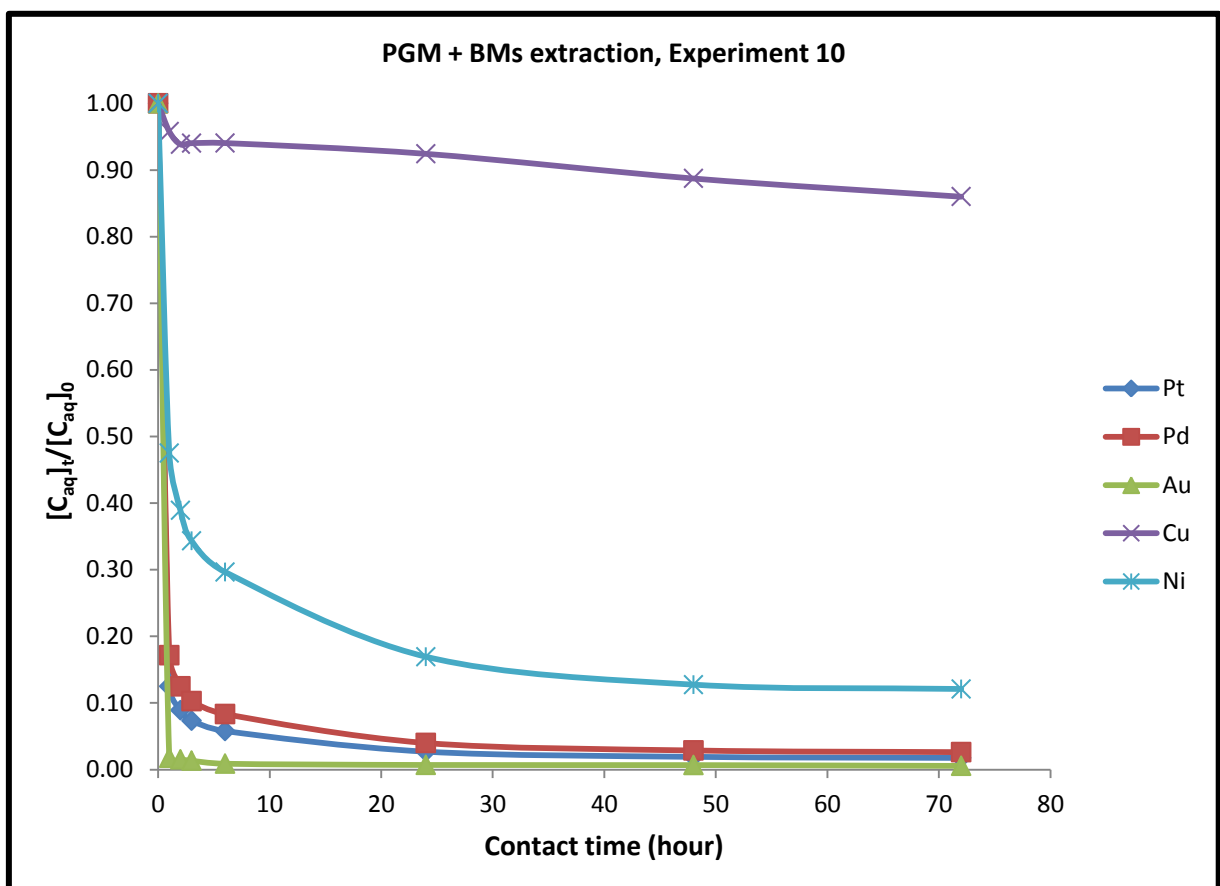
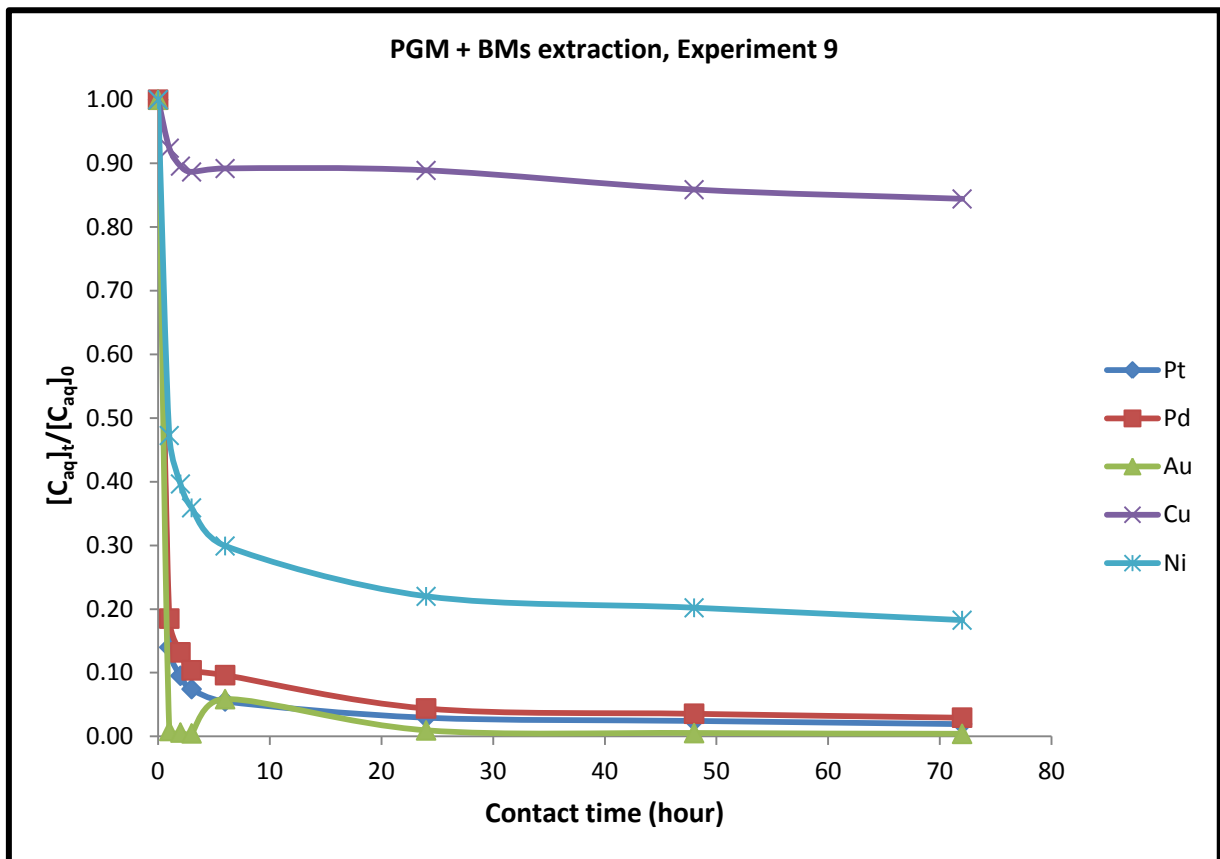
FIGURES

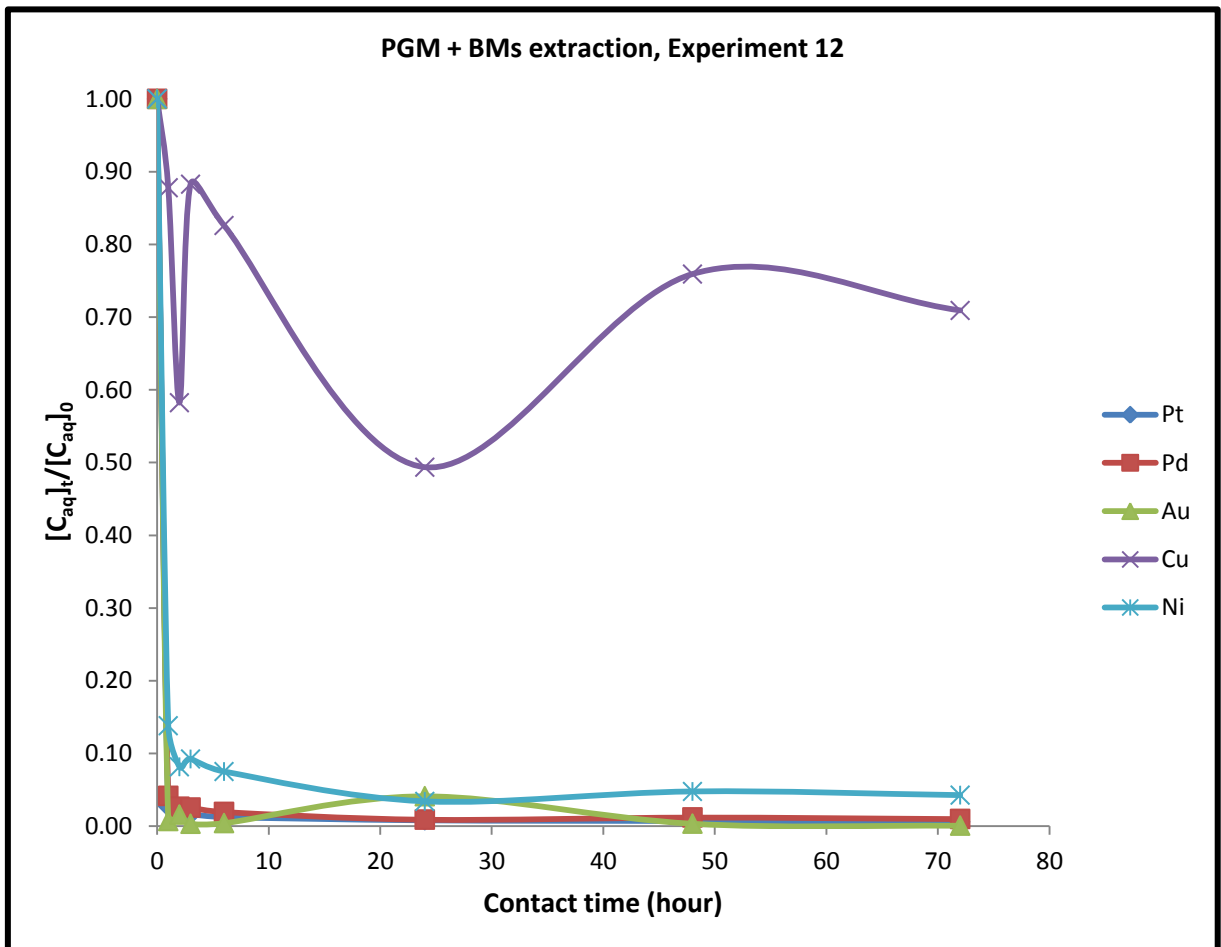
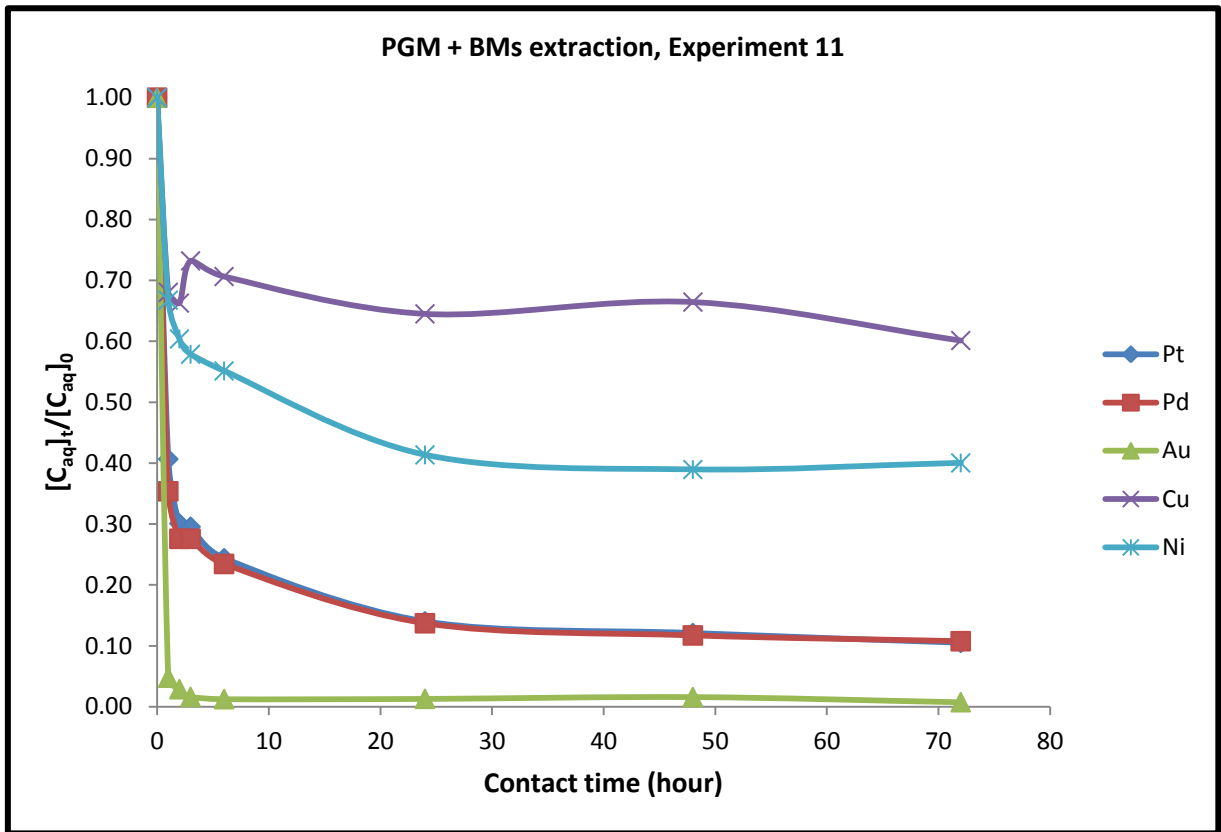


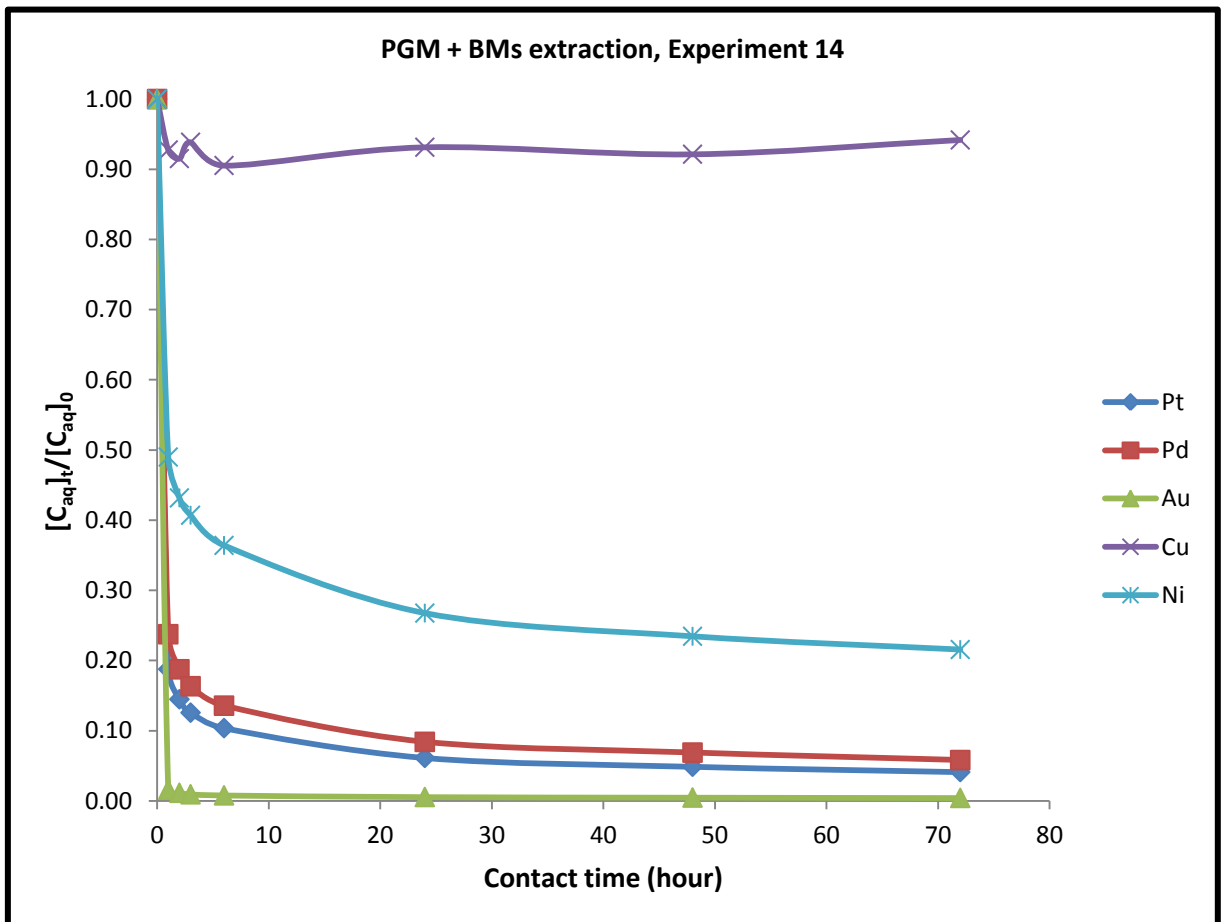
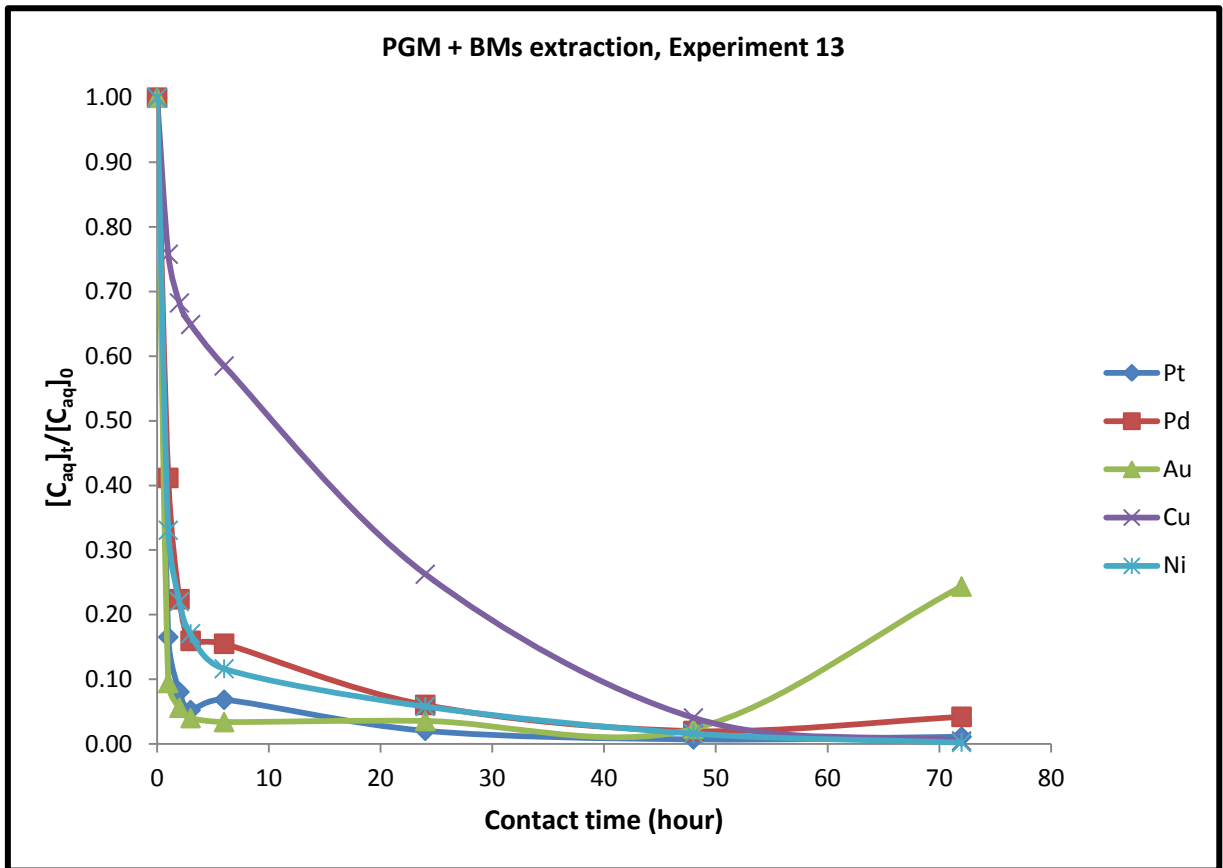


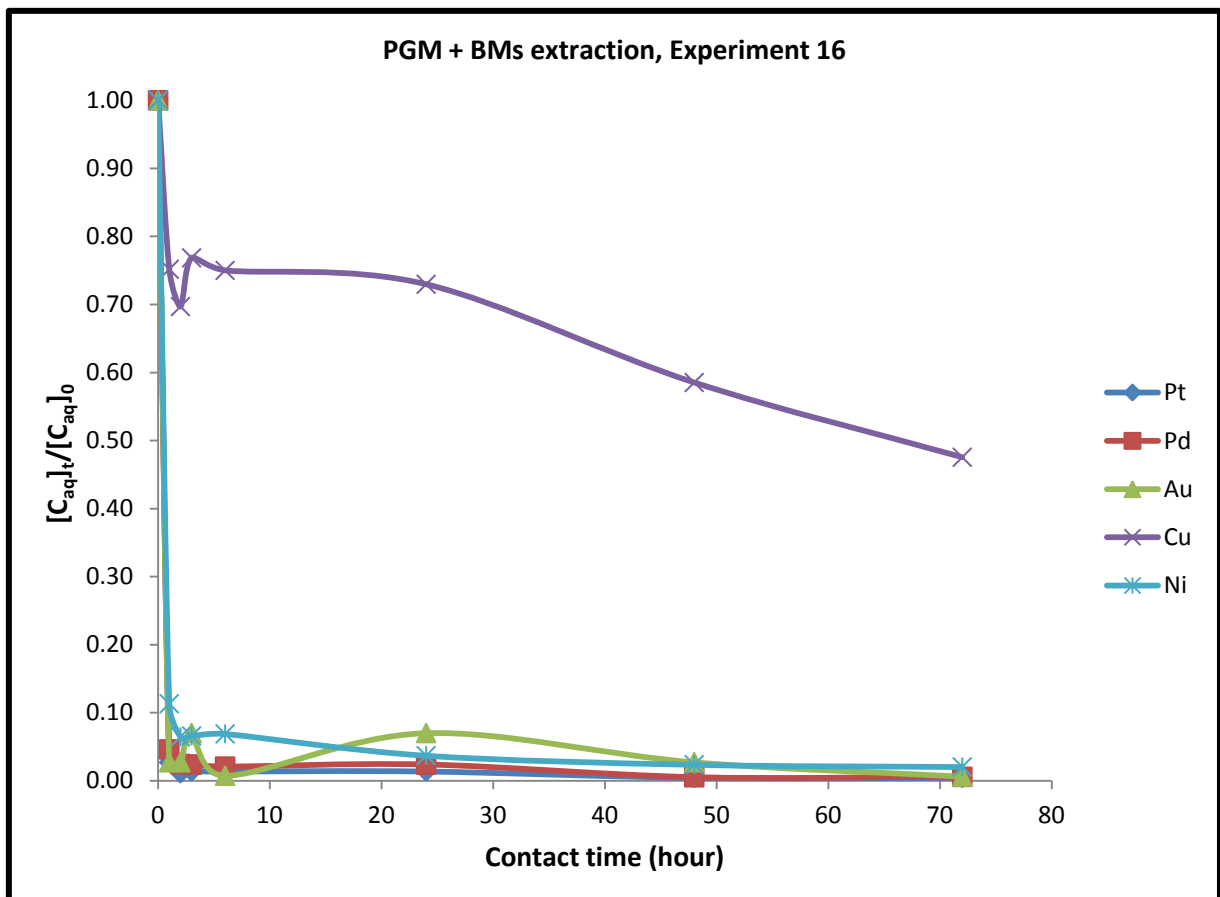
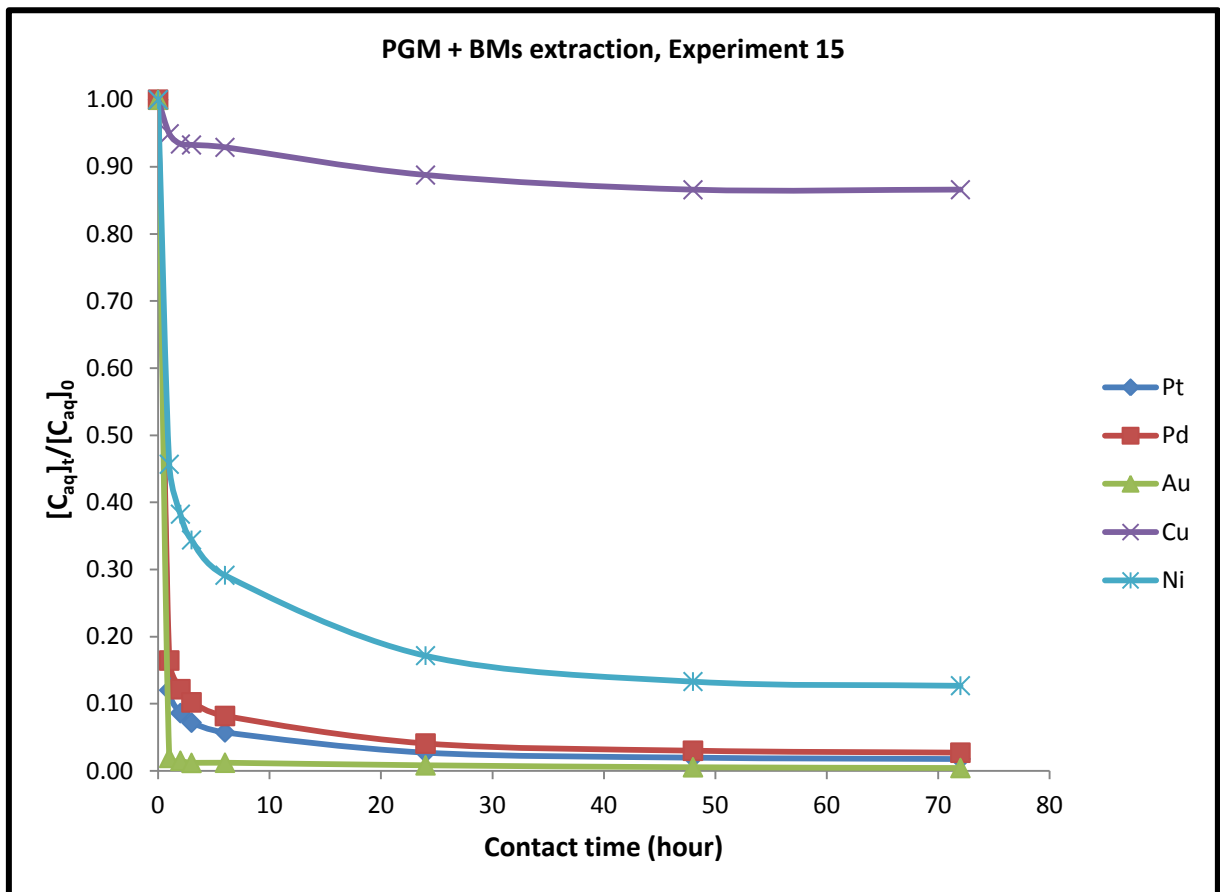


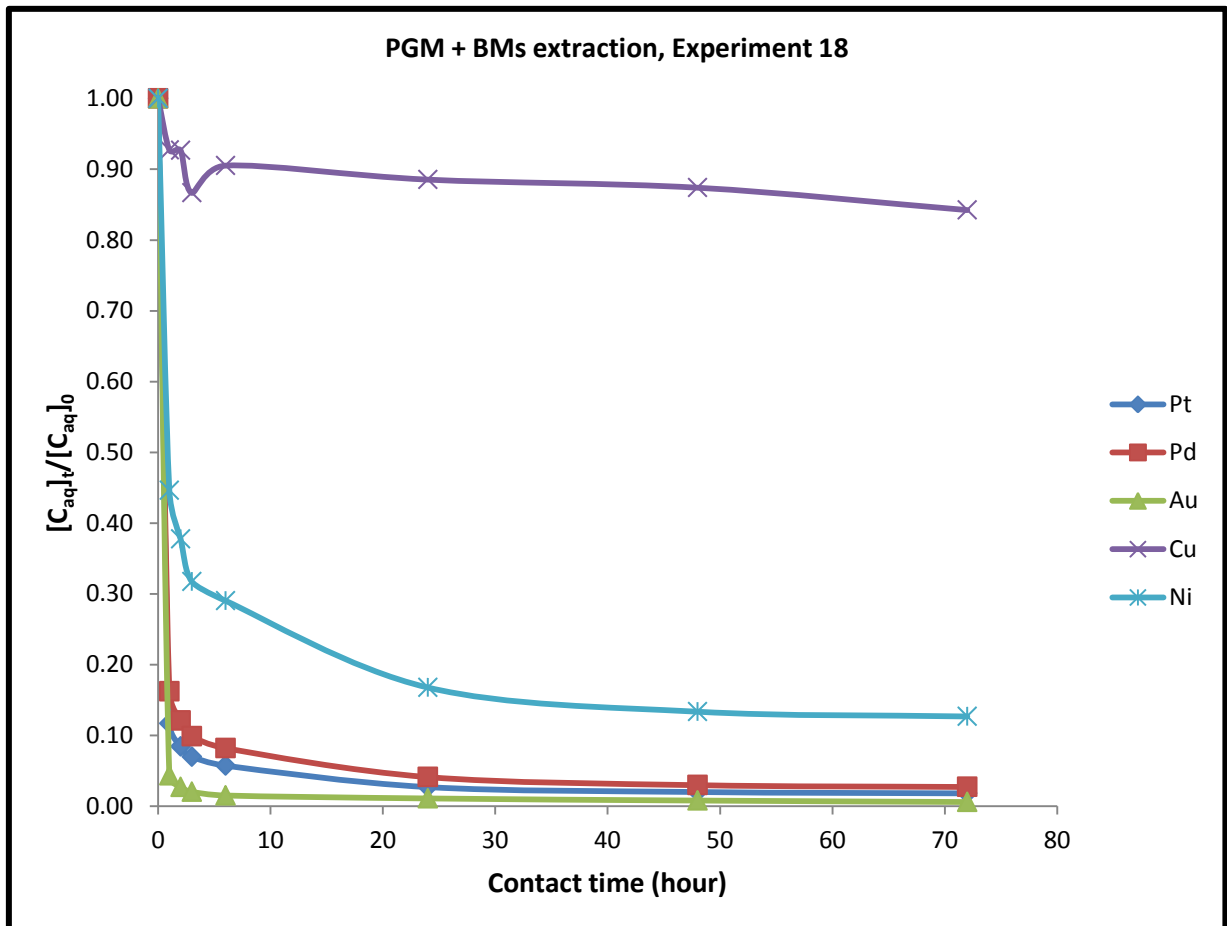
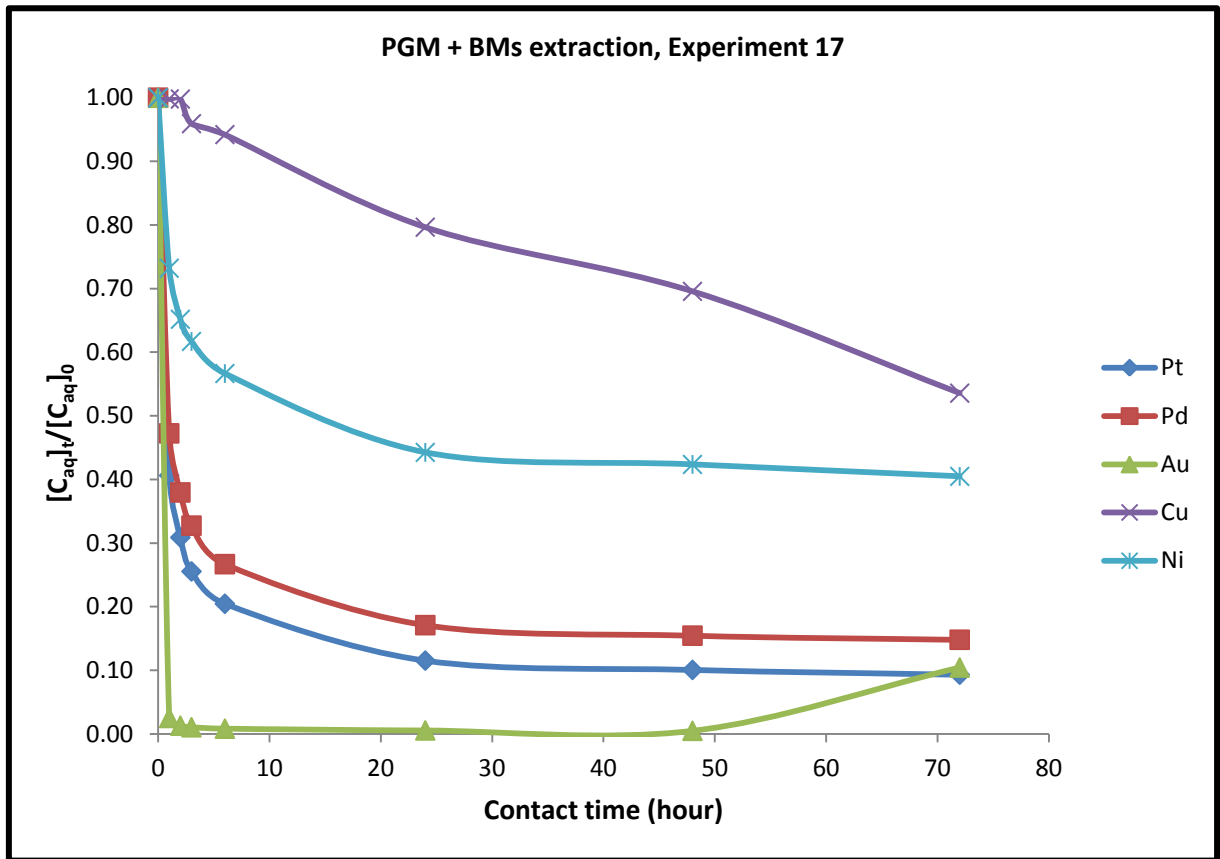


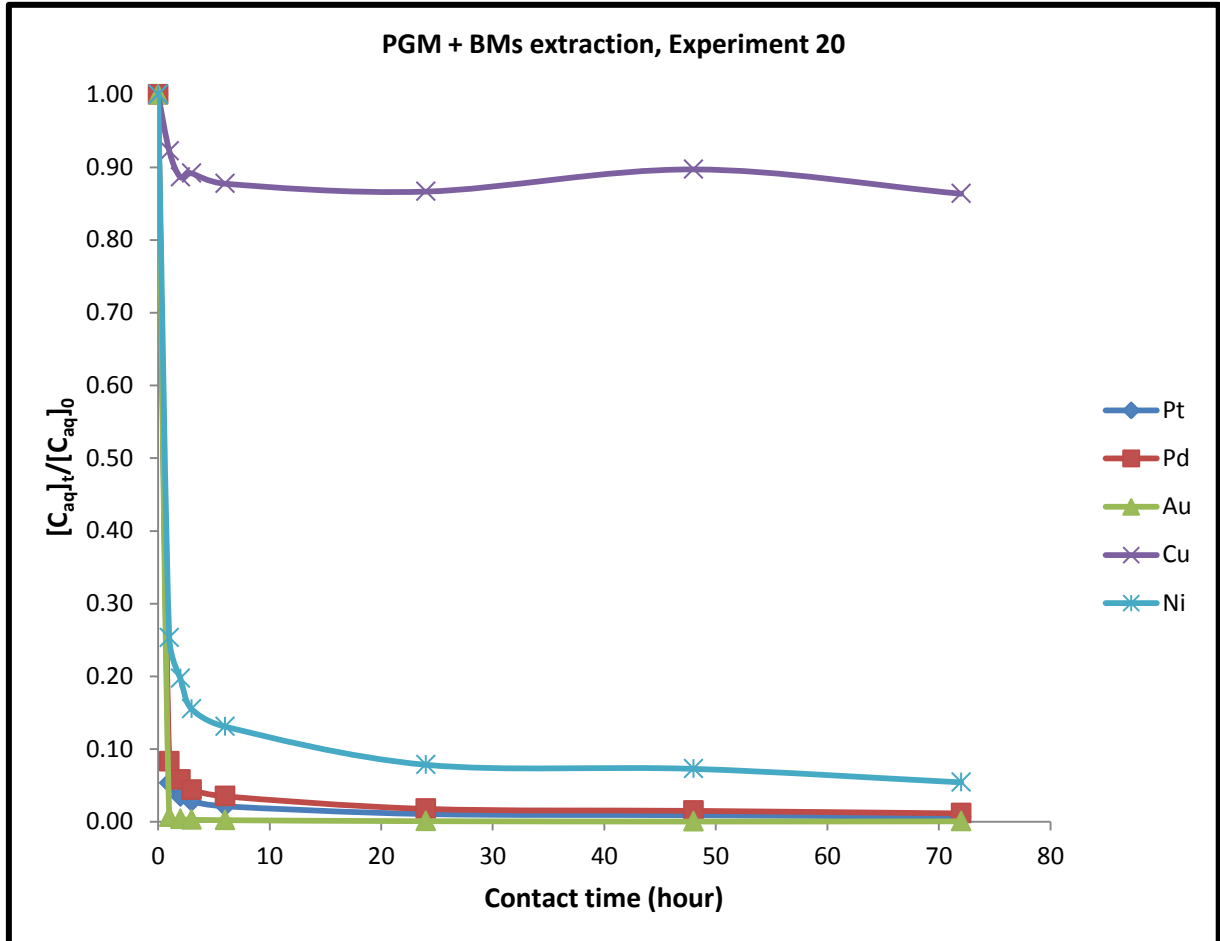
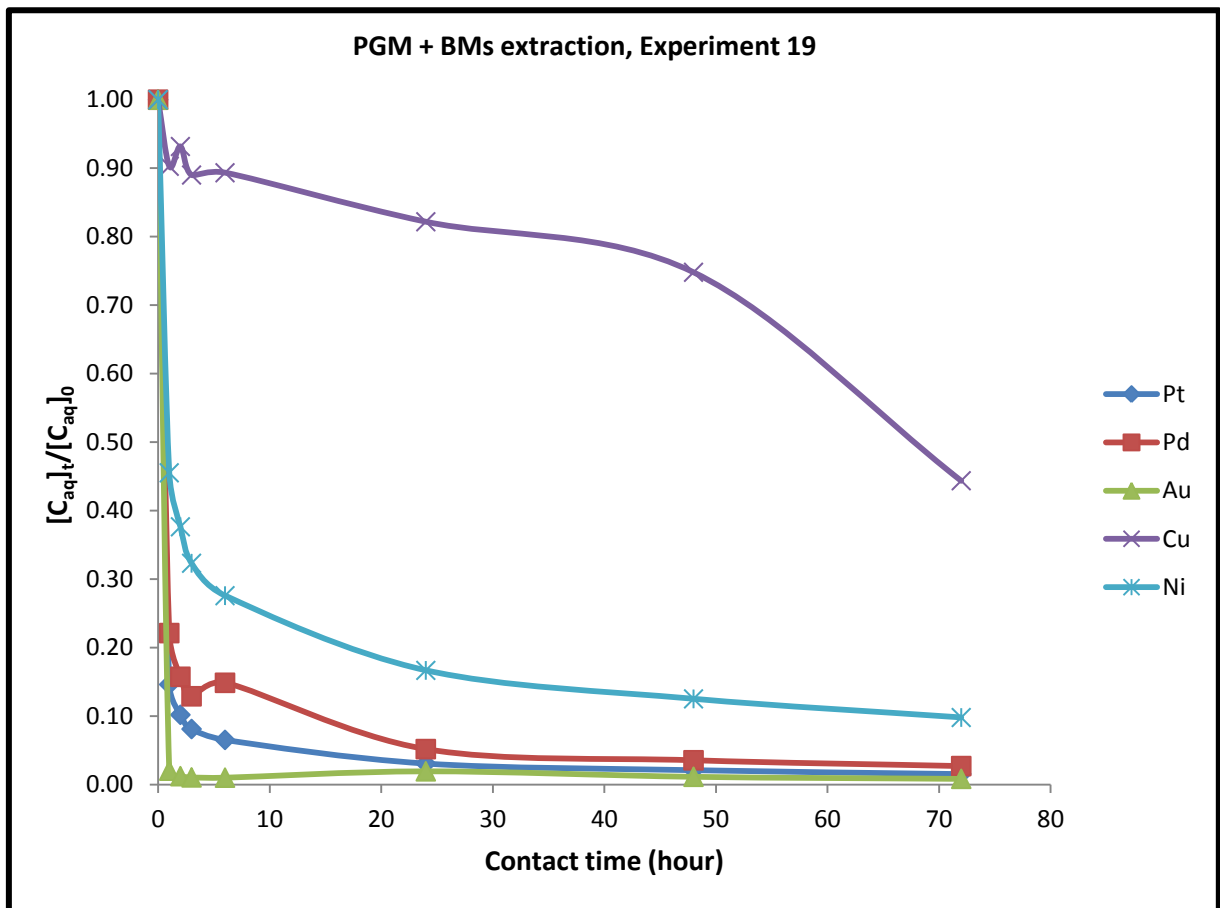


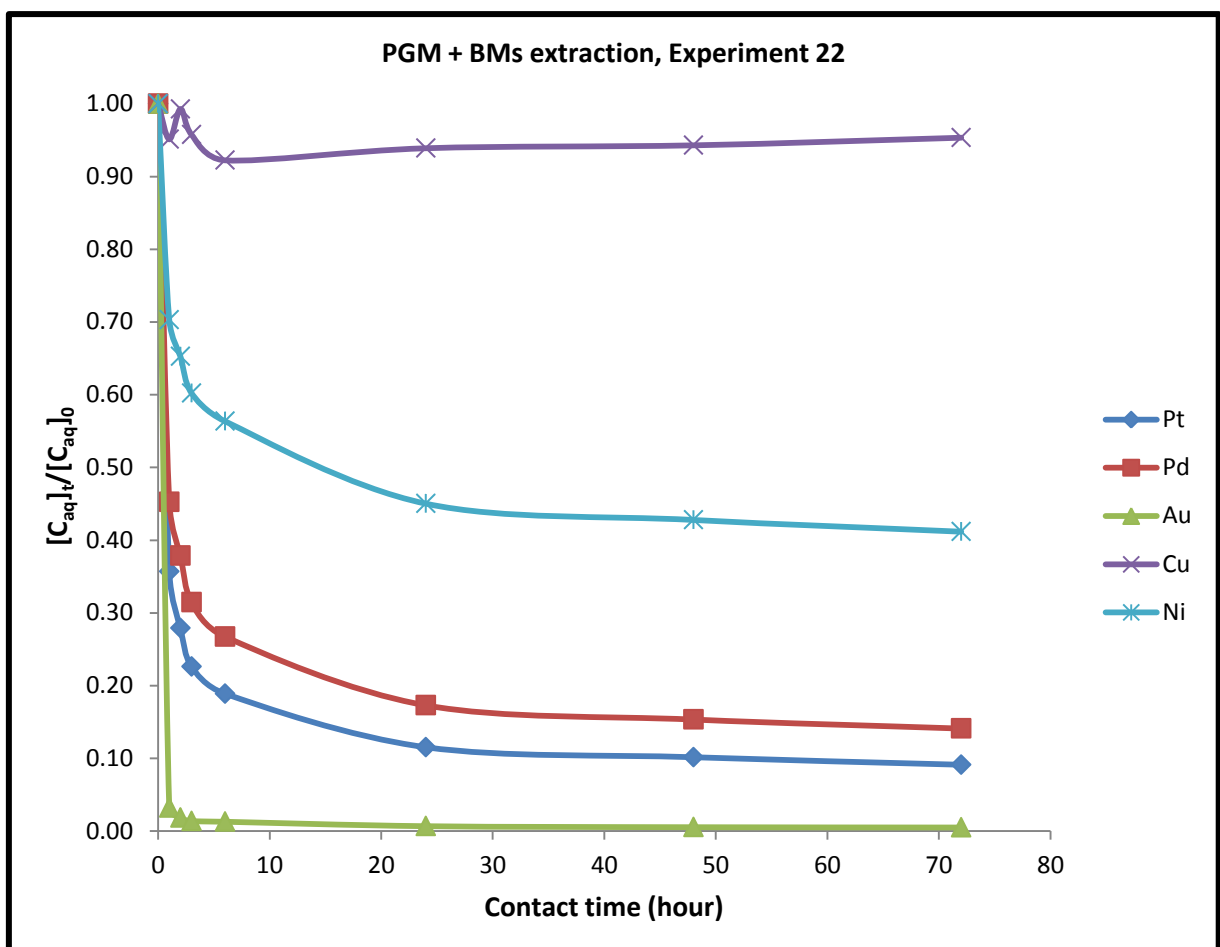
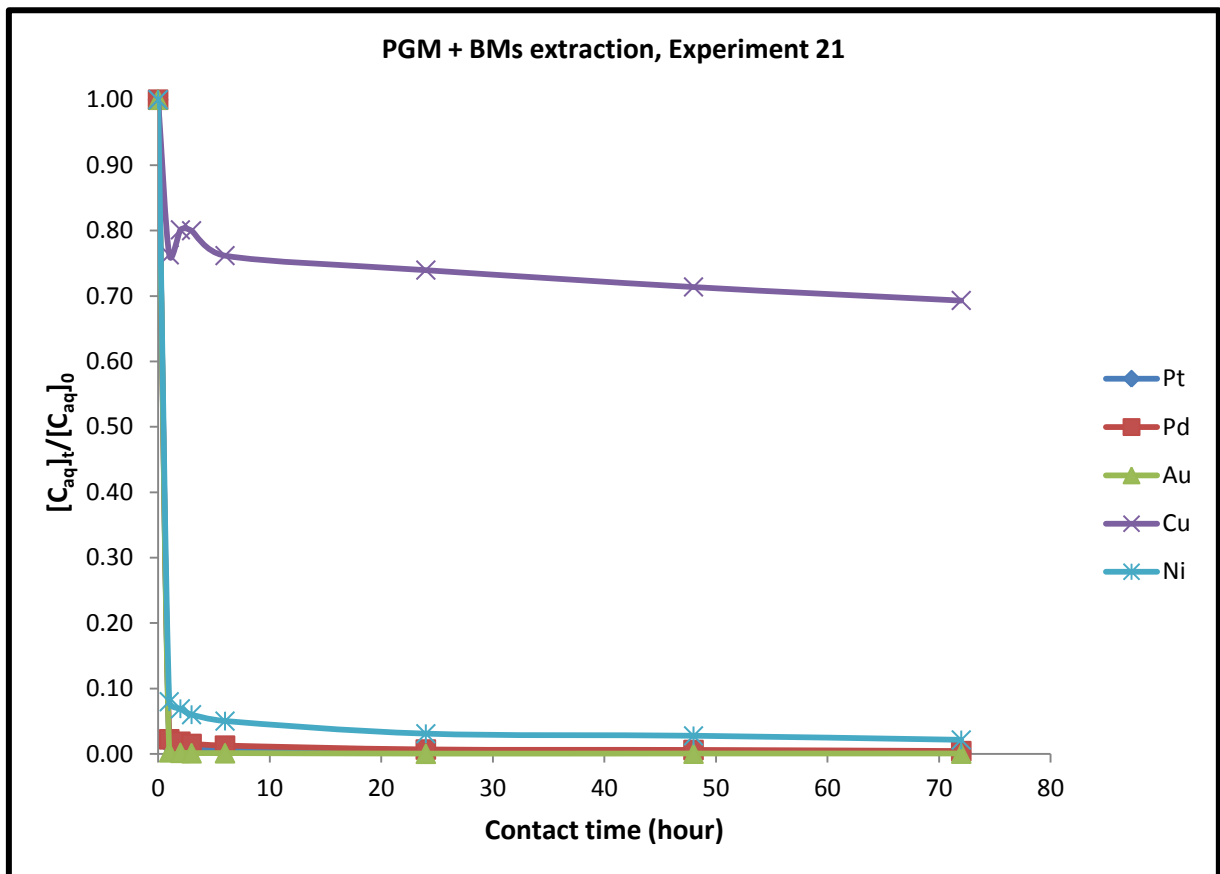


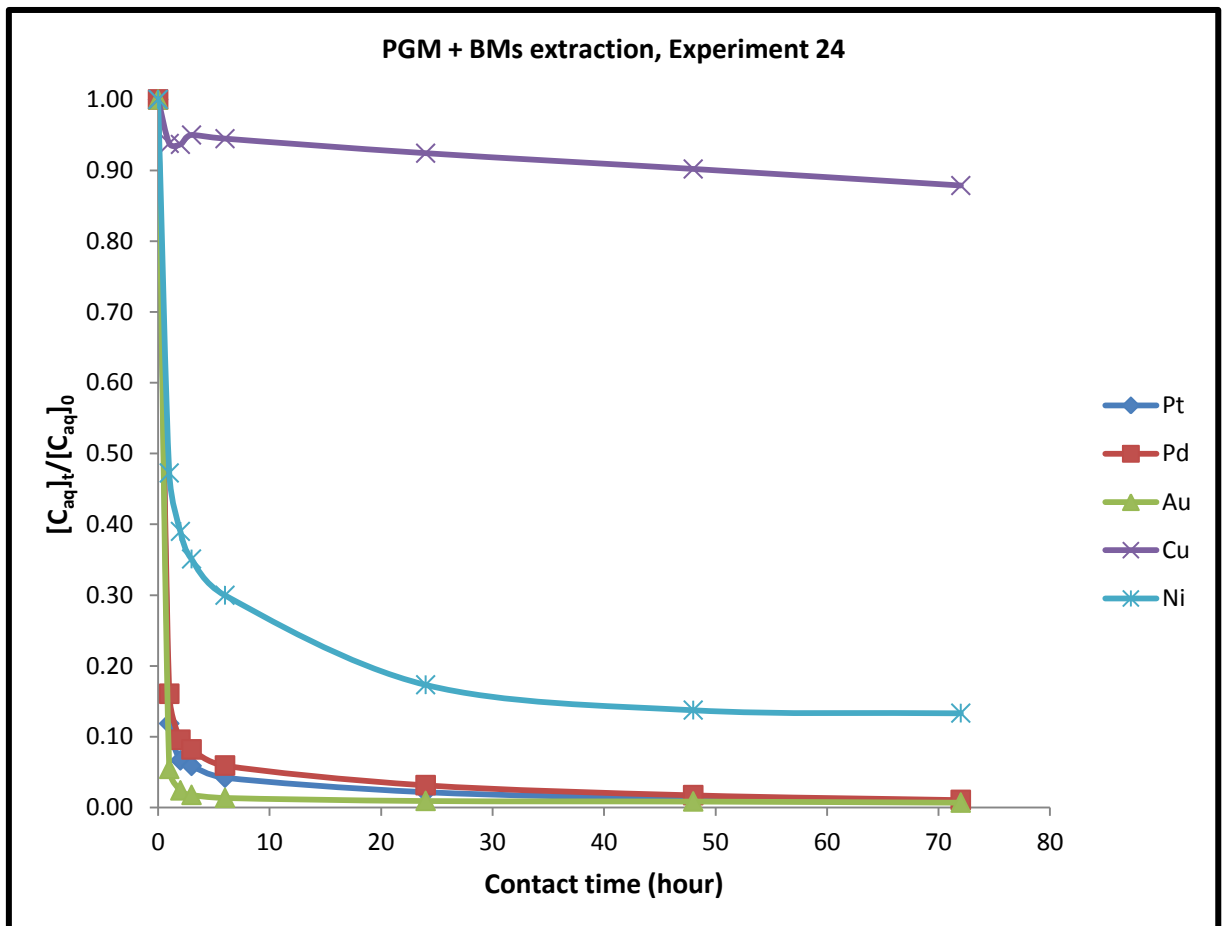
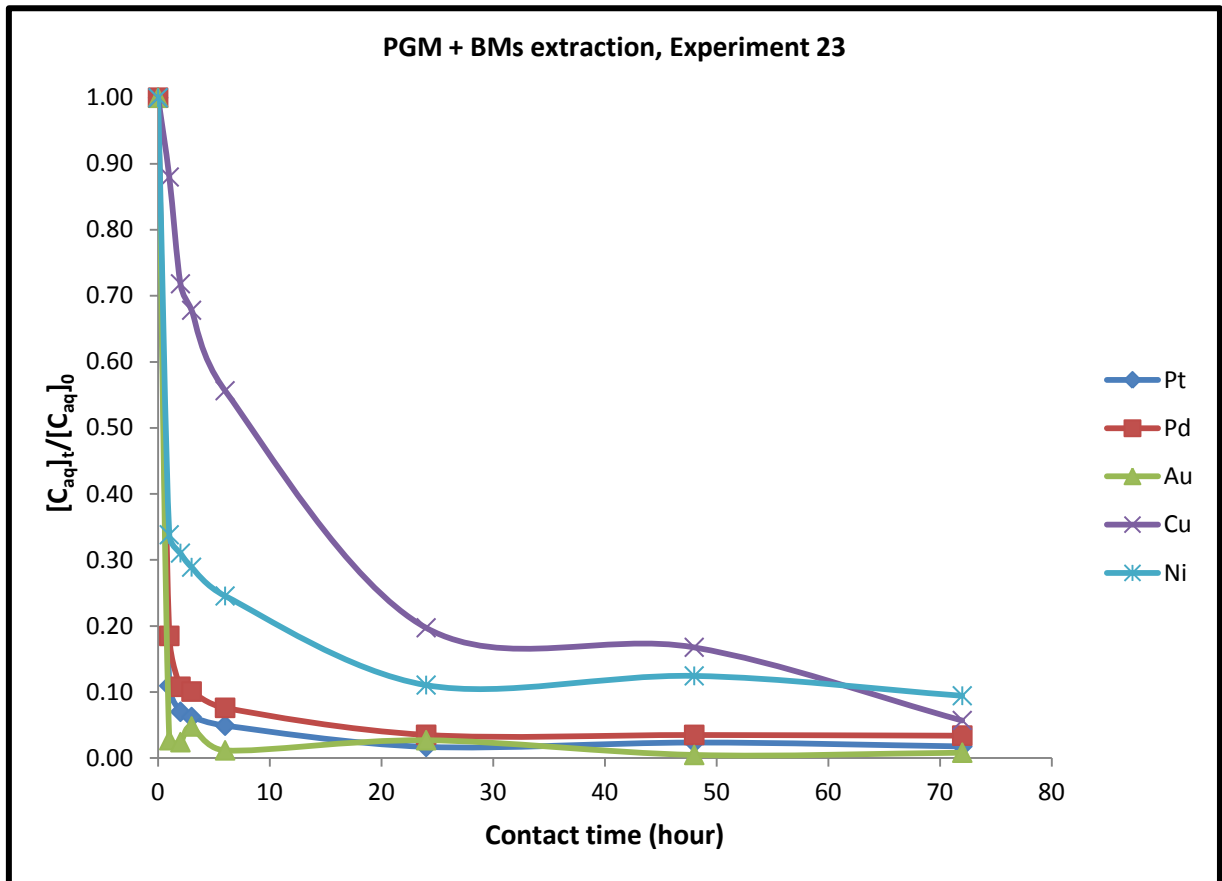


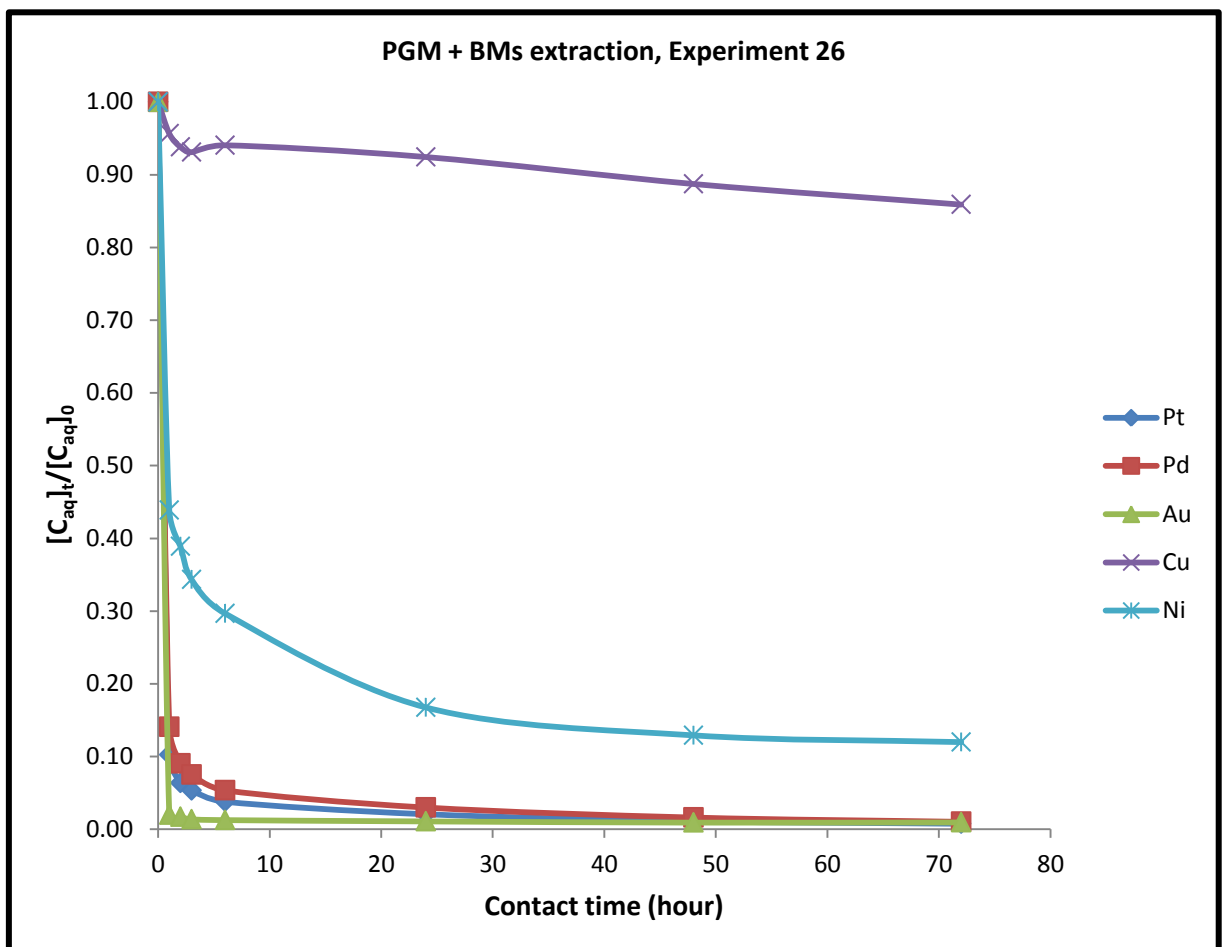
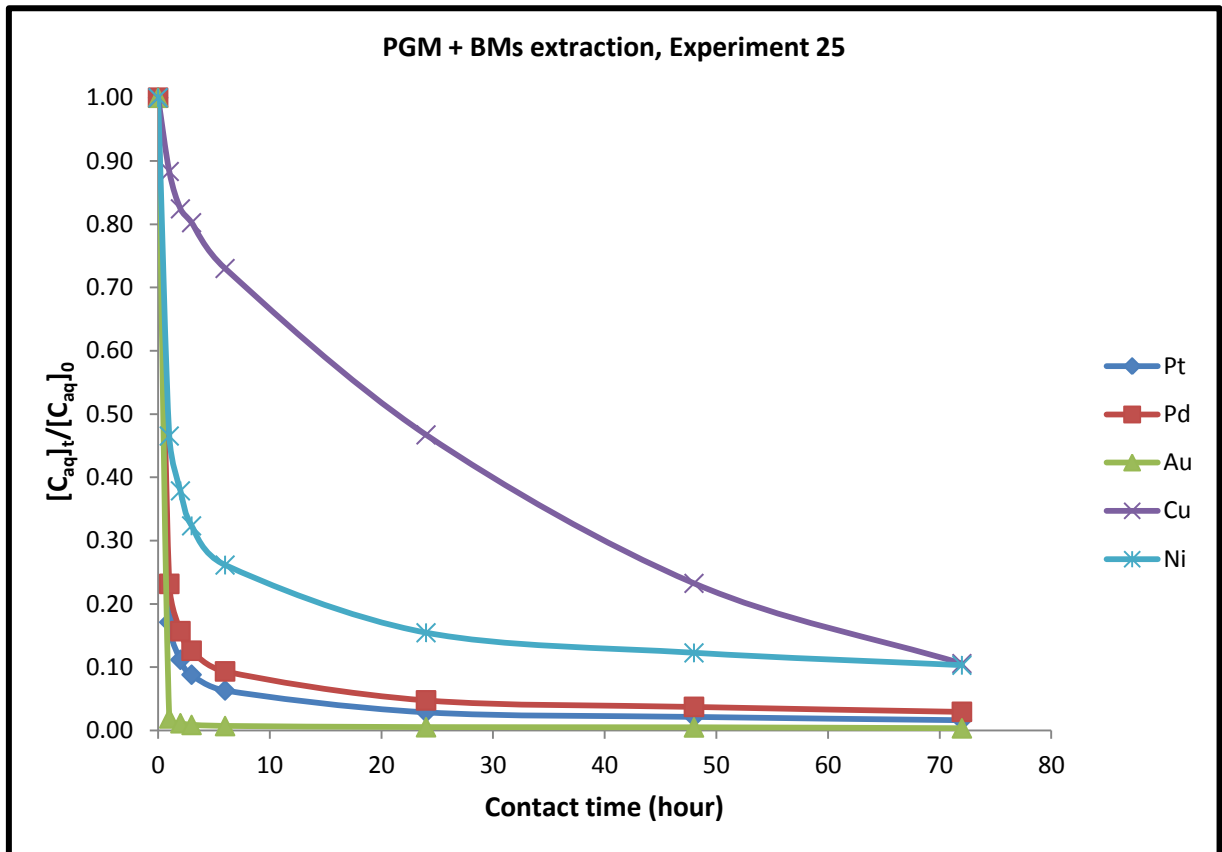


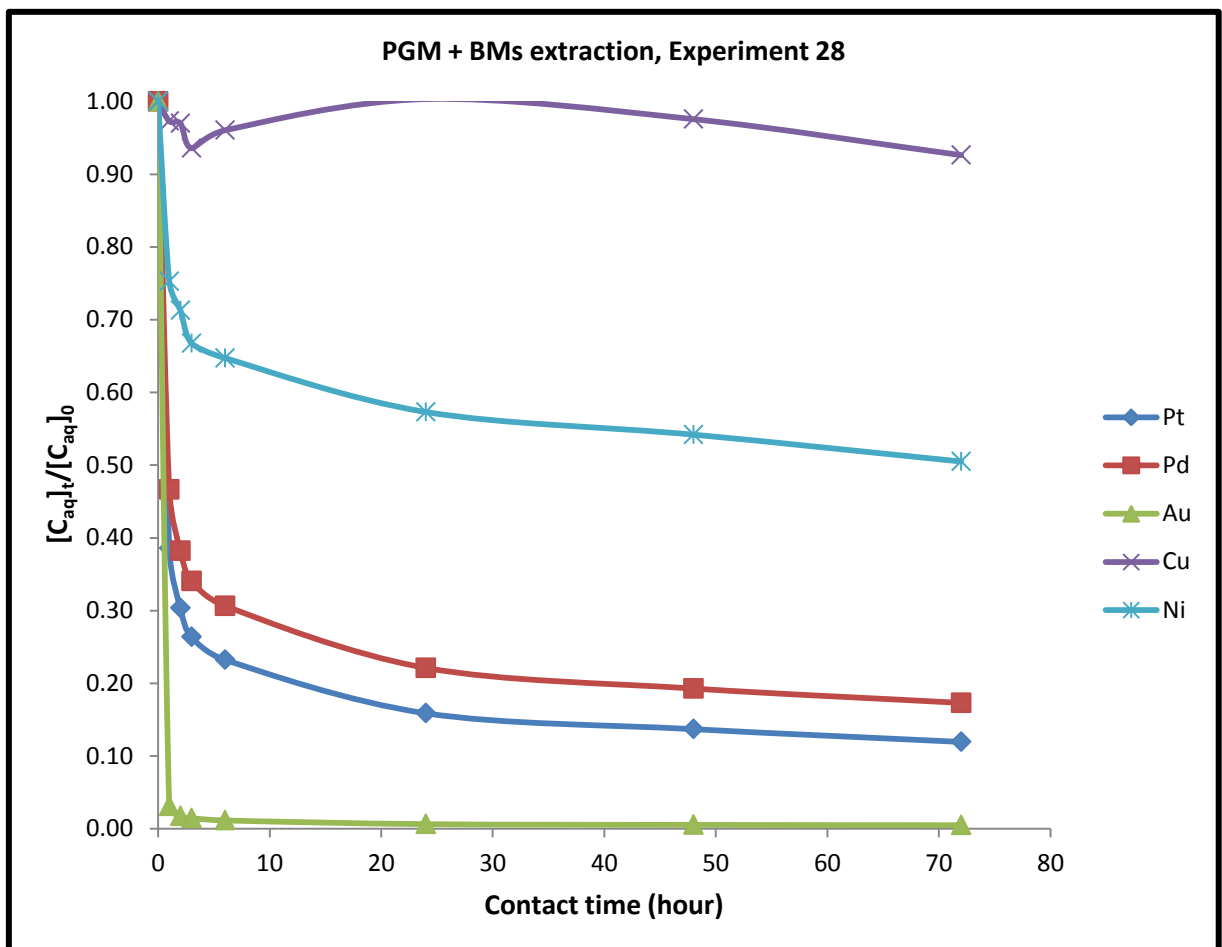
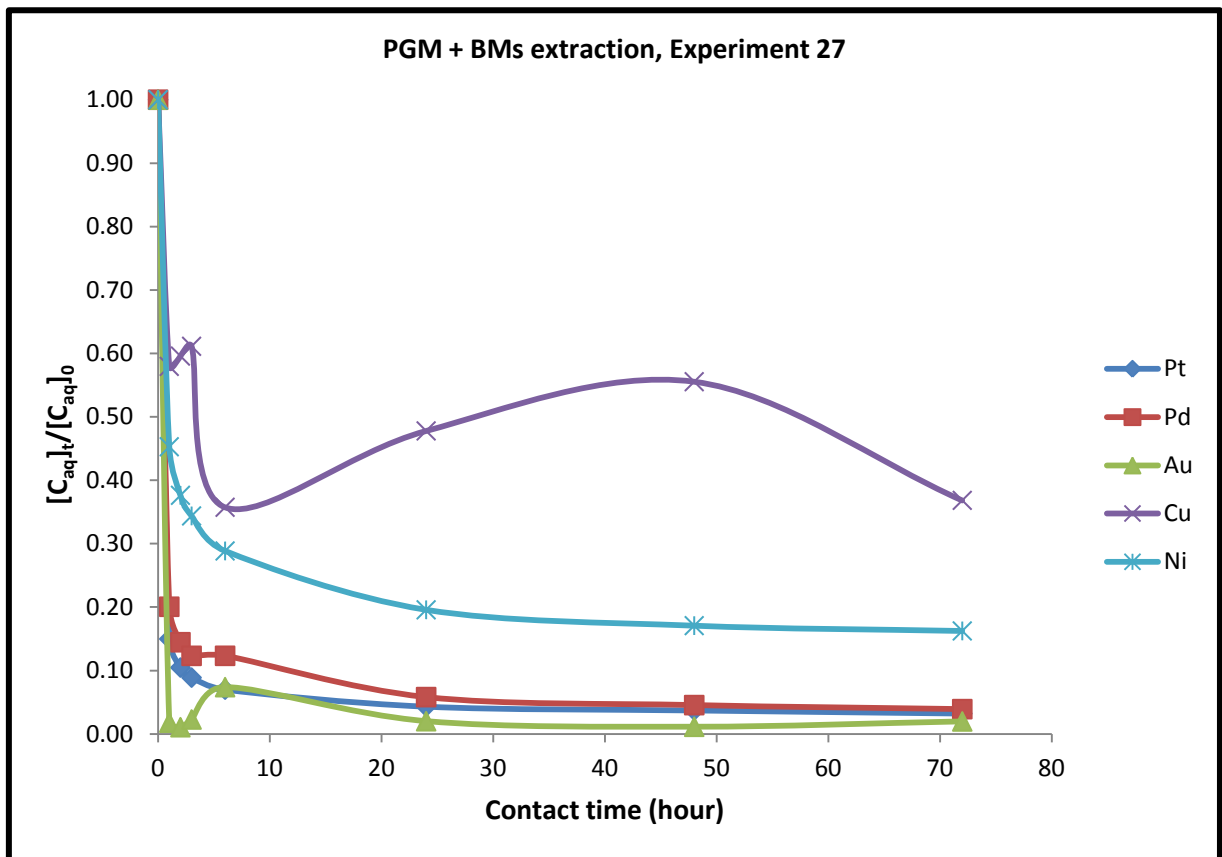


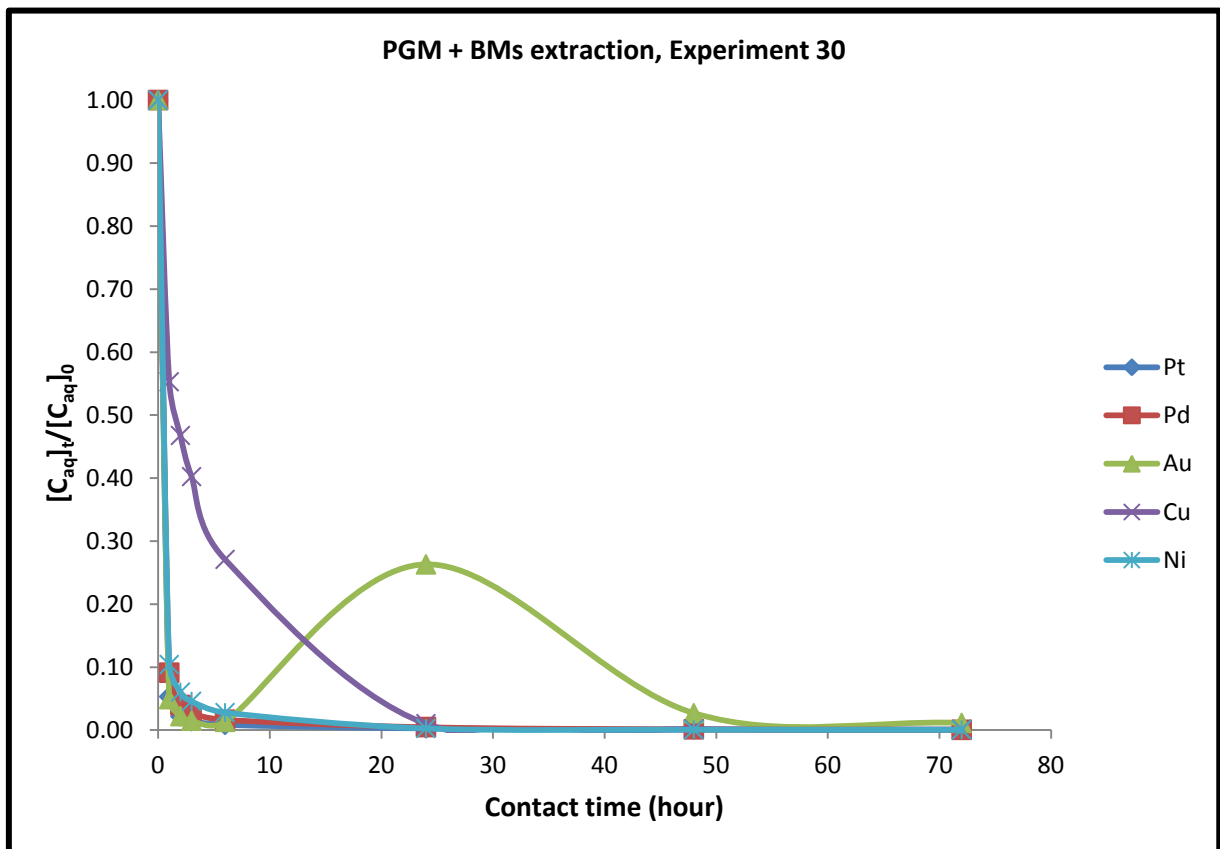
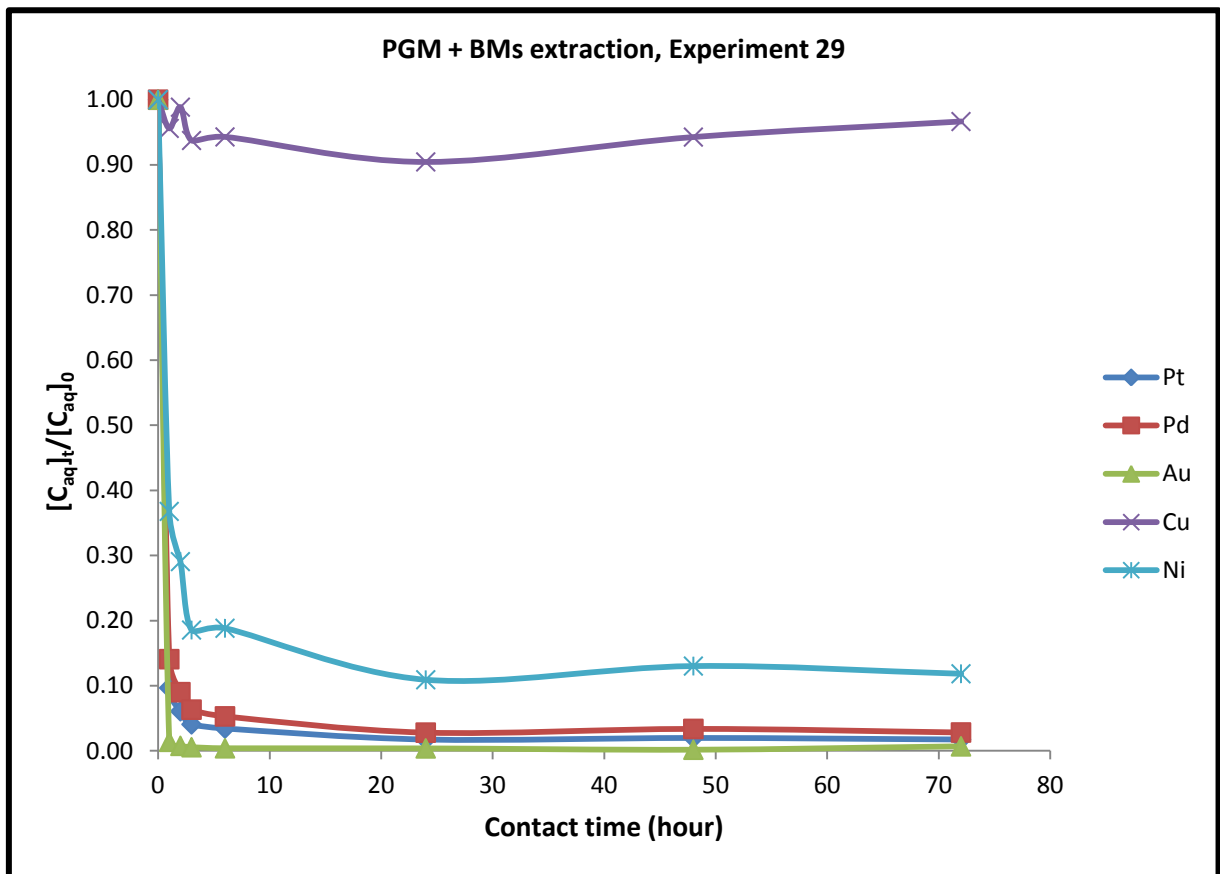


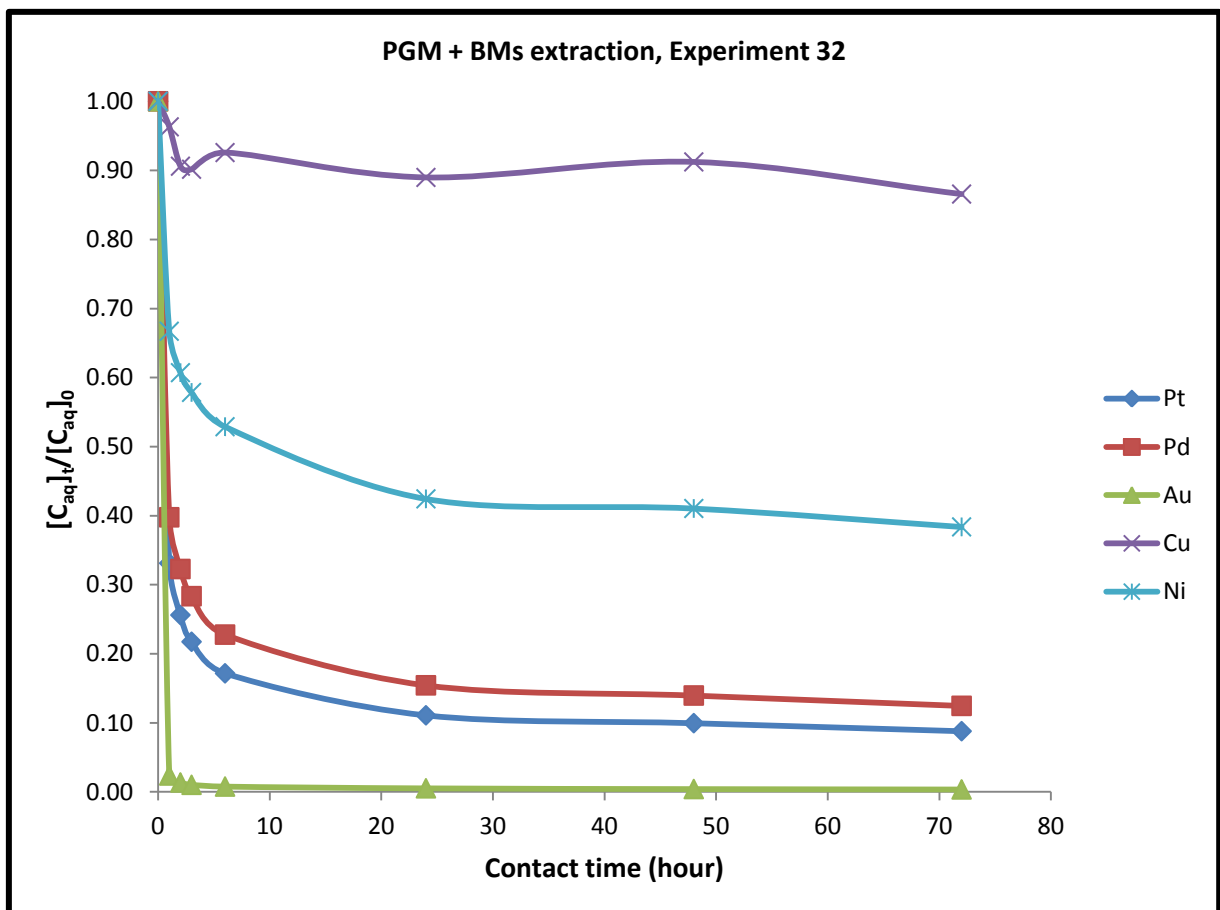
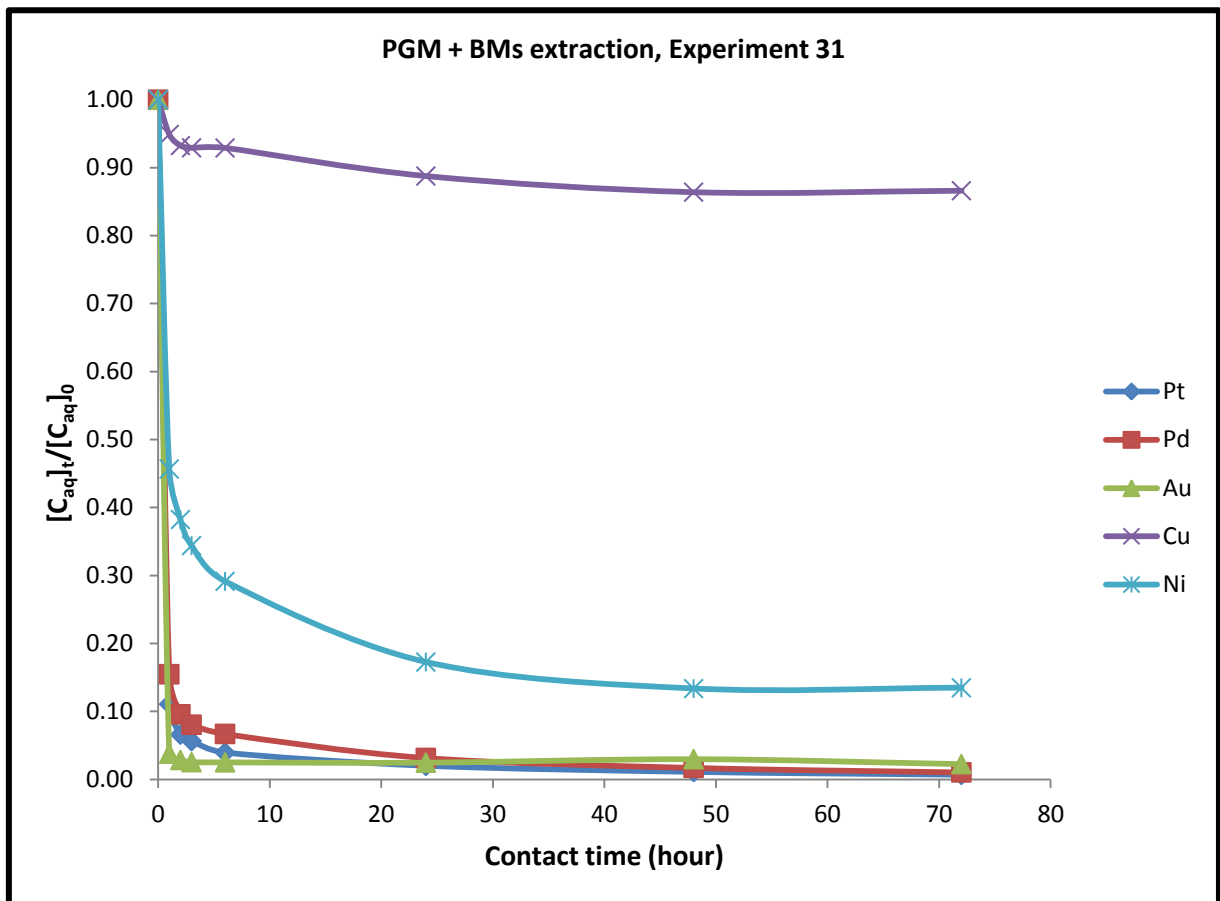


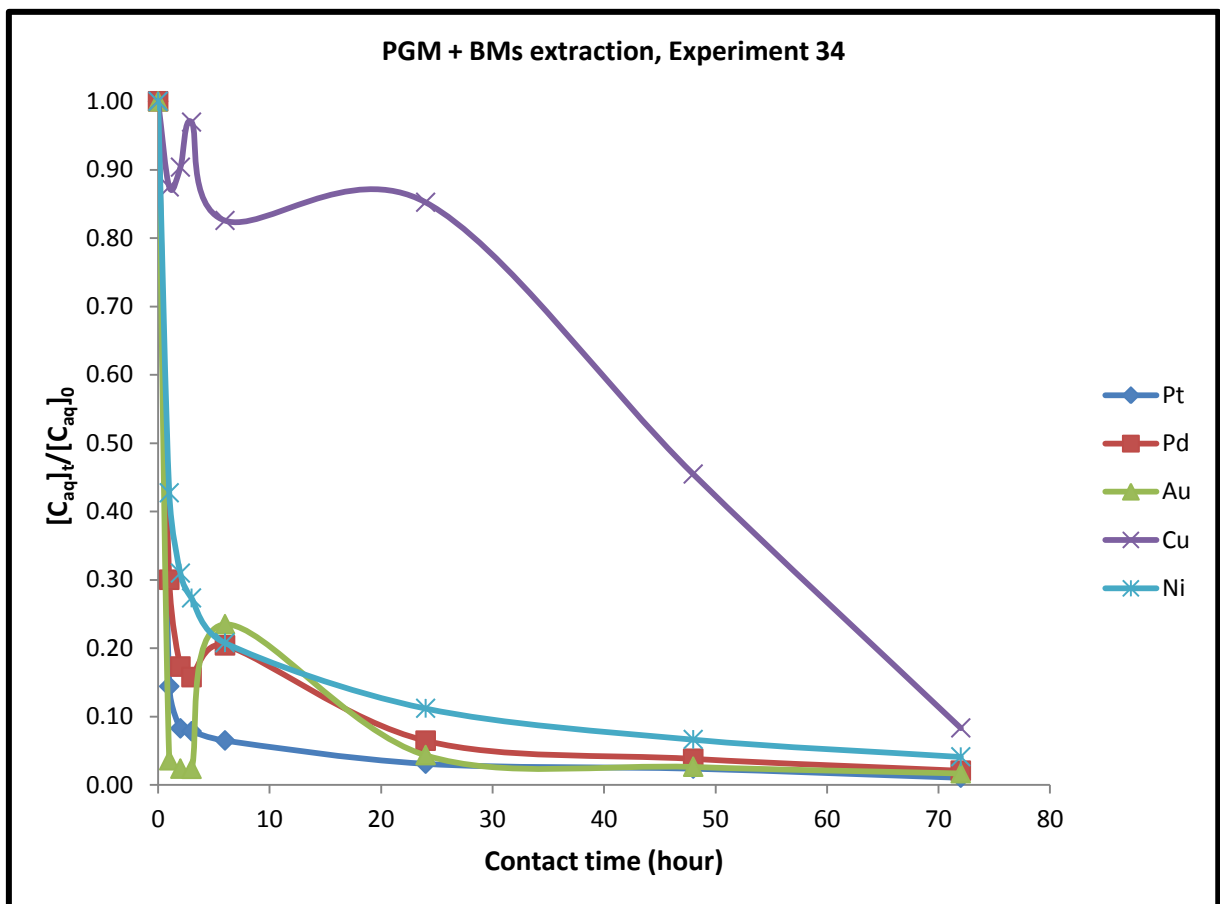
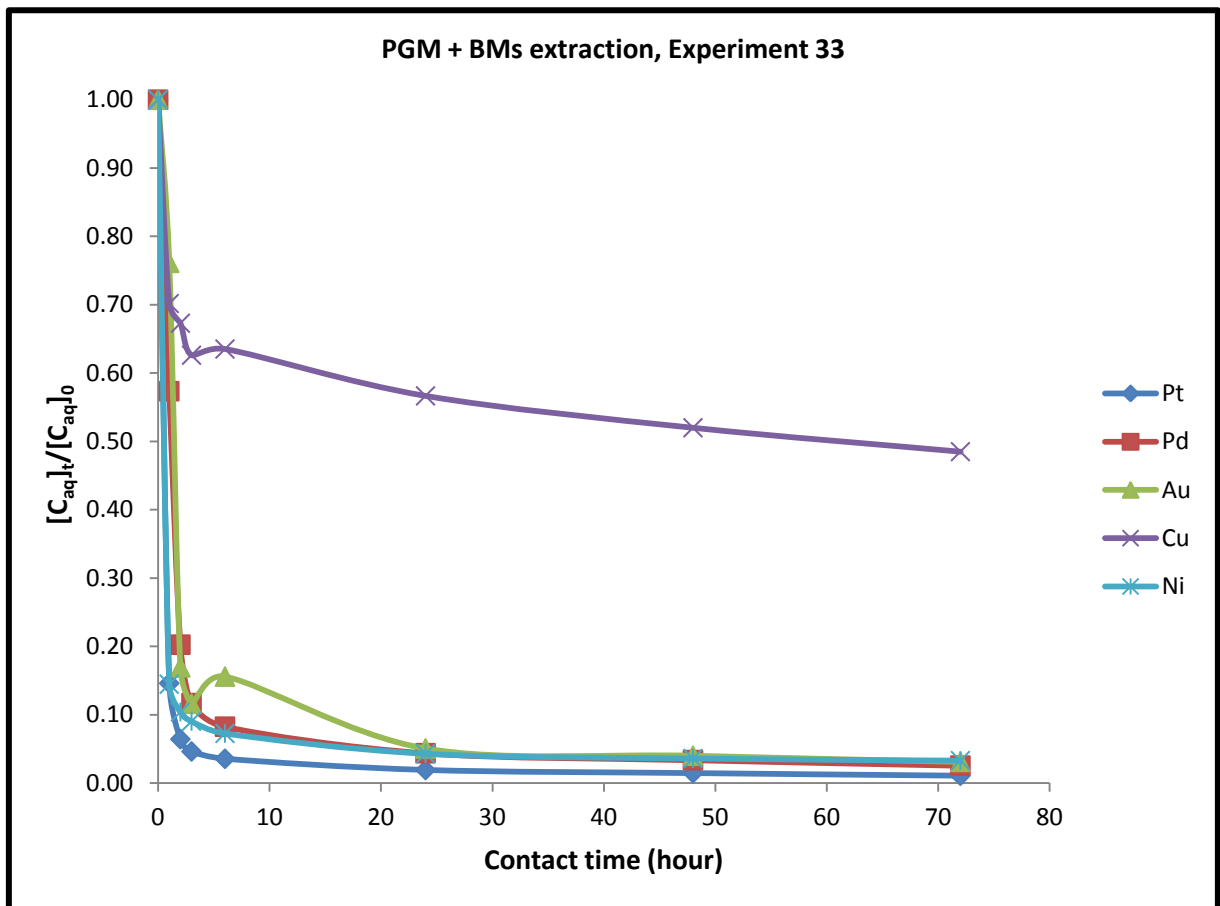


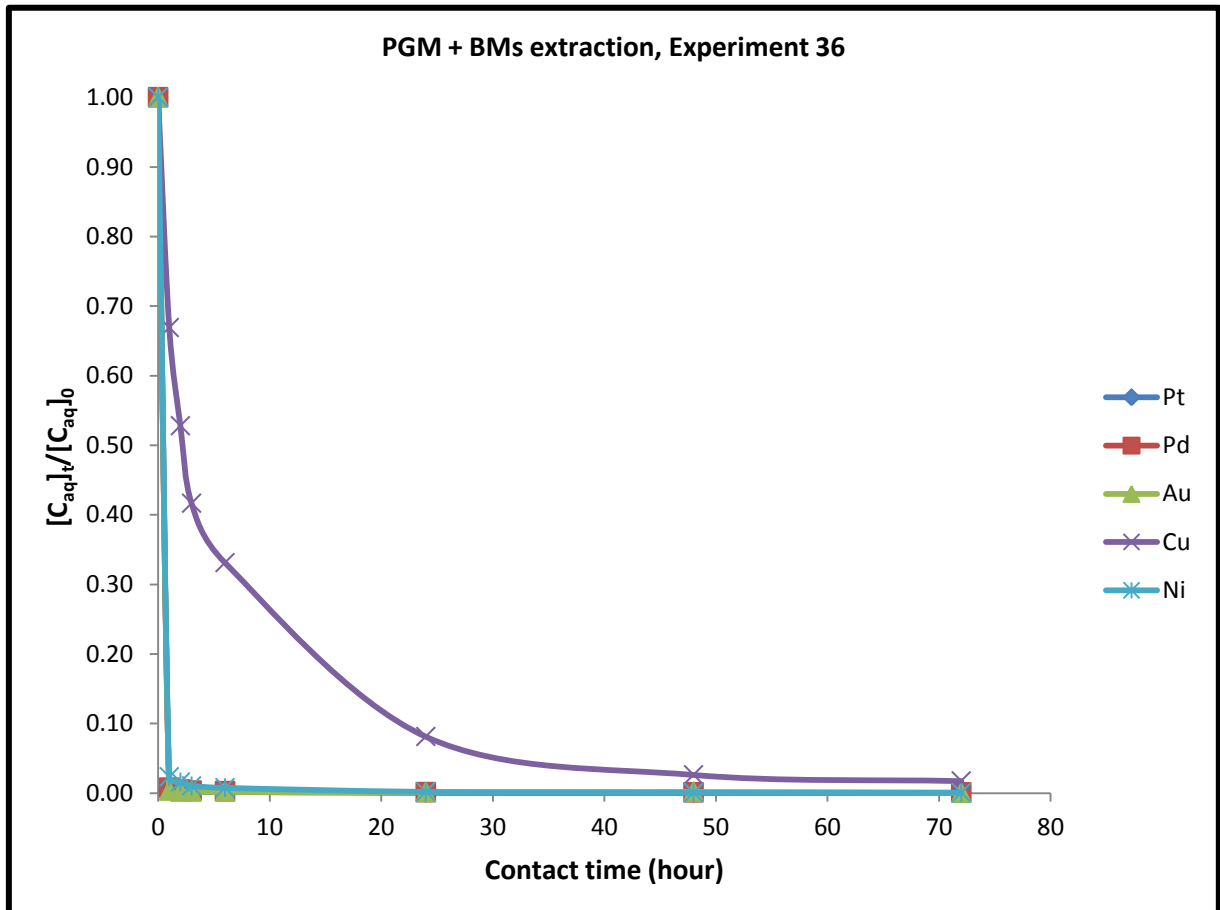
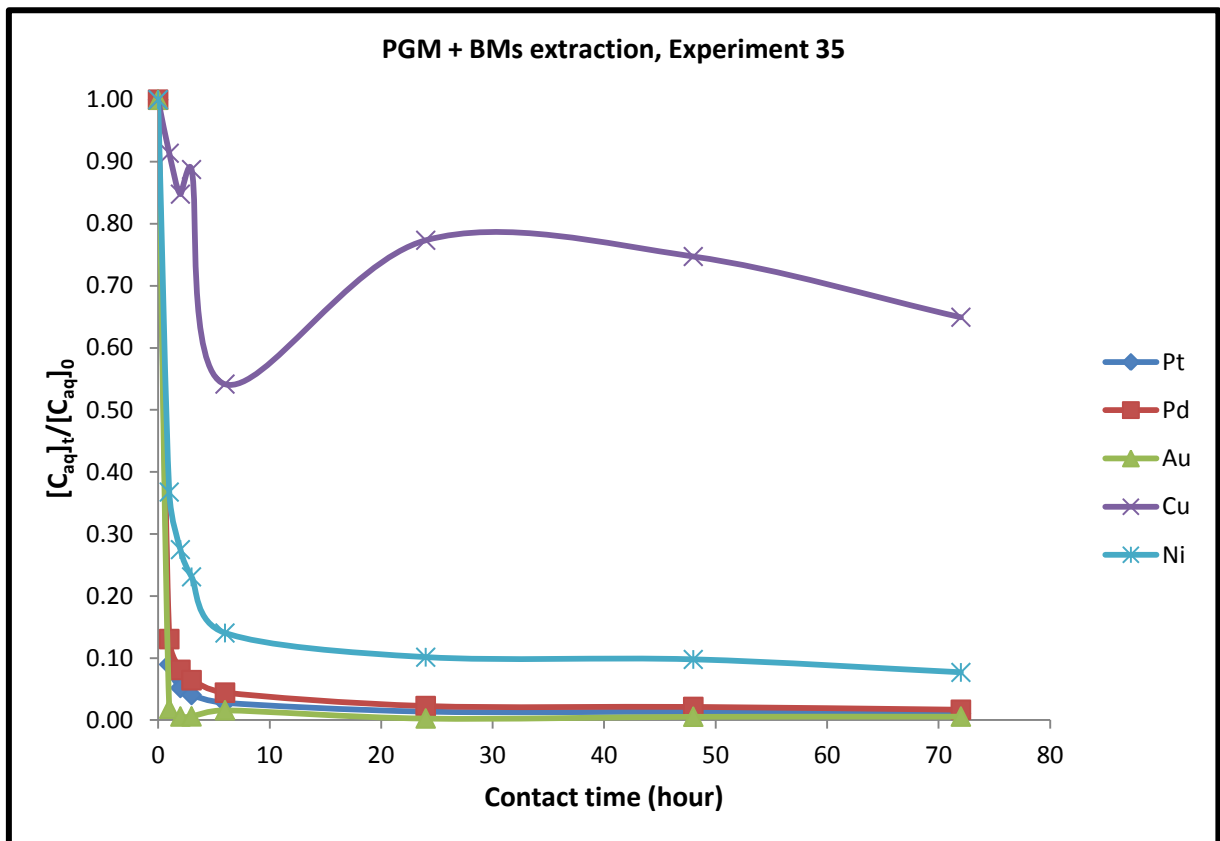


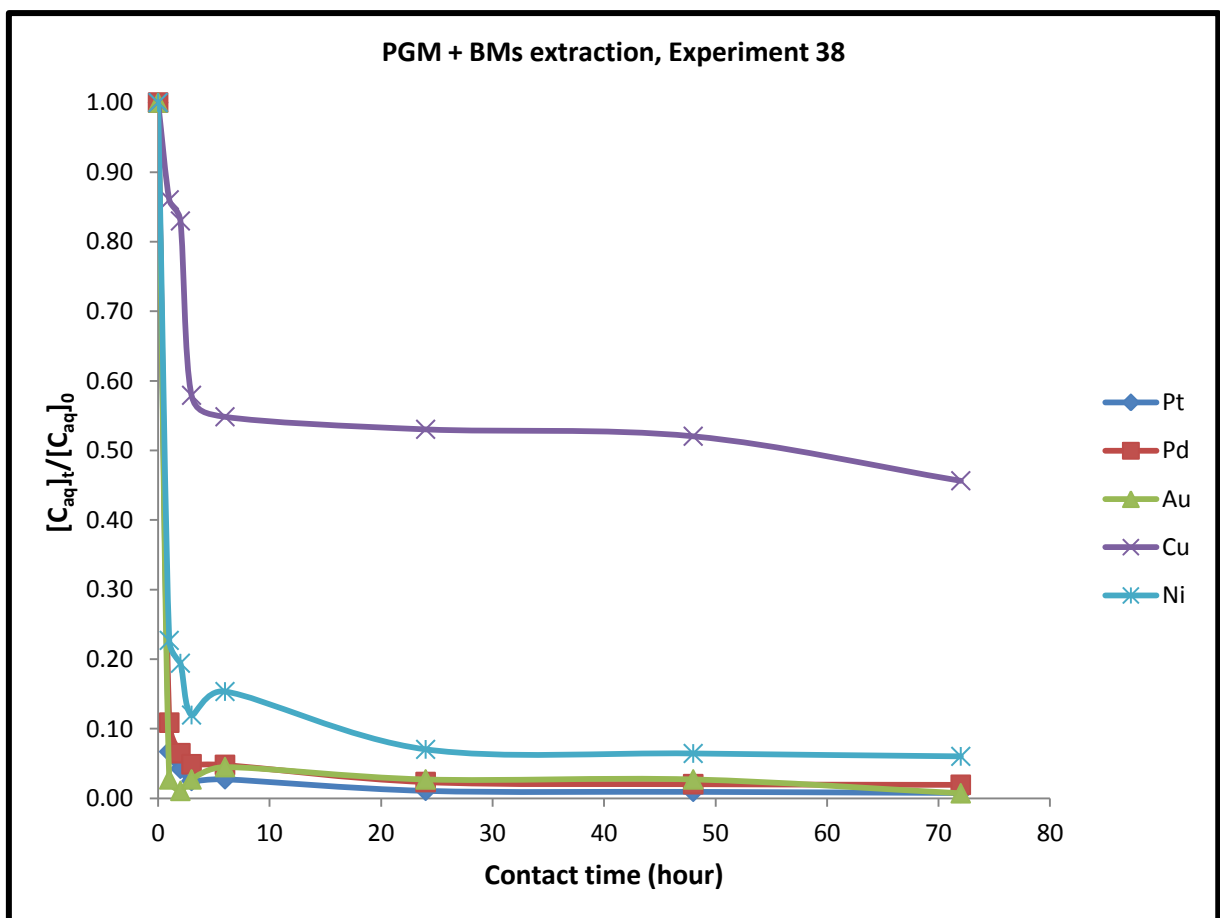
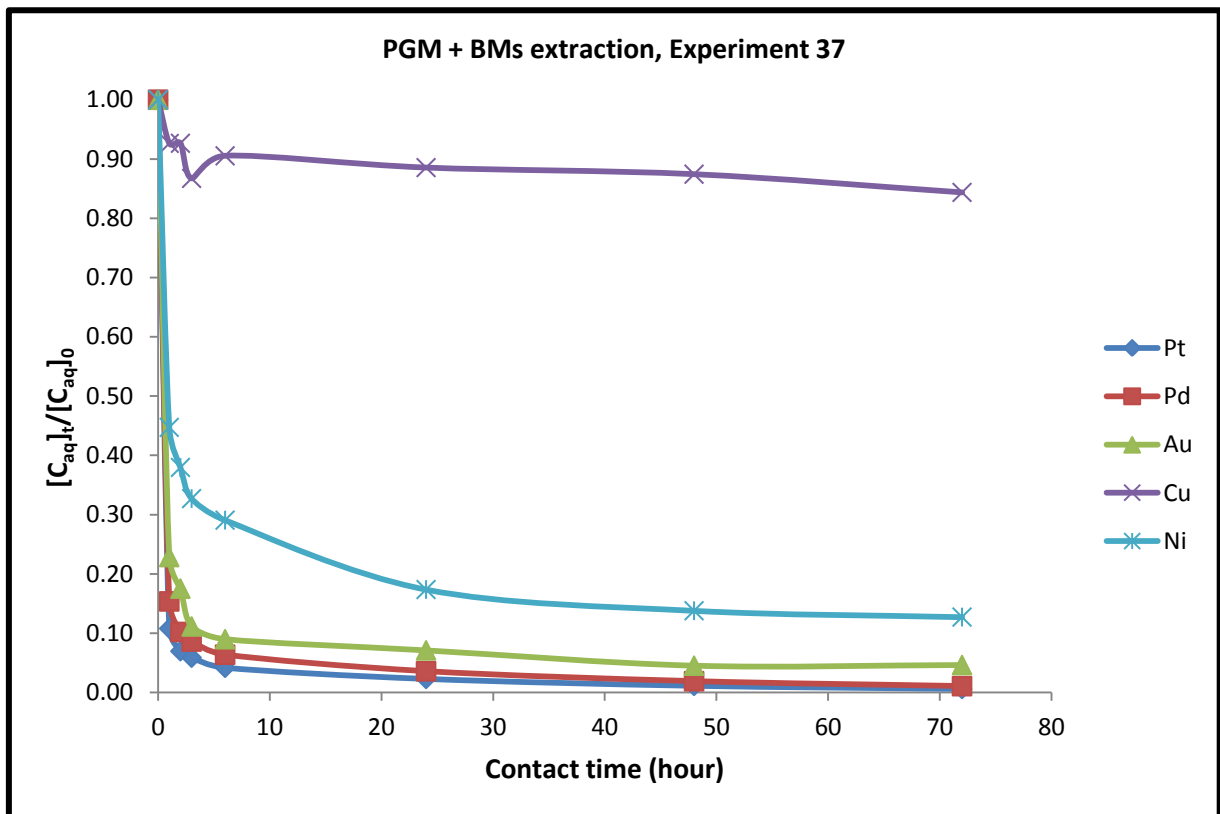


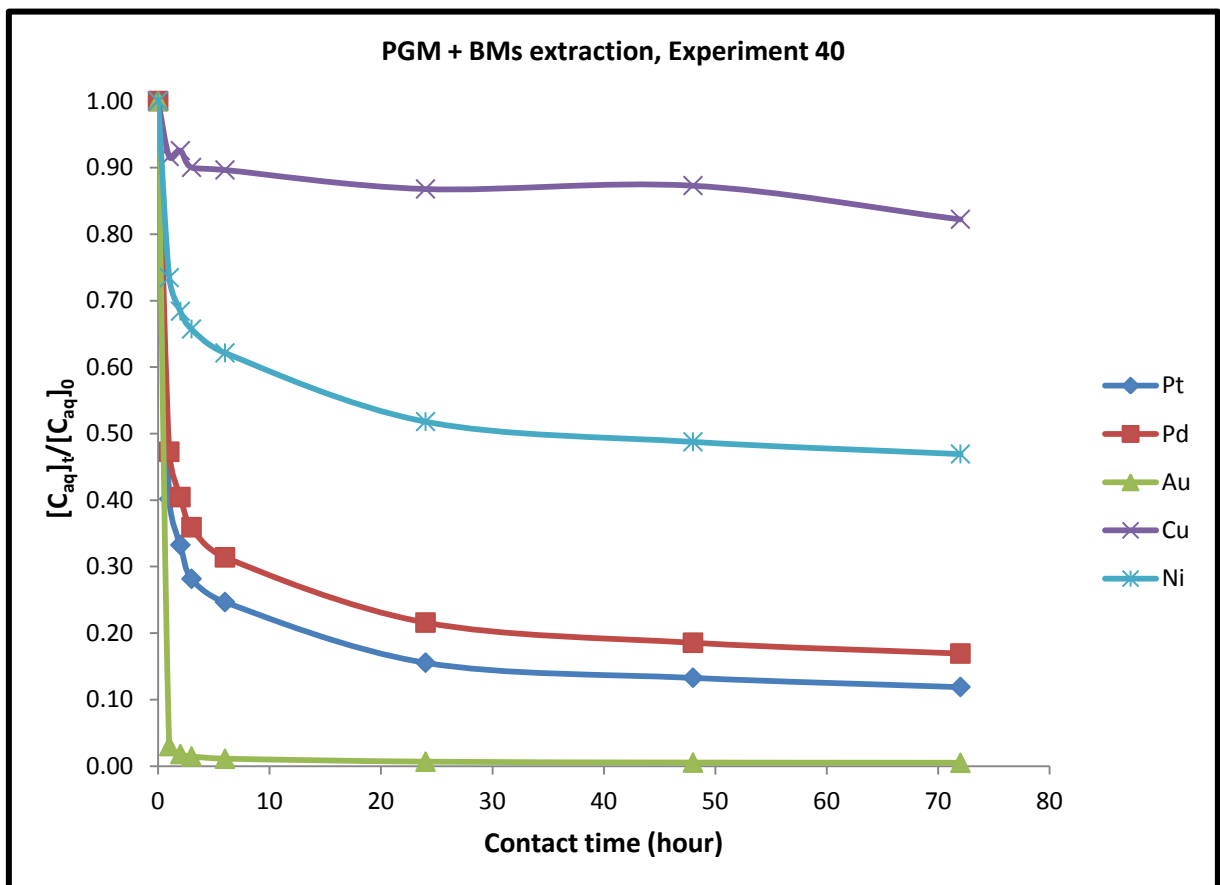
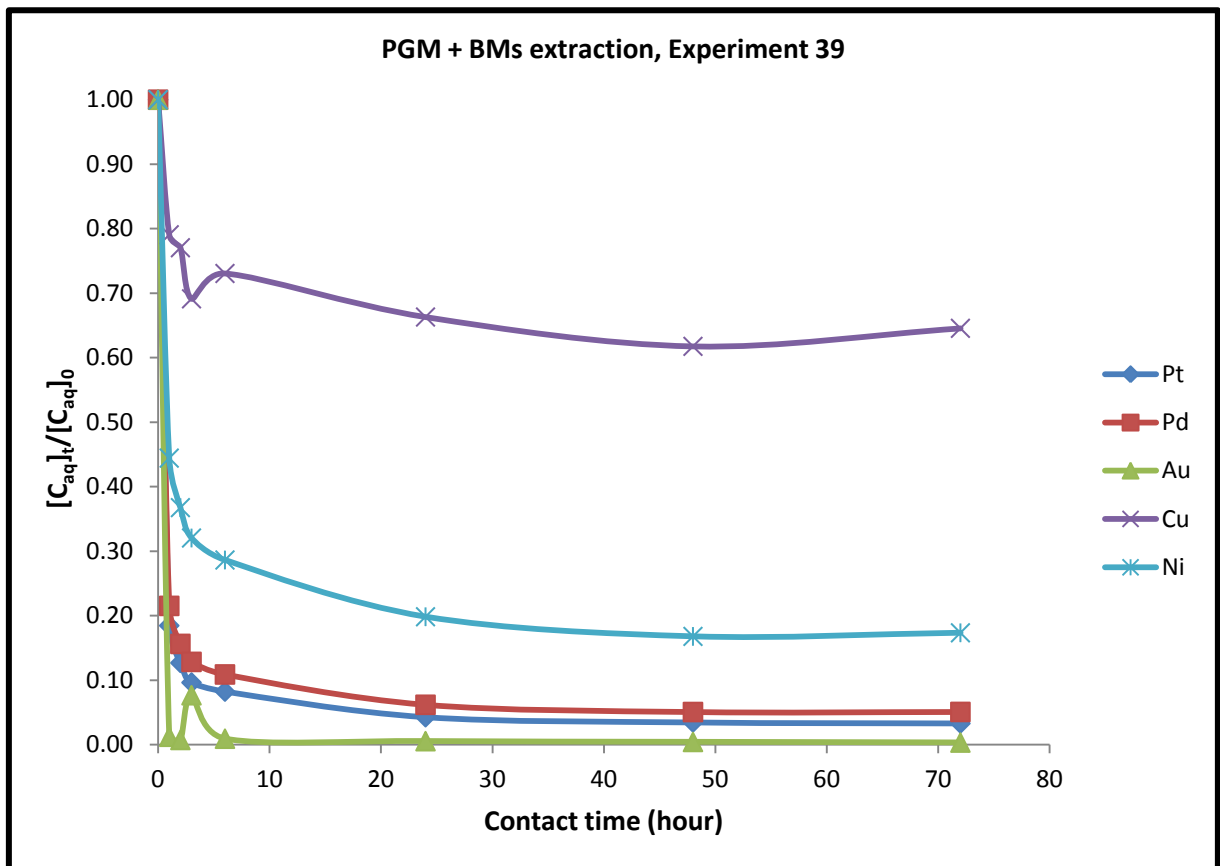












APPENDIX C

TABULATION OF STATISTICAL DATA

Response 1: Pt(II) extraction, ANOVA for selected factorial model

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
Block	18.67	7	2.667517			
Model	3691.19	5	738.2378	314.9059	< 0.0001	significant
A-pH	46.59	1	46.58538	19.87166	0.0001	
B-[Cu(I)]	46.63	1	46.63365	19.89225	0.0001	
C-[Ni(II)]	2221.28	1	2221.278	947.518	< 0.0001	
G-[AC]	950.15	1	950.153	405.3014	< 0.0001	
CG	426.54	1	426.539	181.9464	< 0.0001	
Curvature	127.86	1	127.8599	54.54047	< 0.0001	significant
Residual	60.95	26	2.344312			
Cor Total	3898.67	39				

The model F-value of 105.57 implies the model is significant. There is only a 0.01% chance that a "model F-value" this large could occur due to noise.

Std. Dev.	2.644435	R-squared	0.951337
Mean	88.73175	Adj R-squared	0.942325
C.V. %	2.980258	Pred R-squared	0.906527
PRESS	362.6771	Adeq precision	21.85568

ANOVA summary	Adjusted model		Unadjusted model	
	F-value	p-value	F-value	p-value
Model	314.9059	< 0.0001	105.5676	< 0.0001
Curvature	54.54047	< 0.0001		

Response 2: Pd(II) extraction, ANOVA for selected factorial model

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
Block	316.6363	7	45.23375			
Model	5323.544	9	591.5048	20.73376	< 0.0001	significant
B-[Cu(I)]	142.3406	1	142.3406	4.989403	0.0355	
C-[Ni(II)]	2567.757	1	2567.757	90.00646	< 0.0001	
D-[CN]	22.09463	1	22.09463	0.774473	0.3879	
F-[PMs]	284.5902	1	284.5902	9.975613	0.0044	
G-[AC]	1597.114	1	1597.114	55.98293	< 0.0001	
BD	80.10615	1	80.10615	2.807926	0.1073	
BF	104.582	1	104.582	3.665865	0.0681	
CD	224.773	1	224.773	7.878869	0.0100	
CG	300.1863	1	300.1863	10.5223	0.0036	
Residual	656.1575	23	28.52859			
Cor Total	6296.337	39				

The model F-value of 20.73 implies the model is significant. There is only a 0.01% chance that a "model F-value" this large could occur due to noise.

Std. Dev.	5.341216	R-squared	0.890269
Mean	83.81725	Adj R-squared	0.847331
C.V. %	6.372454	Pred R-squared	0.694125
PRESS	1829.044	Adeq precision	13.74317

ANOVA summary	Adjusted model		Unadjusted model	
	F-value	p-value	F-value	p-value
Model	33.80459	< 0.0001	20.73376	< 0.0001
Curvature	15.4995	0.0007		

Response 3: Au(I) extraction, ANOVA for selected factorial model

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
Block	59.17519	7	8.453599			
Model	450.9022	24	18.78759	4.030609	0.0235	significant
A-pH	10.7764	1	10.7764	2.311923	0.1669	
B-[Cu(I)]	19.39088	1	19.39088	4.160036	0.0757	
C-[Ni(II)]	15.41513	1	15.41513	3.307096	0.1065	
D-[CN]	8.914753	1	8.914753	1.912533	0.2041	
E-[SCN]	4.658878	1	4.658878	0.999496	0.3467	
F-[PMs]	59.26883	1	59.26883	12.71528	0.0073	
G-[AC]	0.002278	1	0.002278	0.000489	0.9829	
AB	11.05127	1	11.05127	2.370891	0.1622	
AC	28.97655	1	28.97655	6.216505	0.0373	
AD	21.40215	1	21.40215	4.591526	0.0645	
AF	9.757153	1	9.757153	2.093258	0.1860	
AG	1.136278	1	1.136278	0.243772	0.6348	
BC	56.34689	1	56.34689	12.08842	0.0084	
BD	17.5084	1	17.5084	3.756178	0.0886	
BF	10.91613	1	10.91613	2.341899	0.1645	
BG	0.512578	1	0.512578	0.109966	0.7487	
CD	12.7134	1	12.7134	2.727479	0.1372	
CF	35.259	1	35.259	7.564316	0.0250	
CG	5.771503	1	5.771503	1.238194	0.2981	
DE	25.06681	1	25.06681	5.377725	0.0490	
DG	3.451878	1	3.451878	0.740551	0.4145	
ADG	31.51513	1	31.51513	6.76112	0.0316	
BDG	23.03565	1	23.03565	4.94197	0.0569	
CDG	38.05426	1	38.05426	8.163997	0.0212	
Residual	37.28983	8	4.661228			
Cor Total	547.3672	39				

The model F-value of 4.03 implies the model is significant. There is only a 2.35% chance that a "model F-value" this large could occur due to noise.

Std. Dev.	2.158988	R-squared	0.923616
Mean	97.3695	Adj R-squared	0.694466
C.V. %	2.217314	Pred R-squared	-2.75087
PRESS	1831.146	Adeq precision	8.446797

ANOVA summary	Adjusted model		Unadjusted model	
	F-value	p-value	F-value	p-value
Model	6.497685	0.0082	4.030609	0.0235
Curvature	5.896681	0.0455		

APPENDIX D

SUPPORTING CALCULATIONS DERIVED

FROM

SYNTHETIC STOCK SOLUTION

PREPARATION

–

MEAN PARTICLE SIZE

OF

ACTIVATED CARBON

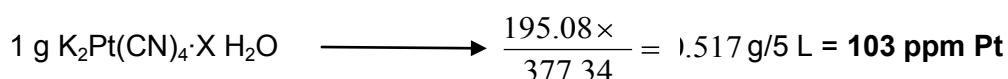
D.1 Preparation of sample synthetic stock solution for each individual base and platinum group metal

Stock standard solutions were prepared by dissolving $\text{K}_2\text{Pt}(\text{CN})_4$, $\text{K}_2\text{Pd}(\text{CN})_4$, $\text{KAu}(\text{CN})_2$ and $\text{K}_2\text{Ni}(\text{CN})_4$ from Sigma Aldrich in an alkaline solution. Here it is noteworthy that $\text{Cu}(\text{I})$ ions began to precipitate in the form of visible flocs when CuCN was dissolved in the alkaline solution. According to Dai and Breuer (2009), at very low cyanide-to-copper ratios, $\text{Cu}(\text{OH})_2$ precipitation can occur depending on the pH of the solution. The pH of precipitation decreases with increasing copper concentration and with decreasing cyanide-to-copper ratio. In order to avoid the precipitation of $\text{Cu}(\text{OH})_2$, which is the dominant thermodynamic species at elevated pH; $\text{Cu}(\text{I})$ standard solution was prepared by dissolving weighted amount of CuCN in alkaline cyanide buffer solution.

1. Platinum standard stock solution

$\text{K}_2\text{Pt}(\text{CN})_4 \cdot \text{X H}_2\text{O}$, Sample mass = 1 g; Molar mass $\text{K}_2\text{Pt}(\text{CN})_4 \cdot \text{X H}_2\text{O}$ = 377.34 g/mol;

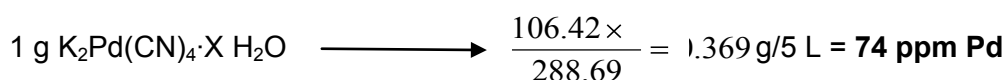
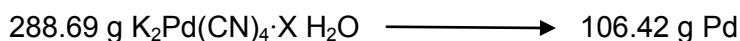
Volume solution = 5 L;



2. Palladium standard stock solution

$\text{K}_2\text{Pd}(\text{CN})_4 \cdot \text{X H}_2\text{O}$, Sample mass = 1 g; Molar mass $\text{K}_2\text{Pd}(\text{CN})_4 \cdot \text{X H}_2\text{O}$ = 288.69 g/mol;

Volume solution = 5 L;

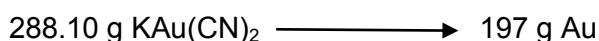
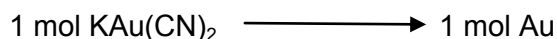


3. Gold standard stock solution

$\text{KAu}(\text{CN})_2$, Sample mass = 1 g; Molar mass $\text{KAu}(\text{CN})_2$ = 288.10 g/mol; Volume solution = 5 L;

Purity = 98%,

$$\text{Purity}(\%) = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100, \text{ Pure mass} = \frac{98 \times}{100} = 1.98 \text{ g}$$

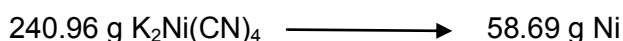
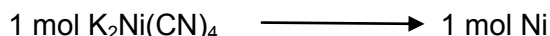


$$0.98 \text{ g KAu(CN)}_2 \longrightarrow \frac{197 \times 0.98}{288.10} = 0.670 \text{ g/5 L Au} = \mathbf{134 \text{ ppm Au}}$$

4. Nickel standard stock solution

$\text{K}_2\text{Ni(CN)}_4 \cdot \text{X H}_2\text{O}$, Sample mass = 5 g; Molar mass $\text{K}_2\text{Ni(CN)}_4$ = 240.96 g/mol; Volume solution = 5 L; Purity = 99.95%,

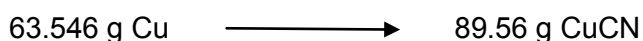
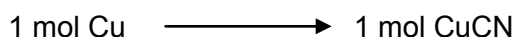
$$\text{Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100, \text{ Pure mass} = \frac{99.95 \times 5}{100} \cong 5 \text{ g}$$



$$5 \text{ g K}_2\text{Ni(CN)}_4 \longrightarrow \frac{58.69 \times 5}{240.96} = 1.218 \text{ g/5 L} = \mathbf{244 \text{ ppm Ni}}$$

5. Copper in buffer solution

Molar mass CuCN = 89.56 g/mol; Purity = 99.0%,



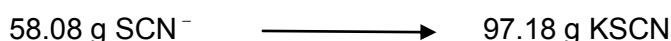
$$100 \text{ ppm Cu} \longrightarrow \frac{89.56 \times 100 \cdot 10^{-6}}{63.546} = 0.141 \text{ g}$$

$$\text{Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100, \text{ Sample mass} = \frac{\text{Pure mass}}{\text{Purity (\%)}} = \frac{0.141}{0.99} = 0.142 \text{ g CuCN}$$

To a 1 L volumetric flask, add 0.142 g CuCN. Dissolve in a buffer solution immediately prior to use. The same calculations can be done for 10 ppm Cu in solution.

6. Thiocyanate in buffer solution

Molar mass KSCN = 97.18 g/mol; Purity = 99.0%,



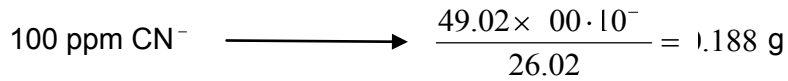
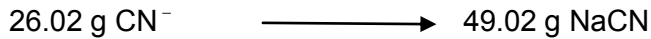
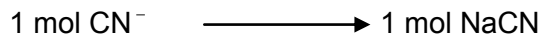
$$100 \text{ ppm SCN}^- \longrightarrow \frac{97.18 \times 100 \cdot 10^{-6}}{58.08} = 0.167 \text{ g}$$

$$\text{Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100, \text{ Sample mass} = \frac{\text{Pure mass}}{\text{Purity (\%)}} = \frac{0.167}{0.99} = 0.169 \text{ g KSCN}$$

To a 1 L volumetric flask, add 0.169 g KSCN. Dissolve in a buffer solution immediately prior to use. The same calculations can be done for 50 ppm SCN^- in solution.

7. Free cyanide in buffer solution

Molar mass NaCN = 49.02 g/mol; Minimum Purity = 95%,



$$\text{Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100, \text{ Sample mass} = \frac{\text{Pure mass}}{\text{Purity (\%)}} = \frac{0.188}{0.95} = 0.198 \text{ g NaCN}$$

To a 1 L volumetric flask, add 0.198 g NaCN. Dissolve in a buffer solution immediately prior to use. The same calculations can be done for 300 ppm CN⁻ in solution.

D.1.2 Makeup of BM and PM cyanide working solutions

To a 2 L volumetric flask (anticipating 4 runs at time, each with 500 mL of solution), add the correct amount of either BM or PMs in accordance with the experimental design layout. Dissolve in the buffer solution. Immediately prior to use, add the required amount of NaCN; 396 or 1190 mg of anhydrous NaCN salt was dissolved in the buffered water to give an initial free cyanide concentration of 100 or 300 ppm. Mix to dissolve and dilute to volume. In order to assess the effect of thiocyanate ions concentration on PMs adsorption rate, a stoichiometric amount of KSCN was dissolved in the buffer solution. Add also required amount of CuCN.

D.1.3 Chemical and protocol for cyanide buffer solution preparation

The working solutions were prepared using a buffered water recipe (prepared from Na₂CO₃ and NaHCO₃) obtained from Sigma Aldrich. By means of the Henderson-Hasselbalch relation expressed in Equation D.1 (McMurry and Fay, 1995), dissolve 0.18 mol NaCO₃ and 1 mol NaHCO₃ in distilled water to make a buffered water adjusted to pH = 9.5 with either NaOH solution or H₂SO₄. The volume of the solution is not critical.

$$pH = pK_a + \log \frac{[Base]}{[Acid]} \quad (D.1)$$

D.1.3.1 Recipe for buffered solution of pH = 9.5

$$\log \frac{[Na_2CO_3]}{[NaHCO_3]} = pH - pK_a = 9.5 - 10.25 \quad (K_a = 5.6 \times 10^{-11}); \frac{[Na_2CO_3]}{[NaHCO_3]} = 0.18$$

The solution must contain 0.18 mol of Na_2CO_3 for every 1 mol of NaHCO_3 .

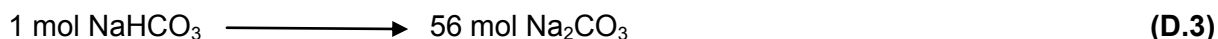


The buffer solution was prepared by combining 8.4 g NaHCO_3 with 1.91 g Na_2CO_3 or the correct proportions.

D.1.3.2 Recipe for buffered solution of pH = 12

$$\log \frac{[\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]} = \text{pH} - \text{pK}_a = 12 - 10.25 \quad (\text{K}_a = 5.6 \times 10^{-11}); \quad \frac{[\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]} = 56$$

The solution must contain 56 mol of Na_2CO_3 for every 1 mol of NaHCO_3 .



The buffer solution can be prepared by combining 0.5 g NaHCO_3 with 35 g Na_2CO_3 or the correct proportions.

D.1.4 Preparation of H_2SO_4 1N

Purity: 95 – 97%, Considered purity: 96%

Density: 1.84 g/mL

$$M = \frac{d \times \% \times 0}{M_m} = \frac{1.84 \times 6 \times 0}{98} = 8.02$$

$$N = M \times 2 = 8.02 \times 2 = 16.04$$

$$N_1 V_1 = N_2 V_2, \quad 16.04 \times V_1 = 1 \times 1000, \quad V_1 = 62.3 \text{ mL H}_2\text{SO}_4$$

Measure 62.3 mL of H_2SO_4 into a 1 L volumetric flask and dilute to volume with distilled water.

D.1.5 Preparation of NaOH 1N

$$M = \frac{\text{Masse}}{M_m \times \%}, \quad \text{Masse} = N \times M_m \times \% = 1 \times 40 \times 100 = 40 \text{ g NaOH}$$

Transfer 40 g of NaOH to a 500 mL beaker. Add 400 mL of distilled water and stir to dissolve. Allow to cool. Transfer to a 1 L volumetric flask and dilute to volume.

D.1.6 Preparation of HCl 5%

Hydrochloric acid solution: 5% (v/v) HCl. Measure 50 mL of concentrated HCl into a 1 L volumetric flask and dilute to volume with distilled water.

D.2 Mean particle size of activated carbon

Size fraction analysis of granular activated carbon MC 110

Screen size (μm)	Weight retained (g)	Sum of
A	B	A.B
3350	76.03	254700.5
2800	425.28	1190784
2360	274.7	648292
2000	102.66	205320
1700	28.95	49215
1400	3.51	4914
1180	0.21	247.8
-1180	0	0
Total	911.34	2353473

$$x = \frac{2353473}{911.34} = 2582 \mu\text{m}$$

APPENDIX E

RISK MANAGEMENT PLAN FOR AKANANI

PLATINUM PROJECT

(Adapted from Mwase, 2011)

E.1 EXECUTIVE SUMMARY

Risk is defined as the likelihood of a desirable or undesirable event occurring and the severity of the consequences (positive or negative) of the occurrence. All projects assume some element of risk and it is through risk management where tools and techniques are applied to monitor and track those events that have the potential to impact the outcome of a project.

Cyanidation is a well established technology for recovery of gold and silver from grades of ores. Despite the toxic nature of cyanide, all hydrometallurgical operations take place in open reactor vessels (open heaps, tanks and vats) with the exception of pressure cyanidation used exclusively for platinum recovery from spent petroleum and autocatalysts. This goes to how well cyanide risk management has developed over time. The question now remains to demonstrate how well cyanide risk management techniques employed in industry and specialist laboratories like Mintek can be applied in the experimental phase of the proposed project titled "Investigating the extraction of PMs from alkaline cyanided pulp by granular activated carbon." The investigation will be conducted by Ngoie Mpinga under the supervision of Prof Steven Bradshaw and Guven Akdogan of Stellenbosch University.

Risk management is an ongoing process that continues through the life of a project. It includes processes for risk management planning, identification, analysis, monitoring and control. Many of these processes are updated throughout the project lifecycle as new risks can be identified at any time.

E.2 PURPOSE

It is the objective of risk management to decrease the probability and impact of events adverse to the project. On the other hand, any event that could have a positive impact should be exploited. The present risk management plan is necessitated by the fact that Stellenbosch University does not possess any dedicated facilities for conducting experimental work with cyanide and as such, the proposed experimental work with cyanide will be conducted in a shared work space with a number of individuals who are not directly linked to the investigation.

This plan documents the processes, tools and procedures that will be used to manage and control those events that could have a negative impact on the Akanani Platinum Project. It is therefore, the controlling document for managing and controlling all project risks. It defines roles and responsibilities for participants in the risk processes, risk management activities that will be carried out.

E.3 PROJECT BACKGROUND

The focus of the project is a low grade material generated by the mineral processing stage in the platinum and base metal recovery process at Lonmin mine. What is being sought is a method to adsorb PMs from a cyanided alkaline medium from bioheap leach process excluding further treatments such as solid-liquid separation.

Given the success of the carbon-in-pulp process with gold bearing materials of a similar nature: low metal value and high tonnage; it has been identified – the material under investigation – as a suitable candidate for evaluation.

E.4 RISK MANAGEMENT STRATEGY

The proposed experimental work will involve PM adsorption tests that will be performed with the traditional bottle-on-rolls method in 2.5 litre bottles containing 500 mL of a cyanided solution. The procedure will be:

- to contact varying amounts of carbon with 500 mL of the cyanided pulp solution of known PM (Pt, Pd, Rh and Au) concentrations and adjusted at appropriate pH. Throughout the adsorption process, bottles will be kept at a constant room temperature.
- Solution sampling taken at regular time intervals, involved withdrawal of 5 mL of pulp using a syringe filter (to remove any carbon fines that might be present in the solution) followed by ICP-MS analysis of the filtrate.
- The uptakes of PMs with activated carbon will be determined from the difference of PM concentrations in the initial and final solutions.

E.4.1 Risk identification

The focus of this section is to outline the risks that cyanide poses to the project, specifically the investigator and individuals with whom the work space will be shared; also to outline measures preventing and containing risks.

Risk identification consists of determining which risks are likely to affect the project and documenting the characteristics of each. Risks can be identified from a number of different sources. Some may be quite obvious and will be identified prior to project kickoff. Others will be identified during the project lifecycle. A risk can be identified by anyone associated or not with the project. Some risk will be inherent to the project itself, while others will be the result of external influences that are completely outside the control of the project team. Throughout all phases of the project, a specific topic of discussion will be risk identification. The intent is to instruct the project team in the need for risk awareness, identification, documentation and communication.

Risk awareness requires that every project team member be aware of what constitutes a risk to the project and being sensitive to specific events or factors that could potentially impact the project in a positive or negative way. At any time during the project, any risk factors or events should be brought to the attention of the Akanani platinum project manager using Email or some other form of written communication to document the item. All identifiable risks should be entered into a risk register and documented as a risk statement.

E.4.2 Health risks

Cyanide salts and solutions can be hazardous, toxic if consumed through the known points of entry being the skin (absorbed), the eyes, inhalation of powder or hydrogen cyanide gas and ingestion of salts or solution. The warning signs of cyanide poisoning include dizziness, numbness, headache, rapid pulse, nausea, reddened skin, and bloodshot eyes. Prolonged exposure results in vomiting, laboured breathing, followed by unconsciousness; cessation of breathing, rapid weak heart beat and death. Severe exposure by inhalation can cause immediate unconsciousness.

E.4.2.1 Inhalation

The threshold limit of HCN is 4.7 ppm and is defined as the maximum average safe exposure limit for a 15-minute period by the Occupational Safety and Health Administration. Exposure to 20 ppm causes slight warning signs after several hours; 50 ppm causes disturbances within an hour and 100 ppm is dangerous for exposures of 30 to 60 minutes while 300 ppm can be rapidly fatal.

E.4.2.2 Skin absorption

Normal skin absorbs HCN slowly, but nonetheless 2% HCN in air may cause poisoning in 3 minutes, 1% is dangerous in 10 minutes and 0.05% may produce symptoms after 30 minutes.

E.4.2.3 Ingestion

1 mg of cyanide salt per 1 kg of body weight can be fatal. The experimental work will proceed with each experiment running with 500 mL of sodium cyanide solution at concentration of 6×10^{-3} M. This means there will be the following amount of cyanide for each run.

$$6 \times 10^{-3} \text{ M} \times 0.5 \text{ L} \times 9.09 = 0.15 \text{ g NaCN} \quad (\text{E.1})$$

Looking at the reaction between free cyanide CN^- and acid proton to produce HCN as expressed in Equation E.2:



This represents a 1 to 1 molar ratio; hence from 0.15 g of NaCN, the following amount of HCN will be evolved:

$$\frac{0.15 \times 7.03}{49.09} = 1.083 \text{ g HCN} \quad (\text{E.3})$$

This amounts to 83 mg of HCN in a 500 mL flask. Taking the immediate area of exposure to the investigator as 1 m³; this amounts to a concentration of 83 mg/1000 L or 0.083 ppm. This is below the maximum average safe exposure limit and can only be reached if all the cyanide is converted.

E.4.3 Risk responsibilities

The responsibility for managing risk is shared amongst all the stakeholders of the project and the rest of the laboratory users. Assigned project members are also responsible for performing the steps of the mitigation plan and reporting progress to the risk officer weekly.

E.4.4 Risk contingency planning

E.4.4.1 The investigator

Gloves, eye goggles, half mask (protection against vapour, gas and dust particles) and a lab coat will be employed when handling the salts and solutions.

All handling of salts and solutions will take place in a fume hood; this will include all experimental procedures-preparation, sampling, filtering and transferring waste solutions to 25 L disposal containers.

Containers containing solutions or salts will be kept closed when not in use. The 25 L disposal containers will additionally be kept in a heavy duty plastic bag as secondary containment.

All glassware will be rinsed with EDTA and a bicarbonate solution to remove any metal ions and acidic residues before using them for the cyanide solutions.

All solutions will be prepared using a buffered water recipe obtained from Sigma Aldrich.

A cyanide anti-dote kit will be kept within reach.

E.4.4.2 Individuals sharing the work space

Inform all students and staff working in the vicinity before working with the cyanide; educate them of the warning signs and first aid measures for dealing with cyanide exposure.

The salts will be kept in a safe place where access is restricted.

Periodic material balances will be carried out on the salts, accounting for what has been used and what remains.

All stored containers having cyanide solutions will be clearly labelled showing the contents, concentration and warning of the hazard.

A Materials Safety Data Sheet (MSDS) and warning labels will be put up in the area where the experimental work is being conducted.

The lab coat used by the investigator will be hung in the lab coat wardrobe in a heavy duty plastic bag.

E.4.5 Risk response – First aid measures

For each identified risk, a response must be identified. It is the responsibility of the Akanani platinum project to select a risk response for each risk.

Eye contact: Immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin contact: Immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient or apply cold water. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious skin contact: Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation: If inhaled but victim is conscious and speaking, with a gas mask and goggles on, remove victim to fresh air. If the victim is unconscious but breathing, break an ampul of amyl nitrite in a cloth and hold it under the victim's nose for 15 seconds. Repeat five or six times. Use a fresh ampul every 3 minutes. Continue until the victim regains consciousness. Amyl nitrite is a powerful cardiac stimulant and should not be used more than necessary. If the patient is not breathing, apply artificial respiration; this can best be done using an oxygen resuscitator. The amyl nitrite antidote should also be administered during resuscitation. Get medical attention.

Ingestion and serious inhalation: If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately. A suggested procedure for physicians or nurses is intravenous administration of 0.3 g (10 mL of a 3% solution) of sodium nitrite at the rate of 2.5 mL/minute followed by 12.5 g (50 mL of a 25% solution) of sodium thiosulfate at the same rate. Watch the patient for 24 to 48 hours, especially in cases of ingestion or skin absorption. If symptoms reappear, repeat the injections in half the original amounts. These solutions should be kept readily available. In some cases, first aid personnel have been trained to use the intravenous medication subject to government regulations.

E.4.6 Risk mitigation

Risk mitigation involves two steps:

- Identifying the various activities or steps, to reduce the probability and/or impact of an adverse risk.
- Creation of a contingency plan to deal with the risk should it occur. Taking early steps to reduce the probability of an adverse risk occurring may be more effective and less costly than repairing the damage after a risk has occurred.

E.4.6.1 Handling and storage

All salt containers will be locked away from heat and sources of ignition. Container will be kept in well ventilated storage where temperature will not exceed 24°C. All empty salt containers will also be kept in the safe until they can be passed on the Enviroserv for disposal. Not water will be added to these containers.

E.4.6.2 Fire risks

Sodium cyanide may be combustible at high temperatures but is flammable in the presence of acids and moisture. It is not known whether there is a risk of explosion in the incidence of mechanical impact or static discharge. But regardless, all the above situations will be avoided in storing and handling the salts and/or solutions.

It must be noted that a fire resulting from the salt is dangerous on contact with acids, acid fumes, water or steam as it results in the immediate formation of toxic and flammable vapours of hydrogen cyanide gas and sodium oxide. When the salt is heated, it will thermally decompose and emit fumes of hydrogen cyanide and oxides of nitrogen.

Small fires can be contained using a dry chemical powder or sand while larger ones using a water spray or foam. If out of control, the Fire alarm will be activated and the emergency number (107) will be dialled.

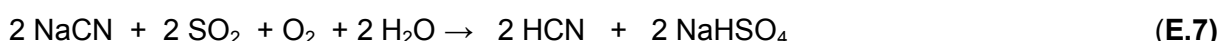
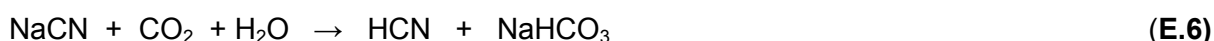
E.4.6.3 Accidental release

All salt handling and solution preparations will proceed on a large plastic tray so that in the case of a spill, the salt or solution will be transferred from the tray back into the container or disposal container, rather than being cleaned from the floor or bench.

In case of a solution spill on the floor, the area will be demarcated with coloured tape or a sign. The solution will be mopped up and transferred to assigned container for disposal. The cleaning aids such as the mop, dust pan, bucket will be dedicated, labelled and isolated for cyanide use. This will be communicated to the rest of the laboratory users.

E.4.6.4 Reactivity and stability risk

Violent reactions occur in contact of NaCN with fluorine gas, magnesium, nitrates and nitric acid. The hazard of producing toxic and flammable vapours of hydrogen cyanide come with the contact of acids, water, steam, strong oxidisers and carbon dioxide gas in ordinary air. These compounds will not be allowed to contact the salts or solutions. To avoid hydrolysis of cyanide (Equation E.4), reaction (i.e. leaching or adsorption) must be carried out under basic conditions. The following reactions illustrate some of the above considerations.



By far, the biggest risk to this project is the formation of hydrogen cyanide gas as a result of any sudden pH drop due to an inappropriate addition of acid. This will be approached through careful pH management above 9.5. As stated earlier, the solutions will be prepared using a buffered water recipe obtained from Sigma Aldrich. The glassware will be rinsed with EDTA and a bicarbonate solution before use and all preparations will proceed in the fume cupboard. A schedule will be worked out to allow the cyanide experiments to run without interference. During that period no acids or oxidisers will be found in the fume hood (see E.5 to E.7 reactions).

To prevent the possibility of any stray reactions in the 25 L disposal containers; the latter will be rinsed with EDTA and bicarbonate solutions to remove metal ions and any acids, then it will be rinsed with deionised water, allowed to stand and dry before being used to store the waste cyanide solutions.

On completion of an experiment, glassware and other equipment will be decontaminated by soaking them in a 0.5 M hydrogen peroxide solution for 1 hour. Other equipment such as mops, clothes, paper towels used for cleaning up spills will be stored in heavy duty plastic bags and handed over to Envirotech for disposal. All waste from experimental work (including solutions and solid waste) will be handed over to Envirotech for disposal.

E.4.6.5 Step by step procedures for handling cyanide

1. All students and staff working in the surrounding vicinity will be informed before work with cyanide commences.
2. All receiving vessels (reactor vessels, tubes, sample bottles, disposal containers) will be soaked in 0.5 M (excess) EDTA solution for 1 hour.

3. The vessels will then be rinsed with deionised water followed by a soak in buffered water prepared from Na_2CO_3 and NaHCO_3 for 1 hour. They will be left to dry over night. In this case, the vessels will not be rinsed as any alkaline residue can only be beneficial to keeping the pH above 10.
4. The equipment for weighing out the salt will be placed on two plastic trays; one for the balance and one for the salt container. A labelled heavy duty paper bag will be kept nearby for the used paper towels, spatulas, etc. A lab coat, double pair of gloves and half mask will be worn at this stage.
5. After measuring the salt, container will be closed and placed out of sight in cupboard to be later locked up in the poisons cupboard.
6. Reactor vessels in which salt was measured will be placed in the fume hood where the cyanide solution will be made up from the salt using buffered water (prepared from Na_2CO_3 and NaHCO_3). The pH of the solution (10 or 12) will be verified using a standard pH meter. All will be conducted in the fume hood.
7. The bulk solution will be labelled and stored in the fridge over night.
8. The bulk solution will be allowed to warm up to room temperature (in the fume hood) and the pH measured before proceeding with experimental work.
9. Experimental work will involve adding 500 mL of bulk solution to 5 or 15 g of activated carbon in bottles. Waste solution will be stored in the disposal container.

E.4.7 Tracking and reporting

Based on trigger events that have been documented during the risk analysis and mitigation processes, the Akanani project managers will have the authority to enact contingency plans as deemed appropriate. As project activities are conducted and completed, risk factors and events will be monitored to determine if in fact trigger events have occurred that would indicate the risk is now a reality.

E.4.8 Processes to address immediate unforeseen risks

The individual identifying the risk will immediately notify the Akanani project managers. If required, they will insinuate a mitigating strategy and assign resources as necessary.

E.4.9 Risk control

The final step is to continually monitor risks, to identify any change in the status, or if they turn into an issue. It is best to hold regular risk reviews to identify actions outstanding, risk probability and impact, remove risks that have passed and identify new risks.

SYMBOLS	DESCRIPTION
EDTA	Ethylenediaminetetraacetic acid
PPE	Personal protective equipment

REFERENCES

Pesce, L.D. 2001. Cyanides Encyclopedia of Chemical Technology-Online. John Wiley & Sons, Inc.

Lengyel, D. 2007. Exploration Systems Risk Management Plan. National Aeronautics and Space Administration.

Northrop Grumman Corporation. 2007. Risk management plan.

APPENDIX F

PUBLICATIONS FROM THIS THESIS

A novel energy efficient process for the extraction of platinum group metals through a sequential stage high temperature heap bioleach and subsequent high temperature cyanide heap leach utilising solar heat. (Eksteen, Mwase, Petersen, Bradshaw, Akdogan, Mpinga, Snyders. *Biohydrometallurgy*, 2012).