SPECIATION OF COPPER, LEAD, MANGANESE AND ZINC AND CHARACTERISATION OF SEWAGE SLUDGE FROM WUPA TREATMENT PLANT, ABUJA, NIGERIA

Speciation of Copper, Lead, Manganese and Zinc ions in three sewage sludge samples (fresh, digested and dry) from Wupa sewage treatment plant, Abuja were investigated using sequential extraction methods. Flame atomic absorption spectrophotometer was used for instrumental analysis. The sludge physicochemical parameters, total metal concentration using aqua regia digestion, speciation of metals under study, using single extraction with EDTA and sequential extraction analytical methods were determined. Analysis of variance (ANOVA) on data obtained from the work was also carried out. Study on physicochemical parameters showed that; Samples had mean pH values of 8.48±0.13.8.50 ±0.02 and 8.37±0.17 for fresh,treated and dry sludge respectively. Samples had electrical conductivities of 520.00±0.01, 340.00±0.01 and 320.00±0.00 µScm^{-1} for fresh,treated and dry sludge respectively. Samples had nitrate contents of; 5.20±0.0, 4.80±0.01 and 2.50±0.01 gkg^{-1} for fresh, treated and dry sludge respectively. Aqua regia digestion for total metal concentration results showed values of;1418.13, 237.50, 4510.00 and 8289.60 mgkg^{-1} for Cu, Pb, Mn an d Zn respectively. Single extraction with EDTA results showed; 66.89, 6.90, 298.46 and 8.10 mgkg^{-1} for Cu, Pb, Mn and Zn respectively. Results for extraction of ions in five operational phases in sequential extraction showed; 202.15, 66.91, 385.59 and 418.79 mgkg^{-1} for Cu, Pb, Mn and Zn respectively. The metals; (Cu, Pb, Mn and Zn) were bound in five operational phases; (exchangeable, acid extractable, reducible, oxidizable and residual) in the sequential extraction method. Pb, Mn and Zn speciated more in the acid extractable, and reducible phases which were the carbonate and Mn/Fe oxide/hydroxide bound respectively. Cu speciated prominently in acid extractable and residual phases which were carbonate bound and occluded in organic matter respectively. The Solubility of all the metals (Cu, Pb, Mn and Zn) ranked highest in the acid extractable phase. Mn and Zn ranked lowest in the residual phase while Cu and Pb ranked lowest in the exchangeable and oxidizable phases respectively. Speciated ions in the exchangeable and acid extractable phases as soluble metal acetates and chlorides respectively are bioavailable to plants and vegetables for uptake. From the results of Cu, Pb, Mn and Zn ions obtained in the three extractions carried out it can be deduced that both ion concentrations are within the limits of regulatory agencies. However, a new method of speciation in handling trace metal pollutants will assist Wupa Treatment Plant in treating sewage sludge better. This will also boost agriculture and human health in the Federal Capital Territory in particular and in Nigeria in general which falls in line with the current Federal Government policies on food security and environmental sanitation.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Frequent discharge of sewage sludge without a proper treatment could have a serious negative impact on the environment, because it is a difficult material to manage (Nessa *et al.*, 2016). Sewage sludge is the residue or waste generated from treatment of wastewater (Emmanuel and Edu, 2017). It is a dark grey deposit, which is a byproduct of treated sewage from homes, offices and abattoirs (Sungur *et al*, 2019). It is also an unavoidable by product of wastewater treatment plants (Hu *et al.*, 2015). Dewatering and disposal of waste sludge is a major economical factor in the operations of wastewater treatment plants (Obianyo, 2015). Sewage contains among other things, toxic metals like copper, lead, manganese and zinc (Duarte and Noguiera, 2014). Heavy metals are mostly present in sludge as they are attached to the solid portion of the wastewater (Abdul-Aziz *et al.*, 2017). The analysis of metal concentrations found in sewage sludge constitutes an important issue in terms of both human health and environmental hazards.

Toxic heavy metals associated with sewage sludge include mercury, cadmium, manganese, nickel, copper, iron, lead and zinc (Daniel, 2017). When the metals are exposed to the environment could pose serious risk to both plants and animals. Cu, Mn, Zn, Pb and Cd pose persistent threat to the ecosystem and human health (Xiaofel *et al.*, 2017). Blood-Mn levels are related to the prevalence of chronic diseases (Koh *et al.*, 2014). Controlling sludge is of essence here, because soil is usually the final destination of metals emitted in to the environment (Ibrahim and Nafiu, 2017).

Metal speciation describes the measure of existence of heavy metals as hydroxides, biomolecules, or even organometallic compounds (Faustin *et al.*, 2018). Operational determination of the various species of Cu, Pb, Mn and Zn in different portions of sludge sample is achieved using both single and sequential extraction techniques (Luana *et al.*, 2015). Sewage sludge can vary from mixed fresh, digested (aerobic or anaerobic) sludge and bed sludge in the sewage treatment plants. Sewage sludge could be hazardous to environment due to its chemical and biological contents but can be useful if well treated (Liang *et al*., 2016). On the other hand, sewage sludge can be beneficial for both agricultural purposes and landfill, to avoid erosion and landslide (Adam, 2018). The knowledge of chemical speciation of heavy metals in sewage sludge disposed in sanitary landfill sites is of great importance to assess the ecological risk of land application of stabilised sewage sludge from the sites (Tyagi and Lo, 2016).

1.2 Statement of the Research Problem

Physicochemical parameters of sewage sludge such as pH, electrical conductivity, moisture and nitrate content can increase the danger posed by sludge to agricultural soil and environment if not controlled properly during sludge treatment (Xavier *et al*., 2019).

Study on the total concentration of a metal alone does not provide adequate information to allow for assessing the bioavailability or toxicity of heavy metals (Egorova and Ananikov, 2017). Understanding metal risk in the environment should go beyond metal measurement (John, 2018).

Species of metals in soil are a potential risk to environment (Reis, 2015). The potential toxic risks from heavy metals of sludge depend on their chemical speciation (Santoro *et al*., 2017).

1.3 Justification of the Study

Safer utilisation of sludge could be achieved only if there is a mechanism in place to control resultant pollution of sludge disposal by controlling its physicochemical parameters.

Effects of pH, electrical conductivity and nitrate contents of sewage sludge can contribute to its potential risk to environment (Li and Yang, 2018).

Understanding the effect of heavy metals in the soil is the key factor to realize the safe utilisation of sewage sludge (Hei *et al*., 2016). Cu, Pb, Mn and Zn concentration will be analysed using aqua regia digestion to extract them (Vhangwale and Miraslav, 2018). Aqua regia method proves suitable for metal extraction for solid phases to have a fair understanding of effect of metals in the environment (Das and Teng, 2016).

Proper understanding and application of the knowledge of chemical speciation of Cu, Pb, Mn and Zn in sanitary landfill can assist greatly in assessing the ecological risk of application of stabilized sewage sludge (Kai *et al*., 2016). Single and sequential extraction techniques in the speciation of Cu, Pb Mn and Zn in sewage sludge can help in evaluating the fractionations of these metals (Shuman, 2015).

1.4 Aim and Objectives of the Study

The aim is to study speciation of Copper, Lead, Manganese and Zinc and characterisation in sewage sludge from Wupa treatment plant, Abuja, Nigeria.

The objectives of this study were:

i. Characterisation of physicochemical parameters of Wupa sewage sludge samples.
ii. Determination of the concentrations of Cu, Pb, Mn and Zn in sewage sludge samples.
iii. Speciation of Cu, Pb, Mn and Zn ions in the sludge using single and sequential extraction analytical techniques.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Sewage Sludge

Sewage sludge is understood to be the solid part of wastewater from industrial and domestic activities (Merla *et al*., 2014). It accompanies wastewater as the solid part, which settles at the bottom of wastewater. According to American Department for International Trade (DIT), liquid wastes are generated from homes and offices (DIT, 2015). Water is used for drinking, industrial and domestic purposes by humans and as a habitat for the aquatics. It is also a means of sustenance for both plants and other animals constituting flora and fauna within the ecosystem (Vladan, 2016).

Both living and non-living things in the environment can contaminate clean water (Dinesen, 2017). When mixed with foreign substances, a clean water is considered to be contaminated and can be harmful. Water is used to remove dirt through bath, washing of pots, cooking utensils and washing of clothes domestically (Baghina *et al*., 2014). Wastewater contains metals, which have been known to concentrate in sewage sludge usually found with effluent from houses, storm runoff, or anything else flushed down the drain (Warren, 2015).

Sewage can be disposed properly by transporting it to sewage treatment plants for processing and final disposal (Uddin *et al*, 2016). In developing nations, not many cities have functional sewage treatment plants for proper disposal of sewage sludge (Iheukwumere *et al*., 2018). Many households in Nigeria resort to constructing septic tanks to dispose their sewage, while poor homes in slums dispose of their sewage on the streets and refuse dumps (Fubara and Butler, 2014).

According to United Nations (UN), the challenge in sewage disposal has become persistent, especially with the current challenge of open defecation in developing countries (UN, 2015a). Septic tanks are still helpful since their discovery. They assist residents in Nigeria to channel sewage to the tanks in the ground (Hassan, 2016). At the beginning of the 20th century, septic tank was introduced as a means of treating domestic sewage from individual households both in urban and rural areas (Chukwu and Oranu, 2018). Lack of sewage treatment plants in urban areas, could pose danger to the environment (Traporte, *et al,* 2014). Untreated sewage is discharged to the environment through gutters and every available channel (Sebastian and Mariosz, 2014). According to American National Organisation for Rare Disorders (NORD), sewage can cause health deficiency in the society as many diseases such as cholera, diarrhea, malaria and typhoid fever can result due to high population density (NORD, 2015).

The most common solution is the use of landfills for disposal of sewage sludge; however, this implies risk to bodies of water and to public health, in addition to operational difficulties and cost (Flicker *et al*, 2014). Public health is in danger in this case and no responsible government will endanger the lives of its people by neglecting environmental sanitation. The disposal of sewage sludge is a particular concern in domestic wastewater treatment and is linked to significant environmental issues (Dan, 2017).

Population gro8wth, urbanisation, improvement of living conditions (Ali, 2016). The increment of the number of inhabitants connected to wastewater treatment plants are responsible for the increases of the amount of sewage produced daily (Thomas *et al*., 2016). Sludge from sewage comes because of the treatment of sewage, which is the solid part of treated sewage (Khaldi, *et al*, 2017). Because of the physicochemical activities in sewage treatment, sewage sludge can be formed (Singh *et al*., 2014).

Sewage sludge contains the residues of metals and biodegradable organic compounds and viruses (Thiara *et al*., 2017). Food and Agriculture Organisation (FAO) asserted that untreated sewage sludge could be more harmful than treated sludge because levels of toxic contents are not known (FAO, 2015a). Fertilizer regulation stipulates that organic residue fertilizer such as compost and sewage sludge must be labelled as such and may be placed only in the market, if their proper use is hazardous to neither soil fertility, human, animal and plant health nor ecosystem (Tim, 2015). Vegetables and other lower plants may not withstand the toxicity of large quantity of heavy metals in disposed sludge to environment (Elophade and Ahammed, 2017). However, the menace of sludge could be reduced if fully treated sludge is used to replace sludge containing heavy metals in soil amelioration (El-Sayed and Mohammed, 2015).

Composting, physicochemical processes as well as biological processes do not curtail the toxicity of these metals in sludge adequately (Ucaroglu and Alkan, 2015). The accumulation of heavy metals in toxic amounts in the soft tissues of the body is known as their toxicity (Bawuro *et al*., 2018). Knowledge of the nutrient requirements of vegetable crops will be of help to farmers and extension workers on how to apply sewage sludge as fertilizer in the farms (Papadimitriou, 2014). Grazing animals end up eating plants with sludge in the environment and that can affect their health and that of humans eventually (Mandal, 2017). The knowledge of chemical speciation of heavy metals in sewage sludge disposed in sanitary landfill sites is of great importance to assess the ecological risk of land application of stabilised sewage sludge from the sites (Timothy *et al*., 2017).

2.2 Heavy Metals Peculiar with Sludge

Heavy metals usually associated with sewage sludge include Cu, Pb, Fe, Hg, Ni, Mn, Au and Zn (Passaro *et al*., 2017). They are peculiar with sewage sludge as components of household items and office equipment (Lata *et al*, 2015). Items containing Pb will be discarded and eventually find their way to dumpsites or waterways (Kin *et al*., 2015). According to World Health Organisation (WHO), such used products release Pb into the environment and it becomes a hazard (WHO, 2017). Cu is a metal used immensely in the automotive industries (Djukanovic, 2019). Cu wires and cables are being produced on a daily basis for electricity generation and coils for generators (Oves *et al*., 2016). These items due to wear and tear, their remains get into sewage and become part of sludge (Arthur and Vincent, 2015).

Mn is found easily in steel, cement and foundry industries (Cipurkovic *et al*., 2014). According to American Chemical Society, Pb pipes and Pb coated sinks are produced for domestic and office purposes in kitchens and toilets (ACS, 2019). Due to wear and tear, lead debris from these materials find their way to wastewater. Moreover, according to American Environmental Protection Agency (EPA) lead can enter drinking water when plumbing materials containing lead corrode (EPA, 2017). Gold (Au) debris obtained in sewage sludge can be economically viable (Nazly *et al*., 2018).

2.2.1 Zinc

Zn is found commonly in soil, water, air and food. It is found naturally in soil but its concentrations are on the increase because of anthropogenic activities, mostly from mining and other industrial processes (Wang *et al*, 2017). Foodstuffs contain some levels of Zn concentrations (West, 2018). Both domestic and industrial sources of Zn including dumpsites could cause health issues (Wang and Mao, 2019). Although Zn production is becoming more popular due its increase usage by man, its increased concentration in the environment can be hazardous to humans (Jian *et al*., 2016). Zn could accumulate in fish when such aquatics live in contaminated waters with high level of Zn (Song *et al,* 2018). Increase of Zn bioavailability and eventual bio magnification in food chain can be harmful (Gundoglu, 2020). Plants do take Zn from soil, but many a times due to its high concentration in the environment the uptake could be higher and such plants cannot handle the high concentration, which affects ecosystem eventually (Labe and Agera, 2017). High concentration of Zn could also affect the activity in soils, thereby disrupting microorganisms’ breakdown of organic matter (Noulas *et al*., 2015).

2.2.2 Manganese

Inhalation or exposure to airborne Mn is common among welders and smelters (Tahiri *et al*, 2017). Inhaled Mn can bypass the liver to enter the blood stream; from there it can enter the brain through the olfactory tract bypassing the blood-brain barrier (Goodson, 2018). Mn deficiencies include; impaired growth, impaired reproductive function, skeletal abnormalities, impaired glucose tolerance and altered carbohydrate and lipid metabolism (Zhang *et al*., 2017). Signs of Mn shortages in the body include diabetes mellitus and epilepsy or seizure diseases (Li and Jing, 2015). Major sources of Mn include; food sources and examples are beans, nut, leafy vegetables whole grains, teas, milk, infant formulae, water and supplements (Gracnaweit and Tadihaka, 2019). Other sources of Mn include cement products, fertilizers, textile printing, iron and steel products and foundries as an alloy of these materials (Tajer, 2018). Mn toxicity is lethal, when inhaled (Sun *et al*, 2017). Methylcyclopentedienly manganesetricarbonyl (MMT), ingested Mn and intravenous Mn are dangerous (Lenntech, 2019). As asserted by Web Medical (WebMD), people who are exposed to Mn susceptibility end up having chronic liver diseases, newborns sicknesses, children brain deficiency and iron deficiency of the population (WebMD, 2015). Consuming more than 11mg per day of Mn could cause serious and harmful effects (Mohammadi, 2014).

2.2.3 Lead

Pb is the most common metal contaminant (Rajaswari and Sailaja, 2014). It is usually found mixed with sulphur (PbS), sulphates (example $PbSO_4$ and carbonates ($PbCO_3$) respectively in the soil (Jasinska, 2018). Common sources of Pb in homes and offices include kitchen sinks, lead pipes and car batteries (Barren, 2017). Prolonged exposure to Pb can lead to several psychological as well as heart complications, as ions of Pb do bridge with sulfur hydryl and other functional groups of enzymes and vital peptides (Monisha *et al*., 2014). The presence of Pb in fuel has also contributed to the accumulation of Pb in the environment. World Health Organisation (WHO) guidelines states that three is no safe Pb concentration (WHO, 2018).

Presence of Pb in ecosystem can be devastating as it affects both plants and animals (Walters, 2018). Once introduced into food chain, it goes around from one victim to another through food intake (Mohammed *et al*., 2016). Pb accumulates in the body gradually due to consistent intake and thus cause devastating effect on victims (Oransky, 2019). The presence of Pb in Pb containing fuel has also aggravated accumulation of Pb in the environment (Abd-Latif *et al*, 2015). As vehicles emit smoke, Pb is released to atmosphere and it falls on leafy vegetables in nearby garden farms, in dams and reservoirs and ponds. When affected leafy vegetables are consumed by man and animals, lead tends to bio accumulate in them thereby causing several diseases (WHO, 2015).

Pb affects miners at mining sites, as it is excavated together with minerals being excavated from the sites (Yu-Pin, 2016). This can easily cause Pb poisoning to miners and surrounding communities, which can lead to mass death in such communities (Yuan *et al*., 2015). American Centre for Diseases Control (CDC) reported that in Zamfara state, Nigeria many miners and villagers died because of Pb poisoning from Au mining sites (CDC, 2018). Pb is usually attached to other compounds of metals, which are found in the soil naturally as a result such compounds become agents of propagation of Pb when they are mined or excavated accidentally (Hsing-Cheng *et al*, 2016). The devastating effect of lead and cadmium in the environment seems to be more pronounced than other toxic metals (Raja and Namburu, 2014). Presence of Pb in sewage sludge is without doubt a thing of concern to governments and people in Nigeria (Ikpeze, 2014).

Tackling the presence of Pb in household items, industrial and office items will go a long way in solving the problem of lead in the environment (UN, 2015b). It is indeed a cheering news that building industries are beginning to reduce the use of Pb as a material for building and for household items (Santosh *et al*., 2014). This indeed underscores the importance of understanding the chemistry of Pb in sewage sludge as to build a mechanism that will immobilize it and thereby mitigating the effect it poses to the environment (khaled *et al*, 2018).

The knowledge of the chemistry of Pb metal in terms of speciation will help in mitigating the unnecessary presence of this metal in the environment (Das *et al*., 2015). It is obvious that Pb metal is no longer desirable in the environment and proper treatment of sewage sludge containing Pb is of paramount importance to environmentalists (John *et al*., 2016).

2.2.4 Copper

Cu is an essential element needed in the human body for proper growth. It functions in the formation of heamoglobin (Vassey *et al*., 2015). It alloys with metals to produce alloys for strength and durability. It is used in electroplating processes through the electrochemical process of electrolysis (Constatino *et al*, 2017). It is an essential material in electrical or electronics industry for the production of copper wires, circuits and cables (Bell, 2015).

According to Food and Agriculture Organisation, Cu can accumulate in the environment and can cause sicknesses and diseases to humans and animals (FAO, 2019). Lower content of it in the body also causes illness (David, 2018). Cu deprivation in animals contribute to instability of heart rhythm, hyperlipidemia, increased thrombosis, breakdown of vascular tissue, cardiac hypertrophy and altered corterial function (Nlemadin *et al*., 2019). Residues of Cu are found in sewage sludge due to wear and tear of copper-coated items and equipment from homes and industries (Huase and Eddy, 2018). Cu can cause kidney failure, sickle cell anaemia and psychological problems (Ayham and Durmus, 2016). Cu poses health risk to man and animal; therefore, it becomes imperative to understand the speciation of Cu in sewage sludge to mitigate its undesirable effect in the environment (Maarouf, 2018).

Cu complexes with organic compounds, which shows only on rare occasions. Cu is found as a single metal in the environment (Anjuola, 2014). Cu exist in different oxidation states being a reactive metal, therefore its speciation is a concern (Adrees *et al.*, 2015). Physicochemical processes such as temperature change and soil pH change can affect water and soil contamination and metal uptake by plants, which occur naturally, this, can lead to environmental contamination (Alexandros and Vassilos, 2014). A lot has to be done in order to reduce the large presence of Cu in the environment and this starts from understanding the speciation of Cu especially in sewage sludge (Joannis, 2017).

2.3 Sources of Toxic Heavy Metals in Sludge

Toxic metals like Cu and Mn in sewage sludge come from household items and office equipment due to wear and tear and end up in soil (Tytia, 2019). Cu plated plumbing materials are also sources of Cu and may be found in sewage sludge (Irena and Bergik, 2017). Mn is found in food humans consume, manganese is a mineral element that is both nutritionally essential and potentially toxic (Highdon, 2019). Zn debris from zinc-coated sinks can accumulate in sewage sludge, which can add to high concentration of Zn in the environment (Jiang *et al.*, 2017). Tin from mining sites, can find its way to waterways and become part of sewage sludge. It can also come from discarded beverage containers from homes and offices. Sludge treatment can be expensive as the cost associated with sludge treatment and disposal can reach 50% of wastewater treatment cost (Jianglong *et al.*, 2014).

Toxic metals could be found in different items, which are necessary for daily use at homes and offices (Alexander and Paulos, 2016). Heavy metal toxicity has no clear warning signs of the damage it causes (Adal and Sage, 2018). Due to increase in population astronomically in the world, many households make use of items of metals and this promises consequences for the environment (Eham, 2014).

2.4 Effects of Toxic Heavy Metals in Sludge

Cu and Mn are toxic because of their speciation while in liquid medium (Anujkumar and Mansoor, 2018). They have different toxic levels in their different forms of existence as species while in sewage sludge (Malwina *et al*., 2015). Mn exists as Mn^{2+} and Mn^{3+} while in human body, which means manganese in these states is soluble (Ahumada *et al*, 2019).

2.5 Sewage Sludge Treatment Plants

The purpose of sewage sludge treatment is to reduce sludge weight and volume to reduce disposal costs and potential risks of disposal options (Nnnekanma, 2018). Sludge in sewage treatment plants can be treated before they are discharged into the environment. In Nigeria, few cities like Lagos, Abuja and Kaduna have sewage treatment plants. Lagos and Kaduna mostly have mini treatment plants owned by private companies and banks, while Abuja has a functional sewage treatment plant (Onakpa *et al*, 2018). Wupa sewage treatment plant Abuja, is made for the Abuja city residents. The treatment plant is used to process liquid waste generated from the city (Kleberg *et al*., 2018). Most of treatment plants are found along rivers or streams for easy treatment of sewage and sludge and eventual disposal (Hassan *et al*., 2015).

Sludge is the result of the treatment of sewage in a treatment plant involving physicochemical processes such as sludge thickening, stabilisation of metals and using lime for pH adjustment of sludge at various stages in a plant (Alexandra *et al*., 2016). Sludge is actually a mixture of biodegradable organic compounds, heavy toxic metals, solid matter and pathogens, which includes bacteria and other microbes (FAO, 2015b). It is very smelly and actually a combination of diseases and hazardous materials to humans, animals and environment (Luciano *et al*., 2016). On the other hand, sludge can be important agriculturally, as a well-treated sludge can serve as a fertilizer and landfill because it is full of nitrogen, phosphorus and other rich and useful organic remnants (Baldessare, 2017). Treated sludge has to be regulated when applied to farms to avoid phytotoxicity in plants and crops. Sludge serves as a landfill to avoid gully erosion and landslide in erosion prone areas; the rich organic matter in sludge helps replenish soil in an erosion site (Kai *et al*., 2018).

Sludge can be charred by burning the solid of sewage at high temperature, which can make it suitable for agricultural purposes (Lechtenberg, 2018). Sludge management by use of sludge as an alternative energy source is emerging in the developed world. Sludge if properly applied can have an advantage over inorganic fertilizer (Hewig, 2016). This is because rich minerals and organic matter that improve soil fertility and thus increasing crop yield are found in treated sewage sludge (Daniel *et al*., 2017). It should be noted that agriculture relies heavily on the breakthroughs made in science and technology to increase crop yield and animal meat and dairy (David and Mineti, 2018). According to United Nations Environmental Programme (UNEP), while inorganic fertilizers contain dangerous chemical contents including radioactive materials like isotopes of potassium and phosphorus, sludge content can be regulated during treatment (UNEP, 2017). Organic fertilizer can increase salinity of soil thereby increasing the chances of crop death and low yield (Kaushal *et al*., 2018). Organic fertilizer can also be potentially dangerous to farmers as they dig wells near their farms for domestic purposes (Aleksandra &Oleszsczuk, 2018). As these minerals from the applied fertilizer percolate into soil, they go to the water table and contaminate it or during rainy season, they dissolve in a runoff water to streams and rivers and subsequently became part of man and animal drink (Pevton *et al*., 2016). Farmers need treated sewage sludge as an organic fertilizer; organic fertilizers have become sought after these days. Regulated sludge can serve same purpose as inorganic fertilizer if not better and with less danger (Gaskin and Mark, 2017). Chemical contents in inorganic fertilizers bio accumulate in the soil and cause havoc but regulated sludge will have with it immobilized metals, which will not cause harm to environment for a long time to come (Dixit *et al*., 2015). Sanitary sewage sludge when treated properly is less harmful to environment and this is achieved when speciation of metals in it are known for proper metal immobilization (Andrew, 2019)

2.6 Sewage Sludge Treatment

Sewage sludge has to be treated in order to control its hazard to the environment and human health (Werle and Dydziak, 2014). When sewage reaches sewage treatment plants fresh sewage passes into grit chamber. This tank slows down the flow for solid components to settle (Al-Salam *et al*., 2017). The mixture moves to primary tank. In this tank about half of suspended solid particles settle out within one and half hour, this makes solid and liquid sewage pollutants remain in the tank (Franz *et al*., 2017). According to American National Science and Environment Management (NASEM), treatment of sewage sludge continues with an overflow of wastewater above continues running for continual cleaning process (NASEM, 2017). Primary solids or raw sewage sludge also known as sediment remains behind in the settling tank (Samer, 2015). At this point, this biosolid is known as fresh sludge, however with time, air is exhausted and microbes begin to act on it in the absence of air. Then microbes succeed in degrading it and a foul smell results eventually (Ismail, 2017). However, to avoid this unpleasant odour, the fresh sludge can be removed immediately (Victor, 2017). As fresh sludge is being removed from settling tank, it is passed on to other tanks for further processing like activated sludge aeration, up flow anaerobic sludge blanked and Imhoff tanks (Andrade *et al*., 2015).

Plate I depict the Fresh sludge basin in which sludge from town is collected and ready for treatment.

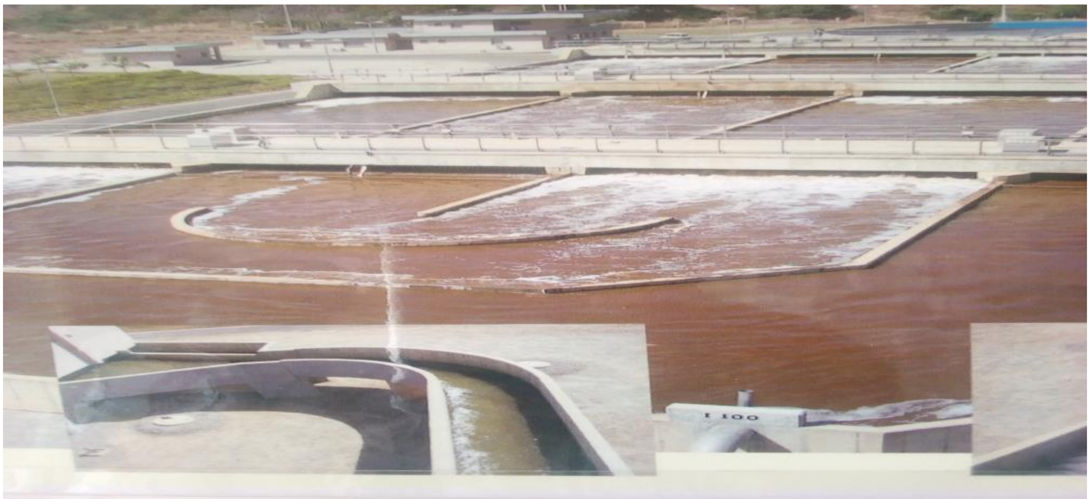


PLATE I: Fresh Sewage with Sludge in a Basin at Wupa Treatment Plant, Abuja.

Sludge treatment by aeration reduces odour of sludge while using an anaeration condition increases sludge odour due to presence of anaerobic bacteria. Aeration is observed to be favoured in sewage processes at sewage plants more than deaeration process; it also increases the yield of sludge in the generation of sludge (Bryen, 2019).

Plate II depicts the treated sewage in a basin in which sludge is separated from wastewater for onward transport to digester tanks.

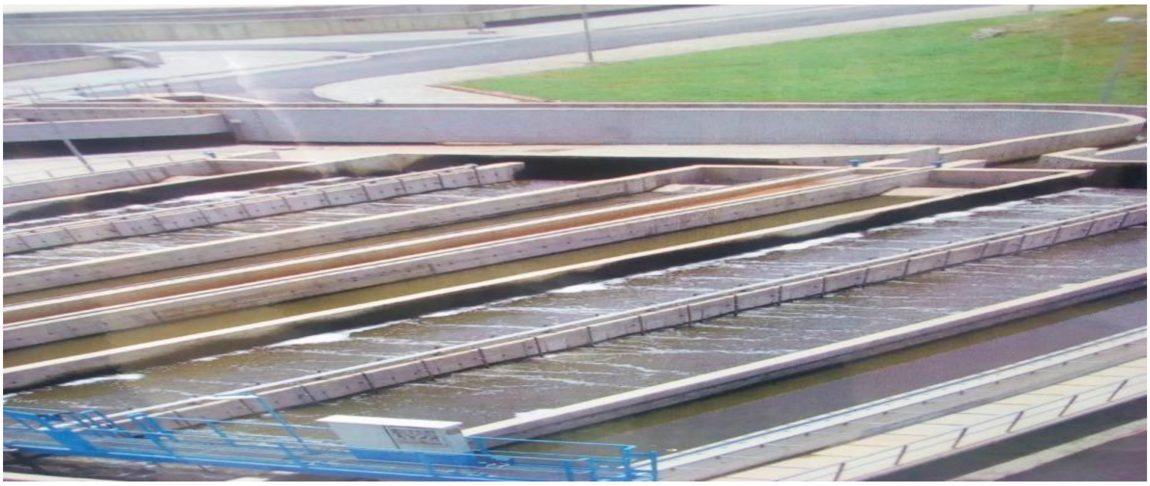


Plate II: Digested Sewage with sludge in a Basin at Wupa Treatment Plant, Abuja.

Biogas is generated from organic sludge using anaerobic digestion technology. Biogas generation is economically viable as it can be used as domestic cooking gas or as energy for electricity generation in the sewage treatment plants or nearby towns and cities. It also saves cost of spending a lot of money in burning away organic sludge. Biogas is generated in sludge digestion tanks called biogas digesters, which operate, at maximum temperature, which makes digestion faster than in other tanks like Imhoff (Abd-Alsalam *et al*., 2017). In many areas, sludge is disposed by drying it and using it for landfilling. Large quantity of treated sludge has to be transported outside to farms or erosion sites for fertilization or landfill respectively (Georges *et al*., 2017).

Sludge treatment is of paramount importance to the environment for the survival of ecosystem (Bred and Lowell, 2015). In Nigeria, many urban centres generate sewage but do not have the facilities to treat such, this helps increase the quantity of sewage deposits in the water channels such as gutters on the streets and rivers or ponds (Otunyo *et al*., 2016). Urban dwellers do eat fish from such ponds and farmers produce vegetables from irrigation farming using such waterways as sources of irrigation water and it should be understood that such vegetables are consumed daily (Eman and Hong, 2018). If such urban areas lack an important public infrastructure as sewage treatment plant, then public health will be always at risk (Jonathan, 2018). Diseases like cholera, diarrhoea and typhoid fever are rampant in developing nations. Sludge treatment has many advantages to cities that adopted it. Cities with sewage treatment plants have higher chances of mitigating the effect of toxic metals on the environment most especially as they can exist in different forms to cause harvock to the environment (Hancock, 2017). Using effective ways of treating sludge containing such metals is imperative in this case.

2.7 Chemical Speciation

Chemical speciation of metals describes their composition, form of association, ionic types and concentration in a given matrix (Adekunle *et al*., 2016). Knowledge of metal speciation is important in treating sludge. Chemical speciation is critical when predicting heavy metals availability in the soil. Chemical speciation enables elements in the environment get in to plants, human and animal systems, thus, it becomes imperative to study their metamorphosis when in the environment (Deng *et al*, 2015). Their bioavailability, which is their proportion as they are absorbed in the body, needs to be checkmated by understanding their risk as they speciate before intake. For metal contaminants, associations with reactive phases and chemical form, which is the speciation, are fundamental controls on their release, transport and environmental impact (Kiri *et al.*, 2015).

Speciation of toxic metals in sludge and eventual deposition in the soil is not only dangerous to humans and animals but to environment if not studied and controlled (Lin, 2020). These metals do not degrade for a long time in the environment as they change into different forms in the soil, they cause gross environmental pollution, which decreases fertility and affects crops, plants and drinking water (Anakpa *et al*., 2018).

Plants and planktons in soil and water (Mitch, 2015) absorb toxic metals from soil. These metal uptakes come with a price because as the metals are transported within the cells of the plants and planktons, toxic metals attack neuro sites and other essential parts of plants and planktons' physiology (Ciencia, 2015). This in turn will result in death of plants, low yield and plant diseases. Grazing animals can eat these plants and feed on them as they take these metals from affected plants in their system toxic metals such as Cu is deposited which in turn can cause illness and death of such animals (Mercola, 2015). Humans do consume the meat of these animals or eat the affected edible plants and in turn allow bioaccumulation of such toxic metals like Cu and Mn in the body (Whitbread, 2019). Toxic metal species are extremely hazardous to ecosystem and environment and proper knowledge of metal speciation will adequately help mitigate potential risks of these species of metals in the environment (Vikzslav and Miraslav, 2018).

Measurement of molecules of both metal and semi metals of biomolecules and organometallic compounds is regarded as metal speciation (Andre *et al*., 2015). Different metals are found in sewage sludge due to usage of their products at homes, industries and offices. Due to wear and tear heavy metal residues, find their way into dustbins, street gutters, incinerators or various waterways, which will be transported eventually to sewage treatment plants or into ponds and streams (Elizbieta, 2017). Understanding of metal speciation therefore gives analysts opportunity to gauge the level of such toxic metals of concern to environment and be able to render their potential risk of none effect. Their distribution and mobility in sludge can be analyzed easily to evaluate their vertical and horizontal movement through operation speciation, which can be determined using sequential extraction steps. Sludge naturally finds its way into soil whether treated or otherwise. Therefore, using sequential extraction to discover their speciation is the best way to tackle their menace to environment. Their bioavailability in the sludge can be verified using sequential extraction technique. This is a good and encouraging way of effectively planning and managing the environment and ecosystem. Bioavailability of Cu to plants and biota is checkmated using metal speciation knowledge (Jacob *et al.,* 2015).

Insoluble metals become soluble in their compounds as they form compounds of for instance oxides in soil when treated sludge is discharged (Zhang *et al*., 2017), this is achieved easily by adding enough anions to sludge for metals to take up. Sediments are the main repository and source of metals in aquatic systems and play an important role in the transport and storage of potentially hazardous metals. Sewage sludge has to be treated properly since metals are found mobilized in sewage sludge and therefore in high concentration (Jolanta and Jaroslaw, 2014).

2.8 Bioavailability and Mobility of Toxic Metals

Bioavailability of metals indicates their abundance in sludge known as contaminants and these abundances can be used to measure their toxic effect or potential danger to humans, animals and environment (Zhujian *et al*., 2017). Bioavailability of toxic metals in sewage sludge gives impetus to the growing contamination of sewage sludge and more work needs to be done for a proper clean up. Increase in the use of metal products at homes and industries, comes because of higher economic empowerment and technological advancement in the populace (Phen *et al*., 2015). More luxury items are being purchased and more machineries for manufacture of items are being procured. This comes with challenges to the environment because this increase in human activity with metals increases the chances of metals being found in sewage sludge (Dorman, 2017).

Mobility of toxic metals implies their increase in concentration via various reactions or mechanisms (Gold, 2018). For instance, Cu concentration by formation of chloride complexes, can be increased through ion exchange. Toxic metals can change their concentrations when in sludge because they are in aqueous phases (Emine and Zuhal, 2018)). This problem can be solved by forming relevant oxides, in the presence of relevant anions through the process of immobilisation. When toxic metals are immobilized, they become ineffective and cannot react with other compounds or elements in the environment thereby becoming less dangerous to environment. Mobility of metals in sludge is discouraged by their immobilisation (Ababu, 2014).

2.9 Mitigating Toxic Heavy Metals in the Environment

Toxic heavy metals have potential risk or hazard to humans, environment and ecosystem when exposed (Kumar *et al*., 2019). Metal toxicity or metal poisoning comes because of metals having dangerous effect in their forms and levels on human, environment and animals (Jaishankar *et al*., 2014). Many heavy metals can be classified as poisonous, although they have their use in day to day lives of humans. Metals that are toxic including Mn are found in the environment either as deposits in the soil or as remnants of their products. They cause gross environmental pollution and therefore have to be contained by environmentalists for a better future. These metals include Cu, Mn, Pb, and Zn. They remain reactive for a long time and may take several years to degrade and thus cause a lot of environmental damage (Ali and Sani, 2014). Allowing them to remain in the environment either in the soil or as they drop on plants and edible crops without taking action on them will not do well to the environment (Sulyman *et al*., 2015). Starting from sewage sludge, chemical treatment of these metals can go a long way in curtailing them and their effect on the environment (Tim *et al*., 2017). Sewage sludge is the embodiment of toxic heavy metals, pathogens and other toxic biological compounds and working seriously on it gives guaranty for a safe environment (Turek *et al*., 2019).

Toxic metals have been posing serious danger to soil and environment not only in the field of agriculture but in the area of geography (Muataz *et al*., 2018). Many geographical features have been tempered with over time due to undesirable presence of such metals once found in the environment. Toxic metals like Mn have contaminated many mining sites that today such sites are not in used and at the same time, such sites are not filled up (Omotola *et al*., 2016). This results in abandoned mining sites that become wider with time and thus causing gully erosions and landslides that consume lives of both man and animals. Landslides have become common especially in mining countries due to erosion and mass movement of sand because the sand is weak due to constant excavation (Hamed and Khairul-Anwar, 2016). Many a times during mining, mercury is encountered, as it is naturally associated with other minerals and after separation is abandoned at surface (Taofeek *et al.*, 2014). This exposure leads to inhalation by humans and causes illnesses. If the naturally occurring toxic metals have to be excavated and be used, they should be used properly. Immobilisation method remains the only viable method of containing these toxic metals in the environment. Proper sludge treatment is important in remediation technique for soil and environment.

Toxic metals mobilisation in sludge and soil is encouraged by lack of proper treatment from sewage treatment plants or when sewage is not treated at all, as it is obtainable in many developing countries (Ariful-Islam *et al*, 2016). Immobilisation, which can involve chemical absorption, ion exchange, formation of complexes with organic ligands and precipitation, is a good method of containing heavy metals in sludge. Two traditional methods employed to checkmate the menace of toxic heavy metals include removing them from sludge and immobilising them from sludge through varying mechanisms like bioleaching or chemical leaching (Ghavidel *et al*., 2017).

Further treatment of separated metals is necessary to avoid secondary pollution, and for secondary pollution to be avoided, separated heavy metals can be taken to stable fractions in the treatment chamber to mitigate their bioavailability and mobility (Cantinho *et al*., 2016). Furthermore, it should be noted that the immobilised metals do remain in the treated sludge, there is then the possibility of them reactivating with time when in the environment. Metals can be immobilised easily by using chemical immobilisation and composting (Xuan *et al*., 2017).

Western countries have functional sewage treatment systems that recycle sewage water into pipe borne water for the populace because there is adequate arrangement for that (Akpen *et al*., 2016). For instance, in the United Kingdom sewage treatment is business that sustains the lives of the society due to lack of adequate fresh water in the kingdom (Mulin, 2018).

2.10 Sewage Sludge Composting

Toxic metals remain mobile in the sludge and therefore remain harmful (Wierzbowska *et al.,* 2018). Composting is a biological process that uses naturally occurring organisms to convert biodegradable organic matter into a humus like product (Selnur and Ukuk, 2015). Sludge composting treatment cannot be compared with sequential extraction technique of treating toxic metals in sewage sludge treatment since the former is capital intensive. Sludge is of two major types, which include primary and secondary sludge. Primary sludge is formed during primary treatment of sewage, while secondary sludge results from secondary treatment of sewage in treatment plants (Graig, 2018).

Sludge is treated after sewage treatment to reduce its volume and weight in order to prevent potential health risks and cost of discharge (Guangying and Youcai, 2017).

2.11 Fixation effect of Cu, Pb, Mn and Zn in a Treated Sludge

The knowledge of the way heavy metal is distributed in the environment and which processes affect the distribution can be used to evaluate the potential of sludge amendment of soil with respect to heavy metal migration. Heavy metals are bound to certain anions during extractions, when treated sludge is discharged to environment; they remain fixed to such anions for a certain period (Gerney and Sin, 2014). However, they are met with other cations in the environment, which tend to displace them, react with their accompanying anions, and render them immobile in soil. Composting of sludge and chemical immobilization of metals in treated sludge have not solved this problem completely (Bozyayor and Siemiakowski, 2018). Using sequential extraction to determine concentrations of Cu, Pb Mn and Zn metals without analysis of their species have been carried out in the past. Concentrations of these metals do not give a sufficient clue to their toxicity in the environment neither their phytotoxicity in plants because they do not exist as species but metals in this case (Juel *et al*., 2015).

Some metals in the soil are more reactive than mobilised metals in treated sludge discharged to agricultural soil and can displace them after sludge discharge as metals bound to anions from treatment and this reverses their immobilisation prior to sludge discharge (Adewuyi and Osobamiro, 2016).

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Equipment/Apparatus

Table 3.1 summarises the list of the equipment and pieces of apparatus used in the study.

Table 3.1: List of Equipment/Apparatus used in the Study

S/N Name	Model	Manufacturer
1. Weighing Balance	B300	Ohaus, USA
2. pH Meter	EIL 7045/46	Kent, England
3. Orbital Shaker	SSL1	United Kingdom
4. Atomic Absorption Spectrometer	Accusys 211	Ohaus, USA
5. Thermometer	EIL 7045/50	Kent, England
6. Conductor meter	1152	Florida, USA
7. Centrifuge	L3-6K	Hunan, China
8. Kjehldahl set up	Micro	Kansas, USA
9. Oven	GVO-072	Kent, England
10. Muffle Furnace	EIE107	Gujarat, India

Source: Step B Laboratory, Federal University of Technology, Minna

3.2 List of Reagents Used in the Study

Table 3.2 summarises the reagents used in the study and all the reagents/chemicals used were of analytical grade.

Table 3.2: List of Reagents Used in the Study

S/N	Name	Formular	Purity	Grade	Manufacturer
1.	Sodium acetate	$C_2H_3NaO_2$	67%	Analytical	BDH, England
2.	Barium chloride	$BaCl_2$	66%	Analytical	BDH, England
3.	Ammonium acetate	$C_2H_7NO_3$	68%	Analytical	BDH, England
4.	Ammoniumhydroxy chloride	$NH_2OH.HCl$	75%	Analytical	KEMLight, India
5.	Nitric acid	HNO_3	75%	Analytical	BDH, England
6.	Ammonium hydroxide	NH_4OH	72%	Analytical	KEMLight, England
7.	Acetic acid	CH_3COOH	70%	Analytical	BDH England
8.	Nitric acid	HNO_3	73%	Analytical	BDH, England
9.	Hydrochloric acid	HCl	70%	Analytical	KEM Light, England
10.	Disodium EDTA	$C_{10}H_{18}N_2Na_{a2}O_8O_8$	75%	Analytical	BDH, England
11.	Perchloric acid	$HClO_4$	75%	Analytical	BDH, England
12.	Sulphuric acid	H_2SO_4	98%	Analytical	BDH, England
13.	Boric acid	HBr	4%	Analytical	KEMLight, England
14.	Ammonium acetate	CH_3COONH_4	75%	Analytical	KEMLight, England

Source: Step B Laboratory, Federal University of Technology, Minna.

3.3 Study Area

Abuja is the capital city of Nigeria and the city has sewage treatment plants in each of its districts according to the master plan. However, only one was functional as of the time of this study, which is Wupa wastewater treatment plant according to Mr. Braimoh, the Deputy Director of Liquid Waste, Abuja Environmental Protection Board in 2019. Wupa wastewater plant is situated at cadastral zone near National Power Training Institute, Wupa district, Abuja, Longitude 6^{o} 45´´ and 7^{o} 39´´ E and Latitude 7^{o} 20´´ and 9^{o} 20´´N (Saminu *et al.*, 2017). Situated close to river Wupa, it covers an area of 297,000 square meters. The plant was constructed in 2007 to address the growing need of the disposal of human waste, as Abuja metamorphosed into a global city (Saminu *et al.*, 2016).

3.3.1 Sample types and sampling points

Three sampling points from Wupa sewage treatment plant were selected and three types of sludge were taken and they were; 1. Fresh (raw) sludge 2. Treated (aerobic) sludge 3. Dry (bed) sludge. The three types of sludge were obtained at three stages of sludge processing at Wupa treatment plant, Abuja. Samples of fresh sludge (sludge with wastewater from town arriving treatment plant), treated sludge (sludge with wastewater during treatment) and dry sludge (sludge discharged to sludge pond after treatment) were collected and taken to laboratory for analysis immediately in order to preserve the texture and physicochemical parameters of samples.

3.3.2 Sample collection

Grab sampling method was employed to take samples in the treatment plant at different stages of processing. Three samples were collected from each of the three sampling points (Fresh, digested and dry) totaling nine samples. 300cm^3 of each sample of fresh, digested and dry sludge was taken in three 100cm^3 bottles, making a total of nine sample bottles.

3.3.3 Sample pretreatment

Samples were pretreated for clean up before analysis. Fresh, digested and dry sludge collected at Wupa plant were decanted and sieved with a mesh of 100mm one after another. The samples were air dried for a day to make the wet samples dry. The dried samples were then taken to oven after the oven temperature was set at 60° C for about 12 hours each (Anujkumar and Mansoor, 2018). The oven dry method was employed to take care of any microbial activity that might have taken place during air-drying.

3.4 Analysis of Physicochemical Parameters of Sludge Samples

The Physical and chemical parameters of the sewage sludge were determined for the analysis of chemical nature of sewage sludge at different phases of processing (Dan *et al*, 2017). The physical and chemical parameters determined, were nitrates, pH, electrical conductivity and moisture contents (Ahmed *et al*, 2019). Different forms of sludge such as mixed fresh sludge, digested sludge and dry sludge physicochemical properties were determined from samples taken from the Wupa treatment plant in Abuja.

3.4.1 Determination of pH

pH value was determined using a calibrated pH meter in the laboratory (Ticesea *et al*, 2021). About 30cm^3 water was added to 1.00g sample of each sludge type and mixed by stirring. The calibrated pH meter was inserted in each of the sample container, using stirring rod to stir the mixture simultaneously until meter displays constant reading (Eom and Ahn, 2017). Readings from each sample were taken in replicates of three and the average was taken as the mean value for each sample.

3.4.2 Determination of moisture content

Moisture content of sludge types was determined by weighing dried sample and recording readings initially and then taken to oven and heated at 105ºC for 3 hours (Alexander *et al*, 2016). After cooling, sample is removed from oven and weighed to constant weight (Qayyum *et al*, 2016). The difference between the initial reading and final reading after heating was evaluated. The experiment was carried out in three replicates and average reading was taken for each sample type as mean value (Huang *et al*, 2016).

3.4.3 Determination of electrical conductivity

This parameter was measured using electrical conductivity probe on wet sample of sludge in the laboratory (Sun *et al*, 2017). 1.00g each of samples of fresh, digested and dry sludge were taken and placed in beakers for each sample and a conductometer tip was placed in each container until a constant reading was observed (Tongchai *et al*, 2021). Average of three replicate readings was taken as mean value for each three-sample type.

3.4.4 Determination of nitrate content

1.00g of homogenous sludge sample was weighed and placed in digestion flask. Two Kjehldahl tablets of 5.00g of the Missouri catalyst was added followed by addition of 20 cm^3 of 98% H_2SO_4 (Shen *et al*, 2014). Sample was suspended by swirling the tube gently and the mixture with the digestion tube were placed in into digestion unit and then into heating block (Liang *et al*, 2017). Mixture was heated at 350-380ºC until white fumes were observed. Heating was sustained for about 180 minutes and vapours of H_2O and H_2SO_4 were bubbled through a solution of NaOH to neutralise them. Digestion was completed, as sample became very transparent (Mitshal *et al*, 2014). Sample was allowed to cool to room temperature and diluted with about $100cm^3$ of H_2O.

The diluted sample was digested with 98% H_2SO_4. 50cm^3 NaOH 50% solution was added to neutralize the pH (Edwards and Patrinha, 20190). Produced. NH_3 was then condensed and a stream of H_2O vapours was bubbled into the sludge sample to obtain the NH_3 formed. NH_3 was captured in a 50 cm^3 HBr 4% that contained 6 drops of Tashiro's indicator (Du *et al*, 2016). Around 150cm^3 of condensate this was titrated with 0.25MolL^{-1} HCl until the solution had a slightly violet colour (Lakakis & Papadoppulos, 2014).

3.5 Determination of the Total Metal Concentration of Cu, Pb, Mn and Zn in the Sludge

Aqua regia method of extraction using HNO_3 and HCl in the ratio of 1:3 was used to carry out total metal wet digestion for 1.00g of each dried sample was weighed into different testubes and 15cm^3 of concentrated HNO_3 with 5cm^3 of concentrated HCl added and placed in a Kjehldahl heating block. This was heated at 100^o C until mixture turns colourless Distilled water was added to each digestion tube after cooling, it was filtered with Whatman no.1 filter paper and each filtrate was made up to 100cm^3 with distilled water and kept for instrumental analysis.

3.6 Speciation of Cu, Pb, Mn and Zn in the Sludge

Sequential extraction was used as a method of leaching out metals out of sludge, sediment and soil. The use of organic reagents in the chemical extraction of metals in Wupa sludge used to achieve such extractions rather than inorganic reagents is due to environmental concerns (Oladapo and Enasi, 2015).

Five methods of extractions were used to remove metals from samples and these include: Aqua regia was used to extract non-silica bound metals (Lapez and Saltzmann, 2018), Hydrogen peroxide was used to extract oxidizable metals (oxidizable phase), Hyroxyammonium chloride was used to extract reducible metals (reducible phase), acetic acid was used to carbonate bound and water-soluble metals (acid extractable phase) and

$BaCl_2$ was used to extract exchangeable metals (Exchangeable phase). In sequential extraction method, an elaborate understanding and characteristics of individual elements can be acquired easily (Barkowska, 2017). Reagents of varying chemical properties are often involved to obtain chemical forms of elements by leaching them out via many chemical mechanisms like acidification and complexation. Although the process seems to be more complex than the simple single extraction, it enables a separation of total composition of elements in fractions with varying bioavailability.

Fractionating columns were used to extract samples of interest at various stages of extraction, which in turn gives efficiency of extraction (UNEP, 2015). Sequential extraction mechanisms involve various groups of extractors, namely extractors with ion exchange properties, extractors with dissolution of carbonates properties, extractors with acid reducing properties and extractors that weaken the metal with organic compounds.

Methods for the speciation of Cu, Pb, Mn and Zn in Wupa sewage sludge included Single and Sequential extractions (Selvi *et al*, 2016). Single extraction with EDTA was carried out for each of the three sludge types in the laboratory.1.00g each of sludge type was placed in an extraction bottle.10cm^3 of 0.01molL^{-1} EDTA and 1.0 cm^3 of 0.01mollL^{-1} CH_3COONH_4 as extractants were added to sample in extraction bottle. pH meter was adjusted to 7.0 by adding 2 drops of concentrated CH_3COOH and 3 drops of concentrated NH_4OH at room temperature intermittently while stirring with rod. The resulting mixture was shaken in orbital shaker for 2 hours at room temperature for proper mixing. Mixture was decanted and filtrate was centrifuged at 2000 revolution per minute for 10 minutes for proper separation. Filtrate collected and made up to mark of 50cm^3 and filtered by Whatman no. 2 filter paper (Zimmermann and David, 2020). Filtrate was collected in 100cm^3 polythene bottle and made up to 50cm^3 and kept for instrumental analysis. The experiments were carried out in three replicates for each of the sludge type.

Sequential extractions were carried out for each of the sludge types in three replicates to obtain mean values. There are five phases or fractions in sequential extractions namely exchangeable, acid extractable, reducible, oxidizable and residual (Olufemi and Augustine, 2018). In exchangeable phase, $BaCl_2$ was used as the extractant and about 16 cm^3 of $BaCl_2$ 0.5$molL^{-1}$ was added to about 1.00g sample. The mixture was stirred and placed in orbital shaker and shaken at 25º C for about 3 hours (Horspool, 2018). The resulting mixture was decanted and filtrate was made up to 50cm^3 with double distilled water in 100cm^3 polythene bottle and kept for instrumental analysis with Flame Atomic Absorption Spectrometer (FAAS). The experiment was repeated in three replicates for each of the sludge types.

In acid extractable (carbonate bound) phase, the major extractant was CH_3COOH and secondary extractant was CH_3COONa. About 17.50cm^3 CH_3COOH 0.06$molL^{-1}$ and 17.50cm^3 CH_3COONa 0.06$molL^{-1}$ were added to the residue from previous experiment in a beaker and stirred. Mixture was shaken with water bath orbital shaker for about 5 hours at 55ºC. Filtrate from mixture was centrifuged at 2000 revolution per minute (rpm) for 10 minutes and supernatant decanted (Rasheed *et al*, 2018). Filtrate was made of to mark to 50cm^3 in a 100cm^3 polythene bottle and kept for instrumental analysis. The experiment was repeated in three replicates for each of the sludge types.

In reducible (oxides and hydroxides) phase, the major extractant was $NH_2OH.HCl$ and the secondary extractant was CH_3COONH_4. About 17.50cm^3 $NH_2OH.HCl$ 0.1$molL^{-1}$ and 17.5cm^3 CH_3COONH_4 0.5$molL^{-1}$ were added to residue from previous experiment. The resulting mixture was shaken for about 1 hours at 45ºC Centrifuge filtrate at 2000 revolution per minute for 10 minutes (Lima *et al*, 2015). Supernatant was decanted, made up to 50 cm^3 in 100cm^3 polythene bottle, and kept for instrumental analysis. The experiment was repeated in three replicates for all the sludge types.

In oxidizable phase, the major extractant was H_2O_2, while the secondary extractants were HNO_3 and CH_3COONH_4. About 10cm^3 of H_2O_2 0.088molL^{-1} and 6cm^3 of HNO_3 0.02molL-^{1} were added to residue from previous experiment (Ma *et al*, 2014). Mixture was shaken for 5 hours at 45ºC and then for 1 hour at 98ºC. 10cm^3 of CH_3COONa 0.5molL^{-1} was added to mixture as extracting agent (Al-Musharafi, 2016). Supernatant was made up to 50cm^3 with distilled water in 100ml polythene bottle and kept for instrumental analysis. The experiment was repeated in three replicates for all sludge types.

About 20 cm^3 concentrated HNO_3 and HCl aqua-regia was added to the final residue from the previous experiment. Residue mixture was placed in silicate crucibles, heated in furnace for about 2 hours at 550ºC, and evaporated to dryness. Residue was diluted with double distilled water and made up to 50cm^3 in 100cm^3 polythene bottle and kept for instrumental analysis. The experiment was repeated in three replicates for all the sludge types. The bioavailable operational phases discovered in the experiment were exchangeable and acid extractable (Zhang *et al*, 2010).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Physicochemical parameters of the samples

Table 4.1 summarises the mean concentration of the physicochemical parameters of Wupa sludge. The pH values of; 8.37±0.17, 8.48±0.03 and 8.50±0.02 for fresh, treated and dry sludge respectively were obtained. Nitrate concentrations of 5.20±0.01, 4.80±0.01 and 2.50±0.01 mgkg^{-1} for fresh, treated and dry sludge respectively were obtained. Moisture content values of; 4.24 and 2.32 and 1.31 % respectively were obtained. Conductivity values of; 520, 340 and 320.00 µScm^{-1} for fresh, treated and dry sludge respectively were obtained. All the results of the parameters under study were found to be within the limit values of the regulatory authorities such as NESREA and WHO, as indicated in the table

Table 4.1: Physicochemical Parameters of the Samples

Parameters	pH	Moisture (%)	Conductivity (µScm^{-1})	Nitrate (gkg^{-1})
Fresh	8.37±0.17	4.24±0.01	520.00±0.72	5.20±0.01
Digested	8.48±0.13	2.32±0.01	340.00±0.47	4.80 ±0.01
Dry	8.50±0.02	1.31±0.01	320.00±0.72	2.50±0.01
Standard:				
NESREA	6.50-8.50	NA	1000	4.0
WHO				

Desirable limits	7.00-8.90	NA	1000	4.0
Maximum permissible limits	6.50-9.50	NA	900	3.7

Source of the Standards = Akharame *et al*., 2017. NA = Not Available Standard

4.1.2 Total metal concentration in sludge samples

Table 4.2 summarises the results of total metal concentrations of Cu, Pb, Mn and Zn in Wupa sludge. Aqua regia results showed Cu concentrations to be; 644.75, 519.25 and 254.13 mgkg^{-1} for fresh, treated and dry sludge respectively. Pb concentrations were; 105.00, 95.00 and 37.50 mg kg^{-1} for fresh, treated and dry sludge respectively. Mn concentrations were; 510.00, 1860.00 and 2140.00 for fresh, treated and dry sludge respectively. Zn concentrations were; 2882.00, 2717.50 and 2690.10 mgkg^{-1} for fresh, treated and dry sludge respectively. Aqua regia results showed that Pb and Zn concentrations in dry sludge were within limits, Mn limit was not available, Cu concentration in dry sludge was within limits of regulatory bodies.

Table 4.2 Results of Total Metal Concentration in Sludge Samples (mgkg^{-1})

Extractions	Cu			Pb			Mn			Zn		
	Fresh	Treated	Dry	Fresh	Treated	Dry	Fresh	Treated	Dry	Fresh	Treated	Dry
Aqua regia	644.75	519.25	254.13	105.00	95.00	37.50	510.00	1860.00	2140.00	2882.00	2717.50	2690.10
Single extraction/EDTA	33.11	21.06	12.72	2.50	1.50	390.00	138.82	145.67	113.97	2.50	2.70	3.90
Sequential extraction	92.55	59.95	49.65	33.104	21.14	12.67	142.85	132.35	111.74	262.03	102.50	54.26
Standards												
NESREA		100			164			NA			421	
WHO		1500			300			NA			2800	

Source of the Standards: Okhareh and Enesi, 2015.

4.1.3 Results of single extraction with EDTA of Cu, Pb, Mn and Zn

Table 4.3a summarises the results of Cu, Pb, Mn and Zn ion fractions in single extraction with EDTA as extractant in Wupa sludge. Cu concentrations were; 33.11, 21.06 and 12.72 mgkg^{-1} for fresh, treated and dry sludge respectively. Pb concentrations were; 2.50, 0.50 and 3.90 mgkg^{-1} for fresh, treated and dry sludge respectively. Mn concentrations were; 138.82, 45.67 and 113.97 mgkg^{-1} for fresh, treated and dry sludge respectively. Zn concentrations were; 2.50, 2.70 and 2.90 mgkg^{-1} for fresh, treated and dry sludge respectively. The results showed Cu, Pb and Zn were within the limits of regulating authorities such as NESREA and WHO. Mn limit was not available as of the time of this study.

Table 4.3 Results of Single Extraction with EDTA of Cu, Pb, Mn and Zn Ions (mgkg^{-1})

Sludge Sample	Cu	Pb	Mn	Zn
Fresh	33.11	2.50	138.82	2.50
Treated	21.06	0.50	45.67	2.70
Dry	12.72	3.90	113.97	2.90

4.1.4 Sequential extraction of Cu, Pb, Mn and Zn ions

Table 4.4 summarises the results of fractions of Cu, Pb, Mn and Zn ions in sludge samples in five operational phases from sequential extraction. Acid extractable phase, which is a bioavailable phase, has the highest concentration of metals extracted and it accounted for about 80.64% of total concentration of ions extracted in sequential extraction. Another bioavailable phase is exchangeable which had about 5.34% of total ions extracted. Oxidizable phase is the phase with the least concentration of ions extracted, which accounted for about 1.91% of total concentration of ions extracted. Non-bioavailable phases in this extraction included reducible, oxidizable and residual phases. The results showed that ions concentration is within the acceptable limits of regulatory bodies like NESREA and WHO.

Table 4.4 Results of Cu, Pb, Mn and Zn Ions Fractions in the Samples (mgkg^{-1})

Extractions		Cu			Pb			Mn			Zn	
	Fresh	Treated	Dry	Fresh	Treated	Dry	Fresh	Treated	Dry	Fresh	Treated	Dry
Exchangeable	0.05	0.05	0.25	0.50	0.50	0.05	10.95	8.65	7.85	16.00	7.05	6.01
Acid extractable	89.00	58.75	49.25	31.00	20.50	12.50	101.10	95.10	100.00	221.5	66.50	21.50
Reducible	1.00	0.05	0.05	0.054	0.05	0.04	15.20	20.75	2.85	24.00	27.50	26.40
Oxidizable	1.00	0.15	0.05	0.05	0.04	0.03	9.70	7.35	1.00	0.50	0.45	0.30
Residual	1.50	0.95	0.05	1.50	0.05	0.05	5.90	0.50	0.04	0.03	1.00	0.05
Total	**92.55**	**59.95**	**49.65**	**33.104**	**21.14**	**12.67**	**142.85**	**132.35**	**111.74**	**262.03**	**102.50**	**54.26**
%BA	**96.21**	**98.08**	**99.70**	**95.15**	**99.33**	**99.05**	**78.43**	**78.40**	**96.51**	**90.64**	**71.76**	**50.70**

Standards:

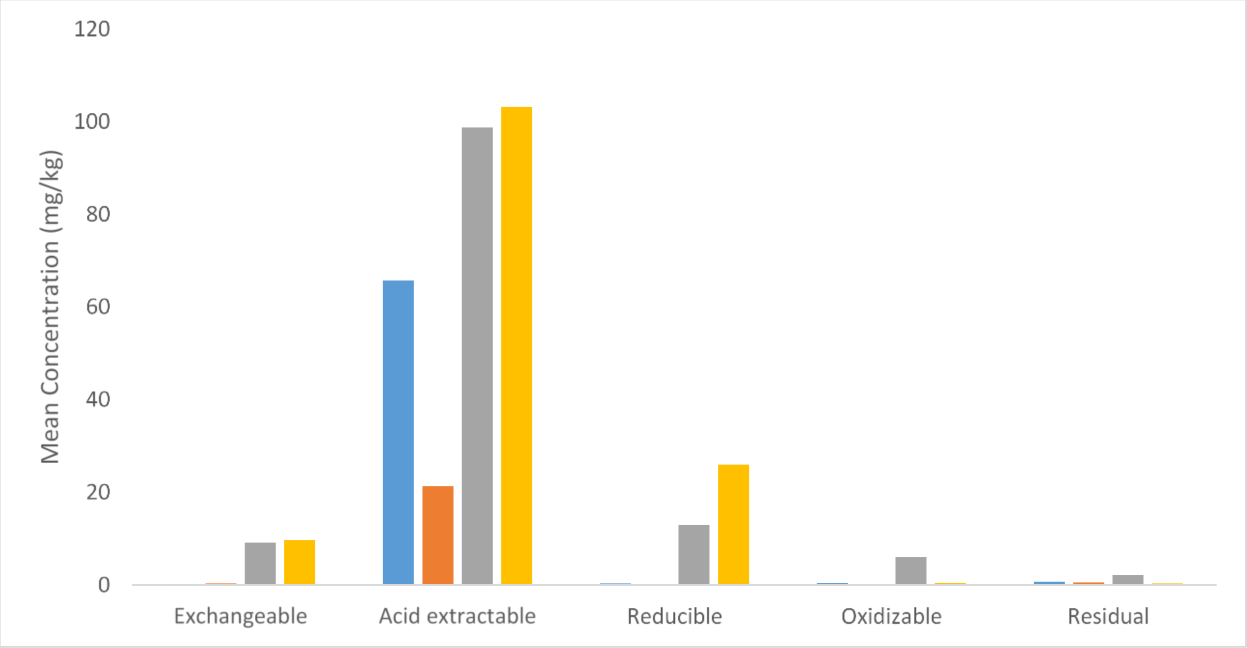
NESREA	100	164	NA	421
WHO	1500	300	NA	2800

Source of the Standards: Okhareh and Enesi, (2015). NA = Not Available %BA= Percent Bioavailability

4.1.5 Bar chart of the sequential extraction results

Figure 4.1 depicts the component bar chart of Cu, Pb, Mn and Zn ions solubility from mean concentration results in five operational phases in sequential extraction technique.

in exchangeable phase, Zn ions have the highest fractions followed by Mn ions, Cu ions and Pb ions. In acid extractable phase, Zn ions have the highest fractions followed by Mn ions, Pb ions and Cu ions, in reducible phase, Zn ions have the highest fractions followed by Mn ions, Cu ions and Pb ions. However, in oxidizable phase Mn ions have the highest fractions followed by Zn ions, Cu ions and Pb ions. In residual phase, Mn ions have the highest fractions followed by Cu ions, Pb ions and Zn ions.



Fgurec4.1 Metal Extraction Results of Cu, Pb, Mn and Zn in Sequential Extraction Technique

From the above charts, the ranking order of extraction efficiencies of Cu, Pb, Mn and Zn in five phases of sequential extraction technique are as outlined below:

Cu: acid extractable>residual>oxidizable>reducible>exchangeable

Pb: acid extractable>residual>exchangeable>reducible>oxidizable

Mn: acid extractable>reducible>exchangeable>oxidizable>residual

Zn: acid extractable>exchangeable>reducible>oxidizable>residual.

4.1.6 Statistical analysis of results

Table 4.5 summarises measurement of the Pearson's correlation coefficients. The positive and negative correlations among Cu, Pb, Mn and Zn in Wupa sludge and their physicochemical parameters were evident. There was a strong positive correlation between Nitrate and pH as well as between Mn and Pb. There was also a strong negative correlation between nitrate, moisture, Pb, conductivity, Mn, and conductivity as well as between Zn and Pb respectively.

Table 4.5: Pearson Correlation Coefficient of the Physicochemical Parameters and Percentage Bioavailability of the Fraction in the Sequential Extraction of Samples

	pH	Moisture	Conductivity	Nitrate	(Cu)	(Pb)	(Mn)	(Zn)
Ph	1							
Moisture	-0.5217	1						
Conductivity	0.5096	-0.0572	1					
Nitrate	0.8493	-0.8140	0.2120	1				
(Cu)	-0.0410	0.2335	0.1198	-0.1841	1			
(Pb)	-0.4519	-0.4923	-0.8067	0.1457	0.3098	1		
(Mn)	-0.6770	-0.0602	-0.8056	0.2545	-0.1461	0.8996	1	
(Zn)	0.2066	0.3529	0.7404	-0.3270	0.3606	-0.8680	0.7687	1

4.2 Discussion

4.2.1 Physicochemical parameters of the sludge samples

4.2.1.1 pH

pH values of; 8.50, 8.48 and 8.48 for fresh, treated and dry sludge respectively were obtained, this conforms to the findings of Grobalak *et al*., (2019), who discovered that treatment of sewage sludge results in increase in its alkalinity which when discharged to agricultural soil, and landfill neutralizes soil acidity. This increment could be due to increase in chemical presence with the addition of stabilization chemicals like brown lime (CaO) during treatment of sludge in the digested sludge basin as attested by Cai *et al*., (2019), who asserted that lime stabilization increases alkalinity. The addition of lime (CaO) or slaked lime $Ca(OH)_2$, could have contributed to the rise in alkalinity of sludge under treatment in the basin. $CaCO_3$ was formed in the metals treatment with CaO or $Ca(OH)_2$ which can reduce corrosion of pipe used to transport treated sludge to dry pond. High alkaline pH of 8.50 was observed in dry sludge as also observed by Shanaszek-Tomal and Fertek, (2016), who showed that dry (bed) sludge, has higher alkalinity than untreated (fresh) sludge.

4.2.1.2 Moisture contents

Moisture contents of; 4.24, 2.32, 1.31 % of fresh, treated and dry sludge respectively were obtained, which showed most of the water in final sludge processing was removed as the dry sludge was separated from the wastewater in the digested basin during sludge thickening process in conformity with the findings of Flotweg, (2020), who demonstrated that moisture content is reduced when sludge is treated efficiently.

4.2.1.3 Electrical conductivity

The electrical conductivity values of sludge samples were; 520, 340 and 320 μScm^{-1} for fresh, digested and dry sludge respectively. The highest electrical conductivity was observed to be in fresh sewage sludge at the fresh sludge entry point. This could be due to domestic and industrial activities such as washing of clothes, industrial cleaning and liquid wastes from construction and dumping sites and hospitals, which have accumulated many ions in the process; this corresponds to the findings of Suanon *et al*., (2016), who affirmed that human activities greatly contribute to the accumulation of metals in the soil.

Treated sludge had electrical conductivity of $340\mu Scm^{-1}$ higher than dry sludge could be due to free manganese, calcium and other ions involved in chemical processes during treatment, this observation is different with the findings of Baawan *et al*., (2015), who proved that Sulphates and Phosphates observed to be sources of conductivity in sludge rather than cations like Calcium. The lowest electrical conductivity was observed in dry sludge, which could be due to reduction of free ions after treatment process this corresponds findings of Wali *et al*., (2014), who observed that conductivity decreases while sludge treatment due removal of ions due chemical processes.

4.2.1.4 Nitrates

Nitrate concentrations of 5.20, 4.80 and 2.50 gkg^{-1} for fresh, treated and dry sludge respectively were obtained. The highest concentration of nitrate is found to be $5.20gkg^{-1}$ in fresh sludge. This could be as result of high nitrate contents in sewage from homes, offices, hotels and offices, usually in protein contained foods and from vegetation around this harmonizes with the findings of

Onodera *et al*., (2019), who understood that vegetation contains nitrate compounds. The lowest concentration was 2.50gkg^{-1} in dry sludge, which could be because of the depletion of nitrate content due to nitrate conversion to nitrogen gas as also observed by Van der Hook *et al*., (2018), who submitted that chemical processes during sludge treatment reduce the concentration of nitrates. 4.80gkg^{-1} concentration of nitrate in treated sludge could be because of high nitrate content in fresh sewage sludge from domestic and industrial activities before treatment but these findings differ slightly with that of Gupta and Thaker, (2016), who observed that not nitrates but highly chlorinated and volatile compounds were found to degrade appreciably in sludge treatment rather than ions of Cu, Pb, Mn and Zn.

4.2.2 Total Metal Concentration in Samples

Cu concentration in fresh sludge was 644.75mgkg^{-1}, which could have come with the sludge directly from homes, offices and industries as debris from utensils and heavy industrial equipment also the high amount of Cu extracted here could be due to Cu oxidized strongly in HNO_3 and HCl digestion. Cu concentration in digested sludge was 519.25mgkg^{-1} lower than fresh sludge, which could be due to reduction of Cu because of chemical processes in the treatment basin. Cu concentration in dry sludge was 254.13mg kg^{-1} in dry sludge due to reduction in Cu from treatment basin. Cu was strongly digested with HNO_3 and HCl this conforms to the findings of by Lima *et al*., (2015), who observed that the strong oxidizing NO_3 ions make digestion done completely. Pb concentrations were; 105.00, 95.00 and 37.50 mgkg^{-1} for fresh, digested and dry sludge respectively.

Mn concentration in treated sludge was 1860.00mg kg^{-1}, which could be due to cement structures at the plant in lime stabilisation of sludge as also observed by Salih *et al*., (2018), who attested that cement contains Mn as an ingredient for its manufacture. High extraction of Mn in the three samples showed that it was abundant in the sludge. In Fresh sludge, Mn concentration was 510.00mgkg^{-1}, which could be attributed to presence of manganese in food remnants from homes and hotels and from cement industries as attested also by Chakraborty, (2014), who observed that food contains Mn. Mn concentration in dry sludge was 2140.00mgkg^{-1}, which is lower than in digested sludge, and this could be due to immobilization of Mn by chemical processes in treatment basin before carrying treated sludge to dry sludge pond. High value of Mn in aqua-regia shows that it was digested by a more efficient aqua regia ratio of HNO_3 and HCl.

Zn concentration in fresh sludge was 2882.00mgkg^{-1}, which could be due to debris from utensils and kitchen equipment and industrial machines and debris from transporting pipes and trucks that convey sewage to manholes or Wupa plant. Zn concentration was 2717.00 mgkg^{-1} in treated sludge, which could be due to metal stabilization process. Zn high value shows that it was strongly digested by HNO_3 and HCl. Zn concentration in dry sludge was 2690.10mgkg^{-1} and could be due to chemical processes and less corrosion of transporting pipes to sludge pond as observed also by Zubala *et al*., (2017), who believed that Zn coated pipes are no longer in use in some treatment plants.

4.2.3 Single Extraction with EDTA of C, Pb, Mn and Zn Ions

High Cu concentration of 33.11mgkg^{-1} in fresh sludge from town could be due to high concentration of Cu in the sludge samples and high complexation ability of Cu with EDTA. Cu concentration was 21.06mgkg^{-1} in treated sludge lower than in fresh sludge and could be due to reduction of Cu in chemical processes during sludge treatment. Cu concentration was 12.72mgkg^{-1} in dry sludge, which can be attributed to removal of most of copper in chemical processes such as metal stabilization before reaching dry sludge pond this conforms to the findings of Soliman *et al*., (2017), who observed that Cu complexes with EDTA to form an organic ligand.

Pb concentration was 2.50 mg kg^{-1} in fresh sludge, showing Pb presence in the sludge was minimal which is not similar to the findings of Karwowska, (2014), who understands that extraction efficiency for Zn and Cd is negligible compared to Cu and Pb during sludge treatment. Pb concentration was 1.50mgkg^{-1} in digested sludge, which showed that it could have undergone chemical reaction in digested tanks. Pb concentration in dry sludge was 3.90mgkg^{-1} slightly higher than in digested sludge which could be due to Pb debris from transporting Pb pipes as also affirmed by Appiah-Effah *et al*., (2015), who observed that treatment plants using Pb coated transporting pipes can have increase in Pb presence in dry sludge due to wear and tear of such pipes.

Mn concentration in fresh sludge was 138.82mgkg^{-1}, high concentration could be due to food remnants from homes and hotels and waste from nearby cement and food manufacturing industries this conforms to the observation of Roberto *et al*., (2015), who agreed that Mn is in manufactured cement products. Mn complexed with EDTA as observed in this work. Treated sludge had Mn concentration of 145.67mgkg^{-1}, which could be due to the presence of brown lime, and cement facilities in the plant, manganese accumulated in digested sludge because it forms part of brown lime and cement products as also observed by Moren, (2018). In dry sludge, Mn concentration was 113.97mgkg^{-1} showing a lower value compared with treated sludge, which could be due to reduction of Mn through metal stabilization after sludge treatment as observed also by Zhu *et al*., (2018) who pointed that Mn could react with other anions to form compound, which stabilizes it.

Zn concentration was 2.50mgkg^{-1} in fresh sludge could have come from zinc coated pipes at homes to Wupa sewage treatment plant this differs with the findings of Russian *et al*., (2018), who observed that increment of Zn was due to complexation of Zn and EDTA even though with higher efficiency. Zinc concentration in digested sludge was 2.70mgkg^{-1}, this could be due to the accumulation of debris from zinc-coated facilities in the treatment basin. Zn amount in dry sludge was 2.90mgkg^{-1}, which had the highest value here, could be due to wear and tear from zinc-coated facilities in the treatment plant as deduced by Kamrul-Islam *et al*., (2015), who observed that sludge processing in Zn coated facility increases concentration of Zn in sludge.

4.2.4 Metal ion fractions in different phases of extraction from sludge samples

In exchangeable phase, $BaCl_2$ was used as the extractant for the ions to be extracted; ion exchange took place through displacement reactions between cations and anions. This is a bioavailable phase in which metal species as plants assimilate metal acetates. Cu ion fraction in exchangeable phase was 0.35mgkg^{-1} Cu ion in this phase can form a chloride of Cu. Pb ion was 1.05mgkg^{-1} and can form $PbCl_2$, while Mn ion was 27.45 mgkg^{-1} a Cl of Mn can be formed here too. Zn ion fraction was 28.06mgkg^{-1}, a Cl of Zn can be formed here. Acetic acid was the main extractant in the acid extractable phase. In this phase, ion fractions were; 197.00, 63.00, 296.20 and 301.50 mgkg^{-1} for Cu, Pb, Mn and Zn respectively. Acid extractable phase had the highest concentration of metal fractions than other phases the above results are in conformity to the findings of Alvarez *et al*, (2014). The results obtained for exchangeable and acid extractable fractions indicated which metal could be readily available for plant absorption in soils treated with Wupa sewage sludge as observed by Campos, (2019) also. Cu, Pb, Mn and Zn ions in treated Wupa sewage sludge were present in forms that require conversion to acid extractable and exchangeable forms by chemical or microbial processes in soils before uptake by plants in sequential extraction in sludge which conforms to the findings of Huang *et al*., (2017), who observed that the introduction of metal stabilizers like $CaSO_4$ significantly lowers the metal availability for plant uptake. Cu, Zn and Mn became easily mobile in acid extractable phase and tend to be less associated with residual phase thus corresponding with the findings of Borgese *et al*., (2014).

Reducible phase had Hyroxyammonium chloride as the major extractant and it extracted all the four metals, which were reducible metals, this phase, is usually iron Fe/Mn oxide phase. Ions are occluded in Mn/Fe oxides as iron and manganese oxides exist as nodules or simply as coating particles and thus not render the ions of Cu, Pb, Mn and Zn available to plants this conforms to the findings of Antonio and Antonio, (2015), who asserted that Mn/Fe are able to oxidize some metals such as Cu, Mn and Pb but shield them in flakes which render them unavailable plants when treated sludge is discharged to agricultural soil. Ion fractions in reducible phase were; 1.10, 0.055, 38.80 and 67.90 mgkg^{-1} for Cu, Pb, Mn and Zn respectively. The ions of these metals do form their carbonates and sulphides in this phase, as the metal carbonates and sulphides are capable of becoming very soluble as a result of microbial oxidation of sulphides to sulphates, which result in the dissolution of metal sulfides and sludge organic constituent binding metals this reflects the findings of Tytia, (2016), who observed that microbial activities do take place during sludge treatment. All of the chemical processes in the laboratory will be influenced by the physical properties such as pH and salinity of the soil receiving the sludge according to Lachassagne *et al*., (2015).

Oxidizable phase major extractant was hydrogen peroxide and it readily oxidized the ions of Cu, Pb, Mn and Zn thereby forming metal oxides, but plants cannot assimilate these oxides at low temperature when sludge is discharged to soil this conform to the findings of Li *et al*, (2018). Residual phase involved digestion using HNO_3 and HCl to extract non-silica bound metals which could be easily assimilated by plants but because they were occluded in organic matter they are not available to plants as this conforms to the findings of Weber *et al*., (2018). Therefore, only exchangeable and acid extractable phases are bioavailable phases and ions in these phases are available to plants when treated sludge is discharged to soil eventually this conforms to the findings of Weng *et al*., (2016). Ion fractions in oxidizable phase were; 1.20, 0.14, 18.05 and 1.80 mgkg^{-1} for Cu, Pb, Mn and Zn respectively, this is in line with the findings of Zhang *et al*, (2017). The results obtained on the fractionation of Cu, Pb, Mn and Zn showed that all were extracted more in acid extractable phase than in other phases, showing that they were more associated with the carbonate fractions as attested also by Radu, (2020) in his findings. This phase was found to contain more of Cu, Zn and Mn than Pb ions.

Residual fraction was found to contain much less concentration of ions in comparison with other phases as also observed by Rodgers *et al.*, (2015). In residual phase, ion fractions were; 1.60, 1.60, 6.44 and 1.08 mgkg^{-1} for Cu, Pb, Mn and Zn respectively, this is in conformity with the findings of (Lago and Vega, (2014). The concentration of Cu and Pb ions associated with exchangeable phase was found to be almost similar. Concentrations of Cu, Pb, Mn and Zn ions associated with reducible and residual phases were found to be different from other phases, this pattern was in conformity with the findings of Guha *et al*., (2015), who observed that reducible and residual phases do not contain metal in the chemical forms due to nature of extractants in such phases and even the in high concentrations, are occluded to plants.

Concentrations of Mn and Zn ions were observed to be more than those of Cu and Pb in Wupa sewage sludge, showing high presence of Mn and Zn in sewage sludge at Wupa treatment plant. Such ions in sludge can be part of sediments in Wupa river, because not all sludge will be removed from treated wastewater which is eventually discharged to the river this also conform to the findings of Ayham *et al*, (2017), who observed that some remnant of treat sludge accompany discharged treated wastewater in to nearby river bodies.

4.2.5 Correlation analysis on physicochemical parameters and heavy metals in sludge samples

Correlations were calculated for both physicochemical parameters and percentage bioavailability of Cu, Pb, Mn and Zn in sewage sludge from Wupa Sewage Treatment Plant. Positive correlation between physicochemical parameters and percentage bioavailability parameters means an increase in the value of one will lead to a corresponding increase in the other which implies a strong relationship between them whereas negative correlation means that an increase in the mean value of one will lead to a decrease of the same in the other this is conformity with the findings of Nikolas, (2019). There was a strong positive correlation between Nitrate and pH and between Mn and Pb as +0.8493 and +0.8996 respectively. Moreover, there was a strong negative correlation between nitrate and moisture and between Pb and conductivity as -0.8140 and -0.8067 respectively. There was also a strong negative correlation between Mn and conductivity and between Zn and Pb as -0.8056, and -0.8680 respectively

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The results of the physicochemical parameters of sewage sludge measured which were pH, moisture content, electrical conductivity and nitrate in the sludge samples were within permissible limits of NESREA and WHO as in 2019 were; 6.50-8.50, na, 1000% and 4.00gkg^{-1} for pH, moisture content, electrical conductivity and nitrate respectively, by NESREA and6.50-9.50, na, 900% and 3.7gkg^{-1} for pH, moisture content, electrical conductivity and nitrate respectively by WHO. Moisture contents standard permissible limits, were not found to be available from both regulatory bodies of NESREA and WHO.

The total metal concentrations reveal that aqua regia digestion extracted the highest concentration of the metals of Cu, Pb, Mn and Zn as; 1418, 237.50, 4510 and 8289.60 mgkg^{-1} respectively. Mn and Zn were discovered to be the metals with highest concentrations in Wupa sewage sludge. Cu and Zn have concentrations within WHO limits. Mn concentration has no available standard from regulatory authorities. Total metal concentration of Pb in the sludge types fresh, treated and dry sludge respectively even though a bit high, was found to be within the limits of both NESREA and WHO in 2019.

Extractions and extracts of single extraction with EDTA gave a fair idea of amounts of heavy metals studied in sequential extraction. Sequential extractions showed highest concentrations of ions in acid extractable phase. Metal ions under study showed to be within the permissible limit of regulatory bodies. Findings in this work will form a baseline for future research and will also afford Wupa treatment plant a new method of speciation of trace metal pollutants rather than total metal concentration approach. This will also boost agriculture and human health in the Federal Capital Territory, which falls in line with the current Federal Government policies on food security and environmental sanitation.

5.2 Recommendations

Chemical processes used in controlling some physicochemical parameters in Wupa sludge as studied in this work should be maintained, if not improved. Physicochemical parameters in sludge are crucial to assessing the risk or safety of treated sludge to agricultural practices as well as solving ecological problems.

Total metal concentrations of Cu, Pb, Mn and Zn in Wupa sludge should be further controlled by employing improved high precision techniques and the use of immobilizing agents like Na bentonite. This is to improve the safety of the discharged sludge to Abuja environment.

Species of Cu, Mn and Zn in acid extractable and exchangeable phases showed significant concentrations in Wupa sludge. Since Cu, Pb, Mn and Zn ions in exchangeable and acid extractable phases are found to be significantly present in acid extractable phase for plant uptake, there is the need to employ more advanced methods to stabilize the sludge before discharging it to agricultural soils and landfills.

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APPENDIX A

ANOVA

concentration

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	106620077.691	2	53310038.845	14.464	.000
Within Groups	121630666.394	33	3685777.770		
Total	228250744.085	35			

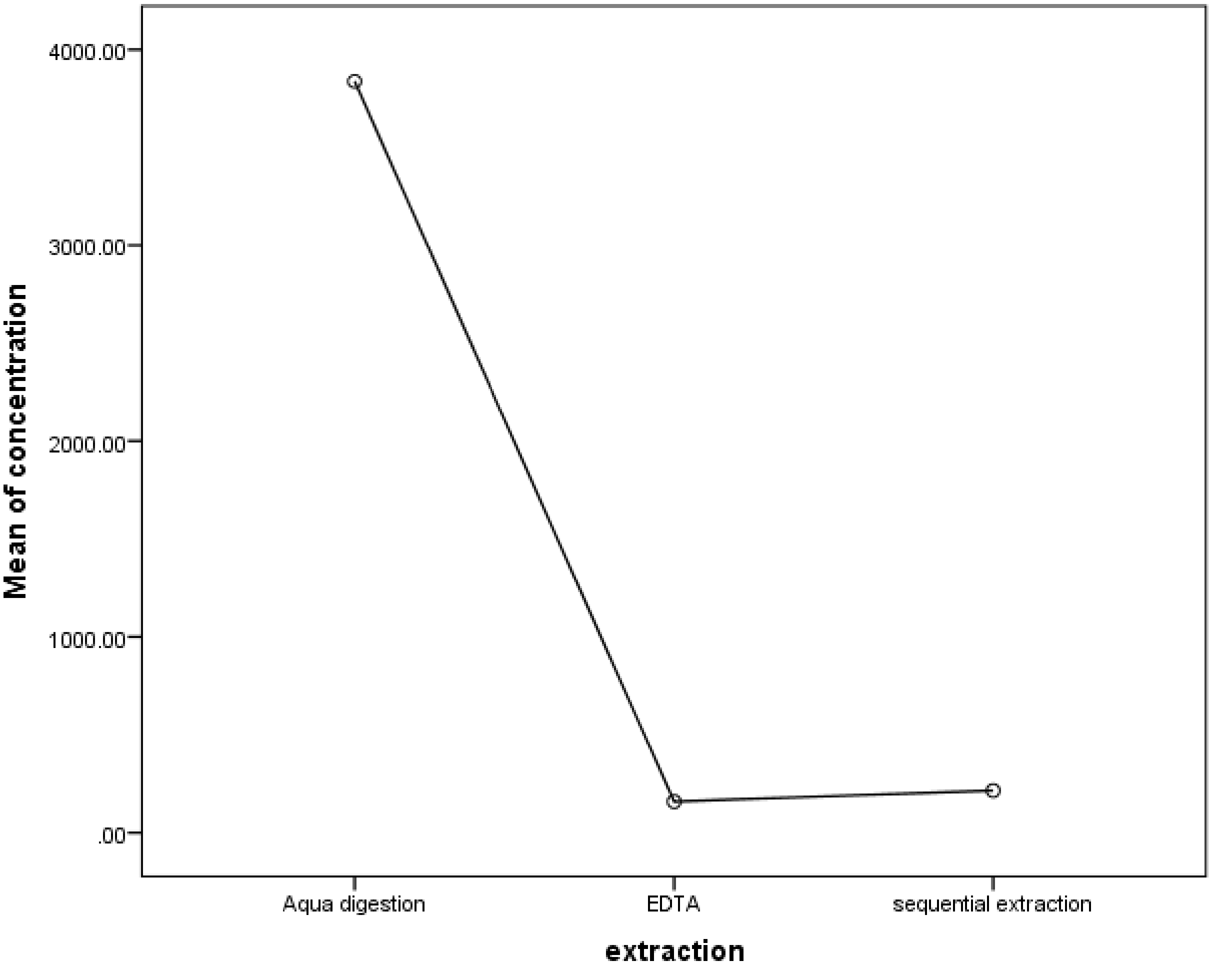

Figure 1: Comparison of Strength of Extraction by the three Extraction s carried out.

APPENDIX B

One way

ANOVA

concentration

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	995674.370	2	497837.185	.072	.930
Within Groups	227255069.715	33	6886517.264		
Total	228250744.085	35			

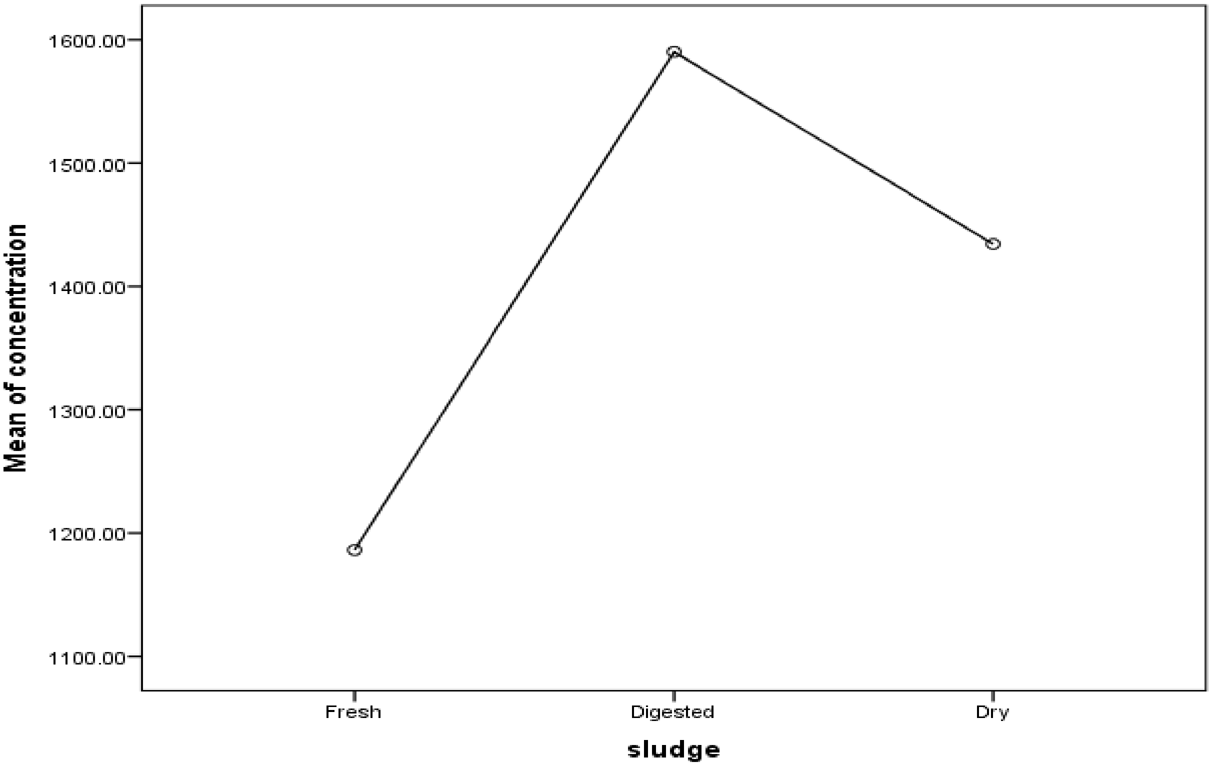

Figure 2: Comparison of Efficiency of Extraction in Sludge Types.

APPENDIX C

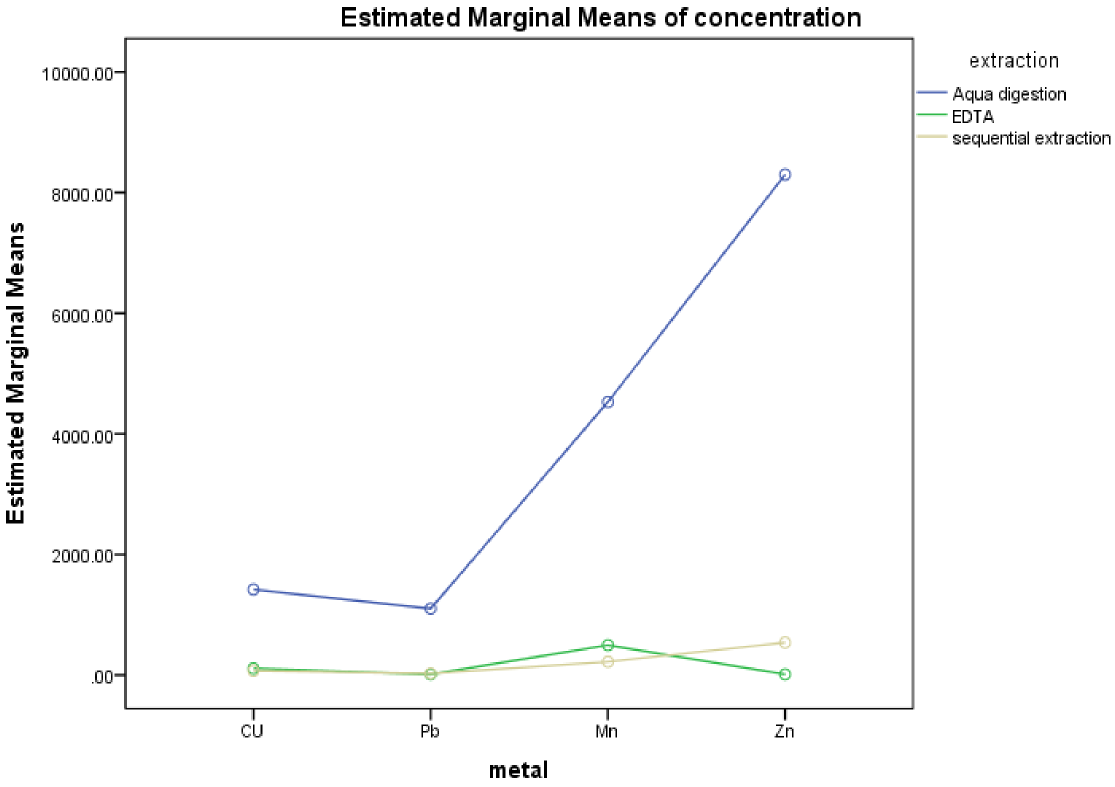

Figure 3: Analysis of Cu, Pb, Mn and Zn Solubility Efficiency in the Three Extractions.

APPENDIX D

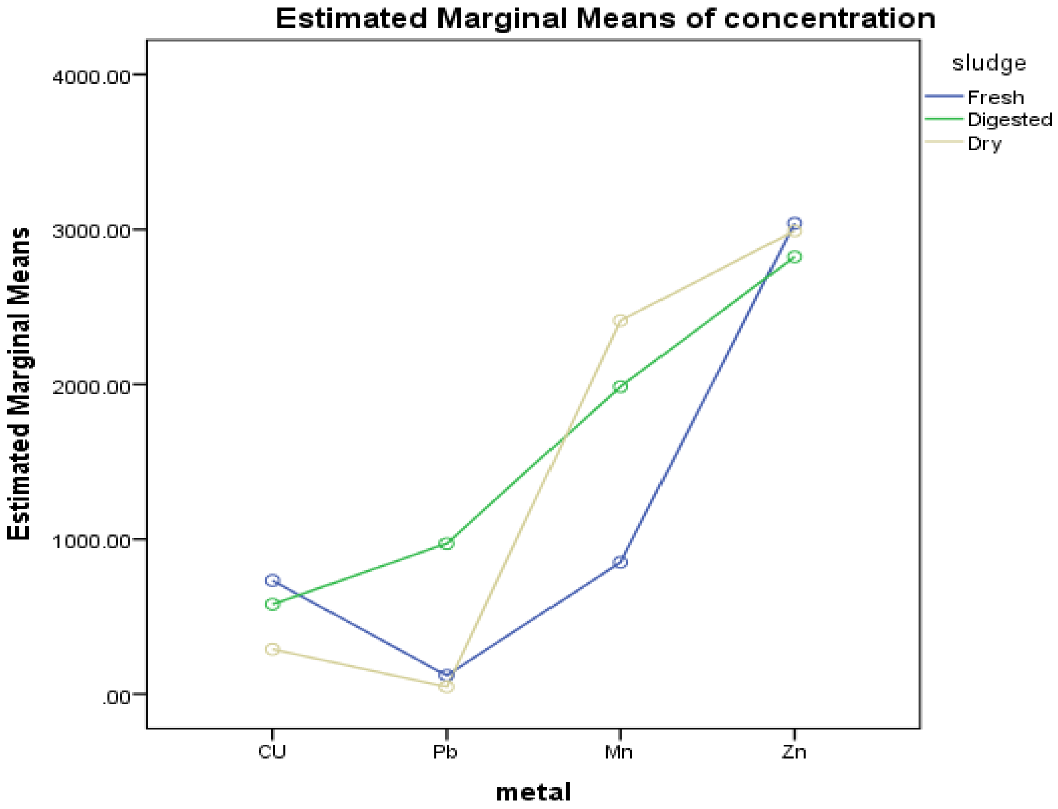

Figure 4 Analysis of Cu, Pb, Mn and Zn extraction in the Three Sludge Types.

APPENDIX E

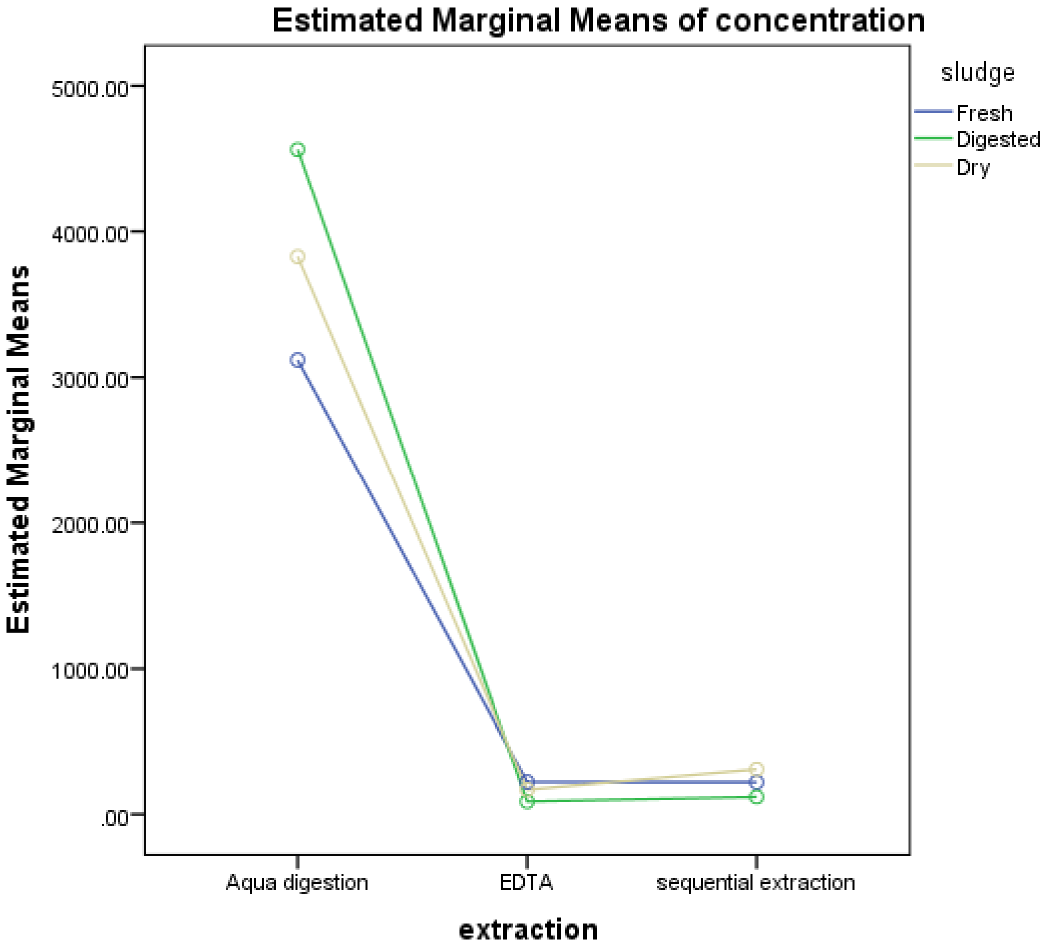

Figure 5: Analysis of Sludge Types' extractions of Metals in Three extractions.

APPENDIX F

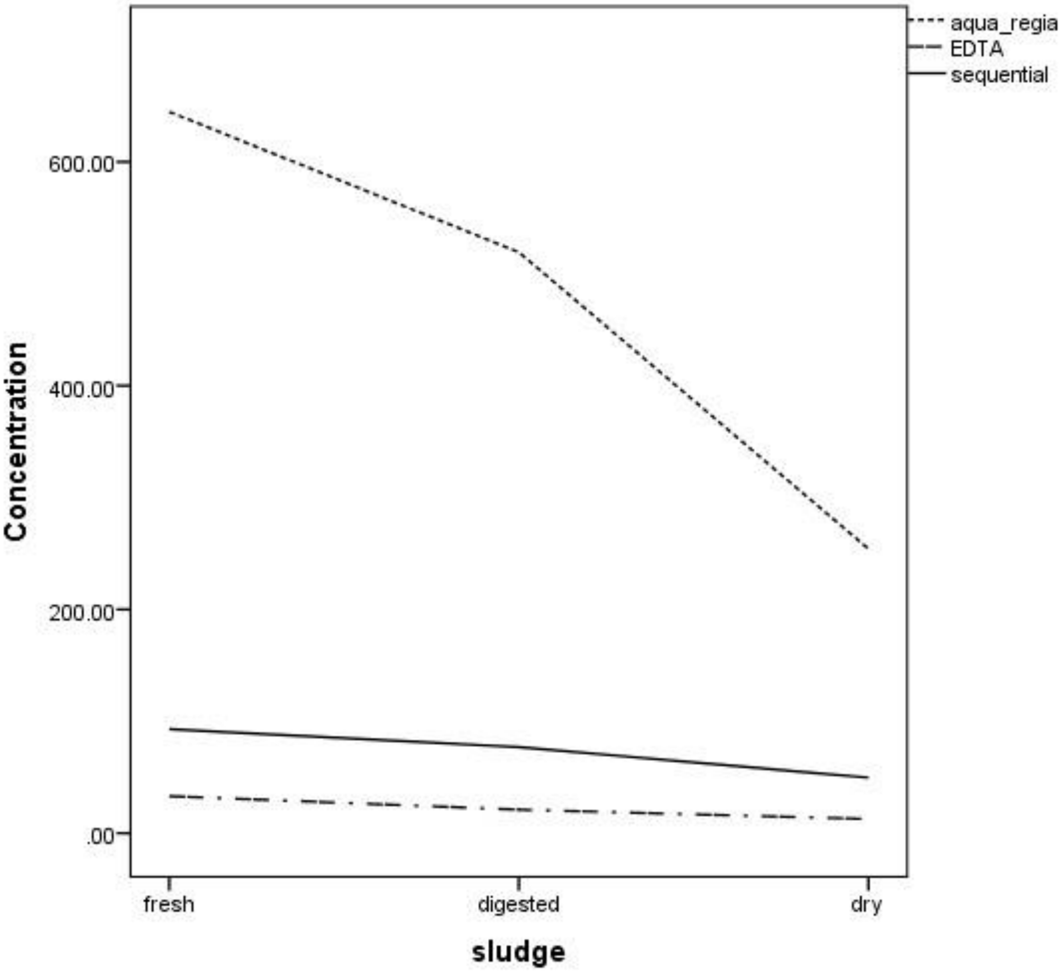

Figure 6: Concentration curves for extractions due to sludge type for Cu.

APPENDIX G

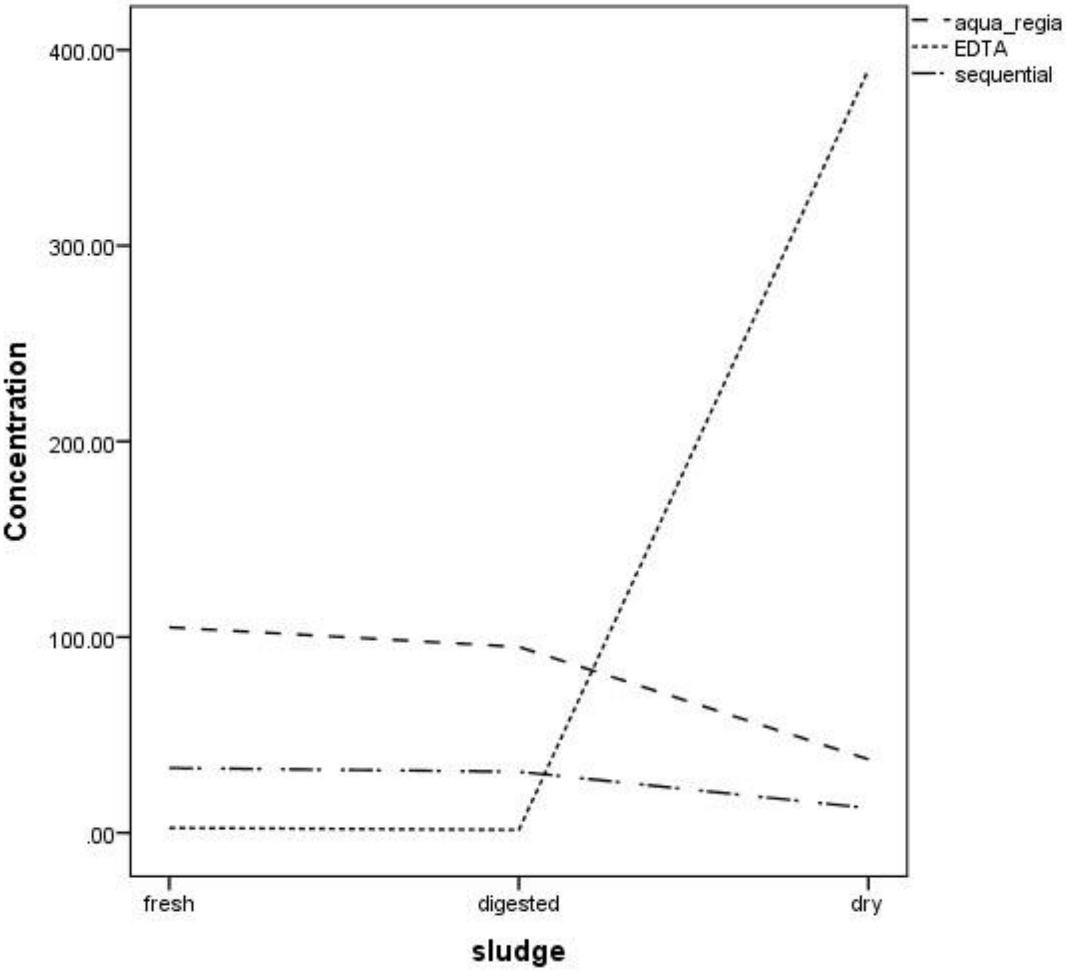

Figure 7: Concentration curves for extractions due to sludge type for Pb.

APPENDIX H

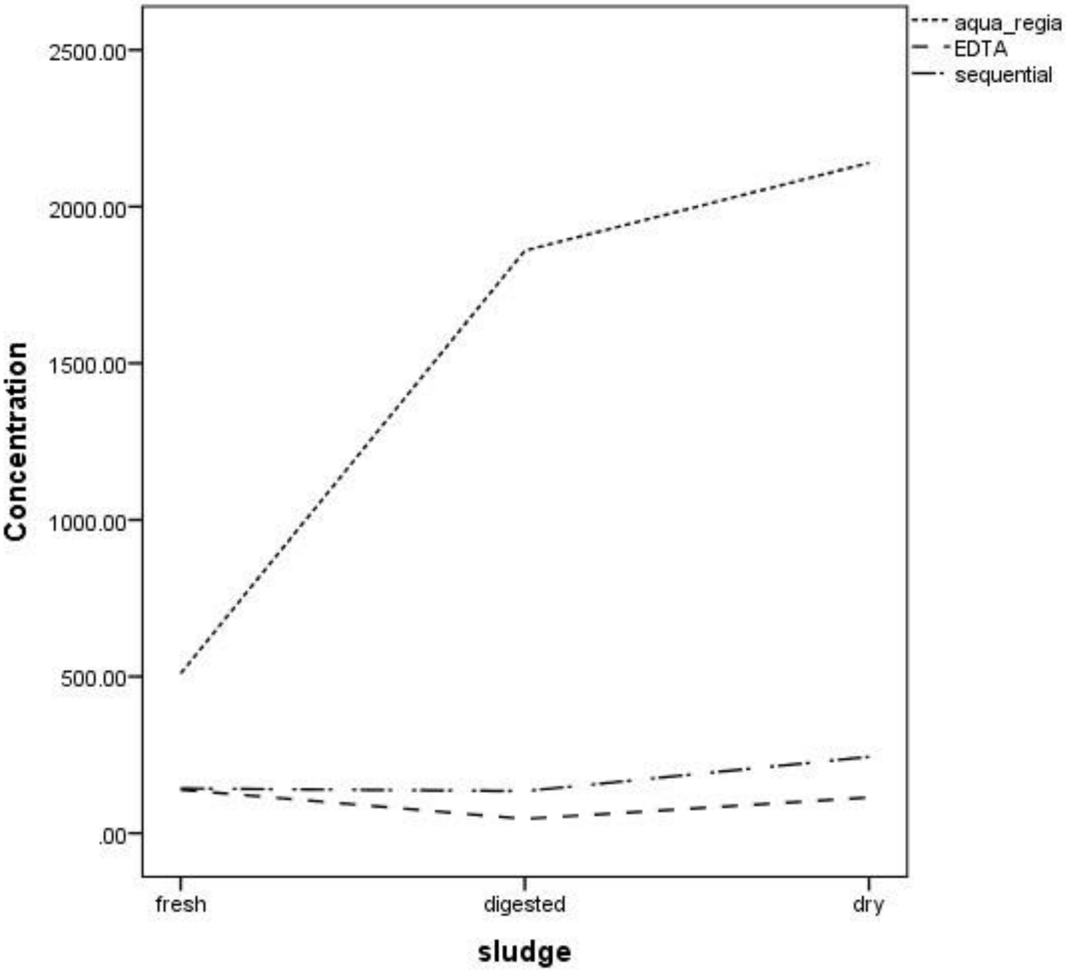

Figure 8: Concentration curves for extractions due to sludge type for Mn.

APPENDIX I

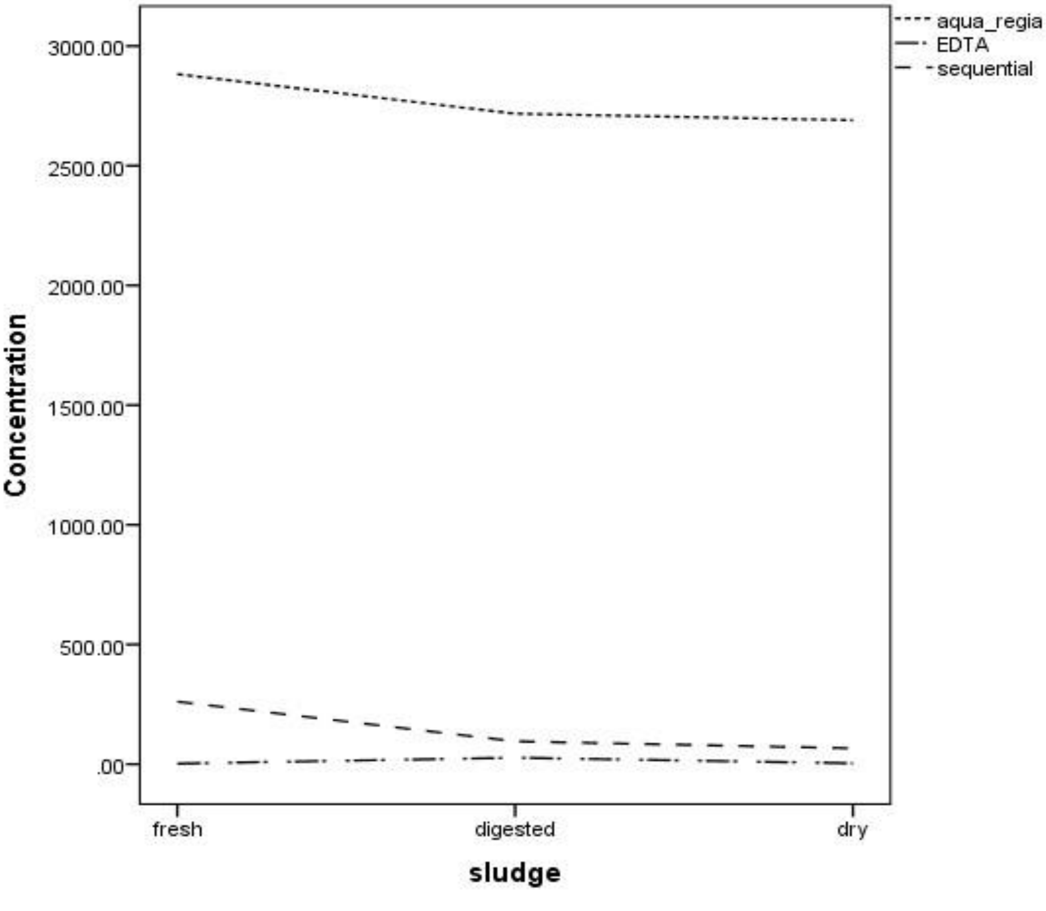

Figure 9: Concentration curves for extractions due to sludge type for Zn.