REMOVAL OF HEAVY METALS IN ANAEROBICALLY DIGESTED SEWAGE SLUDGE FROM KARIOBANGI SEWAGE TREATMENT WORKS USING CITRIC ACID AND CHEMICAL OXIDATION

BY

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DECLARATION

DECLARATION BY THE CANDIDATE:

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DEDICATION

To my wife and sons who are special gifts bestowed on to me by the almighty God in addition to knowledge and intellect.

ABSTRACT

Sewage sludge from municipal wastewater treatment plants has high content of organic matter and substantial N, P and K concentrations that suggest its use preferentially as a fertilizer in agriculture however the presence of heavy metals in the sludges restricts their use. In this connection the objective of this study was to characterise and chemically extract heavy metals in anaerobically digested sewage sludge from Kariobangi Sewerage Treatment Works in Nairobi. In addition, the study sort to determine the optimal values of pH, Hydrogen Peroxide dosage and extraction time for effective heavy metals extraction. Using the full factorial design with three factors at two levels, the chemical extraction was undertaken with the help of Citric acid and Hydrogen peroxide. The two levels considered were: pH (3.0 and 5.0), hydrogen peroxide dosage (1g/l and 5g/l), and extraction time (1day and 10 days). The results were analyzed statistically using the Student's t-test, analysis of variance, F-test, and lack of fit to define the most important process variables affecting the heavy metal removal efficiency. The results revealed that the sewage sludge had high amounts of N, P and K in addition to heavy metals of which the concentrations of Lead and Zinc were higher than the National Environment Management Authority maximum allowable values. The Student's t-test, analysis of variance and F-test revealed that for heavy metals Zn, Pb, Ni and Cu the most significant effect was extraction time followed by Hydrogen peroxide dosage and the interaction of the two. The pH effect and the interaction between pH and time also had an influence in removal efficiency of the heavy metals. There was no significant interaction between pH and Hydrogen peroxide dosage in the extraction of heavy metals under the tested conditions. The optimal conditions of heavy metals Zn, Pb, Ni and Cu extraction obtained using response surface methodology from anaerobically digested sewage sludge were pH value of 3, extraction time of 10 days and Hydrogen peroxide dosage of 1g/l. The percentage extraction at these conditions was Zn (98.4%), Pb (98.8%), Ni (98.6%) and Cu (98.2%). This percentage extraction reduced the heavy metals concentration to below the National Environment Management Authority maximum allowable values. Chemical oxidation with Citric acid acidification was found to bean excellent heavy metals extraction method and sewage treatment plants should consider applying it in their anaerobic treatment processes.

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LIST OF ABBREVIATIONS

PAHs : Poly-nuclear aromatic hydrocarbons

PCBs : Alkyl phenols, polychlorinated biphenyls

NTA : Nitrilotriacetic acid

MAD : Mesophilic Anaerobic Digestion

BOD : Biochemical Oxygen Demand.

AAS : Atomic absorption spectroscopy

HMs : Heavy metals

SS : Sewage sludge

KSTW : Kariobangi Sewerage Treatment Works

ORP : Oxidation-Reduction Potential

g : Grams

ml : Milliters

pH : power of hydrogen

NEMA : National Environment Management Authority

ANOVA :Analysis Of Variance

GoK :Government of Kenya

DEFINITION OF TERMS

Bio-accumulation:	This is the accumulation of substances, such as pesticides, or other organic chemicals in an organism.
Speciation:	Studying the dissipation of heavy metals
Chelate:	A compound formed from complexing of cations with organic compounds resulting in a ring structure
Chelation:	This is the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom**.**
Ligands :	These are organic compounds that are called chelants, chelators, chelating agents, or sequestering agents.
Sewage Sludge:	The solid material removed during the municipal treatment works of wastewaters.
Waste water:	Any water that has been adversely affected in quality by anthropogenic influence.
Sewage :	The subset of wastewater that is contaminated with feaces or urine; waste matter or excrement carried away in sewers
Heavy metals:	Metals which, in their standard state, have a specific gravity (density) of more than about 5 g/cm^3.
Biodegradable:	Ability of a material can be broken down, in a reasonable amount of time, into its base compounds by micro-organisms and other living things, regardless of what those compounds may be.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Municipal wastewater treatment plants produce large amounts of sewage sludge containing high quantities of nutrients and organic matter responsible for plant growth. The sewage sludge may also contain high heavy metal concentrations. Heavy metals can accumulate in soil and in plants when sludge is applied as fertilizer. The potential accumulation of heavy metals in human tissues and biomagnification through the food-chain create both human health problems and environmental impacts (Alvarez et al., 2002). Heavy metals are harmful to both human and animals (Stephanie et al., 2001). They can be present in soluble form in the aqueous solution over a wide range of pH values and quite mobile in the natural environment (Baek and Yang, 2004). Currently, methods such as membrane filtration, ion exchange, reverse osmosis and electrochemical extraction used for heavy metal removal from sewage sludge exist but are quite expensive (Zouboulis et al., 2008). Therefore, efforts have to be directed toward finding strategies that are less expensive.

According to Ku and Jung (2001) chemical precipitation is an effective and the most widely used process in industry to remove heavy metals from waste water, because it is relatively simple and inexpensive to operate In the precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The formed precipitates can be separated from the water by sedimentation or filtration. The treated water is then decanted and appropriately discharged or reused. The application of chemical extraction as a part of the treatment is a feasible option, especially when it is applied as a pre-treatment aiming at heavy metals removal from sewage sludge. Once they are soluble, heavy metals can be precipitated again and further be removed by a physical separation, e.g. flotation (Veeken, and Hamelers, 1999).

The extractive yield of Heavy metals in sludge depend on the kind and concentration of acids used (Ukiwe and Oguzie, 2008). According to Seleem et al. (2011) organic acids such as Citric and Oxalic acids are promising chemical extracting agents for removal of heavy metals from contaminated sludge, since they are biodegradable and can attain a higher metal extraction efficiency at mildly acidic pH compared to other extracting agents.

In this work, investigation was carried out in the Eldoret University Analytical Chemistry Laboratories to test the effect of pH, time and chemical oxidation on the efficiency of heavy metal extraction using Citric acid.

1.2 Problem statement

Sewage sludge containing high concentrations of heavy metals is being disposed by land application in Kenya. In the soil the heavy metals increase their mobility and become easily absorbed by plants. This results in bio-accumulation of heavy metals in plants increasing their ingestion by animals and human beings causing health problems (Kaara, 2012).

1.3 Justification of the study

In Kenya municipal waste water treatment plants produce huge amounts of sewage sludge containing heavy metals. There is need to dispose the sewage sludge safely and economically. There is therefore a need for sustainable and environmentally sound method for sewage sludge disposal. Removal of heavy metals in sewage sludge before land application will be necessary to prevent bioaccumulation of heavy metals in plants which cause subsequent ingestion by humans leading to health problems. The current methods of heavy metals removal from sewage sludge are expensive therefore there is need for alternative technologies and methods that are cost-effective and environmentally acceptable hence the need of this study.

1.4 OBJECTIVES

1.4.1 General objective

To study the efficiency of extraction of heavy metals from anaerobically digested sewage sludge using commercial Citric acid.

1.4.2 Specific objectives

i. To characterize anaerobically digested sewage sludge.

ii. To determine the optimal pH, hydrogen peroxide dosage and extraction time for effective heavy metal removal from sewage sludge.

iii. To determine the heavy metal extraction efficiency from sewage sludge using Citric acid at optimum conditions of pH, Hydrogen peroxide dosage and extraction time.

1.5. Scope of the study

This research was limited to analysis of anaerobically digested sewage sludge from Kariobangi sewage treatment works in Nairobi, Kenya. The experiments and analysis were carried in Eldoret University analytical chemistry laboratories. The chemical leaching process was applied to assess the mobilization of heavy metals present in the anaerobically digested sewage sludge. In addition the possibility of using chemical leaching as an applicable part of the treatment aiming at heavy metals removal from sewage sludge was investigated. In this way Citric acid extraction efficiency was tested at different conditions of pH, leaching time, and chemical oxidation using Hydrogen peroxide. The effect of acidification was tested for dried and crushed anaerobically digested sewage sludge samples.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. Wastewater treatment in Kenya.

According to an assessment report carried out in 2009, there are 43 sewerage systems in Kenya and waste water treatment plants in 15 towns (total population served: 900,000 inhabitants), (WASREB, 2009). Kenya has a mixed sewer system which receives domestic sewage, industrial effluent and surface runoff. This increases the possibility of having heavy metal contamination in the sewage sludge. One of these waste water treatment plants is Kariobangi sewage treatment works (KSTW**)** in Nairobi, which treats sewage sludge through anaerobic digestion.

2.1.1. Sewage sludge

Sewage Sludge is the solid material removed during the treatment of municipal wastewaters (Ronald et al., 2008). Most wastewater treatment processes produce a sludge which has to be disposed off. Bio-solids refer to the solid organic matter recovered from a sewage treatment process and used especially as fertilizer. Biosolids includes excreta, faecal matter, and septage that has been treated and tested and is appropriate for use as fertilizer and/or soil amendment. (Ronald et al., 2008). The distinction between untreated sewage sludge and biosolids is that biosolids have undergone processing during treatment (Harrison & Oakes, 2002). Conventional secondary sewage treatment plants as shown in Figure A11 (appendix 11) typically generate a primary sludge in the primary sedimentation stage of treatment and a secondary sludge in final sedimentation after the digestion process. The characteristics of the secondary sludge vary with the type of digestion process and, often, it is mixed with primary sludge before treatment and disposal. As shown in

Table A6 (Appendix 6), approximately one half of the costs of operating secondary sewage treatment plants can be associated with sludge treatment and disposal. Land application of treated sewage sludge can reduce significantly the sludge disposal cost component of sewage treatment as well as providing a large part of the nitrogen and phosphorus requirements of many crops. The disposal of sewage sludge on soils as a fertilizer or as a regenerative agent for soil is the most attractive application to reutilize the nutrients for crop production owing to sludges' high content of organic matter (Wong and Su, 1996; Zufiaurre et al., 1998; Wong et al., 2001).Very rarely do urban sewerage systems transport only domestic sewage to treatment plants; industrial effluents and storm-water runoff from roads and other paved areas are frequently discharged into sewers. Thus sewage sludge will contain, in addition to organic waste material, traces of many pollutants used in our modern society.

2.1.2. Processing of sewage sludge

Increasing urbanization and industrialization have resulted in a dramatic increase in the volume of waste water produced around the world. The wastewater treatment step concentrates the various pollutants (up to 90%) in the waste water into sludge, normally containing between 1% and 2% by weight dry solids (Wasim and Sengupta, 2008). Prior to disposal options, biosolids stabilisation is of major importance because it must be non-hazardous to humans, biologically inactive, free of offensive odours and aesthetically acceptable (Wasim and Sengupta, 2008).

2.2. Sludge stabilisation

The stabilisation of sewage sludge is done to reduce the undesirable characters such as volatile solids biologically and chemically, pathogen levels, and odour (Lucero, 2000). The technologies for sludge stabilisation include: alkaline stabilisation, thermal drying, composting, aerobic digestion and anaerobic digestion (Nilsson, 2005).

2.2.1. Alkaline Stabilisation

This is where enough lime, about 30% of the dry solid content, is added in order to ensure that no fermentation takes place. According to European Commission (2001) alkaline stabilisation takes advantage of the fact that all biological activity is effectively terminated when the pH rises above 12. Pathogenic micro-organisms are killed effectively during liming, the content of dry solids increases and the handling of the sludge become easier. Also, the lime binds phosphates and heavy metals very securely. Lindquist (2003) observed that when quicklime is added after dewatering, a sharp temperature rise occurs and the high temperature pasteurises the sludge. If quicklime instead is added before dewatering it results in a sludge that is odourless and has much better dewatering characteristics.

2.2.2. Thermal drying

This is a process where heat is transferred directly or indirectly to the sludge to achieve stabilisation and hygienisation when the dry solids content exceeds 90%. This results in the elimination of interstitial water and reduction of sludge volume. At direct transfer, hot gas is used and two important methods are the rotating drum dryer and the fluidised bed dryer. A heat transfer surface is used and the heat is transferred via heat conduction (European Commission, 2001). The drying takes place at different temperatures and if higher temperatures are used (above 300°C) it is important to control it so that no dioxins or furan compounds have been formed. A dry matter content of 35 to 90% is reached and re-growth of pathogens is inhibited mainly due to the reduced water content, (European Commission, 2001). The reduction of pathogens also takes place due to the high temperature (Nilsson, 2005).

2.2.3. Composting

Composting is a biological process in which microorganisms convert organic matter into stabilised, humus like substance (Barker, 1997). Many of the organic materials used for composting are inappropriate in their raw form for use on land or around living organisms because of the presence of odours, weed seeds, human pathogens, and storage and handling constraints. Composting helps to break down organic residues, stabilize nutrients, destroy weed seeds, and control possible toxins or diseases (Barker, 1997). The resulting compost has numerous horticultural and agronomic benefits and is environmentally safe for use on soils around plants, humans, and animals (Barker, 1997). Another advantage is that the final product has little or no odour. In addition to being cheap and simple to use this method substantially reduces greenhouse gas emissions such as methane (Ronald et al., 2008).

2.2.4. Aerobic digestion

This is a process where the sludge is placed in an aerated vessel. The decomposition is performed by aerobic micro-organisms and this generates heat. If the process is working adequately, over 70°C can be reached. Usually the sludge is subjected to 50 to 65°C for 5 to 6 days and most of the harmful organisms are destroyed. One drawback, however is that the energy costs are 5 to 10 times higher than for anaerobic digestion (European Commission, 2001).

2.2.5. Anaerobic digestion

Anaerobic digestion is a sequential process by which organic materials in sludges are fermented by a mixture of fermentative, acetogenic and methanogenic bacteria in the absence of free oxygen to gaseous end products such as methane and carbon dioxide (Dohanyos and Zabranska, 2001; Lucero-Ramirez, 2000). Both mesophilic temperatures (30-38^{o}C) and thermophilic temperatures (50-60^{o}C) are used during the process. The advantage of anaerobic digestion is that the final product is a stable sludge that can be used as a fertilizer in which the pathogen level, the volatile solid content, odour and the volume of sludge are significantly reduced (Dohanyos and Zabranska, 2001; Epstein, 2003). In addition, the biogas produced can be utilised to produce electricity or for heating and lighting purpose (Nilsson, 2002). The major disadvantage is that pathogens reduction during digestion may be achieved partially and to which extent depends on the temperature and retention times used (European Commission, 2001). The widespread use of anaerobic digestion in the treatment of sewage sludges in recent years underlines the importance of investigations in the field of heavy metals removal from anaerobically digested sludges (Marchioretto et al., 2002). Based on these findings and advantages, this research study was based on anaerobically digested sewage sludge.

2.3. Disposal Methods

Considering the huge amount of sewage sludge produced annually, there is a general agreement that long-term goal should be to assess the beneficial use of sewage sludges. Basic options for bio-solids utilization and sludge disposal are land-filling, incineration and application to the land (Marinos et al., 2006).

2.3.1. Land filling

Land filling is where de-watered digested sludge from drying beds and vacuum filters is disposed off by filling low areas, holes at the plant site or in well-designed land fills (Marinos et al., 2006). Land filling is especially useful if there is public concern about incineration or recycling of biosolids to soils and where there is limited land for spreading. Modern landfills are expensive to build and in developed countries, landfill space is becoming more expensive as regulations make siting and operations more costly. As a result this method is becoming less applicable (Ronald et al., 2008).

2.3.2. Incineration

This is where dewatered and/dried sewage sludge is burnt to produce carbon dioxide, water, and ash (Ronald et al., 2008). Incineration greatly reduces the volume of excreta and waste water sludge by rapidly oxidizing the organic matter and it can take advantage of the energy in these materials. Incineration, however, requires a large capital investment in infrastructure and requires fuel (usually fossil fuel) to create the burn. Incinerators in more developed countries are subject to increasingly strict air pollution control standards, which require increased complexity and costs and hence it is not a popular sewage sludge disposal method (Ronald et al., 2008).

2.3.3. Application on the Land

There is an increasing interest in the agricultural application of sludges obtained in waste-water treatment plants, due to the possibility of recycling valuable components: organic matter, Nitrogen, Phosphorous and other plant nutrients (Marchioretto et al., 2002). Programs for utilizing sludge on agricultural land include; application on a farm which grows grain and fodder crops, trees for timber production, land reclamation e.g. mines can be reclaimed by depositing sewage sludge, growth of grass and other herbs and growing ornamental crops in buildings (Epstein, 2003). This is consistent with an overall view that in terms of global environment protection that every effort should be made to use all waste in preference to unproductive disposal (Ronald et al., 2008). According to Gudmundur, (1999) utilizing sludge on agricultural land has several benefits that include; valuable agricultural nutrients like Nitrogen, Phosphorus and Potassium can be returned to the land, soil organic matter levels can be increased to 12% – 15%, ground water and surface water quality are maintained, decrease bulk density and increase the non-capillary pore space in soil, improvement of the aggregation of soil particles, reduction in leaching of soluble nitrogen, increasing the buffer capacity of soil, improving soil structure and improving moisture holding capacity of soil. The only limitation is the presence of heavy metals which can limit the use of sewage sludge for agricultural purpose (Alvarez et al., 2002).

2.4. Characterisation of sewage sludge

Sludge characterisation involves description of sludge behaviour in treatment processes and disposal (Marchioretto et al., 2002). According to Gudmundur (1999), appropriate characterisation methods facilitate understanding and prediction of sludge properties. The nature of the sewage sludge depends on the waste water treatment process and on the source of the sewage. Kenya has a mixed sewer system which receives both domestic sewage and industrial effluent. It is a requirement that all industrial waste waters must be pre-treated before being discharged into the municipal sewer systems and lack of adherence is punishable by law (GoK, 2006). However, the enforcement of various legislations has been lacking (WASREB, 2009). Because of this sewage sludge in Kenya contains both toxic and non-toxic organic wastes.

When material is evaluated for its fertilizer value, total quantity of plant nutrients is of interest (Gudmundur, 1999). Gudmundur (1999) further explains that the plant nutrients of interest are Nitrogen, Phosphorous, Potassium and organic matter. Marinos et al. (2006), highlighted that the quantity of toxic compounds such as heavy metals present should be established because they would limit the use of sewage sludge as a fertiliser.

2.4.1. Nutrient content of sewage sludge

Plant nutrients are among the most important chemical characteristics of biosolids. Farmers value biosolids for the Nitrogen (N) and Phosphorus (P) content (Epstein, 2003). Sewage sludge contains considerable amounts of organic matter, Nitrogen, Potassium and Phosphorus and has significant inorganic fertilizer replacement value for these major plant nutrients (Gudmundur, 1999).

2.4.1.1. Nitrogen

Nitrogen is a macro-nutrient essential in protein and chlorophyll formation. The average Nitrogen content of sewage sludge is around 3.8%, which includes Ammonium, Nitrate and organic forms Seleem et al., (2011). Amounts of each form depend mostly on the extent of treatment, which can alter the forms drastically (Gudmundur, 1999). Gudmundur (1999) further reported that 50-90% of total N could be in organic form, depending on the solids content of the sludge and that a major portion of the organic form was hydrolysable. According to Marchioretto et al.

(2002), the Nitrogen content of anaerobically digested sewage sludge was 71.6g/kg dry matter. Seleem et al. (2011) concluded that the Nitrogen content of anaerobically digested sewage sludge was range between 10.5 and 28.9g/kg dry matter hence having the potential to be used as an organic fertilizer. The fertilizer value of Nitrogen from sewage sludge is variable depending on sludge treatment and soi1 environment. Factors affecting utilization of Nitrogen in soils are temperature, rainfall, immobilization, and ammonia volatilization or denitrification processes (Gudmundur, 1999).

2.4.1.2. Phosphorus

Phosphorus is a limited non-renewable resource, which is indispensable as an essential nutrient for the growth of organisms in most ecosystems, and can be replaced by other elements (Biswas et al., 2009). Phosphorus stimulates root growth and therefore rapid initial plant growth. The demand for phosphorus fertilizer alone increased with the increase in the world's population from $9x10^6$ to $40x10^6$ metric tons between 1960 and 2000 and is expected to increase further to $20x10^6$ metric tons by 2030 (Biswas et al., 2009). In developed countries, annual Phosphorous discharge into sewage systems is about 1 kg per capita, largely from detergents (Gudmundur, 1999). Gudmundur (1999) highlighted that with conventional treatment of sewage, up to 90% of Phosphorous in the treated effluent is removed and ends up in the sludge. According to Marchioretto et al. (2002), reported that the Phosphorous content of anaerobically digested sewage sludge was 25.5g/kg dry matter. Forms of Phosphorous in anaerobically digested sludge, which have undergone tertiary treatment, are mostly inorganic (70%) and the remainder (30%) is in an organic form (Gudmundur, 1999).

2.4.1.3. Potassium

Potassium is a macro-nutrient essential that increases viguor and disease resistance in plants in addition to increasing taste, size and keeping quality of fruits. According to Marchioretto et al. (2002), the Potassium content of anaerobically digested sewage sludge was between 5.8 and 7g/kg dry matter while Seleem et al. (2011) reported it to be between 2.8-6.5 g/kg dry matter.

2.4.1.4. Organic matter

Organic matter contains Carbon and Nitrogen in addition to other elements for plant growth. According to Marchioretto et al. (2002), the organic matter content of anaerobically digested sewage sludge was 14.8g/l while Marinos et al. (2006), estimated it to be between 14.3and 38.6 g/kg fresh weight. In addition analysis by Marinos et al. (2006) revealed that organic carbon was 22.4% dry weight. The increase of water infiltration into the soil and soil moisture-holding capacity, soil compaction reduction, the increase in the ability of the soil to retain and provide nutrients, reduction in soil acidification can be listed as the advantages of the addition of organic matter (Epstein, 2003). The organic matter component is also important because most of nutrients are bound by them reducing leaching by virtue of releasing nutrients slowly (Gudmundur, 1999).

2.4.2. Sewage sludge pH

pH is a physical property of sewage sludge**.** According to Seleem et al. (2011) **t**he pH values ranged from 7.1 to 8.21 which indicate that the sludge is slightly alkaline. A pH value of 8.2 was obtained by Marinos et al. (2006). Gudmundur (1999) obtained a pH average of 7.3 and ranged from 6.7 to 8.0. pH is important because it determines the availability of plant nutrients and mobility of heavy metals (Epstein, 2003).

2.4.3. Heavy metals

Sewage sludge may contain heavy metals like Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Molybdenum, Nickel, Selenium, and Zinc (Whitehouse et al., 2000). These metals are persistent—that is, they do not break down in the environment and therefore build up over time. The heavy metals in land spread sludge therefore become permanent additions to the total quantity in the soil. Even extremely small amounts of heavy metals in sludge, therefore, are dangerous (Harrison & Oakes, 2002).

2.4.3.1. Concentrations of heavy metals in sewage sludge

Sewage sludge composition varies depending on the sources of different wastewater sludge (Marchioretto et al., 2002). Several investigations on the quality of sludge in terms of its heavy metal content have been carried out all over the world.

Aulicino et al. (1998) evaluated heavy metal concentrations of digested sewage sludge samples from domestic wastewater treatment plants located in Italy. The chemical analyses of sewage sludges showed that concentrations of Zinc (Zn) and Copper (Cu) are predominant for both anaerobic and aerobic digested sludge samples. Zn concentrations were 1520 mg/kg and 1472 mg/kg for anaerobic and aerobic digested sludges, respectively. Cu concentrations were 358 mg/kg and 560 mg/kg for anaerobic and aerobic digested sludges, respectively.

Enezi et al. (2004) evaluated sewage sludges from a municipal wastewater treatment plant in Kuwait in order to meet the challenges of agricultural use of sewage sludges. Based on the results of this study, the mean concentrations of heavy metals were Zn=2002 mg/kg, Cu=700mg/kg, Pb=337 mg/kg, Ni=111 mg/kg, Cr=80 mg/kg, Hg=58 mg/kg and Cd=21mg/kg.

Debosz et al. (2002) conducted a survey to quantify the effects of anaerobically digested sewage sludge and composted household waste on selected soil properties, and to describe interactions with ambient climatic conditions. Selected sewage sludge had heavy metals concentrations of Cu, Cr, Cd and Hg as 360mg/kg, 32.5 mg/kg, 2.4 mg/kg and 3.5 mg/kg, respectively.

Goi et al. (2006) monitored heavy metal contents in sludge coming from 10 different municipal wastewater treatment plants located in Italy. For almost all samples, the authors reported Cd and Hg concentration measurements below detection limit and they stated that metal concentrations (Zn, Cu, Cr, Pb, Cd and Ni) were found to be below the maximum concentrations permitted by European regulations.

In Kenya, pure sludge samples collected from Kariobangi Sewage Treatment Plant were studied by Kaara, (2012). The author obtained concentrations of the heavy metals with mean values of; Zinc 1923 mg/g, Copper 456 mg/g, Lead 410 mg/g, Cadmium 5.8 mg/g and mercury 3.3 mg/g of dry matter. Therefore, as reported that the concentration distribution of metals in sludges could be presented in the order of Zn>Cu>Pb>Cd>Hg. Marinos et al. (2006), further specifies that among the heavy metals, Zinc, Copper, Nickel, Lead and Chromium are the principal elements limiting sludge recycling to agricultural land hence Zn, Cu, Cr, Pb, Cd and Ni heavy metals were investigated in this study. A summary for the concentration of these heavy metals in various countries/ regions is shown in Table 2.1.

Table 2.1: Concentration of heavy metals in various Countries/Regions

Serial No.	**Author(s)**	**Country / Region**	**Heavy metals concentration (mg/kg)**					
			Pb	Zn	Cu	Ni	Cd	Cr
1	Aulicino et al. (1998)	Kuwait	337	2002	700	111	21	80
2	Seleem et al. (2011)	Egypt	157.5	790.5	529	277.5	-	31.5
3	Kaara, (2012).	Kenya	410	1923	456	-	5.8	-
4	Marchioretto et al. (2002)	Dutch	195	1925	897.5	30	2.5	420

2.5. Methods of heavy metals removal from sewage sludge

Methods for the removal of heavy metals from sewage sludge include bio-leaching, ion-exchange, electrodialysis, adsorption, reverse osmosis and chemical leaching (Lee et al., 2006).

2.5.1. Bioleaching

The principle of bioleaching is the microbial production of sulphuric acid and subsequent solubilisation of heavy metals. Tichý (1998) defines bioleaching as a process mediated by specific acidophilic bacteria capable of acid production. Since many of these microbes belong to the genus *Thiobacillus,* they are called thiobacilli-like organisms. Thiobacilli are able to oxidize reduced sulphur or ferrous iron and thus produce the acids (Tichý, 1998). The main types of bacteria used in bioleaching are *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* (Lombardi and Garcia, 1999). The bioleaching process aims at especially the solubilisation of heavy metals but it also causes a reduction of pathogenic organisms. This is the result of the extreme pH conditions introduced by Thiobacilli during the bioleaching process operation. Thus, ideally the sludge coming out from a bioleaching system would present reduced amounts of both toxic metals and pathogenic organisms (Lombardi and Garcia, 1999). The major disadvantage of this method is the sensitivity of micro-organisms to high metal toxicity levels (Badmus et al., 2006).

2.5.2. Ion Exchange

Ion-exchange involves the recovery of heavy metal species from solution or solids by directly contacting with ion exchange resin (Ribeiro and Ribeiro 2005). Ion exchangers are insoluble granular substances that have in their molecular structure acidic or basic radicals that can exchange, without any apparent modification in their physical appearance and without deterioration or solubilisation, the positive or negative ions fixed on these radicals for ions of the same sign in solution in the liquid upon contact with them (Zagorodni, 2006). Treatment by ion exchange involves a sequence of operating steps. The material is passed through the resin until the available exchange sites are filled and the contaminant appears in the effluent. At this point treatment is stopped and the bed is backwashed to remove dirt and to re-grade the resin. The bed is then regenerated. After regeneration the bed is rinsed with water to wash out residual regenerant. The major disadvantage of this method is high capital and operation costs when the heavy metals concentrations are high and the sensitivity to particles present. It has the advantage of heavy metals recovery (Ribeiro and Ribeiro, 2005). In addition Ion exchange is a versatile process which accommodates metal ion concentration variations and reasonable changes in flow rate without deterioration in performance (Zagorodni, 2006).

2.5.3. Electrodialysis

This is accomplished by separating a contaminated solution with an ion selective membrane and applying an electrical potential across the system. As the potential is applied, cations (e.g., heavy metals in solution) migrate through semipermeable membranes toward the cathode, thus becoming concentrated in one solution compartment while the in-flow solution becomes purified. The concentrated solution can then be returned to an electroplating cell. Electrodialysis has the disadvantages of limited strength and high cost of the cation selective membrane. In addition high power consumption makes its industrial applications rare (Mohammadi et al., 2004).

2.5.4. Adsorption

Adsorption refers to the ability of certain materials to retain molecules (gas, metallic ions, organic molecules, etc.) on their surface in a more or less reversible manner. There is a mass transfer of sorbate from the bulk of liquid or gas phase to the surface of the solid. The solid sorbent thus acquires superficial (hydrophobic or hydrophilic) properties liable to modify the state of equilibrium of the medium (diffusion, flocculation) (Dabrowski, 1999). The adsorptive capacity of the solid depends on the developed surface area or specific surface area of the material. Examples of adsorbents include clays, silica, activated carbon and alumina. The fact that the adsorbents can be reactivated and reused is a major advantage of this method. However, treating large quantities of waste water would require large beds which will require a large inventory of expensive adsorbents leading to high capital cost. In addition adsorbents progressively deteriorate in capacity as number of cycles increases and as a result the large quantities of spent adsorbents containing heavy metals may be considered a hazardous waste (Batista and Young, 1997).

2.5.5. Reverse Osmosis

Reverse osmosis is based on the separation of the solvent from the influent waste stream by a pressure in excess of the osmotic pressure of the solution. The wastewater flows under high pressure through an inner tube made of a semi-permeable membrane material. The purified solvent is removed from the outer tube, which is at atmospheric pressure (Byrne, 1995). The disadvantages associated with reverse osmosis involve the sensitivity of the membrane. Organics as well as other impurities precipitate lead to membrane fouling. It is therefore necessary to have a consistent composition of the influent waste stream. Apart from the membrane sensitivity, the process also requires elevated pressures that drive up the operating costs due to pumping (Byrne, 1995).

2.5.6. Chemical leaching

The application of chemical extraction as a part of the treatment is a feasible option, especially when it is applied as a pre-treatment aiming at heavy metals removal. Once they are soluble, heavy metals can be precipitated for them to be removed by a physical separation, e.g. membrane filtration or flotation (Veeken and Hamelers, 1999). Chemical treatment of sewage sludge is preferable since sewage sludges are frequently complex and high in pollutant load which present problems in other methods such as bioleaching. In addition, apart from being cheap, chemical treatment systems are more predictable and inherently more subject to control by simple technique while chemicals are usually relatively tolerant to temperature changes

(Badmus et al., 2006). Based on these advantages this research was therefore based on chemical leaching process.

2.6. Acid solubilisation of heavy metals

When acid is added to sludge, the heavy metals present in the sludge are dissolved and then exist in solution. The process is brought about by the exchange of protons (from the acid) through the solubilisation of heavy metals in sludge (Marinos et al., 2006). This reaction proceeds as shown below: M is the heavy metal.

$$\textit{Sludge-M} + \textit{Acid} \longrightarrow \textit{Sludge} + M^{z+} + \textit{Acid}^{z-}$$

After extraction, heavy metals are removed from the extracting solution to recover the extracting agent and prevent environmental impact associated with the discharge of the extracting fluid. Removal of the solubilised heavy metals from the extracting solution can be accomplished by precipitation process followed by a separation step (Dacera and Babel, 2006). Chemical extraction involves the use of both inorganic and organic acids to extract heavy metals from sewage sludge (Marchioretto et al., 2002). The extractive yield of heavy metals in sludge depend on the kind and concentration of acids used (Ukiwe & Oguzie, 2008).

2.6.1. Inorganic acids solubilisation of heavy metals

Sewage sludge that contain heavy metals are so tightly incorporated or absorbed in minerals and organic solids that only under extreme acidic conditions, achieved by chemical leaching or bioleaching, can these metals be satisfactorily solubilised, (Marchioretto et al., 2002). According to Yoshizaki and Tomida (2000), the sufficient removal of heavy metals from sludge can only be achieved by using acids as the extracting solution. These inorganic acids include Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl), Phosphoric and Nitric acid (HNO_3).

2.6.1.1. Sulphuric acid solubilisation of heavy metals

According to Marinos et al. (2006) the optimum condition for extraction was achieved when the sludge samples were in contact with H_2SO_4 20% v/v concentration for 30 minutes at 80°C, as these experimental conditions resulted in the highest heavy metal removal efficiency. This combination led to an efficient percentage of heavy metal removal and more particularly 74% for Ni, 86% for Cu, 99% for total Cr, 11% for Pb and 72% for Zn. It was reported that the extraction of heavy metals in sludges can be presented in the order of Cr>Cu> Ni>Zn>Pb. The heating of the solution means that its application at large scale level will not be applicable because of its high cost.

2.6.1.2. Hydrochloric acid solubilisation of heavy metals

Seleem et al. (2011) reported that solubilisation of metals using HCl started at pH values around 2 and achieved its maximum extraction efficiency (Cr-60%, Cu-76%, Ni-85%, Pb-91%, Zn-79%) at a pH value of around 1. The use of HCl acid to extract heavy metals was also investigated by Marchioretto et al. (2002). He found out that the extraction yield was very sensitive to the type of acid used. HCl was superior to other acids like HNO_3 and H_3PO_4. Copper extraction was highly influenced by oxidation. The best results achieved were: Cr: 85 % with H_2O_2, Cu: 100 % with H_2O_2, Pb: 100 % with aeration and H_2O_2, and Zn: 100 % with aeration and H_2O_2.

2.6.1.3. Phosphoric acid solubilisation of heavy metals

The use of Phosphoric acid to extract heavy metals was investigated by Marchioretto et al. (2002). In this study the author found out that H_3PO_4 required a smaller H_2O_2 dosage than HCl to promote similar Cr, Cu, Pb and Zn extraction. Marchioretto et al. (2002) reported that solubilisation of metals using H_3PO_4 in combination with H_2O_2 achieved its maximum extraction efficiency (Cr-90%, Cu-85%, Ni-85%, Zn-99%) at 24 hours extraction period.

2.6.1.4. Nitric acid solubilisation of heavy metals

Nitric acid is a strong oxidizing agent and therefore good at solubilizing heavy metals (Marchioretto et al., 2002). According to a study conducted by Seleem et al. (2011) solubilisation of metals using Nitric acid started at pH values of around 2 and achieved its maximum extraction efficiency (Cr-88%, Cu-82%, Ni-71%, Pb-94%, Zn-89%) at pH values of around 1. In-organic acids however have associated problems with environmental contamination because they are non-biodegradable (Seleem et al., 2011). This reduces their suitability in heavy metals extraction from sewage sludge that is to be applied in farms for agricultural purposes.

2.6.2. Organic acids solubilisation of heavy metals

Recent studies have suggested organic acids as promising extracting agents since they are biodegradable and they yield high metal efficiency even at mildly acidic pH (Babel & Dacera, 2006). These organic acids include Oxalic acid, Acetic acid, and Citric acid.

2.6.2.1. Oxalic acid solubilisation of heavy metals

According to Seleem et al. (2011) solubilisation of metals using oxalic acid started at pH values of around 4 and achieved its maximum extraction efficiency (Cr-32%, Cu-38%, Ni-35%, Pb-5%, Zn-42%) at pH value of around 2. Marchioretto et al. (2002) observed that oxalic acid is removed from solution by precipitation as Calcium Oxalate hence the low efficiency in the heavy metals solubilisation. Oxalic acid is therefore not suitable for heavy metals solubilisation.

2.6.2.2. Acetic acid solubilisation of heavy metals

Acetic acid alone is known to be a weak chelating agent for removal of heavy metals (Oustan et al., 2011). In another study, Zeng (2007), using concentrations of acetic acid as 0.5mol/l, 1mol/l, 2mol/l, 1.0mol/l, 3mol/l, 5mol/l, H_2O_2 (2%) and reaction time of 0.5h,1h,2h,4h,6h, pH of 4 and room temperature, found out that acetic acid extraction ability was improved. The result obtained by Zeng (2007) showed that Copper and Zinc recovery was 94% and 98% with the extractions performed at pH value of 4, at room temperature and in 4 hours extraction time. Zeng (2007) concluded that using Acetic acid and H_2O_2 to remove Cu and Zn delivered satisfactory results. However the Copper and Zinc in the form of acetic acid complexes may result to the leach liquor not meeting the release standard. This makes acetic acid less favourable as an extracting agent. To solve this problem Xiang et al. (2002) suggested the use of ferrite co-precipitation to remove heavy metals of which density is thicker than 3.8g/L. Although this method of ferrite co-precipitation achieved the goal of avoiding Copper and Zinc acetic acid complexes, it increased the cost of heavy metals extraction making it less favourable (Zeng, 2007).

2.6.2.3. Citric acid solubilisation of heavy metals

In a study conducted by Seleem et al. (2011), solubilisation of metals using Citric acid started at pH values of around 4. Solubilisation achieved its maximum extraction efficiency (Cu-52%, Ni-55%, Pb-46%) at a pH value of 2 and maximum extraction efficiency (Cr-63% Zn-66%) at a pH value of 3. Marchioretto et al. (2002) observed that the difference between Citric and Oxalic acid in the solubilisation of Cr could be due to the chemical structure of both acids. Citric acid is formed by three carboxylic groups whereas oxalic acid contains two carboxylic groups. A high number of carboxylic groups might favour the complexing (or chelating) capacity of the compound. Extraction based on chelation involves the coordination of two or more donor atoms present in the chelating ligand to the same metal ion in such a way so as to form a heterocyclic ring termed a Chelate. Citric acid is an organic alpha hydroxyacid, (Verhoff, 2005). It is a 6-carbon containing tricarboxylic acid and exists as an intermediate in the Citric acid cycle when carbohydrates are oxidized to carbon dioxide. The acidic nature of Citric acid results from the three carboxy groups COOH which can lose a proton in solution forming the Citrate ion. Citrates can chelate metal ions and therefore have been used as chelating and sequestering agents (Dacera et al., 2009).

Citric acid forms mononuclear, binuclear or poly-nuclear and bi-, tri-, and multi-dentate complexes depending on the type of available metallic ions. For example, metals like Fe and Ni, form bidentate, mono-nuclear complexes with two carboxyl acid groups of the Citric acid molecule. On the other hand, Cu, Cd and Pb could form tridentate, mononuclear complexes with Citric acid involving two carboxyl acid groups and the hydroxyl group (Marchioretto et al., 2002). These are some of the reasons why Citric was chosen for this study.

2.7. Solubilisation control parameters

A study conducted on the solubility of metals in sewage sludge showed that heavy metals extraction from sewage sludge depended on factors such as pH, redox potential of the sludge, and the concentration of the metals and ligands (Naoum et al., 2001). In order to determine the extraction efficiencies of heavy metals from sewage sludge, Zhang et al. (2008) noted that in relation to the types of the metals in the sludge, the extraction efficiency depended on the sludge content, dosage of the extractants, reaction time and temperature.

2.7.1. Effect of pH

The amount of heavy metals extracted increased with decrease in pH (Seleem et al., 2011). Marchioretto et al. (2002) noted that pH is one of the most powerful parameters to control the metals transfer from immobile solid-phase forms to more mobile, and therefore more bio-available, solution-phase forms. This parameter influences adsorption equilibria, the stability of organo-mineral complexes and oxidation-reduction potential. Sometimes instant heavy metals solubilisation (Zn for example) can be achieved by merely lowering the pH. Seleem et al. (2011) observed that this was true for both inorganic and organic acids. Solubilisation of metals using inorganic acids (HNO_3, HCl) started at pH values of around 2, achieved its maximum extraction efficiency (Cr-88%, Cu-82%, Ni-71%, Pb-94%, Zn-89%) at pH value of around 1. When a complexing agents like Citric acid or Oxalic acid are applied, metals start solubilisation at higher pH value (3-5) than when a strong acid such as

HNO_3 and HCl are applied at the same pH. Both Oxalic acid and Citric acid had increased heavy metal extraction at mildly acidic pH but Citric acid has better prospects because oxalic acid is removed from solution by precipitation as calcium oxalate. The Calcium oxalate precipitates causes that oxalate become less available for heavy metals leading to a lower extraction for metals compared to Citric acid (Veeken and Hamelers, 1999). The organic acids efficiency in metal solubilisation was not so high; the maximum extraction efficiency achieved was 66% for Zn using Citric acid at a pH value of 3. This might be due to the low pH value required for the metals to solubilize and or to the short acidification time applied in these experiments.

2.7.2. Effect of extraction time

Marchioretto et al. (2002) showed that the amount of heavy metals extracted increased with increase in extraction time. This study highlighted that the maximum extraction yield (79 %) of Cu was achieved with HCl at a pH value of 1 after one day. Almost 100 % of Pb was extracted after 30 minutes with HNO_3 and HCl. The best extraction yield (96 %) for Zn was obtained with HCl at the pH value of 2, after 7 days followed by 93 % after 1 day. HNO_3 was as effective as HCl to promote Cu solubilisation only after a leaching time of about 5 days. Although high extraction efficiencies were achieved using the inorganic acids, the low pH has to be raised before sludge can be released to the environment increasing the cost of treating the sludge. In addition, the inorganic acids are non-biodegradable hence the study proposed the use of organic acids for the extraction.

Seleem et al. (2011) found out that the removal efficiencies of heavy metals using Citric acid are completely changed as the extraction time increased from 1 hour to 10 days. For Cr, the maximum removal of 66% was attained at one day of contact at pH value of 3. For Cu, one day of extraction duration was the optimum condition that achieved higher removal efficiency of 48% at a pH value of 3. The Ni extraction started after one day duration to achieve the removal efficiency of 96% after 5 day of extraction. The Pb maximum removal efficiency of 66% was achieved after 1 day contact with Citric acid at a pH value of 3. For Zn, the optimum extraction time was one day duration it which gave maximum efficiency of 68% at a pH value of 3. High pH values favoured the use Citric acid to inorganic acids. The low extraction efficiencies however suggested that there was need for its improvement hence need for this research.

2.7.3. Effect of oxidation-reduction potential

Marchioretto et al. (2002) found out that heavy metals can be mobilized from sludge particles by changes in pH and Oxidation-Reduction Potential (ORP) conditions and by complexing with synthetic complexing agents Nitrilotri-Acetic acid (NTA) and Ethylene Diamine Tetracetic Acid (EDTA), inorganic complexing agents (Cl^-,NO_3^-, S^{2-}, PO_4^{3-}, CO_3^{2-}), or with natural chelating agents such as Citric acid. The pH value influences adsorption equilibria, the stability of Organo-mineral complexes and ORP. Marchioretto et al. (2002) however observed that a low pH value is not always enough to promote a satisfactory metals release from anaerobic sludge particles to the liquid, unless acidification is preceded by a rise in the sludge ORP. The ORP of the anaerobic sludge can be raised either by means of biological or chemical oxidation, which can be achieved through aerobic conditions. ORP is raised by oxidising the sewage sludge prior to acid extraction. The rise in ORP of the sludge promotes the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH. Chemical oxidation can occur by addition of an oxidizing agent like Hydrogen peroxide. Chemical oxidation applied before acidification increases the ORP of the sludge, promoting the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH.

An investigation into the effect of aeration and acidification on heavy metals solubilisation of sewage sludge using the various experimental procedures, which include, aeration before acidification and aeration after acidification, demonstrated that Mn and Cu were the highest metals extracted when the above experimental procedures were applied in metal extraction (Ukiwe and Nwoko, 2010). However, when only aeration was applied, Cu extraction efficiency dropped remarkably. Ni and Pb were effectively extracted when the aeration after acidification protocol was used. The study further revealed that the extraction yield of Cd was least when the aeration before acidification procedure was employed (Ukiwe and Nwoko, 2010).

In the study of inorganic acids by Marchioretto et al. (2002), the results revealed that the option including chemical oxidation with either aeration or Hydrogen peroxide followed by acidification resulted in the highest extraction percentages of most heavy metals. In addition extraction yield was found to be very sensitive to the type of acid used. HCl was superior in heavy metals extraction to HNO_3 and H_3PO_4. Copper extraction was found to be highly influenced by oxidation. The best results achieved were: Cr: 85 % with H_2O_2, Cu: 100 % with H_2O_2, Pb: 100 % with aeration and H_2O_2, and Zn: 100 % with aeration and H_2O_2. Various complexing agents such as Ethylene Diamine Tetracetic acid (EDTA), Ethylene Diamine Disuccinictrisodium Salt (EDDS), Diethylene-Triamine-Pent-Acetic acid (DTPA), and Nitrilotriacetic acid

(NTA) have been applied to enhance metal solubility and extraction in sludge system (Ukiwe and Nwoko, 2010). The ratio of chelating to heavy metals should be considered when comparing chelating agents for heavy metals decontamination (Marchioretto et al., 2002). Using smaller quantities of chelating agents generates competition of chelates with other complex substances found in the sludge. Citric acid is an organic chelating agent (Ukiwe, 2012). The aim of this research is therefore to investigate the effect of chemical oxidation using Hydrogen Peroxide as a pre-treatment step on the efficiency of heavy metals extraction using Citric acid as a chelating agent from anaerobically digested sewage sludge motivated by observations of Marchioretto et al. (2002).

2.7.3.1. Fenton oxidation

Hydrogen peroxide (H_2O_2) is a strong oxidant. However, oxidation by H_2O_2 alone is not effective because of a slow reaction rate. If ferrous iron is present in the sludge treated with Hydrogen peroxide, the following set of redox reactions, known as Fenton's oxidation may occur (Andersson and Malkoc, 2004).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad \text{(i)}$$

$$Fe^{3+} + H_2O_2 \rightarrow \left[FeOOH^{2+}\right] + H^{+} \quad \text{(ii)}$$

$$\left[FeOOH^{2+}\right] + H^{+} \rightarrow Fe^{2+} + {}^{\bullet}OOH \quad \text{(iii)}$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \quad \text{(iv)}$$

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + {}^{\bullet}OOH \quad \text{(v)}$$

$$Fe^{3+} + {}^{\bullet}OOH \rightarrow Fe^{2+} + O_2 + H^{+} \quad \text{(vi)}$$

Ferrous iron initiates the generation of the Hydroxyl radicals by catalysing the decomposition of Hydrogen peroxide (Eq. i). Ferric ions generate Hydrogen radicals as can be seen in (Eq. ii). The oxidant potential of Hydrogen radicals is 2.8 V which indicates that they are stronger oxidants than ozone (2.1 V) and H_2O_2 (1.8 V). The chain is terminated via reactions (Eq. iv) and (Eq. vi). By adding Hydrogen peroxide to a sewage sludge solution containing ferrous ions the following redox reaction is expected to occur:

Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$ (vii)

Reduction: $H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O$ (viii)

Redox: $2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2H_2O$ (ix)

Municipal sludge has high Phosphate content (Marchioretto et al., 2002). Most of the Phosphates are organically bound but by acidic treatment they can be released in the water phase. At low pH-values, (Eq. ix), it is mostly Ferric phosphate that precipitates (Eq. x) and the sum reaction, when Hydrogen peroxide is added, is then (Eq. xi).

$$Fe^{3+} + H_2PO_4^{-} + 2H^{+} \rightarrow FePO_4 + 2H^{+} \qquad \text{(x)}$$

$$2Fe^{2+} + H_2O_2 + H_2PO_4^{-} \rightarrow 2FePO_4 + 2H_2O + 2H^{+} \qquad \text{(xi)}$$

Depending on the concentrations of iron ions in the solution and the pH-value, Iron hydroxide precipitation can occur, (Eq. xii) and (Eq. xiii). Andersson and Malkoc (2004) suggested the optimal pH for Fenton’s oxidation to be between 2 and 4.

$$Fe^{3+} + 3H_2O \rightarrow (FeOH)_3 + 3H^{+} \qquad \text{(xii)}$$

$$2Fe^{2+} + H_2O_2 + 4H_2O \rightarrow 2(FeOH)_3 + 4H^{+} \qquad \text{(xiii)}$$

As seen in (Eq. xi) and (Eq. xiii) the precipitation of Iron salts result in pH-value decrease.

H_2O_2 added should be varied according to the concentration of Iron present in the sludge to have the ideal proportion of Fe: H_2O_2 necessary for the occurrence of the

Fenton reaction. According to Marchioretto (2002), the typical ranges Fe: H_2O_2 ratios are 1:5, 1:15 and 1:25.

2.8. Precipitation of heavy metals

The removal of the solubilised metals is achieved by chemical precipitation followed by a physical separation step (Stylianou et al., 2007), for example, filtration or centrifugation.

The heavy metal contents of wastewaters can effectively be removed to acceptable levels by precipitating the metal in an insoluble form. Heavy metals are typically precipitated from solution as; hydroxides, sulfides or sometimes sulfates, carbonates and metal co-precipitation during flocculation with Iron or Aluminum salts (Armenante, 1997).

2.8.1. Precipitation of Heavy Metals as Hydroxides

Precipitation by Hydroxide formation is the most common heavy metal precipitation method. The precipitation typically follows the reaction:

$$M^{z+} + zOH \Longleftrightarrow M(OH)_z$$

Many heavy metals are amphoteric (Armenante, 1997). Therefore their solubility reaches a minimum at a specific pH (different for each metal).

2.8.2. Precipitation of Heavy Metals as Sulfides

Metal sulfides are typically very insoluble. Therefore metals can be precipitated by adding Sulfide ions (S^{-2}). Metal Sulfides have much lower solubility than the corresponding metal Hydroxides, thus allowing lower residual metal concentrations in the treated wastewater.

Hydrogen Sulfide (H_2S) is a weak acid and dissociates in two steps according to:

$$\mathbf{H_2S \Longleftrightarrow H^+ + HS^-}$$

$$\mathbf{HS^- \Longleftrightarrow H^+ + S^{-2}}$$

Sulfide salts undergo hydrolysis, partially reforming the undissociated acid:

$$\mathbf{S^{-2} + H_2O \Longleftrightarrow HS^- + OH^-}$$

$$\mathbf{HS^- + H_2O \Longleftrightarrow H_2S + OH^-}$$

S^{-2} is not the dominating species until the pH is very high (~14). Hence, by adding a Sulfide salt, equilibrium is generated resulting in only the partial formation of the S^{-2} ions actually used in precipitation. Sulfide precipitation is always conducted under alkaline conditions to promote Sulfide ion formation, (Armenante, 1997).

2.8.3. Precipitation of Heavy Metals as Carbonates

Some metals (Pb, Cd and Ni) form insoluble carbonates that can be used in carbonate precipitation. Some wastewaters already contain enough carbonates to allow precipitation to occur. Alternatively, inorganic carbonates (e.g., Na_2CO_3) can be added. Carbonate precipitation takes place only if carbonate ions (CO_3^{-2}) are present. Free carbonate ions are present only if the pH is high. A caustic is often added to raise the pH. High pH values also promote the precipitation of the metals as hydroxides. Hence, carbonate precipitation is often a co-precipitation. pH values above 10 promote the formation of metal hydroxy complexes that can increase the metal solubility and reduce the precipitation effectiveness. Carbonate precipitates settle and can be dewatered more easily than the corresponding hydroxide precipitates (Armenante, 1997). This research was limited to solubilisation of the heavy metals using Citric acid and chemical oxidation using Hydrogen peroxide.

CHAPTER THREE

3.0. EXPERIMENTAL MATERIALS AND METHODS

3.1. Experimental design

A full factorial design with three factors at two levels was employed for experimental design. The factors considered were pH, time and H_2O_2 dosage which were less than the four which is the limiting number (Gottipati, 2012). Design©Expert9 software was used in experimental design and data analysis (Antony, 2003).

3.1.1. Selection of factors

The aim of this study was to determine the optimum pH, time and H_2O_2 dosage for heavy metals extraction from sewage sludge using Citric acid. Therefore, the factors that were considered were pH, time and H_2O_2 dosage. The variation levels were as shown in Table 3.1.

Table 3.1: Experimental factors and their variation levels

CODE	NAME OF FACTOR	LOW (-)	HIGH (+)
A	pH	3	5
B	Time (days)	1	10
C	H_2O_2 Dosage (g/l)	1	5

3.2. Factorial experimental design

A three factor two level full factorial design was chosen. A sensible low and high for each factor was chosen to determine the experimental domain (Gottipati, 2012). The levels of the factors are given by – (minus) for low level and + (plus) for high level as shown in Table 3.1. The combinations of 3 factors investigated at two levels result in a factorial design consisting of 2^3= 8 experiments. Table 3.2 shows the factorial design.

Table 3.2: Full factorial design matrix

S/NO	**A (pH)**	**B (Time)**	**C (H_2O_2)**	**Replicates**	**Heavy metals** (Zn, Pb, Cu, Ni)	**Responses**
1	-1	-1	-1	2	4	12
2	+1	-1	-1	2	4	12
3	-1	+1	-1	2	4	12
4	+1	+1	-1	2	4	12
5	-1	-1	+1	2	4	12
6	+1	-1	+1	2	4	12
7	-1	+1	+1	2	4	12
8	+1	+1	+1	2	4	12
Total						**96**

The runs were replicated two times (r = 2) giving a total number of samples of (n × r) =8×2 = 16 samples. The replication was done to reduce experimental errors (Luke et al., 2012). In each experiment a blank (control experiment) was setup. The percentage extraction for the heavy metals Zinc, Copper, Lead and Nickel was taken as the response. The number of responses analysed were 12 x 8= 96 responses. The influences of all experimental, factors, variables and interaction effects on the response were investigated. The general mathematical model for 2^3 factorial design in coded values used was according to (Lazic, 2004) expressed as

$$Y\% = X_O + X_1A + X_2B + X_3C + X_4AB + X_5AC + X_6BC + X_7ABC \text{ ……………..3.1}$$

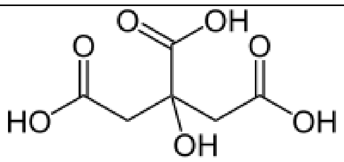
where, *Y%* is the percentage of heavy metals (Zn, Pb, Cu, Ni) extracted from the sewage sludge, X_o is the global mean, X_i represents the other regression coefficients as shown in Table 3.2 and A, B and C are the coded symbols for the factors under study as shown in Table 3.1. After determining the main effects, the effect of interactions were obtained by performing the analysis of variance (ANOVA).

A Pareto plot was used to present the absolute values of the effects of main factors and the effects of interaction of factors. A Pareto diagram is a type of bar chart in which the various factors that contribute to an overall effect are arranged in order according to the magnitude of their effect. This ordering helps identify the “vital few” (the factors that have a major effect) from the “useful many” (factors that, while useful to know about, have a relatively smaller effect, (Hsuan et al., 2004). A reference line is drawn and the factors which extend past this line are potentially important (Antony, 2003). A Pareto plot was therefore used to visually show the contribution of each effect. The plot allows one to detect the factor and interaction of effects which are most important to design optimisation study (Antony, 2003). Bradley, (2007) states that a *t*-test is carried out to identify the significant effects.

3.3. Chemical reagents

Analytical grade chemical reagents were used in this research study. These included Citric acid, Hydrogen peroxide, Potassium dichromate, concentrated Sulphuric acid, Ferrous Ammonium Sulphate, Phenan-throline monohydrate indicator, Selenium powder, Salicylic acid, Sodium citrate, Sodium hydroxide, Sodium Hypochlorite, Sodium nitro-prusside, Sodium salicylate, Sodium tartrate, Antimony potassium-tartrate, Ascorbic acid, Copper II sulphate pentahydrate, EDTA, Lithium sulphate, and distilled water. Frank, (2005) highlighted the properties of are shown in Table 3.3.

Table 3.3: Properties of Citric acid

Properties	
Molecular formula	$C_6H_8O_7$
Structural formula	
Molar mass	192.124 g/mole (anhydrous), 210.14 g/mole (monohydrate)
Appearance	crystalline white solid
Density	1.665 g/cm^3(1.5g/cm^3 for monohydrate)
Boiling point	175 °C, 448 K, 347 °F (decomposes)
Solubility in water	73 g/100 ml (20 °C)
Acidity (pK_a)	$pK_{a1} = 3.09$, $pK_{a2} = 4.75$, $pK_{a3} = 5.41$

American Chemical Society, (1993) highlighted the properties of are shown in Table 3.4.

Table 3.4: Hydrogen peroxide chemical & physical properties

Appearance	Clear colourless liquid with an assay 30.0% (w/w) Hydrogen peroxide in water.
Molecular formula:	H_2O_2
Molecular weight	34.01
Density	1.11 g/ml
Molarity	9.8 M

3.4. Equipment, Glassware and other apparatus

Basic laboratory glassware such as Erlenmeyer flasks, measuring cylinders, funnels, pipettes, beakers, droppers, test tubes, digestion tubes and volumetric flasks were used. They were washed with hot soapy water and rinsed with distilled water. Equipment used included; analytical balance, spectrAA-200 Atomic Absorption Spectrophotometer (AAS), Jenway Flame photometer, Colorimeter, Muffle furnace, Oven, Fume chamber, Shaker, Centrifuge, TBD 200 water deionizer, pH meter, Water distiller and Digestion block. Other apparatus and materials used included; filter papers, spatulas, stickers, plastic reagent bottles, tongs, crucibles, desiccator, shallow trays, porcelain crucibles, stirrer, clock timer, thermometers and screens.

3.5. Sample collection

Samples of freshly deposited anaerobically digested sewage sludge were collected in standard containers from the Kariobangi sewage treatment works, in Nairobi. They were then packaged, labeled and stored in a cold box well. The research experiments and analysis were carried out in the Eldoret University Analytically Chemistry Laboratories.

3.6. Sample preparation and handling

The sludge samples were air dried by placing them in shallow trays. Any big lump was crushed to ensure uniform drying as shown in plate A13 (a) in appendix 13. They were then crushed and sieved through 2mm sieve to remove any material that couldn’t have been crushed e.g. polythene paper pieces. A representative of 250 g was retained by coning and quartering. The samples were then ground in a mortar in order to pass through a 60 mesh screen for Total Nitrogen, Phosphorous and Organic Carbon analysis.

3.6.1. Samples drying

The samples were dried at 40^0C for heavy metals analysis in a dryer as shown in Plate A13 (b) (Appendix 13). The drying was done as quickly as possible to avoid decomposition. The thickness of sewage sludge layer while drying was limited to 2cm to ensure uniform drying.

3.7. Sludge characterization

Physical and chemical characteristics of the sewage sludge were analysed using standard methods and procedures as described by Robert et al. (2002). These included pH, Organic Carbon, Total organic matter, Total Nitrogen and Total Phosphorous, Potassium and Heavy metals (Zn, Pb, Ni, Cu, Cd, Cr and Fe).

3.7.1. Sludge pH

An amount of 20 g of sewage sludge was measured using a weighing balance. An amount of 50 ml of deionized water was measured using a measuring cylinder and added to the 20 g of sewage sludge in a beaker. The pH was then measured using a pH meter.

3.7.2. Determination of Organic Carbon

3.7.2.1. Preparation of Reagents

A mass of 49.024 g of dry Potassium Dichromate was dissolved in 800 ml of distilled water and diluted to 1000 ml to make 1N Potassium Dichromate solution. A mass of 78.39 g of Ferrous Ammonium Sulphate was dissolved in 50 ml of concentrated

Sulphuric acid and diluted to 1000 ml with distilled water to make 0.2 M Ferrous ammonium sulphate solution. A Ferrous Sulphate indicator solution was prepared by dissolving 1.485g of 1.1 Ortho-phenanthroline Monohydrate in 100 ml of 0.025M ferrous sulphate, (Robert et al., 2002).

3.7.2.2. Procedure for determination of Organic Carbon

A mass of 0.1 g of ground sewage sludge was weighed and put into a block digester tube. A volume of 5 ml of Potassium Dichromate solution and 7.5 ml of concentrated solution of Sulphuric acid were added. The tube was then put in a preheated block at 145-155^{0}C for 30 minutes, removed and allowed to cool. The digest was then transferred to a 100 ml conical flask and 0.3 ml volume of the Ferroin indicator solution was added. The digest was then titrated with Ferrous Ammonium solution until a color change from greenish to brownish was reached. Titration was then carried out on the blanks. The amount of Organic carbon (in percent) was then determined as follows:

$$\text{Organic carbon (\%)} = \frac{\text{T x 0.3 x0.2}}{\text{sample weight}}$$

Where,

$T = (V_b - V_s)$

T= Titration volume

V_b = volume in ml of 0.2M Ferrous Ammonium Sulphate used to titrate reagent blank solution.

V_s = volume in ml of 0.2M Ferrous Ammonium Sulphate used to titrate sample solution.

3.7.3. Determination of Total Organic Matter

A mass of 2 g of well mixed dry sewage sludge was weighed in a dry porcelain crucible. They were then heated slowly in a muffle furnace (shown in plate A13(c): Appendix 13) raising the temperature (in steps of 100^0C, 200^0C, and 550 ^{0}C) and maintained at 550 ^{0}C for 4 hrs. The crucibles containing the greyish white ash were then removed and allowed to cool in a desiccator. The cooled crucibles and ash were then weighed.

The percentage ash and organic matter were then determined by differences in weight of the crucibles before and after combustion as follows:

$$\text{Ash}\,(\%) = \left\{\frac{[(W_3 - W_1)]}{[(W_2 - W_1)]}\right\} x100\%\,,$$

Organic matter (%) = {100% - Ash%}

Where,

W_1= The weight of the empty, dry crucible,

W_2= The weight of the dry crucible containing sewage sludge

W_3= The weight of the dry crucible containing ash.

3.7.4. Determination of Total Nitrogen and Total Phosphorous.

3.7.4.1. Digestion mixture preparation

A mass of 3.5 g of selenium powder mixture were dissolved in 1 liter of Sulfuric acid. The solution was then heated to 300 ^{0}C using butane flame. 3.2 g of Salicylic Acid was then dissolved in 100 ml of Sulfuric-selenium mixture.

3.7.4.2. Block digestion

The sludge sample was dried to 70 ^{0}C in an oven to keep the moisture low. A mass 0.3 g of the dried sewage sludge was put into a well labeled dry and clean digestion tubes. 2.5 ml of digestion mixture were added to each of the digestion tubes and the reagent blanks for each batch of the sample. The mixtures were then digested at 110 ^{0}C for 1hr. They were then cooled and three successive 1ml portions of hydrogen peroxide were then added. The temperature of the mixtures was then raised to 330 ^{0}C and heating continued until they became colourless. The mixtures were then allowed to cool. 25 ml of distilled water were then added to the mixtures and the sediments dissolved. The mixtures were then cooled and made up to 50ml with water. The solution was allowed to settle so that a clear solution could be taken from the top of the tube for analysis. The obtained clear solutions were then put in different bottles for determination of Total Nitrogen, Total Phosphorous, Potassium and heavy metals Zinc, Iron, Copper, Lead, Cadmium, Chromium and Nickel (Robert et al., 2002).

3.7.4.3. Colorimetric determination of Total Nitrogen

(a). Preparation of reagents

Reagent N1 was prepared by taking 34g of Sodium Salicylate, 25 g of Sodium citrate together and dissolving them in 750ml of distilled water. A mass of 0.12 g of Sodium Nitroprusside was then added and the solution made-up to 1 litre with distilled water and stored in a dark place. Reagent N2 was prepared by dissolving 30g of NaOH in750ml of distilled water and the solution was allowed to cool. A mass 10g of sodium hypochlorite were then added and the solution made-up to 1 litre with distilled water and stored in a dark place. A stock solution Ammonium Sulphate was prepared by dissolving 11.793 g in 1000 ml of volumetric flask containing distilled water and the solution made-up to the mark (Robert et al., 2002).

(b). Standards

Standards containing 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90 mg Nitrogen/litre were used in the calibration of the colorimeter. The absorbance of each standard was then measured at 650 nm in the colorimeter. The readings are given in Figure A1 (a) appendix 1.

(d). Analysis for Total Nitrogen

A volume of 0.2 ml of the sample digest and blanks was micro-pipetted into well labelled test tubes. A volume of 5 ml of each reagent N1 and N2 was then added and the mixture vortexed to ensure complete mixing. The mixture was allowed to stand for 2 hrs. The absorbance of each sample and blank was then measured at 650 nm in the colorimeter. The readings are given in Figure A1 (a) appendix 1.

3.7.5. Colorimetric determination of Total Phosphorous

3.7.5.1. Reagents preparation

5N Sulphuric acid was prepared by dissolving 148ml of concentrated Sulphuric acid in 500ml of distilled water and making it up to one litre. Ammonium molybdate solution was prepared by dissolving 12 g of Ammonium Molybdate in 250 ml of warm with distilled water at 50 ^{0}C. Antimony Potassium Tartrate solution was solution was prepared by dissolving 0.291g of Antimony Potassium Tartrate in 100 ml of 5N Sulphuric acid. The Ammonium molybdate solution and Antimony potassium Tartrate solution were then mixed thoroughly. The solution allowed to cool and stored in a cool, dark place. Ascorbic acid reducing agent solution was prepared by dissolving 2.108 g of Ascorbic acid in in 400 ml of Ammonium Molybdate / Antimony potassium Tartrate solution and mixed well.

3.7.5.2. Standards

Standards containing 0, 0.5, 1, 2.5, 5, 7.5, 10, and 12.5ppm Phosphorous were used in the calibration of the colorimeter. The absorbance of each standard was then measured at 880 nm in the colorimeter (Robert et al., 2002). The readings are given in Figure A1 (b) in appendix 1).

3.7.5.3. Analysis for Total Phosphorous

A volume of 5 ml of the clear supernatant digest samples solutions was pipetted into well labelled 50 ml volumetric flasks. 20 ml of distilled water and 10ml of ascorbic acid reducing agent were then added to each of the flasks. The solution was then made up to 50 ml mark with distilled water and mixed well. The mixture was allowed to stand for 1hr to permit full colour development. The absorbance of each sample and blank was then measured at 880 nm in the colorimeter (Robert et al., 2002). The readings are given in Figure A1 (b) (appendix 1).

3.7.6. Flame photometry analysis for Potassium in sewage sludge

The instrument was calibrated according to the manufacturer’s standard (Jenway) operating conditions for the analysis of potassium.

3.7.6.1. Preparation of reagents

Potassium stock solution (1000 ppm) was prepared by dissolving 1.907g of dry (100 ^{0}C, 2hr) Potassium chloride in 500 ml of distilled water and making it up to one litre. 100 ppm potassium working solution was prepared by dissolving 20 ml of the stock solution to 200 ml using distilled water.

3.7.6.2 Standards

Standards containing 0, 2, 4, 6, 8, and 10 ppm of Potassium were used in the calibration of the flame photometer. The absorbance of each standard was then measured at 766.5 nm in the flame photometer. The readings are given in Figure A2 (a) (appendix 2).

3.7.6.3. Analysis for Potassium

A volume of 2 ml of the clear supernatant digest samples solutions was pipetted into well labelled 50 ml volumetric flasks. The solution was then made up to 50 ml mark with distilled water and mixed well. The absorbance of each sample and blank was then measured at 766.5 nm in the flame photometer (Robert et al., 2002). The readings are given in Figure A2 (a) (appendix 2). The concentration of the potassium in the dried sewage sludge sample expressed in K% was determined as follows:

$$K\% = \left[\frac{(a - b)\,xVx\;f\;x100}{1000\;x\,Wx1000}\right] \qquad \text{Where;}$$

a = concentration of K in the sample digest solution

b= concentration of K in the blanks digest

V= final volume of the digestion process

W= weight of the sample

f= the dilution factor

3.7.7. Determination of heavy metals in sewage sludge.

Heavy metals are measured by atomic absorption as they absorb radiation from an element specific hollow cathode lamp (Robert et al., 2002). The specific wavelengths for the heavy metals are as shown in Table 3.5.

Table 3.5: Specific wavelengths for the heavy metals

Element	**Pb**	**Cu**	**Fe**	**Zn**	**Ni**	**Cr**	**Cd**
Wavelength	283.3	324.8	248.3	213.9	232.0	357.9	228.8

3.7.7.1. Preparation of reagents

Appropriate amount of heavy metals sulphates were dissolved in 1000 ml volumetric flask and made up to the 1000 ml mark with distilled water to prepare 1000 ppm stock solution for each heavy metal. The working solution of 50 ppm heavy metals was prepared by diluting 25 ml of stock solution in 500 ml volumetric flask and made up to the mark with distilled water (Robert et al., 2002). From the working solution, standards series for each heavy metal as shown in the Table 3.6 were prepared.

Table 3.6: Standards series for heavy metals

Element	**Pb**	**Cu**	**Fe**	**Zn**	**Ni**	**Cr**	**Cd**
Standard Series (ppm)	0,1, 3,5	0,2, 5,10	0,5, 10,15	0,0.5, 1,1.5	0,5, 10,15	0,5, 10,15	0,1, 2,3

3.7.7.2 AAS Analysis for heavy metals

The standard series, suitably diluted sample and blank digests were aspirated into the AAS calibrated for heavy metal measurement at the appropriate wavelength and absorbance measured. A calibration curve of absorbance against the concentrations of the standard series for each heavy metal was plotted as shown in Figure A2 (b), A3 (a), A3 (b), A4 (a), A4 (b), A5 (a), A5 (b) in appendix 2, 3, 4 and 5 respectively. The concentation of the heavy metals in the samples and blanks was then determined. The concentration of the heavy metal in the dried sample, expressed in Hm mg/Kg, was calculated as follows, (Robert et al., 2002).

$$\text{Hm (mg/Kg)} = \left[\frac{(a - b) \, x V x \; f \; x1000}{1000 \, x \, W} \right]$$

Where;

a= Concentration of Hm in the solution

b= Concentration of Hm in the mean values of the blanks

V= Final volume of the digestion process

W= Weight of the sample

f= Dilution factor

Hm= Heavy metal.

3.8. Chemical leaching of heavy metals

3.8.1. Hydrogen peroxide dosage

The extraction efficiency was investigated for three different doses of H_2O_2 calculated according Fe: H_2O_2 ratios of 1:5, 1:15, and 1:25 (wt/wt), (Marchioretto et al., 2002).

3.8.2. Extraction of heavy metals from sewage sludge

A mass of 7 g of sewage sludge was mixed with 140 ml of distilled water in 500 ml Erlenmeyer flask. Citric acid (pK1=3.14) was added to the sewage sludge solution to adjust pH to pH value of 5 and pH value of 3. The mixtures were stirred continuously at 125 rpm at room temperature for 2 hrs. Hydrogen peroxide (H_2O_2) dosages were added to the samples and kept shaking. Citric acid was added to the sewage sludge solution to maintain pH at pH value of 5 to 3±0.1. Samples of 5 ml were collected at times interval of 1day and 10 days). The 15ml samples were centrifuged at 4000 rpm for 30 minutes. The supernatant was filtered through a filter paper. The filtrate was analysed for heavy metals (Cu, Pb, Ni and Zn) using AAS. The experiments were carried out in duplicate. The amount of Citric acid used was calculated according to the equation below.

Mass of Citric acid = Citric acid concentration x Volume used

CHAPTER FOUR

4.0. RESULTS AND DISCUSSIONS

4.1. Sewage Sludge characterisation.

The results for characterisation for anaerobically digested sewage sludge from Kariobangi sewage treatment works compared with the typical contents of bio-solids applied for agriculture, UN HABITAT benchmark, European Union and USA standards (Ronald et al., 2008) were as shown in Table 4.1. The results obtained were also and NEMA standards (GoK, 2006) as shown in Table 4.2

Table 4.1: Standards for sewage sludge for use in agriculture compared to this study.

PARA-METER	UNIT	This Study	Typical values	UN HABITAT 2008 BM	EU	USA
pH		6.75±0.12	7.2	NA	6-7	NA
TN	%	1.21±0.02	1-8	3.5	NA	NA
TP	%	1.93±0.01	0.5-5	3.5	NA	NA
OM	%	41.85±0.07	NA	75	NA	NA
OC	%	14.05±0.02	5.2	NA	NA	NA
K	%	0.10±0.002	<1	0.2	NA	NA
Cu	mg/Kg DM	486.67±12.96	800	500	1000	1500
Pb	mg/Kg DM	338.25±0.47	150	200	750	300
Cr	mg/Kg DM	ND	NA	NA	NA	NA
Cd	mg/Kg DM	ND	NA	3	20	39
Ni	mg/Kg DM	109.17±6.48	60	40	300	420
Zn	mg/Kg DM	777.21±23.39	900	1000	2500	2800
Fe	mg/Kg DM	4010.00±24.75	NA	NA	NA	NA

NA- Not available, ND- Not detected, BM- Benchmark, DM- Dry Matter, TN-Total Nitrogen, TP- Total Phosphorous, OC-Organic Carbon.

Table 4.2: Standards for effluent discharge into the environment in Kenya in comparison with this study.

Heavy Metal	**THIS STUDY (Mean values)**	**NEMA Guide value (max allowable)**
Chromium(mg/l)	ND	2
Cadmium (mg/l)	ND	0.01
Copper (mg/l)	0.6510	1.0
Lead (mg/l)	0.4125	0.1
Nickel (mg/l)	0.2140	0.3
Zinc (mg/l)	0.9603	0.5
pH	6.75	6.5-8.5
TN (%)	1.21	2
TP (%)	1.93	2
K (%)	0.10	Not Available
Iron(mg/l)	5.093	10

The mean pH value of sewage sludge was 6.75 showing that it is slightly acidic. This value was within the EU standards although lower than the typical value. Percentage Nitrogen and Phosphorous were within the NEMA, typical values ranges for agricultural use and the UN habitat benchmark standards. Total organic matter was lower than the UN-habitat benchmark. Organic carbon was higher than the typical value (Ronald et al., 2008).

Heavy metals concentrations of copper were lower than the ceiling concentrations for all the standards considered in this study. However the concentrations of Lead and Nickel were higher than typical values, UN-habitat benchmark although within the EU standards. The concentrations of Lead and Zinc were higher than the NEMA maximum allowable value. The concentrations of Lead were higher than USA standards. Chromium and Cadmium were not detected in the sewage sludge. Iron concentration was the highest among the heavy metals. The amount of iron present (5.1 mg/l) meets the minimal threshold concentration of 3-15 mg/l Fe which allows the Fenton reaction to proceed within a reasonable period of time regardless of the concentration of organic material during chemical extraction of heavy metals (Andersson and Malkoc, 2004). The Iron concentration in the sewage sludge was also within the NEMA standards as shown on Table 4.2. The study by Kaara (2012) of anaerobically digested sewage sludge from KSTW Nairobi obtained concentrations of the heavy metals with mean values as; Zinc 1923 g/Kg, Copper 456g/Kg, Lead 410 g/Kg, Cadmium 5.8 g/Kg of dry matter. These values are comparable to those of this study with the exemption of Cadmium which was not detected in this study. The high Pb and Zinc concentrations could be attributed to the fact that Kariobangi sewage sludge plant receives waste water from industries in Nairobi and also surface runoff water from garages in the surrounding areas.

4.2. Heavy metals extraction

The percentage removal of heavy metals (Zn, Pb, Cu, Ni) at various levels was investigated at different condition of pH, time and Hydrogen peroxide dosage as shown in the experimental design matrix Table 3.2. The responses (Y%) i.e. percentage removal of heavy metals (Zn, Pb, Cu, Ni), for the design matrix shown in Table 3.2, from different conditions of pH, time and Hydrogen peroxide are presented in Table 4.3.

Table 4.3: Mean responses for the heavy metals removal

RUN	RESPONSE Y (%) ZINC (Zn)	RESPONSE Y (%) LEAD (Pb)	RESPONSE Y (%) COPPER (Cu)	RESPONSE Y (%) NICKEL (Ni)
1	92.00	86.00	92.00	93.00
2	89.50	83.82	88.40	90.22
3	98.54	99.02	98.15	98.87
4	99.14	99.42	98.90	99.16
5	99.50	99.82	99.80	99.22
6	96.65	96.87	96.61	96.84
7	99.68	99.90	99.64	99.87
8	99.24	99.52	99.00	99.37

Lead had the highest extraction at 99.90%, followed by Nickel at 99.870%, Copper at 99.80% and Zinc at 99.68%. The highest extraction rates for Pb, Ni and Zn were in run 7. This could be attributed to the fact that time and H_2O_2 setting were at their highest setting while pH was at its lowest setting dosage in run 7 as shown on the experimental design matrix Table 3.2.

4.3. Modelling extraction of Heavy metals (Zn, Pb, Ni and Cu)

The individual runs of experimental design were conducted and the responses were measured as shown in Table 4.3. A linear regression model was fitted for the experimental data. The model coefficients and effects of the factors and interactions are shown in Tables 4.4 (a), (b), (c), and (d). After determining the main effects, the effect of interactions were determined by performing the analysis of variance (ANOVA). Sum of squares (SS) of each factor quantifies its importance in the process and as the value of Sum of squares (SS) increases, the significance of the corresponding factor in the process also increases (Lazic, 2004). The ANOVA results for the heavy metals extraction from sewage sludge are presented in Table 4.5 (a), (b), (c), and (d).

Table 4.4: Regression coefficients of model terms and their effects on heavy metals extraction

(a) Zinc

Factor / Term	Effect	Coefficient	Standard Error	df	Low (-) (95% Cl)	High (+) (95% Cl)
Intercept	-	96.78	0.14	1	92.00	99.24
A	-1.30	-0.65	0.14	1	97.43	96.13
B	4.74	2.37	0.14	1	94.41	99.15
C	3.97	1.99	0.14	1	94.79	98.77
AB	1.38	0.69	0.14	1	96.09	97.47
AC	-0.35	-0.17	0.14	1	96.95	96.61
BC	-3.35	-1.68	0.14	1	98.46	95.11
ABC	-0.17	-0.086	0.14	1	96.87	96.69

(b) Lead

Factor / Term	Effect	Coefficient	Standard Error	df	Low (-) (95%)	High (+) (95%)
Intercept	-	95.55	0.14	1	83.82	99.52
A	-1.28	-0.64	0.14	1	96.18	94.91
B	7.84	3.92	0.14	1	91.63	99.47
C	6.96	3.48	0.14	1	92.06	99.03
AB	1.29	0.64	0.14	1	94.90	96.19
AC	-0.39	-0.195	0.14	1	95.74	95.35
BC	-6.47	-3.235	0.14	1	98.78	92.31
ABC	0.00	0.00	0.14	1	95.55	95.54

(c) Nickel

Factor / Term	Effect	Coefficient	Standard Error	df	Low (-) (95%)	High (+) (95%)
Intercept	-	97.07	0.14	1	93.00	99.37
A	-1.34	-0.67	0.14	1	97.74	96.40
B	4.50	2.25	0.14	1	94.82	99.32
C	3.51	1.76	0.14	1	95.31	98.82
AB	1.24	0.62	0.14	1	96.45	97.69
AC	-0.10	0.00	0.14	1	97.12	97.02
BC	-2.91	-1.45	0.14	1	98.52	95.61
ABC	-0.30	0.00	0.14	1	97.22	96.92

(d) Copper

Factor / Term	Effect	Coefficient	Standard Error	df	Low (-) (95%)	High (+) (95%)
Intercept	-	96.56	0.14	1	92.00	99.00
A	-1.67	-0.84	0.14	1	97.40	95.73
B	4.72	2.36	0.14	1	94.20	98.92
C	4.40	2.20	0.14	1	94.36	98.76
AB	1.73	0.86	0.14	1	95.70	97.43
AC	-0.25	-0.13	0.14	1	96.69	96.44
BC	-3.61	-1.80	0.14	1	98.37	94.76
ABC	-0.45	-0.23	0.14	1	96.79	96.34

Table 4.5: ANOVA results for heavy metals extraction

(a) Zinc

Factors	SS	df	MS	F_0	F table	Statistical Significance	(Alpha)
A	0.00067	1	0.00067	129.74	5.32	Significant	0.05
B	0.00898	1	0.00898	1730.34	5.32	Significant	0.05
C	0.00631	1	0.00631	1216.97	5.32	Significant	0.05
AB	0.00076	1	0.00076	146.31	5.32	Significant	0.05
AC	0.00005	1	0.00005	9.31	5.32	Significant	0.05
BC	0.00449	1	0.00449	866.35	5.32	Significant	0.05
ABC	0.00001	1	0.00001	2.29	5.32	Not Significant	0.05
Error	0.00004	8	0.00001				
Total	0.02132	15					

(b) Lead

Factors	SS	df	MS	F_0	F table	Statistical Significance	(Alpha)
A	0.0007	1	0.0007	49.0870	5.32	Significant	0.05
B	0.0246	1	0.0246	1846.6018	5.32	Significant	0.05
C	0.0194	1	0.0194	1456.6518	5.32	Significant	0.05
AB	0.0007	1	0.0007	49.8858	5.32	Significant	0.05
AC	0.0001	1	0.0001	4.5078	5.32	Not Significant	0.05
BC	0.0168	1	0.0168	1258.9183	5.32	Significant	0.05
ABC	0.0000	1	0.0000	0.0001	5.32	Not Significant	0.05
Error	0.0001	8	0.0000				
Total	0.0622	15					

(c) Nickel

Factors	SS	df	MS	F_0	F table	Statistical Significance	(Alpha)
A	0.0007	1	0.0007	6.46	5.32	Significant	0.05
B	0.0081	1	0.0081	72.61	5.32	Significant	0.05
C	0.0049	1	0.0049	44.28	5.32	Significant	0.05
AB	0.0006	1	0.0006	5.51	5.32	Significant	0.05
AC	0.0000	1	0.0000	0.03	5.32	Not Significant	0.05
BC	0.0034	1	0.0034	30.39	5.32	Significant	0.05
ABC	0.0000	1	0.0000	0.32	5.32	Not Significant	0.05
Error	0.0009	8	0.0001				
Total	0.0187	15					

(d) Copper

Factors	SS	df	MS	F_0	F table	Statistical Significance	(Alpha)
A	0.0011	1	0.0011	133.13	5.32	Significant	0.05
B	0.0089	1	0.0089	1062.01	5.32	Significant	0.05
C	0.0077	1	0.0077	923.47	5.32	Significant	0.05
AB	0.0012	1	0.0012	142.03	5.32	Significant	0.05
AC	0.0000	1	0.0000	2.89	5.32	Not Significant	0.05
BC	0.0052	1	0.0052	620.29	5.32	Significant	0.05
ABC	0.0001	1	0.0001	9.61	5.32	Significant	0.05
Error	0.0001	8	0.0000				
Total	0.0243	15					

In order to determine the important effects of heavy metals extraction from sewage sludge the *F* distribution (F_0) and F_{table} value were employed. Since $F_{table} = 5.32$, the value of 95.0% confidence level, all the effects in Table 4.6 giving F_0 greater than 5.32 have statistical significance (Lazic, 2004). Therefore ABC interaction had insignificant effect in the extraction of heavy metals (Zn, Lead and Nickel) and can be discarded because F_0 is less than F_{table}. In addition AC interaction had insignificant effect in the extraction of heavy metals (Lead, Nickel and Copper) and can be discarded. The model coefficients are obtained by dividing the effects by two (Lazic, 2004). The resultant models are represented as follows:

$$Y\% = 96.78 - 0.65A + 2.37B + 1.99C + 0.69AB - 0.17AC - 1.68BC \quad \text{……… (4.1) for Zinc,}$$

$$Y\% = 95.55 - 0.64A + 3.92B + 3.48C + 0.64AB - 3.235BC \quad \text{……… (4.2) for Lead,}$$

$$Y\% = 97.07 - 0.67A + 2.25B + 1.76C + 0.62AB - 1.45BC \quad \text{………………… (4.3) for Nickel,}$$

$$Y\% = 96.56 - 0.84A + 2.36B + 2.20C + 0.86AB - 1.80BC - 0.225ABC \quad \text{….(4.4) for Copper,}$$

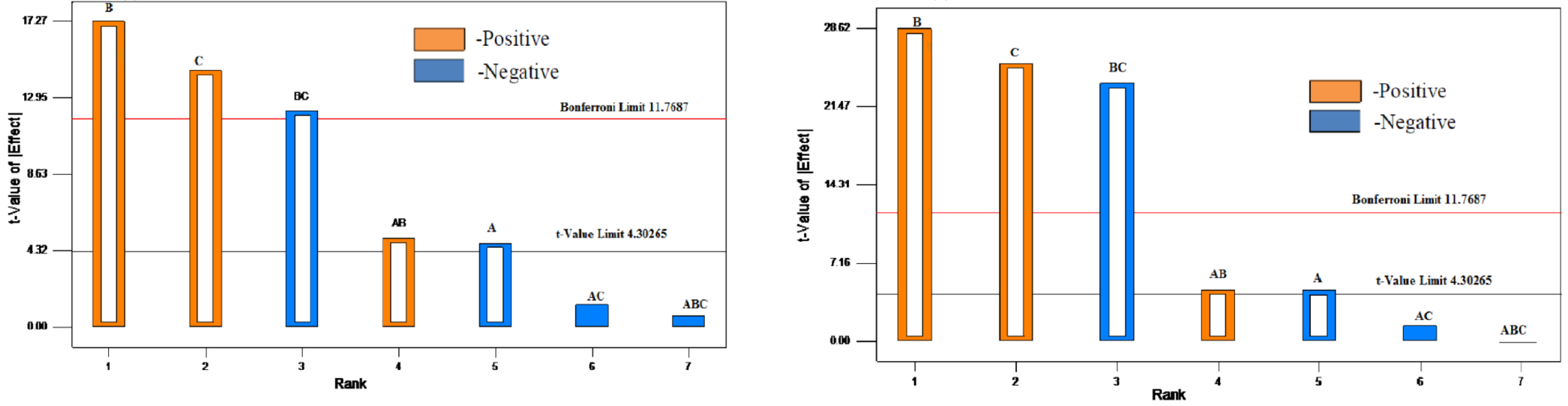
Where Y% is the percentage of heavy metal extracted.

4.3.1. Heavy metals extraction Pareto Plot

To determine whether calculated effects were significant, Student’s *t*-test was used. It was observed that for a 95% confidence level, the *t*-value was equal to 4.30265 for all the heavy metals. Those evaluations are illustrated by means of Pareto charts in Figure 4.1. The horizontal line indicates minimum statistically significant effect magnitude for a 95% confidence level. Effects above t-value (4.303) limit are significant terms in the model. The main factors of Extraction time (B), Hydrogen peroxide dosage (C) and A (pH) and interactions such as BC significantly influenced the extraction of the all the heavy metals. ABC and AC interaction were found to be of no importance in the extraction of heavy metals from sewage sludge. Any factor or interaction of factors above Bonferroni limit (11.769) had a major influence in the extraction of heavy metals.

(a) Zinc

(b) Lead



(c) Nickel

(d) Copper

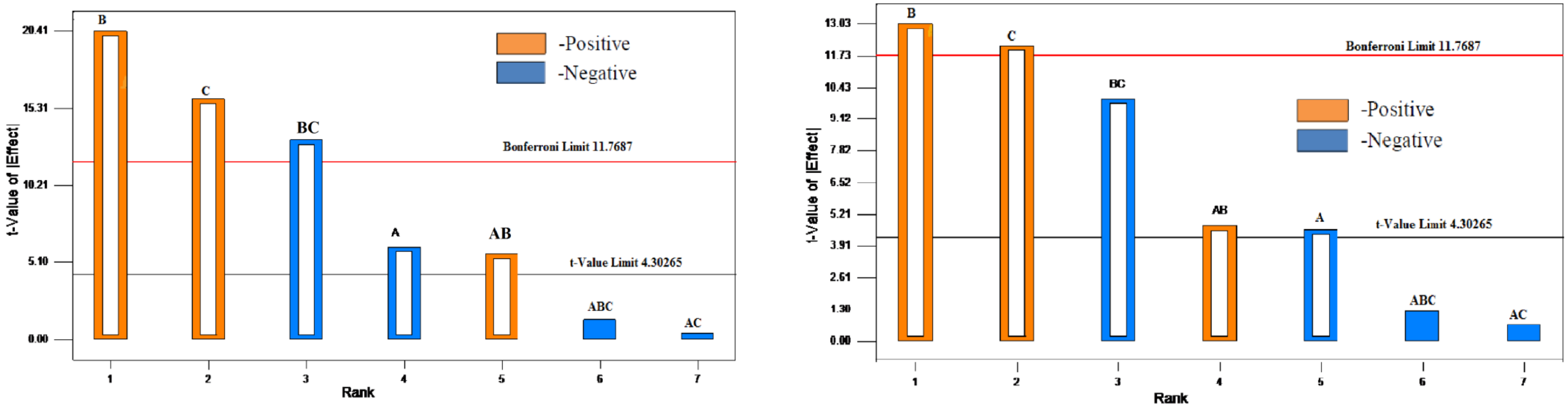
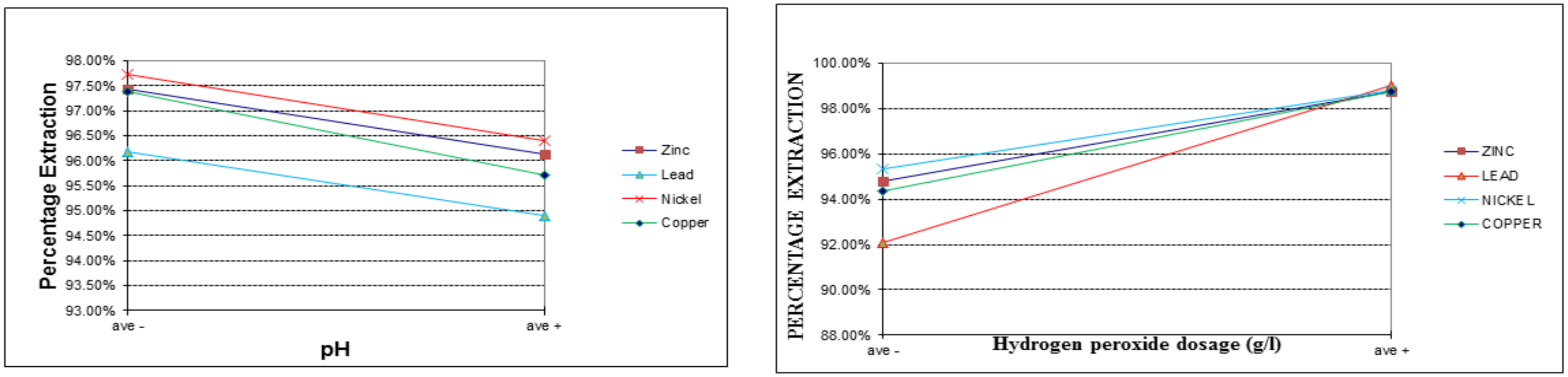


Figure 4.1: Pareto plot for effects of individual factors and interactions for the heavy metals extraction.

4.3.2. Main Effects in extraction of heavy metals

The main factors and their effect on the extraction of heavy metals were shown graphically in Figure 4.2 (a), (b), and (c). The main effect plots are helpful in visualizing which factors affect the response the most (Bradley, 2007). The sign of the main effect indicates the direction of effect. A negative effect means that the response is higher at the low setting.


(a) Effect of pH

(b) Effect of Hydrogen peroxide dosage

(c) Effect of extraction time

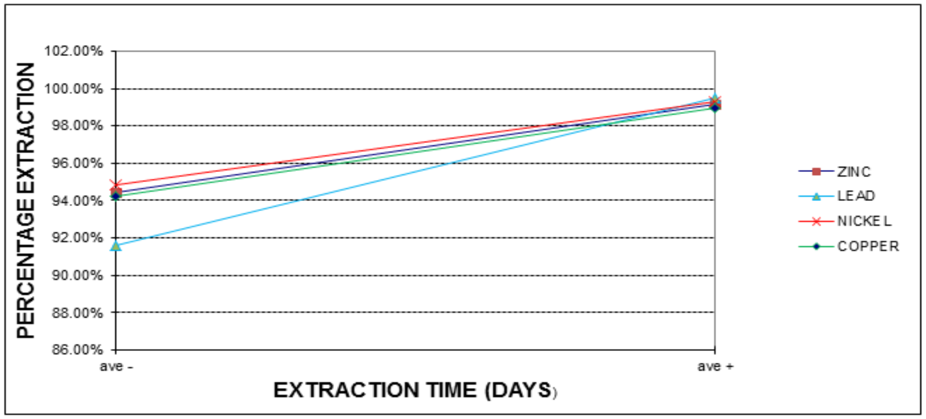


Figure 4.2: Main Effects in extraction of heavy metals

4.3.2.1. Effect of pH

As the pH is lowered, the extraction of all the heavy metals (Zn, Pb, Ni, and Cu) increased as shown in Figure 4.2(a). These results concur with the observation of Seleem et al. (2011) which showed that a low pH value is required for the heavy metals to solubilize where the acid acts as a proton donor. In this case therefore, a low pH was necessary for solubilisation of the heavy metals with the highest value being 97.43% (Zinc), 96.18% (Lead) 97.74% (Nickel) and 99.34% (Copper). Marchioretto et al. (2002) stated that a lower pH favours the solubilisation process hence the increase in percentage of heavy metals extracted as the pH decreased. Effect of pH on extraction of Nickel was highest among the heavy metals and it was least on extraction of Lead. This suggested that Nickel-Organic bond strength is least among the heavy metals and it is highest in Lead. Among the main factors the effect of pH was ranked lowest as shown on the Pareto plot Figure 4.2 (a), (b), (c) and (d). This could be explained from the fact that the change in pH was the smallest (between pH value of 3 and 5) among the main factors because Citric acid is a weak acid. The dosage of Citric acid (pK_1 =3.14) used to reach pH value of 5 was 19.06 g/l while that used to reach pH value of 3 was 80.64 g/l.

4.3.2.2. Effect of Hydrogen peroxide dosage

The dosages of H_2O_2 calculated according Fe: H_2O_2 ratios of 1:5, 1:15, and 1:25 (wt/wt), (Marchioretto et al., 2002) were as shown in Table 4.6.

Table 4:6 H_2O_2 dosages

Ratio Fe: H_2O_2	**Fe mg/140 ml**	**H_2O_2 mg/140 ml**	**H_2O_2. Dosage g/l**	**30% H_2O_2. Dosage ml**
1:5	28.07	140.35	1	0.5
1:15	28.07	421.05	3	1.4
1:25	28.07	701.75	5	2.3

From Figure 4.2 (b) as the Hydrogen peroxide dosage increased the percentage extraction of heavy metals from sewage sludge increased with the highest percentage extraction being 98.77% (Zn), 99.03% (Pb), 98.82% (Ni), 98.76% (Cu). According to Marchioretto (2002), in anaerobic sludges the heavy metals are present usually in their most reducible form, e.g., metal sulphides. Andersson and Malkoc (2004), highlights that the addition of Hydrogen peroxide after acidification increases the oxidation-reduction potential of the sludge. This then results in solubilisation of more heavy metals in the presence of iron ions in the solution. Iron ions were abundant in the solution of the sewage sludge under study as shown in Table 4.2 and could not be exhausted at low Hydrogen peroxide dosage. This applied to the extraction of the heavy metals in this study. Among the main factors, Hydrogen peroxide dosage effect was ranked intermediate as shown on the Pareto plot Figure 4.1 (a), (b), (c) and (d). Effect of Hydrogen peroxide dosage on extraction of Zinc was highest at high dosage among the heavy metals while it was lower than that of Nickel at low dosage. Its effect on extraction of Lead was lowest at low dosage and highest at high dosage. The highest extraction of Zinc increased from 97.43% due to pH to 98.77% due to Hydrogen peroxide dosage. Such behaviour could be justified by the destruction of organic matter due to Hydrogen peroxide treatment, which does not occur only by Citric acid acidification due to the high stability of Zinc complexes with organic matter. Marchioretto et al. (2002) observed that the rise in Oxidation-Reduction Potential (ORP) of the sludge promotes the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH. Oxidation- Reduction Potential (ORP) of the sewage sludge must have increased with addition of Hydrogen peroxide leading to increased extraction of Zinc.

4.3.2.3. Effect of leaching time

As the leaching time increased the percentage extraction of heavy metals under study (Zinc, Lead, Nickel and Copper) from sewage sludge increased as shown in Figure 4.2 (c) above. As the extraction time increased the more stable heavy metals complexes were broken down hence releasing more heavy metals into solution with the highest percentage extraction being 99.15% (Zn), 99.47% (Pb), 99.24% (Ni) and 98.86% (Cu). These results concur with the observation of Seleem et al. (2011) and Marchioretto et al. (2002) who observed that the amount of heavy metals extracted increased with increase in extraction time. Among the main factors, extraction time effect was ranked highest as shown on the Pareto plot Figure 4.1. Extraction time plays a major role because it determines how well the other factors interact for effective extraction of the heavy metals (Marchioretto et al., 2002). The effect of leaching time on extraction of Zinc was highest among the heavy metals at the beginning while it was highest on extraction of Lead at the end of the extraction time. This means that Zinc-Organic bond is broken faster and therefore Zinc is solubilised faster than the other heavy metals.

4.3.3. Interaction Effects

Figures 4.3, 4.4 and 4.5 show the two-factor interactions for heavy metals extraction from sewage sludge. The interactions of different factors influenced the response significantly.

This can be observed from the Pareto chart Figure 4.1. From the Table 4.5 the interaction effects of Time * hydrogen peroxide dosage (BC) and pH*extraction time (AB) are seen to be significant in the extraction of all the heavy metals. The contour plots of interaction of factors are shown in Figures A7 (a), A7 (b), A8 (a), A8 (b), A9 (a), A9 (b) and A10 (a), A10 (b), in Appendix (7), (8), (9) and (10) respectively.

4.3.3.1. Effect of pH (A) *time (B) interaction on the extraction of heavy metals.

The heavy metals percentage extraction plots on Figure 4.3 (a), (b), (c) and (d) are not parallel and therefore there was interaction between pH and time during extraction of Zinc.

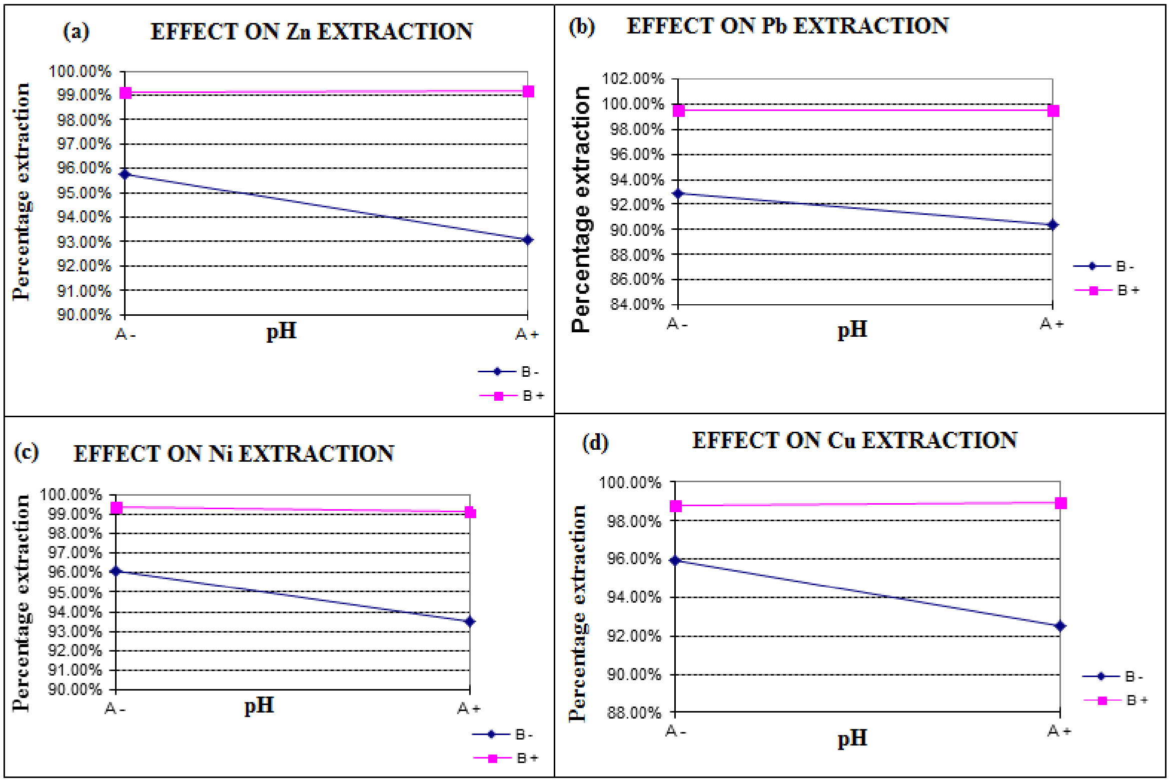


Figure 4.3: Plot of the Effect of pH*Time interaction on the extraction of heavy metals

The curved nature of the contour lines as shown in Figure A7 (a), A8 (a), A9 (a) and A10 (a) in appendix 7, 8, 9 and 10 respectively confirmed that there was interaction between pH and extraction time. The highest heavy metals (Zn, Pb, Ni, Cu) percentage extraction due to this interaction was Zn (95.75%), Pb (99.46%), Ni (99.37%) and Cu (98.95%). The effect of this interaction to the extraction of all heavy metals was low but significant as shown on Figure 4.1 with a t-value effect above the t-value limit.

4.3.3.2. Effect of pH (A)*Hydrogen peroxide dosage (C) interaction on heavy metals extraction.

The heavy metals percentage extraction plots on Figure 4.4 (a), (b), (c) and (d) are parallel showing that there was no interaction between the pH and Hydrogen peroxide dosage. As a result this interaction had no significance in the extraction of all the heavy metals under study.

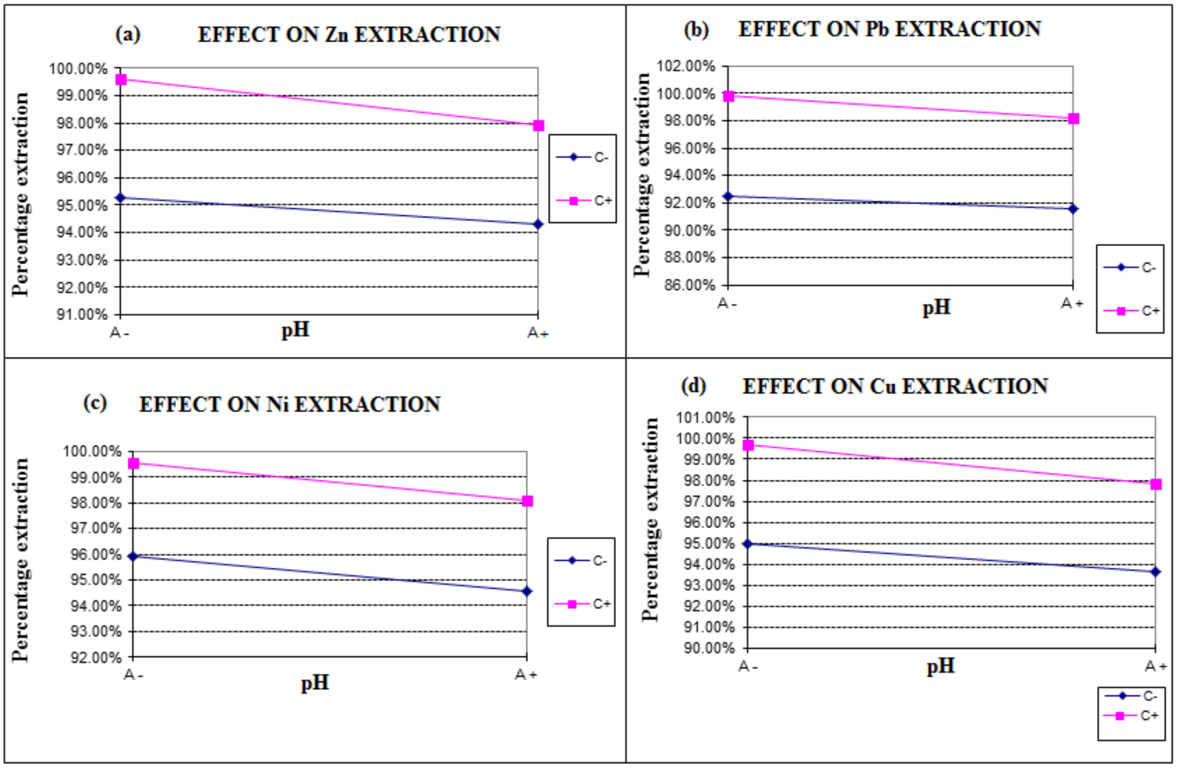


Figure 4.4: Effect of pH*Hydrogen peroxide dosage interaction on the extraction of heavy metals.

This lack of interaction is confirmed by the t-value being less than the t-value limit as shown the Pareto plot Figure 4.1 for heavy metals extraction. This can be attributed to the fact that effect of Hydrogen peroxide dosage oxidation reaction is dependent on the presence of Iron ions in solution (Andersson and Malkoc, 2004). The Iron ions were abundant in the sewage sludge and could be taken as a constant because they were in excess.

4.3.3.3. Effect of Time (B) * Hydrogen peroxide dosage (C) interaction on heavy metals extraction.

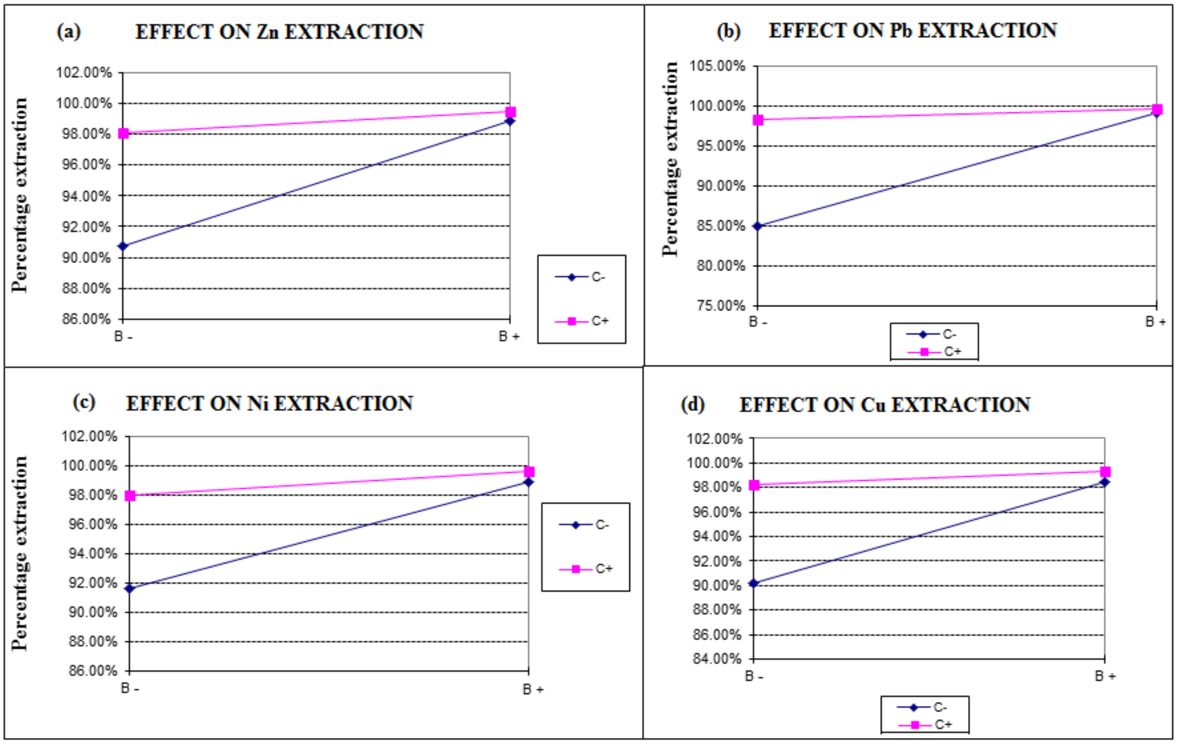


Figure 4.5: Effect of Time *Hydrogen peroxide dosage interaction on heavy metals extraction from sewage sludge.

The lines are not parallel and therefore there was interaction between Hydrogen peroxide dosage and time interaction on the extraction of all the heavy metals as shown on Figure

4.5 (a), (b), (c) and (d). The contour lines are curved as shown in Figure A7 (b), A8 (b), A9 (b) and A10 (b) in appendix 7, 8, 9 and 10 respectively confirmed that there was interaction between Hydrogen peroxide dosage and extraction time. This can be attributed to the fact that the effect of Hydrogen peroxide dosage is dependent on the presence of Iron ions in solution and the more the extraction time the more the interaction between the ions and the more the Fenton oxidation (Andersson and Malkoc, 2004). This caused the higher extraction percentage with increase with time. The highest heavy metals percentage extraction due to this interaction was Zn (99.46%), Pb (99.71%), Ni (99.62%) and Cu (99.32%). The effect of this interaction to the extraction of the heavy metals was high as shown on Pareto plot Figure 4.1. This was confirmed by its t-value being higher than the t-value limit.

4.3.4. The final model equation for heavy metals extraction

Table 4.7: ANOVA for selected factorial models

(a) Zinc

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	**Statistical significance**
Model	106.08	5	21.22	140.94	0.0071	significant
A	*3.37*	*1*	*3.37*	*22.36*	*0.0419*	significant
B	*44.88*	*1*	*44.88*	*298.15*	*0.0033*	significant
C	*31.57*	*1*	*31.57*	*209.70*	*0.0047*	significant
AB	*3.79*	*1*	*3.79*	*25.21*	*0.0375*	significant
BC	*22.47*	*1*	*22.47*	*149.28*	*0.0066*	significant
Residual	0.30	2	0.15			
Cor Total	106.38	7				

R^2 = 0.9972 , **Adjusted R^2**=0.9901, **Predicted R^2**=0.9547

(b) Lead

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	**Statistical Significance**
Model	310.20	5	62.04	413.54	0.0024	Significant
A	*3.27*	*1*	*3.27*	*21.77*	*0.0430*	Significant
B	*122.89*	*1*	*122.89*	*819.15*	*0.0012*	Significant
C	*96.94*	*1*	*96.94*	*646.17*	*0.0015*	Significant
AB	*3.32*	*1*	*3.32*	*22.13*	*0.0423*	Significant
BC	*83.78*	*1*	*83.78*	*558.46*	*0.0018*	Significant
Residual	0.30	2	0.15			
Cor Total	310.50	7				

R^2 = 0.9990, **Adjusted R^2**=0.9966, **Predicted R^2**=0.9845

(c) Nickel

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	**statistical significance**
Model	88.68	5	17.74	182.79	0.0054	significant
A	*3.60*	*1*	*3.60*	*37.08*	*0.0259*	Significant
B	*40.43*	*1*	*40.43*	*416.71*	*0.0024*	Significant
C	*24.66*	*1*	*24.66*	*254.13*	*0.0039*	Significant
AB	*3.07*	*1*	*3.07*	*31.63*	*0.0302*	Significant
BC	*16.92*	*1*	*16.92*	*174.40*	*0.0057*	Significant
Residual	0.19	2	0.097			
Cor Total	88.87	7				

R^2 = 0.9978, **Adjusted R^2**=0.9924, **Predicted R^2**=0.9651

(d) Copper

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	**statistical** significance
Model	120.88	5	24.18	92.18	0.0108	significant
A	*5.59*	*1*	*5.59*	*21.30*	*0.0439*	Significant
B	*44.56*	*1*	*44.56*	*169.90*	*0.0058*	Significant
C	*38.75*	*1*	*38.75*	*147.74*	*0.0067*	Significant
AB	*5.96*	*1*	*5.96*	*22.72*	*0.0413*	Significant
BC	*26.03*	*1*	*26.03*	*99.23*	*0.0099*	significant
Residual	0.52	2	0.26			
Cor Total	121.40	7				

R^2 = 0.9957, **Adjusted R^2**=0.9849, **Predicted R^2**=0.9309

Cl - Confidence Level, A-pH, B-Extraction Time, C-Hydrogen Peroxide Dosage, df- Degrees Of Freedom

Table 4.8: Selected heavy metals extraction model Coefficients

(a) Zinc

	Coefficient		Standard	95% CI	95% CI
Factor	Estimate	df	Error	Low	High
Intercept	96.78	1	0.14	96.19	97.37
A	-0.65	1	0.14	-1.24	-0.058
B	2.37	1	0.14	1.78	2.96
C	1.99	1	0.14	1.40	2.58
AB	0.69	1	0.14	0.099	1.28
BC	-1.68	1	0.14	-2.27	-1.09

(b) Lead

	Coefficient		Standard	95% CI	95% CI
Factor	Estimate	df	Error	Low	High
Intercept	95.55	1	0.14	94.96	96.13
A	-0.64	1	0.14	-1.23	-0.050
B	3.92	1	0.14	3.33	4.51
C	3.48	1	0.14	2.89	4.07
AB	0.64	1	0.14	0.055	1.23
BC	-3.24	1	0.14	-3.83	-2.65

(c) Nickel

	Coefficient		Standard	95% CI	95% CI
Factor	Estimate	df	Error	Low	High
Intercept	97.07	1	0.11	96.59	97.54
A	-0.67	1	0.11	-1.14	-0.20
B	2.25	1	0.11	1.77	2.72
C	1.76	1	0.11	1.28	2.23
AB	0.62	1	0.11	0.15	1.09
BC	-1.45	1	0.11	-1.93	-0.98

(d) Copper

	Coefficient		Standard	95% CI	95% CI
Factor	Estimate	df	Error	Low	High
Intercept	96.56	1	0.18	95.78	97.34
A	-0.84	1	0.18	-1.61	-0.057
B	2.36	1	0.18	1.58	3.14
C	2.20	1	0.18	1.42	2.98
AB	0.86	1	0.18	0.084	1.64
BC	-1.80	1	0.18	-2.58	-1.02

Cl - Confidence Level, A-pH, B-Extraction Time, C-Hydrogen Peroxide Dosage, df- Degrees of Freedom

At $P < 0.05$, the Model F-value of 140.94 (Zn), 413.54 (Pb), 182.79 (Ni) and 92.18 (Cu) implied the models are significant shown in Table 4.7. In this case A, B, C, AB, and BC are significant model terms. Values of "Prob > F" less than 0.0500 indicate model terms are significant. There is only a 0.71%, 0.24%, 0.54%, 1.08%, for Zn, Pb, Ni, and Cu respectively, chance that an F-value this large could occur due to noise. The "Predicted R-Squared" of 0.9547 (Zn), 0.9845 (Pb), 0.9651 (Ni) and 0.9309 (Cu) is in reasonable agreement with the "Adjusted R-Squared" of 0.9901 (Zn), 0.9966 (Pb), 0.9924 (Ni) and 0.9849 (Cu); i.e. the difference is less than 0.2. The R^2 values 0.9972 (Zn), 0.9990 (Pb), 0.9978 (Ni) and 0.9957 (Cu)) indicate that 99.72% (Zn), 99.9% (Pb), 99.78% (Ni) and 99.57% (Cu) of the variability in the response could be explained by the models. In addition, the values of the adjusted determination coefficient (Adjusted R^2 = 0.9901 (Zn), 0.9966 (Pb), 0.9924 (Ni), 0.9849 (Cu)) were also very high to advocate for a high significance of the model. These ensured a satisfactory adjustment of the polynomial model to the experimental data. The adjusted R^2 corrects the R^2 value for the sample size and the number of terms in the models. In this case, the adjusted R^2 values were very close to the R^2 values and therefore the models are good for all the heavy metals under this study. Final heavy metals extraction model equations in terms of coded factors as shown in Table 4.9 are as follows:

$Y\% = 96.78 - 0.65A + 2.37B + 1.99C + 0.69AB - 1.68BC$ ………….. (4.5) for Zinc,

$Y\% = 95.55 - 0.64A + 3.92B + 3.48C + 0.64AB - 3.24BC$ ………….. (4.6) for Lead,

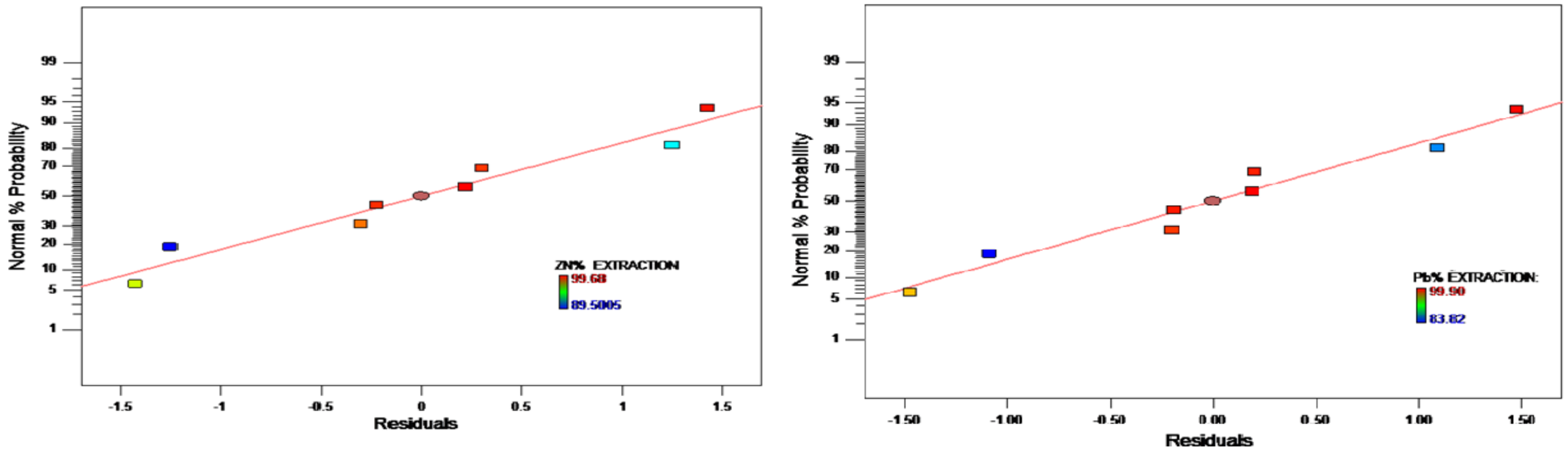
$Y\% = 97.07 - 0.67A + 2.25B + 1.76C + 0.62AB - 1.45BC$ …………… (4.7) for Nickel,

$Y\% = 96.56 - 0.84A + 2.36B + 2.20C + 0.86AB - 1.80BC$ ……………. (4.8) for Copper.

Where Y% is the percentage heavy metal extracted.

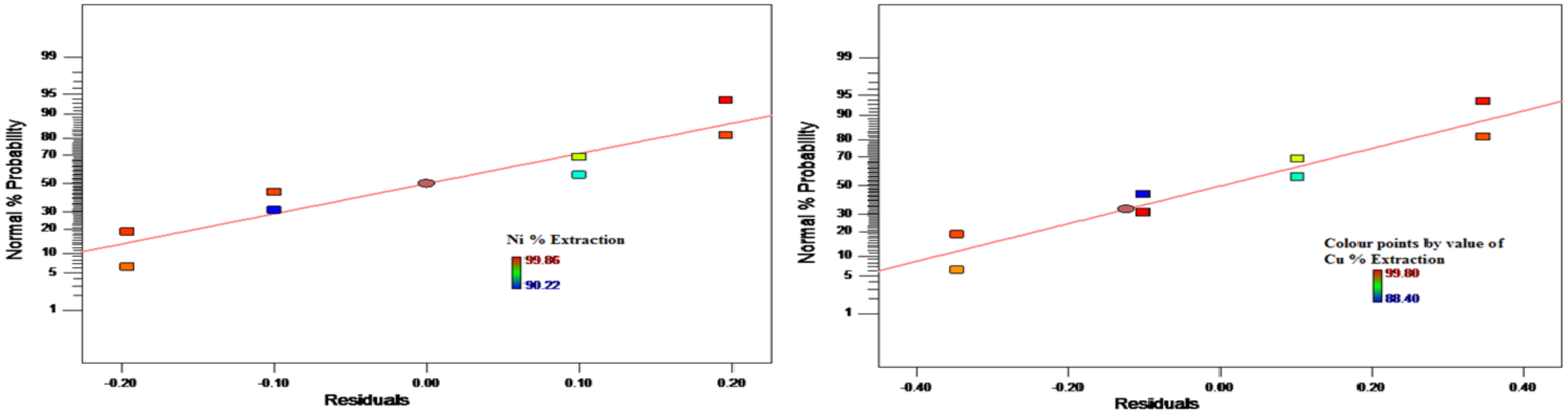
4.3.5. Normal Probability Plot

The normal probability plot of the residuals of the heavy metals under study percentage extraction from sewage sludge is shown in Figure 4.6. The data points fairly close to the straight line indicate that the experiments came from a normally distributed population. The normal probability plot of the residuals indicates no violation of the assumptions underlying the analyses of heavy metals Zn, Pb, Ni and Cu. Therefore the results are a true representation of characteristics of anaerobically digested sewage sludge from KSTW.



(a) Zinc

(b) lead



(c) Nickel

(d) Copper

Figure 4.6: Normal probability plot of residuals for heavy metals extraction

4.3.6. Optimization for heavy metals extraction

The optimization of the heavy metals extraction was performed by using a multiple response method called desirability (D) function to optimize the extraction parameters (liu et al., 2004). The main factors pH, Hydrogen peroxide dosage and extraction time were optimized by targeting maximum removal (D=1) of the heavy metals (Antony, 2003). Figure A12, (a), (b), (c), (d) in Appendix 12 illustrates the cube plot for Zinc, Lead, Nickel and Copper extraction average response values at all combinations for optimization study with three extraction parameters. The 3D surface plots of the heavy metals extraction are shown in Figure 4.7. Hydrogen peroxide dosage was set to be minimised, extraction time were set to be within the studied range, whereas pH was set to lowest (pH value of 3). Hydrogen peroxide dosage and extraction time were targeted for the optimum within the range. This was done in consideration of cost in extraction process and given that the holding time for sewage sludge during treatment is long enough to give the allowance of the studied range of up to 10 days. The optimisation process desirability, D=0.956 (Zn), 0.978 (Pb), 0.958 (Ni), 0.941 (Cu) obtained was close (less than 0.1 deviation) to the targeted value of 1 for all the heavy metals studied. This shows that the obtained model would give an accurate result (Antony, 2003).

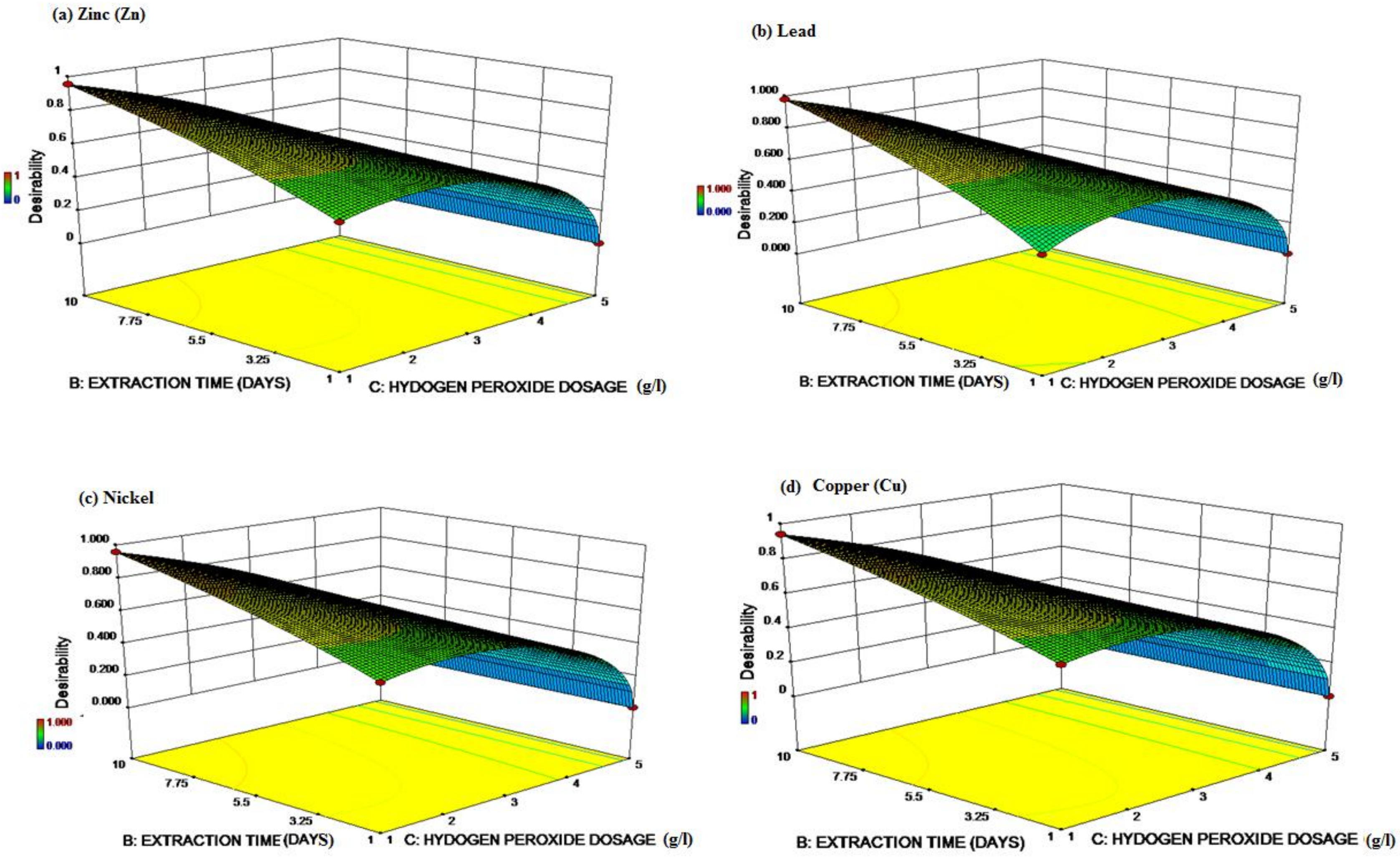


Figure 4.7: Desirability fitted 3D surface plot for Heavy Metals removal at pH value of 3.

4.3.7. Validation Experiments for heavy metals extraction

Validation of the optimized results was done by performing an experiment under predicted conditions by the developed models. The models predicted 98.8% (Zn), 99.22% (Pb), 99.07% (Ni) and 98.5% (Cu) removal at pH value of 3, Hydrogen peroxide dosage of 1mg/L, and extraction time 10 days. The experimental values obtained at these conditions are 98.41% (Zn), 98.78% (Pb), 98.62% (Ni), 98.15% (Cu) and is closely in agreement with the result obtained from the model and hence confirmed the findings of the optimization. This extraction percent was higher than that obtained using Citric acid by Seleem et al. (2011) who obtained 68% (Zn), 66% (Pb), 65% (Ni) and 51% (Cu) using effect of pH and extraction time only. This can be attributed to the use of Hydrogen peroxide causing rise in ORP of the sludge which promoted the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH.

CHAPTER FIVE

5.0. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The results showed that the anaerobically digested sewage sludge from Kariobangi sewage treatment plant contains significant amounts of Nitrogen, Phosphorous and organic matter. The high heavy metals content of the sludge clearly indicated that they must be extracted before its application on agricultural land. The option of using Citric acid and chemical oxidation with Hydrogen peroxide was investigated and found to be a feasible option.

The use of factorial design allowed the identification of the most important parameters for extraction of heavy metals Zn, Pb, Ni and Cu under tested conditions. For heavy metals Zn, Pb, Ni and Cu the most significant effect was ascribed to extraction time followed by Hydrogen peroxide dosage and the interaction of the two. The pH effect and the interaction between pH and time also had an influence in removal heavy metals Zn, Pb, Ni and Cu efficiency. There was no significant interaction between pH and Hydrogen peroxide dosage in the extraction of heavy metals Zn, Pb, Ni and Cu under tested conditions.

The optimal conditions of heavy metals Zn, Pb, Ni and Cu extraction from anaerobically digested sewage sludge were pH value of 3, extraction time of 10 days and Hydrogen peroxide dosage of 1 g/l. The percentage extraction at these conditions was Zn (98.4%), Pb (98.8%), Ni (98.6%) and Cu (98.2%). This percentage extraction reduced the heavy metals concentration to below the National Environment Management Authority maximum allowable values. From this study it is evident that extraction of heavy metals using Citric acid from sewage sludge with chemical oxidation using hydrogen peroxide likely to be an efficient and viable option.

5.2. Recommendations

Analysis of total concentration of heavy metals (HMs) in sewage sludge indicated that Lead and Zinc were in high concentrations beyond the NEMA legal limits. Sequential chemical extraction (SCE) procedures on the sewage sludge from Kariobangi sewage treatment plant should be carried out to give more insight into the forms in which the metals are present.

Chemical oxidation using Hydrogen Peroxide with Citric acid acidification was found to be an excellent heavy metals extraction method from anaerobically digested sludge and sewage treatment plants should consider applying it in their anaerobic treatment processes. Further studies should be carried-out to establish its efficiency in other types of sludges.

REFERENCES

Alvarez, A., Mochón, C., Sánchez, J. and Rodríguez, M. (2002)."Heavy metal extractable forms in sludge from wastewater treatment plants "Chemosphere, 47(7), 765-775

American Chemical Society, (1993). Reagent Chemicals, 8th Ed., p. 376-378.

Andersson, E. and Malkoc, V. (2004). Dewatering of sludge. Lund University, SE-221 00 Lund, Sweden.

Antony, J. (2003). Design of Experiments for Engineers and Scientists, Butterworth-Heinemann, NewYork.

Armenante, p. (1997). Precipitation of heavy metals from waste waters. Environmental Science & Technology, 25(7), 50-59.

Aulicino, F., Colombi, A., Calcaterra, E., Carere, M., Mastrantonio, A., and Orsini, P. (1998). Microbiological and chemical quality of sludges from domestic waste water plants. International Journal of Environmental Health Research vol. 8 pp. 137-144.

Babel, S., and Dacera, D. M. (2006). "Heavy metal removal from contaminated sludge for land application: A review " Waste Management, 26(9), 988-1004

Badmus, M., Audu, K. and Anyata, U. (2007). African Journal of Biotechnology Vol. 6 (3), pp. 238-242, 5 February, 2007.

Baek, K., and Yang, J. (2004). Cross-flow micellar-enhanced ultrafiltration for removal of nitrate and chromate: competitive binding. Journal of Hazardous Materials, 108(1-2), 184-191.

Barker, A.V. (1997). Composition and uses of compost. American Chemical Society, Washington, DC. Pp. 140-162

Batista, J. and Young, C. (1997). Removal of selenium from gold heap leachate by activated alumina adsorption. Min. Met. Proc., 14(2), 29–37.

Biswas, B., Katsutoshi I., Hiroyuki H., Keisuke O., and Hidetaka K.(2009). Leaching of phosphorus from incinerated sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. Journal of Environmental Sciences 21(2009) 1753–1760.

Byrne, W. (1995). Reverse Osmosis, a Practical Guide for Industrial Users, p. 636. Tall Oaks Publishing Inc.,

Dabrowski, A. (1999). Adsorption and its Applications in Industry and Environmental Protection, Applications in Environmental Protection, p. 1090. Elsevier Science.

Dacera, D. and Babel, S. (2006).Use of Citric acid for heavy metals extraction from contaminated sewage sludge for land application. Water Science & Technology 54(9), 129–135.

Dacera D., Babel, S., and Parkpian, P. (2009). Potential for land application of contaminated sewage sludge treated with fermented liquid from pineapple wastes, Journal of Hazardous Materials. vol167. Pg 866–872.

Debosz, K., Petersen, S., Kure, K., and Ambus, P. (2002). Evaluating effects of sewage sludge and household compost on soil physical, chemical and microbiological properties. Applied Soil Ecology, 19, 237-248.

Dohanyos, M., and Zabranska, J. (2001). Sludge into Biosolids and Utilization IWA Publishing, London.

Enezi, G., Hamoda, F., and Fawzi, N. (2004). "Heavy Metal Content of Municipal Wastewater and Sludges in Kuwait." Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances and Environmental Engineering, A39(2), 397-407.

Epstein, E. (2003). Land Application of Sewage Sludge and Biosolids, Lewis Publishers, United States of America.

European Commission, (2001). Disposal and Recycling Routes for Sewage Sludge-Scientific and Technical sub-component report.

Fu, F., and Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management, 92(3), 407-418.

Goi, D., Tubaro, F., and Dolcetti, G. (2006). "Analysis of metals and EOX in sludge from municipal wastewater treatment plants: A case study" Waste Management, 26(2), 167-175.

Gottipati, R. (2012). Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium (VI) from Aqueous Phase. Journal of Hazardous Materials. Vol 187. Pg 67–87.

Government of Kenya (2006). Water quality regulations Environmental management and co-ordination act. Kenya Gazette supplement No. 68 29th September, 2006 (Legislative supplement No. 36). Legal notice no. 120.

Gudmundur, H. J. (1999). Sewage sludge characterization and evaluation of phosphorous availability under greenhouse conditions. Journal of Hazardous Materials. pp. 49–55.

Harrison, E. Z., (1999). The Case for Caution, Recommendations for Land application of Sewage Sludge and an Appraisal of the US EPA's Part 503 Sludge Rules, pp. 22–25.

Harrison, E., and Oakes, R. S. (2002). Investigation of alleged health incidents associated with land application of sewage sludge. New Solutions, 12, 387-408.

Lazic, Z.R. (2004). Design of Experiments in Chemical Engineering. Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim.

Liu, H., Lan, Y., and Cheng, Y. (2004). Optimal production of sulphuric acid by Thiobacillus thiooxidans using response surface methodology. Process Biochemistry 39 (2004)

Kaara, J.N. (2012). Determination of heavy metals in sewage sludge, sewage effluent, garden soils and food crops grown in ordinary and sewage -sludge amended soils. International Journal of Chemistry, 3, 44-54.

Ku, Y., and Jung, I. (2001). Photo-catalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. Water Research, 35, 135-142.

Lee, I., Kuan, Y. and Chern, J. (2006). Factorial experimental design for recovering heavy metals from sludge with ion-exchange resin. Journal of Hazardous Materials B138 (2006) 549–559.

Lindquist, A. (2003). About water treatment, Kemira Kemwater, Helsingborg. Journal of Hazardous Materials (2003) 49–59.

Lombardi, A. and Garcia O. (1999). An evaluation into the potential of biological processing for the removal of metals from sewage sludges. Critical Reviews in Microbiology 25(4): 275-288.

Lucero, R. (2000).The effects of Time and Temperature on the Fate of Pathogens and Indicator Bacteria during Municipal Wastewater Sludge-Mesophilic Anaerobic Digestion, Air Drying, and Composting. International Journal of Chemistry, 2, 64-74.

Marchioretto, M., Bruning, H., Loan, T., and Rulkens, H. (2002).Heavy metals extraction from anaerobically digested sludge. Water Science and Technology, 46, 1-8.

Marinos A., Demetra, K., Katherine, J., Vassilis J., Konstantinos, G., and Maria, L. (2006). Effect of acid treatment on the removal of heavy metals from sewage sludge .Elsevier, Desalination 215 (2007) 73–81.

Mohammadi, T., Razmi, A., and Sadrzadeh, M. (2004). Effect of operating parameters on Pb^{2+} separation from wastewater using electrodialysis. Desalination, 167(1–3), 379-385.

Naoum, C., Fatta, D., Haralambous, K. J., & Loizidou, D. M. (2001). Removal of heavy metals from sewage sludge by acid treatment. Journal of Environmental Science and Health, (A36), 873-881.

Nilsson C. (2005). Treatment and Disposal Methods for Wastewater Sludge in the Area of Beijing, China. Water Science and Technology, 66, 9-18.

Nilsson, I. (2002). Sludge Utilization. New Solutions, 10, 82-94.

Oustan, S., Heidari, S., Neyshabouri, M.R., Reyhanitabar, A., Bybordi, A. (2011). Removal of heavy metals from a contaminated calcareous soil using oxalic and acetic acids as chelating agents. IPCBEE vol.8 67.

Ribeiro, M.H.L. and Ribeiro, I.A.C. (2005). Recovery of erythromycin from fermentation broth by adsorption onto neutral and ion-exchange resins, Sep. Purif. Technol. 45, 232–239.

Robert, J., Paul, L. and Kenneth, G. (2002). Laboratory methods of soil and plant analysis: A working manual.

Ronald, J., Matthews, P. and Roland, P. (2008). Global atlas of excreta, wastewater sludge, and biosolids management: moving forward the sustainable and welcome uses of a global resource.

Seleem, E. G., Mahmoud S. R. and Mohamed. M. Y. (2011). Extraction of certain heavy metals from sewage sludge using different types of acids. Biochemistri Vol 23, No 1, March 31, 41-48.

Stephanie, L. L., Lecomte, P., and Ehrhardt, J. J. (2001). Behavior of hexavalent chromium in a polluted groundwater: Redox processes and immobilization in soils. Environmental Science & Technology, 35(7), 1350-1357.

Stylianou, M. A., Kollia, D., Haralambous, K. J., Inglezakis, V. J., Moustakas, K. G., and Loizidou, M. D. (2007).Effect of acid treatment on the removal of heavy metals from sewage sludge. Desalination, 215, 73-81.

Tichý R. (1998). Bioleaching of metals from soils or sediments using the microbial sulphur cycle. Unpublished PhD. Thesis, Wageningen University, Wageningen, The Netherlands.

Ukiwe, L.N. (2012). Progressive Acidification: An Aspect of Chemical Leaching of Sewage Sludge. International Journal of Chemistry, 13, 7-15.

Ukiwe, L. N., and Nwoko, C. I. A. (2010). The influence of acids and pH in removal efficiency of heavy metals by inorganic coagulants. Terrestrial and Aquatic Environmental Toxicology, 5, 65-76.

Ukiwe, N., and Oguzie, E. (2008). Effect of pH and acid on heavy metal solubilisation of domestic sewage sludge. Terrestrial and Aquatic Environmental Toxicology, 2, 54-58.

Veeken, M. and Hamelers, M. (1999). Removal of heavy metals from sewage sludge by extraction with organic acids. Water Science Technology, 40(1), 129–136.

Verhoff, F. H. (2005). Citric Acid. Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH

Wasim, A.M. and Sengupta, D. (2008). Sewage Sludge Disposal – Land Application - Environmental Problems – An Overview

WASREB Impact Report (2009), Water and Sanitation Coverage pp.20-23.Wikipedia, Citric acid, http://en.wikipedia.org/wiki/Citric_acid#Properties. (accessed on 12/07/2013).

Whitehouse, L. J., Wang, H., and Tomar, M. D. (2000).Guidelines for Utilization of Sewage Effluent on Land Part Two: Issues for Design and Management. New Zealand Land Treatment Collective., New Zealand.

Wong, J. W. C., Lai, K. M., Su, D. C., and Fang, M. (2001). "Availability of Heavy Metals for Brassica Chinensis Grown in an Acidic Loamy Soil Amended with a Domestic and an Industrial Sewage Sludge." Water, Air, and Soil Pollution,128, 339-353.

Wong, J. W. C., and Su, D. C. (1996). "The Growth of a Gropyron Elongatum in an Artificial Soil Mix from Coal Fly Ash and Sewage Sludge."Bioresource Technology, 59, 57-62.

Xiang L, Yin Y P, Jin Y. (2002). Hydrothemal formation of Ni-Zn ferrite from heavy metal co-precipitates. Journal of Materials Science, pg 37 (15):349-352.

Yoshizaki, S., and Tomida, T. (2000). Principle and process of heavy metal removal from sewage sludge. Environmental Science and Technology, 34, 1572-1575.

Zagorodni, A. A. (2006). Ion Exchange Materials: Properties and Applications. Elsevier Science & Technology ,51, 496-595.

Zhang, H., Zhu, Z. H., Zhang, L. H., and Zhao, J. F. (2008). Extraction of heavy metals from sewage sludge using aspartic and Citric acid. Journal of Environmental Science, 29, 733-737.

Zeng, X. (2007). Research on Removal and Recovery of Heavy Metals in Urban Sludge. UK Chinese Association of Resources and Environment Greenwich, 15 Sep. 2007.

Zouboulis, A., Lazaridis, N., Karapantsios T. and Matis, K.(2008) Heavy metals removal from industrial wastewaters by biosorption Int. J. Environment and Pollution, Inderscience Enterprises Ltd.

Zufiaurre, R., Olivar, A., Chamorro, P., Nerin, C., and Callizo, A. (1998). "Speciation of metals in sewage sludge for agricultural uses. " Analyst, 123, 255-259.

APPENDIX 1:

Nitrogen and Phosphorous standards and calibration curves

Figure A1 (a): Nitrogen standards and calibration curve

NITROGEN STANDARDS	
CONC. (ppm)	ABS.
0	0
10	0.228
20	0.39
30	0.692
40	0.85
50	1.045
60	1.204
70	1.39
80	1.636
90	1.82

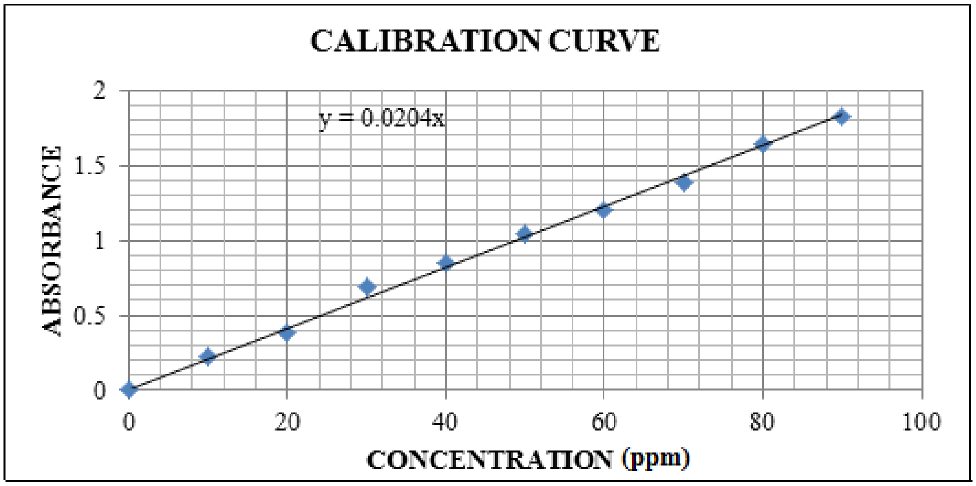
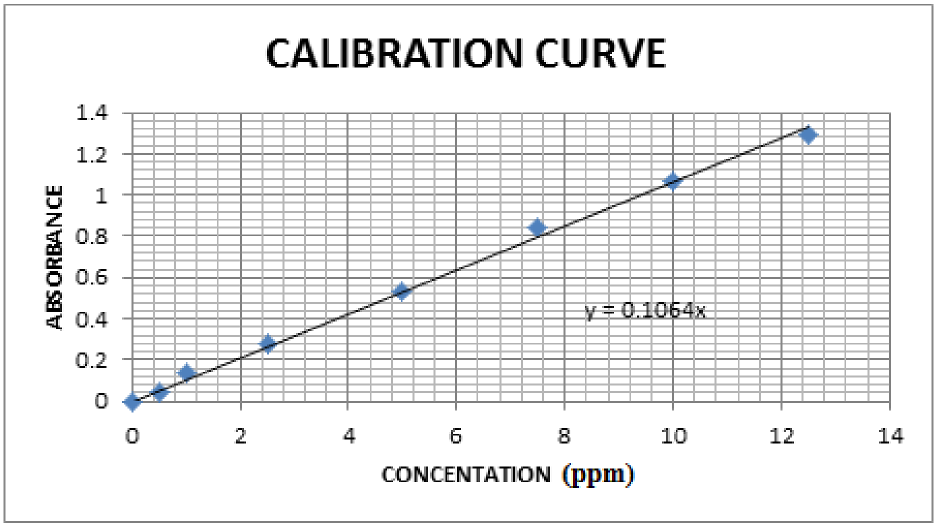


Figure A1 (b): Phosphorous standards and calibration curve

PHOSPHOROUS STANDARDS	
CONC. (ppm)	ABS.
0	0
0.5	0.045
1	0.142
2.5	0.28
5	0.535
7.5	0.842
10	1.067
12.5	1.294



APPENDIX 2:

Potassium and Zinc standards and calibration curves

Figure A2 (a): Potassium standards and calibration curve

STANDARDS	
CONC. (ppm)	ABS.
0	0
2	20
4	41
6	63
8	82
10	100

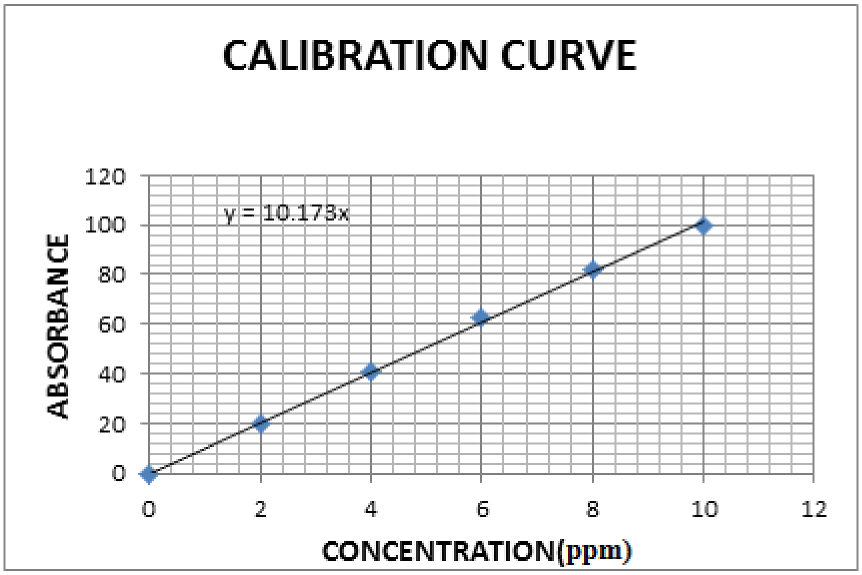
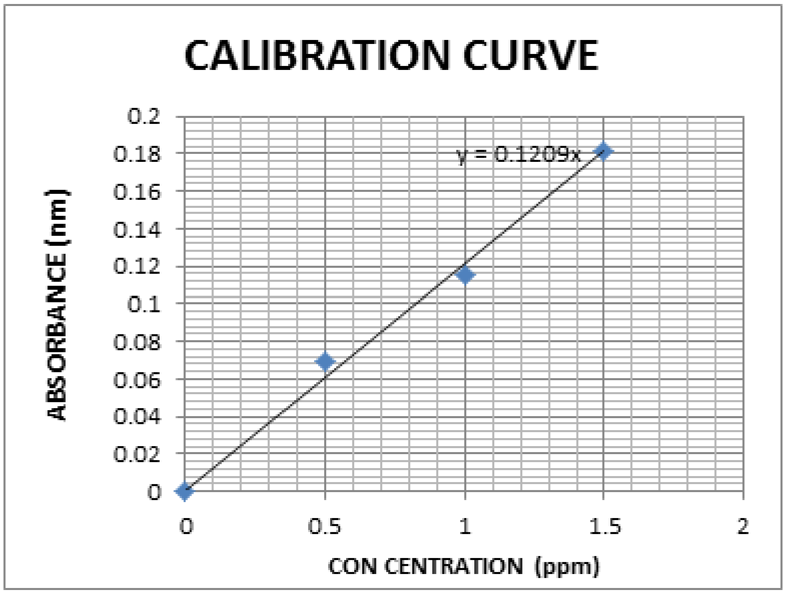


Figure A2 (b): Zinc standards and calibration curve

STANDARDS	
CONC. (ppm)	ABS.
0	0
0.5	0.0696
1	0.1158
1.5	0.1818



APPENDIX 3:

Copper and Nickel standards and calibration curves

Figure A3 (a): Copper standards and calibration curve

STANDARDS	
CONC. (ppm)	ABS.
0	0
2	0.1107
5	0.2498
10	0.5109

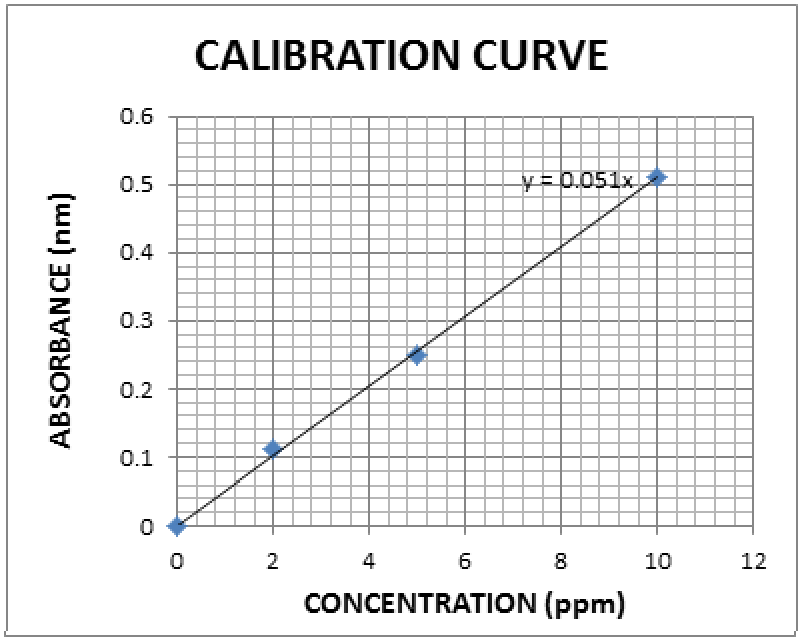
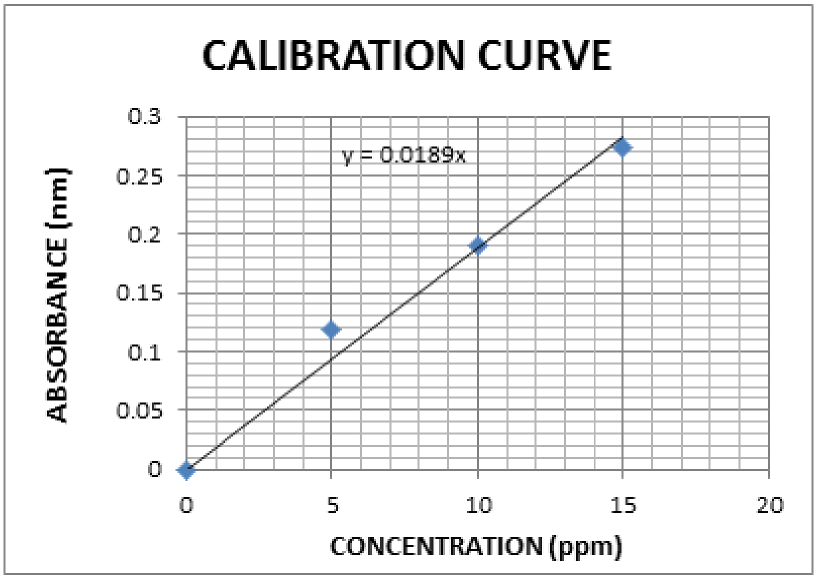


Figure A3 (b): Nickel standards and calibration curve

STANDARDS	
CONC. (ppm)	ABS.
0	0
5	0.1194
10	0.1908
15	0.2731



APPENDIX 4:

Iron and Lead standards and calibration curves

Figure A4 (a): Iron standards and calibration curve

STANDARDS	
CONC. (ppm)	ABS.
0	0
5	0.1347
10	0.2491
15	0.3413

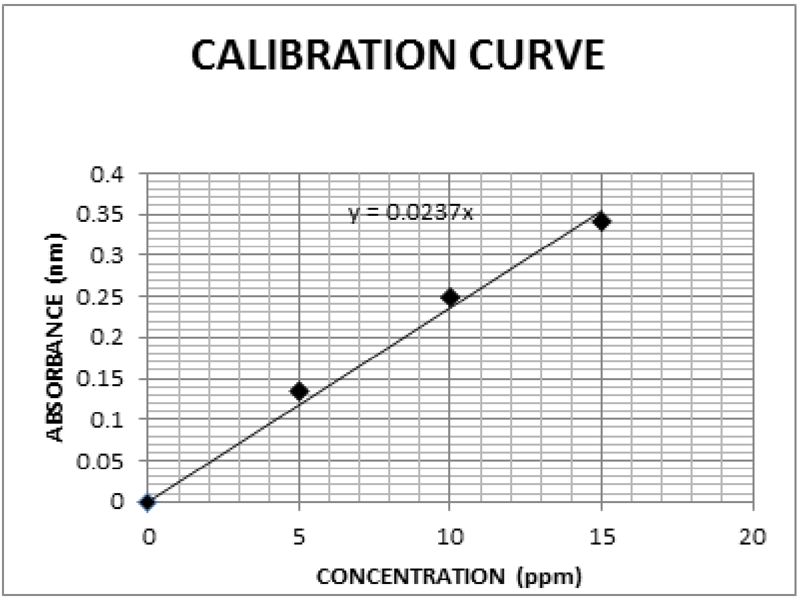
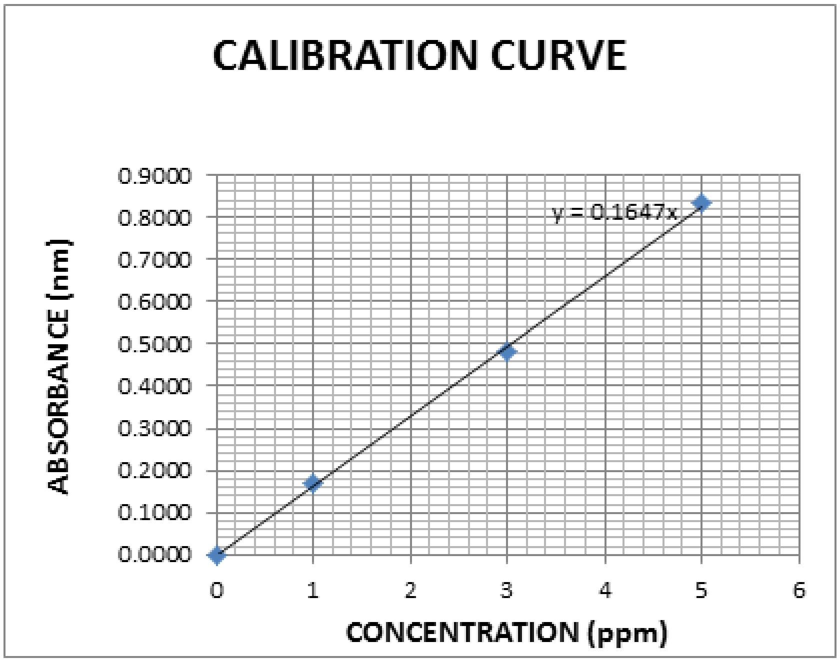


Figure A4 (b): Lead standards and calibration curve

STANDARDS	
CONC. (ppm)	ABS.
0	0.0000
1	0.1700
3	0.4803
5	0.8310



APPENDIX 5:
Chromium and Cadmium standards and calibration curves

Figure A5 (a): Chromium standards and calibration curve

STANDARDS

CONC. (ppm)	ABS.
0	0.0000
5	0.0232
10	0.0444
15	0.0575

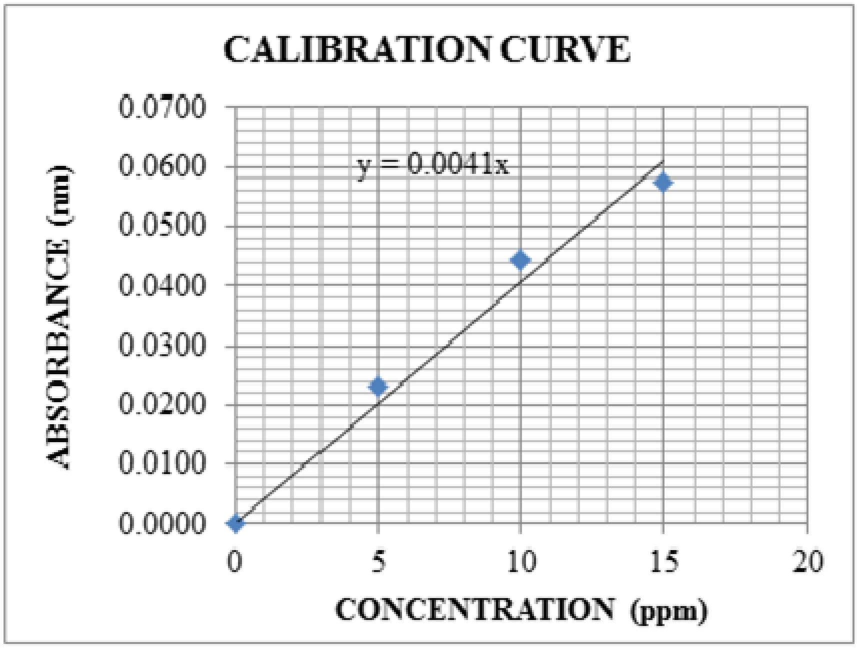
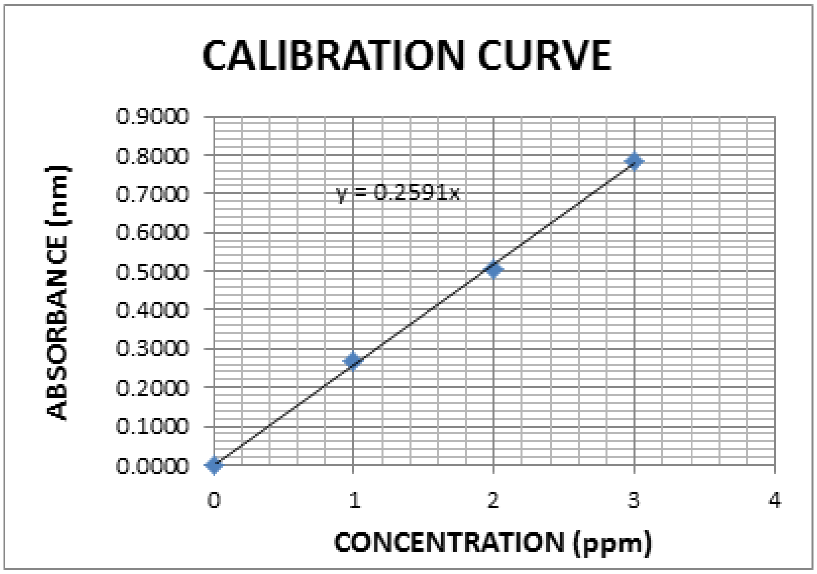


Figure A5 (b): Cadmium standards and calibration curve

STANDARDS	
CONC. (ppm)	ABS.
0	0.0000
1	0.2671
2	0.5050
3	0.7832



APPENDIX 6

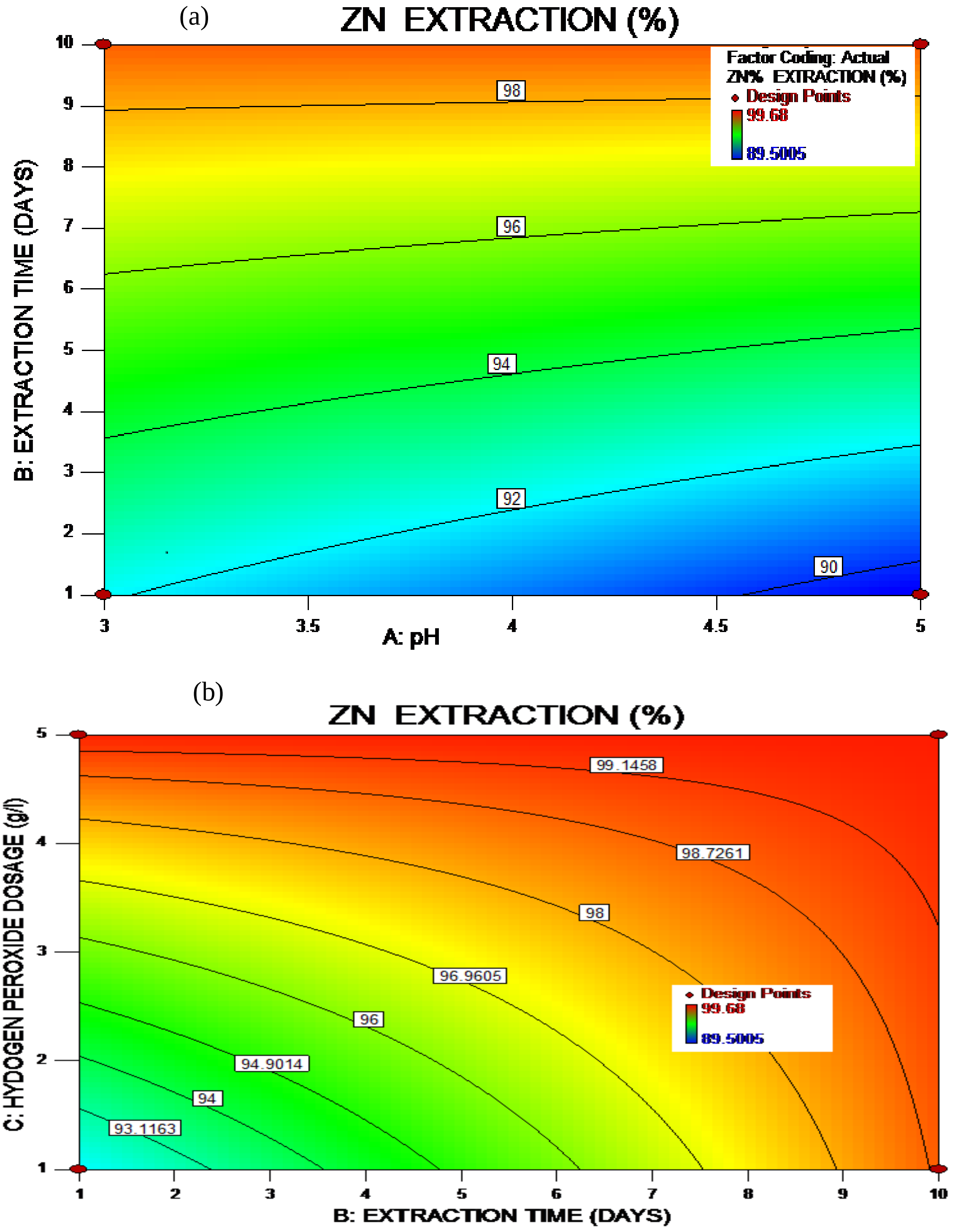
Table A6: Estimated percentage of total waste water costs required for wastewater sludge management.

Country / City	**Estimated percentage of total waste water treatment costs attributable to waste water sludge treatment and management**
Austria	45%
Canada: Greater Moncton	50%
Canada: Ontario	50%
Canada: Montreal, Quebec	45% (Operations and maintenance only)
Czech Republic	57% (Operations and maintenance only)
China	40%
Japan: Tokyo	36%
Norway	50%
Slovakia	40%
Turkey	45%
USA: Milwaukee, WI	57% (Operations and maintenance only)

(Source: Ronald et al., 2008), UN-Habitat Global atlas of excreta, wastewater sludge, and bio-solids management: Moving forward the sustainable and welcome uses of a global resource)

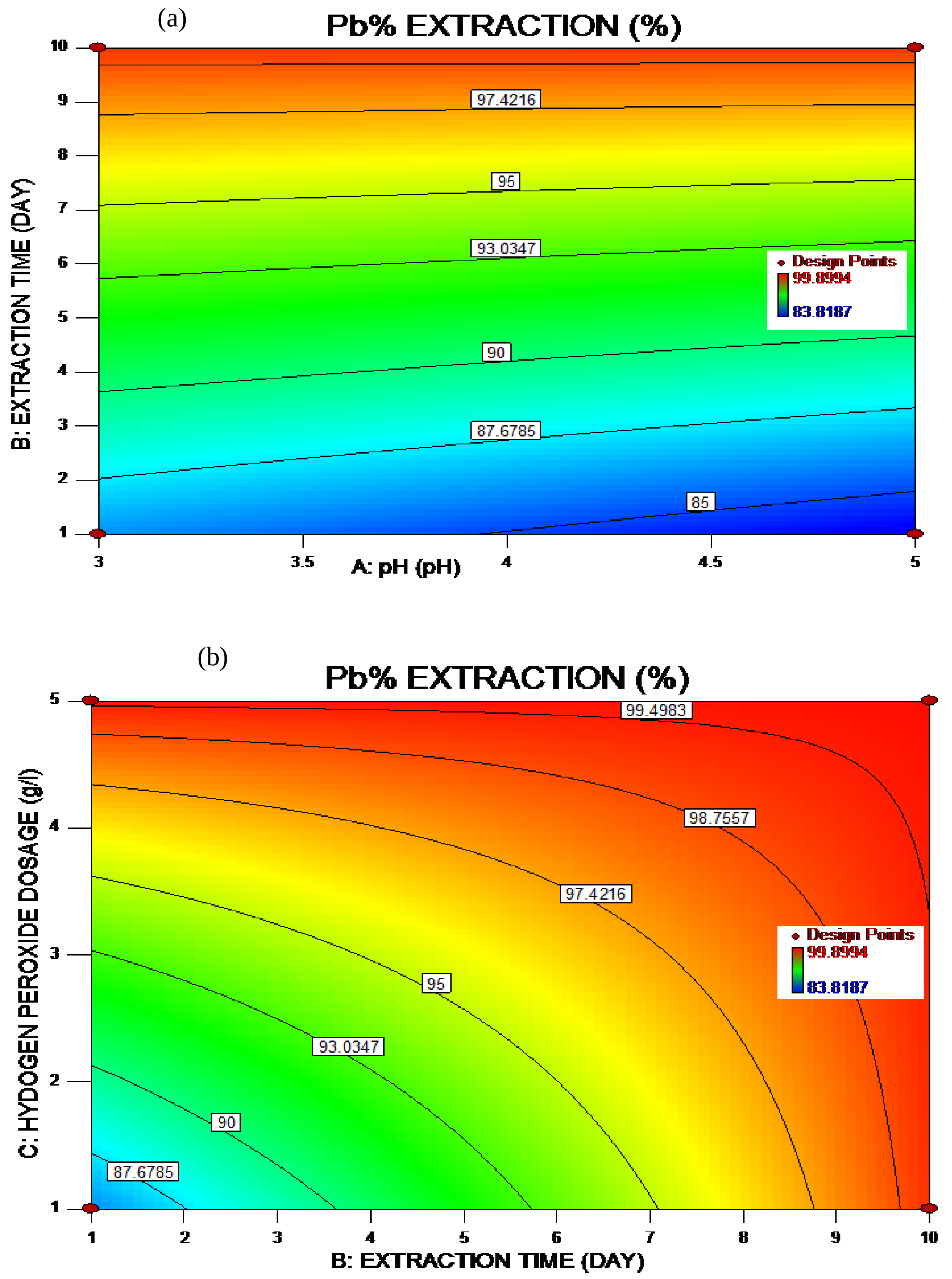
APPENDIX 7

Figure A7: Contour plots of interactions for Zinc (Zn) extraction for the chosen model



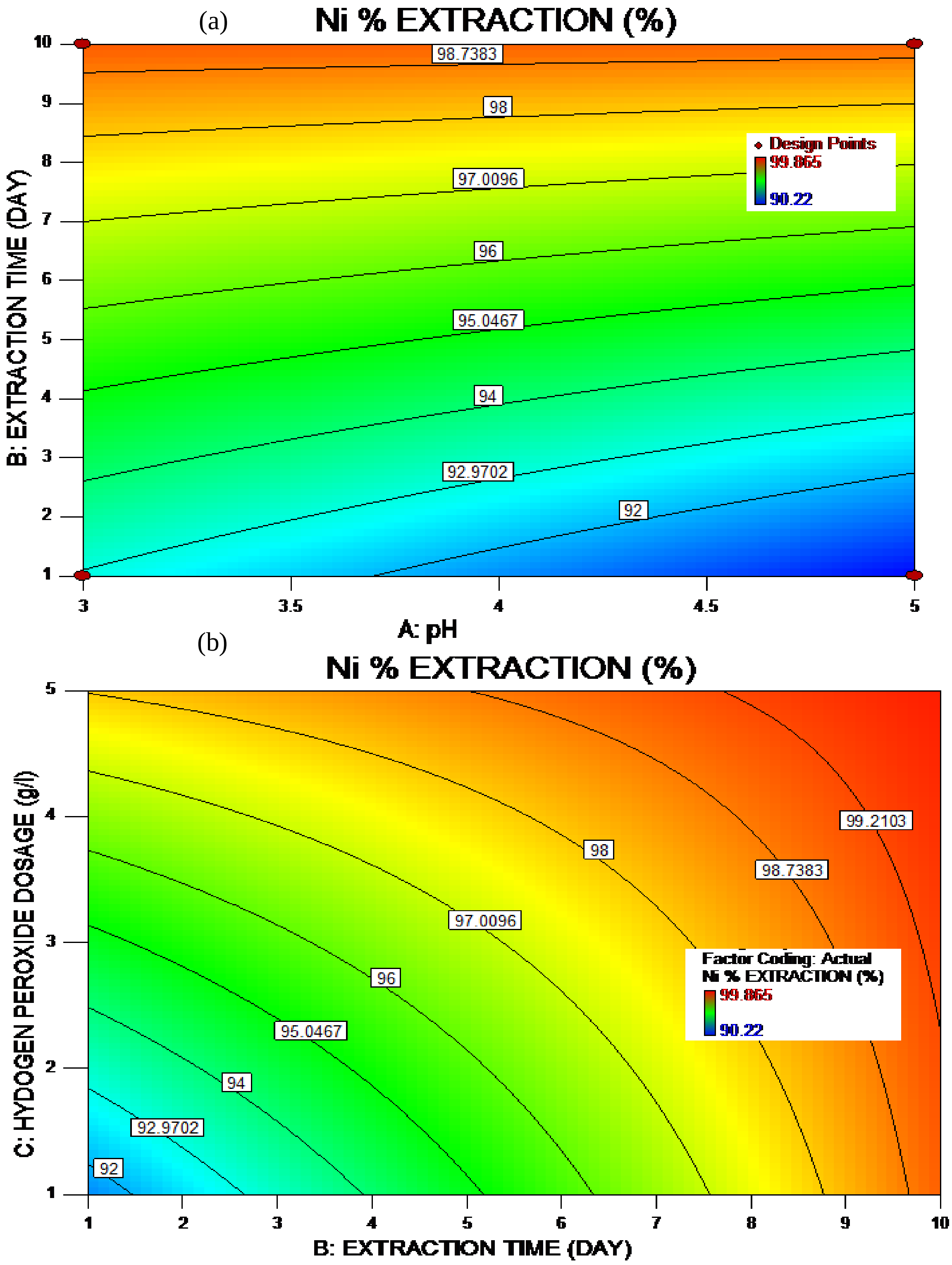
APPENDIX 8

Figure A8: Contour plots of interactions for Lead (Pb) extraction for the chosen model



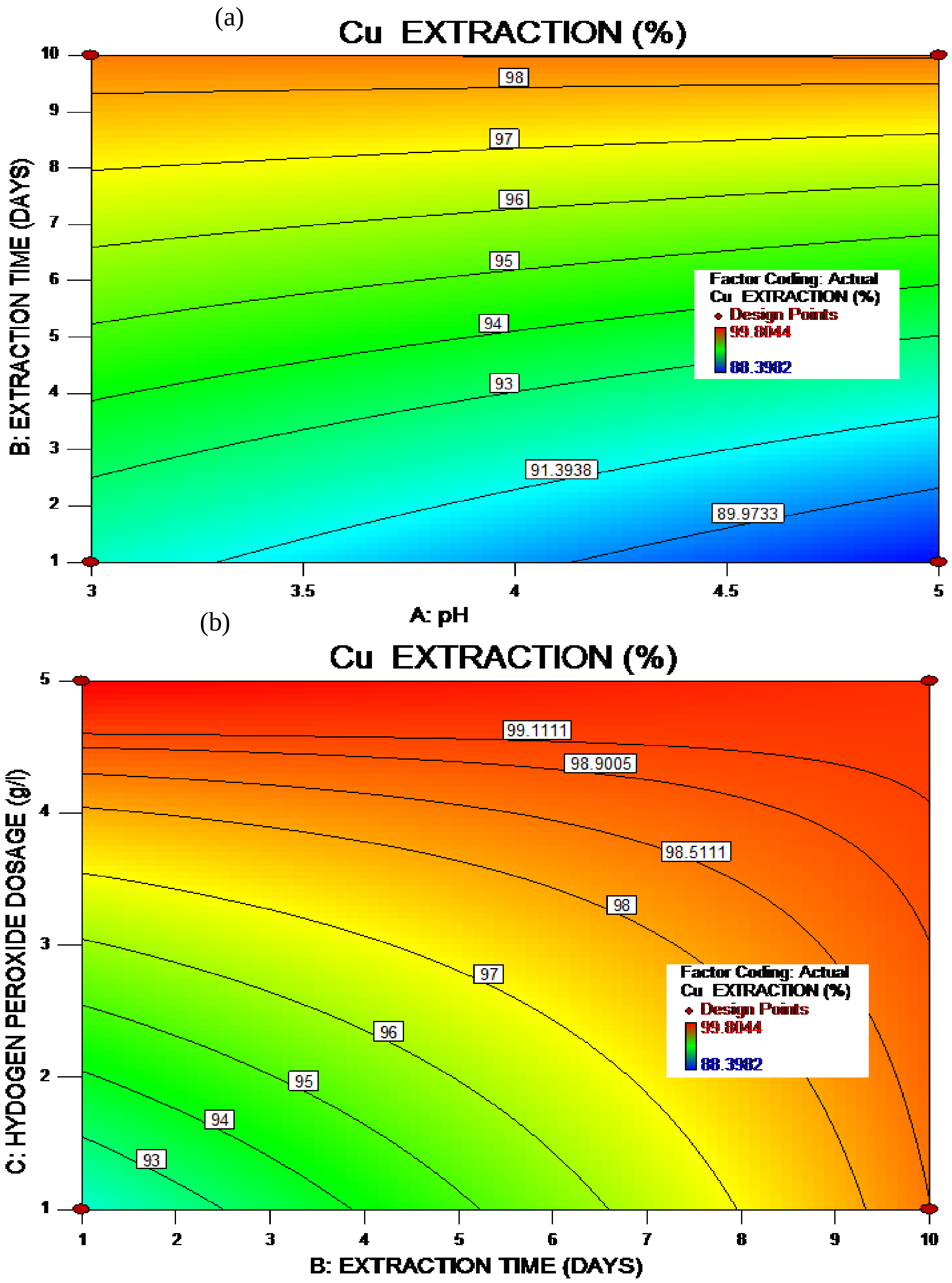
APPENDIX 9

Figure A9: Contour plots of interactions for Nickel (Ni) extraction for the chosen model



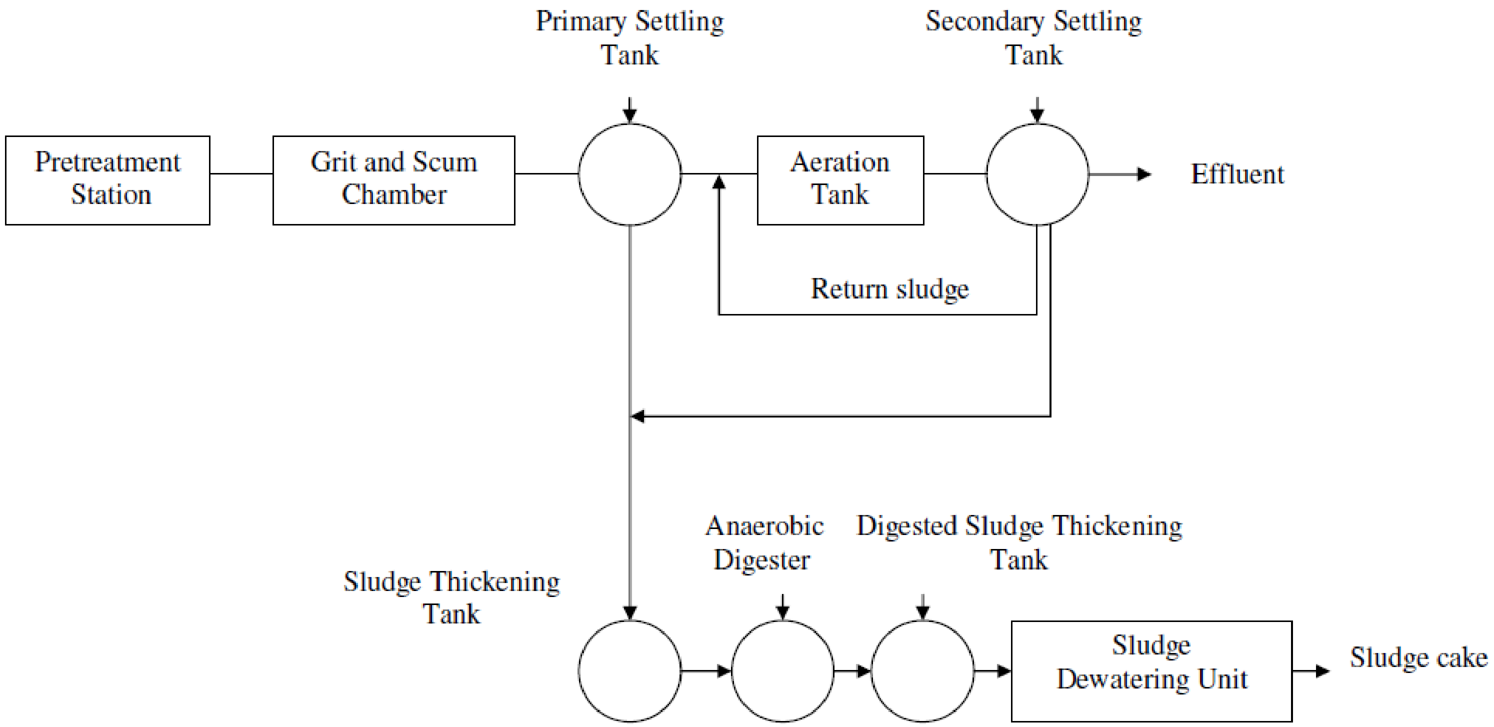
APPENDIX 10

Figure A10: Contour plots of interactions for Copper (Cu) extraction for the chosen model



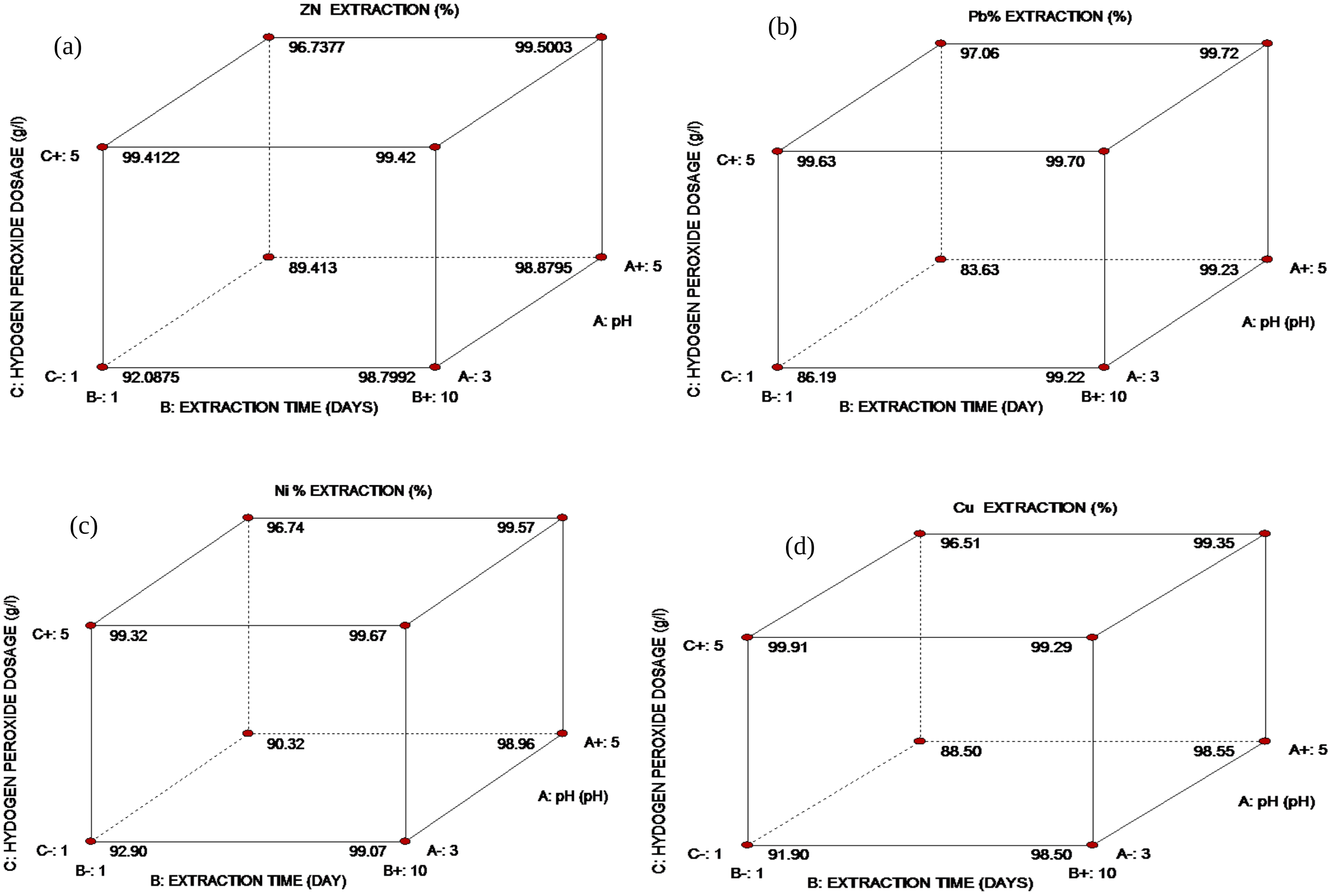
APPENDIX 11

Figure A11: Simplified flow chart of a convectional sewage treatment plant producing anaerobically digested sewage sludge



APPENDIX 12

Figure A12: Cube plots of interactions for heavy metals extraction



APPENDIX 13

Plate A13: Photographs of materials and equipment

(a) Air drying of samples

(b) Samples drying

(c) Muffle furnace and desiccator.

(d) Digested samples and colorimeter

(e) Atomic Absorption Spectrometer (AAS)

(f) Samples for heavy metals for analysis