CHAPTER ONE

INTRODUCTION

1.1 Heavy metals pollution in Malaysia

Rapid industrialization and urbanization in Malaysia has increased alarmingly due to the amount of toxic heavy metals entering the environment. Solid and/or liquid waste containing toxic heavy metals are generated in various industrial processes such as chemical manufacturing, coal and ore mining, smelting and metal refining, metal plating; and others (Nair et al., 2008; Yahya, 2008). The most common toxic heavy metals found in industrial wastes include copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), iron (Fe) and manganese (Mn). Sludge generated during various industrial processes has been found to contain undesirable levels of toxic metals. Disposal of sludge containing heavy metals is a complex and problematic situation for most waste generators because the metals are non-biodegradable and tend to bioaccumulate. Based on the Malaysia Environmental Quality Report (MEQR) 2011 (DOE, 2011), heavy metal sludge was one of the main wastes produced in Malaysia with the amount of 173,837.06 metric tonnes (mt) per year contributing 10.72% of total waste. There was a slight increase in the amount of waste produced when compared to 2010 where the total amount of heavy metal sludge generated was 157,381.38 mt per year or 8.37% of total waste. The waste generated was mostly from the electronic/electrical and metal/engineering industries.

Realizing the potential danger of improper management of toxic and hazardous wastes, the Malaysian Government has taken initiatives to identify the possible options and necessary measures to ensure its proper management since 1979. These include the identification, classification and quantification of various types of toxic and hazardous wastes generated and also its treatment and disposal. This is formulated in the three sets of

regulations in 1989 for the management of toxic and hazardous wastes, termed as scheduled wastes in Malaysia. The regulations aimed to ensure hazardous waste produced in the country is safely managed and in an environmentally sound manner. The Environmental Quality (Scheduled Wastes) Regulation 1989 was further improved when the Environmental Quality (Scheduled Wastes) Regulation 2005 came into force on August 15, 2005.

All this regulations are stipulated under the Environmental Quality Act (EQA), 1974 which are meant to prevent, abate and control pollution, as well as, further enhance the quality of the environment in this country. The Department of Environment (DOE) is responsible for the administration of this legislation to ensure that Malaysia will continuously have the benefit of both industrial growth and a healthy living environment. Scheduled wastes can be defined as any waste falling within the categories of waste listed in the First Schedule in Environmental Quality (Scheduled Wastes) Regulations 2005. According to the World Health Organization (WHO), hazardous waste possesses physical, chemical or biological characteristics, requires special handling and disposal procedures to avoid risk to health and adverse environmental effects. Table 1.1 present the categories of waste that are listed in the First Schedule under the Environmental Quality (Scheduled Wastes) Regulation 2005.

Table 1.1: The categories of waste listed in First Schedule under Environmental Quality

(Scheduled Wastes) Regulation 2005, EQA 1974

Code	Waste Categories
SW 1	Metal and metal bearing wastes.
SW 2	Wastes containing principally inorganic constituent which may contain metals and organic material. As example SW 204 refer to sludges containing one or several metals including Cr, Cu, Zn, Pb, Cd, aluminium (Al), tin (Sn), vanadium (V) and beryllium (Be).
SW 3	Wastes containing principally organic constituents which may contain metals and inorganic materials.
SW 4	Wastes which may contain either inorganic or organic constituents.
SW 5	Other wastes.

DOE has classified heavy metals such as Cd, Cu, Pb, mercury (Hg), arsenic (As) as primary pollutants to the environment (Yahya, 2008). Scheduled wastes classification presented in Table 1.1 is strictly used to identify the different types of scheduled wastes that are produced from all states in Malaysia. This regulation also specifies the disposal of scheduled wastes (Regulation 4(1) and 4(2)), treatment of scheduled wastes (Regulation 5(1) and 5(2)), the responsibility of waste generator (Regulation 8(1) and 8(2)) and storage of scheduled wastes (Regulation 9(1) – 9(7)). Based on the notification of scheduled waste received by the DOE, a total of 1,622,031.54 mt of scheduled wastes were generated in 2011 as compared to 1,880,928.53 mt in 2010 (DOE, 2010; DOE, 2011). This shows a significant decrease in waste generation (13.76%) from 2010 to 2011. In the year 2011, the

industries in Penang generated 194,279.45 mt of scheduled wastes which amounted to 12.0% of the waste generated compared to 273,370.00 mt (14.5%) in 2010 (DOE, 2010; DOE, 2011).

Of the total waste produced, about 937,769.83 mt contributing 28.58% of scheduled wastes were recovered at offsite facilities in 2011 as compared to 877,489.38 mt (7.09%) in 2010 (DOE, 2010; DOE; 2011). An estimated, 340,460.16 mt (10.37%) and 805,365.94 mt (42.82%) were treated on site while about 189,861.05 mt (5.79%) and 35,456.96 mt (1.89%) were stored on site at the premises of the waste generators in 2011 and 2010 respectively (DOE, 2010; DOE, 2011). Moreover, in 2011, the total of 151,979.5 mt of wastes contributing 4.6% were treated and disposed as compared to 162,616.25 mt (6.5%) in 2010 (DOE, 2010; DOE, 2011). These disposal and treatment facilities have been licensed by DOE. There are two companies responsible and authorized for the treatment and disposal of scheduled wastes; Kualiti Alam Sdn. Bhd and Trinekens (Sarawak) Sdn. Bhd. Besides that, two landfarm for on-site treatment and 21 on-site waste incinerators had been licensed by DOE and a total of 404 off-site facilities for the recovery of various categories of scheduled wastes have also been licensed by the department (DOE, 2011).

Due to the high costs and complexity of the treatment and disposal of scheduled wastes especially sludge containing heavy metals, some industries have resorted to the illegal action of dumping the wastes rather than paying for their disposal. Illegal dumping is the disposal of waste generated at undesignated location without legal permission. There seems to be an increase in the number of illegal dumping cases detected by the DOE in the last five years, from three cases in 2001 to 31 cases in 2005 (Lee, 2007). The types of waste found in dumping sites were mainly waste paint, mineral oil and dross. These activities were mostly carried out in secluded areas to avoid detection. Plate 1.1 illustrated the scheduled wastes found to be illegally dumped by irresponsible parties while Plate 1.2

shows the cleanup of illegal dumped scheduled wastes site by DOE in order to remediate the area.

Plate 1.1: Illegal dumping of scheduled wastes (Source: DOE, 2007)

Plate1.2: Clean up of scheduled wastes at illegal dump site (Source: DOE, 2007)

According to DOE, incident that related to illegal dumping however were reduced in 2007. It had been achieved through the gazette amendment of the EQA, 1974, under Section 34B and Section 43. This section specifies that an individual and/or companies that are found guilty of illegally disposing toxic and hazardous wastes, can be fined up to a maximum of RM 500, 000 or sentenced to prison up to five years or both. Illegal dumping can disturb natural processes on land and in the water. Heavy metals contain in the wastes from the illegal dumping activities can leach to the environment and not only pollute the environment but also can cause serious health hazards.

Heavy metals tend to bioaccumulate in plants and animals, bioconcentrate in the food chain, or attack specific organs of the body. Continuous assessment and monitoring of heavy metals in the environment is very important due to their hazard to the public health and environment. According to Cai et al. (2007), metal concentrations in sludge vary widely depending on several factors such as the origin of the sludge and the pre-treatment process of the sludge. It was also determined that there are slight differences in the organic matter-metals association between aerobically and anaerobically digested sludge. During mesophilic anaerobic digestion, microbial transformation will increase the stability of organic matter complexes and precipitate metals as low solubility sulphides (Cai et al., 2007). However, the reduction process of the organic matter associated with the metal will influence the metal conversion from one form to the other (Alvarez et al., 2002). In contrast, during the aerobic digestion, the oxidation process of the reducible fraction will increase the total metal in the residual metal fraction (Alvarez et al., 2002).

In order to ensure the continuous preservation the environment, the Environmental Quality (Schedule Waste) Regulation 2005 stipulates that sludge containing one or several metals including Cr, Cu, Ni, Zn, Pb, Cd, Al, Sn, V and Be (SW 204), shall be disposed of at prescribed premises only. The proper disposal of hazardous waste is imperative due to their

toxicity and impact to the environment as well as human life. However, the determination of heavy metals and their modes of binding are essential in order to estimate their mobility and bioavailability for the proper management of their disposal.

1.2   Problem statement

Although total metal concentration may indicate the overall level of metals in sludge, the mobility of heavy metals, their bioavailability and related eco-toxicity to plants depend strongly on their specific chemical forms or ways of binding. The study of sludge toxicity by chemical speciation is therefore very important to assist in the management of contaminated land.

Metal sludge when recovered for agricultural use affects human and animal health, as well as, soil and water quality. Excess levels of heavy metals introduced to soil by sludge can lead to elevated uptake of heavy metals by plants. This may cause irreparable damage to the plants. It can also affect human health upon the consumption of the plants since these plants consist of accumulated levels of the heavy metals within their tissues.

Different forms of heavy metals have different mobility and phytoavailability. Generally, plant uptake of heavy metals is correlated to extractable forms of the metals rather than to the total metal contents in the soil. Therefore, in order to assess the potential environmental impacts of sludge contaminated with metals, the determination of total, trace and heavy metal content alone is insufficient. The chemical form of the metal in the matrix determines its behaviour in the environment and its mobilization capacity. Availability and metal speciation studies provide more relevant information which is why it is crucial that these studies should be conducted.

The properties of the sludge vary from one to the other because they are generated from various sources. Electroplating sludge is a heavy metals-bearing byproduct that comes

from the electroplating industry's activities. Different metals may be present in different composition. To determine the distribution of metals in the different phases in this type of sludge, sequential extraction for the fractionation of the metals into several groups with different leachibility is widely used. The results obtained will provide valuable information on bioavailability, mobility and transport of the metals in the environment (Shiowatana et al., 2001). Therefore, it is widely used as a method to study the origin and impact of the metal in the environment. Besides that, knowledge and understanding on the speciation of heavy metals in electroplating sludge is necessary for the optimization and monitoring of remediation strategies to be applied for the clean-up of an illegal dumping site, if necessary (Ololade, 2009).

1.3   Scope of the study

In this study, the determination of total concentration and speciation of heavy metals in electroplating sludge were considered. Sludge samples were collected from the wastewater treatment plant (WWTP) from three electroplating industries located in Penang, Malaysia. Cr, Fe, Ni, Cu, Zn, Cd and Pb were the heavy metals chosen for the study. The metals were selected because of their wide use in electroplating industries and their existence in effluents and sludges from industrial processes (Malarkodi et al., 2007; Venkateswaran et al., 2007; Nair et al., 2008). It has been reported that the presence of these metals in the environment has resulted with serious water pollution and is also harmful to human health (Stephenson, 1998; Abbasi et al., 1998).

1.4   Objective of the study

In view of the above observations, this study was carried out with the following objectives:

1. To determine the total concentration of selected heavy metals in sludges from electroplating industry.

2. To determine the speciation of selected metals in sludges from electroplating industry.

3. To understand the mobility of the metals in sludges from electroplating industry.

1.5   Outline of the thesis

This thesis consist of 5 chapters, they are introduction, literature review, materials and methods, results and discussions and conclusion and recommendation.

Chapter 1:   Introduction contains topic of heavy metals pollution in Malaysia, problem statement, scope of the study and objective of the study.

Chapter 2:   Definition of heavy metals, sources of heavy metals in the environment, sludge pollution and general metal behavior in wastewater and/or sludge, disposal of sludge, environmental and health effect of metals in environment, separation methods including total digestion and sequential extraction, electroplating and electroplating industry are discussed in the Literature Review Section.

Chapter 3:   Materials and methods consists of 4 main topics; Apparatus, reagent, sample collection and pre-treatment and procedures. The sub topics in procedures are aqua reqia digestion and sequential extraction.

Chapter 4:   Results and discussion contain pseudototal heavy metals content in sample A, B and C and the total content of Cr, Fe, Ni, Cu, Zn, Cd and Pb.

Percentage of total concentration of heavy metals in sludge samples and the speciation of heavy metals in the electroplating sludges are also discussed.

Chapter 5:   Conclusion of the study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Definition of heavy metals

The term "heavy metal" has been used in various publications and in legislation related to chemical hazards and the safe use of chemicals. The term applies to all metals and metalloids other than alkaline and alkaline earth elements that have been associated with contamination and potential toxicity or ecotoxicity (Karshman, 2002). Besides that, it also can be defined as any metal having a specific gravity greater than Fe (s.g. = 5.5) and this definition is used today to define toxic metal ions (Bohn et al., 2001). However, it is known that several definitions exists which is used in relation to heavy metals.

Encyclopedia of Public Health (2002) (Breslow et al., 2002) defines heavy metals as all metals or metalloids elements that have both metal and nonmetal characteristics, which generally have densities above 5 g cm^{-3}. This includes Cr, As, Cd, Hg, and Mn. According to the chemistry dictionary, heavy metals can be defined as any metal with a high relative atomic mass. The term is usually applied to common transition metals, such as Cu, Pb, and Zn. These metals are known causes of environmental pollution from a number of sources, including Pb in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain. Most of these metal ions (Cd, Cr, Mn, Zn, Fe and Cu) are released from industrial activities in their simple cation forms (Bohn et al., 2001; Yahya, 2008).

Heavy metal in ionic form may be toxic to plants or are found in groundwater at concentrations higher than in native soils (Bohn et al., 2001). It is because they cannot be degraded nor destroyed and are persistent in all parts of the environment. Human activity affects the natural geological and biological redistribution of heavy metals through

pollution of the air, water, and soil. Heavy metal pollution can arise from many sources. Most commonly it arises from the purification of metals, such as the smelting of Cu and the preparation of nuclear fuels.

2.2   Sources of heavy metals in the environment

Most of the heavy metals are introduced into the environment through natural or anthropogenic sources. Commonly, there are two sources of heavy metals pollution to the environment; point source and non-point source of pollution. A point source of pollution is defined as pollution that can be readily identified from a specific source such as a pollutant originating from a particular factory or treatment work. Non-point source is pollution whose origin cannot be specifically defined and are mainly diffused sources such as agricultural activities or surface runoffs (DOE, 2010). The primary anthropogenic sources of heavy metals pollution are point sources such as mines, foundries, smelters, coal-burning power plants and diffuse sources such as combustion by-products and vehicle emissions.

According to DOE (2009) and DOE (2010), 20,348 water pollution point sources were recorded in 2010 in Malaysia as compared to 20,702 in 2009. This shows that there was a slight decrease in water pollution point sources (1.7%) in 2010 compared to 2009. These are mainly generated from manufacturing industries, contributing 44.6% and 47.2%, followed by sewage treatment plants about 49.3% and 46.7% in 2010 and 2009 respectively. Wastewaters from agro-based industries are the least contributors with only 2.5% and 2.4% in 2010 and 2009 respectively. This proves that most of the water pollution point sources are from manufacturing industries in 2009 (DOE, 2009). However, in contrast, the main contributors of pollution in 2010 were from sewage treatment plants (DOE, 2010).

The electroplating industry is one of the primary sources of Cr and Cd contaminations to the environment. Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can localize and lay dormant. The metal industries mainly discharge chromium trivalent (Cr^{3+}) while chromium hexavalent (Cr^{6+}) in industrial wastewater mainly originates from tanning and painting activities. The high demand for Cr usage is because of its use to prevent corrosion, product stability improvement and production of high quality paints. This is because of its high corrosion resistance and hardness. Chromates (CrO_4^{2-}) are also used as rust and corrosion inhibitors in engines. Cr compounds are also added into antifreeze to inhibit corrosion and stop the growth of algae. Most of these compounds exist as zinc chromates ($ZnCrO_4$). Chromic acid (H_2CrO_4) is also used primarily for plating, photoengraving and offset printing. Composition of Cr, Cd and other elements can be extremely variable depending on the industrial activities and other factor such as the raw material used (Nancy, 1992).

The most often mentioned sources of Cd entering the aquatic environment are industrial effluent and sewage. According to Stephenson (1998), small amounts of Cd enter the environment from the natural weathering of minerals, but most is released through human activities. Often it is used in the production of Ni-Cd batteries and for metal plating. In electroplating, Cd is widely used in aircraft industry due to the excellent corrosion resistance of Cd-plated steel components. Cd provides cathodic protection to low-alloyed steels, since it is positioned lower in the galvanic series. The coating is usually passivated by chromate salt (Na_2CrO_4). Treatment of wastewater of any of these industries could result in Cd and Cr being present in the residual sludge.

Bowen (1966) recorded that the concentration of Cu in soils ranged between 2 to 100 ppm by dry weight with a mean value of 20 ppm. In unpolluted waters, concentrations of Cu have been estimated at 0.0006 to 0.4 ppm with a median value of 0.10 ppm (Bowen,

1996). In freshwater sediments which are free from industrial and sewage pollution, the Cu levels were up to 16.8 ppm by dry weight (Taylor, 1976). Among the industrial sources the main contribution of Cu comes from metal pickeling baths, Cu and plating baths, petroleum refining and others. Other man-made pathways by which Cu enters the environment are sewage effluent, fertilizers and pesticide used in agriculture (Abbasi et al., 1998).

As for Cu, environmental releases of Zn from anthropogenic sources far exceeded the release from natural sources. This include those resulting from electroplating, smelting and ore processing, as well as, acid mine drainage, effluents from chemical processes and discharge of untreated domestic sewage (Stephenson, 1998; Abbasi et al., 1998). Zn element is normally found associated with other base metals such as Cu or Pb in ores. Zn has a low affinity for oxides and prefers to bond with sulfides. It is a moderately reactive metal and strong reducing agent. Zn reacts readily with acids, alkalis, and other non-metals. Zn is more reactive than Fe or steel and thus will attract almost all local oxidation until it completely corroded.

Fe oxidizes in air to give iron oxides (Fe_2O_3) or also recognized as rust. Yet, Fe is the most widely used of all the metals, accounting for 95% of worldwide metal production. Furthermore, Fe is of the greatest importance when mixed with other metals and with carbon to form steels. There are various types of steels, all with different properties to manufacture good quality steels. Besides that, Fe is also used in cloth dyeing, as coloring agent in paint and as additive in animal feed.

Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. It is necessary to control the heavy metals present in sludge in order to preserve and protect the environmental.

2.3   Sludge pollution and general metal behavior in wastewater and/or sludge

Generally, sludge is an unwanted byproduct produced from WWTP that exists in many forms and various quantities (Vesilind, 1975; Vesilind and Spinosa, 2001). Wastewater sludge is a suspension of both inorganic and organic solid, basically between 1 to 5%. Because of the nature of this byproduct, the storage and disposal is quiet difficult and expensive.

Electroplating sludge is a final by-product that comes from the electroplating industries activities (Li et al., 2010). It is usually stored in the form of filtered quasi-solid wastes in dumping grounds and contains multiple metals such as Cu, Ni, Zn, Cr, Fe, Pb, Mn and others. According to Wodzki et al. (1999), these wastes are produced in the form of acidic or alkaline solutions, rinse waters, and alkaline sludge which remains after chemical precipitation of heavy metals from effluents. The solid component on the other hand, can be processed and appropriately modified to be reused during recovery and recycling process.

The U.S. Environmental Protection Agency (U.S. EPA) estimated that about 1.3 million wet tons of electroplating sludge was generated a year in the states (Li et al., 2010). The release of these wastes to the environment may lead to contamination of water supplies and soil, spreading of endemic diseases and eutrophication of waterways (Subramanian et al., 2005).

Principally, the two most important sludges generated from WWTP are (i) primary sludge, which is drawn from the bottom of primary clarifier; and (ii) waste activated sludge, which is produced in the activated sludge system as excess biomass. In the primary clarifier (settling tank or sedimentation tank), heavier solids are allowed to settle in the bottom of the tank and lighter solids will float to the top (Kopp and Dichtl, 2001). The floated material also known as scum is usually in smaller amount and conventionally

disposed of to nearby land without further treatment. In addition, the removal of the solids also results in the removal of oxygen demand compound such as biochemical oxygen demand (BOD) (Vesilind, 1975). The quality of the primary sludge depends on the wastewater and the retention time in the pre-sedimentation tank. This type of sludge is biodegradable and the biogas production via digestion is high and its dewaterability is normally very good (Kopp and Dichtl, 2001).

Biodegradability and dewaterability of waste-activated sludges are strongly dependant on the age of the sludge. This waste is different from primary sludge because in this suspended growth process, wastewater is mixed with the active biomass which then assimilates into the organic fraction reducing the demand for oxygen (Vesilind and Spinosa, 2001). This is the most popular process for secondary treatment method for WWTP. Besides that, depending on the treatment plant, there are other types of sludges such as trickling filter sludge which is captured in secondary clarifiers in trickling filter plants and chemical sludges such as aluminum phosphate sludge. The sludges are formed during the chemical nutrient removal or tertiary treatments.

Sludge and biosolids contains a massive variety and complexity of chemical. Most contaminants such as metals are primarily found in the soil phase than the liquid phase of sludges and biosolid because of higher affinity of the absorbed metals (Matthews, 2001; Vesilind and Spinosa, 2001) due to the physical-chemical processes involved in the WWTP (Stylianou et al., 2007). As a result, heavy metals levels are usually higher in the sludge than in the soil. Besides that, the colloidal and particulate metals may be found in hydroxides, oxides, silicates or sulfides or adsorbed to organic matter (Karshman, 2002).

Generally, heavy metals that present in sludge have variable concentration depending on the type of industry. Heavy metals especially Cd, Hg, Cr and Ni are predominant in most industrial effluents. In contrast, Cu and Zn are mainly from domestic

activities and the major source of Pb is both from surface runoff and domestic wastewater (Wang et al., 2005; Pempkowiak and Gajewska, 2008).

Basically, Cr does not react with water at room temperature and most of Cr compounds are relatively water insoluble. Cr^{3+} compounds are water insoluble because they are largely bound to floating particles in water. In contrast, Fe dissolves in water under normal condition. Many Fe compounds share this characteristic. However, Fe that occur naturally such as iron oxide (Fe_2O_3) and iron hydroxide ($Fe(OH)_2$) are water insoluble. The water solubility of some Fe compounds increases at lower pH value. There is a different solubility between Fe^{2+} and Fe^{3+} compounds since Fe^{2+} compounds are water soluble while Fe^{3+} compounds are insoluble. The latter are only soluble in strongly acidic solutions, but water solubility increases when these are reduced to Fe^{2+} under certain conditions.

Ni is insoluble in water at 20 °C and pressure 0.987 atm and does not react with water under normal conditions. Though, some Ni compounds may be water soluble, such as nickel chloride ($NiCl_2$) and nickel carbonate ($NiCO_3$), other Ni compounds such as nickel oxide (Ni_2O_3), nickel sulphide (NiS) and nickel tetracarbonyl ($Ni(CO)_4$) are insoluble. The common aqueous species of Ni is Ni^{2+}. In reducing conditions, insoluble sulfides can form while in aerobic conditions, Ni complexes with hydroxide, carbonates, and organic ligands can form (APHA, 2005). On the other hand, Zn doesn't react with water molecules. The solubility of Zn depends on the temperature and pH of the water. When the pH is fairly neutral, Zn is insoluble. Solubility of the Zn increases with an increase in acidity.

According to Stoeppler (1992), Cd metal is readily soluble in nitric acid (HNO_3), moderately soluble in hydrochloric (HCl) and sulfuric acids (H_2SO_4) while insoluble in basic solution. Salts of Cd with strong acids are soluble in water. Due to its solubility, the amount of Cd found in wastewater is higher compared to that found in sludge.

Pb may exist as both dissolved and suspended species in water (Steve, 1992). The high-molecular humic acid content in some waters may also play an important role in the mobilization and transportation of many heavy metals including Pb (Steve, 1992). The presence of suspended matter may markedly reduce the recovery of Pb compounds from aqueous samples. The tendency of Pb to be bound in suspension is also reflected in the capacity of influent to reduce its Pb burden via sedimentation. This resulted in small variations in the levels of dissolved Pb within discharge effluent. Pb is often heavily bound to suspended particulate and sediment material. Therefore, Pb can be present in the wastewater, as well as in sludge during sedimentation in the treatment plant. Appreciable quantities of Pb may be found in sludges due to the very low mobility of Pb and this characteristic can give rise to a buildup in a localized area.

Karvelas et al. (2003) reported the occurrence and partitioning of heavy metals such as Cd, Pb, Mn, Cu, Zn, Fe and Ni in activated sludge collected from WWTP located at Thessalonica, Greece. From the study, 80 to 93% Ni and 65 to 85% Mn were found mainly in the soluble phase while 65 to 95% of Cu, Cr, Pb, Cd and Zn were mostly associated with the particulate phase (Karvelas et al., 2003). On the other hand, 58 to 75% Fe exhibited association with particles (Karvelas et al., 2003). Fe can form complexes with a wide range of size distribution of soluble organic matter particles while Hg and Pb are only associated with larger soluble complexes (Patrick and Verloo, 1998).

Morel et al. (1975) found that many heavy metals including Cu, Zn, Hg, Ag, Cd and Pb were present as insoluble sulfides while some other metals such as Ni, Mn and Co were relatively soluble. Klinkhammer and Bender (1981) concluded that, Cu, Ni, Cd, Mn and Zn from sewage input were more dominant in the dissolved form whereas Cd, Cu and Fe remained on suspended material. This finding is in agreement with research carried out in Chennai, India (Venkatesawaran et al., 2007).

Alvarez et al. (2002) reported that primary sludge had higher concentration of metals compared to secondary sludge. Concentration of Al, Cr, Fe and Pb in residual fraction (F4) and distribution of Cd and Zn in oxidizable fraction (F3) increased after anaerobic digestion. The conversion of metals during the anaerobic digestion resulted from either the decay of the organic matter associated with the metals, due to formation of insoluble metal sulfides of Fe and Pb or by reduction in the case of Cd and Ni (Alvarez et al., 2002).

Jakubus and Czekala (2001) observed that the fraction of heavy metals in sewage sludge from different WWTP contain varying concentrations of the metals. Generally, Cu was associated with the most stable combinations, the F3 and the F4 fraction (Jakubus and Czekala, 2000). According to Chanpiwat et al. (2010), the amount of metal present, speciation and the reactivity of biomass influence the efficiency in the metal removal. Consequently, various treatment technologies are being studied and developed to reduce the contamination of heavy metals in the environment.

2.4 Disposal of sludge

During the wastewater treatment process, large volumes of sludge are produced. However, sludge cannot be easily or carelessly disposed of due to their microbiological and chemical characteristics. The disposal of the sludge must be done with proper method based on their characteristic (Wang et al., 2005; Chao et al., 2006; Venkateswaran et al., 2007; Chen et al., 2008). Only after proper treatment can they be discharged, that too in a proper way. The treatment and disposal of the sludge is one of the major problems in wastewater treatment and this accounts for about 50% of the total cost (Vesilind and Spinosa, 2001). As the sludge will undergo decay and produce offensive odors it has to be disposed off in a proper way.

There are several options available for the disposal of sludge. This includes disposal in a secured landfill, incineration, or used as a fertilizer. Incineration is particularly useful for sludge containing toxic chemicals. The disposal of the waste through any other routes is environmentally unacceptable due to the presence of the toxic chemicals. Rotary multiple hearth incinerators are widely used for sludge incineration. The uses of fluidized bed furnaces in waste disposal are also gaining popularity. Dewatered sludge with about 30% solid content has sufficient calorific value to maintain self-sustaining combustion. However, most incinerators require fuel oil for efficient combustion. After incineration the ash (basically metal oxides) still has to be handled properly.

In certain cases, sludge is mixed with domestic refuse and treated by various methods of composting. This produces compost which contains nutrients and humus that can be used to condition soil. However, sludge contains potentially toxic chemicals which could be detrimental to the soil. The presence of pathogenic bacteria, particularly *Salmonella sp* and eggs of parasites like *Taenia sp*, make the sludge unsuitable as fertilizer for crops which are eaten uncooked. In addition, treatment of the sludge for use as fertilizer is ultimately too expensive. Certain heavy metals such as Pb, Cd and Hg have been recognized to be potentially toxic and are a potential hazard for human nutrition upon consumption of these crops.

2.5 Environmental and health effect of metals in environment

According to Yahya (2008), heavy metals such as Cu and Zn at low concentration (< 10 mg L^{-1}) are essential trace elements for living organism, but at higher concentrations (>10 mg L^{-1}), it presents with toxic effects. Several heavy metals can affect human health.

(a) Cr

At low concentrations, Cr is an essential micronutrient for humans and animals. But, at high concentration it is carcinogenic when present as CrO_4^{2-} (Nancy, 1992). The chronic effects of Cr species include skin and mucous membrane irritation, broncho-pulmonary effects and systemic effects involving kidney, liver, gastrointestinal tract and circulatory system. Moreover, Cr is generally accepted as the second most common skin allergen in the general population after Ni (Nancy, 1992).

(b) Fe

Fe is a dietary requirement for most organisms and plays an important role in natural processes in its binary and tertiary form. Oxidized Fe^{3+} cannot be applied by organisms freely, except at very low pH value. Still, Fe usually occurs in insoluble form. Adding soluble Fe may rapidly increase productivity in ocean surface layers. Fe is essential for nitrogen binding and nitrate reduction, and it may be a limiting factor for phytoplankton growth. The United Nations Food and Agriculture Organization recommended level of Fe for irrigation water is 5 mg L^{-1} and the U.S. EPA stated that maximum contaminant level (MCL) is 0.3 mg L^{-1} for secondary drinking water standard (APHA, 2005).

(c) Ni

Ni is a dietary requirement for many organisms, but may be toxic in larger doses. Divalent Ni compound are non-toxic for animals, plants and man at prevalent concentration in natural water, soils and food. Ni bioaccumulates in aquatic systems and such elevations above normal concentrations can result in deleterious aquatic effects (Stephenson, 1998). In human beings, adverse effects from inorganic, water soluble Ni compounds frequently occur following skin contact (Stoeppler and

Ostapczuk, 1992; Stephenson, 1998). Alternatively, inhalation of these compounds mainly at the workplace can cause respiratory tract irritation and asthma (Stoeppler and Ostapczuk, 1992).

(d) Zn

Although Zn is an essential requirement for good health, excess Zn can be harmful. Too much absorption of Zn suppresses the absorption of Cu and Fe. The free Zn ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. Ingestion of higher than recommended level of Zn can have adverse effects on health. Consumption 10 to 15 times more than the recommended doses (15 mg day^{-1} for man and 12 mg day^{-1} for women) of Zn can cause stomach cramps, nausea and vomiting (Stephenson, 1998). Ingestion of high levels of Zn for several months may cause anaemia, damage to pancreas and also decreased levels of high-density lipoprotein (HDL) cholesterol (Stephenson, 1998). The United Nations Food and Agriculture Organization recommended level for Zn in irrigation waters is 2 mg L^{-1}. The U.S. EPA secondary drinking water standard MCL is 5 mg L^{-1}. Zn concentration above 5 mg L^{-1} can cause a bitter astringent taste and opalescence in alkaline waters (APHA, 2005).

(e) Cd

Cd has not been shown to be either essential or beneficial to animal or human nutrition. However, Cd is largely recognized due to its toxic characteristics. In Japan, the incident of Cd poisoning or famously known as Itai-itai disease incident has generated an interest in the toxicity of Cd. The concern regarding Cd in environmental toxicity lies with the fact that it can be toxic to aquatic organisms even at very low concentration (Abbasi et al., 1998). Chronic Cd poisoning was first recognized in industrial workers

and mostly involved kidney damage and obstructive lung disease (Abbasi et al., 1998). The United Nations Food and Agriculture Organization recommended that the maximum level for Cd in irrigation water is 10 µg L^{-1}.

(f) Pb

Pb and Pb compounds are generally toxic pollutants that can damage nervous connections especially in young children, and are known to cause blood and brain disorders (Abbasi et al., 1998; Yahya, 2008). As Hg, Pb is a potent neurotoxin that accumulates in soft tissues and bone over time. Pb poisoning typically results from the ingestion of food or water contaminated with Pb, but may also occur after accidental ingestion of contaminated soil, dust, or Pb based paint (Stephenson, 1998).

Prior to the determination of total concentration and speciation of heavy metals in the electroplating sludge samples by means of ICP-MS, a suitable separation method needs to be applied to the samples in order to isolate the heavy metals.

2.6   Separation methods

Previous studies have shown that the ecotoxicity of the environment and mobility of heavy metals is strongly dependent on their specific chemical forms, way of binding as well as the amount present in natural systems (Tokalioglu et al., 2003; Pueyo et al., 2003; Fuentes et al., 2004; Wang et al., 2005; Lemes et al., 2005; Liu et al., 2007; Miao et al., 2007; Venkateswaran et al., 2007; Stylianous et al., 2007; Nair et al., 2008; Chen et al., 2008; Nemati et al., 2009a; Jamali et al., 2009; Lasheen et al., 2009; Davutluoglu et al., 2010; Yuan et al., 2011; Vega and Weng, 2013). Therefore, the toxicity of heavy metals, their effects and biogeochemical pathways should be studied on the basis of the determination of its specific binding forms, rather than by its accumulation rate. The

analytical technique to evaluate the impact on the environment due to the heavy metal content in sludge and or sediments has progressed from the determination of total concentrations to the fractionation of the compounds.

However, most studies have been limited to the determination of the total concentration of metals which does not provide the true understanding of the mobility and bioavailability of potentially toxic elements (Nemati et al., 2009a). Speciation is now recognized by the scientific community as a necessary tool to obtain the valuable information on the heavy metal bioavailability or its mobility to assess their environmental impact (Davidson et al., 1998; Ahnstrom and Parker, 1999; Cid et al., 2001; Gardolinski et al., 2002; Hlavay et al., 2004; Subramanian et al., 2005; Liu et al., 2007; Cai et al., 2007; Martin et al., 2007; Gao et al., 2008; Lasheen and Ammar, 2009; Nemati et al., 2009a; Nemati et al., 2009b; Davutluoglu et al., 2010; Yuan et al., 2011).

Cai et al. (2007) defines chemical speciation as the process of identification and quantification of different species or phases present in a material. On the other hands, metal speciation can also be functionally defined as plant-available, mobile, or exchangeable forms or operationally defined by the procedures or extractants used to isolate them. Furthermore, this allows for the estimation of heavy metal bioavailability and its relation to the different natures of heavy metals, their bonding strength, either in free ionic form or complexes by organic matter or the incorporation of the metals in the mineral fraction of the sample which provides information on the origin, potential mobility and the transport mechanisms of the element in the natural environments. According to Chen et al. (2008), heavy metal speciation can be carried out by means of selective sequential extraction analysis which involves several extraction steps with the use of different chemical reagents and conditions at each step.

The two main extraction approaches commonly used for the isolation of heavy metals species in soil or sediments/sludge are single and sequential extraction method. Initially, single extractions were predominantly used for soil analysis while sequential extraction was preferred for sediments or sludge but errors due to the many steps involved in sequential extraction may give irreproducible results (Sahuquillo et al., 1999). Scancar et al. (2000) determined that the aqua regia extraction is an appropriate digestion procedure for the determination of total concentration of heavy metals in the sludge samples and is comparable to the total acid dissolution of the sludge sample. This finding was further established with studies conducted by Chen et al. (2008); Nemati et al. (2009a) and Nemati et al. (2009b), whereby the aqua regia digestion was applied in their work for the measurement of total concentration and speciation of heavy metals in sludge. Therefore, the aqua regia extraction procedure is a well-established and internationally recognized analytical procedure for the analysis of sediment and sewage sludge.

2.6.1   Total Digestion

For an assessment of the heavy metals burden in sewage sludge (Fuentes et al., 2004; Sprynskyy et al., 2007), sediment/soil (Mossop and Davidson, 2003; Miao et al., 2007; Gao et al., 2008) or industrial/municipal sludge (Wang et al., 2005; Nair et al., 2008) the total concentrations were determined after digestion of samples with strong acids including hydrofluoric acid (HF) treatment (Nemati et al., 2009a; Ahumada et al., 2010) or aqua regia extraction (Tokalioglu et al., 2003; Pueyo et al., 2003; Mossop and Davidson, 2003; Sanchez-Martin et al., 2007; Venkateswaran et al., 2007; Nemati et al., 2009b; Chanpiwat et al., 2010).

The term total metals refer to the concentration of metals determined in an unfiltered sample after vigorous digestion, or the sum of the concentration of metals in the

dissolved and suspended fractions (APHA, 2005). On the other hand, total metals include all metals, inorganically and organically bound, both dissolved and particulate. It's operationally defined by the digestion procedure. HNO_3 will digest most samples adequately. As a general rule, HNO_3 alone is adequate for clean samples or easily oxidized materials while HNO_3-$HClO_4$-HF digestion is necessary for difficult-to-oxidize organic matter or minerals containing silicates (APHA, 2005).

Based on the study by Chen et al. (2008), sludge obtained from the industrial area was found to contain a higher concentration of total heavy metals compared to the other areas studied, and this could be due to the presence of chemical plants in that region suspected of discharging effluent irresponsibly. Scancar et al., (2000) found that the total concentration of heavy metals in sewage sludge fluctuates and could be attributed to the irregular input from the metals industry. The possible use of this sludge in agriculture without bioremediation and/or chemical remediation may potentially contaminate the soil with toxic and labile forms.

Sludge generated from different areas; industrial and treatment plant may contain varying amounts of heavy metals. The content of heavy metals and organic matter in the sludge may differ due to the origin and source of the sludge. According to Yu et al. (2010), the total concentrations of Cr, Cu, Ni, Pb and Zn determined in different regions of China were found to be influenced by the hydraulic conditions and inputs of anthropogenic trace metals. Wastewater discharge from industries and the use of herbicides containing Cu in agriculture were also identified by Yu et al. (2010) as factors contributing to the higher concentration of Cu found in the Pearl River Delta region.

Sludge from industries such as electroplating industry are categorized as hazardous waste and this sludge contain multiple metals such as Cu, Ni, Zn, Cr and Fe (Li et al., 2010). Stylianou et al. (2007) determined that with the addition of acid; heavy metals in

sludge are dissolved and exist in solubilized form. This process occurs with the exchange of protons from the acid through the solubilization of heavy metals in the sludge. The equation is as follows;

$$\text{Sludge-M} + \text{Acid} \longrightarrow \text{Sludge} + \text{M}^{Z+} + \text{Acid}$$
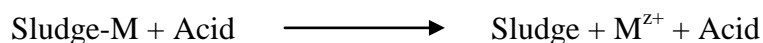
The acid treatment changes the heavy metal partitioning in the sludge and the metals were removed using a precipitation process followed by a separation step.

From a previous study, Zheljazkov and Warman (2002) found that HNO_3 digestion provides the highest recovery for As, Ni, Cd and Pb compared to other digestion methods. Ihnat and Fernandes (1996) found that HNO_3 effectively recovered 21 elements from compost poultry manure, except Mn. Hseu (2004) studied several digestion methods; wet digestion and dry ashing for the evaluation of heavy metals in composts. The study shows that for Cd, Mn and Ni, the HNO_3 digestion method provides the highest efficiency in recovery of the metals. Therefore, Hseu (2004) recommends the use of the HNO_3 procedure in a traditional open-vessel digestion system as a standard method for the digestion of composts due to its cost and time saving effectiveness.

Thus, the determination of heavy metals and their mode of binding are very important in order to estimate their mobility, bioavailability and related eco-toxicity beside the total metal concentrations. Metal remobilization from the solid to the liquid phase have been shown to occur due to changing environmental conditions such as pH, redox potential, or the presence of organic chelators, (Choa et al., 2006; Yu et al., 2010; Lu and Cheng, 2011; Sainger et al., 2011). This results in the heavy metals becoming more bioavailable or more toxic. Therefore, it is essential to study the distribution of metals in sludge and/or sediment in order to predict the mobility, bioavailability, and potential toxicity of metals

(Fan et al., 2002; Yu et al., 2010). The determination of specific chemical species is usually difficult and time consuming due to its complexity. Various single extraction procedures are applied for the investigation of heavy metal availability while different sequential extraction procedures are frequently applied to assess heavy metal mobility in the environment (Scancar et al., 2000; Iwegbue et al., 2007; Lu and Cheng, 2011).

2.6.2 Sequential extraction

During sequential extraction procedures, various chemical extractants are applied to soil, sediment or sludge samples, making the results seldom comparable. Due to the difficulty in comparing results from different laboratories and in order to harmonize the methodology for the determination of metals in soils and sediments, the Community Bureau of Reference (BCR) developed a sequential extraction program (Mossop and Davidson, 2003; Fernandez et al., 2004; Chao et al., 2006; Stylianou et al., 2007; Pan et al., 2009; Yuan et al., 2011; Alba et al, 2011). Originally, this procedure was developed for use in soil but was further expanded for use in a variety of matrices and successfully applied for the determination of metals in sewage sludges including municipal and industrial sludges (Scancar et al., 2000; Cid et al., 2001; Fuentes et al., 2004; Wang et al., 2005; Sprynskyy et al., 2007; Venkateswaran et al., 2007; Chen et al., 2008; Lasheen and Ammar, 2009; Jamali et al., 2009; Donner et al., 2012). Sequential extraction procedures generally focused on differentiating the different association forms of metals in the solid phase.

Extractants could be divided into classes by their extraction efficiency and distinguished by their chemical effects such as weak extractions, reductive extractants, weak acids, strong complexing agents and others (Peijnenburg et al., 2007). Extractants can also be classified according to the metal species to be extracted; whether in the monoatomic or molecular specific forms, or the configuration in which the element exists in the matrix.

Peijnenburg et al. (2007) also states that the interaction between metal ions and the soil matrix occurs through ion exchange, sorption, complexation, precipitation and co-precipitation and also formation of organometallic compounds. Several extracting reagents in the order of increasing aggressiveness or destructiveness; such as unbuffered salts, weak acids or buffered salts, reducing agents, oxidizing agents and strong acids are applied sequentially to the sample to differentiate the metal fractions.

Winistorfer (1995) had grouped the extracted metal species into 4 classes; (i) free hydrated metal ions; (ii) moderately stable metal complexes; (iii) highly stable metal complexes; and (iv) extremely stable metal complexes.

The phase that relevant to heavy metal adsorption in sludge is oxides, sulfides and organic matter. The fractions that are obtained when applying sequential extraction method are; (i) exchangeable and metals mainly bound to carbonates (acid soluble/exchangeable fraction, F1); (ii) metals released in reducible conditions such as those bound to hydrous oxide of Fe and Mn (reducible fraction, F2); (iii) metals bound to oxidizable components such as organic matter and sulfides (oxidizable fraction, F3); and a (iv) residual fraction (F4) metals within lithogenic minerals (Cid et al., 2000; Kim et al., 2002; Fytianos and Lourantou, 2003; Su and Wong, 2003; Fernandez et al., 2004; Iwegbue et al., 2007; Stylianou et al., 2007; Terzano et al., 2007; Sprynskyy et al., 2007; Venkateswaran et al., 2007; Gao et al., 2008; Pan et al., 2009; Ololade, 2009; Rocco and Rubio, 2009; Ahumada et al., 2010; Davutluoglu et al., 2010; Alba et al., 2011; Qia et al., 2012).

The acid soluble and exchangeable fraction (F1) is unstable and susceptible to environmental conditions such as a change in water ionic composition as well as sorption-desorption processes or change in pH (Stylianou et al., 2007; Yuan et al., 2011). This fraction is considered to be weakly bound and may equilibrate with the aqueous phase thus increasing the bioavailability of the metal (Davutluoglu et al., 2010). Due to this, there

could be an increase in the amount of heavy metals released into the environment. This circumstance occurs when the conditions become more acidic and this situation may adversely impact the environment if not monitored responsibly. According to Nair et al. (2008) exchangeable metals are most willingly available to biota and metals in the acid extractable phase are highly sensitive to changes in the pH conditions; leaching occurs readily at low pH. Therefore, these metal fraction are considered mobile and this is supported by Venkateswaran et al. (2007) and Lu and Cheng (2011) who also agrees that the fraction are mobile fraction and are easily bioavailable.

Besides that, this fraction is more available for environmental functions than other fractions, and thus plays an important role in the ecological context. This is agreed with by Chen et al. (2008) Yuan et al. (2011) who suggested that the bioavailability and eco-toxicity of metals is mainly dependent on their speciation in sludge as described in Table 2.1.

Table 2.1: The relation among fraction of heavy metals, eco-toxicity and bioavailability

Fraction of heavy metals	Eco-toxicity	Bioavailability
Acid soluble and exchangeable fraction (F1)	Direct toxicity	Direct effect fraction
Reducible fraction (F2)	Direct toxicity	Direct effect fraction
Oxidizable fraction (F3)	Potential toxicity	Potential effect fraction
Residual fraction (F4)	No toxicity	Stable fraction

Sources: Chan et al., 2008 and Yuan et al., 2011.

The reducible fraction (F2) is a fraction that contains easily and moderately reducible Fe and Mn oxides which are thermodynamically unstable under anoxic

conditions (Templeton et al., 2000; Stylianou et al., 2007; Yuan et al., 2011). This fraction of heavy metal represents the contents of metal bound to Fe and Mn oxides that would be released if the substrate is subjected to more reductive conditions. Davutluoglu et al. (2010) found that the Fe-Mn compounds in the reducible fraction become bioavailable when the metals are mobilized by changes in the redox potential in the sediments. These conditions result in the release of metal ions to the dissolved fraction (Fytianos and Lourantou, 2003). In this extraction step, the destruction of the oxidized compounds especially oxyhydroxides which are only partially crystallized occurs (Baeyens et al., 2003). F1 and F2 fractions are known as direct effect fraction since the heavy metals distributed in the fractions contribute to pollution in the environment when they are readily absorbed by plants or into the water system (Chen et al., 2008; Yuan et al., 2011).

The oxidizable fraction (F3) contains metals associated with organic matter and sulfidic phases (Templeton et al., 2000; Yuan et al., 2011). These metals are bound with organic matter through complexation or bioaccumulation process as living organisms, detritus or coatings on mineral particles (Davutluoglu et al., 2010) and under oxidizing conditions, the slow degradation of organic matter leads to the release of the soluble metals into the environment (Fytianos and Lourantou, 2003). Since this oxidizable fraction is released under oxidizing conditions, it is not considered mobile or bioavailable (Yuan et al., 2011). These metals are integrated into stable high molecular weight humic substances and only a small amount of metals are released over a long period of time. Besides that, the release of the metals bound to the organic components is dependent on the degradation of organic matter under oxidizing conditions. However, heavy metals distributed in F3; also known as the potential effect fraction are easily transformed into F1 and F2 fractions due to an increase in the redox potential and its potential for eco-toxicity should not be ignored (Chen et al., 2008 and Nair et al., 2008; Yuan et al., 2011).

The residual fraction (F4) is identified as the inert fraction since it is often considered stable as well as unaffected by environmental changes (Chen et al., 2008; Lu and Cheng, 2011) and this fraction corresponds to the metals that have strongest relationship with the crystalline structures of the minerals (Yuan et al., 2011). F4 is also the last extraction step corresponding to a total digestion method common for bulk analyses (Baeyens et al., 2003). The extraction of the metals restrained in the residual fraction is not easily done and the conditions for a fast release are not expected to be encountered naturally (Nair et al., 2008; Yuan et al., 2011). This fraction consists of silicates and other refractory minerals which may contain high metal concentrations but these metals are not expected to be released into the environment under the conditions normally encountered in nature (Templeton et al., 2000 and Stylianou et al., 2007; Yuan et al., 2011). In this study, the residual fraction was extracted using aqua regia.

Factors such as redox potential, organic matter, pH and others affect the chemical forms of metals in sludge and soil (Chlopecka et al., 1996; Chlopecka and Adriano, 1996; Su and Wong, 2003; Lu and Cheng, 2011; Singh et al., 2012) and can result in metal remobilization from the solid to liquid phase, thus transforming the metals into more bioavailable or toxic forms (Yu et al., 2010).

Based on the study done by Sahuquillo et al. (1999) using the lake sediment certified reference material (CRM) 601, results show that, Cd, Cr, Ni and Zn were extracted in F1, Cd, Ni and Zn were found in F2 while Cd, Ni, and Pb in F3. It is suggested that Cd also prefers to form complexes with organic matter in the sediment (Chakraborty et al., 2012). However, Cu and Pb were also indicated in F1 and F2 respectively but not certified while due to the high variability of results obtained from laboratories, the remaining metals could not be certified. The study found that Cr, Cu and Pb are more sensitive to pH variations compared to Cd, Ni and Zn. The extractability and reproducibility of Cd, Ni and

Zn are reduced with an increase in pH. Shiowatana et al. (2001) found that the highest amount of Zn in soil was determined in F2 while Cu was more abundantly found in F1.

In contrast, Wang et al. (2005) found that Cd in municipal sludge was principally distributed in F4 whereas for industrial sludge, the highest percentage of Cd was determined in F1 and F2. Ni and Zn were also determined in higher percentages in the F1 and F3 fractions for both municipal and industrial WWTP sludges. From the results obtained in the study by Chen et al. (2008) on the speciation of heavy metals in municipal sludge from Changsha, Zhuzou and Xiangtan in middle-south region of China, it was determined that Cu and Zn were primarily present in F3 which indicates a high potential toxicity and bioavailability. Pb was found primarily in F4 and this could be attributed to the immobilization of Pb to insoluble salts such as phosphates in limiting Pb bioavailabilty. This study also determined that much of Cd in the sludge is bioavailable since the distribution in the various fractions showed no obvious characteristic or pattern.

From the study of distribution of heavy metals in the sewage sludge collected from five WWTP in China using BCR sequential extraction, it was shown that Ni and Cr were predominant in the F4 fraction while Cu and Pb were the primary fraction in F3 (Chao et. al., 2006). Moreover, the authors suggested that metals in the F3 and F4 were regarded to be less mobile and bioavailable compared to other fractions (F1 and F2) indicating that Ni, Cr, Cu and Pb in the sludge studied were not easily mobilized. Zn was found primarily in the F1 and F2 fractions with total concentration ranging from 61 to 93% which indicates the high potential mobility and bioavailability of Zn. Based on the findings, it can be concluded that this type of sludge should not be used on agricultural soil without further treatment (Chao et al., 2006).

In another study conducted by Scancar et al. (2000) on sewage sludge from WWTP in Domzale, Slovenia, it was determined that Pb, Cr, Fe and Cu were less dominant in F1

fraction, Cd was found moderately while high mobility and bioavailability for Zn and Ni were indicated with high percentages found; 46% and 48.5% respectively. More than half of the total Cd concentration (55.7%) was released in the F2 fraction. 61.9% Cr and 55.3% Cu were released in F3 while Fe and Pb were found abundantly in F4 fraction at 60.3% and 53.1% respectively. Stylianou et al. (2007) also found that the distribution of heavy metals in the sludge from municipal WWTP in Psittalia, Athens, Greece shows a similar fraction pattern with the heavy metals found in the sewage sludge at Domzale, Slovenia. These studies have proven that Ni and Zn have high mobility; their potential bioavailability and eco-toxicity should not be ignored and sludge should be treated or disposed of with appropriate measures to reduce their adverse effect to the environment.

Venkateswaran et al. (2007) evaluated the mobility of toxic metals in electroplating industry sludge and wastewater residue. The study determined that the major metal constitute is Fe which was primarily distributed in the F3 and F4 fractions contributing more than 50% from the total concentrations. Fe, a non-toxic metal is found predominantly in the fractions because it is used during the precipitation process in electroplating treatment plants. The high amounts of Fe present may interfere with the efficiency of the sequential extraction. However, less than 20% of Fe is available in F1. In contrast, Cr was present in low quantities in the F1 but mainly found in F2, while Cu is primarily present in F2 followed by F3 fraction. Cu complexes have higher stability with organic matter which leads to its higher concentrations in the organic fraction. The predominant form of Zn was also found in the F2 fraction while F4 fractions in the sludge samples contain higher amounts of Zn compared to wastewater residue. Backes et al. (1995) determined that higher concentration of metals in the F2 fraction can be attributed to diffusion mechanism and the metals could pollute the environment only under extreme reducible conditions. Due to the precipitation of Pb forming stable compounds, the metal shows a higher distribution in the

F2 fraction compared to the other fractions. Both Venkateswaran et al. (2007) and Kazi et al. (2005) found that Cd is the least abundant metal in the plating wastes. Cd was found at 6 to 14% in F1 for wastewater residue samples and found at trace levels in sludge samples.

In another study conducted on sewage sludge in Egypt, it was determined that Ni, Mn and Zn were predominantly present in the F1 and F2 fractions which implies high mobility compared to Cd, Cu, Cr and Fe which were found primarily in the F3 and F4 fractions (Lasheen and Ammar, 2009). This finding is in agreement with the speciation observations by Cai et al. (2007) on composts of sewage sludge and Miao et al. (2007) on sludge. However, the total concentration of Cu and Zn in the final compost shows a remarkable increase after sewage sludge was added with compost material. From the stabilization study conducted, it was indicated that the use of cement kiln dust may influence the distribution of metals by lowering their bioavailability with increasing the percentage of the metal forms in the F2 and F4 fractions. It was demonstrated that the properties of the sludge, the composting process influenced by the content of organic carbon, humic substance as well as the pH will affect the concentration and speciation of heavy metals in the final compost (Cai et al., 2007).

In a study on the chemical speciation of soil amended with fly ash-stabilized sewage sludge (Su and Wong, 2003), the authors mentioned that for the understanding of the bioavailability and mobility of heavy metals in soils, the knowledge of the heavy metal speciation in soil amended with sewage sludge is important. The uptake of heavy metals by plants is correlated to extractable forms of the metals compared to the total metal concentrations in the soil and if excessive amounts of heavy metals are present, the plants may be damaged which could ultimately affect human health upon consumption of said crops. The mobility of metals and their uptake by plants caused by metal hydrolysis or carbonate precipitation could be decreased with the use of lime which increases the pH of

sludge hence killing pathogens and reducing the availability of the metal. The study concludes that the availability of Cu, Zn, Ni and Cd in the sludge could be reduced chemically by modifying their chemical speciation into less available forms with the use of coal fly ash (Su and Wong, 2003).

Davutluoglu et al. (2010), mentioned that the heavy metal concentrations in the sediments were found in higher concentrations at areas with high silt and clay contents. The physical characteristic of silt and clay; consisting of fine particles have a higher adsorptive capability of metals due to their larger surface area. The results show that the rates of the remobilization for the sediments in Akyatan Lagoon for the heavy metals are in the following order: Mn>Pb>Cu>Zn>Cr>Ni. Cr was mainly distributed in the F3 and F4 fractions with the major contribution from the F4 fraction. Similarly, Cu, Ni, Pb and Zn were predominantly found in the residual fraction. The study also suggests that changes in pH and redox potential may not result in significant remobilization of metals such as Pb and Mn.

The results of a study by Yu et al. (2010) on sediments from the Pearl River Estuary and the Daya Bay, Southern China determined that Cr, Ni and Zn were found mostly in the F4 fraction which can be considered as the environmentally safest component due to its stability and inertness, consistent to the analysis results of Lu and Cheng (2011). However, Pb was predominantly present in the non-residual fractions which are unstable under natural environmental conditions and can be solubilized under certain conditions. The study suggests that the origin of the heavy metals found in the sediments studied were mainly due to anthropogenic inputs or human activity (Yu et al., 2010; Lu and Cheng, 2011).

According to Chanpiwat et al. (2010), Cd^{2+} which has low oxidation state and low electronegativity is the dominant chemical species of Cd in water. The study determined that Mn and molybdenum (Mo) were found predominantly in the dissolved phase while Ni

was moderately associated with the dissolved phase but Cu, Zn, Fe, Pb, Cr and Cd were mostly found in the particulate form. Cr, Cu, Fe, Mo and Pb were mostly found in the F4 and F3, therefore showing less mobility and bioavalaibility. In contrast, Cd, Mn, Ni and Zn are predominant in the F1 and F2, thus potentially mobile and bioavailable. The concentration of heavy metals determined in biosludge is dependent on the type and amount of wastewater discharged into the treatment system as well as the performance of the treatment facilities.

Pempkowiak and Gajewska (2008) investigated the influence of sludge treatment processes on heavy metal speciation. The relative occurrence of metals in the wastewater and sludge samples are as follows; Cd<Ni<Cr<Ag<Pb<Cu<Zn. The study suggests that sludge treatment processes such as thickening, stabilization and dewatering affects the composition of the sludge. It was also suggested that some of the metals that were accumulating in sludge could have been released into reject waters during the thickening and dewatering processes. The distribution of Zn, Pb and Cr is greatly affected by mechanical treatment or primary sedimentation while the distribution of Cu, Cd and Ni is mostly influenced by biological processes and secondary sedimentation (Pempkowiak and Gajewska, 2008; Chanpiwat et al., 2010). Moreover, the use of biological method for sewage treatment can increase the heavy metals accumulation in sewage sludge compared to mechanical treatment.

2.7 Electroplating

Electroplating is the process of using an electrical current to coat an electrically conductive object with a thin layer of metal (Schlesinger, 2002). This process is also known as electrodeposition. Electroplating is a popular technique for the prevention of material wear and corrosion especially objects used in the outdoors or exposed to damp conditions.

The electroplating process changes the chemical, physical and mechanical properties of items and it is also used to alter the appearance of items or give the objects special surface properties as illustrated in Plate 2.1.

Plate 2.1: Ni and Zn plate screws.

This process is achieved by placing a negative charge (cathode) on the object to be coated in the electrolysis cell through which a direct current is passed. The positive electrode (anode) is usually a bar of the metal which is to be plated. Both the electrodes are immersed in an aqueous solution referred to as the plating bath. The solution contains the desired metals such as Zn, Ni or Cu which are dissolved and exists as a form of metallic particles (positively charged ion). In the bath, the electric current is carried by the positively charge ion from the anode toward the negatively charge cathode. The metal ions in the bath will migrate towards the cathode since they are attracted towards the extra electrons that are located on the cathode's surface layer. Using the electrolysis process, the metal ions are removed from the solution and are deposited on the surface of the object as a thin layer. Figure 2.1 shows an electroplating cell. The basic equation of the electroplating process is simplified with this formula;

$$\text{Cathode:} \quad M^{2+} \text{ (aq)} + 2e^- \longrightarrow M \text{ (s)}$$

$$\text{Anod} \quad : \quad M \text{ (s)} \longrightarrow M^{2+}\text{(aq)} + 2e^-$$
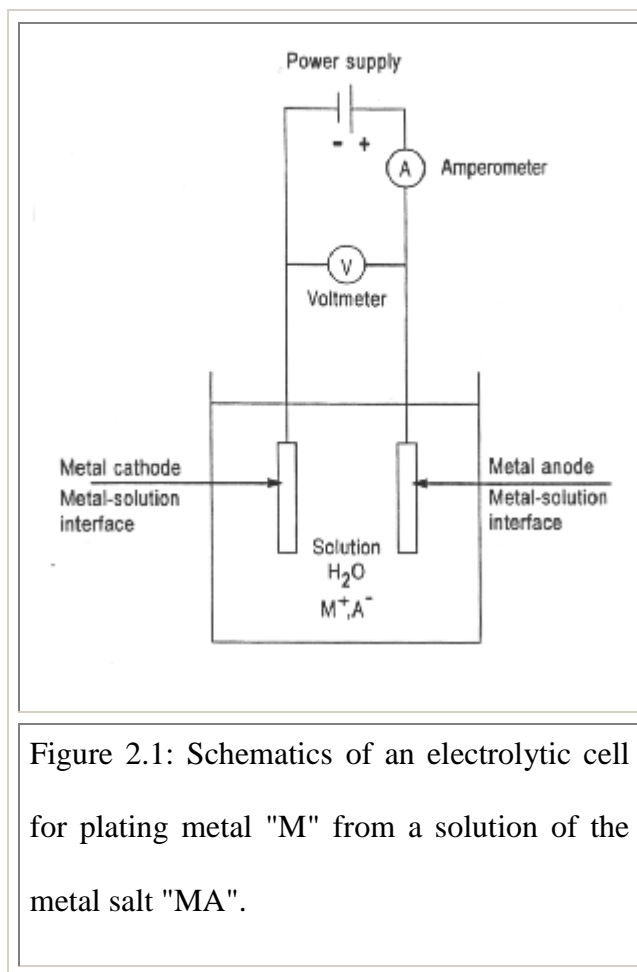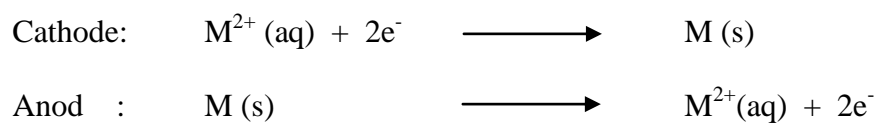
Figure 2.1: Schematics of an electrolytic cell for plating metal "M" from a solution of the metal salt "MA".

There are several types of metals that are most often used in electroplating such as Ni, Zn, Cu, silver, gold and many others. However, during the electroplating process, the transformation of ions cannot be seen but it can be observed by the change in the color of the solution. For example, the Ni solution which is emerald green will change slowly into gray or silver in colour as the metal is being deposited (Devandran, 2007).

2.7.1 Electroplating industry

The increasing demand for plating/surface treatment services in the electrical, electronics, automotive and machinery component industries has created opportunities for new ventures in Malaysia. The Malaysian plating/surface treatment sector has the capabilities to undertake various precision processes such as batch and continuous electroplating, precision electroplating, electroless plating, functional electroplating, cathodic electrodeposit, dacrotised treatment, phosphating, passivation, anodizing, chromating, electroplating for the semiconductor industry including integrated circuits and lead frames, sinter plating and physical vapour deposition. Realizing this, the Malaysian Government encourages the establishment of modern plating plants to complement the country's rapid industrial development and to address environmental concerns linked to the plating industry.

It is a well-known fact that the discharge from the electroplating industry such as plating wastewater mainly contains heavy metals, oil and grease, suspended solids and occasionally organic compounds at the level might be considered hazardous to the environment and could pose risks to public health (Kanluen and Amer, 2001). Due to the high toxicity and corrosiveness of plating waste streams, plating facilities are required by Malaysian legislation as stipulated in the EQA, 1974 to pretreat their wastewater prior to discharge in waterway.

In the electroplating industry, mineral acids such as HNO_3, H_2SO_4 and HCl are used during the removal of rust and scales process. This may result in the presence of more free acids in the electroplating effluent which could reduce the pH of effluent to pH below 2.5 (Malarkodi et al., 2007). Furthermore, this study also determined that the soil around electroplating industries are mostly contaminated with heavy metals such as Ni, Cr and Cu with concentrations of 192.5 mg kg^{-1}, 105.6 mg kg^{-1} and 143.1 mg kg^{-1} respectively

(Malarkodi et al., 2007). This is to be expected because larger quantities of Ni, Cu and Cr are used during Ni, Cu and chrome plating processes which may also contribute to the excessive metal accumulation. The solution used during the plating processes which may consist of mixtures have also contributed to the complexity of waste treatment.

During the wastewater treatment process, the large quantities of sludge generated will have to be treated and when released, it has to be ensured that the sludge will not affect the environment adversely. Due to the physical and chemical processes involved in activated sludge wastewater treatment, heavy metals that are present in the wastewater tend to accumulate in the generated sludge (Pempkowiak and Gajewska, 2008). Therefore, the levels of heavy metals found in the sludge are generally higher than in the wastewater.

Electroplating sludge has been identified as a heavy metals-bearing byproduct that is produced from the activities of the electroplating industry (Li et al., 2010). Multiple metals such as Zn, Ni, Cu, Cr, Fe, Cd and Pb have been found in the discharged residue generated from acidic or alkaline solutions as well as rinse waters which have undergone chemical precipitation.

The most common treatment used during the chemical precipitation process is the hydroxide precipitation treatment. This process involves the use of alkaline material such as caustic soda, soda ash, lime or magnesium hydroxide. The caustic material used will precipitate the metals in the waste to metal hydroxides which are highly soluble and in order to achieve maximum metal hydroxides during the treatment, the pH of the solution should be maintained between 6 to 10 (Devandran, 2007).

In Malaysia, the waste generated by the electroplating industry is classified under scheduled waste and is listed in the First Schedule of the Environmental Quality (Scheduled Wastes) Regulation 2005. Thus, it is the responsibility of the waste generator to manage and treat the hazardous waste properly prior to disposal. Strict regulations and

implementation of the legislation by the authorities is necessary to ensure that the environment is protected and the quality of life for the population is not adversely affected.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Apparatus

An Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500 Series c) was used in this work for the determination of Cd, Cu, Cr, Ni, Pb, Zn, and Fe. The solution was propelled into the nebulizer by a peristaltic pump. A centrifuge instrument, Kubota 2420 (speed range 0-6000 rpm, timer 0-60 min) was used to separate the solid and liquid phase. A WTW 740 pH meter was used for pH reading of the solutions. A horizontal flask electrical shaker (220/60 Hz, Gallenkamp, England) was employed for the shaking of the samples. A water bath and hot plate was also used during the sample digestion process.

3.2 Reagent

All reagents used in this study were of analytical reagent grade unless stated otherwise. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity) was used for the preparation of samples, extraction solutions and standard solutions. Acetic acid (HOAc) (glacial, 100%), hydroxylammonium chloride (NH$_2$OH.HCl), hydrogen peroxide (H$_2$O$_2$) (30%), ammonium acetate (NH$_4$OAc) and HNO$_3$ (69%, sp. gr. 1.42) were of suprapure quality (E. Merck, Fluka). The standard metals solutions (1000$\pm$2 mg L^{-1} in 5% HNO$_3$) were obtained from Merck (Darmstadt, Germany). The plastic and glassware used were soaked in diluted HNO$_3$ for 24 h and were then rinsed with deionized water to remove any impurities present. Extractants were prepared according to the following procedure:-

- *Solution A (HOAc, 0.11 mol L^{-1})* was prepared by dissolving 25$\pm$0.2 mL of glacial *HOAc* in 1000 mL of deionized water. A volume of 250 mL of this solution (*HOAc*,

0.43 mol L^{-1}) was diluted to 1000 mL with deionized water to prepare a final concentration of 0.11 mol L^{-1} of acetic acid.

- *Solution B (NH$_2$OH.HCl, 0.1 mol L^{-1}, pH 2)* was prepared by dissolving 6.95 g of *NH$_2$OH.HCl* in 800 mL of deionized water. The solution was then acidified with concentrated HNO$_3$ to pH 2 and made up to 1000 mL. This solution was prepared fresh for each extraction procedure.

- *Solution C (H$_2$O$_2$, 300 mg g^{-1} i.e. 8.8 mol L^{-1})* which was acid-stabilized to pH 2.0-3.0 was purchased from Merck.

- *Solution D (NH$_4$OAc, 1.0 mol L^{-1})* was prepared by dissolving 77.08 g of *NH$_4$OAc* in 800 mL deionized water. The solution was acidified to pH 2.0 with concentrated HNO$_3$ and made up to 1000 mL with deionized water.

3.3   Sample collection and pre-treatment

Three sludge samples were obtained from the WWTP of three electroplating industries located in Penang, Malaysia. The step at which the samples were collected is indicated in Figure 3.1. The samples were bottled and uniquely labeled for analysis. The samples were dried overnight in an oven at 103±2 °C prior to analysis for the removal of moisture. Samples were then grinded and homogenized in an agate and mortar to reduce the particle size. Then, the samples were sieved through a siever (mesh size 100) and stored
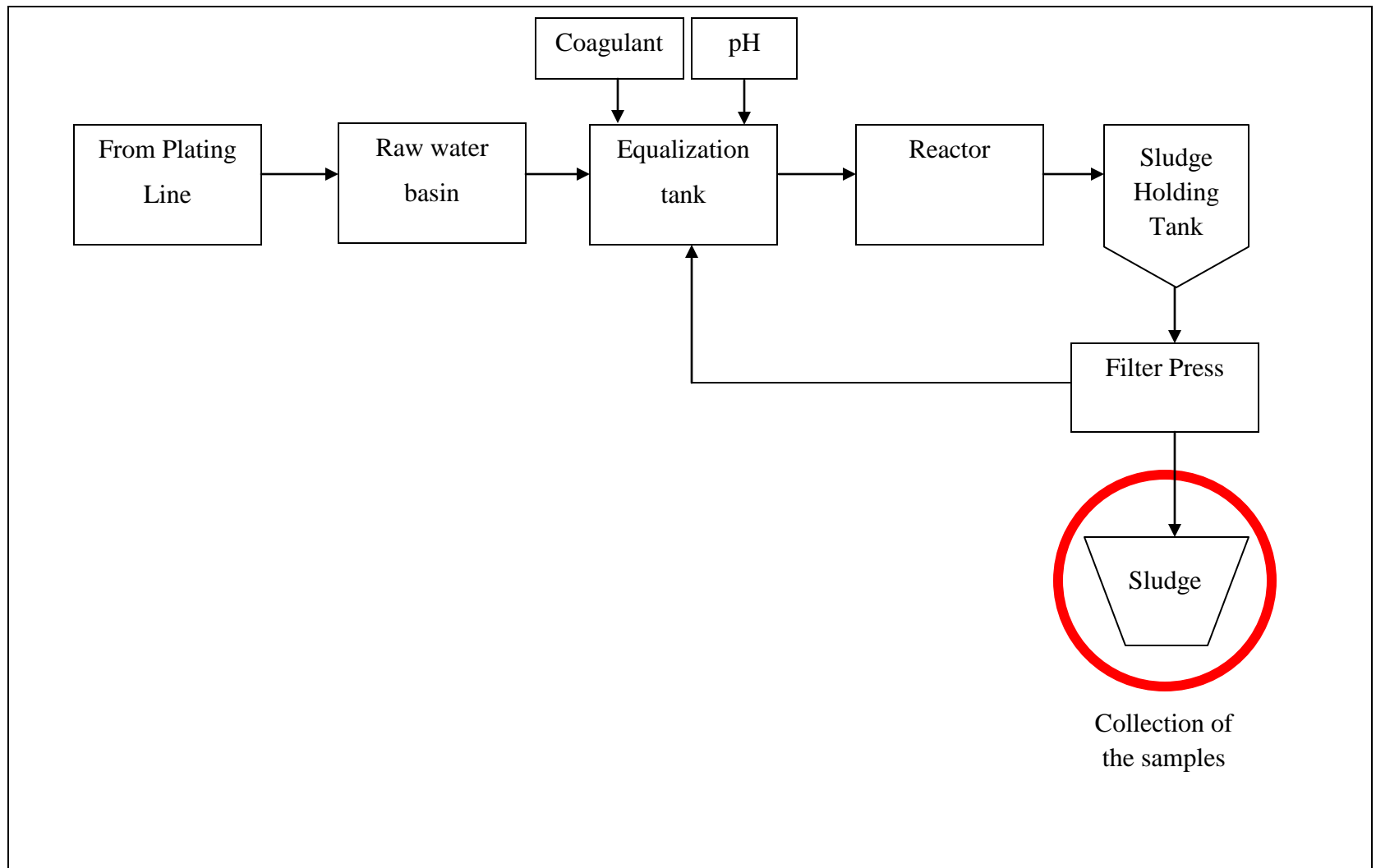
Figure 3.1: Collection of samples after undergoing the filter press step.

in polyethylene containers at room temperature. Prior to the analysis, the dried samples were coned and quartered to 20 g. Homogenized sub-samples weighing 0.5 g each was used for the sequential extraction.

3.4 Procedures

3.4.1 Aqua regia digestion

Pseudototal metal content was determined by means of aqua regia digestion method. A volume of 10 mL of 1:1 HNO_3 was added into the samples, the slurry was then mixed and covered with watching glass. The samples were then heated on a hot plate at 95 ± 5 °C and refluxed for 10 to 15 minutes without boiling. Samples were allowed to cool to room temperature before the addition of 5 mL of concentrated HNO_3 and the sample was further refluxed for 30 minutes. This step was repeated by the addition of 5 mL of concentrated HNO_3 until the brown fumes emitted are no longer released which indicates the complete reaction with HNO_3.

The volume of the solutions was then reduced to approximately 5 mL and allowed to cool. After that, 2 mL of deionized water and 3 mL of 30% H_2O_2 were introduced into the samples. The containers were covered with watching glass and returned to the hot plate for warming in order to start the peroxide reaction. The procedures employed were conducted cautiously to ensure that losses do not occur due to excessive vigorous effervescence. The process was allowed to continue until effervescence present subsides and the samples were then cooled. A suitable volume of 30% H_2O_2, not exceeding 10 mL was added continuously into the solution until the bubbles subside.

The samples were heated during the acid-peroxide digestion until the volume was reduced to approximately 5 mL. Next, 10 mL of concentrated HCl was added to the digested sample and the containers were covered with watching glass. The sample was then

refluxed at 95±5 °C for 15 minutes. After cooling the samples were filtered into 100 mL polyethylene volumetric flask and diluted to the mark with deionized water. Extracts were then transferred into polyethylene container and stored at 4 °C for analysis.

3.4.2 Sequential extraction

The BCR 3-steps sequential extraction procedures described by Wang et al. (2005) and Chen et al. (2008) were used to obtain the information on the non-residual speciation of metals. The next step involves the digestion of residue with the aqua regia. This procedure was introduced to determine the concentration of the elements associated with the residual components of sludges matrix. The sequential extraction protocol which was used in this study as well as the sludge fractions formed which the metals are released into is given as follows:

Step 1 (Acid soluble/exchangeable fraction, F1) was followed by the addition of 20 mL of 0.11 mol L^{-1} HOAc *(Solution A)* to 0.5 g of dry sludge sample in a 50 mL polypropylene centrifuge tube with stopper. The mixture was shaken for 16 h at room temperature. No delay should occur between the addition of the extractant solution and the beginning of the shaking. The solution and solid phase were separated by centrifugation at 4000 rpm for 20 min. The supernatant liquid was filtered into a 100 mL polypropylene volumetric flask. The supernatant was then transferred into the polypropylene container and stored in a refrigerator at about 4 °C prior to analysis. The residues were washed by adding 20 mL of distilled water, shaking for 15 min and then centrifugation at 3000 rpm for 20 min. The second supernatant liquid was discarded without any loss of residue.

Step 2 (Reducible fraction, F2) was continued by adding a portion of a 20 mL volume of freshly prepared 0.1 mol L^{-1} $NH_2OH.HCl$ which had been adjusted to pH 2 with concentrated HNO_3 *(Solution B)* to the residues from Step 1. Sludge was resuspended by manual shaking and then extracted by shaking for 16 h at room temperature. As Step 1, no delay should occur between the addition of the extractant solution and the beginning of the shaking. The extractant was then separated from the solid residue by centrifugation and decantation as described in Step 1. The extractant was transferred to a polypropylene container with stopper and stored in a refrigerator at about 4 °C prior for analysis. The residues were washed by adding 20 mL distilled water, shaking for 15 min and centrifugation for 20 min at 3000 rpm. The supernatant was decanted and discarded without any loss of residue.

Step 3 (Oxidizable fraction, F3) a volume of 5 mL of H_2O_2 (8.8 mol L^{-1}) *(Solution C)* was added carefully to the residue in the centrifuge tube, and was digested at room temperature for 1 h with occasional manual shaking. The procedure was continued for 1 h at 85±2 °C in water bath, and then the volume was allowed to reduce to 1 to 3 mL by further heating of the uncovered tube. A second 5 mL aliquot of H_2O_2 was introduced to the residue and the digestion procedure was repeated. The cover of the centrifuge tube was removed and the volume of liquid was reduced to about 1-2 mL. A volume of 25 mL of NH_4OAc solution (1.0 mol L^{-1}, adjusted to pH 2 with concentrated HNO_3) *(Solution D)*, was added to the cool moist residue and was shaken for 16 h at room temperature. No delay should occur between the addition of the extractant solution and the beginning of the shaking. The extract was separated from the solid residues by centrifugation and decantation (similar to Step 1). The extractant was retained as indicated in Step 1 before analysis.

Step 4 (Residual fraction, F4) the analysis of the residue was performed using aqua regia extraction for the determination of metals that are insoluble in the previous steps. About 5 mL of HNO_3 and 5 mL HCl was added to the residues from Step 3. After adding each aqua regia solution, the contents were heated on a hot plate and evaporated to near dryness. After cooling, the residues were dissolved in 5 % HNO_3. The resultant solutions were used for the determination of the heavy metals concentration.

The concentration of heavy metals in each fraction and the resultant solutions of Step 4 were determined by means of ICP-MS. Each experiment was conducted in triplicates; the average values were calculated and reported.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1   Pseudototal heavy metals content

4.1.1   Sample A

Sample A was collected from one of the Zn plating industry located in Penang. The main processes used in this industry are Zn alloy plating, alkaline Zn plating, Zn-Ni and other plating services. The wastewater generated by the factory was treated prior to discharge. The purpose of the treatment is to remove contaminants from the waste and produce a disposable effluent which will not pose a risk to the surrounding environment and also to prevent pollution.

Physical and chemical methods were used for the treatment of the wastewater. Most of the settleable solids were separated or removed from the wastewater with the use of the physical process of sedimentation. This is a common process and is routinely employed at the beginning and end of the wastewater treatment operation. It was disclosed that alum is used as a coagulating chemical followed by flocculation process as chemical treatment in the plant. Alum is widely used for coagulation for the removal of turbidity and also to speed up sedimentation. When alum is added to water, the metals ions are hydrolyzed to form a series of metal hydrolysis species. This process allows the particles to move closer to each other and large clumps are formed. The particles will then come into contact with each other to form flock during the flocculation process which will then settle out in the sedimentation tank forming sludge. The sludge generated will then undergo thickening and dewatering process prior to disposal.

For the purpose of this study, the sludge samples were collected after undergoing the filter press. The total contents of Cr, Fe, Ni, Cu, Zn, Cd and Pb for sample A is presented in Figure 4.1 (Please refer to Appendix A for the calculation of the concentration of each metal content studied). All data are expressed as mean value (mg kg^{-1}) of dry sludge.
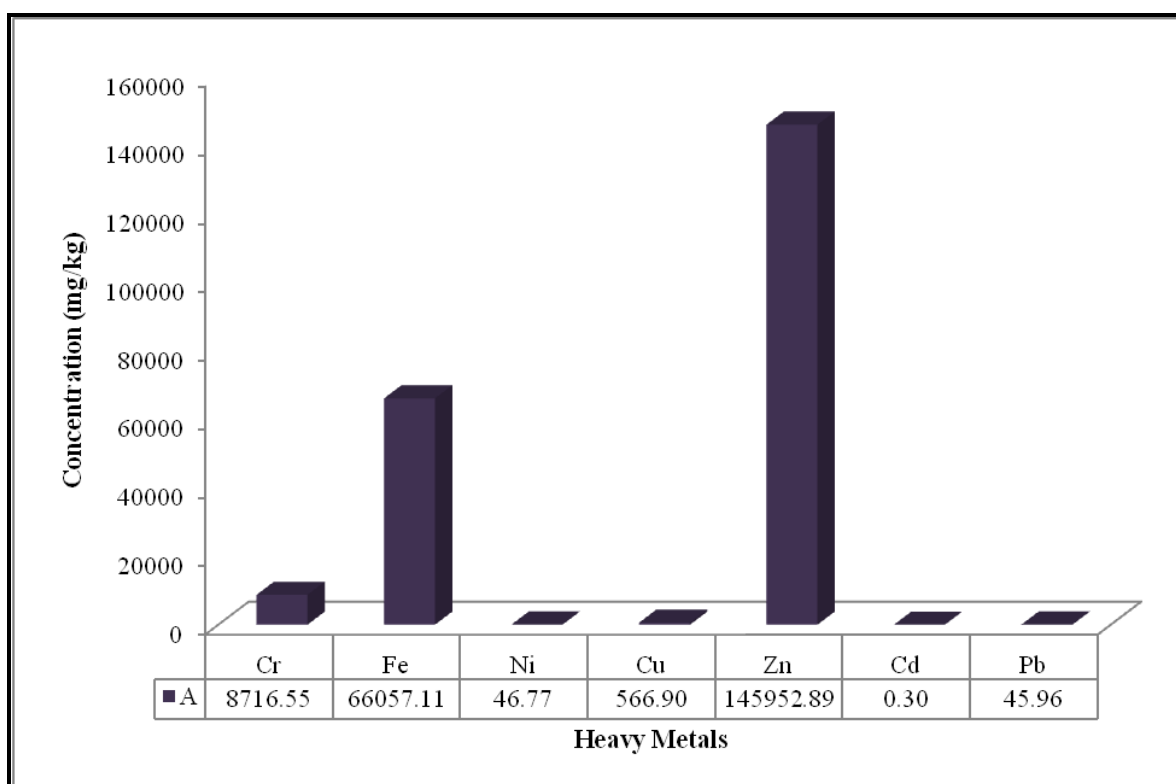

	Cr	Fe	Ni	Cu	Zn	Cd	Pb
A	8716.55	66057.11	46.77	566.90	145952.89	0.30	45.96

Heavy Metals

Figure 4.1: Concentration of heavy metals in sample A by Pseudototal digestion

The results in Figure 4.1 show a wide variation in the concentration of heavy metals determined in the sample. The sludge sample had higher contents of Zn with a total concentration of 145,952.89 mg kg^{-1}, followed by Fe with 66,057.11 mg kg^{-1} and Cr with 8,716.55 mg kg^{-1}. However, only low levels of Ni, Cu, Pb and Cd were found in the sample. A similar wide variation in the concentration range of heavy metals was also

reported by Subramanian et al. (2005) and Venkateswaran et al. (2007). Nevertheless, the total concentration of Cr, Fe, Ni and Zn observed by Venkateswaran et al. (2007) were much lower than the results of the present study. In contrast, the concentration of Cu, Pb and Cd noted in this research were lower than the results of the previous study. The total metal content for this sludge sample is in the following order Zn>Fe>Cr>Cu>Ni>Pb>Cd.

4.1.2 Sample B

Similarly to sample A, sample B was also collected from another Zn plating industry located in Penang. This industry is involved in the production of material for surface treatment and powder coating as their finished products. The raw materials used consist of metals especially Zn which is used extensively compared to other metals. Zn is used to coat surfaces due to the nature the element which is more resistant to corrosion compared to other metals. This factory also applies physical and chemical processes in their treatment plant. However, this industry uses acid treatment for the removal of heavy metals from their wastes.

Figure 4.2, illustrate the total concentration of heavy metals in sample B by Pseudototal digestion (Please refer to Appendix B for the calculation of the concentration of each metal content studied). All results are expressed in mg kg^{-1} of dry sludge. From the results obtained, Zn with total concentration 187,735.84 mg kg^{-1} was the most abundant element found compared to the other elements. The element with the second highest concentration was Fe with a concentration of 68,164.34 mg kg^{-1} followed by Cr with a value of 19,230.87 mg kg^{-1}. However, Ni, Cu and Cd were found at much lower concentrations compared to the other elements. From the findings, Zn was found to be the most abundant metal compared to the other elements and this is consistent with the source of the sample which is from the Zn plating industry. Zn was used as the primary raw

material during the production process. From the results, it is shown that excess Zn had accumulated in the sludge. The order of the metal content in this sludge sample is Zn>Fe>Cr>Pb>Ni>Cu>Cd.
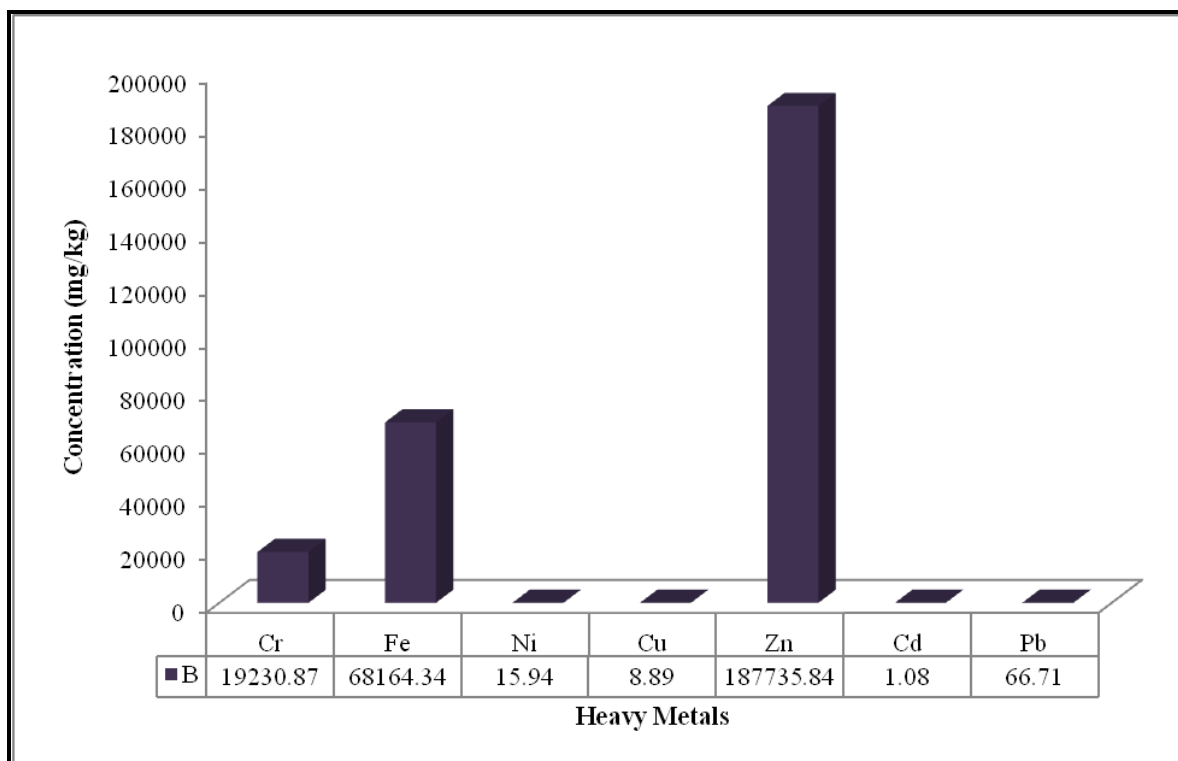
	Cr	Fe	Ni	Cu	Zn	Cd	Pb
■B	19230.87	68164.34	15.94	8.89	187735.84	1.08	66.71

Figure 4.2: Concentration of heavy metals in sample B by Pseudototal digestion.

4.1.3 Sample C

Differing from samples A and B, sample C was obtained from a Ni plating industry located in Penang. This industry is mainly involved in the production of Ni alloy. During the production process, the raw materials used consist of mainly metals especially Ni. In accordance with the regulations stipulated by DOE, this industry has treated the waste generated using physical and chemical treatments prior to their discharge into waterways. Sludge is generated as a by-product from the treatment process.

Figure 4.3, shows the results obtained after the sample was digested using aqua regia and analyzed by ICP-MS (Please refer to Appendix C for the calculation of the concentration of each metal content studied). All data are presented in mg kg^{-1} of dry sludge. As shown in the figure, Ni is the most abundant element with total value 18,312.50 mg kg^{-1}, followed by Fe with total concentration 4,286.50 mg kg^{-1}. Cd is the least element found in this type of sludge with total amount only 0.01 mg kg^{-1}. From the findings, the amount of Ni was much higher compared to the other elements since this sludge was collected from a nickel plating factory and Ni was used as the primary raw material in production. It is to be expected that excess Ni will accumulate in the sludge. The order of the metals found are Ni>Fe>Cr>Cu>Zn>Pb>Cd.

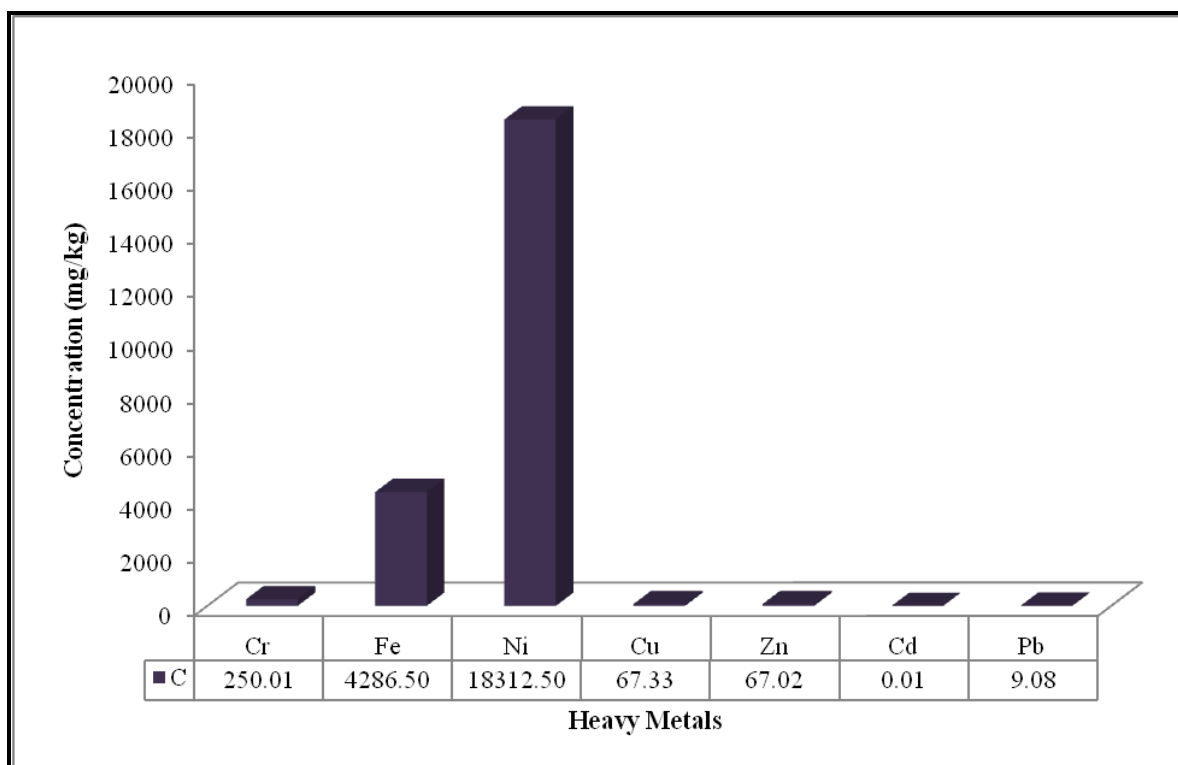|	Cr	Fe	Ni	Cu	Zn	Cd	Pb
C	250.01	4286.50	18312.50	67.33	67.02	0.01	9.08

Heavy Metals

Figure 4.3: Concentration of heavy metals in sample C by Pseudototal digestion.

From the study conducted, an idea on the distribution of the heavy metals in the sludge from the various industries is formed. It can be concluded that the heavy metal content in sludge is highly influenced by the raw materials used during production.

4.1.4 Total content of Cr, Fe, Ni, Cu, Zn, Cd and Pb

The comparison of the percentage of the total content of Cr, Fe, Ni, Cu, Zn, Cd and Pb found in the samples collected from three different electroplating industries located in Penang are shown in Figure 4.4 (a) to Figure 4.4 (g) respectively. The calculated value is the percentage of heavy metals concentrations in each sample compared with the average concentration of heavy metals in all three samples studied. Both samples A and B have higher concentrations of Fe, Zn and Pb but relatively low concentrations of Ni. On the other hand, the most abundant metal found in sample C was Ni with low amounts of Cr, Fe, Cu, Zn, Cd and Pb compared with sample A and B. Samples A and B show a similar trend in their metal content compared to sample C probably because both samples A and B were obtained from the same type of plating industry while sample C was obtained from a different plating industry. According to Venkateswaran et al. (2007), the difference in the concentration of metals may be due to the nature of plating employed by the industry involved. Besides that, the composition of the raw material used in the plating bath also plays an important role to provide an idea on the distribution of heavy metals in sludge sample.

The concentrations of total Cr in the sludge samples varied from 250 mg kg^{-1} to 19,231 mg kg^{-1}. As shown in Figure 4.4 (a), the highest concentration of Cr is in sample B contributing 104.6% from the average of total content of Cr in each sample, followed by sample A (7.3%), while sample C has the lowest amount of total Cr, 97.3% less than sample A and B. During the precipitation process in the WWTP, metals including Cr will

settle and accumulate in the sludge which leads to a higher concentration of Cr found in the sludge samples. This result is in agreement with the study done by Devandran (2007) in determining the concentration of Cr in effluent from plating industry.
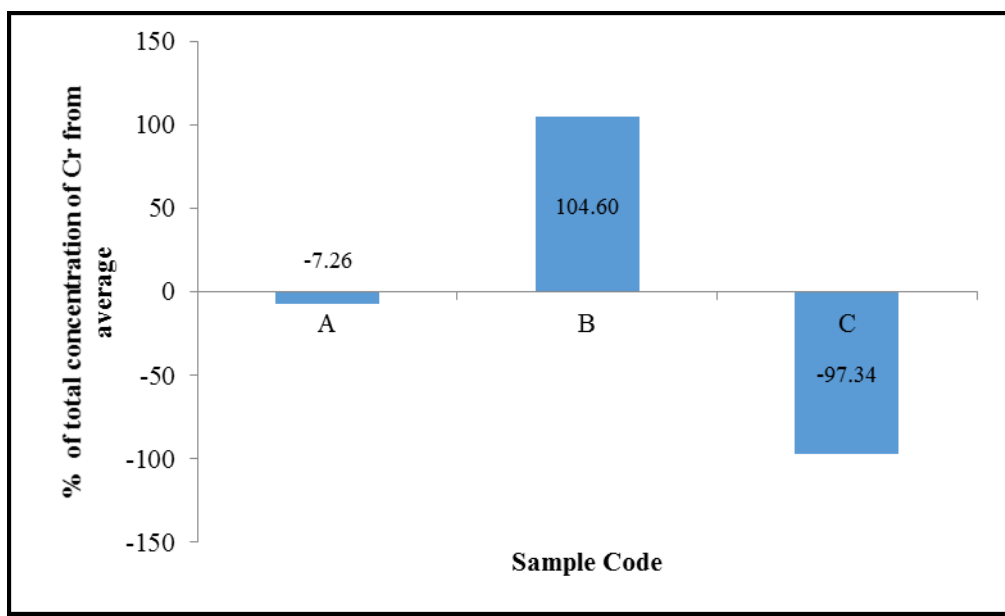

Figure 4.4 (a): Percentage (%) of total concentration of Cr in sludge samples from the average.

Fe was the second highest element found in the sludge samples of sample A and sample B. In sludge sample B, the total concentration of Fe was 68,164. 34 mg kg^{-1} (47.6%) while in sample A it was 66,057.11 mg kg^{-1} (43.1%). 4,286.50 mg kg^{-1} of Fe was found in sample C, 90.7% less than the amount of Fe found in sample A and sample B as shown in Figure 4.4 (b). Because of the higher content of Fe in all sludge samples, this can be used as an indicator that Fe compounds may be used in the precipitation reactions for the removal of heavy metals and other compounds in the wastewater treatment processes. For example, iron (III) chloride ($FeCl_3$) was used during the treatment process as a reducing flocculating agent in the formation of Fe complexes and magnetic Fe oxides and as reducing agent in organic synthesis.
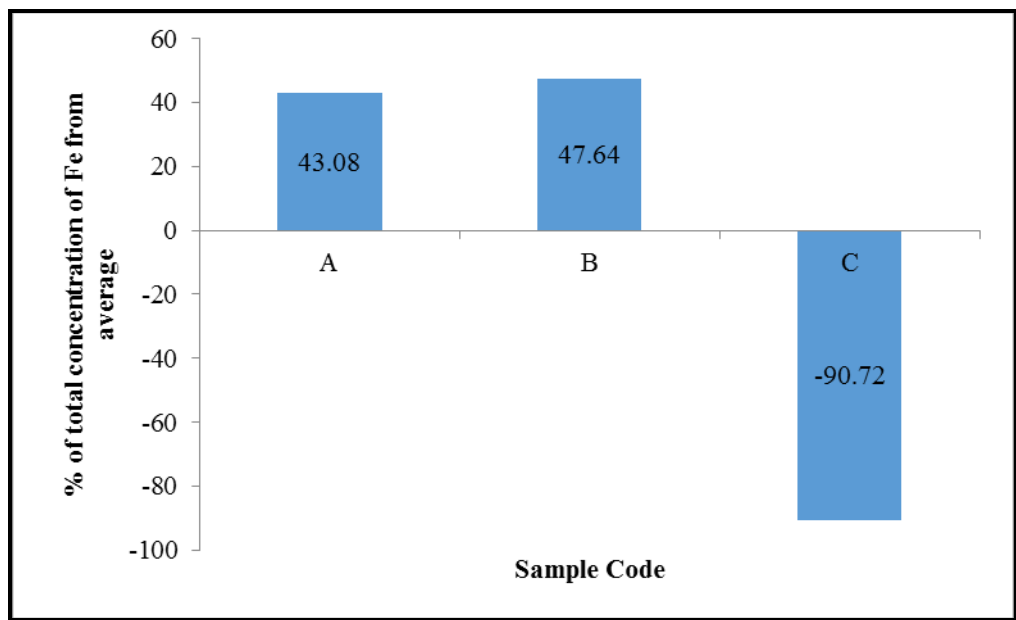
Figure 4.4 (b): Percentage (%) of total concentration of Fe in sludge samples from the average.
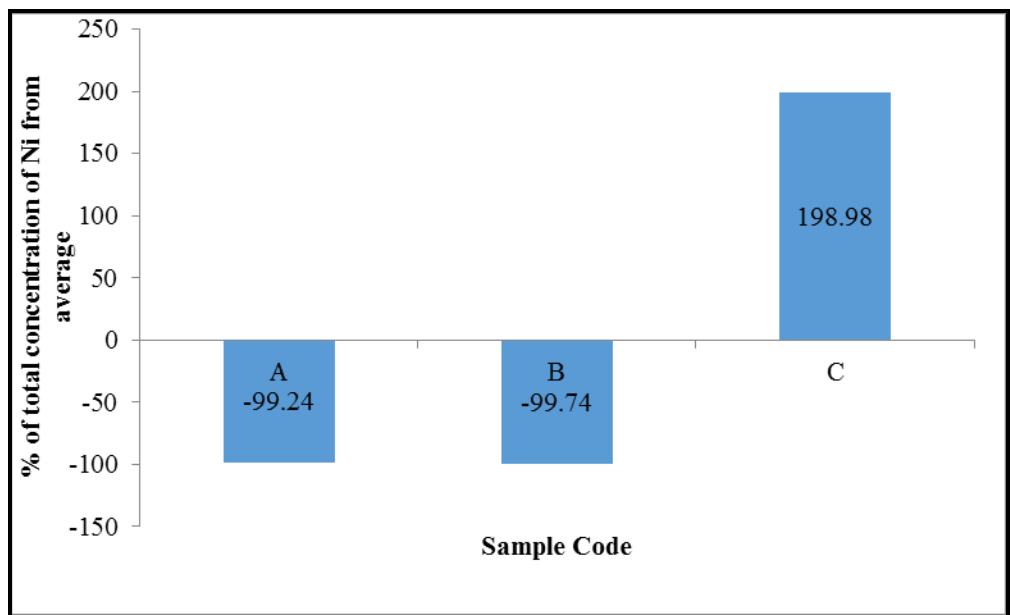

Figure 4.4 (c): Percentage (%) of total concentration of Ni in sludge samples from the average.

In contrast, sample C is sludge that was obtained from a Ni plating industry. Therefore, Ni is the primary raw material that is used during the plating process compared to other metals. Ni that is present in the wastewater needs to be treated prior to discharge to

ensure compliance with regulations and preservation of the environment. During the wastewater treatment, the excess Ni will coagulate and flocculate into the sludge wastes. This explains the higher concentration of Ni determined in sample C (199.0%), compared to samples A and B as illustrated in Figure 4.4 (c). It also demonstrates that industries such as electroplating and steel are the most obvious anthropogenic sources of Ni in the environment.
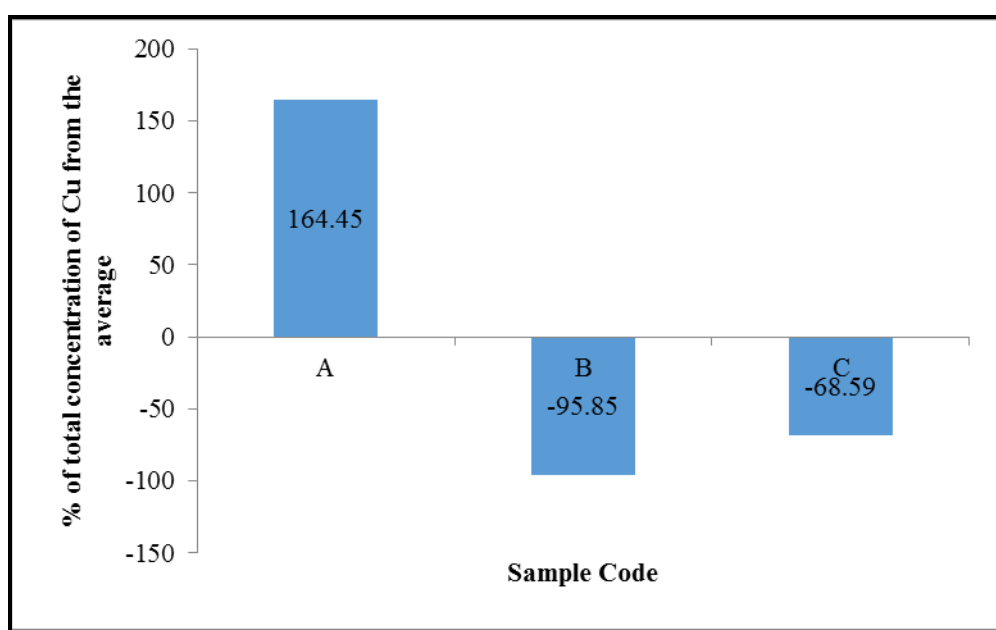

Figure 4.4 (d): Percentage (%) of total concentration of Cu in sludge samples from the average.

In this study, the concentration of Cu determined in the sludge samples range from 8.89 mg kg^{-1} to 566.90 mg kg^{-1}. As observed in Figure 4.4 (d), the highest concentration of Cu was found in sludge sample A (164.5%), followed by sample C (68.6 %) while the sample B contained the 95.9% lowest level of Cu from their average. If these sludges are not properly disposed of as stipulated in the Environmental Quality (Schedule Waste) Regulation 2005, Cu in this sludge will pollute the environment through entry by soil or waterways. Rivers are depositing sludge that is contaminated with Cu onto their banks and

the source of this contamination is from the Cu-containing wastewater of the industries. Cu will coagulate and flocculate in the sludge wastes and the high concentrations of Cu in sludge wastes compared to waste water samples are in agreement with the results of studies conducted by Subramanian et al. (2005); Venkateswaran et al. (2007) and Devandran (2007).
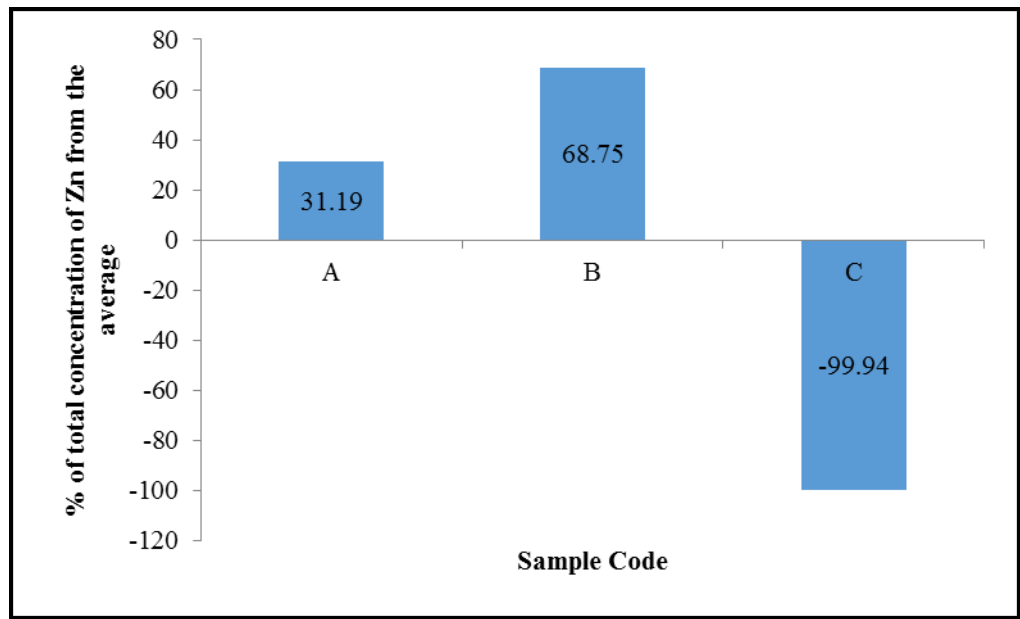

Figure 4.4 (e): Percentage (%) of total concentration of Zn in sludge samples from the average.

The results from Figure 4.4 (e) shown that the quantity of Zn found in sample A (31.2%) and B (68.8%) were higher than found in sample C. The higher content of Zn in these sludge samples can be explained by the fact that the sludge samples were collected from the WWTP from Zn plating industries, while sludge sample C was collected from the Ni plating industry. This proves that the type of industry involved and the raw materials used are an important factor that determines the type of waste generated.
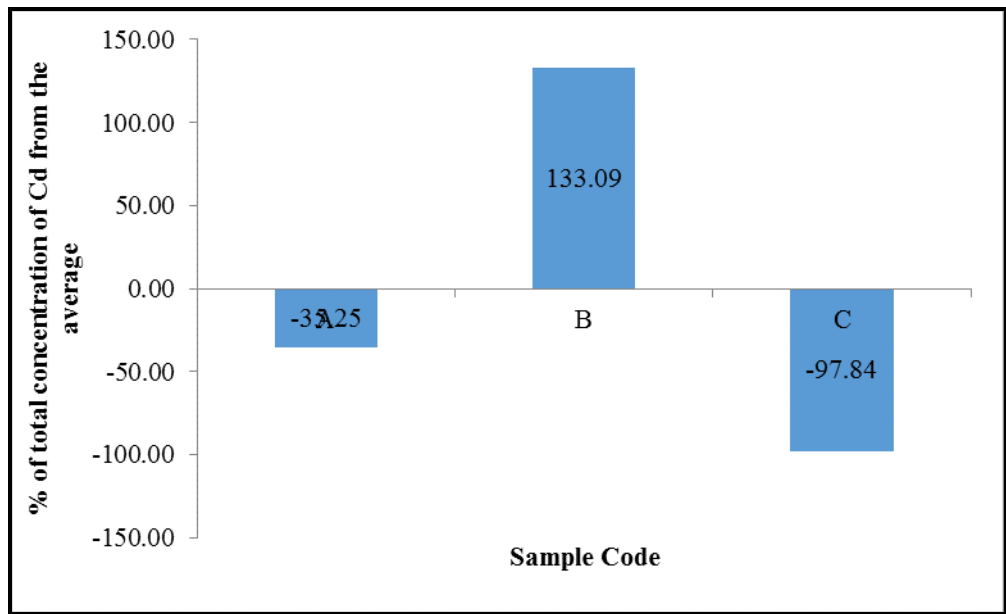
Figure 4.4 (f): Percentage (%) of total concentration of Cd in sludge samples from the average.
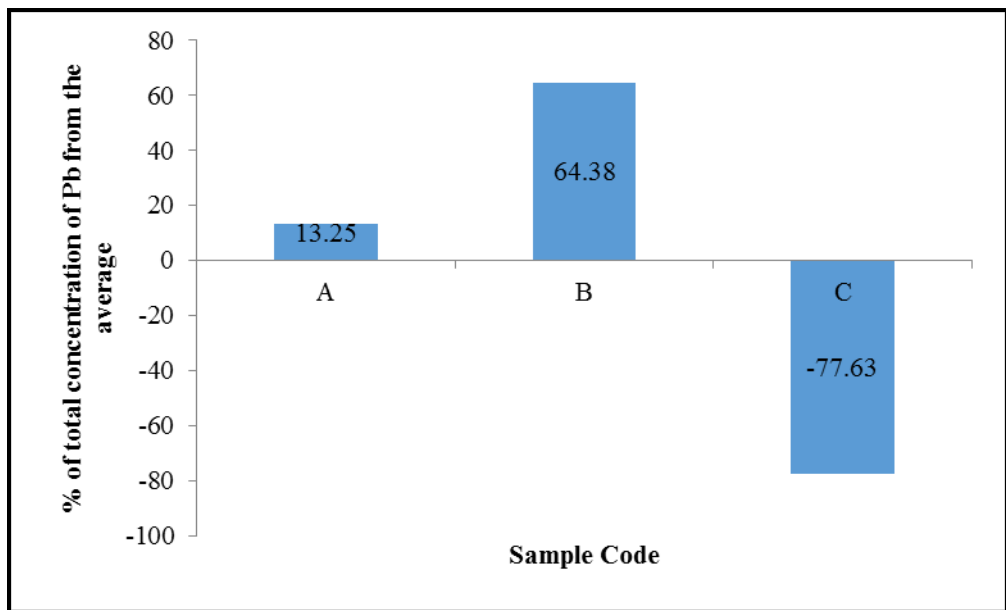

Figure 4.4 (g): Percentage (%) of total concentration of Pb in sludge samples from the average.

From the results illustrated in Figure 4.4 (f), concentration of total Cd in sample C shows 97.8% lower than sample A and B, as well as, Pb in sample C, indicated 77.6% lower than in sample A and B (Figure 4.4 (g)).

4.1.5   Percentage of total concentration of heavy metals in sludge samples

Figure 4.5 (a) to Figure 4.5 (g) show the percentage of total concentration for heavy metals from all the sludge samples. As shown in Figure 4.5 (a), the highest concentration of Zn was found in sample B with 56.25%, followed by sample A at 43.73% and sample C with the lowest amount of Zn at only 0.02% from the total concentration.
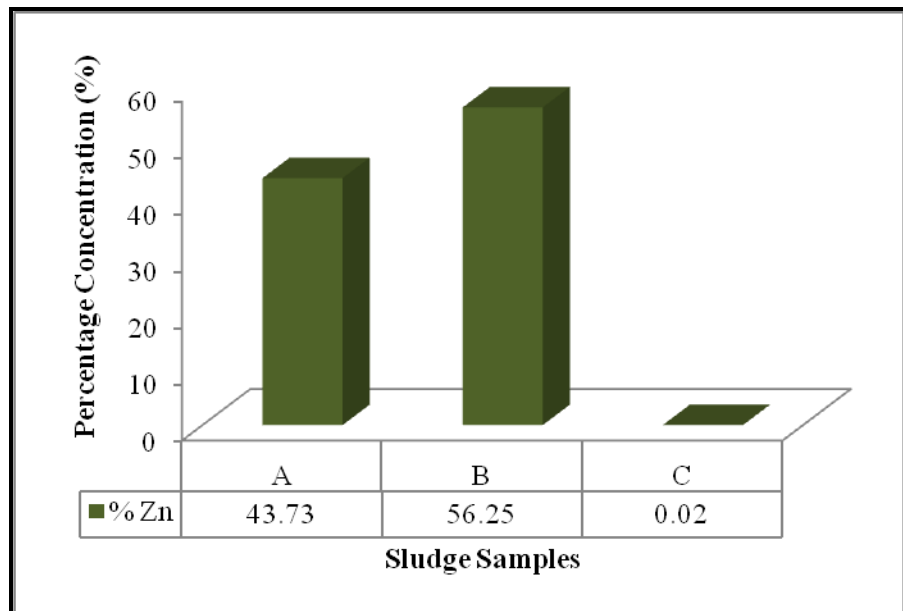

Figure 4.5 (a): Percentage of total concentration of Zn in sludge samples.

As observed in Figure 4.5 (b), the distribution of Fe also shows the same distribution pattern as Zn, with the highest concentration of Fe found in sample B at 49.21%, followed closely by sample A with 47.69% and sample C with only 3.10%.

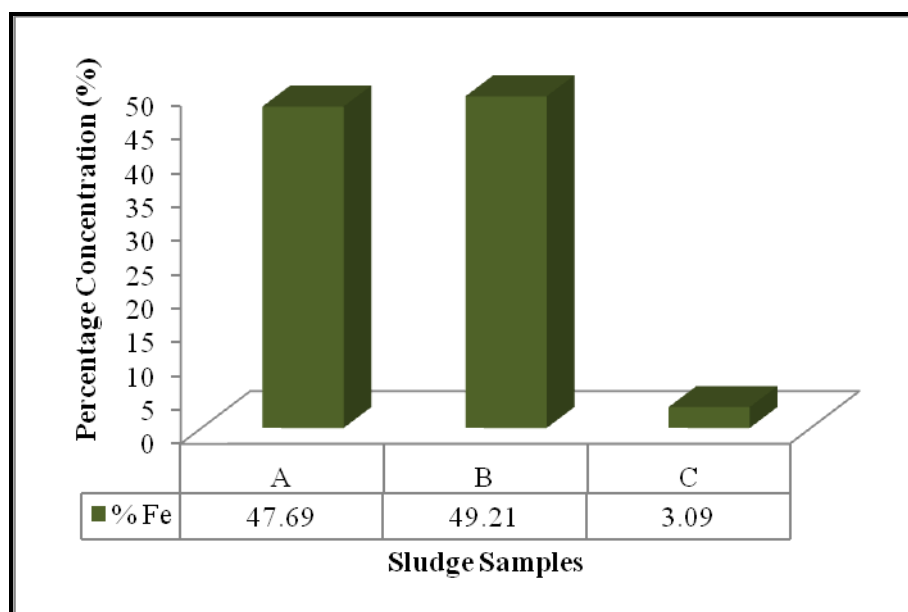Figure 4.5 (b): Percentage of total concentration of Fe in sludge samples.
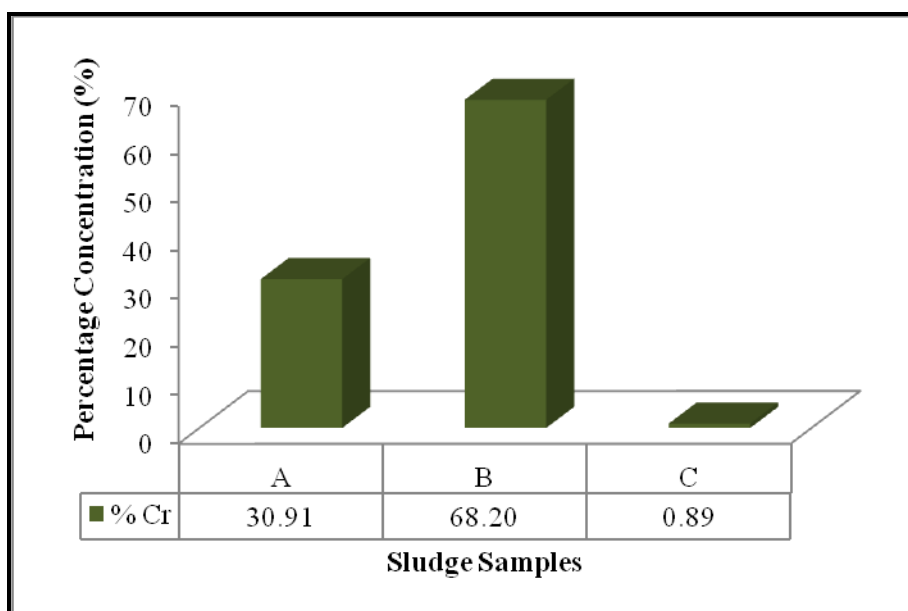

Figure 4.5 (c): Percentage of total concentration of Cr in sludge samples.

As shown in Figure 4.5 (c), the highest concentration of Cr is in sample B at 68.20% followed by sample A with 30.91% and sample C with only 0.89% from the total concentration. When Cr is present at low concentrations, it is an essential micronutrient for

both humans and animals but at high concentrations and when it is present as a chromate, it is known as a carcinogenic (Nancy, 1992).
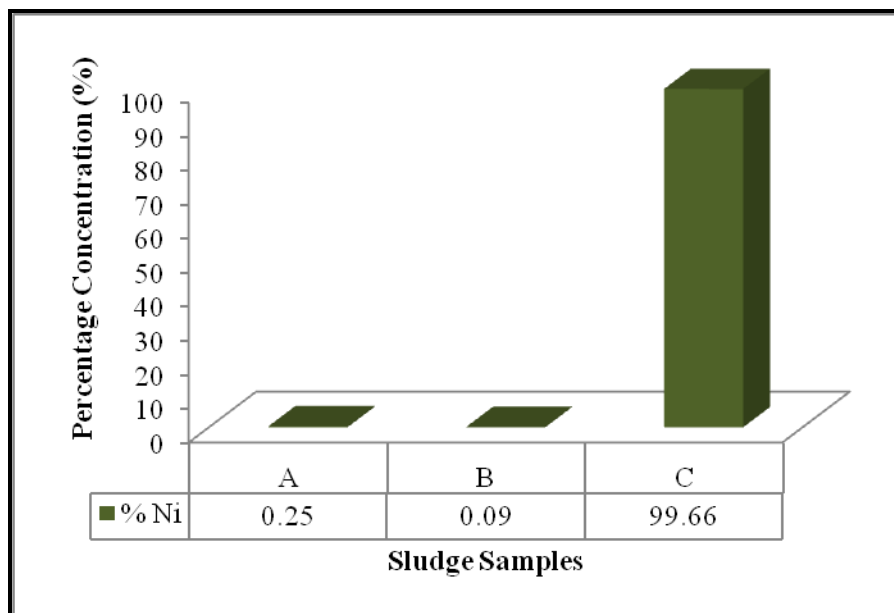
Figure 4.5 (d): Percentage of total concentration of Ni in sludge samples.

In contrast, from Figure 4.5 (d), Ni was most abundant in sample C with total percentage 99.66% followed by sample A with 0.25% and sample B only 0.09%. From Figure 4.5 (e), the highest concentration of Cu found in sample A at 88.15%, followed by sample C with 10.47% and sample C with only 1.38%. As shown in Figure 4.4 (f), the higher concentration of Cd found in sample B contributing 77.7% followed by sample A contributing 21.6% from total amount. Lowest content of Cd was found in sample C contributing only 0.7% from the total.
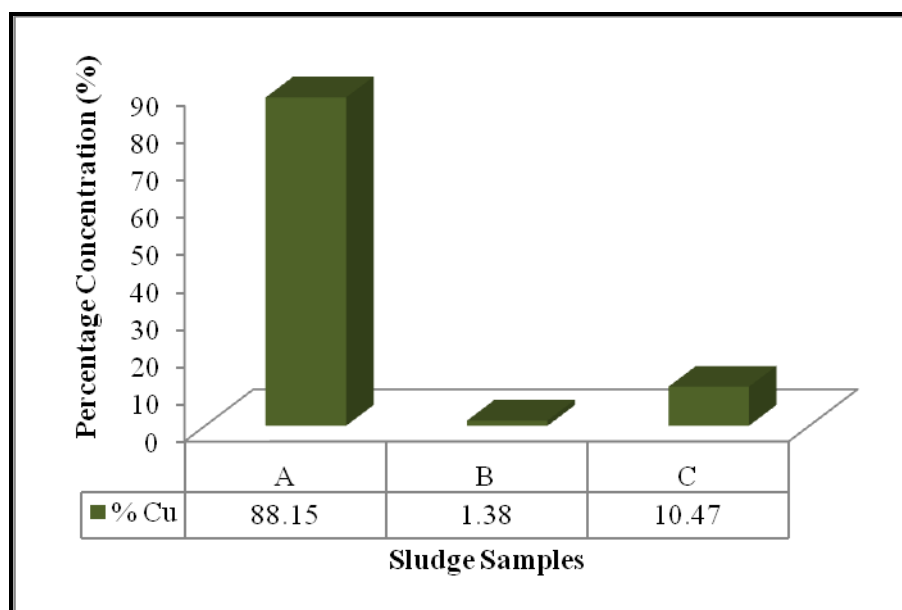
Figure 4.5 (e): Percentage of total concentration of Cu in sludge samples.

	A	B	C
■ % Cu	88.15	1.38	10.47

Figure 4.5 (f): Percentage of total concentration of Cd in sludge samples.

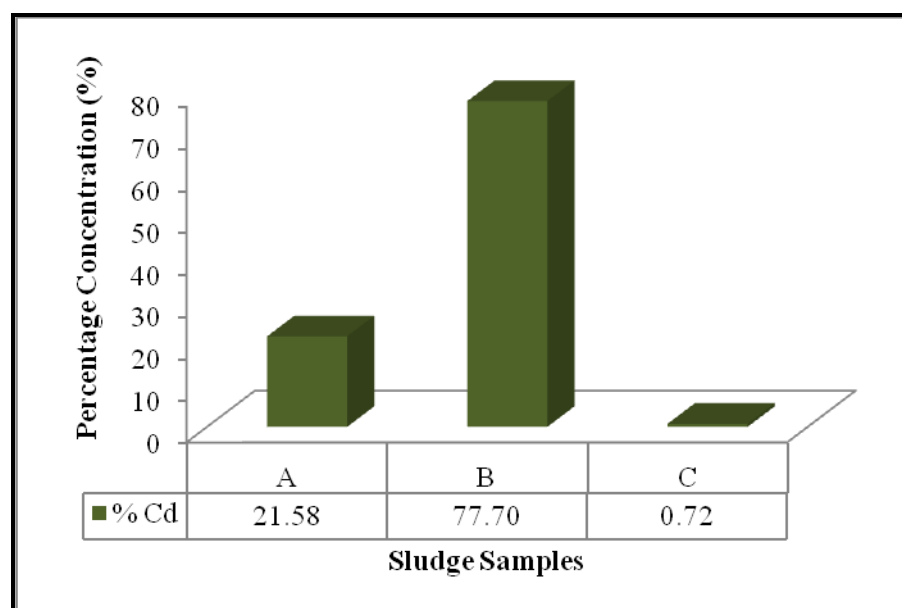|	A	B	C
■ % Cd	21.58	77.70	0.72
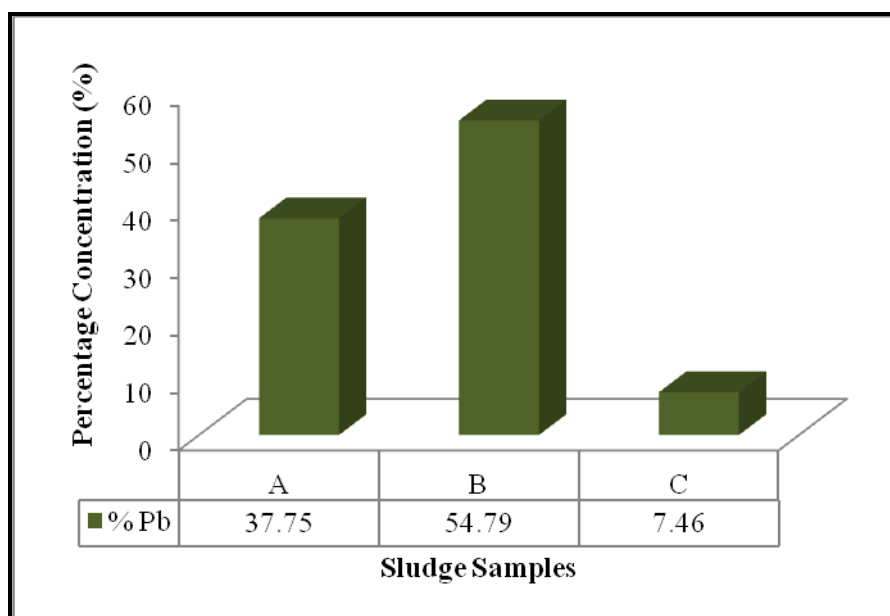
Figure 4.5 (g): Percentage of total concentration of Pb in sludge samples.

As observed in Figure 4.5 (g), the distribution of Pb also shows the same distribution pattern as Cd, with the highest concentration of Pb found in sample B at 54.79%, followed closely by sample A with 37.75% and sample C with 7.46%.

4.2   BCR sequential extraction procedure

Table 4.1 shows the results obtained after the application of the sequential extraction scheme proposed by BCR on all the sludge obtained (Please refer to Appendix D for the calculation of heavy metals studied using a sequential extraction technique). The bioavailability and mobility of heavy metals mainly depend on their speciation. The acid soluble/exchangeable fraction (F1) presents a high bioavailability and mobility of metals on the ground, while reducible fraction (F2) occupies second place regarding the mobility of the metals on the ground. It is because metals associated with this fraction are unstable under anoxic condition. The oxidizable fraction (F3) can be identified as a potential effect

Table 4.1: Metal contents extracted from each step of the BCR sequential extraction procedures and the sum of contents from each step.

Fraction	Sample Code	Cr	Fe	Ni	Cu
F1	A	337.79 ± 20.56	85.08 ± 8.22	9.71 ± 0.72	23.01 ± 3.80
	B	395.34 ± 21.85	43.20 ± 4.89	1.39 ± 0.07	0.67 ± 0.17
	C	19.01 ± 0.49	28.84 ± 0.42	4325.16 ± 116.54	3.91 ± 0.07
F2	A	51.94 ± 8.91	3689.84 ± 426.92	3.24 ± 1.46	10.15 ± 4.94
	B	60.92 ± 9.29	1272.95 ± 182.03	0.63 ± 0.12	0.51 ± 0.20
	C	8.48 ± 0.44	301.25 ± 10.42	1089.04 ± 52.68	5.36 ± 0.44
F3	A	5300.06 ± 115.58	28877.33 ± 1019.69	35.27 ± 1.24	551.83 ± 32.15
	B	9603.50 ± 369.71	8491.33 ± 420.97	7.69 ± 0.52	8.98 ± 1.49
	C	132.30 ± 4.50	236.43 ± 10.42	4603.30 ± 98.99	30.62 ± 0.54
F4	A	2765.38 ± 119.19	24837.51 ± 1074.63	3.15 ± 0.33	52.80 ± 9.82
	B	7677.21 ± 437.80	45987.35 ± 2388.31	6.73 ± 0.90	0.31 ± 0.23
	C	93.63 ± 0.97	3484.20 ± 47.97	7761.03 ± 146.19	42.26 ± 2.29
Total BCR Extraction	A	8455.17	57489.76	51.37	637.79
	B	17736.97	55794.83	16.44	10.47
	C	253.42	4050.72	17778.53	82.15

Results are expressed as the mean ± standard deviations.

Content unit is mg kg^{-1} dry sludge for all elements.

Table 4.1, continued: Metal contents extracted from each step of the BCR sequential extraction procedures and the sum of contents from each step.

Fraction	Sample Code	Zn	Cd	Pb
F1	A	54292.87 ± 1992.23	0.24 ± 0.09	0.70 ± 0.14
	B	44918.53 ± 1056.71	0.08 ± 0.00	0.77 ± 0.18
	C	8.75 ± 1.17	0.01 ± 0.00	1.27 ± 0.21
F2	A	15056.51 ± 2050.75	0.07 ± 0.04	9.24 ± 0.51
	B	11125.73 ± 2659.06	0.36 ± 0.08	8.74 ± 0.21
	C	6.73 ± 0.95	0.00 ± 0.00	1.28 ± 0.07
F3	A	62137.73 ± 925.35	0.00 ± 0.00	12.52 ± 1.09
	B	84896.56 ± 3041.37	0.55 ± 0.07	9.67 ± 0.31
	C	12.93 ± 1.34	0.00 ± 0.00	2.75 ± 0.18
F4	A	9878.81 ± 425.75	0.00 ± 0.00	16.18 ± 0.32
	B	27949.56 ± 1696.70	0.08 ± 0.00	32.02 ± 0.65
	C	29.85 ± 5.15	0.00 ± 0.00	2.34 ± 0.09
Total BCR Extraction	A	141365.92	0.31	38.64
	B	168890.38	1.07	51.2
	C	58.26	0.01	7.64

Results are expressed as the mean ± standard deviations.

Content unit is mg kg^{-1} dry sludge for all elements.

fraction under oxidizing condition. The heavy metals bound to the residual fraction (F4) can be identified as stable fraction because it's mainly contain primary and secondary minerals which may hold metals within their crystal structure.

From the table, Cr was determined in the highest concentration in F3 compared to the other fractions with total concentrations of 5,300.06 mg kg^{-1}, 9,603.50 mg kg^{-1} and 132.30 mg kg-^{1} for samples A, B and C respectively. In contrast, the highest proportion of Fe was determined in the F4 with concentrations of 24,837.51 mg kg^{-1}, 45,987.35 mg kg^{-1} and 3,484.20 mg kg^{-1} respectively for samples A, B and C. Distribution of Cd does not show a distinguishable pattern for the sludge samples and this is probably because of the low concentration of Cd found in the sludge samples.

Based on the data obtained from Table 4.1, the sum of the four fractions is reasonably similar to the total contents determined from the digestion of the original samples with aqua regia digestion method. A recovery study was also conducted to determine the accuracy of the method. The percent recovery of metals was examined with the summation of sequential fractions in relation to the total metals content. The recovery was obtained as follows:

$$\text{Recovery (\%)} = \{(F1 + F2 + F3 + F4) / \text{Pseudototal}\} \times 100$$

Source: Yuan et al. (2011).

The recovery values of heavy metals in the three samples are compared in Figure 4.6. From the study, it was determined that the BCR sequential extraction procedure shows very good recovery from 76.75% to 122.01%. This result is consistent with the study conducted by previous researchers (Davidson et al., 1998; Fuentes et al., 2004; Nemati (a) et al., 2009; Nemati (b) et al., 2009; Yu et al., 2010). The variation in the recovery of the

metals may be attributed to the difference in leaching time, chemical reagents used in the different steps and the total volume extractable (Venkateswaran et al., 2007; Chen et al., 2008; Nair et al., 2008; Nemati (b) et al., 2009).

	Cr	Fe	Ni	Cu	Zn	Cd	Pb
C	101.36	94.50	97.08	122.01	86.93	100.00	84.14
B	92.23	81.85	103.14	117.77	89.96	99.07	76.75
A	97.00	87.03	109.84	112.50	96.86	103.33	84.07
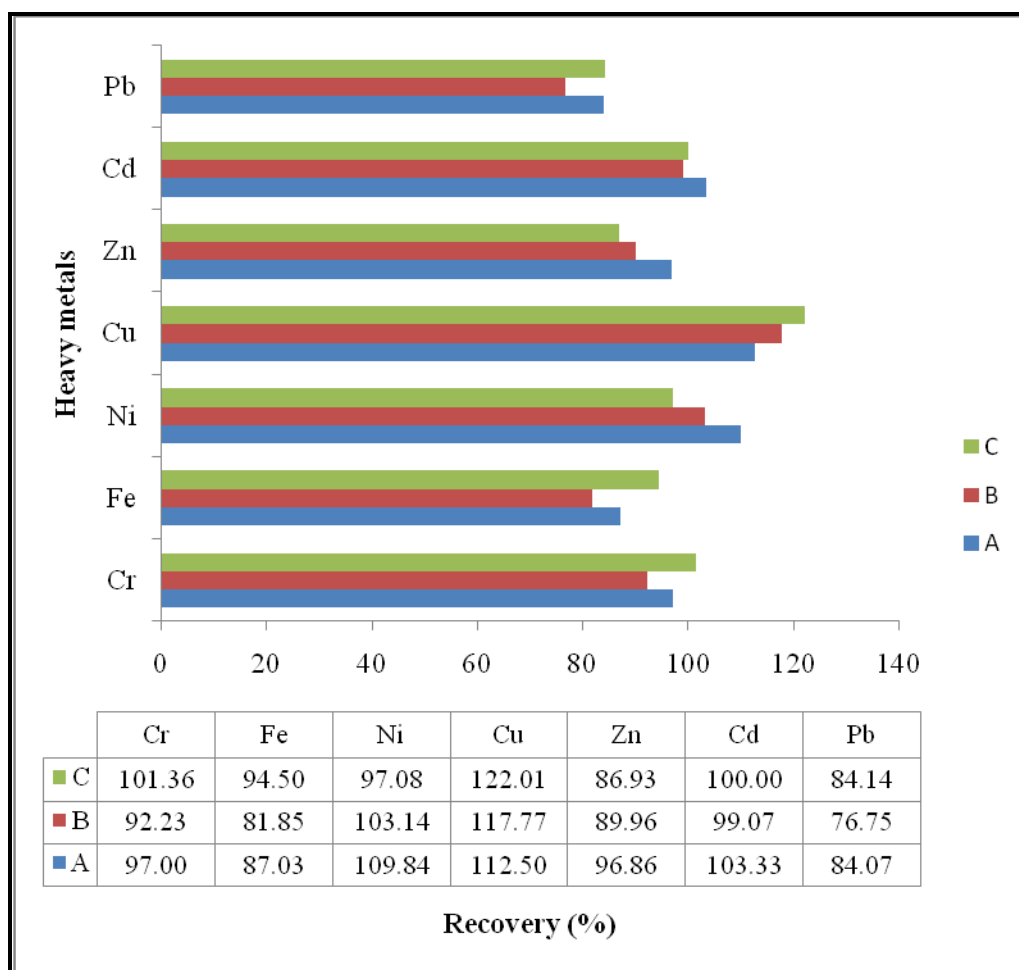
Figure 4.6: Percentage recovery (%) of the metals.

The result of this study provides valuable information on the potential mobility of the trace metals especially in the electroplating industrial sludge. With these findings, coupled with the knowledge on the potential of the migration and contamination of the heavy metals, a suitable treatment method of the wastewater can be developed for the removal of the metals or at the very least, the minimization of the amount of heavy metals

released into the sludge prior to disposal. This study determined that most of the heavy metals are associated with the F3 and F4 forms.

The total concentration of heavy metals was higher than the sum of the metal fraction from the extraction procedure for all the elements studied except for Ni and Cu. This can be attributed to the limitations of the sequential extraction procedures which include metal redistribution during the extraction process, extractability of the metals highly influenced by minor pH differences, as well as possible chemical overloading of the system.

4.2.1   The speciation and mobility of heavy metals in the electroplating sludge

The comparison of the percentage of the fraction (%) for samples A, B and C are demonstrated in Figure 4.7 (a), Figure 4.7 (b) and Figure 4.7 (c). It is shown that more than 80% of the Cr compounds were distributed in the last two fractions, F3 and F4. This is in agreement with previous studies which found that Cr is more likely to be found in the F3 fraction or considered as insoluble sulfide with the F4 fraction (Fuentes et al., 2004; Pan et al., 2009; Lasheen and Ammar, 2009).

Based on study done by Pan et al. (2009), metal sorption by natural organic matter is further reduced at lower pH than metal sorption on oxides. This shows that when metal is associated with organic matter (F3), it is more resistant to acid extraction than the metals associated with metal oxides (F2). In addition, Cr did not exceed 15% in the first two fractions (F1 and F2) in all the samples.

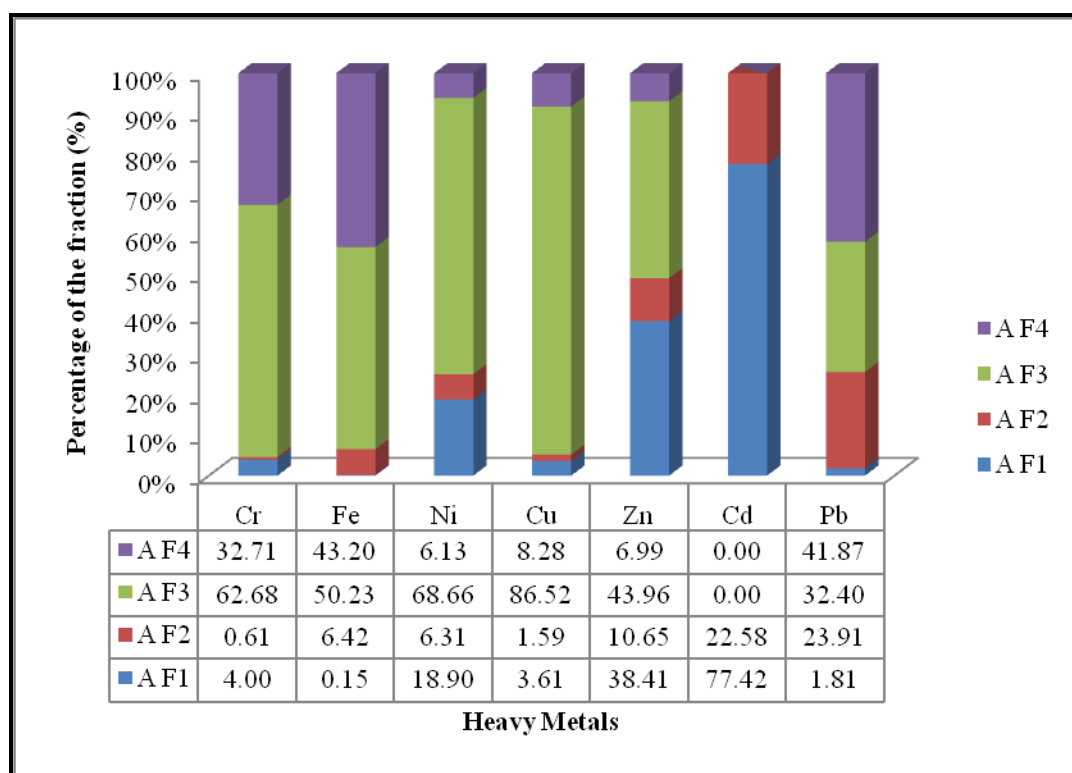| Heavy Metals	Cr	Fe	Ni	Cu	Zn	Cd	Pb
■ A F4	32.71	43.20	6.13	8.28	6.99	0.00	41.87
■ A F3	62.68	50.23	68.66	86.52	43.96	0.00	32.40
■ A F2	0.61	6.42	6.31	1.59	10.65	22.58	23.91
■ A F1	4.00	0.15	18.90	3.61	38.41	77.42	1.81

Figure 4.7 (a): Percentage (%) of the fraction for the sample A.

Yuan et al. (2011) reported that over 90% of Cr was in the last two fractions (F3 and F4). This proves that Cr has low mobility and availability in sludge. It may be because Cr strongly bound to the organic matter and sulphides. Therefore, during the treatment process, decomposition and conversion of organic materials could results Cr release from F3 and combine with a less extractible form in F4. The percentage of Cr in the fractions in all the sludge samples is in the following order: F3>F4>F1>F2 as shown in Table 4.2. This finding is slightly different from the study conducted by Venkateswaran et al. (2007).
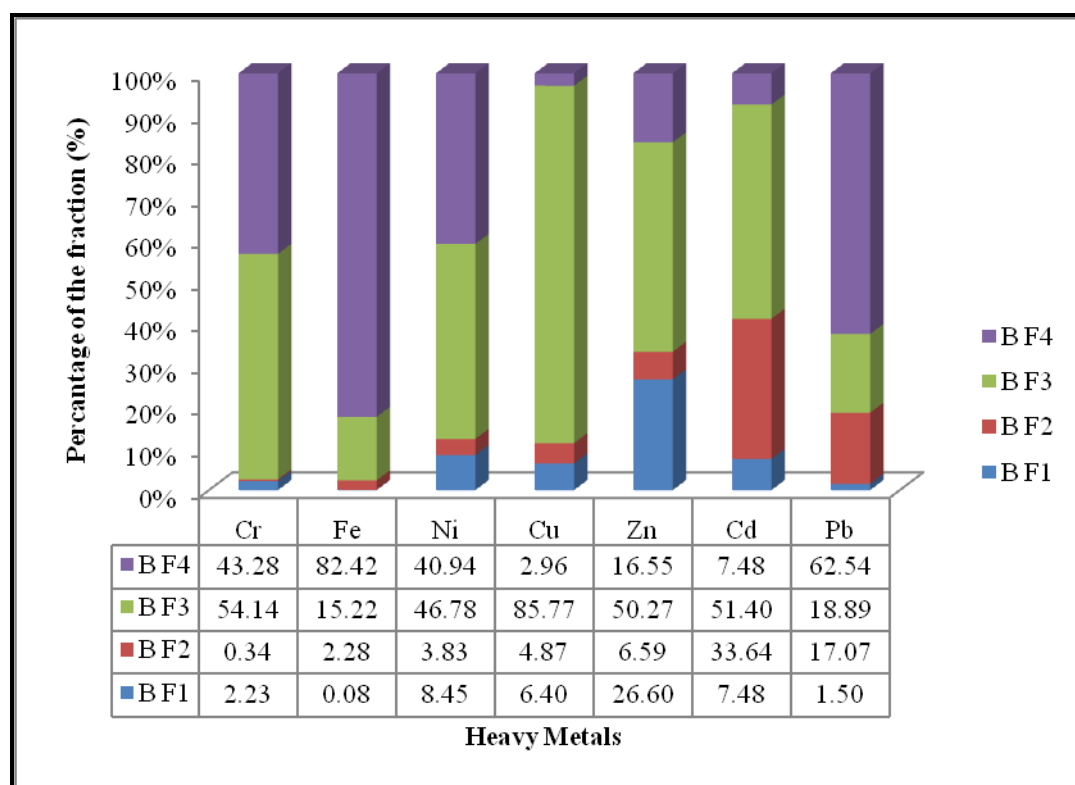
	Cr	Fe	Ni	Cu	Zn	Cd	Pb
■ B F4	43.28	82.42	40.94	2.96	16.55	7.48	62.54
■ B F3	54.14	15.22	46.78	85.77	50.27	51.40	18.89
■ B F2	0.34	2.28	3.83	4.87	6.59	33.64	17.07
■ B F1	2.23	0.08	8.45	6.40	26.60	7.48	1.50

Heavy Metals

Figure 4.7 (b): Percentage (%) of the fraction for the sample B.

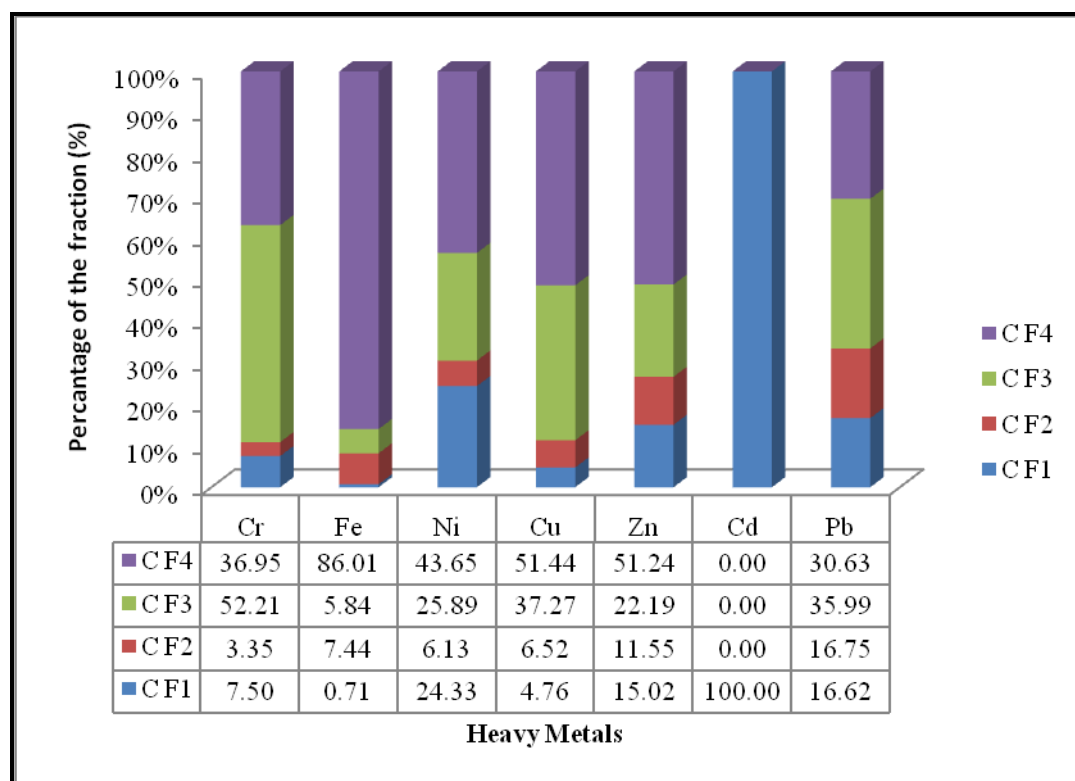|	Cr	Fe	Ni	Cu	Zn	Cd	Pb
■ C F4	36.95	86.01	43.65	51.44	51.24	0.00	30.63
■ C F3	52.21	5.84	25.89	37.27	22.19	0.00	35.99
■ C F2	3.35	7.44	6.13	6.52	11.55	0.00	16.75
■ C F1	7.50	0.71	24.33	4.76	15.02	100.00	16.62

Heavy Metals

Figure 4.7 (c): Percentage (%) of the fraction for the sample C.

Table 4.2: Mobility of elements based on fraction for samples A, B and C.

Sample Code	Elements	Mobility of elements based on fraction
A		F3>F4>F1>F2
B	Cr	F3>F4>F1>F2
C		F3>F4>F1>F2
A		F3>F4>F2>F1
B	Fe	F4>F3>F2>F1
C		F4>F2>F3>F1
A		F3>F1>F2>F4
B	Ni	F3>F4>F1>F2
C		F4>F3>F1>F2
A		F3>F4>F2>F1
B	Cu	F3>F1>F2>F4
C		F4>F3>F2>F1
A		F3>F1>F2>F4
B	Zn	F3>F1>F4>F2
C		F4>F3>F1>F2
A		F1>F2>F3=F4
B	Cd	F3>F2>F1>F4
C		F1>F2=F3=F4
A		F4>F3>F2>F1
B	Pb	F4>F3>F2>F1
C		F3>F4>F2>F1

F1: Ion exchange and acid dissolution

F2: Reduction reaction

F3: Oxidation reaction

F4: Residual

Although Fe is not a toxic heavy metal, it was also analyzed in the present study as it is extensively used in electroplating treatment plants for precipitation purposes and its presence was also determined in all the samples, 66,057.11 mg kg^{-1}, 68,164.34 mg kg^{-1} and 4,286.50 mg kg^{-1} for sample A, B and C respectively. It was found that Fe was mainly associated with the residual fraction (F4) which is consistent with the findings by several authors (Fuentes et al., 2004; Nemati et al., 2009; Lasheen and Ammar, 2009). The percentage of Fe in the F4 is 43.20%, 82.42% and 86.01% respectively for samples A, B and C. This fraction which is also known as the inert phase corresponds to the part of the metal which cannot be mobilized consequently.

The mobility and availability of Fe in the initial fraction especially in F1 is very low. It is because Fe is preferentially bound to F4 beside can form complexes with a wide range of size distribution of soluble organic matter particles, and thus almost not detected in the easily mobile forms. The percentage of Fe determined in this fraction was 0.15%, 0.08% and 0.71% respectively for samples A, B and C. The increasing order of percentage of iron in the fractions are F3>F4>F2>F1; F4>F3 >F2> F1 and F4>F2>F3> F1 for samples A, B and C correspondingly.

The distribution of Ni into the various fractions shows different patterns for each electroplating sludge sample. The total Ni concentrations found in sludge varies from a concentration of 15.9 to 18,312.5 mg kg-1. However, Ni was extracted in large quantities during the last two extraction steps with the sum percentage of F3 and F4 fractions at 74.79%, 87.72% and 69.54% for samples A, B and C respectively. It was found that in all samples, the lowest extraction of Ni was in the F2 fraction with 6.31%, 3.83% and 6.13% respectively in samples A, B and C. This finding is in agreement with the wide mobility of Ni which was also found by Fuentes et al. (2004) in heavy metals speciation of sludge. These result indicate that Ni have a strong association with the crystalline structure of

sludge, whereby Ni^{2+} has stability to form complex with organic ligands in the transition metal cation. The order of availability of Ni in the different fractions in samples A, B and C is F3>F1>F2> F4; F3>F4>F1> F2 and F4>F3>F1> F2.

A number of previous studies on the different kinds of sludge found that Cu is mainly associated with the oxidizable phase (Scancar et al., 2000; Wang et al., 2005; Choa et al., 2006; Chen et al., 2008; Lasheen and Ammar, 2009) and the speciation of Cu found was as organically complexed metal species (Gao et al., 2008). It's in agreement with the current finding. The Cu content found in the F1 and F2 fractions were low in samples A and C, especially for F1 fraction with less than 15%, as found by Nair et al. (2008); Nemati (a) et al. (2009) and Lu and Cheng (2011) in their studies. It is because Cu complexes have higher stability with organic matter which leads to its higher concentrations in the organic fraction. This shows that this element has less direct toxicity to the environment.

In addition, 85.8% to 86.5% from the total Cu present in F3 in samples A and B. This is because that Cu is associated with strong organic ligands and has the property of easily forming organic complexes (Donner at al., 2012) and sulfide copper (Fuentes et al., 2004; Lu and Cheng, 2011). It was also reported that Cu probably occluded in minerals like quartz and feldspars in soil, which are difficult to break down (Fuentes et al., 2004; Lu and Cheng, 2011). This behavior can also be explained by the well-known high affinity of Cu towards humic substances, which are a fraction of natural organic matter which are chemically very active in complexing such metals (Fytianos and Lourantou, 2003). The percentage of fraction Cu are in the order F3>F4>F2>F1; F3>F1>F2>F4 and F4>F3>F2>F1 for sample A, B and C respectively.

However, Cu-organic matter complexes are generally considered relatively stable and the percentage of Cu associated with organic matter fraction is primarily dependent on the quantity of Fe oxides in the soil (Yuan et al., 2011). The evaluation of the

bioavailability of metals to environment is essential to predict the metals behavior in response to changes in the environmental conditions. For example, if this sludge is dumped in an area with high amounts of Fe oxide in the soil, Cu in the F3 will be mobilized and available in this oxidizing condition. Therefore, the Cu in the sludge samples has a high potential for eco-toxicity and bioavailability in this type of soil. This result also indicates that Cu can be leached into the environment only under strong oxidizing conditions.

Zn is highly extracted in the F3 and F1 fractions; with the F3 having the highest percentage at 43.96% and 50.27% respectively for samples A and B. This proves that Zn has a high bioavailability and potential for eco-toxicity. The sum percentage of Zn in the two (F3 and F1) fractions is 82.37%, 76.87% and 37.21% respectively for samples A, B and C. This finding is also consistent with previous studies (Chen et al., 2008; Nemati (a) et al., 2009; Yuan et al., 2011) which mentioned that Zn was mainly associated with the potential mobile forms. Cation exchange and complexation by organic ligands were suggested to be the main Zn mobility controlling mechanisms (Singh et al, 2012). Nevertheless, the efficiency of the fraction may be reduced if the concentration of the metal is too high. Since the concentration of Zn is very high in the sludge samples, this indicates that the sequential extraction may be less effective with other fractionations, as reported by Venkateswaran et al. (2007). The increasing order of fraction of Zn in sludge samples are F3>F1>F2>F4; F3>F1>F4>F2 and F4>F3>F1>F2 for samples A, B and C correspondingly.

Cd is the least abundant metal in the plating wastes when compared to the other available metals. Table 4.1 shows Cd was not found in all the steps of the sequential extraction, but was predominant in the more easily mobilized forms especially for samples A and C. Table 4.2 shows the mobility of elements based on fraction for sample A, B and

C. The distribution of Cd into the various fractions does not show a distinguishable pattern for each of the samples.

It is shown in Figure 4.7 (a) and Figure 4.7 (c) that in the easily assailable fractions F1 and F2 fractions of samples A and C, a relatively high percentage of Cd was obtained for the samples with some of the Cd completely mobilized at 100%. However, in contrast to this, the Cd in sample B was mostly found in the F3 with a total concentration of 51.40% (Figure 4.7 (b)). Therefore, the fractionation of Cd in sludge is distributed in the various chemical forms without showing a definite pattern. The concentration of Cd in the sequential fractions for samples A, B and C are in the order of F1>F2> F3=F4; F3>F2>F1>F4 and F1>F2=F3= F4 respectively.

From the study, Pb was found to be primarily present in the F4 with percentages from 30.63% to 62.54% in the samples. According to Chen et al. (2008), Pb can be immobilized by insoluble salts, such as phosphates and it was also reported that the bioavailability of Pb was also limited by the organic matter of the soil. Therefore, the high concentration of Pb in the F4 poses less of a threat to the environment due to the low direct and potential bioavailability of the metal if this type of sludge was dumped in soil with high amounts of organic matter. The high stability of Pb complexes with organic matter and particularly with humic and fulvic acid as suggested by Stylianous et al. (2007) and Singh et al. (2012) explains the low eco-toxicity of Pb.

This significant concentrations of Pb in the residual fractions suggested that they may be from anthropogenic sources. According to Subramanian et al. (2005), in the urban environment the major sources of Pb are from the industrial processes such as battery manufacturing and petrol driven automobiles. Only a small fraction of Pb in samples A and B (1.81% and 1.50%) were present in F1 while the higher contribution of Pb at the F4 fraction is due to the precipitation of lead as stable compounds, as suggested by Singh et al.

(2012), slightly alkaline medium can reduce mobility Pb by forming Pb-organic matter complex. However, higher alkaline conditions can have a reverse effect on Pb stability due to the amphoteric nature of Pb. The fractionations of Pb in the various fractions are in the following order: F4>F3>F2>F1; F4>F3>F2> F1 and F3>F4>F2> F1 for samples A, B and C respectively.

The sequential results show that Cd was predominant in the F1 fraction which is the most easily assimilable fraction thus increasing the bioavailability of Cd to the environment. It was found that Cr, Ni, Cu and Zn were predominant in the F3 and though the metals are not considered mobile or bioavailable, their potential for eco-toxicity should not be ignored since under the right conditions, the metals could be transformed into the mobile species. It is because some organic bound heavy metals could be degrading under oxidizing conditions, leading to the release of heavy metals.

Fe and Pb were principally distributed in the F4 and the effect on the environment is inconsequential since the metals distributed in this fraction are unaffected by environmental changes. It's show that, the distribution and speciation of heavy metals mainly influenced by their total metal loading and trace metals competitions, beside total organic carbon content (Donner et al., 2012; Chakraborty et al., 2012), characteristic of the sludge such as mineral and particle composition and chemical or physical conditions such as pH (Lu et al., 2011; Singh et al., 2012).

The results of the speciation studies present clear evidence on the distribution pattern of the metals in the sludge samples into the different fractions of the sequential extraction. The knowledge of heavy metal speciation in soil, especially electroplating sludge is important for the understanding on the bioavailability and mobility of heavy metals in soil which provides valuable information for the proper disposal of this waste.

Reduction of heavy metals in industrial sludge can also be realized by the source control of industrial processes or by the extractive removal of metals from the sludge generated. Source control measures include control of the processes and materials used during production at the industries, as well as the removal and controlled disposal of any hazardous constituents which may be present in the wastewater before contamination of the water stream and proper pretreatment of the waste before discharge.

The concern on the presence of heavy metals in the environment is due to its non-biodegradability, toxicity and consequent persistence which could lead to serious and irreparable damage to nature. Working together with the authorities, waste generators play an important role in the preservation of the environment by ensuring that the heavy metal content in the sludge released is within the limits as stipulated in the Environmental Quality (Scheduled Wastes) Regulation 2005.

CHAPTER FIVE

CONCLUSIONS

In this study, the objectives have been successfully achieved. This research had successfully characterized and determined the content of the heavy metals in the electroplating industry sludges. The main metals found in the samples are Cr, Fe, Ni and Zn compared to Cu, Cd and Pb. The concentration of metals in these three samples were in the following order, in this study; Zn>Ni>Fe>Cr>Cu>Pb>Cd.

The bioavailability and mobility of heavy metals mainly depend on their speciation in sludge samples. In the case of mobility potential, Cr and Cu were mainly distributed in the oxidizable fraction (F3). Fe and Pb were extracted to be higher in residue fraction (F4). Cd, Zn and Ni were found frequently in acid soluble/exchangeable fraction (F1), showed relatively high mobility potential compared to other metals. Due to the higher total concentration of Zn and Ni concentration and its high mobility, the investigated sludge should be disposed in landfill after stabilization to prevent the leaching of metals.

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APPENDICES