RECOVERY OF GOLD FROM CHLORIDE CONTAINING SOLUTION USING ELECTROGENERATIVE METHOD

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2017

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by

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Thesis submitted in fulfillment of the requirements

for the Degree of

Master of Science

December 2017

ACKNOWLEDGEMENT

I would like to take this opportunity to express my profound gratitude and deep regards to my supervisor, Dr. Faiz Bukhari Bin Mohd Suah for his guidance, monitoring and constant encouragement which made this study successful.

I would also take this opportunity to thank to Prof. Norita Mohamed as a co-supervisor for her cordial support, valuable information and guidance in completing this project. I would also like to thank School of Chemical Sciences, Institute of Postgraduate Studies and Universiti Sains Malaysia for the support and assistance. Fellow lab members, lab assistants in the School of Chemical Sciences and graduate students although not listed here for their friendship, valuable help and encouragement.

Deepest appreciation to my family members especially my dad, Roslan Bin Shaari and my mom, Nor Azizah Binti Mohd Amin, for their prayers and words of encouragement throughout the study process, all my family members and my friends for their unwavering support and love which gave me strength to complete this study.

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LIST OF SYMBOLS AND ABBREVIATIONS

$\mathrm{A_e}$	specific surface area of cathode, m^{-1}
$\mathrm{A_s}$	active electrode area per unit reactor volume, m^{-1}
$\mathrm{C_o}$	initial concentration, mol cm^{-3}
$\mathrm{C_t}$	metal concentration at time t, mol cm^{-3}
D	diffusion coefficient, cm^2s^{-1}
E_a	standard reduction potential at anode, V
E_c	standard reduction potential at cathode, V
$E°_{cell}$	overall cell potential, V
F	Faraday's constant, 96485.309 C mol^{-1}
$\Delta G°$	standard Gibb's free energy, kJ mol^{-1}
$\mathrm{J_i}$	flux of species I of concentration
$\mathrm{k_m}$	mass transport coefficient, m s^{-1}
n	the number electrons accepted or released by the reaction per mole of reactant
ppi	pores per inch
t	time, s
V_e	cathode volume, m^3
V_R	volume of electrolyte, m^3
ε	porosity of electrode
v	scan rate of the potential, V s^{-1}

PEMULIHAN EMAS DARIPADA LARUTAN KLORIDA MENGGUNAKAN KAEDAH ELEKTROGENERATIF

ABSTRAK

Sistem elektrogeneratif telah diterokai sebagai kaedah alternatif untuk pemulihan emas secara elektrokimia daripada larutan klorida. Dalam proses ini, tindak balas kimia berlaku secara spontan kerana tidak memerlukan bekalan tenaga luar. Sel kelompak statik yang beroperasi dalam mod elektrogeneratif telah digunakan untuk pemulihan emas daripada larutan klorida. Dalam kajian ini, larutan klorida emas telah digunakan untuk menggantikan larutan sianida kerana ketoksikannya. Larutan klorida emas juga merupakan liksivian alternatif yang sesuai dengan merangsang perkembangan baharu dalam teknologi pengekstrakan digabungkan dengan kesedaran terhadap alam sekitar. Dua jenis elektrod telah digunakan dalam sel statik iaitu bahan katod tiga dimensi karbon kekaca berongga (RVC) dan grafit berliang (PG), dan bahan katod dua dimensi iaitu keluli telah digandingkan dengan anod zink. Sistem ini telah menunjukkan > 90% emas dipulihkan dalam masa 3 jam beroperasi. RVC yang diaktifkan merupakan bahan katod yang terbaik dengan kadar pemulihan emas yang paling tinggi sebanyak > 90% dalam masa 1 jam beroperasi tetapi dalam keadaan yang berasid (pH 3.00 ± 0.11). Sel elektrogeneratif aliran terus dengan katod yang diaktifkan telah diterokai. Penilaian prestasi sel ini adalah berdasarkan kepekatan awal emas iaitu 50, 100, 250 dan 500 mg L^{-1} dan jenis bahan katod. Keputusan telah membuktikan bahawa > 99% emas dipulihkan dalam masa 2 jam beroperasi dalam larutan berasid, kadar aliran optimum iaitu 50 mL min^{-1} dan dalam keadaan tanpa oksigen. Bilangan sel aliran terus yang sesuai telah dikaji dalam sistem dan keputusan menunjukkan satu sel aliran terus adalah lebih efektif berbanding dua sel aliran terus dalam bentuk siri. Selain itu, sel aliran terus juga diaplikasikan untuk pemulihan emas daripada larutan buangan elektrik dan elektronik. Sistem menunjukkan > 99% emas telah dipulihkan dalam masa 2 jam beroperasi dengan kepekatan awal emas klorida 100 mg L^{-1}. RVC yang telah diaktifkan adalah bahan katod yang terbaik dengan kadar pemulihan emas sebanyak > 99% dalam masa 2 jam daripada larutan buangan elektronik kerana sifat RVC mempunyai ruang isipadu lowong yang tinggi, struktur berongga yang tinggi, struktur yang tegar dan rintangan aliran yang rendah. Kaedah elektrogeneratif adalah mesra alam dan mampu memulihkan emas walaupun pada kepekatan emas yang rendah (50 mg L^{-1}).

RECOVERY OF GOLD FROM CHLORIDE CONTAINING SOLUTION USING ELECTROGENERATIVE METHOD

ABSTRACT

The electrogenerative system that was developed as an alternative method to the electrochemical recovery of gold from chloride solution is presented. In this process, a chemical reaction takes place spontaneously since it does not require any external supply of energy. A static batch cell operating in electrogenerative mode is used in gold recovery from chloride solutions. In this present work, a gold chloride solution was used to replace cyanide solution due to its toxicity. Gold chloride solution is also a suitable alternative lixiviants which has stimulated new developments in extraction technology combined with environmental concern. Two types of electrodes were used which are three-dimensional cathode materials namely reticulated vitreous carbon (RVC) and porous graphite (PG), and two-dimensional cathode stainless steel plates coupled with a zinc anode. This system showed > 90% of gold being recovered within 3h operation. Activated RVC served as the best cathode material having the highest recovery rate with > 90% of gold being recovered in 1 h operation but in acidic condition (pH 3.00 ± 0.11). An electrogenerative flow-through cell with activated cathodes was developed too. The performance of the cell was evaluated with initial gold concentration of 50, 100, 250 and 500 mg L^{-1} and different types of cathode materials. The result revealed > 99% of gold was recovered within 2 h in acidic solution, an optimum flow rate of 50 mL min^{-1} and deoxygenated state. The suitable number of flow cells used in the system was investigated and it was discovered that a single flow cell system is more effective compared to the two flow cells system in series. Besides, flow-through cell system also was applied to recover gold from an E-waste solution. More than 99% gold in 100 mg L^{-1} of initial gold chloride concentration was recovered within 2h of operation. Overall, the activated RVC is the best cathode material with the highest gold recovery rate > 99% of gold from E-waste in 2 h which is attributed to exceptional high void volume, highly porous surface structure, rigid structure and low resistance to fluid flow. The electrogenerative method is environmentally friendly and could be used to recover the gold even at low gold concentration (50 mg L^{-1}).

CHAPTER 1: INTRODUCTION

1.1 Background

A first approximation of gold market trend over the past decades is the best gained based on the viewing data reported by Shafiee and Topal (2010). Gold is one of the most valued metals known for its beauty and usefulness. It is usually used in the electronics industry because of its good electrical conductivity and had a high corrosion resistance. In addition, electrodeposited gold was important due to its wide application as decorative gold plating in the jewellery industries (Syed, 2012).

Electronic waste (E-waste) can be described as discarded electronic equipment such as unwanted laptops and computers, office electronic equipments and entertainment electronics devices (Cui & Zhang, 2008). The resources contained in E-waste are numerous; mostly it is contains valuable and recyclable metals. Typical materials in E-waste are halogens, toxic elements, non-metals and metalloids such as non-ferrous metals, precious metals and other minor substances such as plastics and glass (Cui & Forssberg, 2007).

Recycling or recovery valuable metals such as gold and platinum are an essential not only on the recovery aspect of precious materials but also in the waste treatment, environmental pollution and adverse human health effects. US Environmental Protection Agency (EPA, 2003) identified that there are seven major benefits when using scrap iron, steel or other metals instead of using virgin metals or materials. These benefits include reduction in pollution, energy saving and reducing potential hazards involved in the mining of the virgin materials, which are the main contributions towards the preference of recovery the E-waste.

In the recovery of gold from E-waste, the most common methods used are hydrometallurgy (Canda et al., 2016; Garlapati, 2016; Sum, 1991; Syed, 2006; Syed, 2012; Karamanoglu & Aydin, 2016), biometallurgy (Dimitrijevic et al., 2013; Kiddee et al., 2013) pyrometallurgy (Zhou et al., 2010; Bigum et al., 2012; Canda et al., 2016; Garlapati, 2016), precipitation and recovery from leachants (Cui & Forssberg, 2003; Vats & Singh, 2015). However, some of these methods involve the use of hazardous chemicals as the stripping solutions, which less environmentally friendly, time-consuming, consume excessive energy, poor recovery for low gold concentrations (< 500 mg L^{-1}). Thus, this pushes for better methods for the recovery of gold from E-waste in particular the method that is less harmful to the environment as well as better gold recovery.

An industrial process streams and cost-effective treatment system to recover and remove heavy metal ions especially gold are needed. In metal finishing and processing industry, a close-loop system was preferred and developed (Pletcher et al., 1993) The system is designed with complete recycling of excess reagents to ensure maximum utilization and minimal waste generation. Gold was labeled a key metal based on the unique chemical and physical properties of gold. The current gold recovery systems (e.g. hydrometallurgy, biometallurgy and electrowinning) are not able to recover the gold fully. Therefore, there is a problem in the E-waste recycling industry due to the requirement of disposing the liquor used to recover gold.

Over the last 100 years, cyanide-leaching process was used in the mining industry. For extracting gold from E-waste, cyanide is the most widely used leachant (Quinet et al., 2005). However, because of its toxicity, much efforts have been made to replace this cyanidation of gold process with suitable alternative lixiviants, like thiourea (Örgül & Atalay, 2002), thiosulfate ion (Aylmore & Muir, 2001), sulfite ion and thiocyanate ion (Senanayake, 2004), ascorbic acid (Osaka et al., 2006) and chloride ion media (Cui & Zhang, 2008; Iglesias et al., 1999; Jeffrey et al, 2001; Puvvada et al., 2003; Viñals et al., 2006). These efforts were due to the significant increased in the price of gold, new developments in extraction technology and environmental concerns (Chatterjee & Kumar, 2009; Gupta et al., 2014; Khaliq et al., 2014; Petersen, 2016).

Effective adsorption of gold(III) (Au(III)), on non-ionic polymeric adsorbents from hydrochloric acid solutions have been demonstrated. In analytical chemistry, this property has been exploited (Koshima, 1986; Tunçeli & Türker, 1997). There are several methods available for metal ion removal and recovery and among these techniques, precipitation is the most widely used because of its simplicity and cost effectiveness. For precipitating the metal as hydroxide, the solution pH was adjusted to the optimum range. In addition, an electrogenerative system (Yap & Mohamed, 2007), ion-exchange resins (Iglesias et al., 1999), cementation (Cui & Zhang, 2008; Quinet et al., 2005), electrodialysis (Sadyrbaeva, 2012), electrowinning (Urbanski et al., 2000) and biosorption (Tay et al., 2013) are the examples of other methods that have been used to recover gold. However, high capital costs are involved in using ion-exchange resins, with strong acid and alkaline solutions being required to regenerate the resins. Metal recycling deals mostly with dilute solutions in low amounts of metal. Hence, in order to control the side reactions there are many factors that should be considered, such as thermodynamics and kinetics of the systems along with the cost of operating.

An ideal solution to solve this problem would be a system that recovers and recycles both metal and water without any need for an external power supply. Therefore, an electrogenerative system or process was introduced to ease the operation of the system, scaling up the system as well as lower the operating cost. In this system, an external flow of current was generated by an electrochemical reaction which takes place spontaneously in a divided cell where a less noble metal anode is oxidized and a more noble metal of high purity is deposited at the cathode. Besides, it also allows for simplicity and for providing a clean electrochemical system that can be applied for fuel cells.

In previous work by Yap and Mohamed (2007), an alternative technology to the current recovery was introduced as an electrogenerative system. The recovery of Au(III) was carried out using a batch cell with different cathode materials. It was found that, in 1 h of operation, activated RVC was the best cathode material than the other electrodes studied with more than 99% of Au(III) recovered. According to Yap and Mohamed (2008) studies, electrolyte flow rate is an important factor for Au(III) recovery in a flow-through. The rate recovery increased when electrolyte flow rate increased for lower gold concentrations. But an optimum flow rate has been determined to achieve highest Au(III) recovery. In this case, the transport of electroactive species to the electrode surface indirectly involved because of the flow rate factor on Au(III) recovery. About 99% of Au(III) was recovered by flow-through reactor within 4 h operation (Yap & Mohamed, 2008).

1.2 Electrogenerative system and its working principle

An electrogenerative process is a galvanic process. The galvanic process is an electrochemical process which a chemical reaction that occurs in a system produces an electrical current. From the thermodynamics view, the Gibbs free energy change, $\Delta G°$, produced is negative for a spontaneous reaction system. Thus, for an electrogenerative process the equation can be written as following:

$$\Delta G° = -nFE°_{cell} = -nF(E_c - E_a)$$

where n is the number of electrons accepted or released by the reaction per mole of reactant, F is a Faraday's constant, $E°_{cell}$ is the overall cell potential, E_c is the standard reduction potential at cathode and E_a is the standard reduction potential at anode. In an electrogenerative process, a chemical reaction takes place spontaneously in a divided cell where a more noble metal is reduced at the cathode and a less noble metal is oxidized to produce electrical energy without an external supply of energy. The roles of these metals as oxidizing and reducing agents are determined by referring to the reduction electrode potentials. The metal ions with more electropositive reduction potentials tend to undergo reduction.

1.2.1 Electrogenerative reactors

Electrogenerative reactors are operated by two coupled electrode reactions. The electrical flow is made through an external wires and current collectors attached to the anode and cathode. A voltmeter is used to measure the overall cell voltage. Generally, by the good choice of anode and cathode materials, specific redox reaction which is thermodynamically favorable can be utilized for metal recovery. Selectivity and the rate of reaction can be controlled by varying the electrode potential using a resistance load in circuit and using suitable electrodes. In electrolytic cells, the selectivity of the system depends on the cathode potential applied to the electrode.

1.2.2 Reactor design and operation modes

In general, electrogenerative reactors can be operated in a batch or continuous mode. Examples of batch reactors are static batch reactor, single-pass reactor and batch-recycle reactor. The flow reactor can be classified in two groups, flow through or flow-by systems as described in Figure 1.1 (Pletcher & Walsh, 1992). The classification is based on the direction of the solution flow with respect to the electrical current through the anode and cathode. When the direction of the solution flow and electrical current flow is perpendicular to each other, it is called a flow-by system. If these directions are parallel to each other, it is called a flow-through system. Figure 1.1 shows the schematic diagram of a flow-by and flow-through system with respect to the directions of current and solution flow. The reactors shown in Figure 1.1 contain two compartments in the cell assembly. Besides, the reactor can be congregated with multiple electrode pairs or multiple reactors which can be gathered in series or in parallel in order to increase the cells accomplishment.

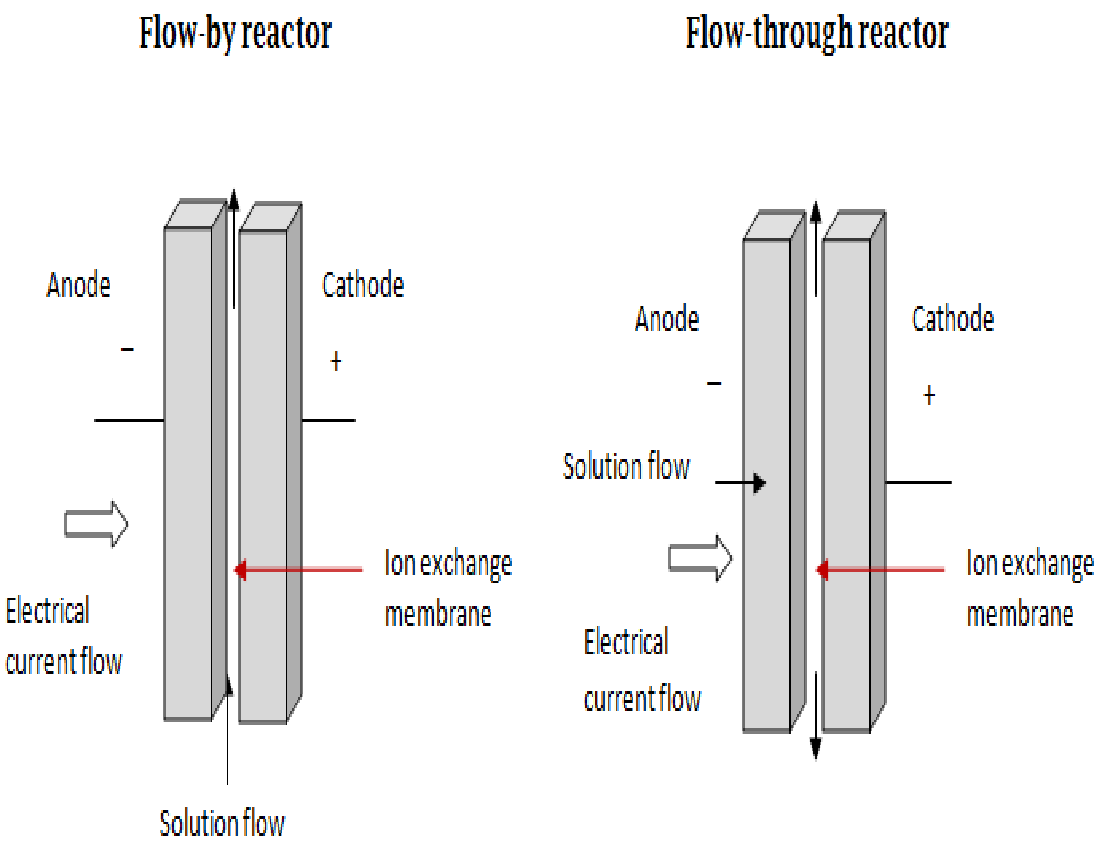

Figure 1.1 Flow-by and flow-through reactor configurations.

1.3 Electrode materials

Electrode is the most important component in the electrochemical reactor. There are two types of classification of electrode which is two and three-dimensional electrodes. These electrodes can be moving such as the rotating disc electrode or rotating cylinder. The movement of electrode contributes to high mass transfer rates while the use of porous, three-dimensional electrode contributes to high surface area. Even at low metal ion concentration, three-dimensional electrodes are more superior compared to the two-dimensional (Pletcher & Walsh, 1992; Walsh & Reade, 1994; Walsh, 2001). Three-dimensional electrodes have their inherent properties; its high surface area to volume ratio and porosity allow the metal ions to be distributed throughout the electrode. This arrangement can overcome the limitation of mass transport and small specific surface area (Min et al., 2012). Examples of the three-dimensional electrodes in are porous graphite electrodes (PG) and reticulated vitreous carbon (RVC). Among the choice of 3D electrodes that being used are fluidized bed electrodes (Rajeshwar et al., 1994), packed bed electrodes (Leon & Pletchert, 1996; Pletcher et al., 1991), carbon felts and reticulated polyurethane (Friedrich et al., 2004).

RVC electrode has a honeycomb structure as shown in Figure 1.2 and open pore foam material composed solely of vitreous carbon. The structure of RVC is attained by polymerization of resin combined with foaming agents, followed by carbonization. A pore size of RVC is usually described as number of pores per inch (ppi). RVC is suitable to be used as an electrode material especially in flow reactor because it is a high voids volume, highly porous surface area, low electrical and fluid flow resistance. It is chemically inert, hydrodynamic and the structural advantages of its open-pore foam structure make it an attractive electrodes material. The brittle of the skeletal structure needs support and low volumetric carbon content to ensure the potential and current distribution through the material.

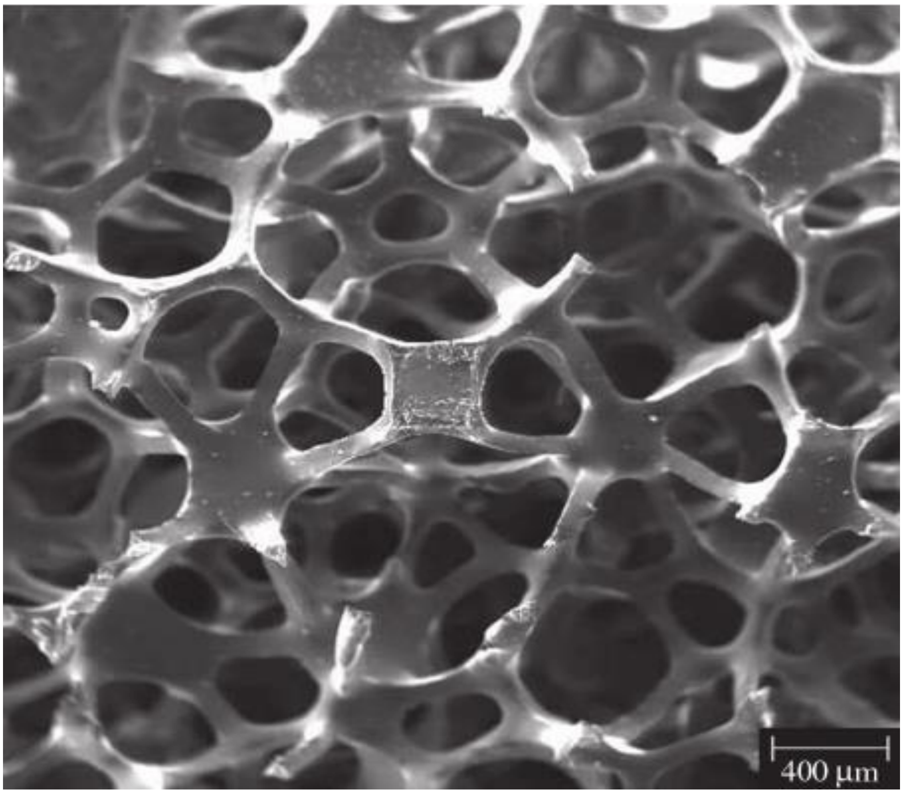

Figure 1.2 Scanning electron micrograpy (SEM) micrograph that shows the three- dimensional honeycomb sructure of RVC 400 × magnification (Pierson, 1993).

Porous graphite is one of the allotropes carbons and it is composed of layers of carbon atoms that are arranged in six-membered, hexagonal rings. These rings are attached to one another on their edges. Layers of fused rings can be modeled as an infinite series of fused benzene rings (without the hydrogen atoms) in Figure 1.3. Carbon atoms in these ring arrays are in the sp^2-hybridized state. In the sp^2 molecular orbital model each carbon atom is attached to three other species carbon atoms in the case of graphite. Porous graphite can manage electricity due to the vast electron delocalization within carbon layers. These valence electrons are free to move and are able to conduct electricity.

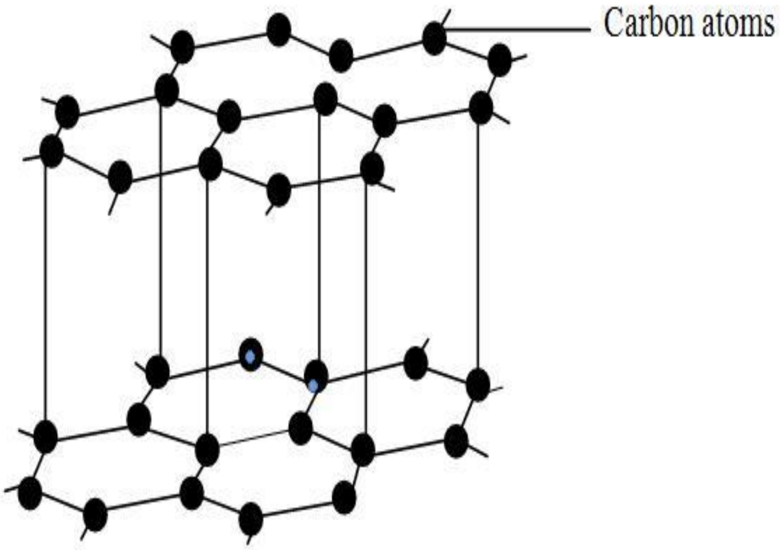

Figure 1.3 Three-dimensional schematic of the graphite structure (Pierson, 1993).

1.4 Ion-Exchange membranes

Ion-exchange membranes also play an important role in electrogenerative system. The membrane functions as a separator between anolyte and catholyte of different compositions which enforces the selectivity in migration of ions between both compartments. There are two classifications of ion-exchange membrane which is an anion exchange membrane and the cation exchange membrane. The anion exchange membrane (AM-1 Neosepta, Tokuyama Corp.) was used in this study. The anion exchange membrane was only permeable to anions. Since positive-charged groups are fixed to anion exchange membrane (Figure 1.4), cations are rebuffed by positive charges (repulsion occur between species of similar charges) and cannot permeate through anion exchange membrane. The Neosepta anion membrane has superior characteristics such as high ionic permeable-selectivity, low electric resistance, low diffusion coefficient, high mechanical strength, high chemical stability and high dimensional stability (Davis et al., 1997).

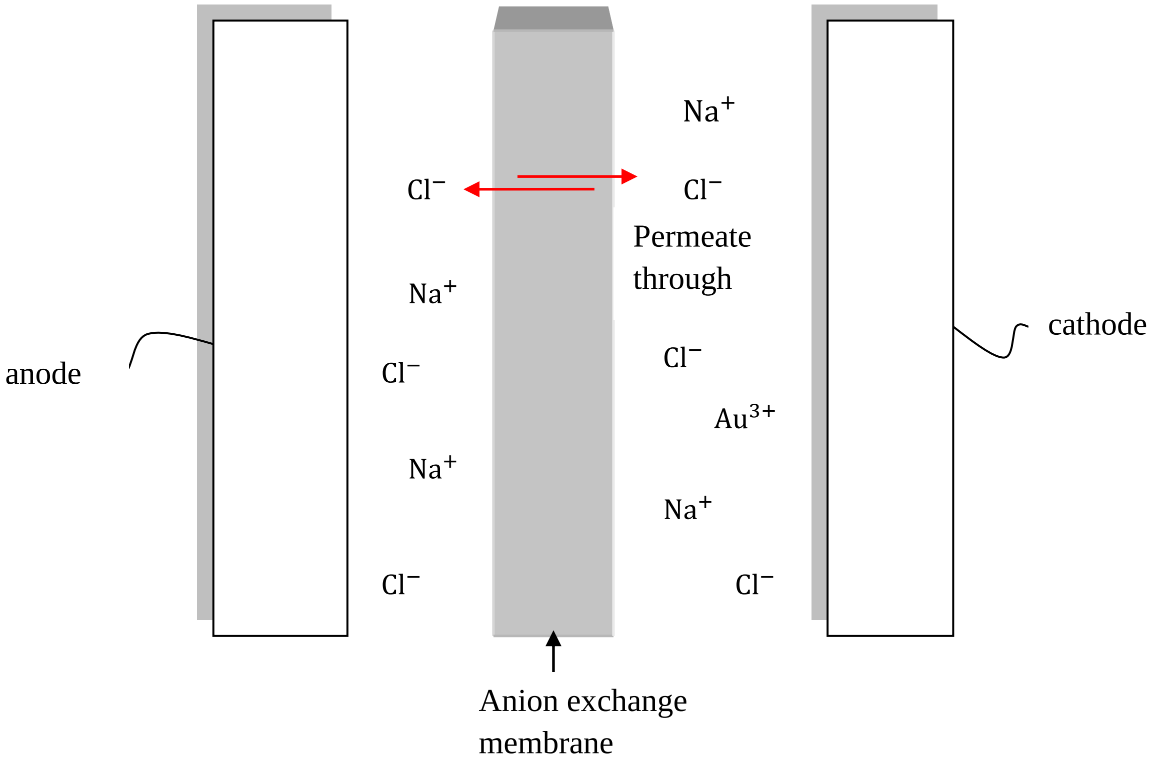

Figure 1.4 Schematic diagram of ion-exchange membrane principle in this study.

1.5 Problem statements

Cyanide is a very powerful ligand which can easily react with gold ions to remove it out from various ore mixtures. Cyanide also the most used leachant for extracting gold from E-waste. However, cyanide extensively used as a strong ligand to leach gold but it has a high toxicity especially in laboratory and industrial scales. Treatment technologies such as electrowinning or electrolytic cannot fully recover Au(III). This project attempted to find an electrogenerative system in which can fully recover Au(III) and to determine the optimum condition to recover gold from E-waste.

1.6 Research aims and objectives

The aim of this study is to evaluate the recovery of Au(III) from chloride solution by an electrogenerative process using different cathode materials. Previously, the recovery of gold by using an electrogenerative process is only performed on gold cyanide solution (Yap & Mohamed, 2007; 2008a).

This study will focus more on the recovery of gold from chloride media by using an electrogenerative system in terms of optimum conditions for maximum Au(III) recovery and the purity of the Au(III) deposited on the cathodes. The feasibility of Au(III) recovery from dilute chloride solutions using a lab scale was applied to E-waste (industrial waste) sample by using flow cell system also investigated. The performance of the system was evaluated as a function of different cathode materials, initial Au(III) concentration, different number of flow cells, the presence of oxygen in the chloride solution, the supporting electrolyte and cathode potential. SEM-energy dispersive X-ray spectroscopy (SEM-EDX) analyses was carried out on Au(III) deposited to confirm and characterize the metallic gold was deposited on RVC cathode.

Overall objectives of this study are as follows:

i. To evaluate the recovery of Au(III) from chloride solution by an electrogenerative process using different cathode materials.

ii. To investigate the optimum condition for the recovery of Au(III) in sodium chloride medium by using a batch cell and a flow-through cell.

CHAPTER 2: LITERATURE REVIEW

2.1 Treatment technologies

The rapid growth of industries has resulted in the generation of large amounts of effluents that contain heavy metals. Apart from industries of gold, the constantly increased value of gold metal frequently makes recovery process important. Therefore, treatment of gold-bearing wastewater usually involves removal and recovery processes. Besides, heavy metals are non-biodegradable, toxic and carcinogenic agents. The release of heavy metals into the environment has become of great concern in recent years due to their hazardous effects. The concentration of metal ions in effluent solutions is normally < 1000 mg L^{-1} (Walsh, 2001). Laws and acts had been proposed to restrain and lower the concentration of heavy metals to below their permissible levels before being discharged into the environment. In view of these issues, various treatment technologies have been exploited to remove and recover metal ions from process solutions. These are described as follows: electrodialysis, ion-exchange, adsorption, cementation, precipitation and electrowinning processes.

2.1.1 Electrodialysis

Electrodialysis is a process involving a selection of ion exchange membranes positioned between a pair of electrodes. The applied voltage drives the flow of ions in solution and the membrane selectively transports ions having positive or negative charges and reject ions of the opposite charge. Removal, separation and pre-concentration of ions can be achieved using this method. The electrodialysis method was applied in removal and recovery of nickel and copper ions from wastewater (Cifuentes et al., 2004; Ogutveren et al., 1997; Spoor & Bertazzoli, 2002; Wong et al., 2002). Millmam and Heller (1982) demonstrated the successful application of the electrodialysis method in a gold plating operation. Electrodialysis was operated at the drag-out rinse following the plating bath. Ions exchange resins were used for the second rinse to recover the remaining gold. Gold recoveries up to 99% were achieved and the concentrate recovered by electrodialysis was returned directly to the plating tank. However, there is a problem about membrane durability which can potentially increase the cost. Electrodialysis has inherent weakness where it is less efficient to remove non-charged, higher molecular weight and less mobile ionic species. Janssen and Koene (2002) reported the fouling of an ion exchange membrane due to clogging would decrease the efficiency of the electrodialysis system.

2.1.2 Ion exchange

Interchange of ions between two electrolytes or between an electrolyte solution and a solid phase is called an ion exchange (Qureshi & Varshney 1991). In most cases the term is used to denote the processes of purification, separation and decontamination of aqueous and other ion-containing solutions with polymeric or mineralic ion exchangers. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. Mendes and Martins (2005) investigated the ion exchange using a chelating resin had been used to remove cobalt. For recovery of gold, an anion exchange membrane was used in the galvanic cementation process. An anion exchange membrane was only permeable to anions (Chang et al., 2007). However, this method is often costly and not all ion-exchanger membrane is suitable and available for all metal ions (Jüttner et al., 2000).

2.1.3 Adsorption

Adsorption is another method which is widely employed in metal recovery. Adhesion of a chemical species onto the surface of particles opposed to absorption in which the molecules actually enter the absorbing medium is called adsorption. Gold cyanide or gold chloride complexes are strongly adsorbed on activated carbon (Adam & Fleming, 1989; Cho et al., 1979; Jia et al., 1998). Although the mechanism has not been fully explained, this recovery system gained wide acceptance in the mining industry. Heap leaching of gold with alkaline sodium cyanide in mining industries will typically produce very dilute solutions containing 0.5-10 mg L^{-1} of gold. The pregnant solution is then transferred to a series of tanks, where carbon is added. The gold is adsorbed onto the surface of the carbon. The carbon with gold attached, is removed by screening. The gold bearing carbon is then passed through a stripping vessel containing heated sodium hydroxide-cyanide-water solution where gold is desorbed. After the stripping process, the activated carbon can be regenerated. This pre-concentration step will subsequently produce solutions of 50-2500 mg L^{-1} of gold. Gold ions eluted from the adsorbents are not in their metallic state and will be subjected to electrolytic recovery or cementation (Barbosa et al., 2001; Stavart et al., 1999).

2.1.4 Cementation

Studies by Cao and Duby (2001) explained that a cementation process is the simplest and oldest hydrometallurgy process. It is a metal displacement reaction where metal ions from an aqueous solution are precipitated spontaneously by a relatively more electropositive metal. Zinc dust was used in the Merril-Crowe process to recover gold from cyanide solution (Gupta et al., 2014). The solution is deoxygenated and soluble lead salts are added to the solution to inhibit passivation of the zinc surfaces which increase the cementation rate (Yannopoulos, 1991). Unfortunately, the resulting product is physically inseparable. The overall chemical reaction is described as follow in Equation 2.1.

$$Zn + Au(CN)_2^- + H_2O + 2CN^- \rightleftharpoons Au + Zn(CN)_4^{2-} + OH^- + 0.5\,H_2O \qquad (2.1)$$

There are two types of behavior of kinetics in the cementation process. The first type was explained the cementation rate is initially slow followed by enhanced rate (faster rate). This is maybe due to large of surface area by deposits, the separation of zero concentration and zero velocity planes near the precipitant metal surface. While the second type, the cementation rate decreases with time due to the formation of the smooth deposits in which results in the difficult diffusion of ions through this layer (Chaudhury & Bhattacharya, 1989). Grosse et al. (2003) found the disadvantages of the cementation process are the other metal ions will be precipitated as well and thus the accompanying metal ions are needed for recycling.

2.1.5 Precipitation

A removal of a dissolved metal in cationic form was involved in precipitation. Studies by Szabadváry (1992) found that the cations are converted to an insoluble form (particle) by a chemical reaction between the precipitating reagent and the soluble metal compounds. The particles formed by this reaction are removed by filtration or resolving from solution. Huang et al. (2004) and Oustadakis et al. (2006) carried out the removal of cobalt through the precipitation process. The precipitation process has economical limitations and the effectiveness of this process is dependent on several factors, including the type and concentration of ionic present in solution, the reaction conditions (especially pH of the solution), the precipitant used and the presence of other constituents that may inhibit the precipitation reaction. The generation of secondary pollutants due to sludge that remains after treatment is the major drawback of this process (Gasparotto et al., 2006; Lanza & Bertazzoli, 2000; Njau et al., 1998).

2.1.7 Electrowinning or electrolysis

Electrolysis can recover gold from solutions, a process that is known in extractive metallurgy industry as electrowinning. A metal can be deposited on negative electrode when two electrodes which are cathode and anode are placed in a solution containing metal ions and electric current is passed between the electrodes. In the recovery of most metals, oxygen evolved from water at the positive electrode. The selection of an electrolyte and a current density generally as to give dense, compact electrodeposits and some addictives should be considered in the electrolyte to further improve product quality.

There are numerous workers negotiating with the electrowinning of gold either from electroplating wastes or mining industries (Barbosa et al., 2001; Reyes-Cruz et al., 2002, 2004; Spitzer & Bertazzoli, 2004; Starvart et al., 1999). Starvart et al., (1999) used carbon felt as the electrode material in a three-dimensional cell and it was found that gold concentration reduced successfully from 30 to 20 mg L^{-1} with current efficiencies from 6% to 12% being achieved.

Actually, Barbosa et al. (2001) used a modified Zadra cell with two different types of cathodes, mild steel wool (MSW) and a stainless steel mesh coil (SSM). The results showed that SSM was a better cathode material compared to MSW in recovering the terms of gold recovery due to distribution of surface area and homogeneity, which allows a better flow of electrolyte solution through it, avoiding the bypass of electrolyte. More than 90% of gold can be recovered with suitable cathode material. It was found that pH of gold cyanide solution has a big impact in the electrolyte conductivity during the electrowinning process.

Reyes-Cruz et al. (2004) managed to recover of 26% of gold and 48% of silver by using a three-dimensional electrochemical reactor (FMDL-LC) with a RVC electrode. While Spitzer and Bertazzoli (2004) used a filter-press type electrochemical reactor and were able to increase the recovery of gold from 67% to 90% of gold, 90% to 95% of silver and 10% to 20% of copper with current efficiencies ranging from 15% to 23%. They used RVC as the cathode for the reported process.

However, electrowinning or electrolytic techniques have disadvantage in which it needs current. When dealing with low concentration of previous metal ions, such reaction as oxygen and water reduction will occur that cause low current efficiencies in the system (Grosse et al., 2003).

2.2 Electrochemical processes

Electrochemical processes are described both as an electrolytic and galvanic processes. The processes are heterogeneous in nature as the reactions are taking place at the interface of the electrode and the electrolyte (Jüttner et al., 2000). Electrochemical processes involve redox reactions where an electron is transferred to or from a molecule or ion by changing its oxidation state. This reaction can occur through the application of an external voltage or through the release of chemical energy. Electrolytic removal of metal had been studied by most authors. The electrolytic removal of lead had been studied by Ponce-de-Leon and Pletchert (1996), Widner et al. (1998) and Gasparotto et al. (2006). Pradhan et al. (2001) and Sharma et al. (2005) had managed electrowinning of cobalt from sulphate solutions while Mishra et al. (2002) had carried out electro-reduction of cobalt. However, the electrolytic process is not cost effective when dealing with very dilute solutions with low metal ion concentrations as parasitic reactions would take place, reducing the current and removal efficiency (Almeida et al., 2008). So, in order to achieve higher recovery, high electrical power input required which would increase the operating costs. Therefore, an electrogenerative process (galvanic process) is introduced as an alternative to the electrolytic process due to less of operating cost and removing metal ions at the same time.

2.2.1 Mass transport studies

There are three forms of mass transport, namely convection, diffusion and migration (Pletcher et al., 1993). Definition of convection is the movement of species due to mechanical forces. Normally, it is influenced by electrode rotation, flowing of electrolyte through the reactor and stirring of solutions. The convection can be classified as forced and free convection. The forced convection can occurs by external influence such as stirring while free convection occurs spontaneously due to temperature variations.

Diffusion is the movement of species down a concentration gradient. Diffusion is described by Fick’s first law as following equation:

$$\mathrm{J_i} = -\mathrm{D_i}\frac{\partial \mathrm{c_i}}{\partial_\mathrm{x}} \tag{2.2}$$

where, $\mathrm{J_i}$ is the flux of species I of concentration $\mathrm{c_i}$ in the x direction, and $\frac{\partial \mathrm{c_i}}{\partial_\mathrm{x}}$ is the concentration gradient. D is the proportionality constant known as diffusion coefficient. In aqueous solution, its value approximately varies between 10^{-5} and 10^{-6} cm^2 s^{-1}. An electrochemical reaction converts a reactant to a product at the surface of electrode. There is a boundary of a layer adjacent to the electrode surface where concentration of reactants and products in the boundary layer is lower and higher than the bulk solution respectively. Hence, reactants will diffuse from the bulk solution to the electrode surface while products will diffuse away from it.

Migration is the movement of charged species due to a potential gradient. The balancing of the current of electrons through an external circuit by the way of ions through the membrane is necessary. If the reaction is consist of high concentration of inert electrolyte in solution, most of the charges will be carried by those inert species and less of electroactive species is transported by migration.

2.2.2 Kinetic studies of electrochemical reactions

Bertazzoli et al. (1997) proposed a model of concentration-time relationship for three-dimensional electrodes can be expressed by Equation (2.3) under mass control:

$$\ln\left[\frac{\mathrm{Ct}}{\mathrm{Co}}\right] = -\frac{V_e}{V_R}\, k_m A_e\, t \qquad (2.3)$$

where C_t is metal concentration at time t, C_o is defined as the initial concentration, k_m is the mass transport coefficient, A_e is the specific surface area of cathode, V_e is the volume of catholyte and V_R is the volume of electrolyte within the reactor. As the effective electrode area is quite difficult to determine to the surface area changes that involved during the recovery process, the ‘volumetric’ mass transport coefficient value will lead to a clear understanding of the comparative performance of the different cathode system (Walsh & Reade, 1994).

Walsh and Reade (1994) stated that $k_m A_e$ and $k_m A_s$ exist as the figures merit for three-dimensional electrode systems and two-dimensional electrode systems respectively. A_s is represent the active electrode area per unit reactor volume which can be defined by Equation (2.4) :

$$A_s = \frac{A}{V_R} \qquad (2.4)$$

The values $k_m A_e$ and $k_m A_s$of can be obtained from the slope of the graph in which representing the rate constant that involved on recovery of gold.

2.3 Application of electrogenerative process for environmental studies

2.3.1 Electrogenerative leaching of sulphide minerals

A chemical energy released from leaching process is transformed to applicable electrical energy in electrogenerative leaching and the purification process is simplified simultaneously. In 1992, Zhang et al. (1992) found out the electrogenerative leaching of Ni_3S_2 with ferric chloride. A dual system separated by an ion exchange membrane was utilized with the sulphide minerals working as anodic materials. Electrogenerative leaching were performed by Wang et al., with various sulphide minerals such as sphalerite (Wang et al., 2006), galena (Wang et al., 2003), nickel sulphide concentrates (Wang et al., 2004) and chalcopyrite concentrates (Wang & Fang, 2006; Wang et al., 2006). Reduction of ferric ions on platinum or the reduction of MnO_2 in acid solution was occurred at the cathode. Instead of producing pollutants as example sulphur dioxide and hydrogen sulphide as in traditional leaching processes, the oxidation of sulphide ores using electrogenerative process produced elemental sulphur (Juarez et al., 2006).

2.3.2 Recovery and removal of copper

The galvanic cementation of copper was used as an initial model system for developing the electrogenerative system and has been among the most extensively studied to-date. Kumar and Vasu (1973) were investigated this system but surprisingly the studies only received little attention. In addition, the authors reported the use of rotating copper foil cathode and a rotating mild steel anode which shown resulted more than 99% purity of copper with minimum anode