

**REMOVAL OF COBALT FROM AMMONIUM
CHLORIDE SOLUTIONS USING A BATCH CELL
THROUGH AN ELECTROGENERATIVE
PROCESS**

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PROCESS**

by

CHEANG CHOR YEE

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LIST OF SYMBOLS

A_e	specific surface area, m^2
C_0	initial metal concentration, mol m^{-3}
C_t	metal concentration at time t , mol m^{-3}
E°	standard reduction potential, V
E°_{cell}	overall cell potential, V
F	Faraday's constant, C mol^{-1}
ΔG°	standard Gibb's free energy, J mol^{-1}
k_m	mass transport coefficient, m s^{-1}
n	number of electrons, mol
t	time, s
V_e	cathode volume, m^3
V_R	volume of the electrolyte, m^3

LIST OF ABBREVIATIONS

2D	two-dimensional
3D	three-dimensional
AAS	atomic absorption spectrometer
AC	activated carbon
CP	cell performance
Cyanex-272	bis-(2,4,4-trimethylpentyl)phosphinic acid
D2EHPA	di-(2-ethylhexyl)phosphoric acid
EDX	energy dispersive X-ray
HER	hydrogen evolution reaction
PC 88A	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
ppi	pores per inch
PVA	polyvinyl alcohol
RVC	reticulated vitreous carbon
SCE	saturated calomel electrode
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
TIBPS	triisobutyl phosphine sulfide
UF	ultrafiltration

**PENYINGKIRAN KOBALT DARIPADA LARUTAN AMONIUM KLORIDA
MENGUNAKAN SEL BERKELOMPOK MELALUI PROSES
ELEKTROGENERATIF**

ABSTRAK

Suatu sistem elektrogeneratif digunakan untuk menyingkirkan kobalt daripada larutan amonium klorida. Dalam proses ini, suatu tindak balas kimia berlaku secara spontan di mana kobalt diturunkan di ruangan katod dan zink dioksidakan di ruangan anod tanpa bekalan tenaga dari luar. Sistem elektrogeneratif untuk menyingkirkan kobalt telah dipertunjukkan dalam sebuah reaktor berkelompok dengan menggunakan elektrod tiga-dimensi: 80 liang per inci (ppi) karbon kaca berongga (RVC) sebagai bahan katod. Kajian atas penyingkiran kobalt daripada larutan amonium klorida telah dilaksanakan dengan menggunakan amonium klorida sebagai media elektrolit pendukung. Pengaruh atas kepekatan katolit dan elektrolit pendukung atas penyingkiran kobalt telah dilaksanakan dengan mengubah kepekatan awal kobalt dan kepekatan amonium klorida masing-masing. Keputusan menunjukkan bahawa 0.5 M amonium klorida merupakan kepekatan optimum bagi penurunan kobalt lebih daripada 95 % selepas beroperasi selama 4 jam dengan kepekatan awal Co(II) sebanyak 200 mg L⁻¹. Keputusan yang diperoleh menunjukkan bahawa RVC bersesuaian sebagai bahan katod dalam sistem ini kerana tenaga bebas yang tinggi sebanyak - 403.89 kJ mole⁻¹ telah dihasilkan dalam proses elektrogeneratif. Pada keadaan optimum, prestasi sel sebanyak 85.6 % telah diperoleh dengan penyingkiran kobalt sebanyak 100 % daripada 200 mg L⁻¹ Co²⁺ dalam 0.5 M NH₄Cl. Pengaruh atas kawalan pH telah dikaji pada pH 7 untuk meningkatkan penyingkiran kobalt. Morfologi kobalt yang diendapkan telah

diperhatikan dengan mikroskop pengimbasan elektron (SEM). Sistem elektrogeneratif ini juga berjaya membuktikan kemungkinan penyingkiran ion serentak dengan kehadiran ion-ion kuprum dan nikel.

**REMOVAL OF COBALT FROM AMMONIUM CHLORIDE SOLUTIONS
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ABSTRACT

An electrogenerative system is applied to remove cobalt from ammonium chloride solution. In this process, a chemical reaction takes place spontaneously where cobalt is reduced at the cathode compartment and zinc is oxidized at the anode compartment without the supply of external energy. The electrogenerative removal of cobalt was conducted in a batch reactor using a three-dimensional electrode: 80 pores per inch (ppi) reticulated vitreous carbon (RVC) as cathode material. Studies of removal of cobalt from ammonium chloride solution were accomplished using ammonium chloride as supporting electrolyte medium. The influence of catholyte and supporting electrolyte concentrations on cobalt recovery were carried out by varying the initial cobalt concentrations and ammonium chloride concentrations respectively. The results showed that 0.50 M of ammonium chloride was the optimum concentration with < 95 % of cobalt being removed from an initial Co(II) concentration of 200 mg L⁻¹ in 4 h of operation. Results obtained showed that RVC serves as a suitable cathode material in the system as a high value of free energy (- 403.89 kJ mole⁻¹) was generated in the electrogenerative process. At optimum conditions, cell performance of 85.6 % with 100 % cobalt recovery was obtained from 200 mg L⁻¹ of Co²⁺ in 0.5 M NH₄Cl. The influence of pH adjustment was examined at pH 7 to improve cobalt recovery. The morphology of cobalt deposited was also observed by scanning electron microscopy (SEM). Use of the

electrogenerative system had also successfully demonstrated the feasibility of recovery of co-ions simultaneously in the presence of copper and nickel ions.

CHAPTER 1

INTRODUCTION

1.1 Cobalt

It is a hard ferromagnetic, silver-white, lustrous and brittle metal. Cobalt is a non-biodegradable heavy metal and chemically active, so cobalt is usually not found as pure metallic element in nature. It commonly occurs in sulfide minerals, associated with copper, nickel and iron in sulfide mineral deposits, or occasionally as cobalt arsenide.

Since cobalt is of low relatively abundance on Earth's crust and natural water, cobalt is not usually mined alone. It is produced as a by-product in the mining process of nickel and copper ores; however, only small amount of cobalt can be extracted from the mining process. Due to the least abundance of cobalt and the high consumption of cobalt in industries, treatment or recovery of cobalt from the industrial wastes are deemed important to solve the problem of scarce production of cobalt.

1.2 Health Concerns

Cobalt is beneficial and a trace mineral in our human body because it is needed for the production of vitamin B₁₂ to stimulate the production of red blood cells. However, cobalt is a non-biodegradable heavy metal and tends to accumulate in our environment. As cobalt is widely dispersed in the surroundings, humans may be exposed to very high levels of cobalt by breathing air, drinking water and eating food. Prolonged exposure to cobalt can give rise to disorders in humans such as causing lung effects including asthma, pneumonia, gastric disturbance with the

symptoms of vomiting and nausea, as well as heart problems and thyroid damage (Suh, Thompson, Brorby, Mittal, & Proctor, 2016). This will cause acute and chronic toxicity to marine life as well (Norwood, Borgmann, & Dixon, 2007). The effects of the use of cobalt in surgical implants, for example the high level of cobalt released by metal-on metal total hip arthroplasties have been reviewed and reported (Simonsen, Harbak, & Bennekou, 2012; Apostoli et al., 2013). Based on the guidelines from Food and Agriculture Organization of the United Nations (FAO) and Ministry of Water, Land and Air Protection, the recommended maximum concentration of cobalt species (predominately Co^{2+} and Co^{3+}) in irrigation water and livestock watering are 50 and 1000 $\mu\text{g L}^{-1}$ respectively. However, there is insufficient data to develop a water quality guidelines to protect marine life from cobalt (Ayers & Westcot, 1994; Nagpal, 2004). Since cobalt receives less attention in Malaysia, discharge of cobalt from industrial effluent is not listed in Department of Environment (DOE) Malaysia. Therefore, to prevent the high toxicity of cobalt in water system, the treatment of cobalt from industrial effluents as well as artificial wastewater is of major concern (Hussain, Din, Nayab, & Islam, 2013).

1.3 Application of Cobalt in Industries

Cobalt is diversely used in many industries due to several of its unique properties. Along with the growth in automotive and electronic fields, the demand of cobalt became predominant as cobalt is required in the manufacture of electronic devices. Due to its magnetic properties, cobalt is suitable in the production of superalloys. These high performance cobalt-base alloys which are resistant to high temperature and corrosion are used in jet turbines and gas turbine generators. Cobalt

can be magnetized and uses as a magnet when alloyed with aluminum and nickel (Cobalt and Cobalt Alloys, 2015).

The use of cobalt in battery technology has increased because the demand for portable rechargeable electronic devices such as camcorders, portable telephones and laptop computers has grown rapidly. A huge amount of cobalt needed to meet the demand in battery production (Cobalt demand grows, 2017). Cobalt salts which carry the physical properties of transition metals have been used to produce the brilliant blue colour in paint, glass, pottery and ceramic pigments. Another important use of cobalt compounds is as catalysts, which is commonly used in the petrochemical and plastic industries. In the Gas-to-Liquid (GTL) technology, cobalt is used as the catalyst to allow a high selectivity to desired products, has a high mechanical resistance and a high sustained activity with long-term low deactivation rates. Cobalt is also widely used in cancer treatment as it is an important source of gamma rays (The Cobalt Development Institute, 2006; Cobalt, 2012).

1.4 Waste Treatment Technologies

Due to the rapid growth and high consumption of cobalt in industries, especially in developing country, the treatment or recovery of cobalt from industrial waste is important because cobalt is produced as a by-product of the mining and processing of copper and nickel ores and only a small amount of cobalt will be produced from the extraction of the ores. Another concern of the importance of the recovery of cobalt from industrial waste is due to the recalcitrance and persistence of heavy metals in the environment. Therefore, various methods for heavy metal removal from effluent were studied extensively in recent years to minimize the

concentration of heavy metals in the industrial effluents (Fu & Wang, 2011). In view of these issues, treatment techniques for the removal of cobalt such as chemical precipitation, ion exchange, adsorption, membrane filtration, solvent extraction and electrochemical processes are discussed at length as follows.

1.4.1 Chemical Precipitation

Precipitation removes a dissolved metal which is in the ionic form from a solution. The ionic metals are converted to an insoluble particle by chemical reactions between the soluble metal compounds and the precipitating reagent. The particles are further processed by settling and filtration to be effectively removed from the solution. Although chemical precipitation is a simple and inexpensive process, it is ineffective when dealing with low concentration of metal ions and it is not economically friendly as large amount of sludge was retained after treatment. The effectiveness of the precipitating process is affected by several factors, such as the concentration of ionic metals in the solution, the precipitant used, the reaction conditions (pH of the solution), and the presence of other constituents that may inhibit the precipitation reaction. Cobalt removal from simulated wastewater by ferrite co-precipitation was done by Becker, Rodríguez, & Schwab (2012). The application of ferrites became an attractive alternative compared to conventional precipitation treatment as they have the spinel structure and ferromagnetic behavior. The incorporation of the cobalt ions to the ferrite structure formed precipitations which are chemically stable and being ferromagnetic that can be removed magnetically. In the work done by Becker *et al.* (2012), efficiency of 99 % cobalt incorporation to the ferrite structure was obtained and successfully removed by magnetic removal.

1.4.2 Ion Exchange

Ion exchange is a technique that involves an interchange of ions between two electrolytes, or between an electrolyte solution and a solid phase. There are two types of ion exchangers: cation exchanger that exchange positively charged ions (cations) and anions exchanger that exchange negatively charged ions (anions). The advantages of using ion exchange are high treatment capacity, high removal efficiency and fast kinetic. However, the major drawback of this method is the regenerated ion exchange resin by chemical reagents when they are exhausted, which can cause serious secondary pollution. There are some studies on cobalt recovery by using an ion exchange method done by Mendes & Martins (2005) and Xiong, Feng, Yao, & Shen (2010). In the study by Mendes & Martins (2005), a polymeric resin, Amberlite IRC 748® was selected in the application of resin-in-pulp (RIP) technology for the extraction of nickel and cobalt. The result concluded that nickel and cobalt would probably co-extract where the total recovery of cobalt from liquid and solid phase was 99.7 % and 20.0 % respectively. A macroporous strong acidic exchange resin (NKC-9) was used by Xiong *et al.* (2010) as a new adsorbent material for removal of cobalt ion from aqueous solutions. Compared to other adsorbents, NKC-9 resin showed a maximum adsorption capacity of 361.0 mg/g for Co(II) recovery. The result reported that the Co(II) adsorbed by the resin can fully be desorbed by 0.5 mol/L HCl eluent solution.

1.4.3 Adsorption

Adsorption is the adhesion of a chemical species onto the surface of a solid or a liquid (adsorbent). Activated carbon (AC) adsorbent is widely used due to its large micropore and mesopore volumes and the resulting high surface area (Fu & Wang,

2011). However, the depleted source of commercial coal-based AC results in the increase of price, therefore low-cost adsorbents from agricultural wastes, industrial by-products and natural substances have been reviewed to replace AC (Gu & Evans, 2008; Wan Ngah & Hanafiah, 2008; Parab et al., 2010). Kyzas, Deliyanni, & Matis (2016) had carried out a study to investigate the use of AC for the removal of Co(II) ions from synthesis wastewater. The waste potato peels was chemically activated by phosphoric acid (H_3PO_4) and served as adsorbents for Co(II) ions. The adsorption performance of cobalt was affected by the surface area, pore size distribution, and surface chemistry of AC. From the study, result showed a better contribution of cobalt onto a larger pores AC.

1.4.4 Membrane Filtration

Membrane filtration technology gives the advantages of high removal efficiency and space saving but its problems such as high cost, membrane fouling and low permeate flux have limited the use of this technology in heavy metal removal. A satisfying result of cobalt removal was obtained by Uzal, Jaworska, Miśkiewicz, Zakrzewska-Trznadel, & Cojocar (2011) using polymer enhanced ultrafiltration (UF) technology. Polyvinyl alcohol (PVA) and sulfonated PVA were used as chelating agents in the study. The properties of sulfonated PVA such as water solubility, metal ion binding capacity, and selectivity were improved compared to non-modified PVA. By comparing the results with PVA and sulfonated PVA, Co^{2+} removal ability of sulfonated PVA (removal efficiency of 99.98 %) was found about threefold higher than that of PVA (removal efficiency of 31.81 %). Karate & Marathe (2008) had conducted an experiment to remove nickel and cobalt simultaneously from aqueous stream using cross flow micellar enhanced

ultrafiltration. Sodium dodecyl sulfate (SDS) was introduced as surfactant to remove dissolved metal ions from aqueous streams. As a result, maximum rejection for cobalt was obtained as 99.7 % under optimized inlet flow rate of 150 mL/min.

1.4.5 Solvent Extraction

A mixture of two components is separated by a solvent to extract the solutes (metal ions) from the mixture. Previously, studies have done on cobalt recovery by using this method. Sodium salts of di-(2-ethylhexyl)phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC 88A) and bis-(2,4,4-trimethylpentyl)phosphinic acid (Cyanex-272) were used by Devi, Nathsarma, & Chakravortty (1998) as extractants for the separation of cobalt and nickel from sulphate solutions. From the study, the cobalt and nickel separation efficiency of the three extractants were concluded in the order: NaCyanex-272 > NaPC 88A > NaD2EHPA. This gave the evidence that Cyanex-272 is the best extractant for the cobalt separation with 100 % cobalt extraction and 2.0 g/m³ nickel contamination compared to PC 88A with the result of almost 100 % cobalt extraction and 4.0 g/m³ nickel contamination. In the research done by Reddy, Rao, & Park (2009), a mixture of TOPS 99 (an equivalent of D2EHPA) and triisobutyl phosphine sulfide (TIBPS) was used as an extractant for the recovery of cobalt and nickel from sulphate medium. It was observed that addition of TOPS 99 increased the selectivity for the separation of cobalt over nickel by suppressed the extraction of nickel. The result indicated a cobalt recovery of 99.5 % in the addition of 0.1 M TOPS 99 and 0.05 M TIBPS in acidic condition. A number of synergistic solvent extraction systems have been developed as an alternative to replace the highly selective solvent extraction

extractants which is rare and prohibitively expensive (Cheng, Barnard, Zhang, Zhu, & Pranolo, 2016).

1.4.6 Electrochemical Process

Electrochemical processes include both electrolytic and galvanic processes. An electrochemical reaction will only take place when electricity is applied to the system or through the release of chemical energy. Redox reactions occur where electrons are transferred to or from a molecule or ion with a change in oxidation state. Electrolytic removal of cobalt had been recently studied by Santos, Santos, Pontual, Monteiro, & Mainier (2016). Galvanized carbon steel was used as cathode and platinum plate was used as anode, both were connected to a power supply with a maximum voltage of 30 V. In a removal time of 185 min, Santos *et al.* successfully removed cobalt ions from 100, 200 and 400 mgL⁻¹ simulated industrial wastewater with satisfying results of 84, 88, and 73 % recovery respectively. Dell'Era, Pasquali, Lupi, & Zaza (2014) had also conducted an electrolysis process for the removal of cobalt from experimental baths containing Ni²⁺ and Co²⁺ ions. A flow-by electrolytic cell was used to perform the experiment. In their work, reticulated vitreous carbon (RVC) and platinized titanium were used as cathode and anode respectively. For the depletion of Co(II) ions, the electrolysis process was performed at the potential range of – 1.0 and – 1.3 V. As reported by Dell'Era *et al.*, a satisfactory decrease of Co²⁺ ions was obtained with an average current efficiency of 15 % in less than 1 hour.

Although electrolytic process can provide good reduction yields and produce less sludge, it requires expensive electricity supply and more time consumption. However, electrolytic processes are not cost effective because low removal

efficiencies resulted when dealing with dilute solutions and high electrical power input is required. Therefore, an electrogenerative process (galvanic process) is introduced as an alternative.

1.4.6(a) Electrogenerative Process

An electrogenerative process is an electrochemical process that does not require an external energy supply. An exothermic energy of chemical reaction is converted to direct electric current while a desired chemical product is produced. Electrogenerative systems would eliminate the external power resource and give advantages in terms of ease of operation and lower operating cost (Gomathi & Sridevi, 2015). From the thermodynamics view, the change of Gibbs' free energy, ΔG° for a favourable overall reaction is negative (Langer, 1992). Thus, for an electrogenerative process can be calculated by:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad (1.1)$$

where n is the number of electrons accepted or released by the reaction per mole of reagent, F is Faraday's constant, E_{cell}° is the overall cell potential. In the electrogenerative process, oxidation-reduction reactions occur spontaneously in a divided cell where a more noble metal (stronger oxidizing agent) is reduced at cathode and a less noble metal (stronger reducing agent) is oxidized at anode to produce electrical energy. The strength of oxidizing and reducing agents are determined by referring to their standard reduction electrode potential.

The recovery of copper from dilute electroplating rinse water had been demonstrated by Hor & Mohamed using a single-pass reactor (2003) and batch-recycle reactor (2005). The electrogenerative system was proved to be suitable in treating low conductivity wastewater. With the flow rate of 500 mL min^{-1} , an initial copper(II) concentration of 74.2 mg L^{-1} was recovered to less than 1.0 mg L^{-1} in 150 min.

Yap & Mohamed had successfully remove gold from cyanide solutions using a batch reactor (2007) and flow-through reactor (2008). In the studies, more than 99 % of gold was recovered within 1 h using activated reticulated vitreous carbon (RVC) as cathode material in batch reactor system. For flow-through reactor system, the reactor was efficiently recovered more than 99 % of gold within 4 h of operation for lower initial gold concentration.

1.5 Electrogenerative Removal of Cobalt from Ammonium Chloride

Solutions

The electrogenerative removal of cobalt will be carried out in a batch reactor. A three dimensional porous electrode will be used as cathode material in catholyte compartment and zinc will be used as anode in anolyte compartment. An anion exchange membrane was used to separate the electrolytes between cathode and anode compartments. When the reactor is completely connected, zinc metal with a lower reduction potential will be oxidized and cobalt ions will be reduced on the cathode at the same time. The flow of electrons from Zn terminal is shown in Fig 1.1. The half-cell reactions involved in the removal of cobalt can be expressed by the following equations:

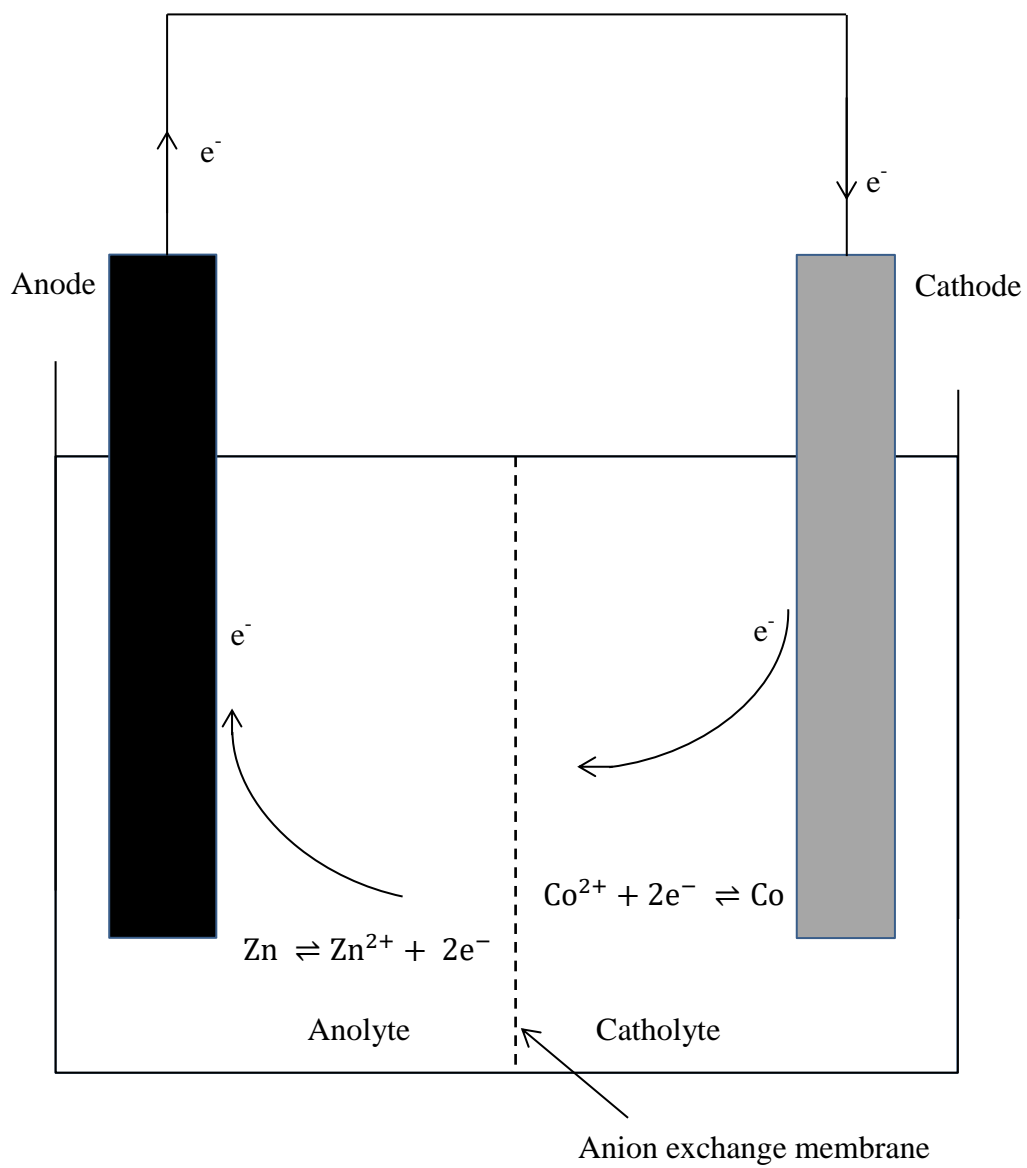
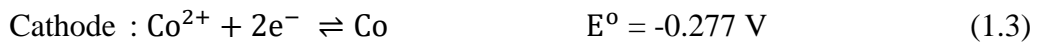


Figure 1.1 Electron transport in an electrogenerative reactor with an anion exchange membrane.



E° values in Eqs. 1.2 and 1.3 are standard oxidation potential of Zn and standard reduction potential of Co^{2+} respectively. The positive value of overall cell potential (Eq. 1.4) indicates that the electrochemical process occurs spontaneously without the supply of energy and Co^{2+} ions will be reduced on the cathode.

1.6 Reticulated Vitreous Carbon

Electrode materials can be classified into two groups: two-dimensional (2D) electrodes and three-dimensional (3D) electrodes. However, 3D electrodes are more superior to 2D electrodes due to their inherent properties: its high surface area to volume ratio and porosity enable the metal ions to distribute throughout the electrode. This arrangement can encounter the limitations of mass transport and low specific surfaces area (Soh, Rahim, & Mohamed, 2012). Among the choice of 3D electrodes such as packed bed electrode, fluidized bed electrode, porous graphite, reticulated vitreous carbon (RVC) and reticulated polyurethane, RVC was chosen as cathode materials in this work.

Reticulated vitreous carbon (RVC) foam was first developed in the mid to late 1960s as an inert, electrically and thermally conductive, and corrosion resistant microporous glassy carbon electrode material. RVC is an open-pore foam material of honeycomb structure which is formed by strands of carbon (struts) (Friedrich, Ponce-de-León, Reade, & Walsh, 2004). RVC has a better arrangement of the carbon atoms

in the basal planes, forming graphitic lamellar planes, which are stacked in the carbon structure (Gonçalves, Rezende, Takahashi, & Ferreira, 2006). The skeleton structure of RVC is shown in Fig. 1.2.

RVC is a useful cathode material, owing to its properties such as large void volume, high surface area, high porosity, high corrosion resistance, high electrical conductivity, low resistance to fluid flow, chemical inertness and good fluid permeability. The advantages of an RVC electrode in the electrochemical cell are uniform current and potential distribution, low ohmic internal resistance and high rates of mass transport of the electroactive species to the electrode surface (Pec *et al.*, 2010).

Many studies showed that the recovery of heavy metals using RVC electrodes can offer a highly efficient and low cost process. Due to the RVC properties, nearly 100% of electrolysis yield can be achieved, provided the electrode is still sufficiently porous to allow for low flow resistance after the deposition of metals on the electrode itself (Pec *et al.*, 2010). There is a large number of works dealing with the removal of other metal ions such as lead, gold and nickel by using RVC electrodes (De Leon & Pletcher, 1996; Yap & Mohamed, 2007; Yap & Mohamed, 2008; Dell'Era, Pasquali, Lupi, & Zaza, 2014).

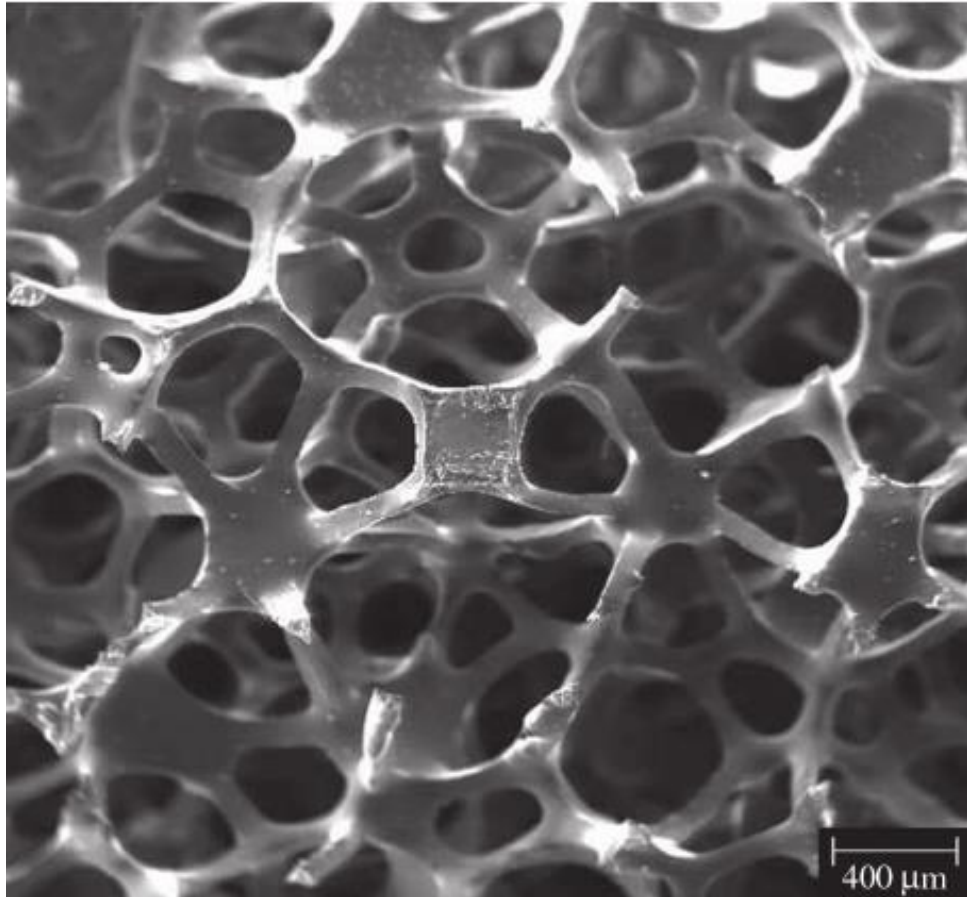


Figure 1.2 The skeleton structure of RVC observed by SEM. (adapted from Gonçalves, Rezende, Takahashi, & Ferreira, 2006)

1.7 Anion Exchange Membrane

An anion exchange membrane was introduced in the electrogenerative system to avoid the mixing of the electrolyte. Anion exchange membrane selectively influences the transportation of the anionic species. Since positively-charged groups are fixed to anion exchange membrane, cations are rejected by the positive charges due to the repulsion between species of similar charge. Hence, cations are unable to permeate through the anion exchange membrane and the membrane is only permeable to anions. The ionic selectivity principle of anion exchange membrane is shown in Fig. 1.3. There are some excellent characteristics of Neosepta membrane, such as high ionic perm-selectivity, low electric resistance, high mechanical strength, high chemical stability, high dimensional stability, , low diffusion coefficient and ability to separate monovalent and multivalent ions (ASTOM Corporation, 2013).

1.8 Choice of Supporting Electrolyte

Supporting electrolyte plays an important role in the electrogenerative system as it is added into the solutions to be treated to support the current flow and sufficient conductivity of the medium, which can have appreciable effect on the cell performance (Izquierdo et al., 2010). In previous work, the electrogenerative system had been demonstrated successfully to remove cobalt from different supporting electrolyte. Tan & Mohamed (2011) had successfully removed more than 99 % Co^{2+} ions from 200 mgL^{-1} solution in 0.2 M sodium sulfate and 0.4 M boric acid. The studies were performed in a batch reactor using RVC and porous graphite as cathode material. Under similar experimental conditions, Tan, Hasnat, Ramalan, Soh, & Mohamed (2012) had also demonstrated the removal of Co^{2+} ions by using a flow-by reactor. As reported by Tan *et al.*, removal of > 99 % Co^{2+} ions with current

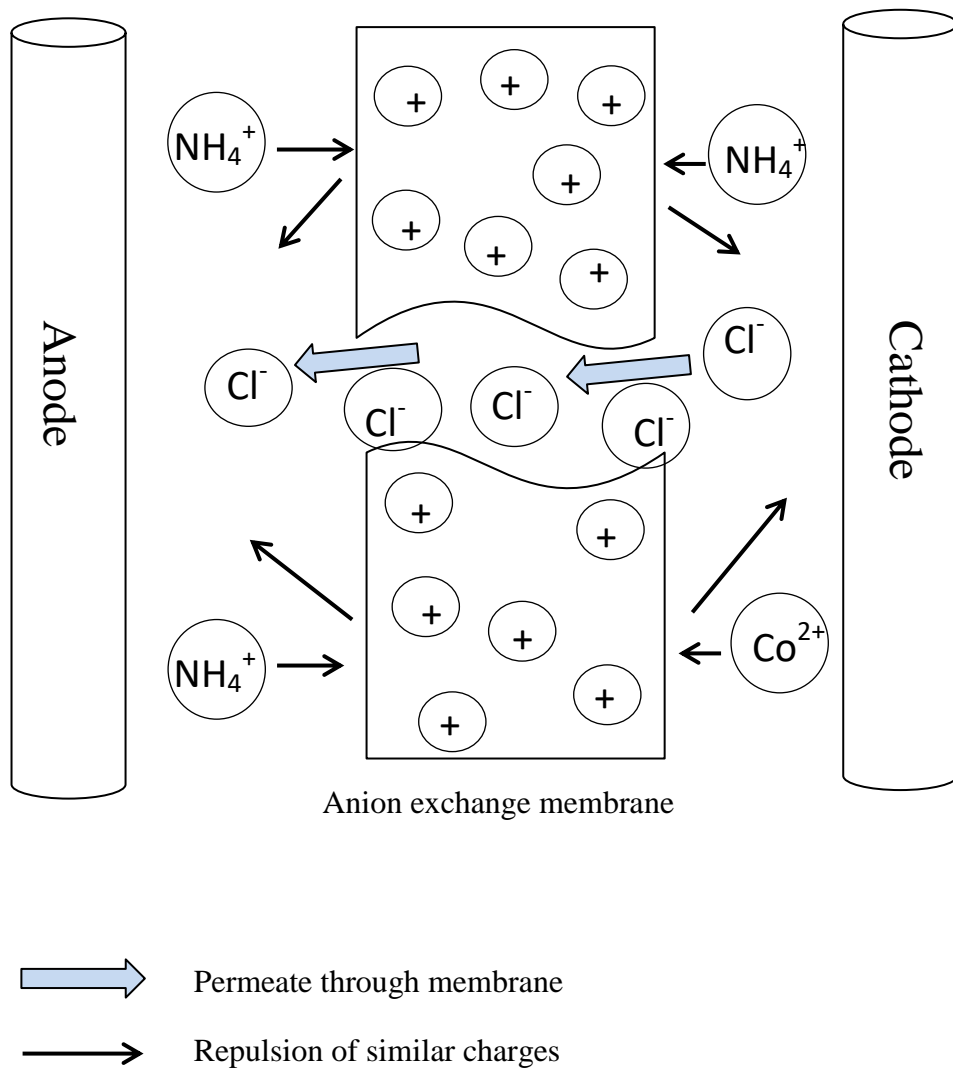


Figure 1.3 The ionic selectivity principle of an anion exchange membrane.

efficiency of 82 % from 200 mgL⁻¹ was achieved at all flow rates. Instead of using sodium sulfate, Soh, Hasnat, Rahim, & Mohamed (2013) used sodium chloride as supporting electrolyte in their study. A promising result of 99 % cobalt recovery with current efficiency of 83 % from 100 mgL⁻¹ Co²⁺ solution was achieved. In the present work, ammonium chloride electrolytes are used to replace chloride electrolytes to improve the recovery performance and deposition condition.

1.9 Problem Statement

Ammonium chloride supporting electrolyte was used in the present work to improve on the recovery process and morphology of the deposited cobalt. Besides having the advantages of higher electrical conductivity in the electrolyte, lower overpotential for deposition of cobalt, and higher current efficiency, the addition of ammonium chloride can improve the uniformity of electrode surface by removing oxygen atom or oxide layer on the electrode surface so that cobalt ions can deposit better on the electrode surface. Also, the ammonium ions can help in modulating and enhancing the morphology of the deposited cobalt (Grujicic & Pesic, 2004; Ramos-Lora, Mendoza-Huizar, & Rios Reyes, 2011). The NH₄⁺ ions were partially absorbed on the negatively charged electrode and the deposited cobalt surfaces, therefore changing the cobalt nucleation environment to improve the deposition conditions. In the studies conducted by Hashemzadeh, Raeissi, Ashrafizadeh, & Khorsand (2015), ammonium chloride was added as the crystal modifier to facilitate the regular morphology.

In the studies on electrodeposition of cobalt, it was found that an active site on electrode plays a major role in the early stages of the formation of the nuclei. In

ammoniacal medium, cobalt electrodeposition and hydrogen evolution reaction (HER) can be treated separately, the mechanism and the crystal growth of cobalt electrodeposition can be evaluated (Soto, Arce, Palomar-Pardavé, & González, 1996).

Based on the basis of electrogenerative process, the feasibility of recovering more than one metal is one of the modifications that can be made on the method of the recovery system in the present work. By adding multiple ions (Co^{2+} , Cu^{2+} and Ni^{2+}) into the same solution, all the different ions can be reduced in the solution simultaneously.

1.10 Objectives of Research

In this work, the use of electrogenerative process is introduced as an alternative treatment technology for the removal of cobalt. The purpose of this work was to study the feasibility of ammonium chloride supporting electrolyte in cobalt recovery at RVC cathodes using a batch cell system through electrogenerative process.

The performance of batch cell system was evaluated with different parameters, viz. initial Co(II) concentration, concentration of ammonium chloride as supporting electrolyte and pH adjustment. Optimum conditions for the recovery of cobalt using an electrogenerative process were also investigated. The efficiency of Co^{2+} recovery has been explained on the basis of cell performance. The morphology of the cobalt has also been observed. The feasibility of the removal system of co-ions simultaneously was introduced in this study.

The summary of the overall objectives of this study are listed as the following:

- i. To evaluate the cell performance of cobalt removal in ammonium chloride medium.
- ii. To investigate the optimum conditions for the recovery of cobalt in ammonium chloride medium.
- iii. To monitor the effects of pH adjustments on cobalt recovery.
- iv. To investigate the feasibility of recovery of co-ions simultaneously in the presence of copper and nickel ions.

CHAPTER 2

EXPERIMENTAL

2.1 Materials and Apparatus

The electrogenerative cell compartments were separated by an anion exchange membrane Neosepta[®] AM-01 (Tokuyama Corp.). It was cut into dimensions according to the cell and placed between the catholyte and anolyte compartments, acting as a restrictive barrier to prevent the mixture of both electrolytes. A three-dimensional electrode, reticulated vitreous carbon (RVC) 80 pores per inch (ppi) (Electrolytica Inc.) was used as cathode. The dimension of RVC was 2 cm x 5 cm x 0.3 cm. The anode used was pure zinc foil (> 99 % purity, R & M chemicals) with dimensions 2 cm x 5 cm x 0.05 cm and it acted as a sacrificial electrode. Zinc was easily oxidized when exposed to the air and the oxide layer that formed on the surface of the zinc foil will hinder the contact between the electrolyte and zinc anode, hence the zinc foil needed to be cleaned with sand paper each time before use.

The different concentrations of Co(II) solutions were prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salt (QRĒC) and the supporting electrolyte was prepared from ammonium chloride salt (Bendosen Lab Chemicals). Stock solutions (1000 ppm) of cobalt and zinc (Merck) served for preparation of standard solutions for the calibration purpose. In the section of pH adjustment, the pH of the Co(II) solution was adjusted to the desired pH by adding NaOH solution (QRĒC).

2.2 Experimental Procedure

2.2.1 Treatment of Cathodes

Before the experiment can be carried out, the cathode was activated to remove the surface residues and prevent the contamination of organic compounds. Therefore, the cathode was treated for 8 hours before use.

During the treatment, the cathode was first immersed in a mixture of ethanol and distilled water (95:5 v/v) for 4 hours. After the 4 hours treatment, the cathode was taken out and rinsed thoroughly with distilled water. Then, the cathode was immersed in concentrated sulfuric acid for another 4 hours. Lastly, the cathode was taken out and rinsed with distilled water again. When the cathode was not in use, it needs to be stored in distilled water to maintain their surface moisture. This can help to ensure maximum contact between the cathode and the solution during experiments.

2.2.2 Electrogenerative Removal of Cobalt using a Batch Cell

The schematic diagram of the batch cell is shown in Fig. 2.1. The batch cell has two electrolyte compartments each of dimensions 4.5 cm x 4.5 cm x 6.5 cm separated by an anion exchange membrane Neosepta[®] AM-01 (Tokuyama Corp.). The cell compartments were sandwiched together by six nuts and bolts. Reticulated vitreous carbon (RVC) (Electrolytica Inc.) was used as cathode material with dimensions 2.0 cm x 4.5 cm x 0.5 cm. The RVC porosity studied was 80 pores per inch (ppi). Zinc foil (> 99 % purity, R & M chemicals) with dimensions 2.0 cm x 4.5 cm x 0.1 cm was used as anode material. The electrodes were then attached to copper plates using Teflon tape. The copper plates functioned as current collectors. The circuit was then completed by connecting the current collectors to a digital

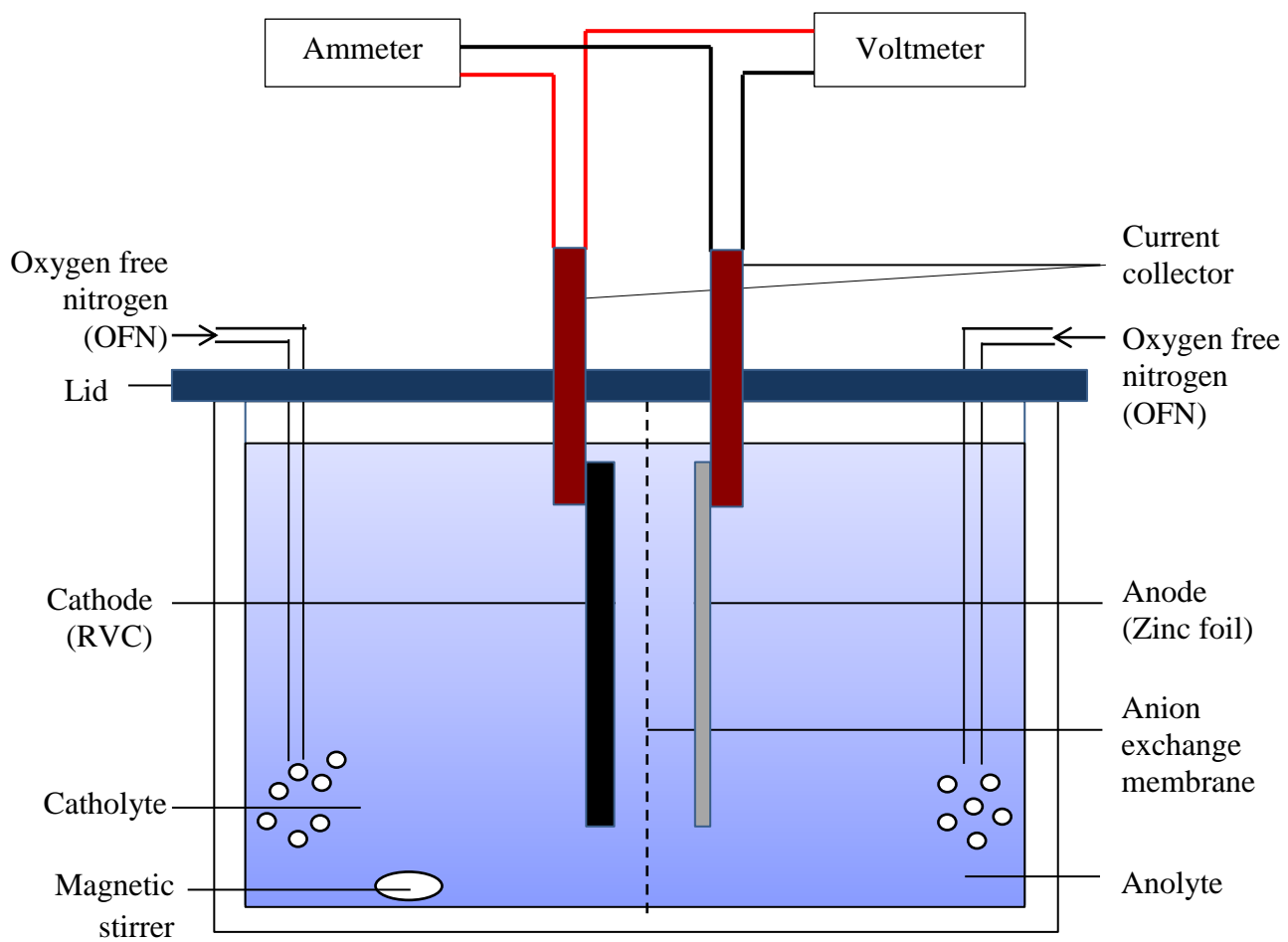


Figure 2.1 Experimental setup for an electrogenerative cell.

multimeter (Sanwa CD800A) using external conducting wire. A magnetic stirrer is used in cathode compartment to agitate the catholyte.

All the electrolytes were prepared in distilled, deionized water using analytical grade reagents (System[®] ChemAR[®]). The Co(II) solutions were prepared from CoCl₂·6H₂O salt. The catholytes of 100, 200 and 500 mg L⁻¹ Co(II) were prepared in 0.10 M ammonium chloride. The anolyte used was 0.10 M ammonium chloride. The effect of supporting electrolyte was investigated by varying the concentration of ammonium chloride to 0.50, 1.0 and 2.0 M. The effect of pH adjustment was done by increasing the initial pH 5.5 to pH 7.0 by adding 1.0 M sodium hydroxide solution into the catholyte. The details of the parameters applied are listed in Table 2.1.

Before each experiment, nitrogen gas was used to purge out dissolved oxygen in both compartments for 10 minutes and a flux of nitrogen was maintained above the electrolyte surface throughout the experiment to ensure an inert atmosphere. All the experiments were carried out at room temperature (~25 °C). Due to the high toxicity of zinc, the hazardous Zn²⁺ solution in the anode compartment was collected in a container for further recovery after each experiment. As a test of reproducibility, a particular experimental run was performed three times.

Before the experiment started, aliquots of 500 µL of catholyte and anolyte were collected to determine the initial amount of cobalt and zinc in the solutions respectively. At every 30 minutes intervals, 500 µL of catholyte and anolyte were collected to examine the amount of cobalt left in the catholyte and the amount of zinc

Table 2.1 Detail of experimental conditions for batch cell.

Cathode compartment		Anode compartment	
Catholyte		Anolyte	
(a) Co(II) concentration	100, 200, 500 mgL ⁻¹	(a) NH ₄ Cl concentration	0.10, 0.50, 1.0, and 2.0 M
(b) NH ₄ Cl concentration	0.10, 0.50, 1.0, and 2.0 M	pH adjustment	~5.5 (natural pH), 7
pH adjustment	~5.5 (natural pH), 7	Anode	Zinc foil > 99 % (Dimensions 2.0 cm × 4.5 cm × 0.1 cm)
Cathode	RVC 80 ppi (Dimensions 2.0 cm × 4.5 cm × 0.5 cm)		