Toxic and precious metals removal from wastewater using freeze concentration and electrodeionization

By

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Abstract

Industrial wastewater may contain metals such as chromium (VI), nickel, cobalt and palladium. These metals are toxic to aquatic organisms and also have an adverse impact on human health and environment. Due to limited availability and high demand, the value of the precious metals such as palladium has increased significantly. There has long been an interest in recovering toxic and precious metals from industrial effluents for sustainable use of resources and compensate the cost of wastewater treatment, in addition, to reduce environmental pollution. However, the low concentrations of precious metals in wastewater make recycle and recovery difficult. Some removal and recovery processes have been developed in recent years, but the costs of treatments are usually high and some processes also generate large volumes of secondary wastes. There is a need for a cost-effective treatment method for precious and toxic metal removal/recovery from wastewater.

This research was carried out to investigate the potential of freeze concentration, electrodeionization and combination of the two processes for removal and recovery of wide concentration range of chromium (VI), nickel, cobalt and palladium in synthetic wastewater.

The feedwater with metal concentrations starting from 20 mg/L was frozen at -15°C. By freezing only 80% (volume) of the feedwater, about 99% reduction of metal concentration in ice was achieved in single stage freeze concentration. The concentrated unfrozen liquid was then used as feedwater for the electrodeionization system. Multi-stage (two and three stages) freeze concentration were also used for further treatment of the unfrozen liquid with high concentrations of metals. By freezing only 80% (volume) of the feedwater and with the washing of the ice, about 99% reduction of metal content in ice and 99% volume reduction of feedwater were achieved by multi-stage freeze concentration process. Palladium concentrations of 160-fold increment of the initial feedwater concentration could be achieved using multi-stage freezing. Overall, it was found that freeze concentration is an effective method for chromium (VI), nickel, cobalt and palladium removal from synthetic wastewater.

In the electrodeionization approach, using commercially available resins, the removal efficiencies for chromium (VI), nickel, cobalt and palladium using the unfrozen liquids from freeze concentration process as feedwater were investigated. The feedwater concentrations in the range of 120 - 650 mg/L examined using 15 mA and 50 mA current. Removal efficiencies were 97% for 120 mg/L of chromium (VI), 65% for 500 mg/L of cobalt and 90% for 250 mg/L of palladium. Promising results were shown by combination of freeze concentration and electrodeionization approach for the removal and recovery of toxic and precious metals from industrial wastewater.

Results of freeze concentration and electrodeionization showed that using 80% freezing of the initial feedwater volume, very high removal efficiencies were achieved for freeze concentration process for separation of chromium (VI), nickel, cobalt and palladium while similar results were only possible in chromium (VI) and palladium using EDI. Overall, freeze concentration process was not so sensitive to changes in influent metal concentration and chemical natures of the metals as EDI.

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Abbreviations and notations

AEM	Anion Exchange Membranes
C_0	Initial Concentration
CEM	Cation Exchange Membranes
C_f	Final Concentration
C_{FW}	Concentration of initial feedwater
C_{FW}	Concentration of initial feedwater
C_i	Impurity Concentration in the Ice Phase
C_{ice-1}	Concentration of ice from single/ first stage FC
C_{Ice-2}	Concentration of ice from second stage FC
C_{Ice-3}	Concentration of ice from third FC
C_L	Impurity Concentration in the Unfrozen Liquid
Co	Cobalt
Cr (VI)	Chromium (VI)
C_r	Concentration Ratio
C_{UFL-1}	Concentration of unfrozen liquid from single FC/ feedwater for second stage FC
C_{UFL-1}	Concentration of unfrozen liquid from single stage FC

C_{UFL-2}	Concentration of unfrozen liquid from second stage FC/ feedwater for the third stage FC
C_{UFL-2}	Concentration of unfrozen liquid from second stage FC/ feedwater for the third stage FC
C_{UFL-3}	Concentration of unfrozen liquid from third stage FC
ED	Electrodialysis
EDI	Electrodeionization
FC	Freeze Concentration Process
Ice-1	Ice from single/first stage of freezing
Ice-2	Ice from the second stage of freezing
Ice-3	Ice from the third stage of freezing
Ni	Nickel
Pd	Palladium
pH_{FW}	pH value of the initial feedwater
pH_{ice-1}	pH value of the ice from single/first stage FC
pH_{UFL-1}	pH value of the unfrozen liquid from single/first stage FC
Re	Removal Efficiency
UFL-1	Unfrozen liquid from single/first stage of freezing

UFL-2	Unfrozen liquid from the second stage of freezing
UFL-3	Unfrozen liquid from the third stage of freezing
V_0	Volume of Feedwater
VFW	Volume of Feedwater
V_i	Volume of Melted Ice
V_L	Volume of Unfrozen Liquid
Vr	Volume Reduction
V_{UFL-1}	Volume of unfrozen liquid from single/first stage
V_{UFL-2}	Volume of unfrozen liquid from the second stage
V_{ULF-3}	Volume of unfrozen liquid from the third stage

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Chapter 1: Introduction

Industrial effluents are the main source of toxic metals that are released to the aquatic environment *(Agrawal et al., 2007; Cavas et al.,2005; Gan,2000; Lothongkum et al, 2008; Onikura et al., 2008; Silva et al., 2008; Verma et al., 2010).* Metals such as chromium, copper, lead, mercury, nickel are discharged with industrial effluents at various concentrations and are known to have adverse effects on human and the environment *(Mohan et al., 2007, United States EPA, 2014).* Over the past decade, great efforts have been made by industries to reduce the amount of toxic metals discharged into aquatic environments *(Govind et al., 2014).* On the other hand, precious metals such as gold and palladium utilization have increased tremendously *(Abughusa et al., 2013).* Due to limited availability and high demand for these precious metals, the market values have skyrocketed *(Abughusa et al., 2013).* Therefore, there is a great interest in extracting these precious metals from industrial wastewater which could compensate the cost of wastewater treatment. However, it is very challenging to recover these metal ions because of the very low concentrations in the industrial wastewater *(Abughusa et al., 2013).*

Various treatment processes, for example, chemical precipitation, membrane filtration, ion exchange and electrochemical treatment methods have been used for removal of metals from wastewater *(Carolin et al., 2017; Ahmed et al., 2017; Barakat, 2011)*. Due to limited purification efficiencies of the available treatment methods for metal removal, industrial effluents can accumulate in water bodies which could lead to serious consequences on the ecosystem *(Govind et al., 2014).* Even though some of the treatment methods may be effective for removal of metals from wastewater they require high capital and operational costs, use of additional chemicals and, generate large volumes of sludge *(Carolin et al., 2017).* In addition, reducing the fresh water consumption, recycling and reuse of partial or entire treated wastewater are becoming an option for many industries *(Gao et al., 2009)*.

Freeze concentration has shown great potential in treating various industrial wastewater *(Gao et al., 2009)*. Without any chemical addition or pre-treatment, freeze concentration was able to remove various organic and inorganic contaminants from industrial effluents. Furthermore, the ice samples recovered from freezing could be reused or recycled within the treatment systems or discharge to the environment depending on the quality of ice. Electrodeionization (EDI) has shown great potential in wastewater treatment for recovery of ions *(Alvarado et. al, 2014).* EDI is a chemical-free technology that reduces ions in water. EDI processes use cations and/or anion exchange resins that are continuously regenerated by an electrical current *(Alvarado et. al, 2014).*

Limited research has been done using freeze concentration to remove or recover toxic and precious metals from industrial effluents or liquid wastes. Also, no study has been done to examine the potential of using freeze concentration as a pre-treatment for EDI processes to enhance removal and recovery of toxic and precious metals from wastewater

1.1 Objectives

The objectives of this study are to investigate:

1. The effectiveness of freeze concentration on the removal and recovery of toxic and precious metals in industrial wastewater.
    a. The effect of initial metal concentrations, chemical nature and the mixing methods on the freeze concentration efficiency
    b. The effectiveness of using multiple stages of freezing for the treatment of the unfrozen liquid
    c. The capacity of the freeze concentration on the wastewater volume reduction and
    d. Effect of the percentage of freezing on the removal efficiency and the partitioning of the metals in ice and liquid phases during freezing will be examined
2. The effectiveness of EDI for the removal and recovery of toxic and precious metals from wastewater using commercially available resins and
    a. The effect of the chemical nature of the metals,
    b. The feedwater metal concentrations and
    c. The level of electric current applied to the EDI cell on the treatment efficiency will be examined
3. The effectiveness of using freeze concentration as a pre-treatment method for the removal and recovery of toxic and precious metals from wastewater

1.2 The scope of this thesis

This thesis is composed of six chapters. The research background and the study objectives are presented in this chapter followed by a comprehensive literature review in chapter 2. Chapter 2 will include information regarding toxic and precious metals that are found in industrial wastewater, their effects on the human and aquatic environment, reasons for recovering precious metals from industrial wastewater and finally, treatment methods that are currently available for recovery/removal of toxic and precious metals from industrial wastewater. Chapters 3 to 5 will include the experimental studies of metal removal using freeze concentration, EDI as well as, using freezing as a pre-treatment for EDI, respectively. Chapter 6 will summarize the results and provide recommendations for future research on the basis of the experimental studies.

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Chapter 2: Literature Review: Toxic and precious metals in wastewater and treatment technologies

2.1 Toxic metals in wastewater

2.1.1 Toxic metals

Toxic metals are individual metals or metal compounds that have an adverse effect on human life and the environment *(Mohan et al., 2007).* Metals such as antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc are considered priority pollutants by United States Environmental Protection Agency *(United States EPA, 2014).* These priority pollutants are known to cause multiple organ damages even at low concentrations *(Tchounwou et al., 2012).*

In recent years, there has been an increased concern on ecological and global public health associated with toxic metals *(Tchounwou et al., 2014).* Even though these metals are naturally occurring, due to exponential use of these metals in industrial, agricultural, domestic and technological applications, human exposure and environmental contamination have increased drastically *(Tchounwou et al., 2014).*

2.1.2 Main sources of toxic metals in wastewater

There are numerous sources of industrial effluents that lead to enrichment of toxic metals in aquatic environments *(Agrawal et al., 2007; Bruggen et al.,2001; Cavas et al.,2005; Gan,2000; Lothongkum et al, 2008; Onikura et al., 2008; Silva et al., 2008; Verma et al., 2010).*

Mining is one of the most important sources of toxic metals in the aquatic environment. Mining operations and disposal of tailing ponds, leave behind a wide range of toxic metals including chromium, nickel, and cobalt. *(Meldrum et al., 2001)*. Pollution of water with toxic metals is mainly associated with acid mine drainage *(Razo et al., 2004)*. For example, mining of certain minerals such as nickel, and copper are associated with acid drainage problems that can cause long-term damage to waterways and biodiversity *(Akcil et al., 2006)*. In a study conducted by *Huang et al., (2016) and Zou et al., (2015),* it was found that the chromium, nickel and cobalt concentrations in the water in the mining regions were in the range of 0.1 - 10 mg/L.

Pulp and paper industry effluent contains chromium, copper, magnesium, lead and nickel. These metals are used in different stages of production in pulp and paper industry *(Onikura et al., 2008)*. Petrochemical industry effluent contains cobalt, manganese, chromium, iron, magnesium and aluminium in various concentrations. Metals such as chromium and chromium compounds are used as de-flocculants in the petrochemical industry *(Cavas et al., 2005).* Fertilizer industry effluent contains toxic metals such as cadmium, chromium, copper, lead and nickel. *(Lidia et al., 1997).* In textile and leather tanning industries, chromium is used to remove the outer skin and dirt from hides. Also, in the second stage in the tanning of leather, chromium compounds are frequently used to keep the leather soft *(Forstner et al., 1981).* Steel industrial effluent contains toxic metals such as cadmium, chromium, copper, iron, lead and nickel *(Lothongkum et al., 2009).* Electrochemical methods are used in metal plating industry for protection and decoration of variety of metal surfaces. Most of the processes are followed by rinsing operations to remove excess chemicals and other wastes materials from the treated surface. This leads to a rise in metal concentrations in plating industries (*Silva et al., 2008).* Table 2.1 shows the toxic metals that are used in major manufacturing industries.

Table 2.1: Toxic metals in major industrial effluents

Industry	**Cd**	**Cr**	**Cu**	**Hg**	**Pb**	**Ni**	**Sn**	**Zn**	**Reference**
Pulp and paper		×	×	×	×	×		×	*(Onikura et al., 2008)*
Petrochemicals	×	×		×	×		×	×	*(Verma et al., 2010)*
Fertilizers	×	×	×	×	×	×		×	*(Lidia et al., 1997)*
Petroleum refinery	×	×	×		×	×		×	*(Cavas et al., 2005)*
Steel industry	×	×	×	×	×	×	×	×	*(Lothongkum et al., 2009)*
Metal plating	×	×	×	×		×			*(Silva et al., 2008)*
Textile	×	×	×	×	×	×		×	*(Bruggen et al., 2001)*
Leather tanning		×							*(Agrawal et al., 2007)*
PCB manufacturing		×	×					×	*(Gan, 2000)*
Electroplating		×	×		×			×	*(Agrawal et al., 2007)*

The major industrial uses of toxic metals have been compiled in Table 2.1. The toxic metals under consideration are employed in widely diversified fields such as petrochemical, steel, metal plating, etc. On the other hand, industries such as leather tanning uses only one specific toxic metal; chromium.

2.1.3 Characteristics of toxic metals

2.1.3.1 Chromium

Chromium is a naturally occurring element that exists in the earth's crust. It has oxidation states ranging from chromium (II) to chromium (VI) *(Jacobs et al., 2005).* Chromium (III) compounds are considered most stable and can be found in nature in the form of ferro-chromite ore. The second most stable form of chromium is hexavalent chromium [Cr (VI)]. On the other hand, elemental chromium [Cr (0)] does not occur naturally in the environment. Chromium enters into the environment via different sources such as natural and results of human activities. Industries such as metal processing, chromate production, stainless steel welding and chrome pigment production contribute the most chromium to the environment. Chromium that is released to the environment as a result of human activities is in hexavalent form *(Tchounwou et al., 2014).* It is considered a toxic industrial pollutant and a carcinogen by various regulatory agencies *(Tchounwou et al., 2014)*. The toxicity of chromium depends on the oxidation state which ranges from low toxicity of the metal form to high toxicity in hexavalent form (*Cohen et al., 1993).* Many chromium (III) compounds are relatively water insoluble. However, chromium (VI) can make excellent water-soluble compounds such as chromium (VI) oxide which has a solubility of 1680 g/L *(Lenntech, 2017).* Table 2.2 shows the typical average concentrations of chromium in industrial wastewater.

Table 2.2: Typical concentrations of chromium in major industrial effluents

Industry	**Typical concentration (mg/L)**	**Reference**
Steel	408.58	*(Lothongkum et al., 2009)*
Sugar	5.5	*(Gupta et al., 2004)*
Plating	18.54	*(Hunsom et al., 2005)*
Pulp and paper	0.05	*(Bishnoi et al., 2005)*
Petrochemicals	10-100	*(Mirbagheri et al., 2004)*
Fertilizers	10.4- 72.7	*(Camelo et al., 1997)*
Textile	< 20	*(Bruggen et al., 2001)*
Leather tanning	0.5- 5	*(Agrawal et al., 2007)*
PCB manufacturing	0.8	*(Gan, 2000)*
Electroplating	0.1- 286	*(Agrawal et al., 2007)*

As seen in Table 2.2, the steel industry has the highest concentration of chromium in effluent followed by electroplating industry. Pulp and paper industry and textile industry have one of the lowest concentrations of chromium in industrial wastewater.

2.1.3.2 Nickel

Nickel is a naturally occurring metal that exists in the earth's crust. In nature, nickel exists in the forms of sulphides and silicates which are in both soluble and insoluble forms *(Denkhaus et al., 2002).* Nickel and nickel compounds are widely used in various industries due to its unique physical and chemical properties. This high usage of nickel leads to environmental pollution at all stages of production, recycling and disposal *(Denkhaus et al., 2002).* Nickel has oxidation states ranging from -1 to +4 and +2 oxidation state is the most common state in the bio-systems *(Denkhaus et al., 2002).* Nickel compounds are heavily used in industries such as electroplating, electroforming and for the production of nickel-cadmium batteries *(Denkhaus et al., 2002).* Moreover, nickel alloys are used in stainless steel, machinery, jewellery industries and in medical applications worldwide *(Denkhaus et al., 2002).*

Human activities are the main source of nickel in the environment followed by direct leaching from rocks and sediments *(Denkhaus et al., 2002).* Exposure to nickel compounds can have adverse effects on human health *(Denkhaus et al., 2001).* In addition, even though nickel is a dietary requirement, it was found that nickel compounds, except for metallic nickel, are carcinogenic to humans *(Denkhaus et al., 2001)*. In addition, elementary nickel is not water soluble at 20°C and 1 bar. However, nickel compounds are water soluble. Nickel chloride is said to be the most water-soluble compound out of various nickel compounds (*Lenntech, 2017).* Table 2.3 shows the average concentration of nickel in industrial effluents.

Table 2.3: Typical concentrations of nickel in major industrial effluents

Industry	**Typical concentration (mg/L)**	**Reference**
Steel	8.12	*(Lothongkum et al., 2009)*
Sugar	12	*(Gupta et al., 2004)*
Metal plating	7.97	*(Hunsom et al., 2005)*
Pulp and paper	0.03	*(Bishnoi et al., 2005)*
Fertilizers	7-26.9	*(Camelo et al., 1997)*
Textile	2.19	*(Bruggen et al., 2001)*
Electroplating	65-670	*(Benvenuti et al., 2014)*
Slaughterhouse	55.35	*(Gonzalez et al., 2014)*
Automotive	0.44	*(Adeli et al., 2017)*

As seen in Table 2.3, the concentration of nickel in industrial wastewater varies between 0.03 - 670 mg/L. Steel, metal plating and mining industries have similar concentrations of nickel in the industrial effluent. Lowest concentrations of nickel were reported in pulp and paper industry.

2.1.3.3 Cobalt

Cobalt is also a naturally occurring element in the environment. Cobalt is present in small amounts in rocks, soils, water and plants. Generally, cobalt is more associated with other minerals such as nickel, iron and copper *(Santos et al., 2016)*. Cobalt has many oxidation states, and +2 oxidation state is considered the most common state *(Gault et al., 2010)*. In the last century, cobalt had very little industrial usage, but now, it is used widely in many applications *(Santos et al., 2016)*.

Cobalt enters into the environment via natural sources as well as through human activities. The largest source of cobalt exposure for humans is through food or skin contact with substances containing trace amounts of cobalt. However, workers in an industrial setting could be exposed to cobalt via inhalation. Cobalt and its compounds are considered as human carcinogens based on experiments conducted on animals *(Gault et al., 2010).* The main application of cobalt is the production of high-performance alloys *(Gault et al., 2010).* In addition, cobalt salts are used as catalysts, fertilizers, batteries and ceramics (*Santos et al., 2016).* Table 2.4 below shows the average concentrations of major industrial effluents that contain cobalt.

Table 2.4: Typical concentrations of cobalt in major industrial effluents

Industry	**Typical concentration (mg/L)**	**Reference**
Apex steel	0.68	*(Singh et al., 2011)*
Pharmaceutical	0.009-0.085	*(Amin et al., 2015)*
Paint	1.15	*(Malakootian et al., 2008)*
Tannery	0.02-1.1	*(Bhuiyan et al., 2010)*
Nuclear waste	145 Bq/l	*(Saleh et al., 2017)*

The concentrations of cobalt in the industrial effluent are tabulated in Table 2.4 and the values are very low compared to other metals such as chromium and nickel.

2.1.3.4 Copper

Copper is one of the few metals that are found in metallic form in nature. As a result, copper was used in various applications throughout human history *(Gaetke et al., 2003).* Copper is known to exist in both oxidized (Cu^{2+}) and reduced (Cu^{+}) states *(Gaetke et al., 2003).* Copper is mainly used as a metal or as an alloy in modern industries. For example, copper is widely used in machinery, construction, transportation and military industries. In addition, copper is used in the jewellery industry, dental products and in cosmetics *(Gaetke et al., 2003).* Elemental copper does not react with water; however copper-based minerals are water-soluble *(Sauve et al., 1996).*

Moreover, copper is found in trace amounts in human's cells and tissues with the highest concentrations in the liver. However, copper in high concentrations can be poisonous to organisms and environment (*Saha et al., 2009).*

2.1.3.5 Arsenic

Arsenic is considered a common element that is in low concentrations in the environment. Natural phenomena such as volcanic eruptions and soil erosions as well as human activities lead to arsenic pollution in the environment (*Tchounwou et al., 2012).* There are many arsenic-rich compounds that are made mainly for the agriculture industry. For examples, insecticides, herbicides, fungicides, sheep dips and wood preservations (*Centeno et al., 2005).* Arsenic is also used for eradication of tapeworms in sheep and cattle. In addition, arsenic compounds have been used for syphilis, yaws, amoebic dysentery and trypanosomiasis for at least a century (*Centeno et al., 2005).* Arsenic in groundwater is a serious issue in many countries. It is estimated that several million people are exposed to arsenic through drinking water. In addition, arsenic toxicity highly depends on the oxidation state and solubility as well many other intrinsic and extrinsic parameters (*Tchounwou et al., 2012).*

2.1.3.6 Cadmium

Cadmium is a toxic metal which has considerable environmental and occupational concern. It is widely available in the earth's crust (*Tchounwou et al., 2012).* The highest concentration of cadmium can be found in sedimentary rocks and marine phosphates (*Tchounwou et al., 2012).* In addition, cadmium is usually found in +2 oxidation state *(Holleman et al., 1985).* Cadmium is frequently used in numerous industries. As a result, large amounts of cadmium is released into the environment. The major use of cadmium is for production of alloys, pigments and batteries

(*Wilson, 1988).* However, the cadmium use in batteries is decreasing due to environmental concerns and strict regulations (*Dong et al., 2015).* Exposure to cadmium can occur through a number of sources such as employment in cadmium containing industry, eating contaminated food and smoking cigarettes. Cadmium compounds are considered as human carcinogens by multiple regulatory agencies (*Tchounwou et al., 2012).*

2.1.3.7 Lead

Lead is a naturally occurring, bluish-grey metal that is present in the earth's crust in small amounts. Even though lead is naturally occurring, human activities such as fossil fuel burning, mining and manufacturing contribute to the release of lead in high concentrations to the environment (*Gabby, 2006).* Lead has many uses in industrial, agricultural and domestic applications due to characteristics such as high density, low melting point, ductility and relative inertness to oxidation. Lead is currently used in lead-acid battery production, ammunition, and metal products. In recent years, lead has been replaced from paints, ceramic products and pipes (*Gabby, 2003).* In addition, under standard conditions, lead does not dissolve in water. However, lead carbonates are dissolved in water. Lead compounds are usually found in +2 oxidation state rather than +4 oxidation state (*Tchounwou et al., 2012).*

2.1.3.8 Mercury

Mercury can be found in three forms in nature (Elemental, inorganic and organic). It is a unique toxic metal that belongs to the transitional element series in the periodic table (*Guzzi et al., 2008).* The toxicity of mercury depends on the form of mercury. At room temperature, elemental mercury exists in the liquid form which has a high vapour pressure and is released into the environment as mercury vapour (*Dopp et al., 2004).* In addition, mercury exists as a cation with oxidation states of +1 or +2. Methylmercury is the most frequent organic compound that is found in the environment and is formed as a result of methylation of inorganic forms of mercury by microorganisms in soil and water (*Tchounwou et al., 2012).* Mercury is utilized in the electrical industry (switches, thermostats and batteries), dentistry and many industrial processes including the production of caustic soda, in nuclear reactors, as anti-fungal agents for wood processing, as a solvent for reactive and precious metals (*Tchounwou et al., 2003).*

2.1.4 Contamination of aquatic environments

2.1.4.1 Chromium

Chromium enters into the natural water by weathering of chromium-containing rocks, direct discharge from industrial wastewater and leaching from the soil *(Kimbrough et al., 1999).* When in water, transformations such as reduction, oxidation, sorption, desorption, dissolution and precipitation can occur *(Kimbrough et al., 1999).* The discharging by industries can contaminate surface water as well as groundwater due to high concentrations of chromium *(Chandra, 2014).* Discharging untreated chromium into rivers has caused environmental disasters in the past. For example, in 1975, it was witnessed that ground drinking water in Tokyo was contaminated by chromium (VI) containing spoil heaps. The concentration of chromium in groundwater was more than 200 times the legal limit (*Chandra, 2014).*

2.1.4.2 Nickel

Nickel is used in numerous industries and as a result, nickel-containing wastewater is released to the environment. In addition, there are a number of other sources for nickel in the environment such as natural weathering, atmospheric deposition and surface runoff *(Brix et al., 2016).* In lakes, nickel is mostly found in ionic form or with organic matter. Also, there is extensive precipitation of nickel in the catchment area of the lake if there is a point source nearby *(Cempel et al., 2006).* In rivers, nickel is transported mainly as a precipitated coating on particles and in association with organic matter.

2.1.4.3 Cobalt

Mining, smelting and other industrial activities are the main sources of cobalt in the wastewater. Moreover, groundwater contamination by radioactive cobalt has also occurred throughout North America as a result of inappropriate disposal or leakage from nuclear waste repositories used by Chalk Ridge-Ontario, Hanford-Washington, Oak Ridge-Tennessee *(Collins et al., 2010).* In addition, cobalt is not biodegradable and the presence in lakes and rivers leads to bioaccumulation in living organisms, animals, plants and humans *(Malakootian et al., 2008).*

2.1.5 Toxicity on human health and the aquatic environment

2.1.5.1 Chromium

Chromium (III) is considered an essential nutrient that plays a vital role in the metabolism of glucose, fat and protein *(Kimbrough et al., 1999).* However, chromium (VI) is considered toxic and has been a major concern due to the dynamic interconversion of chromium (III) to chromium (VI) in aqueous environments. Due to contamination of the environment and water, human population, as well as some wildlife, are at risk (*Tchounwou et al., 2012).* Human health effects of chromium (VI) are lung cancer, respiratory irritation, dermatosis, dermatitis, kidney and liver damage *(Kimbrough et al., 1999).* It was found that chromium in large quantities is toxic for aquatic animals (*Kimbrough et al., 1999).*

2.1.5.2 Nickel

Humans are exposed to nickel in various ways such as inhalation, ingestion and absorption through the skin. Ingestion is considered to be the most significant method of exposure. Nickel is normally present in human tissues and, under high exposure, these levels can increase significantly *(Cempel et al., 2006).* The absorption of nickel is dependent on the solubility and physiochemical form. Humans exposed to high nickel polluted environments show a range of pathological effects. For example, skin allergies, lung fibrosis, cancer and nickel poisoning *(Cempel et al., 2006).* Levels of precipitation of nickel of 0.9 mg/m^2 /year over long periods were found to be dangerous for biological systems of freshwater catchments *(Cempel et al., 2006).*

2.1.5.3 Cobalt

Cobalt is an essential element for humans and a constituent of vitamin B_{12}. However, cobalt compounds can be highly toxic to individuals and the environment *(Gault et al., 2010).* Most common exposure for cobalt for the general population is through food. In addition, skin exposure and inhalation are the most common occupational risks for workers in metal and nuclear industries *(Gault et al., 2010).* Harmful effects include asthma, pneumonia, wheezing and allergies. Based on experiments on animals, cobalt and its compounds are listed as possible carcinogens *(Gault et al., 2010).*

2.1.5.4 Arsenic

Millions of people are exposed to arsenic throughout the world due to groundwater contamination (*Tchounwou et al., 2012).* Exposure to arsenic can occur via ingestion, inhalation, dermal contact and parenteral route to some extent (*Centeno et al., 2005).* Usually, arsenic concentration in water is 10µg/L but the concentration could rise if there are mineral deposits or mining industries nearby (*Tchounwou et al., 2012).* Diet is considered the most common source of exposure for humans. In addition, workers in vineyards, ceramics, glass making, smelting, refining of metallic ores, pesticide manufacturing wood preservation and semi-conductor manufacturing are exposed to higher levels of arsenic (*Centeno et al., 2005)* Exposure to higher levels of arsenic can cause a number of human health effects. Arsenic is considered carcinogenic and can cause systemic health effects. Also, if exposed via drinking water, cardiovascular and peripheral vascular disease, development anomalies, neurologic, nervous, hepatobiliary, renal, gastro-intestinal and respiratory system failure can occur (*Tchounwou et al., 2012).*

2.1.5.5 Cadmium

Cadmium is a toxic metal that has considerable environmental and occupations concern. The main route of cadmium exposure is via inhalation. Cigarette smoke is one of the main sources of inhalation (*Tchounwou et al., 2012).* Ingestion is the second common exposure to cadmium. Cadmium exposure via skin absorption is rare (*Tchounwou et al., 2012).* The main sources of cadmium exposure are working in cadmium-rich industries such as metal industries. In addition, consuming contaminated food and smoking cigarettes are also major sources of cadmium exposure (*Tchounwou et al., 2012).* Other sources include emissions from industries such as mining, smelting, battery and alloy manufacturing. Cadmium can cause severe pulmonary and gastrointestinal irritation which can be fatal. In addition, cadmium can cause abdominal pain, nausea, vomiting, salivation, muscle cramps, vertigo, shock, loss of consciousness and convulsions within 15 to 30 minutes of ingestion (*Tchounwou et al., 2012).* Moreover, cadmium is considered carcinogenetic by multiple regulatory agencies (*Tchounwou et al., 2012).*

2.1.5.6 Lead

As mentioned earlier, lead is a naturally occurring element that is present in the earth's crust (*Tchounwou et al., 2012).* However, due to human activities, lead exposure has increased significantly. Exposure to lead can occur via inhalation and ingestion of lead-contaminated food and water (*Gabby, 2006).* The nervous system is the most vulnerable target of lead poisoning. As a result, headache, poor attention span, irritability, loss of memory and dullness can occur (*Gabby, 2006).* If children are exposed to lead, they may suffer delayed or impaired neurobehavioral development, decreased hearing, speech and language handicaps, growth retardation, poor attention span and anti-social behaviour. Moreover, acute brain and kidney damage and gastrointestinal diseases are common in adults if exposed to lead (*Tchounwou et al., 2012).* Table 2.5 shows the toxicity of some of the metals that are found in industrial wastewater.

Table 2.5: Toxic metals and toxicity (Barakat, 2011)

Toxic Metal	**Toxicity**
Arsenic	Skin manifestations, visceral cancers, vascular disease
Cadmium	Kidney damage, renal disorder, human carcinogen
Chromium	Headache, diarrhea, nausea, insomnia
Copper	Liver damage, Wilson disease, insomnia
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen
Zinc	Depression, lethargy, neurological signs and increased thirst
Lead	Damage the fetal brain, diseases of kidneys, circulatory and nervous system
Mercury	Rheumatoid arthritis, and diseases of kidneys, circulatory and nervous systems

As seen in Table 2.5, the toxic metals can cause many toxic effects on humans such as insomnia, depression and cancer.

2.2 Precious metals in wastewater

2.2.1 Precious metals

Precious metals can be classified as rare, naturally occurring metallic chemicals with a high economic value *(Reeves et al., 1999).* They are also difficult to extract and widely scattered in the natural environment (*Wang et al., 2017).* However, precious metals have shown a broad range of applications in fields like machinery, energy, aviation and chemical industries *(Wang et al., 2017).* This is due to their excellent physical and chemical properties such as high-temperature oxidation resistance, corrosion resistance, good conductivity, and high-temperature thermoelectrical properties *(Wang et al., 2017).* Increasing demand for catalysts and electronic devices has encouraged recovery and recycling of precious metals *(Parajuli et al., 2009).*

Precious metals include gold, silver, platinum-group metals, ruthenium, palladium, osmium, rhodium and iridium *(Wang et al., 2017).*

2.2.2 Main sources of precious metals

In the mining industry, tailing ponds contain trace amounts of precious metals *(Abughusa et al., 2006).* Mining of certain metals such as gold is associated with acid drainage problems that can cause long-term damage to waterways and biodiversity *(Akcil et al., 2006)*. The concentrations of precious metals in mining wastewater ranges from 0.08 - 1 mg/L depending on the mine site *(Vogeli et al., 2011).* Precious metal concentrations in wastewater are prominent in cities with a strong jewellery-making industry, in regions (ancient and modern) with a strong gold mining industry, dental industry waste, automobile exhaust (particularly platinum from catalytic converters) and abrasion of jewellery *(Reeves et al., 1999).* In addition, precious metals are used extensively in biomedicine, electric and electronic industries and aerospace construction *(Duru et al., 2016).*

Silver, gold, platinum and palladium are widely used in jewelry and electronics industries. In the electronics industry, these precious metals are used as a mixed paste during the production process of printed circuit boards to improve the electrical conductivity of joints *(Wang et al., 2017).* In addition, precious metals are used extensively in a variety of industrial products and chemical reagents such as glass, ceramics, oil and pharmaceuticals *(Wang et al., 2017).* Table 2.6 shows the precious metals that are found in industrial effluents.

Table 2.6: Precious metals in industrial effluents

Industry	**Gold**	**Silver**	**Platinum**	**Palladium**	**Rhodium**	**Iridium**	**Ruthenium**
Jewellery	×	×	×	×			
Chemistry			×	×	×		
Electronics	×	×	×	×	×	×	×
Fuel cells			×	×	×		×
Glass, ceramics			×		×		
Medical, dental	×	×	×	×		×	
Oil		×	×				
Pharmaceuticals	×		×	×			×
Photovoltaics		×					×
Super-alloys	×		×				×

As seen in Table 2.6, the precious metals are used widely in all kinds of industries spanning from jewellery to mining. Palladium is one of the most commonly used precious metals, as seen from Table 2.6. Therefore, following sections will be focused on the characteristics of palladium, toxicity, concentrations in various industrial effluents and benefits for recovering it from industrial wastewaters.

2.2.3 Characteristics of Palladium

Palladium is a shiny silvery-white metal that is found mostly in sulfide minerals *(Royal society of chemistry, 2017).* It has no known biological role. Palladium belongs to the platinum group metals and used extensively in catalytic converters since the 1970s *(Chen et al., 2015).* Palladium is considered to have the lowest melting point and has the least density in the platinum group metals *(Liu et al., 1979).* Palladium has many oxidation states but 4, 2 and 0 are the most common states. In addition, palladium is known to resist corrosion *(Royal society of chemistry, 2017)*. Palladium can also be used for organic coupling reactions, hydrogen purification and storage, and hydrogen sensors *(Konda et al., 2017).*

Table 2.7 shows the typical palladium concentrations found in various in industrial effluents.

Table 2.7: Palladium concentrations in industrial effluents

Industry	Typical concentration (mg/L)	Reference
Recycling process plant	183.1	*(Umeda et al., 2011)*
Electronics manufacturing	10	*(Gurung et al., 2012)*
Steel industry	60	*(Kakoi et al., 1996)*
Electro-plating	6- 10	*(Noah et al., 2016)*
Metal recycling facility	0.02	*(Parajuli et al., 2009)*

As seen in Table 2.7, the concentration of palladium in industrial wastewater varies between 0.02 - 183 mg/L. Recycling process plant effluent contained the highest concentration of palladium in water while metal recycling plant facility effluent contained very low concentrations of palladium.

2.2.4 Contamination of the aquatic environment

The development of catalytic converters in automobiles led to palladium contamination of aquatic environment *(Luderwald, 2016)*. Nano-sized palladium is used in catalytic converters of vehicles and palladium is reduced or oxidized within these converters. The contamination of soils along major highways shows high levels of palladium *(Luderwald, 2016)*. During heavy rains, palladium transfers into water bodies via surface runoff *(Luderwald, 2016)*. In addition, palladium can also be introduced to water bodies through palladium-induced rainwater from the atmosphere *(Luderwald, 2016)*. Moreover, unattended dumping of obsolete electronic devices and proliferated mining also lead to high concentrations of palladium in the environment *(Parajuli et al., 2009).*

2.2.5 Toxicity on human health and the aquatic environment

The accumulated levels of palladium are increasing worldwide *(Awual et al., 2015).* As a result, toxic palladium compounds are increasing in the environment. These compounds are considered toxic to mammals, fish and higher plants *(Awual et al., 2015).* In addition, palladium compounds can easily transport to the biological material through plant roots and can have adverse effects on human health causing primary skin problems, eye irritations and substantial degradation of DNA *(Awual et al., 2015).* In addition, exposure to palladium can cause acute toxicity or hypersensitivity with respiratory systems *(Noah et al., 2016).* High concentrations of palladium also have adverse effects on the aquatic life *(Luderwald et al., 2016).*

2.2.6 Benefits of recovering precious metals

According to *Behnamfard et al., (2013),* gold has the highest economic incentive ($15,200 per ton of Printed Circuit Board) followed by palladium ($1850 per ton of Printed Circuit Board) and then copper ($1400 per ton of Printed Circuit Board). In addition, recovery of precious metals could potentially make treatment processes more cost-effective and sustainable *(Wang et al., 2014).* In 2011, U.S. Water Environment Research Foundation reported that 10 million gallons per day wastewater treatment plant can recover up to $8849-$3,904,664 worth of silver per year *(Wang et al., 2014).* In another study, it was found that approximately $4600 worth of gold can be recovered from 10 m^3 of electroplating wastewater *(Chen et al., 2013).* Increasing demand and limited availability have led to a great increase in price and thus it is important to recover precious metals from industrial effluents *(Wang et al., 2014).* Palladium is one of the scarce precious metals that has a very high industrial usage and a high economic value *(Noah et al., 2016).* Due to these reasons, recovery of palladium from different kinds of wastewater is given much attention *(Parajuli et al., 2009)*.

2.3 Current treatment methods for removal/recovery of toxic and precious metals from industrial wastewaters

Current methods of removal can be categorized into three main categories. Physical treatment, chemical treatment and biological treatment methods *(Barakat, 2011).* Most of the times, combinations of one or more methods are used for removal of metals. It is important to note that the most suitable treatment method for metal removal depends on pH, initial metal concentration, capital investment, operational costs, plant flexibility, reliability and overall treatment performance *(Barakat, 2011).*

2.3.1 Ion Exchange

Ion exchange is a system which utilizes the exchange of ions between the solution and an insoluble material (resins) that is capable of exchanging cations and anions *(Alvarado et al., 2014)*. When a chemical potential gradient occurs between the solution and the resin, the ions in the solution displace the mobile species in the resin, which are retained due to intermolecular attractions (*Alvarado et al., 2014)*. When in contact with certain solids, water containing dissolved electrolytes undergo changes. Ions can be exchanged from the surface or in the interior of the solid ion exchange resin. In order to maintain the law of electro-neutrality, the total number of ions entering the solution is equal to the total number of ions leaving the solution *(Al-Enezi et al., 2004).*

Ion exchange is a versatile process which can be used to separate metal ions from wastewater *(Al-Enezi et al., 2004).* Since ion exchange is efficient in removing dissolved solids from normally dilute spent rinse waters, it is well-matched for water purification and recycling *(Al-Enezi et al., 2004).* Moreover, ion exchange can also be used for removing most plating chemicals, acids and bases used in metal finishing *(Al-Enezi et al., 2004).* Due to their many advantages such as high treatment capacity, high removal efficiency, and fast kinetics, ion exchange is widely used to remove metals from wastewater (*Al-Enezi et al., 2004).* Lab scale studies were conducted using either synthetic or natural solid resins for improving removal efficiencies for toxic metals such as chromium and nickel (*Al-Enezi et al., 2004).* However, due to the resins being saturated on a regular basis, operational costs and sludge production are high for ion exchange processes *(Zhao et al., 2016).*

Table 2.8: Levels of metals in water before and after ion exchange process

Metal	**Before ion exchange (µg/L)**	**After ion exchange**
Cadmium	21	<1 µg/L
Chromium	80	<1 µg/L
Copper	700	<1 µg/L
Mercury	58	<1 µg/L
Nickel	111	<1 µg/L
Lead	337	<1 µg/L
Zinc	2002	<1 µg/L

As seen in Table 2.8, after the experiments, it was found that all the metal concentrations in the water were found to be less than 1 µg/L in the effluent from the ion exchange system. Almost 99.9% removal efficiency could be achieved. This shows that ion exchange is a very effective system to get rid of metals from wastewater *(Al-Enezi et al., 2004).*

2.3.2 Membrane filtration

Membrane filtration is a pressure-driven separation technique that is used in water and wastewater treatment. Membrane filtration separates particles based on its size, solution concentration, pH and applied pressure *(Carolin et al., 2017).* Depending on the size of the particle, the membrane filtration can be subdivided into microfiltration, ultrafiltration, nano-filtration and reverse-osmosis as seen in Figure 2.1 *(Barakat, 2011).* The membranes are made out of special porous material which plays a major role in removing metals from wastewater *(Carolin et al., 2017).* This porous material can be made out of ceramic or polymer

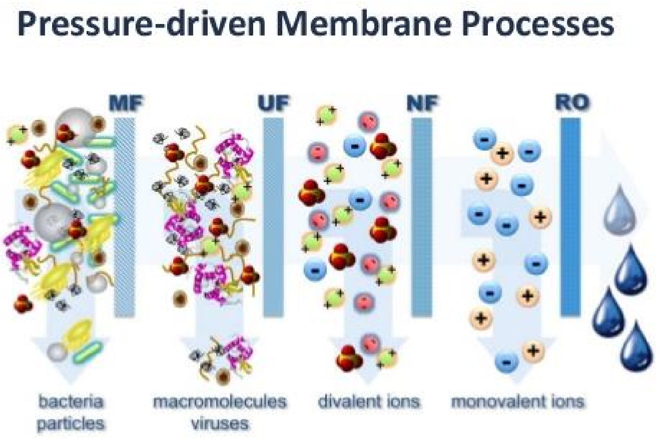

Figure 2.1: Membrane filtration *(Barakat, 2011)*

In ultrafiltration, the pore size of 10-100nm is used to separate metals *(Carolin et al., 2017).* This allows the water and low-molecular solutes to pass through the membrane while retaining macromolecules which are larger than the pore size. Moreover, the metal removal efficiency depends on the parameters such as pH, ionic strength and concentrations of the metals *(Fu et al., 2011).*

Using micellar-enhanced ultrafiltration in lab-scale experiments, *Fu et al., (2011)* were able to improve removal efficiencies for metals such as copper, nickel, zinc, and chromium. *Fu et al., (2011)* and *Ahmed et al., (2017)* could achieve over 96% removal efficiencies for metals such as copper, nickel, zinc and chromium from synthetic wastewater with concentrations in the range of 0.5 - 500 mg/L by using micellar-enhanced ultrafiltration system in a lab-scale study. Nano-filtration is a promising technology for removal of metal ions such as nickel, chromium, copper and arsenic from wastewater *(Fu et al., 2011).* Nano-filtration has many advantages such as ease of use, comparatively low energy consumption and high efficiency *(Fu et al., 2011).* Using a thin film composite polyamide nanofiltration membrane, very high nickel separation could be achieved *(Fu et al., 2011).* It was reported that 92%-98% removal efficiency could be achieved for a feed concentration of 5- 250mg/L *(Fu et al., 2011).* Reverse osmosis process uses a semi-permeable membrane which allows the fluid that is being purified to pass through the membrane while rejecting the contaminants *(Fu et al., 2011).* Reverse osmosis is considered to be one of the methods that are capable of removing a wide range of dissolved contaminants from water which is mainly used for desalination *(Fu et al., 2011).* Table 2.9 (*Fu et al., 2011)* shows the metals removed by reverse osmosis and nanofiltration.

Table 2.9: Metals removed by reverse osmosis and nanofiltration

Membrane	Metal	Concentration (mg/L)	Removal Efficiency
Reverse Osmosis	Copper, Nickel	500	99.5%
Reverse Osmosis	Copper	20-100	70-95%
Reverse Osmosis	Arsenic	<0.5	91-99%
Reverse Osmosis	Nickel, Zinc	44-170	99%
Nanofiltration	Copper	10	47-66%
Nanofiltration	Chromium (VI)	-	100%
Nanofiltration	Copper	0.47	96-98%

As seen in Table 2.9, very high removal efficiencies could be achieved using reverse osmosis and/or nanofiltration for metals such as copper, nickel, arsenic, zinc and chromium. However, high initial costs, complex processes and membrane fouling issues need to be considered before using a membrane filtration system *(Ahmed et al., 2017).* In order to avoid membrane fouling, wastewater has to be pre-treated to remove organic matter which could hinder the process of membranes. However, membrane filtration is an attractive method for metal removal as it is very efficient, easy to use and requires less footprint *(Barakat, 2011).*

2.3.3 Chemical precipitation

Chemical precipitation is a comparably cheap and widely used technique for metal removal. For chemical precipitation to work, chemicals are added to the solution that changes the pH to form precipitation *(Chon et al., 2014).* The precipitation is removed using the sedimentation process and the remaining solution is further treated to match the standards before discharging into the environment *(Fu et al, 2016).* Chemical precipitation can be used effectively for removing metals such as copper, cadmium, manganese and zinc *(Ahmad et al., 2016).* Moreover, chemical precipitation is very effective at treating high concentrations of metals in wastewater *(Kuan et al., 2010).* However, the main drawback of chemical precipitation is the production of excessive sludge with high water content due to the precipitation of insoluble metals which are difficult to treat and considered as a hazardous waste (*Kuan et al., 2010).*

There are two major precipitation processes that are used today; hydroxide precipitation and sulphide precipitation *(Carolin et al., 2017).* Hydroxide precipitation is the most preferred method for handling metals. This is due to the ease of handling and low cost associated with hydroxide precipitation. Metal hydroxides can be removed by flocculation and sedimentation (*Fu et al, 2016).* Different types of precipitants such as lime, calcium hydroxide, sodium hydroxide can be used to form hydroxide precipitate *(Carolin et al., 2017).* Addition of coagulants such as alum, iron salts and organic polymers can also increase the efficiency of metal removal. As mentioned earlier, hydroxide precipitation generates large volumes of low-density sludge which leads to dewatering and disposal problems *(Fu et al, 2016).* Moreover, some of the metal hydroxides are known to be amphoteric and this leads to problems in precipitation since the ideal pH for one metal may put another metal back into solution *(Fu et al, 2016).*

Sulphide precipitation is also an effective method for removing metals from wastewater *(Fu et al, 2016).* One of the main advantages of using sulphide precipitation is that the solubility of the metal sulphides is lower than hydroxide precipitates. Also, sulphide precipitates are not amphoteric. Due to this reason, metal removal over a broad pH range can be achieved *(Fu et al, 2016).* In addition, metal sulphides have better thickening and dewatering properties than the corresponding hydroxide sludge *(Fu et al, 2016).* However, using metal sulphides could be hazardous due to in acidic conditions, metal sulphides could react and release hydrogen sulphide gas. Therefore, it is important to control pH so that the process is performed in the neutral or basic medium. In addition, metal sulphides tend to form colloidal precipitates that can cause separation difficulties in settling or filtration processes *(Fu et al, 2016).* Table 2.10 shows the efficiency of chemical precipitation in removing metals such as chromium, zinc and nickel.

Table 2.10: Efficiency of chemical precipitation

Metal	**Removal Efficiency**	**Reference**
Zinc	99.7%	*(Ghosh et al., 2011)*
Chromium	99.7%	*(Ramakrishnaiah et al., 2012)*
Nickel	98.4%	*(Fu et al., 2012)*
Copper	99.37%-99.6%	*(Zhao et al., 2016)*
Lead	92%	*(Zhao et al., 2016)*

As seen in Table 2.10, very high removal efficiencies could be achieved by chemical precipitation for metals such as zinc, chromium, nickel, copper and lead.

2.3.4 Adsorption

Adsorption is the adhesion of atoms to a surface and is considered an effective method for removing metals from wastewater *(Jusoh et al., 2007)*. The adsorption process offers flexibility in design and operation and has the ability to produce high-quality treated effluent *(Jusoh et al., 2007)*. However, adsorption process is reversible and adsorbents can be regenerated by an appropriate desorption process *(Jusoh et al., 2007)*. Activated carbon is one of the widely used methods of adsorption for metal removal (*Jusoh et al., 2007)*. This is because of the large micro-pore and mesopore volumes resulting in a high surface area (*Jusoh et al., 2007). Jusoh and colleagues (2007),* studied the effectiveness of granular activated carbon to remove metals such as cadmium and lead from synthetic wastewater. Results showed that at a flow rate of 4 mL/min, 99.5% and 99.9% removal of cadmium and lead could be achieved using activated carbon.

Carbon nano-tubes can also be used as adsorbents for metal removal *(Rao et al., 2007).* As a new material, carbon nano-tubes have shown potential for removing metal ions such as lead, cadmium, chromium, copper and nickel from wastewater *(Rao et al., 2007).* The mechanism of adsorption depends on the properties such as electrostatic attraction, sorption-precipitation and chemical interactions between the metal ions and the surface of carbon nano-tubes *(Rao et al., 2007).* However, extensive use of carbon nano-tubes will eventually pollute the environment and poses a risk to humans. Therefore, environmentally friendly adsorbents are used to mitigate this problem *(Li et al., 2010).*

Biosorption is an alternative method of adsorption which utilizes adsorbents derived from chitinous materials, algal biomass or microbial biomass such as bark, lignin, shrimp, krill, squid and crab shell *(Apiratikul et al., 2008).* It is a relatively new process that has the potential for removing metal contaminants. The primary advantage of biosorption is that it is very inexpensive and can have very high effectiveness in removing the metal ions *(Apiratikul et al., 2008).* In a study conducted by *Apiratikul and colleagues, (2008),* using algal biomass, up to 83% removal of lead, copper and cadmium could be achieved for concentrations between 0.01- 0.15 mol/m^3. However, the downsides of bio-sorbents are most of it is still under theoretical and experimental phase *(Apiratikul et al., 2008).*

2.3.5 Electrochemical treatment

Electrochemical methods include plating-out of metal ions on a cathode surface. The electrochemical method allows for recovery of metals in elemental form *(Fu et al, 2016).* Electrocoagulation is an electrochemical treatment method which involves the production of coagulants in-situ by dissolving aluminum or iron ion from aluminum or iron electrodes *(Chen et al., 2004).* The metal ion generation occurs in the anode and hydrogen gas is produced in the cathode. This hydrogen gas helps to float the flocculated particles out of the water *(Chen et al., 2004).* Electrocoagulation treatment processes have a wide range of applications in wastewater treatment. In addition, it is very effective in removing organic contaminants and pathogens. Since these processes produce very little sludge, it can easily replace the conventional chemical coagulation tanks and very little modification is needed. For example, by using an aluminum electrode, removal efficiencies of over 99% were achieved for zinc, copper, nickel, silver and chromium *(Chen et al., 2004).* Table 2.11 shows a summary of metal removal efficiency in electrochemical methods.

Electrochemical methods require a relatively large capital investment and an expensive electric current supply. The efficiency could be increased by the development of new electrodes. Moreover, it is considered a clean technology because of little or no addition of chemicals *(Fu et al., 2016).* Electrochemical treatment methods have the potential to become one of the most efficient ways for treating wastewater *(Fu et al, 2016).*

Table 2.11: Metal removal from electrochemical methods

Metal	**Initial concentration (mg/L)**	**Removal Efficiency**	**Reference**
Manganese	100	78.2%	*(Shafaei et al.,2010)*
Nickel	236-248	99.9%	*(Kabdasli et al., 2010)*
Arsenic	2.24	>99%	*(Parga et al., 2005)*
Chromium (VI)	1470	99%	*(Olmez et al., 2009)*
Zinc	20-250	96%	*(Casqueira et al., 2006)*
Copper	100	98%-99%	*(Khelifa et al., 2005)*

2.3.6 Freeze concentration for wastewater treatment

Freeze concentration is a physical treatment method that consists of fractional crystallization of water followed by removal of ice (*Gao et al., 2009).* Freeze concentration has been widely investigated and used in the food industry on liquid food products *(Sanchez et al., 2009).* Lately, interest in freeze concentration for wastewater has increased due to few factors such as high separation ratio, high-energy efficiency, low operational costs, and low capital investment in comparison to other treatment processes such as reverse osmosis and electrodialysis *(Williams et al., 2013).* Freeze concentration has been used for removal of various organic and inorganic contaminants from industrial effluents such as petroleum refinery, pulp and paper effluents, pharmaceutical active compounds, glucose solutions, polypepton wastewater, cutting oil wastewater, urban wastewater and desalination *(Gao et al., 2008; Gao et al., 1999; Gao and*

Shao, 2009; Wakisaka et al., 2001; Lu et al., 2017; Lorain et al., 2001; Fujioka et al., 2013,). In a recent study, *Melak and his coworkers (2016)* conducted a study using freeze concentration to remove chromium (VI) from synthetic wastewater. Solutions of chromium (VI) with varying concentrations from 1 – 300 mg/L and variable chloride ion concentrations (5, 10, 250 and 3550 mg/L) were frozen and removal efficiency of chromium (VI) under various salinity was examined. Chromium (VI) removal efficiency between 85% - 97% was achieved and removal efficiency of chromium (VI) decreased with increasing salinity *(Melak et al., 2016).* Boron removal using single stage freeze concentration was studied by *(Wang, 2017).* Synthetic wastewater containing boron samples of 100 mg/L, 500 mg/L, and 1000 mg/L were used to determine the effects of the advance speed of the ice front, the circumferential velocity of the stirrer and the initial boron concentration. With single stage, FC, the concentration of the unfrozen liquid samples were increased 3-4 times while boron removal ratio between 90% - 99% was also achieved (*Wang, 2017).* The results from the study showed that the effectiveness of boron removal improved with a lower advance speed of the ice front, a higher circumferential velocity of the stirrer and a lower initial boron concentration *(Wang, 2017).* Zinc and lead-containing synthetic wastewater samples were used by *(Gay et al., 2003)* to determine the residual concentrations in the treated medium (ice) and the effects of mixing in FC. Wastewater samples containing zinc, lead and a mixture of zinc and lead between concentrations of 500 - 1000 mg/L were used. Over 98% removal ratio of zinc and lead could be achieved via single stage freeze concentration, and it was also found that mixing makes the separation mechanism more efficient *(Gay et al., 2003).*

During the freeze concentration, contaminants are separated from the wastewater due to the formation of ice crystals leaving impurities in the remaining liquid *(Halde, 1980).* This leads to a concentration gradient between the solid and the liquid phase. According to *Sanchez et al., (2009),* there are two types of freeze concentration methods; suspension crystallization and progressive crystallization. Suspension crystallization involves the formation, growth, and separation of various ice crystals where progressive crystallization involves the formation, growth, and separation of a single ice crystal as seen in Figure 2.2 *(Sanchez et al., 2009).*

Suspension crystallization, even though has higher efficiency, is a complicated and expensive system *(Miyawaki et al., 2005)*. Therefore, practical applications are limited to the food industry. In contrast, progressive crystallization offers a simple, easy-to-use process which can be cheaper. Therefore, it has drawn more attention in wastewater treatment *(Miyawaki et al., 2005).*

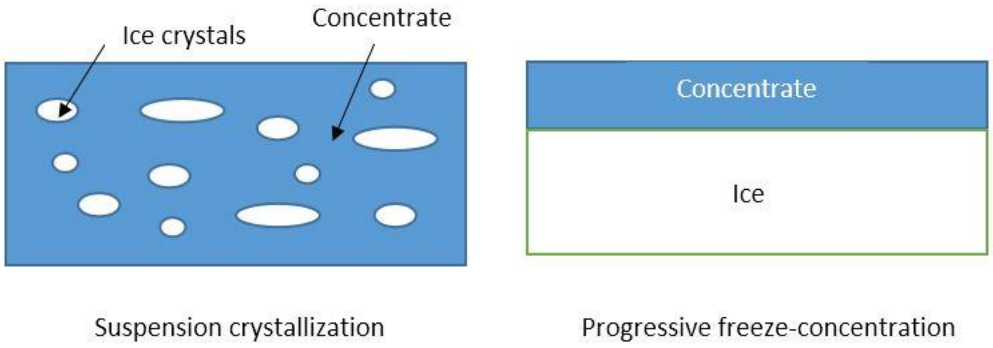

Figure 2.2: Figure of suspension and progressive freezing *(Miyawaki et al., 2005)*

2.3.6.1 Advantages of freeze concentration

One of the main advantages of freeze concentration is the flexibility of feedwater concentration. For example, changes in the feedwater composition can influence the efficiency of biological treatment methods (*Ruemekorf et al., 2000).* Also, biological treatment is sensitive to toxic metals or compounds but freeze concentration can be used effectively in similar scenarios

(Partyka, 1986). In addition, high purity ice crystals that are formed during the treatment can be reused within an industrial operation or used for air conditioning systems especially in warmer climates *(Wakisaka et al., 2001).* Moreover, compared to evaporation, freeze concentration has high energy efficiency since the latent heat of freezing is low compared to the latent heat of evaporation (333.5 kJ/kg vs 2256.7 kJ/kg), no biological fouling, scaling and corrosion problems due to low operating temperature, less use of chemicals and thus lower operating costs, no discharge of toxic chemicals to the environment due to lack of chemical pre-treatment and can operate for a long time with little maintenance*(Williams et al., 2015; Fujioka et al., 2013).*

2.3.6.2 Factors that influence freeze concentration

The removal efficiency of metals in freeze concentration may be affected by many factors such as the freezing rate, initial feedwater concentration, mixing speed and particle size *(Luo et al., 2010; Fujioka et al., 2013*; *Gao et al., 2009*). For example, the advancing speed of the ice front should be low enough to let the impurities be rejected from the growing ice crystals at the interface of ice and water (*Luo et al., 2010).* Also, higher removal efficiency can be achieved when fed with a lower initial concentration *(Luo et al., 2010). Halde, (1980*) reported that there is a substantial difference in the effectiveness of forming a concentration gradient for a variety of different sizes of impurities. It was reported that coarser particles were much more effectively removed than finer particles.

2.3.6.3 Partition constant

A comprehensive analysis of progressive freeze concentration was conducted by *Miyawaki et al., (1998)* in which theoretical breakdown and experimental operating conditions on the effectiveness of freeze-concentration were provided. The effectiveness of progressive freeze concentration could be defined by the effective partition constant.

The effective partition constant of solute could be defined as the concentration ratio between the solid and liquid phases. The effective partition coefficient can be calculated using Equation 2.1 *(Liu et al., 1999).*

$$K = {}^{C_s}/_{C_L} \tag{2.1}$$

Where,

K- Effective partition constant of solute
C_s -solute concentration in the ice phase at the boundary
C_L- solute concentration in the bulk liquid phase

This parameter K defines the effectiveness of progressive freeze concentration and can be experimentally determined by the following equation. Experimental calculation of effective partition constant can be calculated using Equation 2.2 *(Liu et al., 1999).*

$$(1-K)\, log\left({}^{V_L}/_{v_0}\right) = log({}^{C_0}/_{C_L}) \tag{2.2}$$

Where,

V_0- liquid phase volume at the beginning of time

V_L- liquid phase volume at an arbitrary time

C_0- solute concentration in the liquid phase

C_L- solute concentration at an arbitrary time

2.3.7 Electrodeionization

2.3.7.1 Introduction

Electrodeionization (EDI) is a hybrid separation process consisting of electrodialysis (ED) and ion exchange (IX) methods *(Song et al., 2007).* In an EDI setup, cation and anion exchange membranes are alternately placed between the electrodes. The central compartment is filled with ion exchange materials that improve the transport of cations and anions under the driving force of a direct current *(Song et al., 2007).* Water dissociation reaction happens during the EDI operation which produces hydrogen (H^+) and hydroxyl ions (OH^-). These H^+ and OH^- ions continuously regenerate the ion exchange resins electrochemically without the use of regenerating chemicals *(Song et al., 2007).*

A typical EDI device contains membranes that are placed alternately between the cathode and the anode *(Tanaka et al., 2012).* The space between the membranes is set up to allow liquid to flow into the compartments via inlets and outlets. An electric field is applied by an external power source through the electrodes at the ends of the membranes and compartments *(Tanaka et al., 2012).*

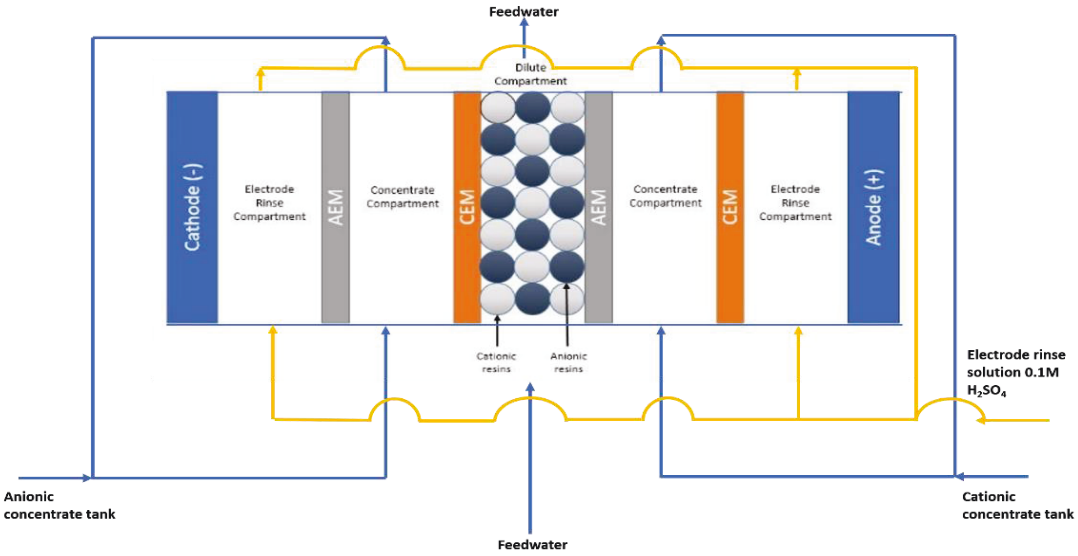

Figure 2.3: A typical EDI device setup *(Alvarado et al., 2014)*

As seen in Figure 2.3 *(Alvarado et. al, 2014),* in a continuous electrodeionization (CEDI) device, the dilute compartment and in some cases, concentrate compartments are filled with ion exchange resins *(Wood et al., 2010).* These resins improve the transportation of ions and can also participate as a substrate for electrochemical reactions such as splitting of water into H^+ and OH^- ions *(Wood et al., 2010).* As a result of electro-regeneration, EDI has far better results compared to electrodialysis and ion exchange in the separation of ions (*Wood et al., 2010).* In an EDI system, different configurations of media can be used depending on the feedwater parameters. For example, a mixture of anion and cation exchange resins or separate sections of ion exchange resins can be used accordingly *(Arar et al., 2014).*

Due to selective properties of the ion exchange membranes and the direction of the electrical potential gradient, ions in the dilute compartment move to the adjacent concentrate compartments *(Tanaka et al., 2012).* This is possible due to the use of ion exchange resins in the dilute compartment. One of the reasons for this is that, without the ionic conductivity of the resins, the ion transfer does not occur at a practical rate *(Tanaka et al., 2012).*

Another reason for having resins in the dilute compartment is that there is an important electrochemical relationship between the applied potential and the equilibrium concentration of H^+ and OH^- ions in water *(Wang et al., 2000).* Localized areas with high potential gradients can produce a substantial amount of H^+ and OH^- ions. This production of H^+ and OH^- ions can lead to localized pH fluctuations that can hinder the performance of the EDI cell *(Wang et al., 2000).*

The main consumable in an EDI cell is electricity. The average cost of running an EDI system is usually between \$0.2-3.0 / 1000 gallons of water produced. However, these numbers vary depending on the feedwater quality and specifications of the EDI cell. Recent developments in EDI technology has led to a decrease in electricity costs *(Khoiruddin et al., 2014).*

2.3.7.2 Mechanisms of ion removal

A CEDI device has two separate operating regions: ion removal region and water splitting region. In the ion removal region, resins act as the transport medium for the transportation of ions to the ion exchange membranes *(Wood et al., 2010).*

At the water splitting region, due to electrically induced water dissociation, continuous regeneration of resins occurs by hydrogen and hydroxide ions *(Ganzi et al., 1997).* This dissociation occurs at the bipolar interfaces (resin/resin interface or resin/membrane interface) in the dilute compartments. In a mixed-bed setup, water splitting can occur at both types of interfaces. This leads to very effective resin regeneration (*Ganzi et al., 1997).* A current-voltage graph can be seen in Figure 2.4 below.

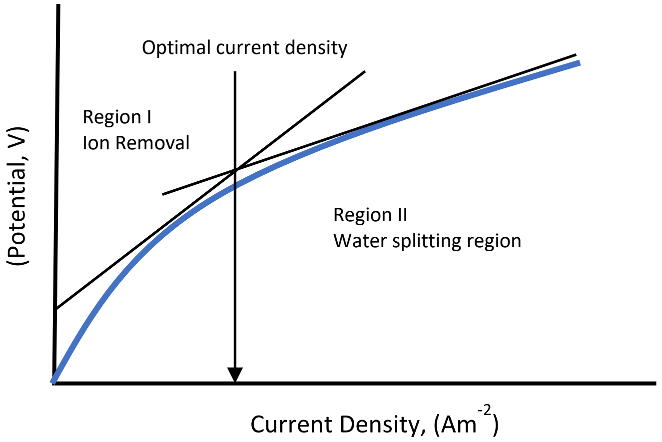

Figure 2.4: Current-voltage graph *(Alvarado et al., 2014)*

As seen in Figure 2.4 *(Alvarado et. al, 2014),* as the current density increases, the potential increases exponentially. Using two different slopes, as shown in Figure 2.4, the optimal current density can be found. Region I is the ion removal region while the region II, is the water splitting region.

Since various types of resins can be used for the EDI system, Table 2.12 shows the types of resins that can be used for each type of metals.

Table 2.12: Types of resins used for each metal

Metal	**Resin**	**Reference**
Chromium	Lewatit MPC 64	*Bergmann et al., 2009*
	Wolfatit SZ 30	*Bergmann et al., 2009*
	CET cellulose	*Elleunch et al., 2006*
	Amberlite IR-120	*Lee et al., 2007*
	D354	*Xing et al., 2007*
Nickel	D072	*Lu et al., 2011*
	Dowex 50 WX 2%	*Spoor et al., 2001*
	Dowex 50 WX 4%	*Spoor et al., 2001*
	Dowex MSC-1	*Rozhdestevenska et al., 2006*
	Purolite C100E	*Pailin et al., 2011*
	Amberlite IRN 77	*Wang et al., 2000*
	Zirconium hidrophosphaste	*Rozhdestevenska et al., 2006*
Cobalt	Purolite 100E	*Dermentzis et al., 2010*
	Amberlite IRA-67	*Willauer et al., 2011*
	Diaion SKN1	*Ganzi et al., 1991*
	Amberlite IRA-77	*Song et al., 2004*

Table 2.12 shows that various brands offering different types of resins for particular needs. The selection of resins is based on the feedwater parameters such as concentration, content and pH etc. *(Alvarado et al., 2009).*

2.3.7.3 Removal of metals

Lately, EDI has received a great interest in metal removal. However, due to the precipitation of bivalent metal hydroxide as a result of metal ions reacting with hydroxide ions that are in EDI cell, the applications in wastewater treatment has been greatly limited *(Arar et al., 2014).* EDI is widely used in metal removal from different types of industries such as mining, electroplating and nuclear processes (Usually, mining waste is treated using precipitation. Since precipitation creates sludge, scientists are looking at new methods to decrease sludge production and/or replace precipitation techniques) (*Alvarado et. al, 2014).*

2.3.7.3.1 Removal of Chromium (VI)

Research on the removal of chromium (VI) using electrodeionization has been conducted by many researchers *(Xing et al., 2009)*. A comparison of electrodeionization, ion exchange and electrodialysis was conducted for removal of chromium (VI) in order to evaluate the sturdiness of electrodeionization by *Alvarado et al., (2009).* The results showed that 99.8% of 100 mg/L of chromium (VI) was efficiently removed by electrodeionization. Moreover, using a completely saturated mixed resin bed with identical concentrations as before, 98.5% removal could be achieved with a CEDI process at an applied current of 6.6 mA *(Alvarado et al., 2009).*

Xing and his colleagues (2009) used an EDI cell to remove chromium (VI) from wastewater. According to their findings, migration rate of $Cr_20_4^{2-}$ is linearly proportional to the current density, flow rate and initial concentration. Furthermore, *Xing et al, (2009)* found that using a continuous electrodeionization system, chromium (VI) concentrations of 40 mg/L and 100 mg/L could be reduced to 0.09 mg/L and 0.49 mg/L respectively.

2.3.7.3.2 Removal of Nickel

Spoor et al., (2001) studied the removal of 602 mol/ m^3 of nickel ions from the aqueous solutions by the EDI. The flux of nickel ions and current efficiency for transportation of nickel ions increased with increasing the concentrations in the resin. In addition, the removal rate of nickel ions decreased at pH <2. However, using an acidic feed, the formation of $Ni(OH)_2$ was decreased *(Spoor et al., 2001)*. The nickel ions were removed in many ways. By the transport through the solution phase to the cathode compartment, by sorption in the ion-exchanger and subsequent transport to the cathode compartment or by precipitation as a hydroxide in the central compartment *(Spoor et al., 2001)*.

Lu et al., (2011) studied the effects of resin particle size on the removal of nickel ions by EDI. It was found that the particle size in the dilute compartment affects the removal efficiency significantly. The best performance could be achieved by using 0.71-0.90 mm resin particle size range *(Lu et al., 2011).* In another work by the same author, the effects of voltage in nickel removal were also discussed. According to the findings, applying 12V to the system, 99.8% removal efficiency for 50 mg/L of nickel ions could be achieved.

2.3.7.3.3 Removal of Cobalt

Cobalt removal from nuclear power plant waste was studied by *Yeon et al., (2003)*. The media type and ion exchange bed configuration to achieve best results were studied for cobalt removal. It was found that the ion-exchange textile was better than ion-conducting spacers in terms of efficiency and faster kinetics. Moreover, it was found that having a three parts configuration for the ion exchange resin bed, over 99% ion removal and 30% current efficiency could be achieved for 10 mg/L of cobalt solution *(Yeon et al., 2003)*.

In another study conducted by the same researcher*,* it was found that using a two-stage EDI system, 97% removal 10 mg/L of cobalt ions could be achieved using a mixed-bed ion exchange resin. In the same study, ion exchange capacity, electrical conductivity and zeta potential of the resin beds were also investigated. No significant difference was found between the conductivity of the ion exchange resin and the voltage drop (*Yeon et al., 2003)*.

In a study conducted by *Dermentzis et al., (2010)* removal of cobalt ions was achieved by using graphite powder beds between the anode and cathode as intermediate electrodes inside an electrolytic set-up. This membrane less method could achieve ion concentrations less than 0.1 mg/L from 100 mg/L initial feedwater *(Dermentzis et al., 2010).*

Available physical and chemical methods to remove toxic and precious metals from industrial effluent include chemical precipitation, membrane filtration, adsorption, ion exchange and electrochemical treatment methods such as electrocoagulation *(Carolin et al., 2017, Ahmed et al., 2017, Barakat, 2011).* The removal using these methods is often uneconomical because of the requirement of high capital and operational costs, generation of sludge, high chemical usage and complex processes. In contrast, freeze concentration and electrodeionization (which are still on a limited scale) offer simplicity, cost-effectiveness and high feasibility in operations to remove a variety of metals.

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Chapter 3- Toxic and precious metal removal from wastewater using freeze concentration

3.1 Introduction

Metals such as antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, thallium and zinc are known to have adverse effects on life and the environment and are considered as toxic metals *(Mohan et al., 2007, United States EPA, 2014).* These toxic metals are known to cause multiple organ damages even at low concentrations such as kidney and liver damage, asthma, headache and cancer *(Tchounwou et al., 2012, Barakat, 2011).* Currently, there has been a raised concern about ecological and global public health associated with toxic metals *(Tchounwou et al., 2014).* On the other hand, metals such as gold, platinum, palladium ruthenium, osmium, rhodium, iridium, and silver have a very high economic value and are considered precious metals *(Wang et al., 2017).* Gold and silver nanoparticles are known to have adverse effects such as the formation of reactive oxygen species and cytotoxicity on rainbow trout (*Farkas et al., 2010).* Exposure to palladium through water has known to cause skin problems, eye irritations and degradation of DNA in humans *(Awual et al., 2015).* In addition, high levels of palladium can have lethal effects on aquatic life *(Luderwald et al., 2016).* Even though these metals are naturally occurring, due to exponential use of these metals in industrial, agricultural, domestic and technological applications, human exposure and environmental contamination have increased radically *(Tchounwou et al., 2014).* Toxic metals such as chromium, copper, cadmium, lead, mercury and nickel are extensively used in many industries such as mining, pulp and paper, petrochemicals, fertilizers, steel, metal plating and textile *(Onikura et al., 2008, Verma et al., 2010, Cavas et al., 2005, Lothongkum et al., 2009, Silva et al., 2008, Bruggen et al., 2001, Agrawal et al., 2007, Gan, 2000).* For example, effluent from mining, steel industries, sugar industries, petrochemical industries, textile industries, and leather tanning industries all contain chromium with concentrations varying from about 1 - 500 mg/L *(Dakiky et al., 2002; Lothongkum et al., 2009; Gupta et al., 2004; Mirbagheri et al., 2004; Bruggen et al., 2001; Agrawal et al., 2007).* Nickel-containing wastewater is much more prominent in industries such as steel, fertilizer, electroplating and mining and the nickel concentrations in the wastewater were in the range of 7 - 275 mg/L *(Price et al., 2016; Lothongkum et al., 2009; Camelo et al., 1997; Benvenuti et al., 2014; Huang et al., 2016)*. Furthermore, cobalt is common in wastewater from industries such as steel, pharmaceutical, paint, mining, and tannery. The effluent cobalt concentrations were found to be in the range of 9 µg/L to 1 mg/L *(Keranen et al., 2015; Singh et al., 2013; Amin et al., 2015; Malakootian et al., 2008; Bhuiyan et al., 2010)* In addition, palladium is commonly found in effluents from mining, jewelry, electronics and medical industries and the concentrations of palladium in the effluents are between 1 µg/L to 31 mg/L *(Wang et al., 2017, Abughusa et al., 2006, Parajuli et al., 2009).* Removing and recovering these toxic and precious metals not only reduce the adverse environmental impact but also compensate the cost of wastewater treatment *(Parajuli et al., 2009, Chen et al., 2015).*

Metals such as chromium, cobalt, nickel, and palladium are employed in widely diversified fields such as mining, petrochemical, steel, metal plating etc. *(Onikura et al., 2008, Verma et al., 2010, Cavas et al., 2005, Lothongkum et al., 2009, Silva et al., 2008, Bruggen et al., 2001, Agrawal et al., 2007, Gan, 2000).* Depending on the desired final water quality, a mine may use coagulation and flocculant methods, ion exchange methods, and/or membrane filtration *(Rankin et al., 2011)*. Furthermore, in the mining industry, as the mining area is exhausted, these mining areas are abandoned, leaving behind tailing ponds containing a wide range of toxic and precious metals *(Meldrum et al., 2001)*. Mining of certain minerals such as nickel, gold, and copper is also associated with acid drainage problems that can cause long-term damage to waterways and biodiversity *(Akcil et al., 2006)*. The most environmentally effective methods available for mitigating acid mine drainage are internal neutralization methods, water-covers, and biological/natural degradation processes. However, these techniques are expensive, slow and require maintenance *(Hilson et al., 2001).*

Chromium removal from industrial wastewater is commonly done using ion exchange, membrane filtration, adsorption and chemical precipitation *(Al-Enezi et al., 2004; Ahmed et al., 2017 Fu et al., 2011; Wang et al., 2011).* Ion exchange, membrane filtration, electrochemical treatment and chemical precipitation methods are often used for nickel removal from industrial wastewater *(Al-Enezi et al., 2004; Ahmed et al., 2017; Fu et al., 2011).* Cobalt and palladium removal from industrial wastewater is conducted mainly by electrochemical treatment methods *(Shafaei et al., 2010, Kabdasli et al., 2010, Parga et al., 2005, Olmze et al., 2009, Casqueira et al., 2006, Khelifa et al., 2005)*. In addition, precious metals can be recovered using adsorbents, liquid-liquid extraction, ion exchange, and using aminated lignin derivatives *(Matsubara et al., 2002; Kramer et al., 2004; Guibal et al., 2002; Jia et al., 2003).* Due to their many advantages such as high treatment capacity, high removal efficiency, and fast kinetics, ion exchange is widely used to remove metals from wastewater (*Al-Enezi et al., 2004).* Lab scale studies were conducted using either synthetic or natural solid resins for improving removal efficiencies for toxic metals such as chromium and nickel (*Al-Enezi et al., 2004). Ahmed et al., (2017)* and *Al-Enezi et al., (2004)* have reported 99.9% removal of cadmium, chromium, copper, mercury, nickel, lead and zinc from synthetic wastewater with concentrations in the range of 0.021 - 2 mg/L using ion-exchange system in laboratory studies. However, due to the resins being saturated on a regular basis, operational costs and sludge production are high for ion exchange processes *(Zhao et al., 2016).* Membrane filtration is a pressure-driven separation process often used for metal removal from wastewater *(Fu et al., 2011).* It offers high efficiency, easy operation, and lower space requirement compared to other methods *(Zhao et al., 2016).* Depending on the contaminant particle size, different types of membrane filtrations such as ultrafiltration, nanofiltration and reverse osmosis could be used *(Zhao et al., 2016).* Using micellar-enhanced ultrafiltration in lab-scale experiments, *Fu et al., (2011)* were able to improve removal efficiencies for metals such as copper, nickel, zinc, and chromium. *Fu et al., (2011)* and *Ahmed et al., (2017)* could achieve over 96% removal efficiencies for metals such as copper, nickel, zinc and chromium from synthetic wastewater with concentrations in the range of 0.5 - 500 mg/L by using micellar-enhanced ultrafiltration system in a lab-scale study. However, high initial costs, complex processes and membrane fouling issues need to be considered before using a membrane filtration system *(Ahmed et al., 2017).* Chemical precipitation by far is the most widely used process by the industries for metal removal *(Fu et al., 2011).* This is due to its relatively simple and inexpensive operation *(Carolin et al., 2017).* Chemicals are added to alter the pH and to form metal precipitants. Through sedimentation, these precipitates are removed from the solution. Lab scale studies were conducted to optimize the process and 99.7% removal of zinc, nickel, chromium, and copper were achieved for concentrations from 100 - 5363 mg/L by researchers such as *Ghost* *et al., (2011), Ramakirshnaiah et al., (2012), Fu et al., (2012) and Zhao et al., (2016)* using chemical precipitation. However, chemical precipitation cannot be used effectively for low metal concentrations and produces a considerable amount of sludge with high water content which is difficult to treat and dispose of and considered a hazardous waste *(Carolin et al., 2017).* Adsorption is a low cost, easy to use treatment method which offers high quality treated effluents *(Barakat, 2011).* It is a process which uses mass conversion by transferring the waste through physical or chemical means into the active sites present in the adsorbent *(Carolin et al., 2017).* Very high removal ratios of 96.24% - 99.99% could be achieved for concentrations around 2 mg/L of lead, copper, chromium, gold, and cadmium in a lab-scale study conducted by *Lo et al., (2012)* and *Acheampong et al., (2010)*. Due to the adsorption process being reversible, desorption can occur during the metal removal and metals could end back in the solution *(Wang et al., 2011).* Electrochemical (EC) treatment methods including plating-out of metal ions on a cathode surface were also examined for toxic metal removal from wastewater *(Fu et al., 2016).* EC treatment is considered a clean technology due to lack of chemical addition and has the potential to become one of the most effective ways to treat wastewater *(Fu et al., 2016)*. However, it requires relatively large capital investment and an electric current supply *(Fu et al., 2016).* Very high removal ratios (98% - 99%) could be achieved for concentrations from 50 - 5000 mg/L for metals such as manganese, nickel, arsenic, chromium, zinc, cobalt and copper using EC treatment methods with varying electrodes in studies conducted by various researchers, for example *Shafaei et al., (2010), Kabdasli et al., (2010), Parga et al., (2005), Olmze et al.,(2009), Casqueira et al., (2006), Khelifa et al.,(2005).* High capital and operational costs, use of additional chemicals and, high volumes of sludge generation are some of the limitations of these technologies *(Carolin et al., 2017).*

Freeze concentration (FC) is a physical treatment method that consists of fractional crystallization of water followed by removal of ice (*Gao et al., 2009).* Freeze concentration has been widely investigated and used in the food industry on liquid food products *(Sanchez et al., 2009)*. Lately, interest in freeze concentration for wastewater has increased due to few factors such as high separation ratio, high-energy efficiency, low operational costs, high water recovery, and low capital investment *(Williams et al., 2013).* Freeze concentration has been used for removal of various organic and inorganic contaminants from industrial effluents such as petroleum refinery, pulp and paper effluents, pharmaceutical active compounds, glucose solutions, polypepton wastewater, cutting oil wastewater, urban wastewater and desalination *(Gao et al., 2008; Gao et al., 1999; Gao and Shao, 2009; Wakisaka et al., 2001; Lu et al., 2017; Lorain et al., 2001; Fujioka et al., 2013,).* In a recent study, *Melak and his coworkers (2016)* conducted a study using freeze concentration to remove chromium (VI) from synthetic wastewater. Solutions of chromium (VI) with varying concentrations from 1 – 300 mg/L and variable chloride ion concentrations (5, 10, 250 and 3550 mg/L) were frozen and removal efficiency of chromium (VI) under various salinity was examined. Chromium (VI) removal efficiency between 85% - 97% was achieved and removal efficiency of chromium (VI) decreased with increasing salinity *(Melak et al., 2016).* Boron removal using single stage freeze concentration was studied by *(Wang, 2017).* Synthetic wastewater containing boron samples of 100 mg/L, 500 mg/L, and 1000 mg/L were used to determine the effects of the advance speed of the ice front, the circumferential velocity of the stirrer and the initial boron concentration. With single stage, FC, the concentration of the unfrozen liquid samples were increased 3-4 times while boron removal ratio between 90% - 99% was also achieved (*Wang, 2017).* The results from the study showed that the effectiveness of boron removal improved with a lower advance speed of the ice front, a higher circumferential velocity of the stirrer and a lower initial boron concentration *(Wang, 2017).* Zinc and lead-containing synthetic wastewater samples were used by *(Gay et al., 2003)* to determine the residual concentrations in the treated medium (ice) and the effects of mixing in FC. Wastewater samples containing zinc, lead and a mixture of zinc and lead between concentrations of 500 - 1000 mg/L were used. Over 98% removal ratio of zinc and lead could be achieved via single stage freeze concentration, and it was also found that mixing makes the separation mechanism more efficient *(Gay et al., 2003).*

Limited research has been done using freeze concentration to remove or recover toxic and precious metals from industrial effluents or liquid wastes. The potential of removal and recovery of toxic and precious metals using multiple stage freeze concentration processes, the capacity of freeze concentration on wastewater volume reduction, and using freeze concentration as a pre-treatment process for electrodeionization (EDI) have not been examined. In addition, no information on the behaviour/partitioning of toxic and precious metals such as chromium (VI), nickel, cobalt, and palladium, in ice and liquid phases during freezing process is available. The objectives of the research were to investigate:

1. The effectiveness of freeze concentration on the removal and recovery of toxic and precious metals namely, chromium (VI), cobalt, nickel and palladium in synthetic wastewater

2. The effect of initial metal concentrations, chemical nature of the selected metals, and mixing methods on freeze concentration efficiency
3. The effectiveness of using multiple stage freeze concentration for the treatment of the unfrozen liquid with high concentrations of the metals
4. The capacity of freeze concentration on wastewater volume reduction
5. Effect of degree of freezing on removal efficiency, and partitioning of the selected metals in ice and liquid phases during freezing

Furthermore, unfrozen liquids with various concentrations of the selected metals from freeze concentration process will be used as the feedwater for EDI process to examine the concept of using the combined freeze concentration-EDI treatment options for the selected toxic and precious metal removal/recovery. The combined freeze concentration and EDI treatment will be discussed later in detail in Chapter 4.

3.2 Materials and Methods

3.2.1 Water samples preparation

Synthetic wastewater samples with chromium (VI), nickel, cobalt, and palladium were prepared using potassium dichromate ($K_2Cr_2O_7$,>99.0% purity), nickel chloride ($NiCl_2.6H_2 0$, 98% purity), cobalt nitrate ($CoN_2 0_6.6H_2 0$, 98% purity), and palladium chloride ($PdCl_2$,99% purity). The chemicals were purchased from Sigma-Aldrich Canada (Oakville, Ontario, Canada). The samples were prepared using purified water from Thermo Scientific Barnstead Easypure II RF (Marietta, Ohio, United States).

3.2.1.1 Potassium dichromate ($K_2Cr_2O_7$)

Potassium dichromate is a reddish-orange coloured solid. At 600˚C, it decomposes to give oxygen, potassium dichromate and chromium (III) oxide. It acts as a strong oxidizing agent in acidic media *(Sigma Aldrich, 2017).* It has a molar mass of 294.185 g/mol and odourless. The solubility in water is 13g/100 mL at 20˚C *(Sigma Aldrich, 2017).* It is in solid form at room temperature and has a melting point of 398˚C and a boiling point of 500˚C. It is considered toxic if swallowed, fatal if inhaled and harmful if in contact with skin *(Sigma Aldrich, 2017).* Figure 3.1 shows the chemical structure of potassium dichromate.

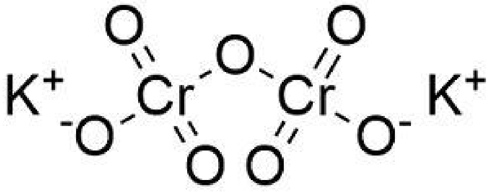

Figure 3.1: Potassium dichromate chemical structure *(Sigma Aldrich, 2017)*

3.2.1.2 Nickel chloride ($NiCl_2$)

Nickel chloride is an odourless, green crystal. It has a molar mass of 237.69 g/mol *(Sigma Aldrich, 2017).* The solubility in water is 67.5g/100 mL at 20˚C. It is in solid form at room temperature and has a melting point of 140˚C. It is considered toxic if swallowed and may cause skin sensitization by skin contact. In addition, it is considered toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment (*Sigma Aldrich, 2017).* Figure 3.2 shows the chemical structure of nickel chloride.

Figure 3.2: Nickel chloride chemical structure *(Sigma Aldrich, 2017)*

3.2.1.3 Cobalt nitrate ($CoN_2O_6.6H_2$0)

Cobalt nitrate hexahydrate is an odourless red crystal. It has a molar mass of 291.03 g/mol *(Sigma Aldrich, 2017).* It is in solid form at room temperature and has a melting point of 55˚C and a boiling point of 74˚C, at which point it decomposes *(Sigma Aldrich, 2017).* The solubility in water is 334.9 g/mol. It also considered toxic and causes abdominal pain, nausea, vomiting, rash, and ringing in the ears if ingested. Cobalt nitrate can cause irritation if contacted via skin and eye *(Sigma Aldrich, 2017).* Figure 3.3 shows the chemical structure of cobalt nitrate.

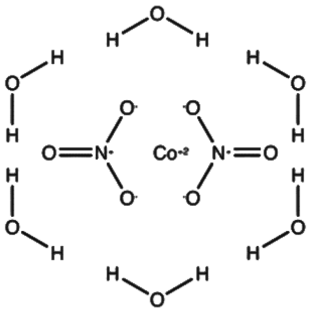

Figure 3.3: Cobalt nitrate chemical structure *(Sigma Aldrich, 2017)*

3.2.1.4 Palladium chloride ($PdCl_2$)

Palladium chloride is dark brown and in crystalline form. It has a molar mass of 177.326 g/mol *(Sigma Aldrich, 2017).* It is also in solid form at room temperature and has a melting point of

679˚C *(Sigma Aldrich, 2017).* The solubility in water is very low but dissolves rapidly in HCl acid *(Sigma Aldrich, 2017).* Palladium chloride is considered hazardous in case of eye contact and slightly hazardous in case of skin contact *(Sigma Aldrich, 2017).* Chemical structure of palladium chloride is shown in Figure 3.4

Figure 3.4: Palladium chloride chemical structure *(Sigma Aldrich, 2017)*

3.2.2 Metal concentrations

The concentration range of the selected metals was determined according to the literature review of various industrial wastewater/effluents. For chromium (VI), the concentration range was from 0.7 - 350 mg/L *(Lothongkum et al., 2009; Gupta et al., 2004; Hunsom et al., 2005; Bishnoi et al., 2005; Mirbagheri et al., 2004; Camelo et al., 1997; Bruggen et al., 2001; Agrawal et al., 2007; Gan, 2000; Agrawal et al., 2007)*. Nickel concentration range varied from 0.1 - 675 mg/L *(Lothongkum et al., 2009; Gupta et al., 2004; Hunsom et al., 2005; Bishnoi et al., 2005; Camelo et al., 1997; Bruggen et al., 2001; Benvenuti et al., 2014; Gonzalez et al., 2014; Adeli et al., 2017; Huang et al., 2016)*. Cobalt concentration was from 0.7 - 134 mg/L *(Singh et al., 2011; Amin et al., 2015; Malakootian et al., 2008; Bhuiyan et al., 2010; Saleh et al., 2017)* and Palladium concentration was from 50 µg/L to 60 mg/L (*Abughusa et al., 2006; Umeda et al., 2011; Gurung et al., 2012; Kakoi et al., 1996; Noah et al., 2016; Parajuli et al., 2009).*

Initial feedwater samples were prepared by making a stock solution of each metal that was used for the experiment. For chromium (VI) and nickel, a stock solution of 1000 mg/L was prepared separately. For cobalt, a stock solution of 500 mg/L was used, and for palladium, a stock solution of 100 mg/L was used. Desired concentrations were achieved by diluting the stock solution.

The details of the wastewater samples that were prepared are listed in Table 3.1.

Table 3.1: Metal concentrations and pH in synthetic wastewater samples used as the feedwater for first stage/single stage freeze concentration (FC)

Metal	**Concentration (mg/L)**	**pH**
Chromium (VI)	19.9 ± 0.4	4.5 ± 0.2
Nickel	19.7 ± 0.4	4.2 ± 0.1
Cobalt	18.8 ± 0.4	5.5± 0.2
Palladium	19.3 ± 2.0	1.8± 0.2

3.2.3 Freezing Tests

The freezing apparatus and the freezing procedures used by *Reynolds (2013)* were implemented in the freezing tests. The overall setup of freeze concentration apparatus is shown in Figure 3.5.

Control of the temperature of the freezing bath was done by Thomas programmable ultra-low refrigerating/heating circulator (Thomas Scientific, Swedesboro, NJ, United States). Motomaster long-life premixed antifreeze which has a -33.6°C was used as the coolant for the freezing bath. The temperature of the freezing bath was kept at -15°C for all the experiments.

400 mL of feedwater samples were contained in two 600mL stainless steel beakers and kept at room temperature before the freeze concentration experiment. These two beakers were lowered into the freezing bath at a constant speed. Once the freezing tests start, this constant speed was achieved by using a planetary gearbox. One of the two beakers was mixed using an ultrasonic probe while the other was mixed using a mechanical mixer with four horizontal blades

during freezing. The two mixers were placed closely above the ice front in the feedwater beakers. Constant mixing settings were used for the ultrasonic mixer and the mechanical mixer. The ultrasonic mixer was set at S/30 (1 second on, 30 seconds off) with 20% amplitude and the mechanical mixer was set at 300 rpm.

To investigate the effect of degree of freezing on metal removal efficiency, various percentages of freezing (20%, 40%, 60%, 80% and 90% of initial/total sample volume) was used. Trial runs were conducted prior to the experiments to find the approximate time needed for freezing various volumes of feedwater. In order to achieve the desired freezing ratio, the volume indicators on the outside of the steel beakers were used. Approximately 80% freezing ratio could be achieved by submerging the beakers until the 320 mL mark in the freezing bath. This process usually takes about 3 to 4 hours. Once the desired freezing ratio was achieved, the unfrozen liquid was separated from the ice, and the ice was melted at room temperature prior to washing the top layer of ice with 10 mL of pure water using a syringe. Next, the volume of ice samples and the volume of unfrozen liquid were measured using a graduated cylinder.

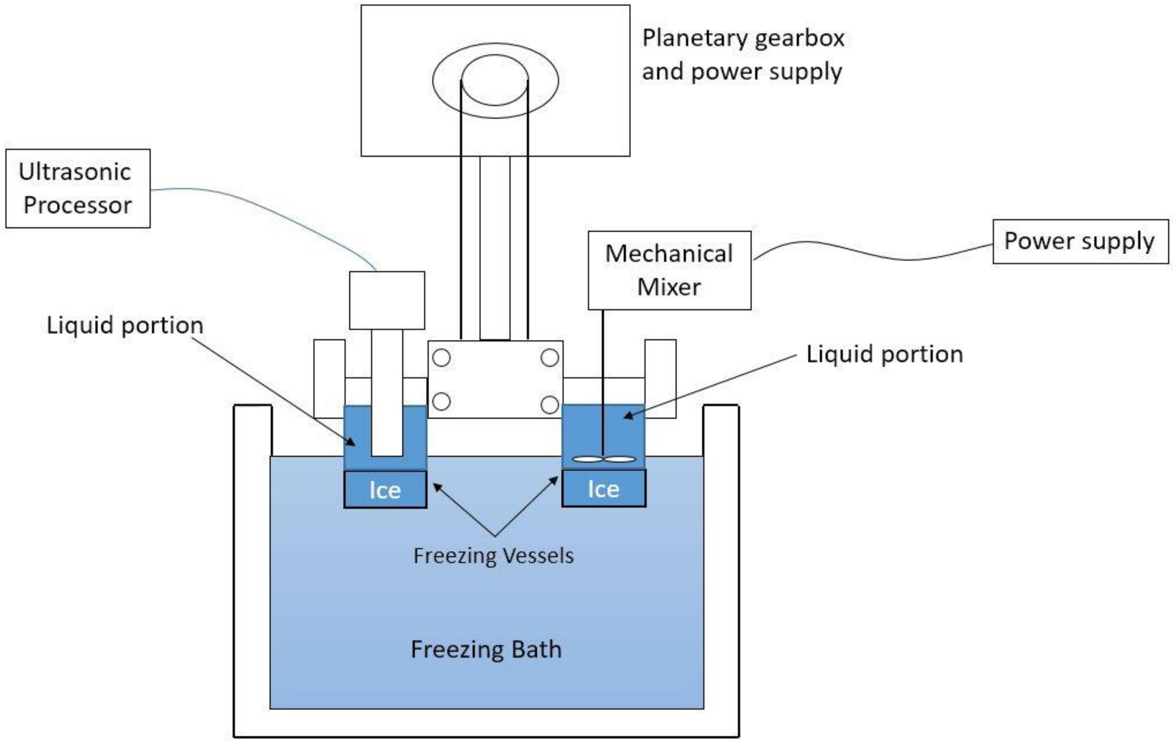

Figure 3.5: Freezing bath schematics *(Reynolds., 2013)*

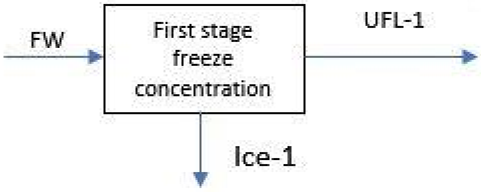

Figure 3.6: Schematic of single/first stage freeze concentration test

FW: feedwater
Ice-1: ice from single/first stage FC
UFL-1: unfrozen liquid from single/first stage FC

In the first stage of freeze concentration, for synthetic wastewater with concentrations described in Table 3.1 were used for chromium (VI), nickel, cobalt, and palladium as the feedwater (FW). After the desired freeze concentration ratio was achieved, ice (ice-1) samples were melted at room temperature, and the volume and concentration of ice were measured using a graduated cylinder. The unfrozen liquid (UFL-1) samples were also collected, and the volume and concentration were also measured separately using a separate graduated cylinder. Figure 3.6 shows the schematic of single/first stage of freeze concentration test.

Also, different percentages (20%, 40%, 60%, and 80%) of freezing were conducted with 20 mg/L concentration of chromium (VI), nickel, cobalt, and palladium in the first stage of freezing to determine the partition coefficient. Furthermore, 90% freezing tests were conducted on all the metals except for palladium.

For multi-stage freeze concentration processes, depending on the final/product water quality requirements for reuse (within an industrial operation) or discharge to a receiving water body, both ice and unfrozen liquids could be treated through multiple stages or only unfrozen liquid is treated through multiple stages.

For this study, only the unfrozen liquid was treated using multiple stage freeze concentrations. The following figures illustrate two and three stages of freeze concentration and the samples generated from each stage.

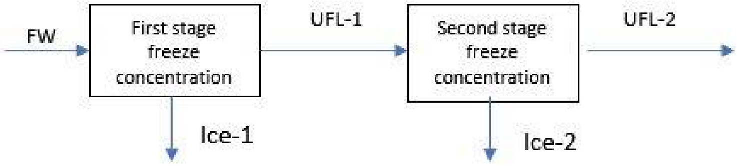

Figure 3.7: Schematic of two-stage freeze concentration test

FW: feedwater
Ice-1: ice from single/first stage FC
Ice-2: ice from two-stage FC

UFL-1: unfrozen liquid from single stage freeze concentration/feedwater for two-stage FC
UFL-2: unfrozen liquid from two-stage FC

During the two-stage freeze concentration process, as seen in Figure 3.7, unfrozen liquid (UFL-1) from the first stage of freeze concentration was used as the feedwater for this stage. Ice (ice-2) and unfrozen liquid (UFL-2) samples were collected after the desired percentage of freezing of initial feedwater volume was achieved. Ice (ice-2) samples were melted at room temperature and the volume of unfrozen liquid and ice samples were then measured using a graduated cylinder.

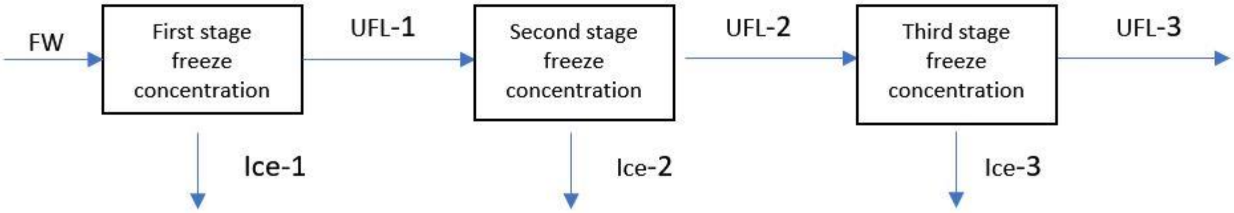

Figure 3.8: Schematic of three-stage freeze concentration test

FW: feedwater
Ice-1: ice from single/first stage FC
Ice-2: ice from two-stage FC
Ice-3: ice from three-stage FC
UFL-1: unfrozen liquid from single FC/ feedwater for two-stage FC
UFL-2: unfrozen liquid from two-stage FC/ feedwater for three-stage FC
UFL-3: unfrozen liquid from three-stage FC

For the feedwater for the third stage FC, unfrozen liquid from the two-stage FC (UFL-2) was used as seen in Figure 3.8. After the desired percentage freezing (of the feedwater volume) was achieved, ice (ice-3) was melted at room temperature, and the volumes of ice and unfrozen liquid samples were measured using a graduated cylinder. The samples were ready for metal concentration analysis.

In the case of palladium, the fourth stage of freeze concentration was also performed using the unfrozen liquid from the third stage (UFL-3) as the feedwater. Ice (ice-4) and unfrozen liquid (UFL-4) were measured after the experiment was completed.

To summarize, after the first stage, unfrozen liquid samples with chromium (VI), nickel, and cobalt were treated with two additional stages of freeze concentration while unfrozen liquid samples containing palladium went through three additional stages of freeze concentration.

3.2.4 Analytical methods

Initial feedwater, ice and unfrozen liquid samples from each freeze concentration stage were collected. The pH of the samples was measured with VWR® SympHony™ SB20 pH meter. (Mississauga, Ontario, Canada). Metal concentrations of the samples were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Varian Vista Pro) (Palo Alto, California, United States) and UV-Visible spectrophotometer (Cary 50) (Thermo Fisher Scientific, Mississauga, Ontario, Canada). All analysis were performed according to *Standard Methods for the Examination of Water and Wastewater (AHPA, 2005)*. Before analysis, calibration of the analytical instruments was carried out. The following Figure 3.9 is a sample calibration curve for determining the concentration of chromium (VI) using a UV-Visible spectrophotometer.

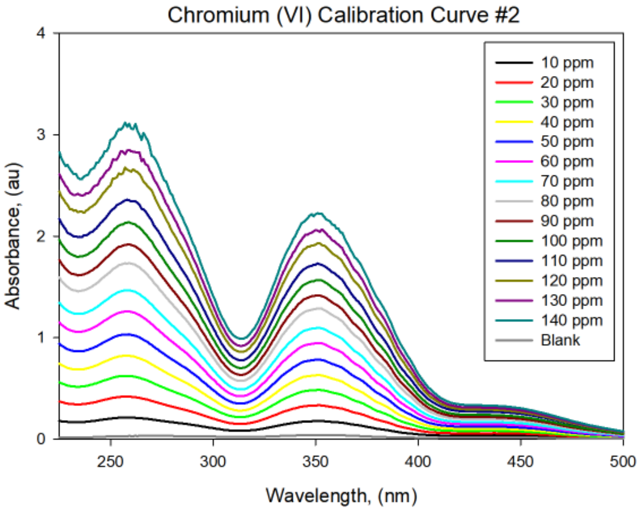

Figure 3.9: Chromium (VI) calibration curve for the UV-Visible spectrophotometer

3.2.5 Data Analysis

Removal efficiency and concentration ratio for each stage were calculated.

3.2.5.1 Single stage/first stage freeze concentration

Percentage removal of metal concentration in ice expressed as removal efficiency (Equation 3.1), concentration of metals in the unfrozen liquid was expressed as concentration ratio (Equation 3.2), volume reduction in comparison to initial feedwater volume is expressed as ratio of volume of unfrozen liquid to that of that initial feedwater (Equation 3.3) and pH ratio of unfrozen liquid pH to feedwater pH (Equation 3.4), and ice pH to feedwater pH (Equation 3.5) were calculated using following equations for single stage/ first stage of FC

$$Removal\ efficiency\ (Re) = 1 - \left({}^{C_{ice-1}}/_{C_{FW}} \right) \times 100\% \qquad (3.1)$$

$$Concentration\ ratio\ (Cr) = ({}^{C_{UFL-1}}/_{C_{FW}}) \qquad (3.2)$$

$$Volume\ reduction\ (Vr) = 1 - \left({}^{V_{UFL-1}}/_{V_{FW}} \right) \times 100\% \qquad (3.3)$$

$$pH\ ratio = {}^{pH_{UFL-1}}/_{pH_{FW}} \qquad (3.4)$$

$$pH\ ratio = {}^{pH_{ice-1}}/_{pH_{FW}} \qquad (3.5)$$

C_{ice-1}: concentration of ice from single/ first stage FC
C_{FW}: concentration of initial feedwater
C_{UFL-1}: concentration of unfrozen liquid from single/first stage FC
C_{FW}: concentration of initial feedwater
V_{UFL-1}: volume of unfrozen liquid from single/first stage
V_{FW}: volume of feedwater
pH_{UFL-1}: pH value of the unfrozen liquid from single/first stage FC
pH_{ice-1}: pH value of the ice from single/first stage FC
pH_{FW}: pH value of the initial feedwater

3.2.5.2 Second stage freeze concentration

Percentage removal of metal in ice samples (Equation 3.6) and the ratio of the concentration of metal in the unfrozen liquid to that in feedwater (Equation 3.7) and were calculated for the second stage of freeze concentration. Metal removal efficiency in ice samples (in the second stage FC) from the unfrozen liquid from single stage FC process and the concentration ratio of unfrozen liquid from the first stage to unfrozen liquid in the second stage were determined using the following equations.

$$Removal\ efficiency\ (Re) = 1 - \left({}^{C_{ice-2}}/_{C_{UFL-1}} \right) \times 100\% \qquad (3.6)$$

$$Concentration\ ratio\ (Cr) = ({}^{C_{UFL-2}}/_{C_{UFL-1}}) \qquad (3.7)$$

C_{Ice-2}: concentration of ice from second stage FC
C_{UFL-1}: concentration of unfrozen liquid from single FC/ feedwater for second stage FC
C_{UFL-2}: concentration of unfrozen liquid from second stage FC/ feedwater for the third stage FC

3.2.5.3 *Third stage freeze concentration*

For the third stage, contaminant removal in ice observed from the feedwater (unfrozen liquid from the second stage) was calculated as a percentage using the Equation 3.8. Also, the ratio of the concentration of the unfrozen liquid from the second stage to unfrozen liquid from the third stage was calculated using Equation 3.9.

$$Removal\ efficiency\ (Re) = 1 - \left({C_{ice-3}}/{C_{UFL-2}} \right) \times 100\% \qquad (3.8)$$

$$Concentration\ ratio\ (Cr) = ({C_{UFL-3}}/{C_{UFL-2}}) \qquad (3.9)$$

C_{Ice-3}: concentration of ice from third FC
C_{UFL-2}: concentration of unfrozen liquid from second stage FC/ feedwater for the third stage FC
C_{UFL-3}: concentration of unfrozen liquid from third stage FC

Duplicate or triplicate runs were carried out for each treatment and data were reported as the average value of replicates. One-way ANOVA was performed (with α= 0.05) to determine if a significant difference existed among the data obtained from various tests using Microsoft Excel 2016 (Microsoft Cooperation, 2018).

3.3 Results and discussions

The ability of freeze concentration to remove different metals from synthetic wastewater at various levels of concentrations, varying degrees of freezing and varying stages of freeze concentration were determined by measuring concentrations and volumes each ice, unfrozen liquid and feedwater samples. Furthermore, volume reduction was also measured.

3.3.1 Single stage/ First stage of freeze concentration

20 mg/L samples were prepared according to section 3.3.1 for the four metals (chromium (VI), nickel, cobalt, and palladium) and various percentage of freezing tests (20%, 40%, 60%, 80% and 90% of initial/total sample volume) were conducted.

3.3.1.1 Chromium (VI)

3.3.1.1.1 Effect of degree of freezing on chromium (VI) removal/separation efficiency

The removal efficiency of chromium (VI) was at various percentages of freezing (percentage volume of the initial volume of feedwater) and is shown in Figure 3.10.

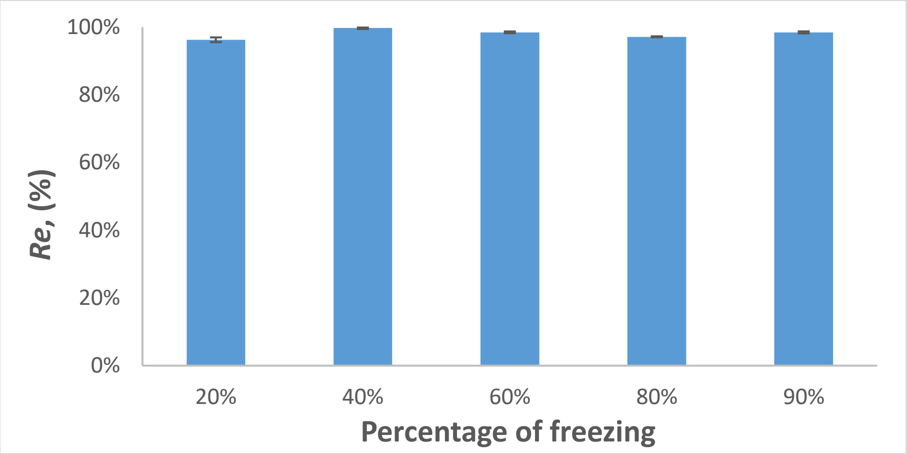

Figure 3.10: Effect of percentage of freezing on Chromium (VI) removal efficiency

Samples frozen at 20%, 40%, 60%, 80% and 90% all reported very high removal ratios for chromium (VI). The removal efficiencies were in the range of 97% to 99% indicating that as long as the wastewater is frozen, the high separation efficiency of chromium (VI) in the ice samples was achieved. The high removal efficiency achieved at 20% to 90% freezing of the initial volume of the feedwater, freezing was very effective to remove chromium (VI) at this concentration (20 mg/L). Similar results were achieved by *Melak et al., (2016)*, in his study of chromium (VI) removal from synthetic wastewater at 30% to 90% freeze concentration of 10 - 100 mg/L. Removal efficiencies were similar for the mechanical and ultrasonic mixing methods.

3.3.1.1.2 The concentration of chromium (VI) in unfrozen liquid

The concentration ratio of chromium (VI) was calculated and plotted vs. the percentage of freezing and shown in Figure 3.11.

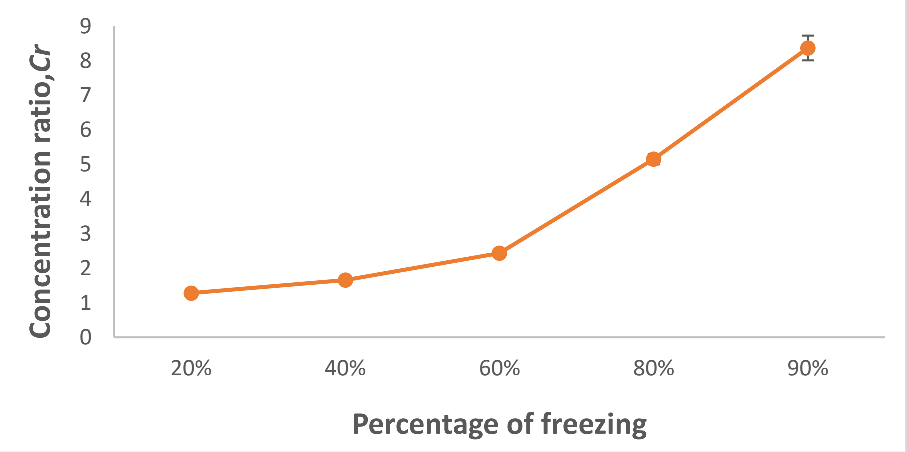

Figure 3.11: Effect of percentage of freezing on Chromium (VI) concentration ratio

As shown in Figure 3.11, as freezing proceeded from 20% to 60%, the concentration of chromium (VI) started to increase slowly in the unfrozen liquid. At 20% freezing, chromium (VI) concentration in the unfrozen liquid was about 1.2 times of that of control (initial feedwater). As freezing continued, chromium (VI) concentration reached 2.4 times at 60% freezing. From 60% freezing to 90%, the accumulation of chromium (VI) in unfrozen liquid enhanced, indicated by the change of the slope of the line. More and more chromium (VI) ions were rejected from ice structure as freezing progressed and their concentration in the unfrozen liquid increased quickly.

The concentration of chromium (VI) in unfrozen liquid reached about 8 times of the control when 90% of the feedwater was frozen. The high concentration of chromium (VI) in unfrozen liquid suggests that freezing is quite effective in separating/removing chromium (VI) from the water.

3.3.1.1.3 pH ratio in Chromium (VI)

Figure 3.12 shows the pH ratios of the unfrozen liquid and the ice samples to that of feedwater versus the percentage of freezing.

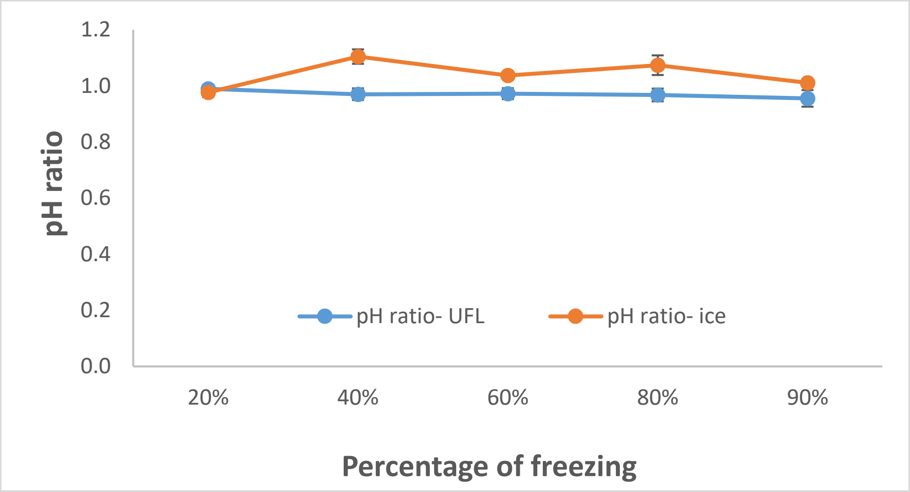

Figure 3.12: pH change of chromium (VI) in unfrozen liquid and ice

As shown in Figure 3.12, as the freezing advanced from 20% to 90%, the pH of the unfrozen liquid dropped from 1.0 to 0.9. This phenomenon may be explained by the factor that more H^+ ions were concentrated in the unfrozen liquid than feedwater since dichromate ion dissolute in water as follows, $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ CrO_4^{2-} + 2\ H^+$. On the other hand, as a result of less H^+ ions in the ice, the pH ratio of ice increased with the percentage of freezing.

3.3.1.2 Nickel

3.3.1.2.1 Effect of degree of freezing on nickel removal/separation efficiency

The removal efficiency versus the percentage of freezing was calculated for nickel at 20 mg/L and is shown in Figure 3.13.

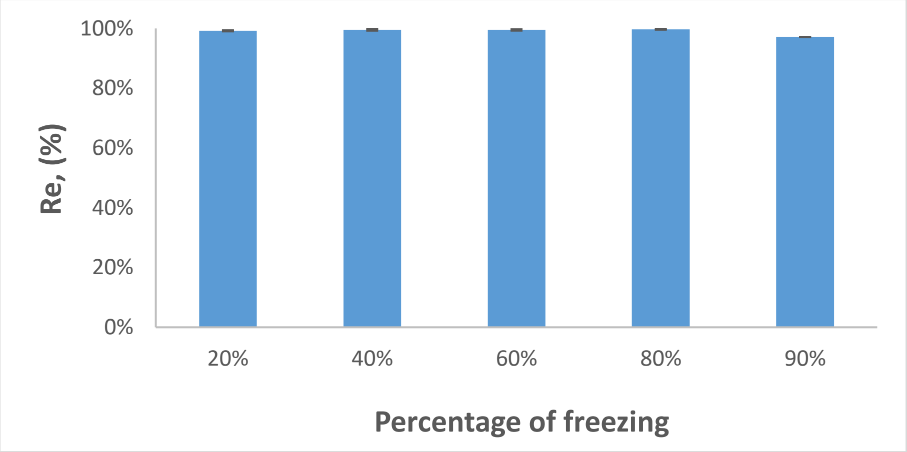

Figure 3.13: Effect of percentage of freezing on Nickel removal efficiency

As seen in Figure 3.13, samples were frozen at various percentages of freezing from 20% to 90%. Very high removal efficiencies of nickel from ice samples were achieved. The removal efficiencies were in the range of 97% to 99% which suggests that freeze concentration was very effective at separating nickel from water at 20 mg/L. Similar results were achieved by mechanical and ultrasonic mixing methods.

3.3.1.2.2 Nickel concentration and the pH ratio of unfrozen liquid

The concentration and pH change of unfrozen liquid was plotted against the percentage of freezing and the results are shown in Figure 3.14.

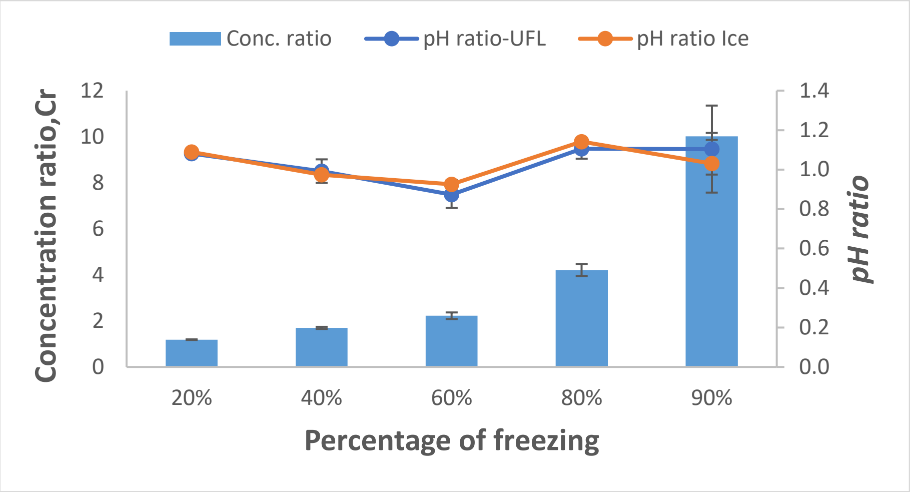

Figure 3.14: Effect of percentage of freezing on nickel concentration ratio and pH ratio

The concentration ratios of the unfrozen liquid to the initial feedwater/control of nickel at various percentages of freezing is shown in Figure 3.14. As the percentage of freezing increased, the concentration of nickel ions in the unfrozen liquid also increased compared to the feedwater concentration. At 20% freezing, the nickel concentration in the unfrozen liquid was about 1.2 times of that of the initial feedwater concentration. The concentration increment was steady until freezing reached 80% of initial feedwater volume and the nickel concentration in the unfrozen liquid reached approximately 4.2 times (of feedwater). The change in the slope from 80% freezing to 90% freezing was even more obvious. There was about 10 times more of nickel ions in the unfrozen liquid as compared to the control (feedwater), i.e. a concentration ratio of 10 was reached at 90% freeze concentration. The high concentration of nickel in the unfrozen liquid suggest that freezing is effective at separating nickel ions from wastewater. The pH values of the unfrozen liquid samples fluctuated, it first dropped steadily with increasing percentage of freezing until 60%, then from 80% freezing onwards, the pH ratio stayed constant at 1.1, which suggests that the H^+ ions moved from the ice lattice to the unfrozen liquid at a constant rate. pH values of the ice samples followed a similar pattern to pH values of unfrozen liquid. However, at 90% freezing, the pH values dropped lower than pH values of the unfrozen liquid indicating that H^+ ions were trapped inside the ice samples.

3.3.1.3 Cobalt

3.3.1.3.1 Effect of degree of freezing on cobalt removal/separation efficiency and concentration

Removal efficiency (Re) and concentration changes of cobalt (Cr) were calculated versus the percentage of freezing and the results are plotted in Figure 3.15.

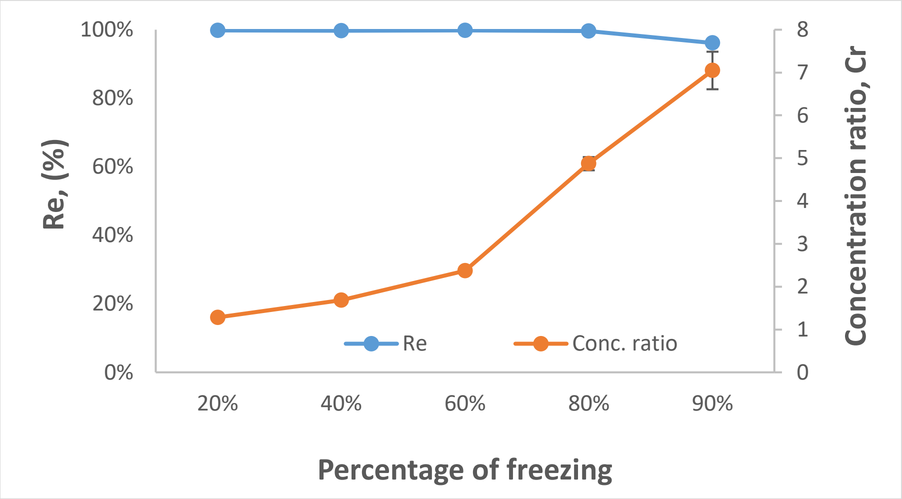

Figure 3.15: Effect of percentage of freezing on cobalt removal efficiency and concentration ratio

Samples frozen at 20%, 40%, 60%, 80% and 90% all reported very high removal ratios for cobalt. The removal efficiencies of cobalt in the ice samples were to be found in the range 96% to 99%. The high removal efficiencies suggest that freeze concentration is very effective at removing cobalt at a concentration of 20 mg/L. The slightly lower removal efficiency (96%) observed at 90% freezing might be due to more impurities attached to the surface of the ice *(Gao, 2013)*. Furthermore, the concentration changes in the unfrozen liquid versus the percentage of freezing is also shown in Figure 3.15. A similar trend as that observed in the unfrozen liquid collected from the freezing of chromium (VI), from 20% to 60% freezing, the concentration of cobalt increases slowly in the unfrozen liquid. The concentration of cobalt in the unfrozen liquid after freezing of 20% of the feedwater (volume) is approximately 1.3 times of that in of feedwater. Then, the cobalt accumulation in the unfrozen liquid increased rapidly from 60% to 90% freezing and it is indicated by the change of slope of the line. More cobalt ions were rejected from the advancing ice structure as freezing continued and the cobalt concentration in the unfrozen liquid increased accordingly. At 90% freezing, a maximum of 7-fold increment of the feedwater concentration was reached. The high concentration of cobalt in the unfrozen liquid suggests that freezing is also very effective in removing cobalt ions from water. Mechanical mixing and ultrasonic mixing both were similarly effective at removing cobalt ions from ice.

3.3.1.3.2 Change of pH values

pH values of the unfrozen liquid and ice samples were recorded as a ratio against the initial feedwater pH value and plotted versus the percentage of freezing as shown in Figure 3.16.

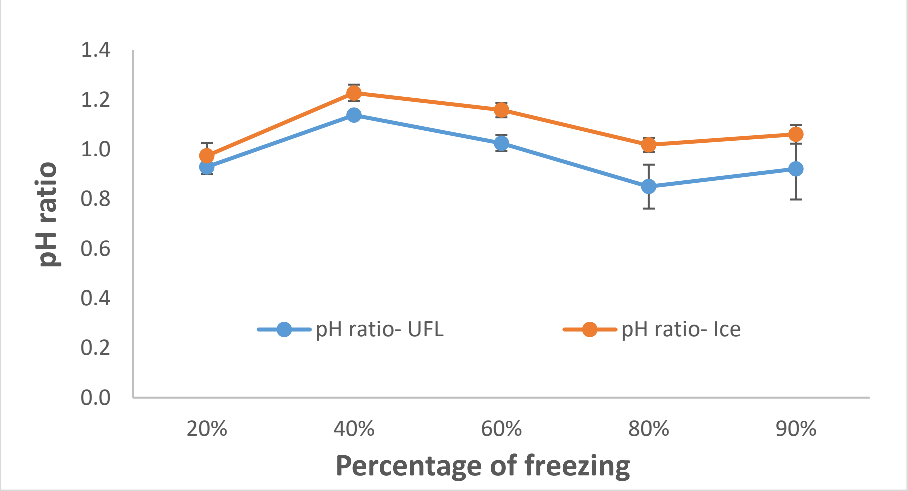

Figure 3.16: pH values versus the percentage of freezing

As shown in Figure 3.16, overall, pH values of ice samples were slightly higher than those of unfrozen liquid samples, similar to those observed in chromium (VI) samples. As freezing advanced from 20% to 90%, the pH in the unfrozen liquid fluctuated from1.1 to 0.9 with slightly lower pH at 80% and 90% freezing. pH ratios lower than 1 was recorded for unfrozen liquid samples throughout indicating accumulation of H^+ ions during formation of ice crystals. pH in the ice samples followed a similar trend (but with higher pH values).

3.3.1.4 Palladium

3.3.1.4.1 Effect of degree of freezing on palladium removal/separation efficiency and concentration

The removal efficiency of palladium from ice samples, along with the concentration changes versus the percentage of freezing are depicted in Figure 3.17.

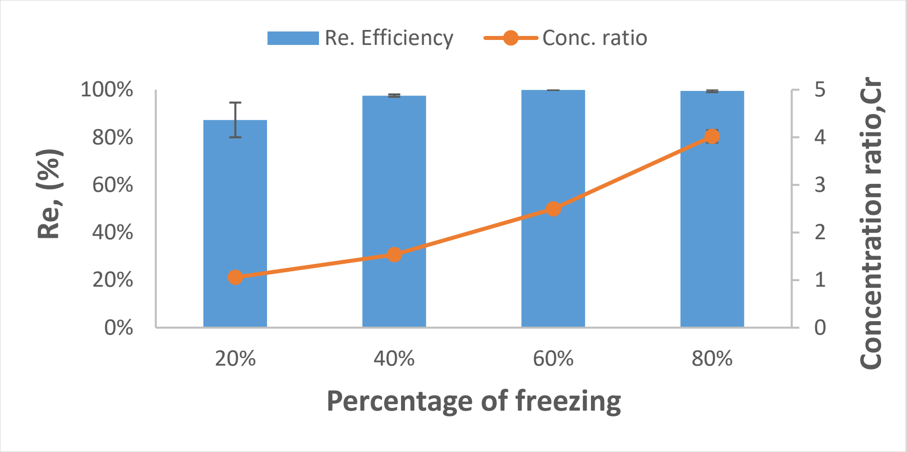

Figure 3.17: Effect of percentage of freezing on palladium removal efficiency and concentration

Samples were frozen at 20%, 40%, 60%, and 80% all reported high removal efficiencies for palladium in the ice samples. The removal efficiencies were in the range of 87% to 99%. Mechanical mixing and ultrasonic mixing were equally effective at removing palladium from ice samples. As seen in Figure 3.17, the concentration ratios of the unfrozen liquid demonstrate that the unfrozen liquid contained high concentrations of palladium. At 20% freezing, the palladium concentration in the unfrozen liquid was about 1.1 times of that of the initial feedwater. The palladium concentration increased steadily to four times of that in the feedwater when 80% of the feedwater was frozen. The difference in the slope indicated that the accumulation of palladium ions in the unfrozen liquid enhanced with each percentage of freezing. The high concentration of palladium in the unfrozen liquid suggests that freezing is very effective in separating palladium from the water.

3.3.1.4.2 Relationship of pH of palladium and the percentages of freezing

pH value changes of palladium unfrozen liquid and ice samples were measured and plotted against the percentage of freezing in Figure 3.18.

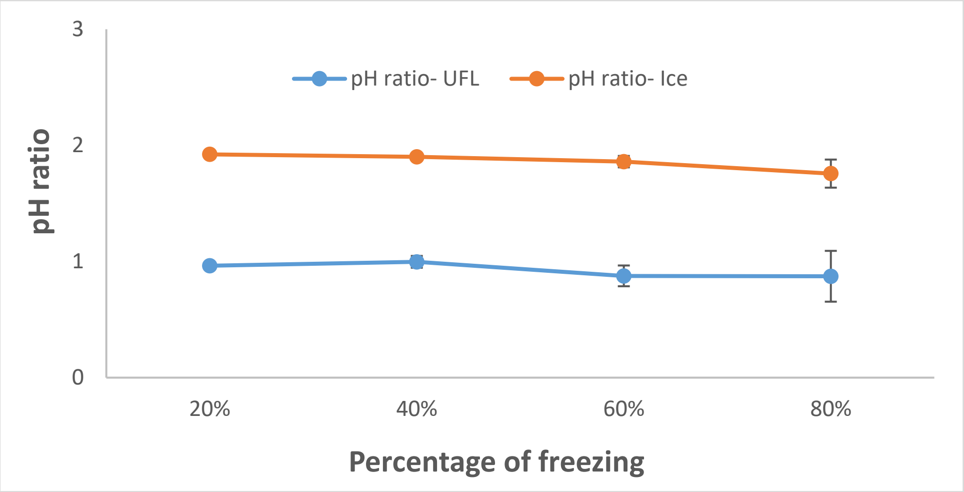

Figure 3.18: pH values of palladium unfrozen liquid and ice

As seen in the Figure 3.18, overall, the pH values of the ice samples were on average 2 values higher than those of unfrozen liquid sample, which may be due to more and more H^+ ions leaving the ice samples. A similar trend was observed in chromium (VI) and cobalt but with lower difference between the pH values of the unfrozen liquid and the ice samples. The pH values of palladium unfrozen liquid samples fluctuated between 0.8 and 1.0 as freezing progressed from 20% to 80%. A value of 0.9 was reported at 20% freezing and as freezing advanced, pH values increased to 1 at 40% freezing followed by 0.8 at 60% and 90% freezing. pH ratio lower than 1 suggested that the accumulation of H^+ ions during the formation of ice crystals in the unfrozen liquid samples. The pH ratios dropped from 1.9 to 1.7 at 20% to 90% freezing. pH values for the ice samples decreased with the increasing freezing suggesting that more and more hydrogen ions were being trapped inside the ice lattice.

3.3.1.5 Effect of chemical nature of the metal on removal efficiency

Removal efficiencies of metals at 80% freezing were compared in Figure 3.19.

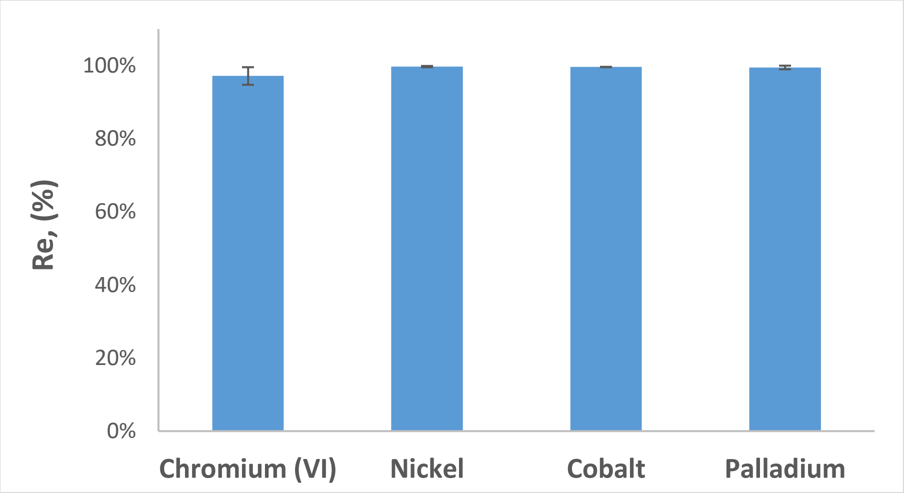

Figure 3.19: Removal efficiency of metals at 80% freezing

Figure 3.19 shows the average removal efficiencies for ice samples achieved for the four metals using 80% freeze concentration. Overall, high removal/separation efficiencies were observed for all the metals examined. The removal efficiencies were in the range of 97% to 99%. Among the four metals, highest average removal efficiency was observed for nickel at 99.7% and lowest for chromium (VI) at 97.1%. Cobalt and palladium showed similar removal efficiencies to that of nickel. The difference in removal efficiency for the four metals was not statistically significant (p = 0.128). Hydration radii of each metal might play a role in the removal efficiency as described by *(Malek et al., 2016)*. Size of the ion is inversely proportional to the hydration radii, and larger the hydration radii, larger the hydration energy which in turn results in a low removal efficiency *(Malek et al., 2016)*. If based on the size of the ion, the removal efficiency of the tested ions should be in the order of palladium>cobalt> nickel> chromium (VI). As seen in Figure 3.19, chromium (VI) has the lowest removal efficiency. However, the other metals are not according to the order mentioned above. This could be due to the sensitivity of the measuring device since nickel, cobalt, and palladium have very similar hydration radii, and therefore, the removal efficiencies are very similar to each other.

3.3.1.5.1 Comparison of concentration ratios

Concentration ratios of metals at 80% FC are shown in Figure 3.20.

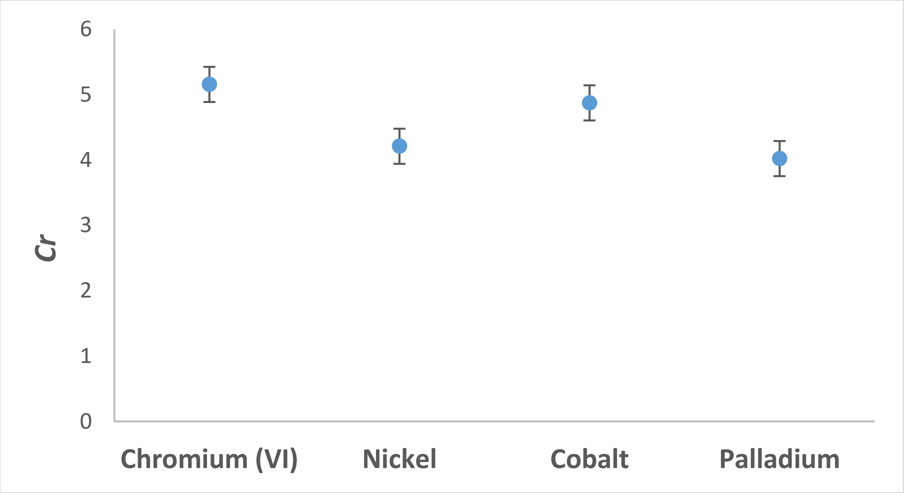

Figure 3.20: Concentration ratios of the metals in 80% freezing

The concentration ratios of the chromium (VI), nickel, cobalt, and palladium at 80% freezing were the average of the mechanical and ultrasonic mixing and is shown in Figure 3.20. The highest concentration ratio was shown by chromium (VI) at 5.2 times followed by cobalt at 4.87 and the lowest for palladium at 4.0 times. Palladium had second highest removal efficiency in ice, but the lowest concentration ratio which could be a measurement error. Overall, high concentration ratios were achieved for all four metals indicating that freeze concentration is also effective at separating these metals from water.

3.3.1.5.2 Effect of mixing methods

Ultrasonic mixing (US) and mechanical mixing (MM) methods were used for the agitation within the liquid during the freeze concentration process. The average time for freezing using mechanical mixing (MM) and ultrasonic mixing (US) was recorded and the results revealed that the time used for completing the same percentage of (volume) of freezing (of feedwater) was similar for mechanical and ultrasonic mixing, no statistical difference in terms of treatment efficiency.

3.3.1.6 Partition Coefficient (K)

The partition coefficient (K) is a measurement used to determine the effectiveness of freeze concentration processes as it examines the behaviour of an impurity to get incorporated into or rejected from ice crystals during freezing of a liquid *(Gu et al., 2005).* The relationship between the relative concentration (C_0/C_L) of the metals in the liquid phase and the volume ratio (V_L/V_0) of the unfrozen phase can be experimentally determined using the Equation 3.9 *(Gu et al., 2005)*.

$$(1-K\,)log\left(\frac{V_L}{V_0}\right)=log(\frac{C_0}{C_L}) \tag{3.10}$$

Where, V_0 and V_L are liquid phase volumes at the beginning and at an arbitrary time, and C_0 and C_L are solute concentrations in the liquid phase at the beginning and at an arbitrary time. K, determines the effectiveness of freeze concentration. K value for the metals was obtained by plotting the relative concentration (C_0/C_L) versus the volume ratio (V_L/V_0) of the liquid phase. The resulting graphs are shown below in Figure 3.21.

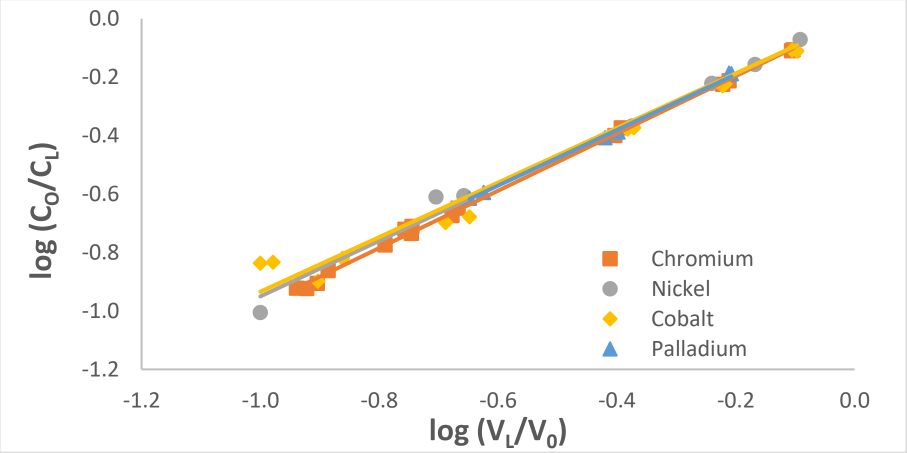

Figure 3.21: Partition coefficient graph

As is shown, a linear relationship exists between the volume ratio and the concentration ratio. A K-value closer to zero suggests very high separation while a K-value closer to 1 suggests very low separation. K values that were calculated for the four metals from the synthetic wastewater samples are shown below in Table 3.2.

Table 3.2: Partition coefficient values

Metal	**K**	**R^2**
Chromium (VI)	0.0191	0.9985
Nickel	0.0498	0.9884
Cobalt	0.0661	0.9712
Palladium	0.0485	0.9712

As shown in Table 3.2, the low K values that were obtained for chromium (VI) (K= 0.0191), nickel (K= 0.0498), cobalt (K=0.0661), and palladium (K=0.0485) for the partition coefficient suggest that the effective concentration of contaminants in the liquid phase and as a result, reduced levels in the solid phase. R^2 values were closer to 1 suggesting a very high correlation. Very low chromium (VI) partition coefficient reflects on the removal efficiencies of chromium (VI) as discussed in section 3.6.1.5. Based on the K values, cobalt (K= 0.06) would have higher tendency to get incorporated into ice structure as compared to chromium (VI), cobalt and nickel. A similar pattern was noted by *Melak et al., (2016)* for chromium removal.

3.3.2 Second stage FC

Second stage freeze concentration was conducted on chromium (VI), cobalt and palladium samples following first stage/single stage freeze concentration using unfrozen liquid (UFL-1) from the first stage of freeze concentration.

3.3.2.1 Chromium (VI) removal efficiency

Feedwater (UFL-1) concentration of 120 mg/L was used for the second stage of freezing of chromium (VI). After 80% freezing, the concentration of chromium (VI) in the ice (ice-2) samples were 0.8 mg/L which leads to 99.3% removal efficiency. Furthermore, the concentration of chromium in the unfrozen liquid reached 570 mg/L, which was an approximately 4.8-fold increase from that of feedwater. Following Figure 3.22 shows the average removal efficiency of chromium (VI) in the first and second stage of freeze concentration.

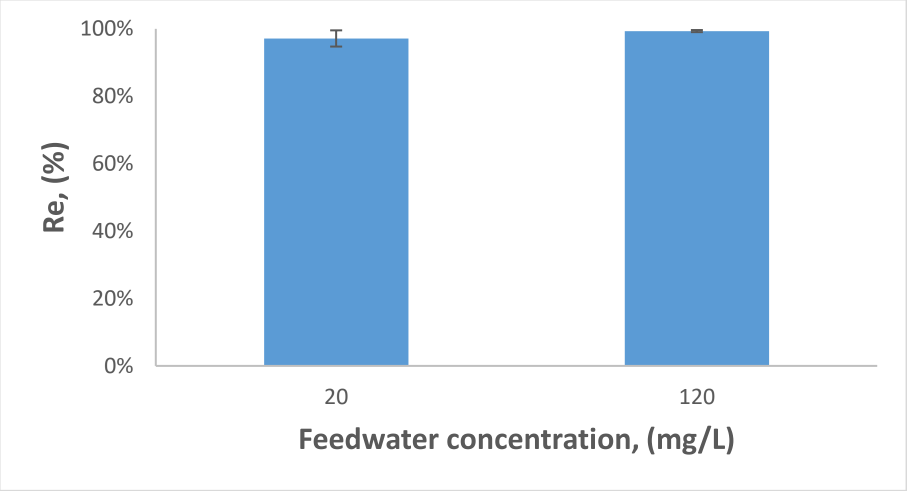

Figure 3.22: Chromium (VI) removal efficiency in the first and second stage freezing

Figure 3.22 compares the removal efficiency of chromium (VI) of ice samples versus the initial feedwater concentrations used in the first and second stages of freeze concentration. As shown in figure 3.22, the removal efficiency of the second stage was actually slightly higher than that of the first stage. Although the initial feedwater concentration increased from 20 - 120 mg/L in the second stage (increased approximately 6 times), the removal efficiency was not affected, which suggests that freeze concentration was not sensitive to the feedwater impurity concentration, at least not at this concentration range. The pH values were measured and are shown in Table 3.3.

Table 3.3: Average pH ratios of chromium (VI) in single stage freezing

Initial feedwater concentration	**pH ratio**	
	UFL	**Ice**
20 mg/L	0.95± 0.03	1.07± 0.01
120 mg/L	0.97± 0.03	1.07± 0.07

Table 3.3 shows the pH ratios that were calculated using Equation 3.4 and 3.5. The pH ratios of chromium (VI) unfrozen liquid changed slightly with the increasing feedwater concentration suggesting less accumulation of H^+ ions at higher feedwater concentration. However, the pH ratios of ice did not change with the feedwater concentration which suggests that at least in this concentration range pH values are not sensitive to the feedwater concentration changes.

3.3.2.2 Nickel removal efficiency

Nickel concentration of 670 mg/L, highest concentration reported for nickel from the literature review, was used as the feedwater for the second stage freezing process. After 80% freezing, ice samples collected from the second stage (ice-2) contained 35 mg/L of nickel. As a result, 94% removal efficiency was achieved for the second stage of freeze concentration. Figure 3.23 compares the removal efficiency and concentration ratio of nickel versus the initial feedwater concentration used in first and second stages of freezing.

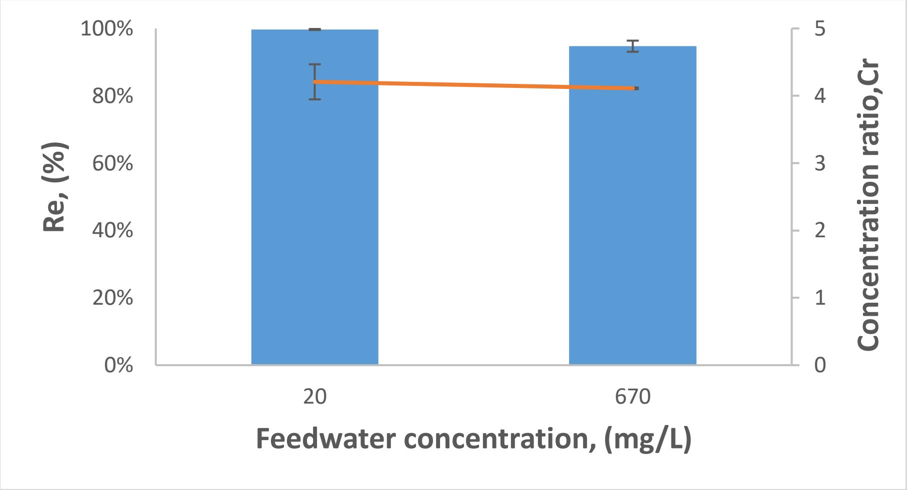

Figure 3.23: Nickel removal efficiency and concentration ratio in the first and second stages of freezing

As seen in figure 3.23, the removal efficiencies of nickel in the ice samples drop as the feedwater concentration increases. At 20 mg/L, a removal efficiency of 99% was achieved and the removal efficiency dropped to 94% at 670 mg/L. In a study conducted by *Wang, (2017),* using 100 -1000 mg/L synthetic boron wastewater, it was found that higher concentrated feedwater has low removal efficiencies. This is due to higher concentrated feedwater having more contaminants and thus more chance of said contaminants getting into the ice lattice while freezing. This phenomenon may be applied for nickel since the removal efficiency dropped with the increasing feedwater concentration. Furthermore, the concentration ratio also changed slightly with the feedwater concentration. A concentration ratio of 4.2 and 4.1 was achieved for 20 mg/L and 670 mg/L respectively. High concentration ratios suggest that freezing is also very effective at removing nickel from the water. Figure 3.24 shows the average changes in the pH values of the nickel unfrozen liquid (UFL-2) and ice (ice-2) samples.

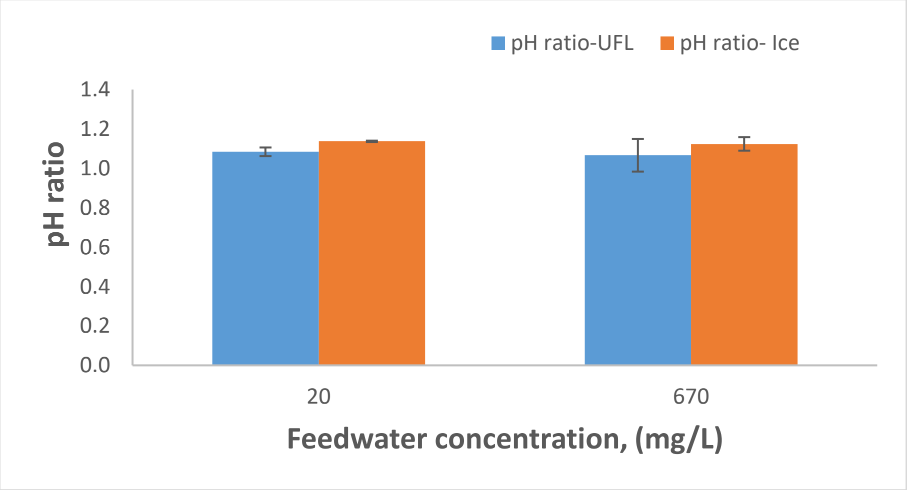

Figure 3.24: Average pH ratios of nickel samples

Figure 3.24 compares the pH ratios of nickel unfrozen liquid (UFL-2) and ice (ice-2) samples at 20 mg/L and 670 mg/L. As the feedwater concentration increased, the pH ratio of nickel unfrozen liquid increased slightly. A similar pattern was observed for pH values of nickel ice samples.

3.3.2.3 Cobalt removal efficiency

Feedwater (UFL-1) cobalt concentration of 135 mg/L was used for the second stage of freezing. The concentration of cobalt in ice (ice-2) samples, after 80% freezing, was at 6 mg/L which results in a 95% removal. In addition, the concentration of cobalt unfrozen liquid (UFL-2) reached 538 mg/L, which was an approximately 4-fold increase from that of feedwater. Figure 3.25 shows the average removal efficiency and concentration ratios of cobalt at 20 mg/L and 135 mg/L.

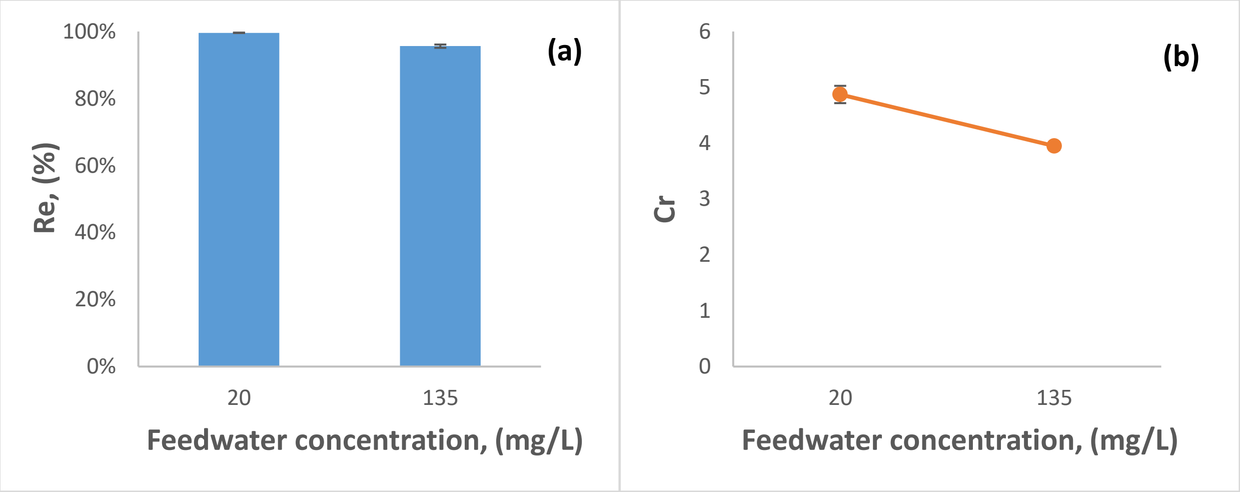

Figure 3.25: Removal efficiency and concentration ratio of cobalt

Figure 3.25 compares the removal efficiency (a) and concentration ratio (b) against the feedwater concentrations used in first and second stages of freezing. As seen in figure 3.25a, the removal efficiency of the second stage is lower than the removal efficiency of the first stage. As the feedwater impurity concentration increased, the removal efficiency decreased accordingly. A similar pattern was observed in nickel in section 3.6.2.2. Figure 3.25b shows the concentration changes (as a ratio) in the cobalt unfrozen liquid (UFL-2) versus the feedwater concentration. The concentration ratio decreased with higher feedwater impurity concentration as seen in Figure 3.25b. The concentration ratios dropped from 4.8 to 3.9 indicating more metal ions left in ice. High concentration ratios observed for cobalt suggests that freezing is also effective for separation of cobalt from water between 20 mg/L- 135 mg/L.

Table 3.4: pH values of cobalt in the second stage of freezing

Initial feedwater concentration	**pH ratio**	
	UFL	**Ice**
20 mg/L	0.85± 0.09	1.02± 0.03
135 mg/L	1.05± 0.12	1.01± 0.02

Table 3.4 shows cobalt pH values in the unfrozen liquid and ice samples with the respective feedwater concentration. As seen in Table 3.4, the pH values of the cobalt unfrozen liquid samples increase with higher feedwater concentration. In the first stage of freezing, using 20 mg/L of cobalt, unfrozen liquid samples recorded pH values less than 1 suggesting that H^+ ions were moving to the unfrozen liquid, however, as the feedwater concentration changes, the values were over 1. However, the ice samples stayed constant throughout the multiple stages of freezing.

3.3.2.4 Palladium removal efficiency and concentration ratio

Feedwater (UFL-1) concentration of 68 mg/L was used for the second stage of freezing of palladium. After 80% freezing, ice samples (ice-2) collected from the second stage contained 1.6

mg/L of palladium which resulted in a removal efficiency of 97%. Palladium unfrozen liquid (UFL-2) sample was concentrated 4.1-fold that of the feedwater. Figure 3.26 shows the average removal efficiency of ice samples collected during the first and second stages of freezing.

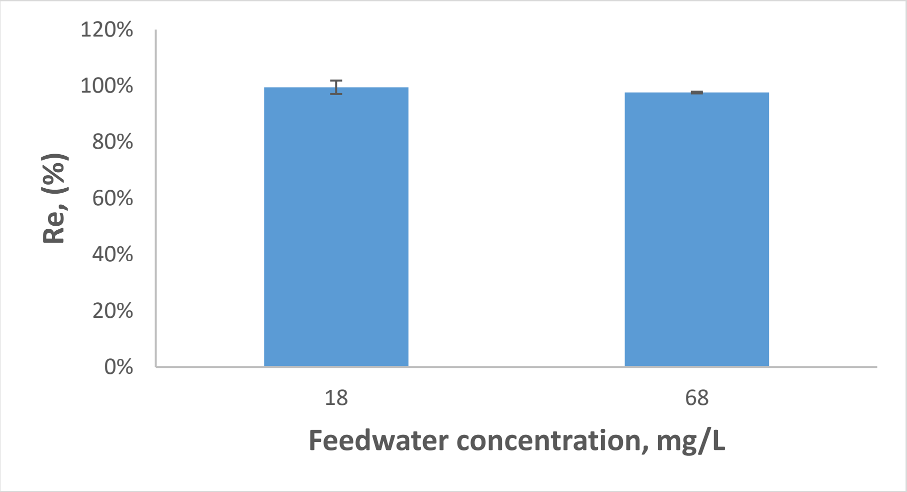

Figure 3.26: Palladium removal efficiency

As seen in Figure 3.26, the removal efficiencies of palladium in the ice samples decreased with the higher feedwater concentration. 99% removal efficiency was achieved in the first stage of freezing with palladium concentration of 18 mg/L followed by 97% removal efficiency in the second stage with palladium concentration of 68 mg/L as feedwater. With the increasing feedwater concentration, slightly fewer palladium ions were removed from the ice samples. Table 3.5 shows the pH values of palladium unfrozen liquid (UFL-2), ice (ice-2) samples, and the concentration ratio.

Table 3.5: pH ratios and concentration ratios of palladium

Initial feedwater concentration	pH ratio		Concentration ratio
	UFL	Ice	UFL
20 mg/L	0.9± 0.2	1.8± 0.03	4.0± 0.13
65 mg/L	1.1± 0.04	1.8± 0.1	4.1± 0.05

Table 3.5 shows the average pH ratios of palladium unfrozen liquid (UFL-2) and ice (ice-2) samples with the respective feedwater concentration. While the pH ratios in the unfrozen liquid differ slightly with the increasing feedwater concentration, the pH ratios in the ice samples were identical in both the first stage and second stage of freezing. Similar results were recorded in nickel samples in section 3.6.2.3. In addition, both stages have similar concentration ratios which suggest that freeze concentration is not susceptible to concentration changes in the feedwater for palladium at these concentrations. Also, palladium can be effectively separated using freeze concentration since high concentration ratios were achieved, at least in this concentration range.

3.3.2.5 Comparison of removal efficiencies of metals in second stage freezing

Removal efficiencies of chromium (VI), nickel, cobalt, and palladium in the second stage of freezing are shown in Table 3.6.

Table 3.6: Comparison of removal efficiency of metals in second stage freeze concentration

Metal	Feedwater concentration (mg/L)	Removal efficiency	Concentration ratio
Chromium (VI)	120	99.3% ± 0.3%	4.8
Nickel	671	94.7% ± 1.6%	4.1
Cobalt	136	95.6% ± 0.1%	4.0
Palladium	68	97.6% ± 0.4%	4.1

Table 3.6 shows the removal efficiencies and the concentration ratios of the four metals from the second stage of freeze concentration. All four metals showed very high removal efficiencies in the range of 94% to 99%. Chromium (VI) showed the highest removal efficiency out of the four metals while nickel showed the lowest removal efficiency since the feedwater concentration was very high compared to the rest of the metals. *Wang, (2017)* explains that higher concentrated feedwater has less removal efficiencies. Higher concentrated feedwater has more contaminants and more chance of said contaminants getting into the ice lattice while freezing, compared to lower concentrated feedwater and thus increasing the probability of contaminating the ice. However, with the lowest feedwater concentration, palladium showed lower removal efficiency than chromium (VI) at a removal efficiency of 97.6%. Impurity size may also have played a role since according to *Halde, (1979),* coarser particles are more easily separated than finer particles. Overall, the removal efficiency for the four metals was comparable although feedwater impurity concentration varied widely from 68 -671 mg/L.

3.3.3 Three-stage FC

Three stage freeze concentration was conducted on chromium (VI), nickel, cobalt and palladium samples following the second stage freeze concentration using unfrozen liquid (UFL-2) from the second stage of freeze concentration.

3.3.3.1 Chromium (VI) removal efficiency

Unfrozen liquid (UFL-2) from the second stage of freezing was used as the feedwater for the third stage of freeze concentration. After 80% freezing, 593 mg/L of chromium (VI) feedwater was concentrated to 2780 mg/L in the unfrozen liquid (UFL-3) while 94% removal was achieved in the ice sample in this stage of freeze concentration.

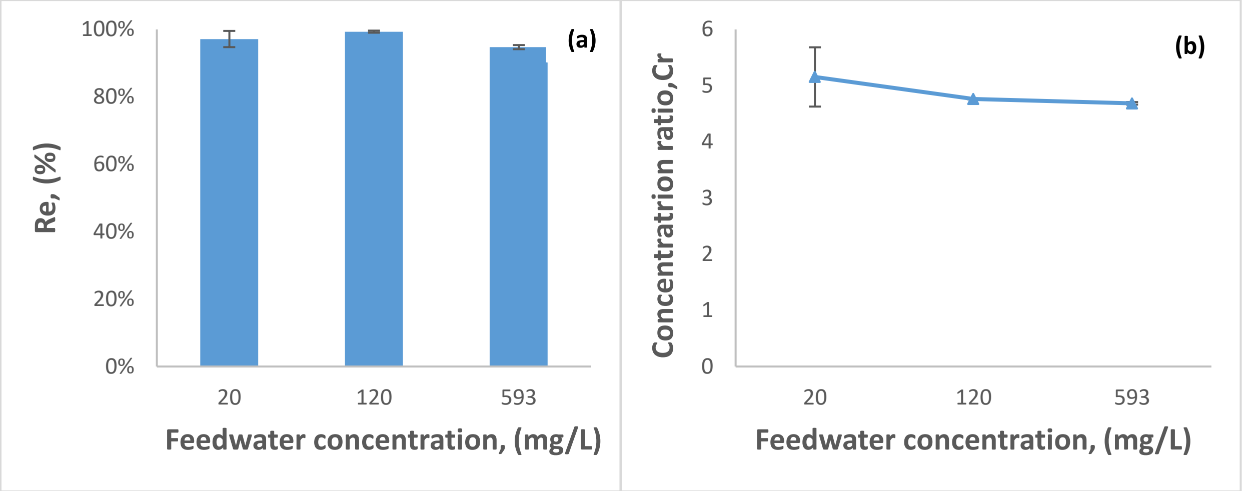

Figure 3.27: Chromium (VI) removal efficiency and concentration ratios in third stage freezing

Figure 3.27(a) shows the removal efficiency of chromium (VI) samples at various feedwater concentrations used in the three stages of freezing. As the freezing progressed from the second stage freezing to third stage freezing, the removal efficiency dropped from 99% to 94%. Until the second stage freezing, freeze concentration was not sensitive to the initial feedwater concentration of chromium (VI). As the initial feedwater concentration further increased, the removal efficiency dropped slightly. The reasoning behind lower removal efficiency at higher feedwater concentrations was explained by *Wang, 2017* in section 3.6.2.2. Overall, very high removal efficiencies of chromium (VI) were achieved by freeze concentration in all three stages. In addition, as seen in figure 3.27b, the concentration ratios in the unfrozen liquid (UFL-3) decreased with the higher initial feedwater concentration. The accumulation of chromium (VI) ions in the unfrozen liquid reduced slightly with the increasing freezing as seen by the changes in the slope of the Figure 3.27b. High concentration of chromium (VI) in unfrozen liquids suggests that freezing is quite effective in separating chromium from water at this concentration range.

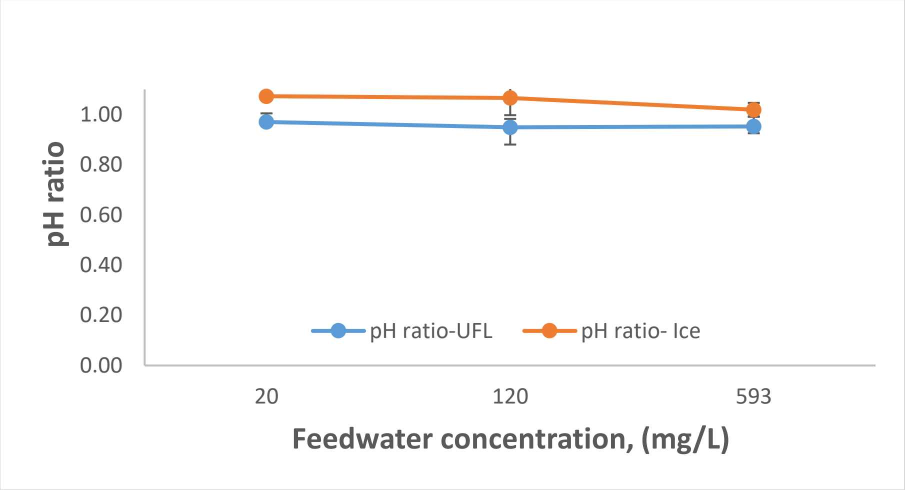

Figure 3.28: Changes in pH ratios of unfrozen liquid and ice

Figure 3.28 compares the pH ratios of unfrozen liquid (UFL-3) and ice (ice-3) samples at 20 mg/L 120 mg/L and 593 mg/L. As the feedwater concentration increased, the pH ratio of unfrozen liquid decreased slightly. pH ratios decreased from 0.97 to 0.95 with increasing freezing percentage and lower than 1 pH values suggest that H^+ ions were moving into the unfrozen liquid from the advancing ice front. A similar pattern was observed for pH values for ice samples with higher pH values (pH ratio = 1.0).

3.3.3.2 Nickel removal efficiency

Feedwater (UFL-2) concentration of 2750 mg/L was used for the third stage of freezing of nickel. After 80% freezing of the unfrozen liquid, the concentration of nickel in the ice (ice-3) samples were at 844 mg/L which was 69% removal. In addition, the concentration of the nickel in the unfrozen liquid reached 5553 mg/L, which was an approximately 2-fold increase from that of feedwater.

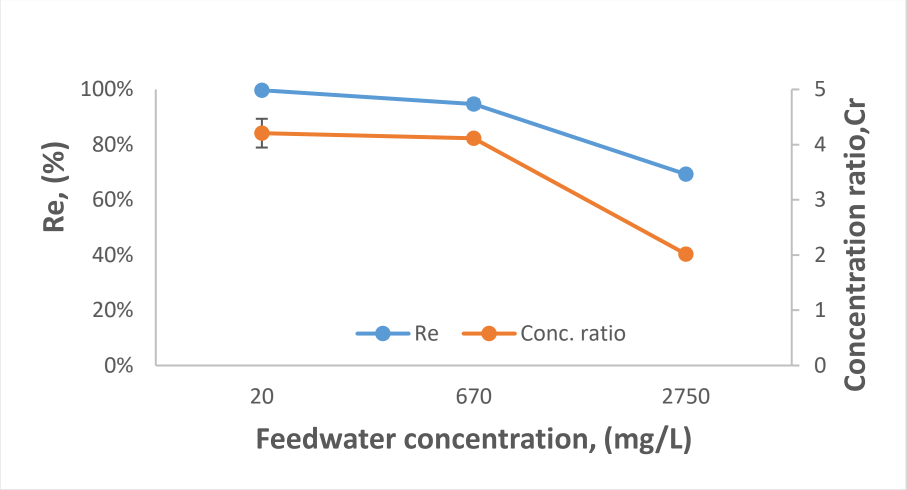

Figure 3.29: Removal efficiency of nickel in three stages freezing

Figure 3.29 compares the removal efficiency and concentration ratio of nickel versus the feedwater concentrations used in the three stages of freezing. As shown in Figure 3.29, the removal efficiency of nickel decreased with increasing feedwater metal concentrations. The removal efficiency dropped from 99% to 69% when the feedwater concentration increased from 20 -2750 mg/L at the end of the third stage of freezing. In addition, the concentration changes in the unfrozen liquid are also shown in Figure 3.29. As seen from the slope of the concentration ratio graph, the accumulation of nickel in the unfrozen liquid is reduced with the increasing feedwater nickel concentration. The concentration ratios dropped from 4.2 to 2.0 at the end of three stage freeze concentration.

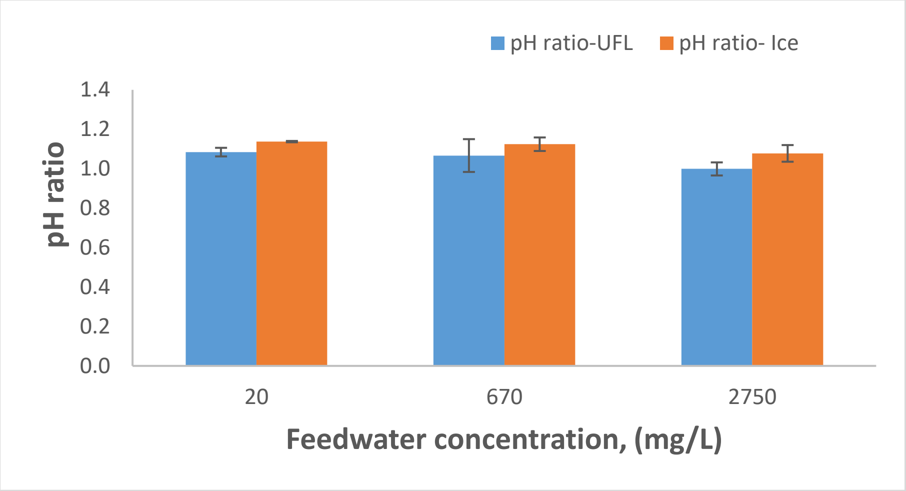

Figure 3.30: pH changes in the unfrozen liquid and ice samples

Figure 3.30 compares the changes in pH values in the unfrozen liquid and the ice samples. The pH ratios dropped slightly with the increasing feedwater concentration. pH ratio of 1.1 dropped to 1.0 at 2750 mg/L concentrations. However, there was no significant change in pH ratio from the second stage freezing to the third stage of freezing in the unfrozen liquid samples. Similarly, pH ratios of ice samples also decreased with increasing feedwater concentrations as seen in Figure 3.30. pH ratios of ice samples dropped from 1.1 to 1.0 in the three stages of freezing.

3.3.3.3 Cobalt removal efficiency

Feedwater concentration (UFL-2) of 540 mg/L was used for the third stage of freezing. At 80% freezing, a removal efficiency of 91% was recorded as the ice (ice-3) samples. Moreover, the unfrozen liquid (UFL-3) samples were concentrated to 2135 mg/L as a result of 80% freezing, i.e. 3.9 times increment from that of the feedwater concentration.

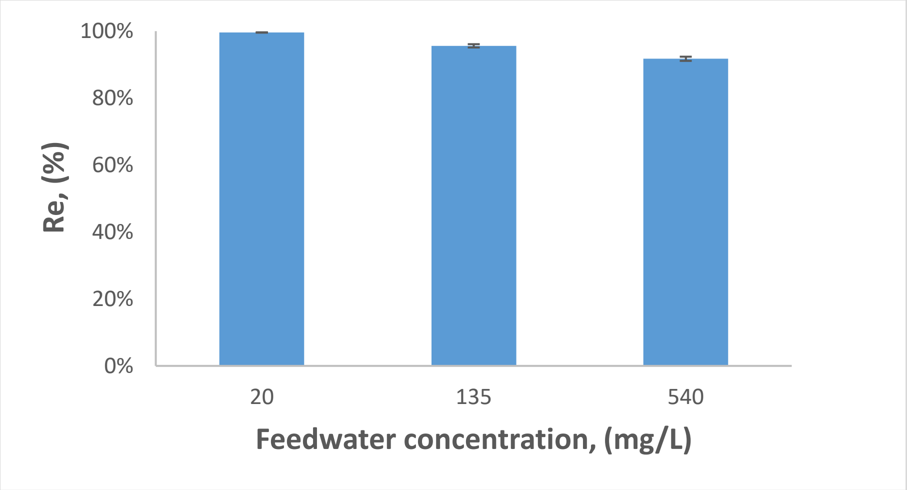

Figure 3.31: Removal efficiency of cobalt at three stages of freezing

As seen in Figure 3.31, the removal efficiency versus the feedwater concentration used in each stage is shown. The removal efficiency is decreased slightly with increasing feedwater concentration. The removal efficiency dropped from 99% in 20 mg/L to 91% in 540 mg/L of cobalt. Overall, over 90% removal efficiencies were achieved in all the stages of freeze concentration. Similar removal efficiencies were seen for nickel at this concentration range.

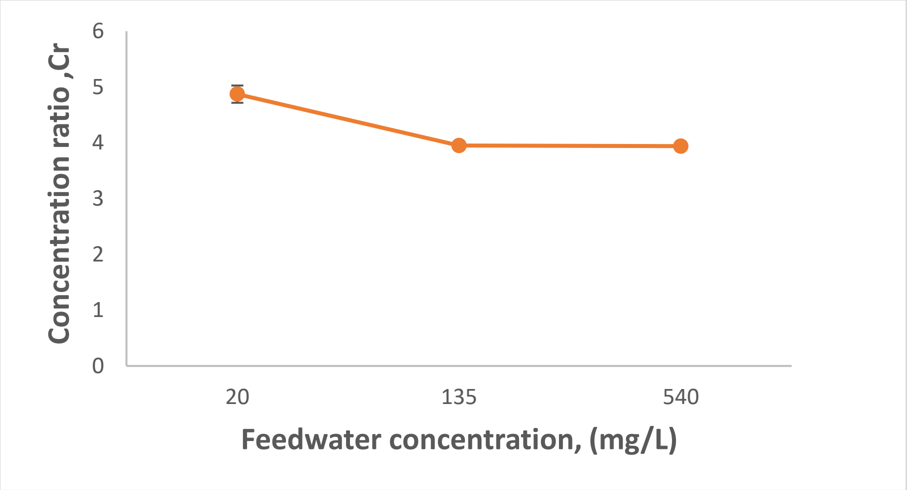

Figure 3.32: Concentration ratio of cobalt

Figure 3.32 compares the concentration ratios versus the initial feedwater concentration used in the first, second and third stages of freezing. As shown, the concentration ratios decreased slightly with the increasing freezing stages. The changes in the accumulation of cobalt ions in the unfrozen liquid are shown by the changes in the slope of Figure 3.32. From 20 -135 mg/L, the rejection of cobalt ions from the ice was much greater than the rejection between 135 -540 mg/L. However, approximately 4 to 5 concentration ratios were achieved suggesting that freezing is effective at separating cobalt ions in water.

Table 3.7: pH ratios of unfrozen liquid and ice samples

Initial feedwater concentration	**pH ratio**	
	UFL	**Ice**
20 mg/L	0.9	1.0
135 mg/L	1.0	1.0
540 mg/L	1.1	1.0

Tabulated values of cobalt pH ratios of in the unfrozen liquid and the ice samples are shown in Table 3.7. The pH ratio of the unfrozen liquid increased slightly with the increasing feedwater concentrations as seen in Table 3.7, a pH ratio of 0.9 with 20 mg/L increased to 1.1 with 540 mg/L, but the cobalt pH ratios in the ice samples remained constant. At this concentration range of palladium, it seems that the pH changes in the ice samples are not sensitive to the freezing.

3.3.3.4 Palladium removal efficiency

Feedwater concentration (UFL-2) of 279 mg/L was used in the third stage of freezing. After 80% freezing, ice (ice-3) samples of palladium reported a concentration 12 of mg/L which leads to 95%

removal. Furthermore, the palladium unfrozen liquid samples were concentrated to 1285 mg/L at the end of the freezing test which was a 4.6-fold increase from that of the feedwater.

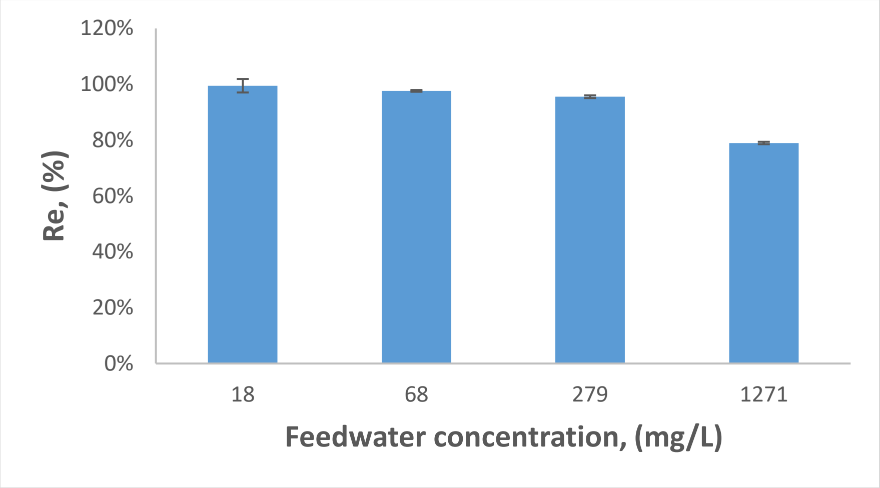

Figure 3.33: Removal efficiencies of palladium in the three stages of freezing

Figure 3.33 compares the removal efficiencies of palladium with different feedwater concentrations used in the first, second and third stages of freezing. As seen from the Figure 3.33, as the concentration of the initial feedwater increases, the removal efficiency of palladium from ice, decreases. The removal efficiencies dropped from 99% to 95% for the feedwater concentrations of 18 -279 mg/L. High removal efficiencies achieved by the freeze concentration suggests that it is very effective at removing palladium ions water at this concentration range. In addition, the fourth stage of freezing was conducted on palladium using the unfrozen liquid from the third stage. A concentration of 1271 mg/L was used as the feedwater (UFL-3) and after 80% freezing, a removal efficiency of 79% was achieved as the palladium concentration in the ice (ice-4). The feedwater with 1271 mg/L of palladium was concentrated to 3270 mg/L in the unfrozen liquid which leads to 2.5 times of that of the control feed (UFL-3) as a result of 80% freezing.

Table 3.8: Concentration ratios and pH ratios of palladium

Initial feedwater concentration	**pH ratio**		**Concentration ratio**
	UFL	**Ice**	**UFL**
20 mg/L	0.9 ± 0.2	1.8 ± 0.0	4.0 ± 0.1
65 mg/L	1.1 ± 0.1	1.8 ± 0.1	4.1 ± 0.1
279 mg/L	1.1 ± 0.1	1.5± 0.0	4.6 ± 0.1
1271 mg/L	1.1± 0.1	1.6± 0.1	2.5 ± 0.0

Table 3.8 shows the palladium pH ratios of unfrozen liquid and ice samples along with the concentration ratios at different feedwater concentrations used for each freezing stage. pH changes in the unfrozen liquid changed slightly with the increasing feedwater concentrations. However, between the 65 -279 mg/L, there was no change in pH ratios for unfrozen liquid samples which suggests that higher feedwater concentration did not affect the pH ratios, at least at this concentration range. pH ratios of the ice samples, on the other hand, remained constant at 1.8 until 65 mg/L and then decreased to a ratio of 1.5 at the 279 mg/L. In addition, the concentration ratio increased with the increasing feedwater concentration. The accumulation of palladium ions in the unfrozen liquid increased with higher feedwater concentrations as the seen in Table 3.8. The concentration of unfrozen liquid increased 4-fold at 20 mg/L while the concentration of unfrozen liquid increased 4.6-fold at 279 mg/L which suggests that the separation of palladium ions in water was not affected by freezing at this concentration range.

3.3.3.5 Comparison of removal efficiencies of metals in third-stage freeze concentration

Removal efficiencies of chromium (VI), nickel, cobalt, and palladium in the third-stage freeze concentration are shown in Table 3.9

Table 3.9: Removal efficiencies of metals in the third-stage of freezing

Metal	Feedwater concentration (mg/L)	Removal efficiency
Chromium (VI)	594	94.7% ± 0.4%
Nickel	2750	69.3% ± 1.7%
Cobalt	542	91.7% ± 0.0%
Palladium	279	95.5% ± 0.4%

Table 3.9 shows the removal efficiency of the four metals from the third stage of freeze concentration. All metals except nickel showed high removal efficiencies that were in the range of 91% to 95%. Palladium showed the highest removal efficiency out of the four metals while nickel showed the lowest removal efficiency due to very high feedwater concentration. The results are expected as the initial concentration of nickel for the third stage was about 5 to 10 times higher than those of other three metals. For nickel, the removal efficiency was actually comparable or slightly better than those of other three metals at 670 mg/L. The removal efficiency was 94.7%, as reported earlier. The experimental data indicated that freeze concentration was not sensitive/selective to the chemical nature of the metals. All four metals were removed effectively at similar levels. The effect of feedwater metal concentration on the removal efficiency was noticed when feedwater concentration of palladium was increased to about 1300 mg/L and nickel concentration was increased to 2750 mg/L.

The experimental data demonstrated that as a physical treatment process, freeze concentration was effective to remove or recover the selected metals from wastewater without the addition of chemicals. For practical applications, single stage or multi-stage freeze concentration could be used for effective treatment and volume reduction of industrial wastewater or liquid waste.

Depending on the requirements for the final/product water quality for discharge or reuse, ice and unfrozen liquid could be treated through different stages of freeze concentration. The ultimate goal is to get the maximum amount of product water with desired quality while keeping operating costs at a minimum *(Gao et al., 2008).* If only unfrozen liquid is treated through multiple stages of freeze concentration the process could not only effectively remove/separate the metals but also significantly reduce the volume of the waste. For example, with 80% freezing of feedwater (volume), the volume reduction achieved is 80% in the single/first stage, and for two stages the volume reduction is increased to 96% (or, 0.2x0.2 = 0.04 of the initial feedwater volume). With three stage freeze concentration, the volume reduction is greater than 99%, i.e. the volume of the unfrozen liquid (or residue) collected is only about 1% of the original feedwater volume. In multiple stage freeze concentration, only the unfrozen liquid (portion) is effective for recovery of precious metals, as demonstrated by the experimental results of palladium. The concentration of palladium increased from 20 -3270 mg/l, i.e. more than 160 times increase. Volume reduction is also important for waste residue management. Reducing the volume of residue/sludge generated from treatment processes at wastewater treatment plants will lead to a reduction of the cost for residue disposal.

3.4 Summary and Conclusions

This study was conducted to investigate the effectiveness of removal/ recovery of toxic and precious metals from synthetic wastewater using freeze concentration. The following conclusions can be drawn from this study:

- High removal/separation efficiencies were observed for chromium (VI), nickel, cobalt, and palladium synthetic wastewater samples. The removal efficiencies were in the range of 97% to 99% in the first stage of freezing
- The chemical nature of the metal type did not influence the removal efficiencies
- Ultrasonic and mechanical mixing methods were equally effective in removing/separating metals from wastewater
- Increasing feedwater metal concentration from 20 -670mg/l had little impact on the treatment efficiency. The metal removal efficiency of 92% to 99% was observed in the second and third stage of freeze concentration. However, at extremely high feedwater metal concentration (e.g. 2750 mg/l), freeze concentration efficiency dropped considerably (to 69%)
- Freeze concentration could effectively recover precious metals. More than 160 times increase of palladium concentration was observed in the unfrozen liquid after multiple stages of freeze concentration. Significant waste volume reduction could also be achieved using freeze concentration

In general, freeze concentration was very effective for removal or recovery of chromium (VI), nickel, cobalt and palladium from the water.

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Chapter 4- Electrodeionization (EDI) for toxic and precious metal removal from wastewater

4.1 Introduction

Toxic metals can be described as metals or metal compounds that have a harmful effect on life and environment (*Mohan et al., 2007).* Metals such as antimony, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, thallium, and zinc can cause multiple organ damages even at low concentrations *(Tchounwou et al., 2012).* Further, metals such as gold, platinum, palladium, ruthenium, osmium, rhodium, iridium, and silver are expensive and are considered precious metals *(Wang et al., 2017).* Gold and silver nanoparticles are known to have adverse effects, such as the formation of reactive oxygen species and cytotoxicity, in rainbow trout (*Farkas et al., 2010).* Exposure to palladium through water has been known to cause skin problems, eye irritation, and the degradation of DNA in humans *(Awual et al., 2015).* In addition, high levels of palladium can have lethal effects on aquatic life *(Luderwald et al., 2016).* Due to the exponential upsurge in the use of these metals in industrial, agricultural, domestic, and technological applications, human exposure and environmental pollution has increased significantly *(Tchounwou et al., 2012).* In many industries, such as mining, pulp and paper, petrochemicals, fertilizers, steel, metal plating, and textiles, toxic metals such as chromium, copper, cadmium, lead, mercury, and nickel are extensively employed *(Onikura et al., 2008, Verma et al., 2010, Cavas et al., 2005, Lothongkum et al., 2009, Silva et al., 2008, Bruggen et al.,* *2001, Agrawal et al., 2007, Gan, 2000).* For example, chromium with concentrations varying from ~1 -500 mg/L can be found in mining, steel industries, sugar industries, petrochemical industries, textile industries, and leather tanning industries *(Dakiky et al., 2002; Lothongkum et al., 2009; Gupta et al., 2004; Mirbagheri et al., 2004; Bruggen et al., 2001; Agrawal et al., 2007).* Nickel-containing wastewater is much more prominent in industries such as steel, fertilizer, electroplating, and mining, where nickel concentrations in wastewater can range from 7 -275 mg/L *(Price et al., 2016; Lothongkum et al., 2009; Camelo et al., 1997; Benvenuti et al., 2014; Huang et al., 2016)*. Furthermore, cobalt is common in wastewater from industries such as steel, pharmaceutical, paint, mining, and tanneries, where cobalt concentrations were found to be in the range from 9 µg/L to 1 mg/L *(Keranen et al., 2015; Singh et al., 2013; Amin et al., 2015; Malakootian et al., 2008; Bhuiyan et al., 2010).* In addition, effluents from mining, jewelry, electronics, and medical industries were found to be high in palladium, with concentrations between 1 µg/L to 31 mg/L *(Wang et al., 2017, Abughusa et al., 2006, Parajuli et al., 2009).* If these metals can be effectively recovered from wastewater, not only will environmental contamination be reduced and human health problems prevented; they will also compensate for expenditures in wastewater treatment *(Parajuli et al., 2009, Chen et al., 2013).*

Many strategies such as membrane filtration, chemical precipitation, adsorption, ion exchange, and electrodialysis have been implemented for the removal of metals such as chromium, cobalt, nickel, and palladium from wastewater *(Caroline et al., 2017, Ahmed et al., 2017, Barakat, 2011).*

Membrane filtration is a highly efficient, pressure-driven, easy to operate separation method which segregates particles based on their size, solution concentration, pH, and applied pressure *(Carolin et al., 2017)*. Moreover, contingent on the particle size being removed, membrane filtration may be subdivided as ultrafiltration, nanofiltration, and reverse-osmosis *(Barakat, 2011).* High removal efficiencies of over 99% might be achieved for concentrations between 0.5 - 500 mg/L of copper, nickel, zinc, and chromium-containing synthetic wastewater *(Fu et al., 2011, Ahmed et al., 2017)*. However, some of the complications inherent to membrane filtration are high initial costs, complex processes, and membrane fouling *(Ahmed et al., 2017).*

The most widely used wastewater treatment process in the industry is chemical precipitation, due to its relatively simple and inexpensive operation. In chemical precipitation, metal precipitants are formed by changing the pH through the addition of chemicals. These precipitants are subsequently removed through sedimentation from the solution *(Carolin et al., 2017)*. Chemical precipitation is known to have treated concentrations of 100 -5363 mg/L of zinc, nickel, chromium, and copper while achieving 99.7% removal *(Ghosh et al., 2011, Ramakirshnaiah et al., 2012, Fu et al., 2012 and Zhao et al., 2016).*

Adsorption is a process that uses mass conversion by transferring contaminants to the active sites of an adsorbent. Very high removal efficiencies of 96.24% - 99.99% may be achieved for concentrations of ~2.00 mg/L of lead, copper, chromium, and cadmium *(Lo et al., 2012)*. Even though this process is a low cost, easy to use treatment method, its reversibility is considered to be a disadvantage *(Wang et al., 2011).*

Ion exchange is extensively employed for the removal of metals due to its many advantages such as high treatment capacity, high removal efficiency, and rapid kinetics *(Al-Enezi et al., 2004)*. Through the use of ion-exchange systems, removal efficiencies of 99.9% may be achieved for concentrations from 0.021 - 2 mg/L of cadmium, chromium, copper, mercury, nickel, lead, and zinc-containing synthetic wastewater *(Ahmed et al., 2017, Al-Enezi et al., 2004).* In ion exchange, resins are used for the removal of metals from wastewater; however, this is not a continuous process as the resins may easily become saturated. Therefore, the regeneration of ions with acids and bases are required *(Zhang et al., 2014).*

Electrodialysis (ED) has been employed for metal removal in the past. ED is a separation process that is based on the selective migration of ions in a solution through ion exchange membranes, with the assistance of an electric current *(Alvarado et al., 2014)*. ED has a number of advantages, such as high removal efficiencies and high-water recovery *(Carolin et al., 2017).* A chromium removal rate of >99.5% was achieved in a study conducted by *Sadyrbaeva*, *(2016).* However, when the ion concentration becomes low, the removal efficiency is lowered along with higher energy consumption *(Zhang et al., 2014).*

Electrodeionization (EDI) is a separation technique that combines electrodialysis (ED) and ion exchange methods *(Song et al., 2007).* In an EDI setup, cation and anion exchange membranes are alternately placed between the electrodes as shown in Figure 4.1. An external power source is used to apply an electric current through the electrodes *(Tanaka et al., 2012).* Ion exchange resins are filled in the central compartment to improve the transport of cations and anions under the driving force of a direct current *(Song et al., 2007).*

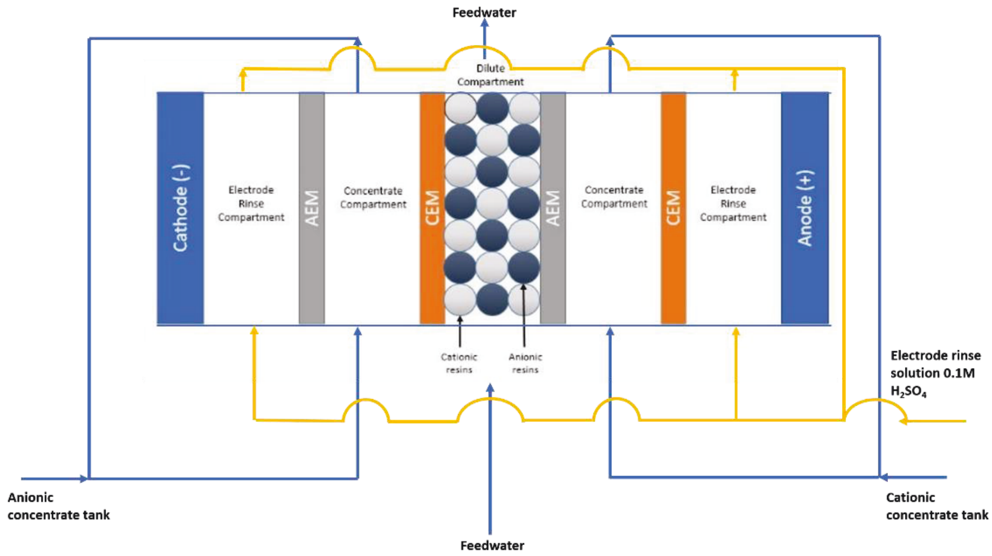

Figure 4.1: A typical EDI device setup *(Alvarado et. al, 2014).*

While the resins improve the transport of ions, they can also participate as a substrate for electrochemical reactions, such as the splitting of water into H^+ and OH^- ions *(Wood et al., 2010).* As the result of electro regeneration, EDI has far better results in contrast to electrodialysis and ion exchange in the separation of ions (*Wood et al., 2010).* Different configurations of media may be used in an EDI system depending on the feedwater parameters. For example, a mixture of anion and cation exchange resins, or separate sections of ion exchange resins, may be used accordingly *(Arar et al., 2014).*

Ions in the dilute compartment move to the adjacent concentrate compartments, due to the selective properties of the ion exchange membranes, and the direction of the electrical potential gradient *(Tanaka et al., 2012).* This is possible due to the use of ion exchange resins in the dilute compartment. One of the reasons for this is that, without the ionic conductivity of the resins, the transfer of ions does not occur at a practical rate *(Tanaka et al., 2012).*

EDI has been employed for many applications, primarily metal removal, organic compound separation, and high purity water production *(Alvarado et al., 2014).* In a study conducted by *(Zhang et al., 2014),* the continuous separation and recovery of chromium (III) and chromium (VI) along with the saturation of resins, and its roles in removal efficiency and energy consumption were studied. From their findings, it was reported that 95.5% to 98.5% chromium (III) and 90.0% to 99.0% chromium (VI) removal efficiencies could be achieved. The study also reported that once the resins were fully saturated, the removal efficiencies and energy consumption remained stable *(Zhang et al., 2014).* According to the study by *(Xing et al., 2009),* using 40 - 100 mg/L synthetic chromium (VI) wastewater, it was found that the current density, flow rate, and initial concentration were linearly proportional to the removal efficiencies.

The removal of nickel using EDI has also been studied *(Spoor et al., 2001, Dzyazko et al., 2006, Dermentzis et al., 2010 and Lu et al., 2011).* Spoor et al. investigated the relationship between removal efficiencies, current, and initial concentration. It was found that the transport of nickel ions increased with the increase of the concentration of nickel ions in the resin. Dermentzis et al. found that the effective diffusion coefficient of nickel ions was dependant on the acidity and flow rate of the feed solution. For an initial nickel concentration of 100 mg/L, the removal of ~90% of the nickel could be achieved when the initial feedwater concentration was <500 mg/L *Dermentzis et al. (2010)* and *Lu et al. (2011)* studied the effects of resin particle distribution on the removal of nickel ions, and it was found that the particle size distribution of the resins packed in the dilute compartments affected the EDI performance.

The removal of cobalt was studied by *Yeon et al., (2003) and Dermentzis et al., (2010)*. Yeon et al., *(2003)* found that the ion exchange resin bed configuration was significant toward the removal of cobalt ions from nuclear power plant waste. Furthermore, it was found that ion exchange textiles were superior to ion exchange resins in terms of faster kinetics and the overall cobalt removal *(Yeon et al., 2003).*

Metals such as chromium, cobalt, nickel, and palladium are employed in widely diversified fields such as petrochemical, steel, metal plating, etc. *(Onikura et al., 2008, Verma et al., 2010, Cavas et al., 2005, Lothongkum et al., 2009, Silva et al., 2008, Bruggen et al., 2001, Agrawal et al., 2007, Gan, 2000).* The objective of this study was to investigate the effectiveness of EDI in the removal of toxic and precious metals; namely, chromium (VI), nickel, cobalt and palladium from synthetic industrial effluent, using commercially available resins. The data obtained from this study will be used for the possible integration of electrodeionization and freeze concentration for the removal and recovery of these metals and volume reduction of wastewater.

4.2 Materials and methods

The ion selective membranes used in these experiments were cation exchange membranes (CMI-7000S) and anion exchange membranes (AMI-7001S), which were purchased from Membrane International Inc. (New Jersey, USA). The cation exchange membrane contained a gel polystyrene that was crosslinked with divinylbenzene via sulphonic acid functional groups, with a total capacity of 1.6±0.1 meq/g. The anionic exchange membrane possessed the same matrix with divinylbenzene and quaternary ammonium functional groups, with a total exchange capacity of 1.3±0.1 meg/g. Moreover, fibres were utilized to reinforce both membranes.

Amberlite™ IRC 86 Hydrogen Form, having a methacrylic gel matrix and a capacity of 4.1 meq/mL, was employed as the cation exchange resin, which was purchased from Sigma Aldrich, Canada. For the anion exchange resin, Purolite FerrIX™ A33E (Pennsylvania, United States), which has a polystyrene polymer structure crosslinked with divinylbenzene, was used,

4.2.1 Synthetic wastewater samples

Synthetic wastewater samples were prepared using the same method as described in the section: 3.3. The concentrations of the samples were determined according to freeze concentration results, where the chromium (VI) samples were 120 mg/L and 500 mg/L, nickel samples were 350 mg/L, 500 mg/L, and 650 mg/L/, cobalt samples were 135 mg/L, 500 mg/L, and 550 mg/L, and palladium samples were 55 mg/L and 200 mg/L.

4.2.2 Analytical methods

The concentrations of chromium, nickel, cobalt and palladium were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Varian Vista Pro). Both current-voltage and time-voltage curves were recorded using a Voltalab (PGZ 402 Universal Potentiostat.)

4.2.3 Pre-treatment of ion exchange membranes and resins

Prior to installation, the cation exchange membranes were submerged in 0.1M H_2S0_4 and the anion exchange membranes were submerged in 0.1M KOH for 24 hours. This allowed the membranes to hydrate and expand. After 24 hours, the membranes were rinsed with deionized water to remove any excess reagents.

The cationic resins (Amberlite™ IRC 86) were initially submerged in 0.1M H_2S0_4 and stirred for 1 hour. The anionic resins (Purolite FerrIX™ A33E) were submerged in 0.1 KOH and stirred for 1 hour. Subsequently, the resins were separately rinsed twice using deionized water and completely dried at a temperature of 50°C.

4.2.4 EDI cell setup

A lab-scale EDI cell setup established by *Zhang et al., (2014)* was used for the experiments. Two cationic exchange membranes (CEM) and two anionic exchange membranes (AEM) were alternatively placed in between the two electrodes. A stainless-steel plate (6 cm x 10 cm) was used as the cathode and a Ti/Ta_2O_5-$Ir0_2$ mesh was employed as the anode. The active surface area of the membranes was of 60 cm^2 (6 cm x 10 cm). The width of the dilute compartment was

10 mm, whereas the width of the concentrate compartments was 10 mm, and the width of the electrode rinse compartments was 15 mm. The dilute compartment was fully packed with mixed resins (~50g) at a ratio of 1:1 by weight. The EDI cell was operated by a Voltalab (PGZ 402 Universal Potentiostat) with a constant current through the cathode and the anode.

4.2.5 Operation of CEDI system

The synthetic solution (250 mL) was circulated through the dilute compartment with a peristaltic pump while 250 mL of 0.1M H_2S0_4 was separately circulated through the other compartments. A flow rate of 6 mL/min was constantly maintained throughout the experiments. Hourly samples were then taken from the dilute tank of the recirculation line to monitor the concentrations of chromium (VI), nickel, cobalt and palladium. Following each run, a 0.1M HCl solution was used to clean the concentrate compartments to remove any possible precipitation on the membranes, followed by ultrapure water to eliminate any residues. All of the solutions entered through the bottom of the cell and exited from the top of the cell at a continuous flow rate of 6 mL/min.

4.3 Results and discussion

4.3.1 Concentration change in the EDI cell

A limiting current for the experiment was determined according to *Zhang et al., (2014).* A limiting current of 15 mA was used for the experiments. However, some experiments were conducted with a higher limiting current of 50 mA due to the removal efficiencies being too low.

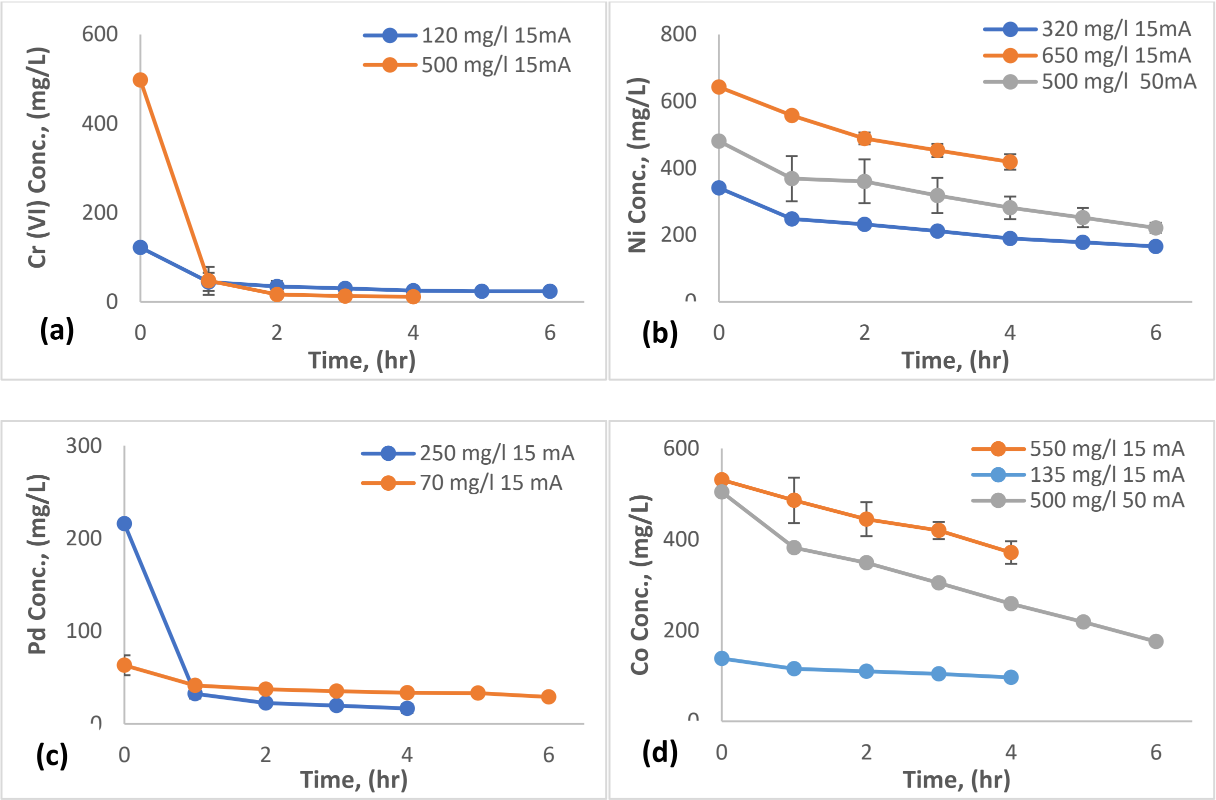

Figure 4.2: Concentration profile of chromium (VI)(a), nickel (b), palladium (c) cobalt (d) in the concentrate compartment of the CEDI

As shown in Figure 4.2a, 500 mg/L of chromium (VI) was reduced to 10.61 mg/L within in four hours of running the EDI cell at 15 mA current. Within the first hour alone, the concentration dropped to 47.2 mg/L. On the other hand, 120 mg/L of chromium (VI) was reduced to 25.4 mg/L in four hours. The continuous operation of the EDI cell for two more hours reduced the concentration to only 23.8 mg/L. A 215 mg/L concentration of palladium was reduced to 13.12 mg/L in four hours using a 15 mA current as seen in Figure 4.2c. When a 55 mg/L palladium feedwater was used, it was reduced to 33.6 mg/L in six hours under 15 mA. Similar to chromium

(VI), palladium concentration dropped from 215 -70 mg/L in the first hour. The chromium (VI) and palladium showed similar results with high and low initial feedwater concentrations. Similar results were achieved by *Zhang et al., (2014) and Alvarado et al., (2013)* for chromium (VI) removal using similar concentrations of wastewater*.*

As seen in Figure 4.2b, the nickel concentration of 650 mg/L was only reduced to 418 mg/L after four hours of continuous operation of the EDI cell under a 15 mA current. A concentration of 320 mg/L of nickel was reduced to only 166 mg/L within six hours. To determine if the limiting current was a factor for having high concentrations of nickel even after four hours of operation, the limiting current was increased to 50 mA, and the experiment time was increased to six hours. Yet the concentration was lowered only from 500 -211 mg/L in six hours. This might have been due to the influence of the resin size on the removal efficiencies. According to *Lu et al., (2010),* the best performance for nickel removal could be achieved using a resin particle size of 0.71- 0.90 mm. Amberlite™ IRC 86 which was used as the resin for the experiment has a particle size of 0.58 – 0.78 mm which not in the optimal range for nickel removal *(Dow.com, 2018)*. Also, it could be due to the EDI cell being optimized for chromium removal.

A cobalt concentration of 530 mg/L was reduced to 388 mg/L after four hours, while a 138 mg/L concentration was reduced to 95 mg/L under a 15 mA as seen in Figure 4.2d. However, much-improved results could be achieved by increasing the limiting current to 50 mA, whereby the concentration was reduced from 503 - 148 mg/L within in six hours. As pointed out by *(Xing et* *al., 2009)*, higher influent concentrations result in enhanced removal efficiencies due to having higher ion concentrations in the resins which assists the ions to migrate more quickly.

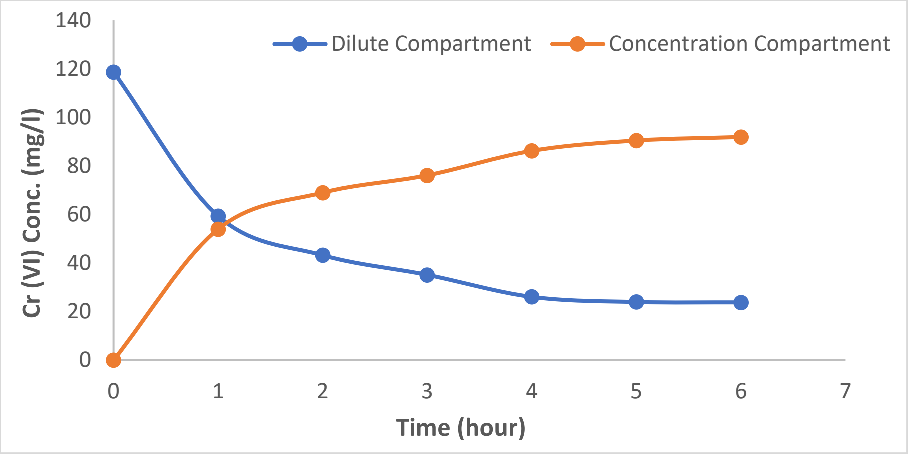

Figure 4.3: Concentrations in the dilute and concentrated compartments over time

As seen in Figure 4.3, the chromium initial concentration of 120 mg/L in the concentrated compartment was reduced to 25.4 mg/L in six hours while the concentration in the dilute compartment was increased to 92 mg/L at the end of six hours. A mass loss of 2.1% occurred during the test, which might have been due to differences in the water pressure in the dilute compartment and the concentrating compartment. As a result, diluted water could be forced into the concentrating compartment through the ion exchange membranes *(Lu et al., 2015)* and could be also due to minor leaks in the EDI cell setup. Similar trends were seen for other metals such as nickel, cobalt, and palladium with mass losses of 3.16%, 3.57%, and 5.23% respectively.

4.3.2 Removal efficiencies in the EDI cell

Removal efficiencies *(Re)* was used to evaluate the performance of the CEDI system by using Equation 4.1 *(Xing et al., 2009)*:

$$Re\ (\%) = \ (C_o - C_f)/\ C_o \times 100\% \tag{4.1}$$

Where C_0 and C_f are initial feedwater concentration and concentration in the dilute compartment after arbitrary time, respectively.

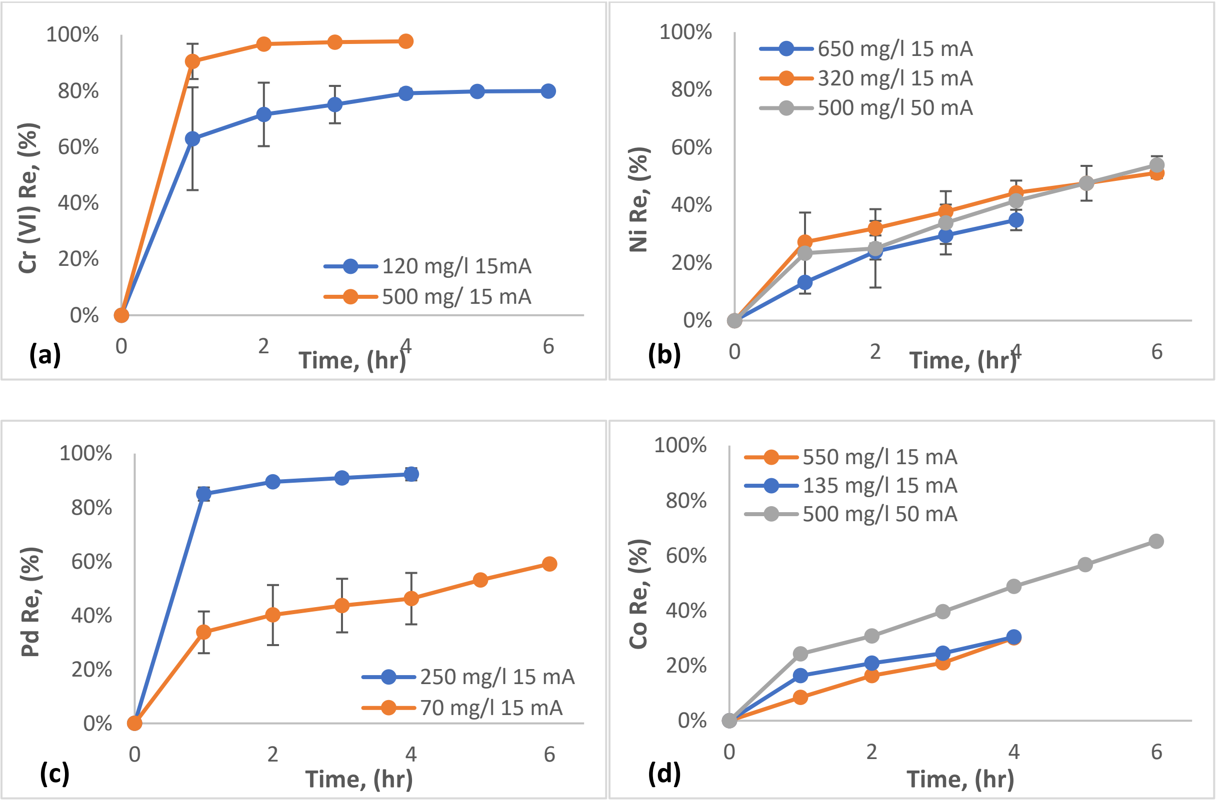

Figure 4.4: Removal efficiencies of chromium (VI)(a), nickel (b), palladium (c), cobalt (d) in the dilute compartment of the CEDI

As seen in Figure 4.4a, the chromium (VI) removal efficiencies were over 97% for the 500 mg/L sample. The chromium (VI) removal efficiencies were found to be 97.67% on average after four hours of running the cell at 15 mA and 6 mL/min. Using the same parameters, the 120 mg/L chromium (VI) samples had only 80% removal efficiencies even after six hours of continuous operation. Palladium showed similar results as seen in Figure 4.4c to that of chromium (VI) in 250 mg/L samples. Removal efficiencies of 92% were achieved in four hours of operation using 15 mA and 6 mL/min. However, only 60% removal efficiencies could be achieved with 70 mg/L samples. Lower removal efficiencies were shown on all the low concentration samples used for the experiment. The 650 mg/L nickel sample could only achieve ~35% removal using a 15 mA current and 6 mL/min as seen in Figure 4.4b. By increasing the current to 50mA, higher removal efficiencies of 54% could be achieved under the same experimental conditions. A 320 mg/L concentration nickel sample achieved only 50% removal efficiencies with a 15 mA current and 6 mL/min flow rate. This might be due to the resin particle size as explained earlier. As seen in Figure 4.4d, cobalt samples behaved in a similar pattern to that of nickel samples. The 550 mg/L and 135 mg/L samples achieved 30% removal efficiencies after four hours of operation at 6 mL/min, while with increasing the current, higher removal efficiencies could be achieved (e.g., 70% removal efficiencies could be achieved by increasing the current to 50 mA). As pointed out by *Xing et al., (2009),* higher influent concentrations resulted in higher removal efficiencies due to having higher ion concentrations in the resins, which assists the ions in migrating faster.

4.4 Conclusion

This study investigated the feasibility of using a CEDI system for the simultaneous removal and recovery of toxic and precious metals from synthetic industrial wastewater. On the basis of the results obtained, EDI is recommended for the removal of chromium (VI) concentrations of up to 500 mg/L and palladium concentrations of up to 250 mg/L using a 15mA current and 6 mL/min flow rate by using cationic resins (Amberlite™ IRC 86) and anionic resins (Purolite FerrIX™ A33E). Cobalt can be effectively removed and recovered using a 50 mA current with the same equipment. For Nickel, a different type of resin is recommended for removal and recovery under experimental conditions. Under the operating conditions, the removal efficiencies were 97.87%, and 90.73% for chromium (VI) and palladium, while cobalt achieved a 70.5% removal efficiency. The results show a promising removal and recovery of toxic and precious metals from industrial wastewater using electrodeionization.

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Chapter 5- Comparison of freeze concentration and electrodeionization in treatment of high concentrations of toxic and precious metals

5.1 Introduction

Industrial wastewater contains a wide variety of toxic and precious metals. Toxic and precious metals such as chromium (VI), cobalt, nickel and palladium have been found in mining, pulp and paper, petrochemicals, steel, textiles, jewellery and electronics industrial wastewater *(Onikura et al., 2008, Verma et al., 2010, Cavas et al., 2005, Lothongkum et al., 2009, Silva et al., 2008; Agrawal et al., 2007, Gan, 2000)*. The concentrations of these metals in wastewater vary greatly depending on the industrial operations. Nevertheless, these toxic and precious metals need to be removed/recovered due to adverse effects on human and aquatic eco-system *(Mohan et al., 2007)*. The high economic values of precious metals also make it necessary to recover them from wastewater *(Parajuli et al., 2009*).

Freezing is used as a potential option for the removal and recovery of high concentrated metals from synthetic wastewater in this study. Freeze concentration (FC) is a physical treatment method which uses partial crystallization of water followed by the removal of ice (*Gao et al., 2009).* No addition of chemicals and low maintenance are one of the key advantages of freezing over other conventional methods *(Williams et al., 2013).* The results from the Chapter 3 showed that freeze concentration is an effective method for removing toxic and precious metals from wastewater.

Electrodeionization (EDI) is considered a green technology for the removal and recovery of ions from water due to no addition of chemicals *(Alvarado et. al, 2014)*. EDI is a membrane separation process that is based on the forced transportation of ions through selective membranes. Cationic and anionic exchange membranes are alternately placed between the anode and the cathode *(Alvarado et. al, 2014).* The ability of freeze concentration and EDI processes for removal/recovery of high concentrations of toxic and precious metals from wastewater have not been evaluated. The objective of this study is to examine the capacity of two processes: freeze concentration and EDI for removal and recovery of relatively high concentrations of selected metals from synthetic wastewater.

5.2 Materials and methods

Freeze concentration apparatus and the EDI cell setup from the section 3.2 were used in this study. The procedures implement by *Reynolds (2013)* were used for the freeze concentration tests and the EDI procedure for pre-treatment of resins, EDI cell setup (shown in Chapter 4, Figure 1) and operation of the cell were same as section 4.2.

5.2.1 Synthetic wastewater samples

The synthetic wastewater samples were prepared using the same technique as in section 4.2. The concentrations of the samples were determined by the freeze concentration results.

5.2.2 Analytical methods

Initial feedwater, ice and unfrozen liquid samples from each freeze concentration stage were collected and the concentrations from each compartment in the EDI cell were also collected and analyzed. Metal concentrations of the samples were analyzed using Inductively Coupled Plasma

Atomic Emission Spectroscopy (ICP-AES) (Varian Vista Pro) (Palo Alto, California, United States) and UV-Visible spectrophotometer (Cary 50) (Thermo Fisher Scientific, Mississauga, Ontario, Canada) according to *Standard Methods for the Examination of Water and Wastewater (AHPA, 2005)*.

5.3 Results and discussion

5.3.1 Chromium (VI)

5.3.1.1 Treatment efficiencies for wastewater with 120 mg/L of chromium (VI)

Figure 5.1 shows the removal efficiencies of chromium (VI) using freezing and EDI.

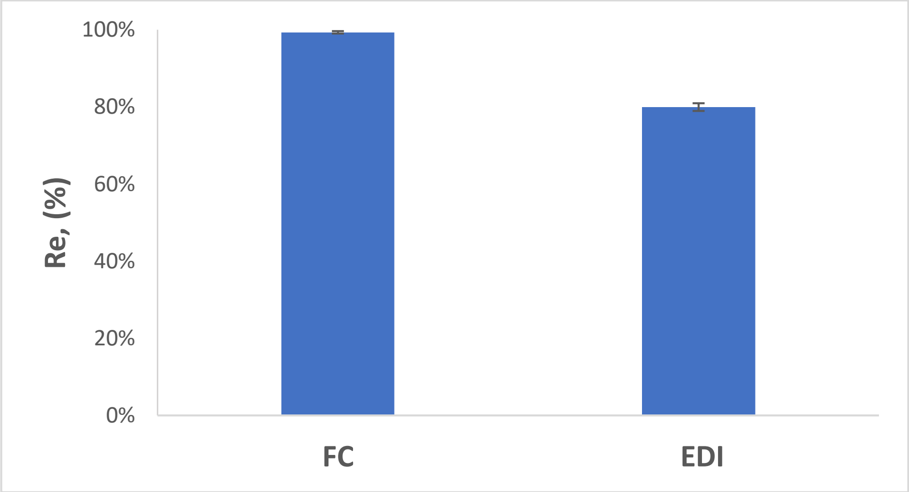

Figure 5.1: Removal efficiencies of FC and EDI at 120 mg/L of chromium (VI)

Figure 5.1 reveals the removal efficiencies of freeze concentration (FC) and electrodeionization (EDI) of feedwater with 120 mg/L of chromium (VI). Both treatment methods achieved high removal efficiencies but freezing showed better results compared to EDI. The lower removal efficiency from EDI unit could be caused by low chromium (VI) concentration in the feedwater, i.e. 120 mg/L was not an optimum input concentration for EDI. As pointed out by *Xing et al., (2009),* using 40 - 100 mg/L chromium (VI), better removal efficiencies were achieved with higher influent concentrations due to having higher ion concentrations in the resins helps the ions migrate faster. The unfrozen liquid from the freezing was concentrated to 570 mg/L while the concentrating compartment in the EDI cell reported a concentration of 92 mg/L of chromium (VI) ions resulting in a mass loss of 2.1% due to minor leaks in the EDI cell.

5.3.1.2 Comparison of removal efficiencies for wastewater with chromium concentration between 500 – 593 mg/L

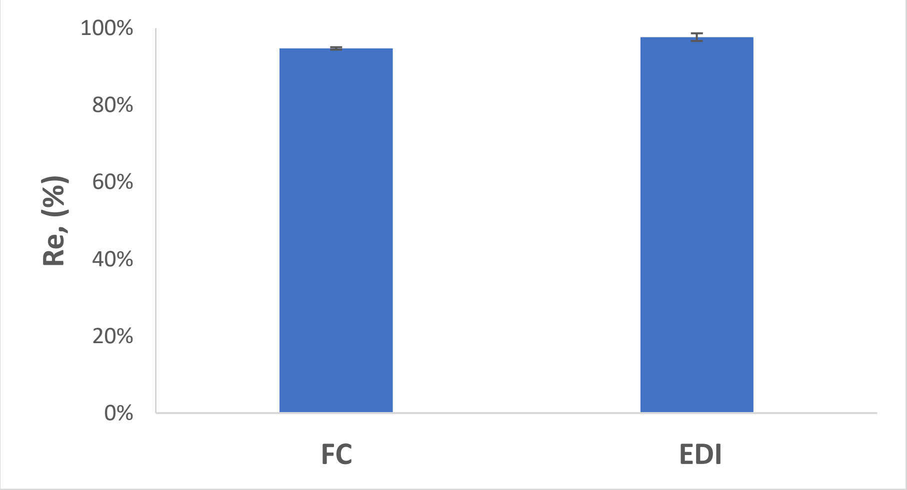

Figure 5.2: chromium (VI) removal efficiency over 500 mg/L metal concentrations

Feedwater with chromium (VI) concentration of 593 mg/L was treated using freeze concentration and a 500 mg/L of feedwater was treated using EDI. Figure 5.2 shows removal efficiencies of chromium (VI) for corresponding treatment methods. Very high removal efficiencies were achieved by both methods. EDI showed slightly higher removal efficiency of 98% as compared to

95% removal efficiency in FC. For EDI process, the performance for removal of 500 mg/L of chromium (VI) was better than that at 120 mg/L. The results from Figure 5.1 and Figure 5.2 suggest that both methods were effective for treatment of wastewater with chromium (VI) concentrations in the range of 120 – 600 mg/L.

5.3.2 Nickel

5.3.2.1 Nickel removal efficiencies at 650 - 670 mg/L

A 95% removal efficiency was observed for freeze concentration process when feedwater nickel concentration was at 670 mg/L. For EDI cell, when feedwater with 650 mg/L of nickel was treated, the highest treatment efficiency was 34%, lowering feedwater nickel concentration to 320 mg/L and 500mg/L, the treatment efficiency increased to 51- 54%. The low removal efficiency of EDI could be due to resin size in the EDI cell influencing the removal efficiencies. According to *(Lu et al., 2010),* the best performance for nickel removal could be achieved by using a resin particle size of 0.71- 0.90mm. Amberlite™ IRC 86, the resin used for this study, has a particle size of 0.58 – 0.78 mm *(Dow.com, 2018)*. The selected resin size was not optimized for removal of nickel and thus, low removal efficiencies were achieved for EDI. Also, it could be due to the EDI cell being optimized for chromium removal.

5.3.3 Cobalt

5.3.3.1 Comparison of removal efficiencies

Table 5.1: Removal efficiencies of Cobalt using freezing and EDI

Cobalt	FC	EDI
135 mg/L	95% ± 0.1%	33% ± 0.3%
500 - 540 mg/L	91% ± 1.0%	70% ± 0.0%

Table 5.1 shows the removal efficiencies of cobalt using freezing and EDI, at two different concentrations. At 135 mg/L concentration, freezing shows considerably higher (more than 60% higher) removal efficiencies than that of EDI. The low removal efficiency in EDI is, due to the lower current used for the operation of the EDI cell. After increasing the applied current from 15 mA to 50 mA, the removal efficiency of cobalt increased significantly to approximately 70% when the feedwater concentration was in the range of 500 – 540 mg/L. Freezing showed better removal efficiency (at 91%) for the same concentration range, although the removal efficiency was even higher at 135 mg/L.

5.3.4 Palladium

5.3.4.1 Removal efficiencies comparison of FC and EDI

Table 5.2: Removal efficiencies of palladium in freezing and EDI

Palladium	FC	EDI
~70 mg/L	98%± 0.4%	60%±2.0%
~280 mg/L	96%± 0.0%	90%± 1.0%
1271 mg/L	79% ± 0.8%	-

Freezing treatment achieved very high removal efficiencies for palladium in the concentrations range of 70 - 280 mg/L. The removal efficiency was between 96% - 98%. EDI, on the other hand, reported 90% removal efficiency only for palladium concentration at 250 mg/L. As shown in Table 5.2, treatment efficiency of EDI was 60% for palladium concentration at about 70 mg/L and the process was fairly sensitive to the change in the feedwater palladium concentration. At feedwater palladium concentrations around 250 mg/L, both freeze concentration and EDI showed very high removal efficiencies but freezing showed slightly better removal efficiencies compared to EDI. For wastewater with low concentrations (<70 mg/L) of palladium feedwater, freezing treatment was more effective. For very high input palladium concentration (~1300 mg/l), freeze concentration efficiency was reduced to 78%, still acceptable. Freezing showed great capacity in recovering palladium from feedwater with a wide range of concentration.

5.4 Conclusion

Removal efficiencies of two treatment methods, namely, freeze concentration and electrodeionization were studied for the removal of toxic and precious metals from synthetic wastewater. Using 80% freezing of the initial feedwater volume, very high removal efficiencies were achieved for freeze concentration process for separation of chromium (VI), nickel, cobalt and palladium while similar results were only possible in chromium (VI) and palladium using EDI. Overall, freeze concentration process was not so sensitive to changes in influent metal concentration and chemical natures of the metals. Treatment efficiency of the EDI system was affected by chemical nature of the metals, feedwater metal concentrations and the level of electric current applied.

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Chapter 6: Summary and suggestions for future work

This study was carried out to investigate the potential of freeze concentration, electrodeionization, and the combination of freeze concentration (as a pre-treatment method) and electrodeionization techniques for removal/recovery of chromium (VI), nickel, cobalt and palladium in wastewater. The following is a summary and the conclusions drawn from the study:

- Industrial wastewater contains numerous toxic and precious metals with varying concentrations depending on the industrial operations. Toxic metals can be removed and recovered to lower the adverse effects on human health and the aquatic environment
- Precious metals can be recovered to compensate the costs of water treatment
- Various techniques such as ion exchange, membrane filtration, chemical precipitation and electrochemical methods are available for removal of these metals, high capital and operational costs, use of additional chemicals and, high volumes of sludge generation are some of the limitations of these technologies
- High removal efficiencies (97%-99%) were achieved for chromium (VI), nickel, cobalt and palladium using single stage freeze concentration
- Chemical nature of the metals and mixing methods did not influence the removal efficiencies in freeze concentration
- Feedwater metal concentrations from 20 - 670 mg/L had little effect on the removal efficiencies as observed in the second and third stages of freezing, but treatment efficiency decreased (to 69%) at extremely high feedwater concentrations (e.g.: 2750 mg/L)

- More than 160-fold increase of palladium concentrations of that of feedwater water could be achieved through multiple stages of freezing. Significant waste volume reduction could also be achieved using freeze concentration
- Preconcentration of dilute metals in wastewater using freeze concentration could improve the performance of EDI. Removal efficiencies of 70% - 99% were achieved for chromium (VI), cobalt and palladium in EDI system using the unfrozen liquid from freeze concertation as feedwater
- Resin type, applied electric current influenced the removal efficiencies in the EDI
- Feedwater metal concentration also affected the removal efficiency of the EDI
- For removal of high concentrations of metals, using 80% freezing of the initial feedwater volume, very high removal efficiencies were achieved for freeze concentration process for separation of chromium (VI), nickel, cobalt and palladium while similar results were only possible in chromium (VI) and palladium using EDI

6.1 Future research:

This study only examined single metal removal/recovery. For future research, a combination of metals should be used for the removal and recovery using freeze concentration and electrodeionization.