POLLUTION IMPACT, PHYTOREMEDIATION AND KINETICS OF ADSORPTION OF SELECTED METAL IONS FROM RIVER AND WASTE WATERS USING ARROWROOTS (*AMARANTA ARUNDINACEA*)

BY

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DECLARATION

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To my Father, John W. Tenge

ABSTRACT

Increased human activities have led to a rise in pollutants in the environment among them heavy metals. Conventional technologies for removal of metal ions from polluted water are numerous. Most of these methods are, however, expensive and sometimes inefficient. Adsorption utilizing natural adsorbents is found to be cost effective and adaptable to local needs. A study on the removal efficiency of Cu^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{2+} metal ions from River Malakisi water and wastewater from Eldoret municipal treatment plant using arrowroot biomass adsorbent has been done. The rhizomes of arrowroots planted in distilled water were harvested, sun and oven dried and then used for biosorption. Adjusting pH from 2.5 to 9.5, residual metal ion levels were measured using UV visible spectrophotometer. The procedure was repeated using residual metal ion levels at intervals of 10 minutes and at optimum pH of 5.5. Batch experiments were done by monitoring two model solutions of low 5 and high 25 ppm for mixed and single solutions containing the metal ions. A model constructed wetland was also set up by planting arrowroots in the influent and effluent of municipal wastewater where the % metal removal rates were compared with the wastewater that does not pass through the wetland. Other parameters determined in river water were coliforms, BOD, COD, anionic pollutants: NO_3^- , PO_4^{3-}, SO_4^{2-} and F^- , total hardness, turbidity, conductivity and pH. The Langmuir and Freundlich isotherm models, kinetic order of reaction and inter-particle diffusion models were evaluated to study the adsorption process for the metal ions using arrowroots. The paired t-test statistical parameter and relative treatment efficiency index were also used to compare the percent metal removal efficiency from municipal wastewater with and without live arrowroot plants. The results showed that all the heavy metals, except Zn, coliforms and turbidity were above the WHO limits while other pollutants were within, implying the general pollution of River Malakisi. The % metal removal efficiency from river water by arrowroots followed the trend, $Fe^{2+} > Cu^{2+} > Mn^{2+} > Zn^{2+}$. The R^2 for both Langmuir and Freundlich isotherms showed that the adsorption data for the metal ions in river water using arrowroots best fitted the Freundlich isotherm, that is mainly by hetero layer mechanism. Results of batch experiments showed that adsorption of all the metal ions in model solutions containing mixed ions of low and high concentrations, adopted pseudo second order mechanism while solutions containing single ions at high concentrations adopted pseudo first order mechanism. Adsorption of the metal ions by dry arrowroots from model solutions involving higher concentrations than river water, best fitted the Langmuir isotherm. The metal removal rates in wastewater cultivated with live arrowroots were however, higher than that without arrowroots, suggesting that arrowroots could be of significant benefit providing a tertiary wastewater treatment alternative.

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LIST OF ABBREVIATIONS

ANOVA - Analysis Of Variance

APHA - American Public Health Organization

ATSDR - Agency for Toxic Substances and Disease Registry

BOD - Biological Oxygen Demand

COD - Chemical Oxygen Demand

ELDOWAS - Eldoret Water And Sanitation Company

NBI - Nile Basin Initiative

NTU - Nephelometric Turbidity Units

RTEI - Relative Treatment Efficiency Index

S.A.C.N -Scientific Advisory Committee on Nutrition

UNEP - United Nations Environmental Programme

WRSEB - Water Resource Service Board

WHO - World Health Organization

BAT - British American Tobacco

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CHAPTER ONE

INTRODUCTION

1.1 Background

The scarce water resources globally are being polluted by both organic and inorganic pollutants from domestic, industrial waste, municipal waste, agricultural, mining activities and geological origin. Heavy metals and pathogens in water sources such as rivers are known to have adverse effects in humans. Rivers play a major role to the community especially in the fishing industry and to supply water for people. River contamination either directly or indirectly finally affects humans.

New methods of removal of pollutants such as heavy metals from polluted waters are being researched on to replace conventional methods which have been discovered to be costly and not eco-friendly (Mousa *et al*., 2013; Reeb & Werckmann, 2005). Biosorption using dead biomass and live plants have been discovered as the best alternatives which are cheap and environmentally friendly. Heavy metal-tolerant plant species are used for removing heavy metals from the soil and contaminated water and translocating them to above the ground biomass which is subsequently harvested and utilized. Phytoremediation is an emerging technology, environmentally friendly method for large-scale cleanup of contaminated water and soil (Igwe & Abia, 2007; Volesky, 2007). It is a process that involves uptake and degradation of organic pollutants and heavy metals by plants from soil and water. Phytorestoration or phytoremediation is thus a term covering all technologies using plants to restore soils, ecosystems, and/or water integrity.

Municipal wastewater contains high levels of pollutants since it is a collection of wastes from various sources such as domestic waste, industrial effluents from various industries within that municipality and sewage among others. Municipal treatment of such wastewater is usually aimed at lowering the level of available pollutants such as heavy metals, odour, nutrients, turbidity and colour to permissible levels before discharge into recipient environment such as rivers and streams. Several methods such as chemical precipitation, conventional adsorption, ion exchange, membrane separation and electro- remediation methods are available for treatment of wastewater. However, most of the methods are not economically viable due to their secondary effluent impact on the recipient environment (Achanai *et al*., 2012a; Phiri *et al*., 2009).

Data showing metal and metalloid removal rates by different plant species and standardized procedures have been emphasized for further research. Other suggestions include; carrying out studies in a micro- or mesocosm scale experiment which would not aim at exactly mimicking natural ecosystems but allow visualization of plant responses to the conditions prevailing in wastewater, such as metal concentrations, redox conditions and pH (Abdel & Elchanghaby, 2007; Marchand *et al*., 2010).

Other suggestions have emphasized the fact that experiments aimed at testing metal removal should use the following criteria of measurement of system efficiency via the assessment of a mass balance of water and pollutants, such as measuring concentration differences between inlet and outlet, ensuring the system is hydrologically isolated, and properly replicated, and inclusion of unplanted control. Others include, carrying out studies using bio-racks, which are completely soil free and proper experimental design such as, relative treatment efficiency index (RTEI), to achieve quantification and standardization of various conditions and their effects (Marchand *et al.*, 2010). In this study, efficiency of arrowroots as one of the emergent macrophytes plant in removal of heavy metals in river water and municipal wastewater was investigated.

1.2 Study area

A study was carried out on Malakisi River which traverses through Bungoma west, Mount Elgon and Teso sub-counties, and on municipal wastewater in Eldoret to establish their quality and assess the effectiveness of purple arrowroots in removing selected heavy metals from the river water and highly contaminated wastewater.

Bungoma West is in Bungoma County, Western Kenya, coordinates, $0^{o}35^{/}$N, $34^{o}35^{/}$E. The Sio-Malakisi river basin is shared by Kenya and Uganda. The Malaba-Malakisi catchment has an area of 1750 km^{2}. The Sio- Malaba-Malakisi river basin has a population of about 4 million people, 80% of whom are engaged in agriculture (NBI, 2011).

Rainfall is in two seasons, where the highest is between the months of April, and June. The second season is between the month of September and November while dry season is between the month of December and March.

1.3 Problem statement

The problems associated with lack of clean water are estimated to cost in excess of US $ 10 billion per year to correct such problems if ground and surface water contamination goes unchecked (Pink, 2006; UNEP, 2006; West, 2006; WHO, 2008). In majority of the rural parts of Kenya, over 60 percent of local people depend on rivers and groundwater aquifers for water (WRSEB, 2002), due to lack of piped water.

In Mount Elgon, Teso and Bungoma West sub-counties in western Kenya, the only water treatment plant which had been constructed along the Malakisi River upstream at Nasara in Mount Elgon failed to work several years ago due to poor piping, lack of new technology, poor gravity, generators among others. The plant was to provide clean water for residents of these sub-counties. As a result, the residents do use untreated raw water from the river and springs for drinking and other domestic purposes.

However, the quality of this water has never been determined and the number of people suffering from water related diseases is on the rise and this is of great concern (http://westfm.co.ke/mobile/index.php?page=news$id7593:2012-4-25). Despite the fact that Mt Elgon is a water catchment area, lack of piped water and incidences of typhoid and other water related diseases have been witnessed in some schools and health centres, (Kapchangablogsport.com/2012-4-11-archive.html).

The municipal wastewater treatment plant in Eldoret is a collection of wastewater from various sources including domestic sewage and industrial effluents from textile industries, Kenya cooperative creameries (KCC), Brookside, among others. The main method of treatment of such wastewater is through natural biological degradation, where the wastewater is left to degrade in unplanted maturation ponds for around one week, before being discharged to river Sosiani. Although this method drastically reduces the level of BOD and COD, the effluent could still contain phosphates, nitrates and some finely dissolved suspended organics and metal ions

1.4 Justification of study

Water scarcity and water pollution have become a serious problem worldwide (Enuneka *et al.*, 2013; Kuforiji & Ayandiran, 2013; Younus & Enaam, 2014). Reduced water quality can also lead to reduced biodiversity (UNEP, 2006). Most of the rivers in the developing world are the end points of effluents discharged from industries and untreated or partially treated sewage, which contain different pollutants such as heavy metals, organic contaminants, xenobiotics, nutrients, among others (Phiri *et al.*, 2009). Presence of heavy metals in high levels in water has been found to have adverse effects to human health and living organisms. Apart from health impacts to humans, water contamination places other resources such as fisheries and land at risk. In most cases, down-stream fish and vegetable crops become heavily contaminated with heavy metals (Dara, 2004).

Malakisi River, being the main source of water in Bungoma West district should be used sustainably and extent of pollution of the river needs to be established in order to come up with possible management strategies to curtail environmental degradation. Mount Elgon is a source of the Malakisi River, which discharges into Lake Kyoga at an elevation of 950 metres above sea level. The mountain was formed as a result of volcanic eruption and hence comprises of volcanic rocks. Mineral veins have been found to occur in eastern part of Uganda which shares part of Mount Elgon, where mining of copper and cobalt deposits is being carried out (www.oilinuganda.org/.../copper-waste-poisoning-kasese-river.html). Main inorganic ground water quality problems with high levels of fluoride, iron and manganese above 0.3 mg/l and high chloride concentrations have been reported in eastern Uganda because of volcanic rocks (WaterAid Country Office, 2001). There is thus a possibility of finding some of these metals in Malakisi River due to geological origin or erosion.

The Bungoma West, Teso and Mount Elgon sub-counties are agricultural areas and the river traverses them. Substantial vegetable production, sugarcane production, purple arrowroots, bananas, and nappier grass have been planted along the river bank. A few coffee factories have been constructed along the river bank where they discharge their treated effluents. Main crops grown in the Malakisi river catchment area include coffee, onions, maize, beans, Irish potatoes (upstream), tobacco, cassava, millet (downstream). Purple arrowroots have been grown both upstream and downstream. Examples of fertilizers, insecticides, fungicides, insecticides and herbicides used in Malakisi catchment area of study include: Mancozeb (dithane) fungicide, a product of zinc ion (0.9%) and manganese ethylene bisdithiocabamate (7.4%) are commonly used in tobacco farming. Others include copper nordox and redomil (metalxyl). The region is also poorly served with sewage system hence most of the wastes find their way into the river through run off. There is also lack of adequate piped water in the region. Most of the residents depend on raw water from the river, which could be polluted due to human activities or geological origin. Following the above activities, which are likely to lead to river pollution, a study that will check on the levels of major pollutants and reduce pollutant levels is necessary.

Therefore, this study is important because not only will it provide vital information concerning the quality of the water from the Malakisi river and measures to take to ensure safe drinking water, but also provide a cheap, efficient and environmentally friendly phytoremediation technology of removing pollutants from river and wastewater using arrowroots.

1.5 Rationale

Malakisi River is the main source of water to residents of Bungoma West, Teso and Mount Elgon sub-counties. This river could probably contain high levels of some of the heavy metals due to geological origin or pollution.

Studies to investigate the level of pollution have been done on some rivers and available water sources in some parts of Kenya (Dulo, 2008; Gathenya *et al*., 2009). A survey done under the umbrella of wetlands for community livelihoods with an aim of establishing artificial wetlands along Ngong river in Kenya in order to purify the highly polluted river water, showed that arrowroots can be good accumulators of heavy metals but suggested for a more comprehensive research, since the results were not scientifically represented (Constance *et al*., 2011). Elsewhere, studies have also been done on other macrophyte plants to show their pollutant removal efficiency but the pollutant removal rate using arrowroots and other rotundifolia species is yet to be done (Marchand *et al*., 2010). In Bungoma County, studies on river pollution have not been done on most rivers including Malakisi river (NBI, 2011).

1.6 Objectives

1.6.1 Overall objective

The general objective of the study was to determine the concentration levels of heavy metals, and the adsorption capacity of the arrowroots for the selected metal ions from Malakisi river and waste water from Eldoret water treatment plant.

1.6.2 Specific objectives

The specific objectives of this research were:

1) To determine the amounts of heavy metals in water (Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}) using UV visible spectrophotometer
2) To determine phosphates, nitrates, fluorides and sulphates in river water
3) To determine the presence and level of faecal coliforms, and physico-chemical parameters (BOD, COD, turbidity, conductivity, total hardness and pH) in river water
4) To investigate the adsorption kinetics of the arrowroots for the Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}metal ions from river and wastewater, using Langmuir and Freundlich isotherms, Pseudo first and second order kinetic models and inter-particle diffusion models

1.7 Research questions

1) Are there high or low concentration levels of Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+} in the water from Malakisi river and in the influent and effluent wastewaters of Eldoret treatment plant?
2) Are the concentrations of phosphates, nitrates, fluorides and sulphates in the water from Malakisi worrying?

3) Are there faecal coliforms in Malakisi river and, what are the amounts of the physico-chemical parameters (BOD, COD, turbidity, conductivity, total hardness and pH) in the river water?
4) Can purple arrowroots effectively reduce levels of heavy metals from river water and tolerate high concentrations of the pollutants in wastewater?

CHAPTER TWO

LITERATURE REVIEW

2.1 General

Water quality is the ability of a water body to support all appropriate beneficial uses. Nitrates, pH, heavy metals, sulphates, fluorides, BOD, COD, phosphates, conductivity, turbidity and coliforms are some of the basic parameters that describe water quality.

2.1.1 Nitrates

Nitrate levels can be high in streams and rivers due to runoff of nitrogen fertilizers from agricultural fields and urban lawns. Nitrate levels above 10 ppm have been reported to present a serious health concern for infants and pregnant or nursing women (Williams *et al*., 2006). High nitrate levels have been reported to interfere with the ability of the blood to carry oxygen to vital tissues of the body in infants of six months old or younger. The resulting illness is called methemoglobinemia or "blue baby syndrome"(Dara, 2004).

Little is known about the long-term effects of drinking water with elevated nitrate levels. Some research has suggested that nitrate may play a role in spontaneous miscarriages, thyroid disorders, birth defects, and in the development of some cancers in adults (Selman, 2007). Recent human epidemiologic studies have shown that nitrate ingestion may be linked to gastric or bladder cancer (Dara, 2004). The most likely mechanism for human cancer related to nitrate is the body’s formation of N-nitroso compounds (NOC), which have been shown to cause tumours at multiple organ sites in every animal species tested, including neurological system cancers following transplacental exposure (Schindler & Vallentyne, 2008). Nitrite, the reduced form of nitrate, reacts in the acidic stomach to form nitrosating agents that then react with certain compounds from protein or other sources such as medications to form NOCs (Dara, 2004). In humans, it is the nitrosamines and NOCs that are suspected brain and central nervous system carcinogens. Maximum WHO levels of nitrates and nitrites are 10 ppm and 1 ppm, respectively (Phiri *et al*., 2009).

2.1.2 Phosphates

Fertilizers, failing septic system, wastewater treatment plant discharges, and wastes from pets and farm animals are typical sources of excess nutrients of phosphates and nitrates in surface waters. Phosphates have been considered as the primary cause of eutrophication, where it promotes excessive plant growth and decay, favouring simple algae and plankton over other more complicated plants, and causes a severe reduction in water quality. Phosphates adhere tightly to soil, and hence are mainly carried by erosion and then translocated to lakes or rivers. The extraction of phosphates into water have been found to be slow and hence difficulty for reversing the effects of eutrophication. Eutrophication decreases the resource value of streams or rivers such that recreation, fishing and aesthetic enjoyment is hindered. Health problems have been identified to occur where eutrophic conditions interfere with drinking water treatment (Selman, 2007; West, 2006). Eutrophication is depriving the river of oxygen (also called oxygen debt). The growth of water plants is suppressed resulting in death of these plants as algae dominate and turn water green. This disrupts the food chain, which further results in death of invertebrates and then fish which in turn results in excess bacterial activity during decomposition, hence reducing oxygen levels further (Womach, 2005). Surface water quality with high nutrient levels has increased biomass and algal growth, increased blooms of gelatinous zooplanktons, depletion of dissolved oxygen, increased turbidity and increased rate of sedimentation, development of anoxic conditions and water treatment problems ranging from odour, bad taste, increased filtration costs and disinfection by- products- trihalomethanes with potential health effects. Increased vegetation also impedes water flow and navigation and leads to disappearance of important species such as salmonids and coregonids or water fish (Phiri *et al.*, 2009). The WHO maximum limit of phosphate levels in water is 5.0 mg/l (WHO. 2008).

2.1.3 pH

pH is the negative logarithm of the hydrogen-ion activity of a solution. It is a measure of the acidity or alkalinity of an aqueous media. Most natural waters are buffered by a carbon dioxide- bicarbonate system. Buffering capacity is the water's ability to resist changes in pH, and is critical to the survival of aquatic life. This reaction keeps pH of most water bodies at pH range of 7-7.5, unless large amounts of acid or base are added to the water. pH values higher than 8.5 have been known to interfere with chlorination during water treatment. pH outside range of 6.5- 8.5 reduces the diversity in the stream by stressing the physiological systems of most organisms thereby reducing reproduction (Williams *et al.*, 2006).

2.1.4 Sulphates

Sulphate levels in natural waters have been found to be between 2 and 80 mg/l but higher than 1,000 mg/l near industrial discharges or in arid regions where sulphate minerals, such as gypsum, are present. High concentrations (> 400 mg/l), which is the WHO maximum limit, may make water unpleasant to drink (Johathan, 2010).

2.1.5 Fluoride

Fluoride concentrations in natural waters have been established to vary from 0.05 to 100 mg/l, with most fresh waters having less than 0.1 mg/l. Very high concentrations of fluoride, far exceeding the WHO guideline value of 1.5 mg/l have been encountered in volcanic aquifers and lakes in the East African Rift system and in Hawaii. A high concentration fluoride is toxic to humans and animals and can cause bone diseases. However, a slight increase in natural concentrations can help prevent dental caries although, at higher concentrations (above 1.5-2.0 mg/l), mottling of teeth can occur (Ayoob & Gupta, 2006; Kahama *et al.*, 1997).

2.1.6 Biological oxygen demand and chemical oxygen demand

Biological oxygen demand (BOD) is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions. High BOD levels in a stream or a river accelerates bacterial growth which consumes the available oxygen levels in the river. The oxygen may diminish to levels that are lethal for most fish and aquatic insects. Chemical oxygen demand (COD) is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. COD values are always greater than BOD values. COD measurements can be made in a few hours while BOD measurements take five days (Manta, 2003; Schindler &Vallentyne, 2008). BOD > 6 mg/l have been classified as grossly polluted, BOD between 3 – 6 mg/l as moderately polluted and rivers with BOD <3 mg/l as relatively polluted (Selman, 2007). The WHO maximum limits of BOD and COD are 20 mg/l and 50 mg/l respectively (WHO, 2008).

2.1.7 Conductivity

Conductivity is the ability of a substance to conduct electricity. The conductivity of water is a function of the concentration of dissolved ions. A sudden increase of the conductivity of a stream indicates that there is a source of dissolved ions in the vicinity. Hence, conductivity measurements can be used as a quick way to locate potential water quality problems (Williams *et al.*, 2006). A maximum limit of conductivity levels in water is 1500 µs/cm (WHO, 2008).

2.1.8 Turbidity

Turbidity is another indicator of the amount of material suspended in water. It measures the amount of light that is scattered or absorbed. Suspended silt and clay, organic matter, and plankton contribute to turbidity. Photoelectric turbid meters measure turbidity in nephelometric turbidity units (NTU). Researchers have established that native fish populations can only be maintained in rivers and streams if random monthly values of turbidity never exceed 100 NTU. Turbidity of 10 NTU or less represent very clear waters, 50 NTU or greater represents cloudy water and river water with turbidity range of 100-500 is very cloudy and muddy. In drinking water, the higher the turbidity level, the higher the risk that people may develop gastrointestinal diseases, where contaminants such as viruses or bacteria can become attached to the suspended solids. The suspended solids have also been discovered to interfere with water disinfection with chlorine because the particles act as shields for viruses and bacteria. Similarly, suspended solids can protect bacteria from ultraviolet (UV) sterilization of water. The WHO maximum limit of turbidity is 5.0 NTU. Topography, vegetation, geology, agricultural activities, and precipitation greatly influence raw water turbidity (Goransson *et al.*, 2013; Younus & Enaam, 2014).

2.1.9 Coliforms

Faecal coliform (FC) are the most common pollutants in rivers and streams (Dagne *et al.*, 2006; Oliver & Ismaila, 2011). Coliforms or indicator microorganisms are present in the intestinal tracts of warm blooded animals, including humans and can be excreted in the faeces of these animals. Indicator organisms are commonly used to assess the quality of surface waters where FC is the most commonly used bacterial indicator of faecal pollution (Edberg *et al*., 2000). The coliforms are indicative of the general hygienic quality of the water and potential risk of infectious diseases. High FC and total coliform (TC) counts in water are usually manifested in the form of diarrhoea, fever and other secondary complications (Sivaraja & Nagarajan, 2014). A zero Cfu/100 ml is the WHO required maximum limit of coliform levels in water (WHO, 2008).

2.1.10 Water Hardness

Temporary hard water contains soluble hydrogen carbonates of calcium or magnesium while permanent hard water contains soluble sulphates of calcium and magnesium. The general classification for hardness of water is 75 –150 mg/l of $CaCO_3$ for soft water and 150 mg/l and above as for hard water (Kuforiji & Ayandiran, 2013). The WHO maximum limit of total hardness in water is 100 mg/l (WHO, 2008). Calcium is important for strong bone formation in humans while magnesium deficiency have been implicated in the pathogenesis of hypertension. Studies have also documented importance of magnesium in type 2 diabetes mellitus (WHO, 2011). Although consumption of water containing soluble calcium and magnesium ions is essential for human health, high intake of calcium have been reported to exert acute effects on iron absorption. Drinking-water in which both magnesium and sulfate are present in high concentrations (above 250 mg/l each) has been reported to have laxative effect.

Concern for excess calcium has also been directed to those who are prone to milk alkali syndrome (the simultaneous presence of hypercalcaemia, metabolic alkalosis and renal insulin insufficiency) and hypercalcaemia (WHO, 2011). Individuals are protected from excess intake of calcium by a tightly regulated intestinal absorption and elimination mechanism through the action of 1, 25-dihydroxyvitamin D, the hormonally active form of vitamin D. When calcium is absorbed in excess of need, the excess is excreted by the kidney in healthy people who don't have renal impairment.

Depending upon interaction with other factors, such as pH and alkalinity, hard water can cause increased soap consumption and scale deposition in the water distribution system, as well as in heated water applications where insoluble metal carbonates are formed, coating surfaces and reducing the efficiency of heat exchangers. Excessively hard water can also have corrosion tendencies (WHO, 2009).

2.1.11 Heavy metals

2.1.11.1 Sources and effects of Copper

Copper is mostly found in copper water pipes, pesticides, swimming pools, intra-uterine devices, and dental amalgams, nutritional supplements especially prenatal vitamins, birth control, weak adrenal glands and occupational exposure. Effects of high levels of copper metal include irritation of the nose and liver damage. One may be exposed to copper by breathing air, eating food or drinking water containing copper as well as through skin contact with soil, water. In drinking water, the WHO minimum limit of copper is 0.05mg/l (WHO, 2008). Copper is an essential element, small amounts are necessary in diets to ensure good health for living organisms including human beings. However, if daily intake of 0.9 mg/day is exceeded, deficiency and toxic effects are observed (Singh & Garg, 2006). The main problem with copper is that if its concentration increases too sharply, the body's absorption of zinc will be impeded. Zinc deficiency contributes to infertility. Copper has also been associated with liver damage and kidney disease and is suspected to cause infant liver damages (Dara, 2004). Acute symptoms of excess copper include salivation, epigastric pain, vomiting, diarrhoea, stomach cramps, nausea, irritation of eyes and respiratory tract (Araya *et al*., 2001). Vomiting and diarrhoea usually present more serious manifestations of copper toxicity that can include coma, shock, oliguria (diminished urine secretion), hemolytic anaemia, acute renal (kidney) failure with tubular damage, hepatic necrosis (liver cell death), vascular collapse and death. Exposure to skin can cause inflammation, itching and burns. Other effects include: acne, adrenal hyperactivity and insufficiency, agoraphobia, allergies, hair loss, anaemia, anxiety, arthritis, autism, cancer, chronic *candida albicans* infection, depression, elevated cholesterol, cystic fibrosis, diabetes, dyslexia, elevated estrogen, failure to thrive, fatigue, fears, fractures of the bones, headaches, heart attacks, hypertension, hypothyroidism, infections, insomnia, iron storage diseases, decreased libido, multiple sclerosis, nervousness, osteoporosis, panic attacks, premenstrual syndrome, schizophrenia, strokes, tooth decay, vitamin C and other vitamin deficiencies (Singh & Garg, 2006).

2.1.11.2 Sources and effects of Iron

Iron is used as a construction material, inter alia for drinking water pipes. Iron oxides are used as pigments in paints and plastics. It is also used as food colours and for treatment of iron deficiency in humans. Various iron salts are used as coagulants in water treatment. Water colour has been known to be affected by the quality of organic matter and prevalence of iron. Browning of inland waters over large parts of the northern hemisphere has been a phenomenon with both ecological and societal consequences (Kritzberg & Ekstrum, 2012). In drinking water supplies, iron (II) salts are unstable and are precipitated as insoluble iron (III) hydroxide, which settles out as a rust- coloured silt. Turbidity and colour have been discovered to develop in piped systems at iron levels above 0.05 mg/l. Staining of laundry and plumbing also takes place due to iron concentrations above 0.3 mg/l (WHO, 2008). Iron is an essential metal to human body; it is vital to biological processes as in transport of oxygen in the body. However, intake beyond a range of 8-18 mg/day gives rise to deficiency and toxic effects (Singh & Garg, 2006). Iron may cause conjunctivitis, choroiditis and retinitis if it contacts and remains in the tissues. The large amounts of ingested iron can cause excessive levels of iron in the blood which react with peroxides to produce free radicals, which are highly reactive and can damage DNA, proteins, lipids and other cellular components (Clifford, 2010). Acute high doses of iron can also damage the intestinal mucosa and cause systemic shock and death. Iron supplementation may favour infectious pathogens by providing them with a supply of iron for their growth and replication. Carcinogenic effects of several heavy metals have been discovered including iron. Deficiency of iron in the body causes anaemia, while continuous exposure to lower amounts may interfere with the metabolism of copper and zinc (Clifford, 2010).

2.1.11.3 Sources and effects of Zinc

Zinc enters the air, water and soil as a result of both natural processes and human activities. Most zinc enters the environment as a result of mining, purification of zinc ores, lead and cadmium ores, steel production, coal burning and burning of wastes. Levels of zinc in soil increases mainly from disposal of domestic wastewater, zinc wastes from metal manufacturing industries and coal ash from electrical utilities. Sludge and fertilizers also contribute to increased levels of zinc in the soil (ATSDR, 2005). Other sources include: corrosion and leaching of plumbing, water-proofing products (zinc formate, zinc oxide), anti-pest products (zinc arsenate - in insecticides, zinc dithioamine as fungicide, rat poison, rabbit and deer repellents, zinc fluorosilicate as anti-moth agent), wood preservatives (as zinc arsenate), deodorants and cosmetics (as zinc chloride and zinc oxide), medicines and ointments (zinc chloride and oxide as astringent and antiseptic, zinc formate as antiseptic), paints and pigments (zinc oxide, zinc carbonate, zinc sulphide), printing inks and artists paints (zinc oxide and carbonate), colouring agent in various formulations (zinc oxide) and a UV absorbent agent in various formulations (Dara, 2004).

Zinc is an essential metal to human beings; it is extraordinarily useful in biological systems. However, beyond intake range of 8-11 mg/day deficiency and toxic effects are observed (Singh & Garg, 2006). Toxicity of zinc in human beings is minimal; its major effect is interference with copper metabolism. Symptoms of an acute oral zinc dose may include: tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhoea and damage of hepatic parenchyma (Bigdeli & Seilsepour, 2008).

Excessive absorption of zinc suppresses copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates and even vertebrate fish. The free ion activity model is well-established in the literature and shows that just micromolar amounts of the free ion kills some organisms. A recent example showed 6 micromolar killed 93% of all *Daphnia* in water (Muyssen *et al*., 2006). The WHO maximum limit of zinc levels in water is 1.5 mg/l (WHO, 2008).

The free zinc ion is a powerful Lewis acid up to the point of being corrosive. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride. Swallowing a post-1982 American one cent piece (97.5% zinc) can cause damage to the stomach lining due to the high solubility of the zinc ion in the acidic stomach (Bothwell *et al*., 2003). Recent research suggests that the topical antimicrobial zinc pyrithione is a potent heat shock response inducer that may impair genomic integrity with induction of PARP-dependent energy crisis in cultured human keratinocytes and melanocytes (Lamore *et al*., 2010).

2.1.11.4 Sources and effects of manganese

Manganese is an essential nutrient, comprising approximately 0.1% of the earth's crust. Manganese does not exist in nature as an elemental form, but is found mainly as oxides, carbonates, and silicates in over 100 minerals with pyrolusite (manganese dioxide) as the most common naturally-occurring form. As an essential nutrient, several enzyme systems have been reported to interact with or depend on manganese for their catalytic or regulatory function. As such, manganese is required for the formation of healthy cartilage and bone and the urea cycle; it aids in the maintenance of mitochondria and the production of glucose. It also plays a key role in wound-healing (Casarett & Doull, 2001).

Manganese exists in both inorganic and organic forms. An essential ingredient in steel, inorganic manganese is also used in the production of dry-cell batteries, glass and fireworks, in chemical manufacturing, in the leather and textile industries and as a fertilizer. The inorganic pigment known as manganese violet (manganese ammonium pyrophosphate complex) has nearly ubiquitous use in cosmetics and is also found in certain paints. Organic forms of manganese are used as fungicides, pesticides (for example, maneb), fuel-oil additives, smoke inhibitors, an anti-knock additive in gasoline, and a medical imaging agent (Bowler *et al*., 2007; ATSDR, 2000).

The principal sources of manganese in the atmosphere are natural sources including continental dust, volcanic gas and dust and forest fires. Other sources are industrial emissions and combustion of forest fires. In water, manganese is reported to undergo chemical reactions and persist for up to several hundred years. Studies in animals and humans indicate that acute inhalation of high levels of manganese dust cause inflammatory response in the lungs (Bowler *et al.*, 2007). Symptoms of lethargy, increased muscle tone, spasm, tremors and mental abnormalities in persons drinking water contaminated by manganese from dry cell batteries buried nearby were noted in another study where the tested water contained manganese at a concentration of 14.3 mg/l.

In a similar study that was conducted to evaluate populations in three areas in Greece, each containing different levels of manganese in their drinking water, neurological scores, indicating weakness/fatigue, disturbance in walking, and tremors were found in the area with the highest manganese levels (1.6 – 2.3 ppm in water) compared with the area having the lowest. Different findings also established that neurological and neurobehavioral deficits occurred when one is exposed to low levels of manganese (< 0.2 mg/m^3) in welding fumes. A few reports have also associated intake of manganese with reproductive effects in humans including impotency in males and birth defects (ATSDR, 2008).

The secondary maximum contaminant level of 0.05 ppm is an acceptable level of manganese in drinking water based on the aesthetic qualities of taste, smell and staining of bath fixtures rather than on the potential to cause adverse effects (WHO, 2008). Manganese staining of fixtures produces a brownish-black colour, compared to blue-green for copper and reddish- brown for iron (Casarett & Doull, 2001).

2.2 Methods of treatment of metal contaminated waters

Methods of treatment of metal contaminated water include chemical precipitation, reverse osmosis, electro- dialysis, ion exchange, coagulation, flotation, membrane processes, ultra-filtration and adsorption. Of these methods, adsorption has been established to be highly efficient, inexpensive and easy to adopt (Maine, 2006). For municipal wastewater treatment, conventional methods have been associated with secondary effluent impact on the recipient environment such as rivers and streams (Abdel & Elchaghaby, 2007; Achanai *et al*., 2012a; Agbozu & Emoruwa, 2014; Kapellakis *et al*., 2004; Mollel *et al*., 2005). Besides, conventional methods of water treatment have also been established to be inefficient for metal removal from dilute solutions containing from 1 to 100 mg/L of dissolved metal (Abdel & Elchaghaby, 2007; Brisson & Chazarenc, 2009).

2.2.1 Biosorption of heavy metals

Biosorption is based on metal binding capacities of various biological materials. The term biosorption is used to describe the accumulation of metal ions by material of biological origin. It is a process that utilizes inexpensive biomass to sequester heavy metals. Biosorption has been defined as the property of certain biomolecules or types of biomass to bind and concentrate selected ions or other molecules from aqueous solutions (Volesky, 2007). According to Ahalya *et al*. (2003), biosorption is the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. Biosorption uses raw materials which are either abundant or wastes from industrial operations. Biosorption is an effective and versatile method which can easily be adopted as a low cost method of removing heavy metals from large amount of municipal and industrial wastewaters (Igwe & Abia, 2007; Oboh *et al*., 2009).

2.2.2 The biosorbents

Biosorbents for removal of metals and dyes include algae, fungi, bacteria, industrial wastes, and other polysaccharide materials, all of which have shown good biosorption capacities towards all types of metal ions (Achanai *et al*., 2012a; Agbozu & Emoruwa, 2014; El-Sayed *et al*., 2011). For bacterial biomass, they have polysaccharide slime layers and readily provide amino, carboxyl, phosphate and sulphate groups for biosorption. The sequestration of metallic species by fungal biomass has mainly been traced to the cell wall. The vegetative phases of fungi and algae are multicellular and various polysaccharides are the main constituents of the fungal cell wall, which are complexed with proteins, lipids and pigments. Large quantities of phosphate and glucouronic acid and chitin-chitosan complex exist in the cell wall which offers extensive possibilities for binding metals through ion exchange and coordination. In the fungal cell wall, several types of ionizable sites such as the phosphate group, carboxyl groups on uranic acids and proteins, and nitrogen containing ligands on protein and on chitosan affect the metal uptake capacity

2.3 Constructed Wetlands for Wastewater Treatment

Constructed wetlands can be considered as treatment systems that use natural processes to stabilize, sequester, accumulate, degrade, metabolize, and/or mineralize contaminants. These wetland treatment systems use rooted wetland plants and shallow, flooded or saturated soil to provide wastewater treatment. They are designed to take advantage of the chemical and biological processes of natural wetlands to remove contaminants from the wastewater (Benyamine *et al*., 2004; Brisson & Chazaren 2009).

Wetlands remove metals using a variety of processes including filtration of solids, sorption onto organic matter, oxidation and hydrolysis, formation of carbonates, formation of insoluble sulphides, binding to iron and manganese oxides, reduction to immobile forms by bacterial activity, and uptake by plants and bacteria. Metal removal rates in both subsurface flow and surface flow wetlands can be high, but can vary greatly depending upon the influent concentrations and the mass-loading rate. Removal rates of greater than 90% for copper, lead and zinc have been demonstrated in operating surface flow and subsurface flow wetlands. Wetlands possess a rich microbial population in the sediment to bring about the biochemical transformation of pollutants, are biologically productive, and are self-sustaining. Constructed wetlands also have significantly lower total lifetime costs and often lower capital costs than conventional treatment systems. Constructed wetland is an innovative and inexpensive treatment approach that has the potential to treat organic and inorganic compounds in wastewater from a range of sources (Calheiros *et al*., 2007).

Constructed wetlands have proven to be a very effective method for the treatment of municipal wastewater. For a small community with limited funds for expanding or updating wastewater treatment plants, constructed wetlands are an attractive option. Rural municipalities have access to adequate inexpensive land, and wetlands blend into a natural landscape setting. Once the wetlands are designed and constructed, annual maintenance costs are low. In addition, wetlands add aesthetic value, and provide wildlife habitat and recreation opportunities (Brisson & Chazarenc, 2009).

The application of constructed wetlands for municipal wastewater treatment has led to the study of their use for other kinds of wastewater. Acid mine drainage, agricultural wastewater, industrial wastewater, stormwater runoff, landfill leachate and airport runoff are all good candidates for remediation using constructed wetlands. Site specific designs that carefully consider factors such as hydrology, native plant species, and seasonal temperature fluctuation can lead to efficient removal of contaminants in wastewater. Demonstration projects have shown that wetlands are effective at removing both organic and inorganic contaminants. The relatively inexpensive nature of this type of treatment makes it a potentially cost-effective option for remediation (Marchand *et al*., 2010).

2.3.1 Metal removal processes in wetlands

Contaminants are removed from wastewater through several mechanisms. Processes of sedimentation, microbial degradation, precipitation and plant uptake remove most contaminants. Heavy metals in a wetland system may be sorbed to wetland soil or sediment, or may be chelated or complexed with organic matter. Metals can precipitate out as sulfides and carbonates, or get taken up by plants. Compounds in sediment, such as iron oxides, show preference for certain metals. This behaviour can affect how efficiently a metal is adsorbed in a wetland. A system that has reached the limits of its adsorption capacity can exhibit a reduction in contaminant removal rates. After a system has reached its capacity for metal sorption, metal sulfide formation becomes the main method of metal removal. Sulfate-reducing bacteria oxidize organic matter and reduce sulfate to form hydrogen sulfide. Hydrogen sulfide reacts with metals to form metal sulfides, which precipitate. Compared to sediments, plants not only take up metals but they are also involved in oxygenation and microbiological processes that contribute to the ability of the wetland to remove metals. Organic compounds can be broken down for consumption by microorganisms in a wetland system (Tondeski *et al*., 2005).

This biodegradation removes the organic compounds from water as they provide energy for the organisms. Organics can also be degraded when taken up by plants

(Marchand *et al.*, 2010). They can also sorb to surfaces in the wetland, usually to plant debris. Organic compounds containing nitrogen sorb to surfaces in the wetland, and organic nitrogen is converted to ammonia. Ammonia can volatilize, be exchanged with other cations in the sediment, or be nitrified if oxygen is present. Nitrate is the form of N taken up by plants, so emergent plants use it during the growing season. Excess nitrate in an anaerobic system is reduced to N_2 and N_2O gases as a result of denitrification, the main mechanism of nitrate removal. Some wastewaters contain phosphates from cleaning products. Storm water and agricultural wastewater may contain fertilizer runoff containing phosphates. Phosphates can sorb to surface plants and floating plant litter, as well as to sediment surfaces. They may precipitate out of solution with metals at more alkaline pH levels. Soluble inorganic phosphate is taken up by plants, and cycled through their growth and decomposition. Most phosphate is removed from wastewater through sediment retention. Phosphates sorb to sediment surfaces through bonds to positively charged clay particles and by substituting for silicate in clay structures.

It is not completely understood how explosives are removed in a wetland system. Wastewaters contaminated with the explosive compounds have been successfully treated by constructed wetlands. It is suspected that several processes working in conjunction contribute to their degradation. Enzymes reduce nitro groups to amino groups in some explosives, such as trinitrotoluene. These compounds are broken down further by ring cleavage. Degradation also occurs in plants that take up the compounds (Karanthanasis & Johnson, 2003).

Four mechanisms affect metal removal in wetlands. They include adsorption to fine textured sediments and organic matter, precipitation as insoluble salts in form of sulphides and oxyhydroxides, absorption and induced changes in biogeochemical cycles by plants and bacteria and lastly, deposition of suspended solids due to low flow rates. All these processes lead to accumulation of metals in the substrate of wetlands where the efficiency of systems depends strongly on inlet metal concentrations and hydraulic loading (Marchand *et al*., 2010).

2.3.2 Adsorption

Sorption, the transfer of ions from a soluble phase to a solid phase, has been identified as an important mechanism for removal of metals in wetlands. It may result in short-term retention or long-term stabilization. Sorption describes a group of processes which includes adsorption (physisorption, that is, physical processes with weak bindings, chemisorption, that is, chemical processes with strong bindings), absorption (that is, with biochemical processes when a compound from the external media is entering into an organism) and precipitation reactions. Metals are adsorbed to particles by either ion exchange depending upon factors such as the type of element and the presence of other elements competing for adsorption sites or chemisorption. For example, retention of Pb, Cu, and Cr by adsorption has been found to be greater than Zn, Ni, and Cd (Marchand *et al*., 2010). Several factors including the pH value, initial concentration, contact time, the speciation of metal ions and surface charge affect the adsorption of metal species from aqueous solutions (Agbozu & Emoruwa, 2014; El- Sayed *et al*., 2011; Jenny, 2006; Mousa *et al*., 2013; Mustaqeem *et al*., 2014; Namatollah *et al*., 2014; Sevil & Bilge, 2007; Shahmohammadi *et al*., 2011 and Zhanming *et al*., 2009).

2.4 Kinetics of Adsorption

Adsorption can be described by adsorption isotherms. In order to study the adsorption kinetics, Langmuir and Freundlich isotherms can be used by fitting in the experimental data so as to understand the extent and degree of favourability of adsorption (Achanai, 2012b; Igwe & Abia, 2007; Marchand *et al.*, 2010; Peter, 2006). The fitness of the data can be established using a single statistical parameter R^2 (Kothari, 2011). An adsorption isotherm is an invaluable curve describing the retention or mobility of a substance from the aqueous environment to a solid phase at a constant temperature and pH. Freundlich adsorption isotherm has been widely used for determining the adsorption capacity of adsorbents (Babu & Ramakrisna, 2003).

2.4.1 The Langmuir isotherm

The Langmuir isotherm assumes that the uptake of metal ions occurs on an energetically homogenous surface by monolayer adsorption without any interaction between adsorbed ions (Igwe & Abia, 2007; Shahmohammadi *et al.*, 2011). It can be represented by the Langmuir equation,

$q = abCe/(1 + bCe)$……………………………………………………………2.1

Where,

q = mass of metal adsorbed to the substrate (mg/g),

Ce =concentration at the equilibrium (mg/l),

a =adsorption capacity maximum to the substrate (mg/g), and

b =a constant linked to the metal fixation force.

The Langmuir equation can also be represented as,

$C_e/q_e = q_m k_L C_e/1+k_L C_e$……………………………………………………………2.2

or

$C_e/q_e = 1/q_m k_L + C_e/q_m$……………………………………………………………2.3

Where,

q_e= amount adsorbed

k_L = Langmuir constant related to the energy of adsorption

q_m= maximum amount of adsorbed metal per unit mass of sorbent corresponding to complete coverage of the adsorptive sites.

The equation can also be represented as

$$\frac{Y}{M} = \frac{abCe}{1+aCe} \text{.........} 2.4$$

Where,

Y = concentration of contaminant adsorbed

M = adsorbent concentration

C = equilibrium concentration of contaminant

a = constant related to energy of adsorption

b = constant, adsorption capacity (amount of adsorbate per weight of adsorbent)

The constant, b denotes the maximum value of adsorbate (metal ion) that can be obtained at equilibrium concentrations. The other constant, a, represents the energy associated with adsorption, and increases as the strength of the adsorption bond increases (Babu & Ramakrishna, 2003). The Langmuir constant values can be determined from the linearized Langmuir graph plotted from the linear equation.

The equation can be rearranged in the linear form,

$$\frac{M}{Y} = \frac{1}{ab} X \frac{1}{C} + \frac{I}{b} \text{.........} 2.5$$

If a graph of $\frac{M}{Y}$ is plotted against $\frac{1}{C}$, then

Slope = $\frac{1}{ab}$ and

Y-intercept = $\frac{1}{b}$

2.4.2 The Freundlich isotherm

The Freundlich equation is an empirical equation based on adsorption on an energetically heterogeneous surface. The equation is represented as;

$q_e = KCe^{(1/n)}$ ……………………………………………………………………2.6

Where,

q = adsorption capacity (metal concentration on adsorbing material, mg/g),

K = constant linked to adsorption capacity,

Ce = equilibrium concentration of the contaminant and

n = empirical parameter linked to sorption intensity, where high 1/n show preference for sorption of the metal while high K imply greater adsorption tendency towards the adsorbent (Agbozu & Emoruwa, 2014; Shahmohammadi *et al.*, 2011; Peter, 2006).

The Freundlich equation can also be represented as

$\frac{x}{m} = KC^{1/n}$ ……………………………………………………………………2.7

Where,

x = mass of adsorbate

m = mass of adsorbent

C = equilibrium concentration of adsorbate

n = constant, degree of favourability of adsorption

K = constant, adsorption capacity

The equation can be arranged to a linear form;

$\text{Log}\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log C$ ……………………………………………………………2.8

A plot of log x/m against log C gives a straight line where

Slope = $\frac{1}{n}$

Y intercept = log K

A smaller 1/n indicates stronger bond between adsorbate and adsorbent, while higher K indicates the rate of adsorbate removal is high or adsorbate adsorbed increases with K. It has been reported in literature that the value of n that is in the range of 1 to 10 indicates favourable adsorption, where, for majority of adsorbents, n lies in the range of 0.9 to 10 (Agbozu & Emoruwa, 2014; Shahmohammadi *et al.*, 2011; Peter, 2006). Freundlich and Langmuir models have been used to determine maximum metal immobilization and their retention capacity over time.

2.5 Mechanism of adsorption of metal ions unto adsorbents

Rate of adsorption depends on reactants remaining

$\mathrm{Rate} \propto [\mathrm{reactant}]^{\mathrm{p}}$

Where p is the number which states how rate depends on the $[reactant]$ and is the order of reaction. Thus,

$\mathrm{Rate} = \mathrm{k}[\mathrm{reactant}]^{\mathrm{p}}$ where

k = rate constant/ constant of proportionality

When p = 0 (zero order)

p = 1 (first order)

p = 2 (second order)

The rate constant k has been found to be significant compared to rate because the rate constant k is a constant at a given temperature and is independent of concentration (Margaret, 2004). Also, if the rate constant and order are known then it is easy to calculate the rate for any reaction (Skoog *et al.*, 2004). Several methods can be used to determine the rate, rate constant and order of reaction. Some of these include:

i. Log/log graphical procedure, where ; log rate = log k + plog$[reactant]$where a plot of log rate against log [reactant] gives p = slope and log k = intercept

ii. A systematic numerical procedure, where:

$$\frac{\text{rate in experiment 2}}{\text{rate in experiment 1}} = \frac{\text{K 2}}{\text{K1}}\frac{[\text{concentration in experiment 2}]}{[\text{concentration in experiment 1}]}$$

Ratio of rates = (rations of concentration)^{p} or log (ratio of rates) = plog (ration of concentrations).

iii. Integrated rate expressions

The rate of reaction is the negative of the gradient of the tangent to the curve [reactant] versus time. For first order, rate = k [A] and $\frac{dA}{dt}$ = k[A], while for the second order, rate = k$[A]^{p}$ or -$\frac{dA}{dt}$ = k$[A]^{2}$

Linear plots are drawn upon differentiation which gives linear equations.

2.5.1 Pseudo first-order and pseudo second-order kinetic models

Some kinetic models such as pseudo-first order, pseudo-second order, Elovich equation, parabolic diffusion and intra-particle diffusion model have successfully been used to investigate the mechanism of adsorption of metal ions unto adsorbents (Alkpokpodion *et al*., 2010; Ho *et al.* 2000; Ho, 2006; Ungarish *et al*., 1998). In these models, linear regressions are used to determine the best fitting kinetic models, where, the most commonly used method is the coefficient of determination R^2, since a kinetic model is concerned with the effect of observable parameters on the overall rate (Ho, 2006). The best fitting kinetic model for the adsorption of metal ions by the adsorbent is the one with the highest coefficient of determination that is, the kinetic model with R^2values closest to unity is taken as the most appropriate mechanism of sorption (Alkpokpodion *et al*., 2010).

The influence of initial concentration on the rate of reaction can be described by the rate of biosorption, where, the rate equation gives an expression of the variation in concentration with time. The order of reaction can be deduced from the integrated rate equation by appropriate plot to give a linearized plot. A reaction can either be pseudo first order or pseudo second order. The first order rate equation for metal adsorption on the adsorbent is;

$\log q_t = -K_1 t/2.303 + \log q_o$……………………………………………………………2.9

where, q_t = equilibrium concentration at time t, q_o = initial concentration at time t = 0 and k_1 is the first order rate constant. A plot of log q_t versus t gives a straight line where k_1 and q_o can be determined.

For the second order kinetics, the following equation can be used:

$1/q_t - 1/q_o = k_2 t$ ……………………………………………………………………2.10

or,

$1/q_t = k_2 t + 1/q_o$ …………………………………………………………………2.11

Where, q_t = equilibrium concentration at time t, q_o = initial concentration at time t = 0 and k_2 is the second order rate constant. A plot of $1/q_t$ versus t gives a straight line where k_2 and q_o can be determined. In this study, the kinetic modeling of the four metal ions adsorption mechanism was also compared using pseudo – first and second order kinetic models and results recorded in tables.

2.5.2 The intra- particle diffusion model

The intra-particle diffusion model expressed as: $r = K_{id}(t)^y$ (Alkpokpodion *et al.*, 2010), where, a linearised form of the equation is followed by:

$$\text{Log } r = \log K_{id} + y \log (t) \qquad \text{……} 2.12$$

Where,

r = the percent metal ion adsorbed

t = contact time

y = the intraparticle diffusion rate constant

K_{id} = the rate factor or percent metal ion adsorbed per unit time

If the mechanism of adsorption fits the inter-particle diffusion model, then, a plot of log r against log (t) will yield a straight line, where, the

Slope = y

Intercept = log K_{id}

Higher values of K_{id} illustrate enhancement in the rate of adsorption and better adsorption mechanism which is related to an improved bonding between sorbate and adsorbent particles. If R^2 (coefficient of determination) is high in addition to the linear curve, then it implies that, the initial concentration of the metal ion could be a factor that determine the pattern of intra- particle diffusion mechanism (Kothari, 2011; Skoog *et al.*, 2004; Ungarish *et al.*, 1998). In this work, the intra- particle diffusion constants of the metal ions were determined at different initial concentrations both when single and when mixed and recorded.

2.6 The arrowroots as bioadsorbents

Arrowroot is a common name of tropical plants whose botanical name is *maranta arundinacea L.* and family name is *marantaceae* (Nishaa *et al.*, 2013). The plant grow well in deep, well drained, slightly acidic soils and a hot humid climate. Harvesting involves breaking off the rhizome from the shoot. Planting and harvesting are interchanged in that when the rhizomes are harvested, the shoot is replanted at the same time.

The rhizome of maranta arundinacea possess various chemical components such as alkaloids, carbohydrates, cardiac glycosides, proteins, amino acids, phenolic compounds, terpenolds, saponins, flavones and gum. These are bioactive constituents of the plant (Shintu *et al*., 2015). Terpenoids and alkoloids are secondary metabolites and are important for plant defence mechanism. Flavonoids, triterpenoids and tannins are known for their hepatoprotective activities (Anderson & Chase, 2001). According to Elvren (2010), arrowroots contain phenolic phytochemicals such as salicyclic acid that protect the plant cells from environmental hazards such as pollution, stress, drought, uv exposure and pathogenic attack.

The flavonoids and other plant phenolics are reported in addition to their free radical scavenging activity, to have multiple biological activities, including vasodilatory, anticarcinogenic, anti-inflammatory, ant-bacterial, immune- stimulating, antiallergic, antiviral and estrogenic effects (Anderson & Chase, 2001 ; Pradeepkumar *et al*., 2008). Arrowroot tubers contain 23% starch, where amylose and amylopectin are the major fractions (Ghosh and Ray, 2011). Being polysaccaride materials, arrowroots are considered to have polysaccaride slimelayers and readily provide amino, carboxyl, phosphate and sulphate functional groups for biosorption (Pradeepkumar *et al*., 2008). Since phenolics mainly comprise of flavonoids, phenolic acids and polyphenols, then arrowroots also contain hydroxyl (-OH) class of chemical compunds that provide hydroxyl functional groups for biosorption. The polysaccarides can also be complexed with proteins, lipids and pigments. Studies show that the presence of phosphate and glucouronic acid and chitin- chitosan complex in arrowroots also assist in binding of the metals through ion exchange and coordination (Anderson & Chase, 2001).

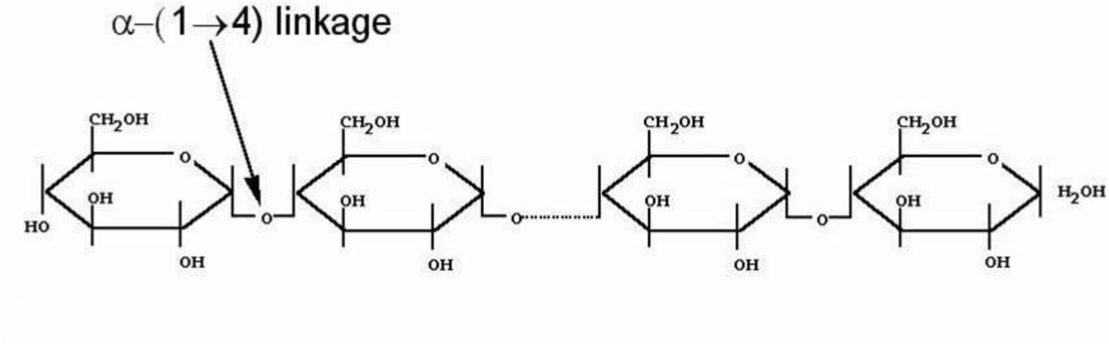

Figure 2.1 : Structure of amylose molecule

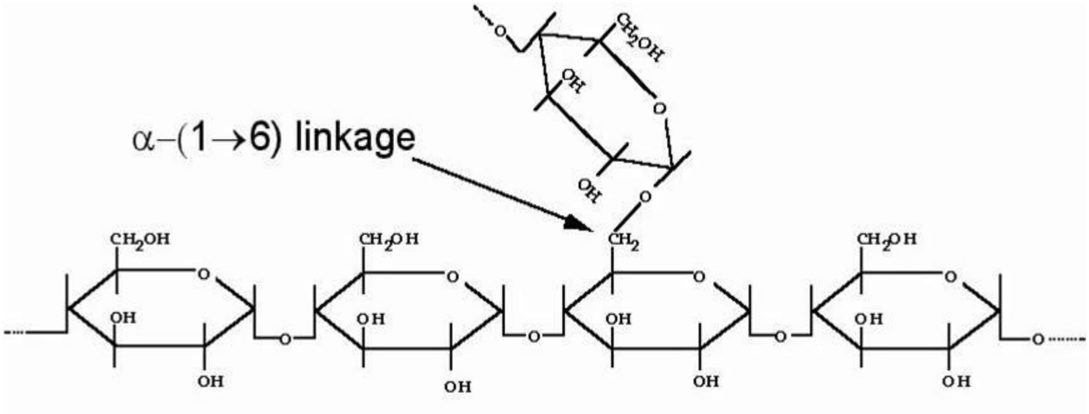

Figure 2.2 : Structure of amylopectin molecule

Studies done by Nohinee *et al*. (2010) show that the enhancement of the solubility of iron (III) in aqueous solutions can be achieved by complexing it with polysaccharides from locally available starch such as cassava and arrowroots. It was established that the polysaccharides prevent the hydrolysis and precipitation of the iron (III) as iron-oxide and hence providing the alternative treatment for iron deficiency anaemia. The cassava and arrowroot starch are able to stabilize iron (III) and hence enhance its solubility in the aqueous solution by providing multiple hydroxyl groups to bind to the surface of iron oxyhydroxide to prevent further hydrolysis and precipitation.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials and reagents

The sampling bottles and glassware were cleaned according to the recommended methods (APHA, 2002). The arrowroots were used as biosorbent for the biosorption of the metal ions from river water at different concentrations. Roots of arrowroots were collected from the western region of Kenya and washed several times with tap then distilled water to remove impurities and salts. The biomass was sun-dried and then oven dried at 60 °C for 48 hours. The dried arrowroots were cut into small pieces, ground using a pestle and mortar and subsequently sieved and the particles with an average size of 1.0 mm were used for biosorption. Raw arrowroots and municipal wastewater were also used.

3.1.1 Chemicals

All the chemicals used in this work were of analytical grade. In addition to the common laboratory chemicals, the following were also used.

- Endo agar media
- Potassium dichromate
- Silver sulphate
- Sulphuric acid
- Ammonium molybdate
- Stannous chloride
- Potassium antimonyl tartrate
- Mercury sulphate
- BOD nutrient buffer pillow

- Deionised water
- Sodium hydroxide
- Zinc nitrate
- Copper nitrate
- Iron (II) sulphate
- Manganese sulphate
- Calcium and magnesium indicator
- EDTA reagent
- Barium sulphate
- Sodium periodate
- Cyclohexane
- Bicinchoninate

3.1.2 Instruments and apparatus

- HACN DR 4000 spectrophotometer
- COD reactor
- Ice boxes
- BOD track sample bottles
- Thermostat
- Incubator
- Sample cells
- Sample bottles
- pH meter model sension- 51935
- Conductivity meter
- Pocket turbid meter
- Volumetric flasks

- Magnetic stirrer and stirring bars
- Nessler tubes
- Measuring cylinders
- Beakers

3.2 Summary of the experimental work

Water was sampled from the river and levels of pollutants determined. Physical-chemical parameters like conductivity, pH, turbidity, total hardness, chemical oxygen demand, biological oxygen demand were analysed. Sulphates, nitrates, fluoride and phosphates were also determined. Metals analysed in this study were copper, zinc, iron and manganese. Faecal coliforms were also analysed. Laboratory model experiments were then set up where the initial concentrations of the river water were then varied and effect of contact time, concentration and pH analysed with dry roots of the arrowroots. This was done in order to establish the adsorption behaviour of the arrowroots. The level of the pollutants was initially determined at 0 minutes and then after at a selected time interval after introducing the arrowroots. Effect of pH on metal ion adsorption by the arrowroots was also determined. The level of the pollutants was varied to establish the tolerance levels of the arrowroots in these pollutants. Adsorption can be described by adsorption isotherms. In order to study the adsorption kinetics, Langmuir and Freundlich isotherms, Pseudo first and second order kinetic models and inter-particle diffusion models were used by fitting in the experimental data so as to understand the extent and degree of favourability of adsorption (Achanai, 2012b;Igwe & Abia, 2007; Marchand *et al*., 2010; Peter, 2006).

The kinetic study of the rate of metal ion absorption in relation to the initial concentration was then studied. The absorption curves were applied to both the

Freundlich, Langmuir, Pseudo first and second order kinetics and inter-particle diffusion equations to give the coefficients for the linearised form of the isotherm models for the absorption of the heavy metals by the arrowroots. The adequacy or inadequacy of the isotherm models were used to explain the absorption process of the arrowroots. The correlation coefficient R^2 was used to determine whether the adsorption of the heavy metals by arrowroots fits an isotherm model (Kothari, 2011). Thus the correlation factor R^2 was critically compared.

In order to determine whether arrowroots can tolerate high levels of the pollutants under natural set up and whether they are indeed of significance, live arrowroots and raw waste water were used. Pollutant removal efficiency levels from wastewater using arrowroots was carried out by setting up a model constructed wetland where arrowroots were planted in raw influent of wastewater obtained at a wastewater treatment plant at a quarry in Eldoret and concentration levels of both influent and effluent determined. Pollutant removal efficiency of both treated (with arrowroots) and untreated wastewater (without arrowroots) was compared by using the relative treatment efficiency index (RTEI) technique as suggested by Marchand *et al*. (2010). The effluent composition of the planted and the unplanted treated wastewater were also compared.

3.3 Sampling

Figure 3.1 shows the stations along the Malakisi River where samples were collected throughout the study.

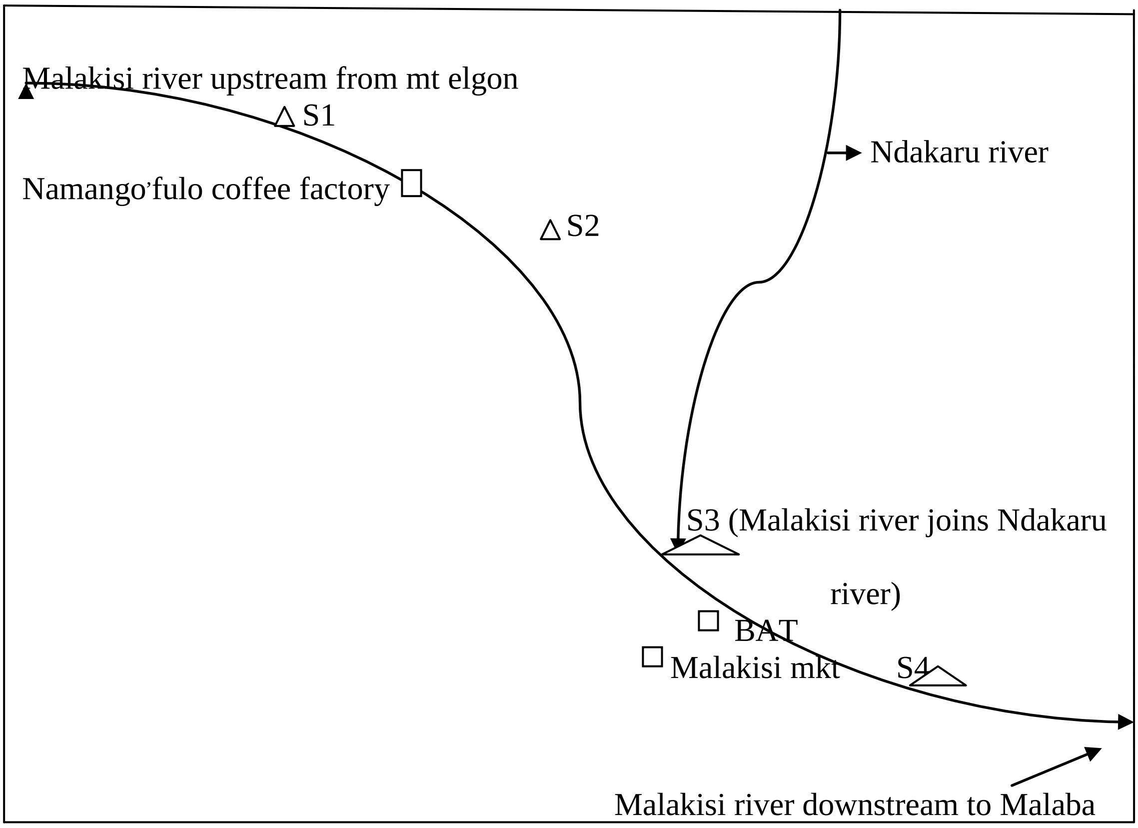

Figure 3.1: Sampling stations along the Malakisi River

In Figure 3.1, four sampling stations were selected starting from the farthest upstream in Mount Elgon to the lowest downstream to Malaba at intervals of 4 km a part. The stations were designated S1, S2, S3 and S4. The isokinetic sampling technique was used to ensure that the velocity of the sample river was equal to the velocity of the water being sampled in order to ensure that samples obtained had identical constituent concentrations. The contact time with water was minimised by making the length of the sampling line as short as possible to ensure a high linear velocity through them. Each unit of the river discharge was equally represented in the sample by dividing the river cross section into intervals of equal width (EWI). A total of thirty water samples were collected from each sampling station during dry and wet seasons respectively for six months. The dry season comprised of; January, February and March whereas the wet season comprised of; April, May and June. Sampling was done twice per month. The samples were transported to the laboratory in ice boxes containing ice to maintain a temperature range of-20^{O}C to -10^{O}C and were analysed within 48 hours of sampling. Samples for Coliform analysis were collected in sterilized plastic containers which had been carefully washed and rinsed with deionized water and sterilized using an autoclave at 121^{O}C for 15 minutes and were analysed within six hours after sampling. All samples were analysed at the Eldoret Water and Sanitation Company (ELDOWAS).

3.4 Determination of the level of pollutants in Malakisi river

3.4.1 Determination of coliforms

A 100 ml of sample was filtered using a 0.45µm filter paper. A 1.66 g of endo agar media placed in 40 ml of the sample was heated to boil and then autoclaved for 15 minutes. A 10 ml of the sample was then placed in sterilized petri dishes and left to solidify. The prepared culture were placed in an incubator upside down and set at 44^{o}C for faecal Coliform and 37 ^{O}C for total Coliform and then left for 24 hours in the thermostat (APHA, 2002; WHO, 2003).

3.4.2 Determination of chemical oxygen demand

The COD in the samples was determined using the standard method (APHA, 2002). The low range reagent mixture of $K_2Cr_2O_7$, $AgSO_4$, $HgSO_4$ and concentrated H_2SO_4 were used. A 2 ml of each sample was pipetted and each homogenously mixed with the reagent and placed in a COD reactor at a temperature of 150^{O}C and left for 2 hours. The results were recorded in mg/l.

3.4.3 Determination of biological oxygen demand

The BOD Track test procedure was used to test for BOD in the samples (APHA, 2002). The sample was heated to 20^{o}C of its incubation temperature (20^{O}C, 68F) and 420 ml was measured and poured into a BOD track sample bottle. A 3.8 cm (11/2 inch) magnetic stir bar was placed in each sample where the contents of one BOD nutrient buffer pillow was added to each sample bottle for optimum bacterial growth. The bottles were stoppered carefully and placed on the chassis of the BOD track which was appropriately connected to the sample bottle and the cup firmly tightened and placed in the incubator at a temperature of 20^{O}C for the BOD test. A 0-35 mgl-1 range was selected and the results in mgl^{-1}were read after 5 days.

3.4.4 Determination of fluoride

Fluoride was analysed using the SPADNS method at a wavelength of 580 nm using HACN DR 4000 spectrophotometer (HACN DR 4000 spectrophotometer operating Manual).A 10 ml of the sample was pipetted into a dry sample cell. A 10 ml of the deionized water was also pipetted and placed into the second dry sample cell and labeled as the blank. The sample and the deionised water were maintained at the same temperature. A 2 ml of SPADNS reagent was carefully measured and added into 10 ml of the sample in each sample cell and the mixture swirled to mix and fluoride measured in mg/l (HACN DR 4000 spectrophotometer operating manual).

3.4.5 Determination of phosphates

Phosphate analysis was achieved using the spectrophotometer at wavelength of 880 nm. A 10 ml of each sample was measured. The phosphate was measured through phosphorous as an orthophosphate. Phosver 3 reagent (a mixture of ammonium molybdate, stannous chloride and ascorbic acid in the required amounts) was added to each sample where blue colour indicated presence of the phosphate after 2-3 minutes.

The blue colour developed was measured within 10-12 minutes after development of the colour using the blank. The blank was distilled water which was prepared in the same way as the sample. Phosphate levels were recorded in mg/l (WHO, 2004; APHA, 2000).

3.4.6 Determination of total hardness

Total hardness was determined using the colorimetric method at a wavelength of 522 nm. The pH adjusted to between 3 and 8 with 5.0 N sodium hydroxide standard solution before analysis. A 100 ml of the sample was measured and 1.0 ml of calcium and magnesium indicator added. A 25 ml solution of each of the sample was measured and each poured into three sample cells. One drop of 1M EDTA solution was added to one cell which was used as the blank and another drop of EDTA was added to the prepared sample and total hardness determined in mg/l (APHA, 2002; HACN DR 4000 spectrophotometer operating manual).

3.4.7 Determination of Nitrates

Total nitrogen was determined by Hach spectrophotometer DR/4000 at wavelength of 400nm. A 10 ml of the sample and the blank were measured and carefully mixed. Nitraver 5 reagent (a mixture of phenol disulphonic acid reagent, ammonium hydroxide, EDTA, aluminium hydroxide and potassium manganese VII) was then added to each sample and the mixture shaken well for 1 minute using a vortex shaker. The sample cell was wiped dry and left to stand for 5 minutes before putting it in the spectrophotometer. The blank was first analysed and then instrument set at zero followed by the samples. Nitrate levels were recorded in mg/g.

3.4.8 Determination of pH

The pH was determined by potentiometric method, using digital pH meter model sension-51935. Calibration of the electrode was done with 2 buffer solutions of pH 4 and 7 prior to its use. A pH 4 buffer solution was prepared by dissolving 10.12g potassium hydrogen phthalate in distilled water and diluted to 1L. A pH 7 buffer solution was prepared by dissolving 1.361g anhydrous potassium dihydrogen phosphate and 1.42g anhydrous disodium hydrogen phosphate which had been dried at 110^{o}C and diluted to 1L with boiled distilled water. Before use, the electrodes were removed from storage solution and rinsed with distilled water. The electrodes were dried by gently blotting with a soft tissue. The instrument was standardized with electrodes immersed in a buffer solution of 4. The electrodes were removed from the buffer, rinsed thoroughly with distilled water, blot dried and then immersed in the second buffer of pH 7, where the pH reading was within 0.1 pH unit of the second buffer. The results were recorded to the nearest plus or minus 0.1 pH unit (APHA, 2005).

3.4.9 Measurement of Conductivity

The digital conductivity meter model 1152 by Emcee electronics was used. The probe was rinsed with deionized or distilled water before use to remove any Impurities adhering to the probe body and then Shaken to dry. To avoid contamination or dilution of the sample, the probe was rinsed with a small volume of the sample. The conductivity meter was turned on. The probe was then dipped into the sample. After stabilization, the reading on the display was noted. The conductivity measurements were done in triplicate. When dipping the probe into the sample, care was taken to ensure that the liquid level was above the upper steel band. The sample was gently stirred with the probe to create a homogenous sample. The conductivity measurement was recorded in micro Siemens.

3.4.10 Measurement of Turbidity

A 5 ml of sample was poured into the Hach 1720E low range Pocket Turbid meter sample cell and then capped. The outside surface of the cell was wiped with the oiling cloth to remove any liquid where care was taken not to scratch the cell. The READ key was pressed until the reading stabilized (approximately 5sec.) and then released and displayed reading recorded. Turbidity measurements were recorded in nephelometric turbidity units in triplicate.

3.4.11 Determination of Sulphates

Sulphates was analysed using a Hach spectrophotometer DR/4000 at wavelength of 450 nm. A 25 ml of the sample was measured and placed in one cell. Another cell was the blank with the same volume of the sample. The content of one sulfaver 4 ($BaCl_4$) reagent pillow was added to the sample cell and swirled to mix for five minutes after which the blank was placed in the cell holder, the light shield closed and soft key under zero was pressed. The prepared sample was then put into the cell holder and results in mg/l sulfate displayed. For proof of accuracy, the calibration standards containing 10, 20, 30, 40, 50, 60, and 70 mg/l of SO_4^{2-} were prepared from the 1000 mg/l of anhydrous sodium sulphate standard solution by pipetting 1, 2, 3, 4, 5, 6, and 7 ml into 100 ml volumetric flask and diluting to the mark with deionized water and a calibration curve generated from the standards (APHA, 2002).

3.4.12 Determination of levels of metal ions in river and waste water

Levels of Zn^{2+}, Cu^{2+}, Mn^{2+} and Fe^{2+} in river and waste water were determined using UV visible Hach DR/4000 spectrophotometer. The method was preferred to other analytical methods because of the many intensity coloured complexes known and the degree of selectivity introduced by proper choice of organic reagents and masking reactions or by solvent extraction. The method is moderate to high selectivity since a wavelength can be found at which the analyte alone absorbs, thus making preliminary separations unnecessary. Where overlapping absorption bands do occur, corrections based on additional measurements at other wavelengths hence eliminating the need for a separation step.

It also has a good accuracy with relative errors ranging from 1% to 5% and with special precautions; the errors are decreased to a few tenths of a percent. The method is also easy and convenient since spectrophotometric and photometric measurements are readily available, easily and rapidly performed with modern instruments which are automated such as Hach DR 4000 spectrophotometer. The method also has a high sensitivity with detection limits ranging from 10-4 to 10-5M and 10-7M with procedural modification (Gary, 2004). It has a wide applicability since enormous numbers of organic, inorganic and biochemical species absorb ultraviolet or visible radiation and are thus amenable to direct quantitative determination. Many non absorbing species can also be determined after chemical conversion to absorbing derivatives. The metals analysed were transition elements which are good at forming complexes since they have small highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by other groups or ligands.

3.4.12.1 Determination of Mn^{2+} levels

The concentration of Mn was determined by the periodate oxidation method using Hach DR 4000 spectrophotometer at a wavelength of 525 nm (Hach DR 4000 operating manual). The cell was filled with 10 ml of the sample and the contents of one buffer powder pillow, citrate type for manganese added, followed by sodium periodate and swirled to mix for 2 minutes. Another sample cell was filled with 10 ml of the sample which acted as a blank. After 2 minutes, the blank was placed in the cell holder, light shield closed and instrument set to zero. The prepared sample was then placed in the cell holder and results in mg/l Mn displayed. Samples were adjusted to pH 4-5 with 5.0N sodium hydroxide before analysis. A manganese calibration curve was also performed using the periodate oxidation method. A 100 mg/l Mn stock solution was prepared by pipetting 10 ml of 1000 mg/l manganese standard solution into a 100 ml volumetric flask and diluted to the mark with deionized water and then mixed thoroughly. Calibration standards containing 2, 4, 8, 12, 16, and 20 mg/l Mn were prepared by pipetting 2, 4, 8, 12, 16 and 20 ml of the 100 mg/l Mn stock solution into 100 ml volumetric flaks and diluting to the mark with deionized water. Using periodate oxidation method, a calibration curve was generated for the standards.

The manganese in the sample was oxidized to the purple permanganate by sodium periodate, after buffering the sample with citrate. The purple colour was directly proportional to the manganese concentration.

3.4.12.2 Determination of Zn^{2+} levels

Zinc was analysed using the zincon method at a wavelength of 620 nm. A 25 ml graduated mixing cylinder was filled with 20 ml of the sample and the contents of one zincover 5 reagent powder pillow (2- carboxyl-2- hydroxyl-5-sulfoformazyl benzene and cyanide) added to the cylinder, stoppered and inverted several times to dissolve the powder completely. 10 ml of this sample was placed into another sample cell and used as a blank. 0.5 ml of cyclohexanone was added to the remaining solution in the graduated mixing cylinder using a plastic dropper since rubber bulbs on glass droppers contaminates the cyclohexanone. The cylinder was stoppered and shaken vigorously for 30 seconds. This was the prepared sample. The soft key under the start timer was pressed for a 3 minutes reaction period. During this reaction period, the solution from the cylinder was poured into the sample cell (the prepared sample). After 3 minutes, the blank was placed in the cell holder and light shield closed and zero soft key pressed. The prepared sample was then placed in the cell holder and light shield closed and results in mg/l zinc displayed.

Before analysis, the pH was adjusted to 4-5, with 5.0 sodium hydroxide to prevent oxidation of zinc above pH 5. Zinc calibration was performed using the zincon method by preparing calibration standards containing 0.2, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mg/l zinc. A 10 mg/l zinc stock solution working standard was prepared. A 10 ml of a 1000 mg/l zinc standard solution was pipetted into a 1 litre volumetric flask and diluted to the mark with deionized water, stoppered and inverted several times to mix. A 2, 5, 10, 15, 20, 25 and 30 ml of the 10 mg/l zinc stock working standards were pipetted into seven different 100 ml volumetric flasks respectively and diluted to the mark with deionized water, stoppered and inverted several times to mix. Using the zincon method, a calibration curve was generated from the prepared standards.

Zinc and other metals in the sample are complexed with cyanide. Adding cyclohexanone causes a selective release of zinc. The zinc then reacts with 2-carboxyl-2- hydroxyl-5-sulfoformazyl benzene (zincon) indicator to form a blue coloured species. The intensity of the blue colour is proportional to the amount of zinc present.

3.4.12.3 Determination of Cu^{2+} levels

The levels of Cu^{2+} were determined using bicinchoninate method. The sample cell was first filled with 10 ml of the filtered sample whose pH had been adjusted to 4-6 with 8N KOH, and One Cuver 1 copper reagent powder pillow (bicinchoninate reagent) added and swirled for 2 minutes. After which, the blank which was copper-free deionized water was put into the cell holder and set at zero. The prepared sample was then placed in the cell holder, light shield closed and results recorded in mg/l copper at a. wavelength of 560 nm (Hach DR/4000 spectrophotometer operating manual).

To prepare a copper calibration using the bicinchoninate method, a 40 mg/l copper stock solution was prepared by pipetting a 4.0 ml of a 1000 mg/l copper standard solution into a 100 ml volumetric flask and diluted to the mark with deionized water. Calibration standards containing 0.4, 0.8, 1.6, 2.4, 3.2, 4.0, and 4.8 mg/l Cu were prepared by pipetting 1, 2, 4, 6, 8, 10, and 12 ml of 40 mg/l Cu stock solution into different 100 ml volumetric flasks and calibration curve generated from the standards.

3.4.12.4 Determination of Fe^{2+} levels

The concentration of Fe was determined by ferrover method and levels analysed using a Hach DR 4000 spectrophotometer at a wavelength of 510 nm (Hach DR 4000 operating manual). A clean sample cell was filled with 10 ml of the sample and the contents of one ferrover iron reagent powder pillow added and swirled to mix for 3 minutes. Another sample cell was filled with the blank which was 10 ml of the sample. After 3 minutes, the blank was placed into the cell holder and light shield closed and instrument adjusted to zero. The prepared sample was then placed in the cell holder and results in mg/l iron displayed. The ferrover iron reagent was used to convert all soluble iron and most insoluble forms of iron to soluble ferrous iron, which reacted with 1, 10 phenanthroline indicator in the reagent to form an orange colour proportion to the iron concentration.

For proof of accuracy, 1.0 mg/l iron standard was used. Calibration standards containing 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, and 2.8 mg/l were prepared by pipetting 1, 2, 3, 4, 5, 6, and 7 ml of 40 mg/l iron stock solution into a 100 ml volumetric flask and diluted to the mark using deionized water and calibration curve generated using the ferrover procedure.

3.5 Model experiments using dry Arrowroots

The rhizomes of the mature arrowroots were harvested and shoots replanted in distilled water for two months to allow regrowth of the roots and the leaves where the roots were selectively cut, washed several times with tap and distilled water to remove salt and other impurities. The roots were sun-dried and then dried in an oven at 80^oC for two hours. The dried arrowroot biomass was cut into small pieces, ground using a pestle and a mortar and subsequently sieved to particle average size of approximately 1.0 mm which was then used for biosorption. A 0.3 g of the arrowroot biomass was used with river water, while 0.5 g was used with model solutions during batch experiments which had higher concentrations of the metal ions compared to river water.

The samples were collected at four sampling stations (figure 3.1) in acid-cleaned plastic containers, filtered and 2 ml concentrated nitric acid added per litre and the preserved samples stored at room temperature. These were later used for adsorption studies with arrowroots. The samples were mixed and metal concentration levels determined respectively using DR 4000 UV visible spectrophotometer, followed by adsorption experiments using arrowroots at the established initial metal ion concentrations and effect of pH and contact time on maximum metal ion bioadsorption by the arrowroots determined in triplicate respectively, in order to establish the optimum pH and optimum time for maximum biosorption of the heavy metals by the arrowroots. The concentration of each metal ion adsorbed, the adsorbent concentration and equilibrium concentration obtained after every 10 minutes and at a constant pH were subjected to Langmuir and Freundlich isotherm equations and the favourability of the adsorption process described for each metal.

Model solutions of different metal ion concentrations at the established constant optimum pH were then prepared and effect of concentration of metal ions both when single and when mixed on biosorption capacity of arrowroots was investigated at a selected time interval.

3.5.1 Effect of pH and contact time on biosorption efficiency of arrowroots of metal ions from river water

To the contents in each plastic bottle and at a particular pH, 0.3 g of arrowroot per 100 ml river water was added followed by periodic shaking and allowed to settle before taking heavy metal measurements. pH was adjusted at intervals of 1, between 2.5 to 9.5 and residual metal ion concentrations measured. The percentage reduction of the metal concentrations was calculated. One set of measurement was taken for water without arrowroots and another with arrowroot added. Percent absorption was calculated by evaluating changes in concentrations at various times with respect to changes based on maximum biosorption, using the expression;

$$R = \frac{Co - Ct}{Co} \qquad \text{3.1}$$

Where,

R = biosorption efficiency (%).

Co = original concentration and

Ct = concentration at time t.

The arrowroot biomass metal ion uptake capacities after different experiments were calculated from the initial metal cation concentration in water according to the following equation

$$Q = \frac{(Ci - Cf)}{S} \qquad \text{3.2}$$

Where,

Q = metal uptake capacity (mg/g dry arrowroot)

S = dry weight of arrowroot sample (g)

C_f =final metal cation concentration in the solution, after the absorption test

C_i = initial metal ion concentration in the solution, before the adsorption test

V = volume of the sample used

Langmuir and Freundlich adsorption models were adopted to describe the adsorption isotherms. Langmuir adsorption isotherm equation 2.5 was used with river water and Langmuir equation 2.3 used for mixed model solutions during laboratory batch experiments. Freundlich adsorption isotherm equation 2.8 was applied both with river water and model solutions containing different concentrations of the metal ions during laboratory batch experiments.

3.6 Laboratory experiment (Batch experiment)

In order to evaluate the ability of dry arrowroots corresponding with the removal of dissolved heavy metals from wastewater or industrial effluents; a batch experiment was conducted. A number of model solutions at pH of 5.5 were set up.

1. A model solution of 25 ppm (to represent high concentration) containing Cu^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{2+} ions was prepared in different containers and 0.5 g arrowroot was added for every 100 ml solution, the contents stirred and concentration of each metal ion monitored at intervals of ten minutes.
2. A model solution of 25 ppm that contained Cu^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{2+} ions in the same container was prepared; 0.5 g arrowroots was placed in for every 100 ml solution and change in concentration levels of each metal ion was monitored.
3. A model solution of 5 ppm (to represent low concentration) each containing Cu^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{2+} ions separately was prepared in different containers and dry arrowroot was placed in for every 100 ml solution, and concentration of each metal ion monitored at the intervals of ten minutes.
4. A model solution of 5 ppm that contained Cu^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{2+} ions in the same container was prepared; 0.5 g of dry arrowroot placed in for every 100 ml solution and change in concentration levels of each metal ion was monitored at intervals of ten minutes.

Metal concentrations were measured by UV visible spectrophotometer; Hach DR/4000 at their respective wavelengths and experimental procedures 3.4.12.1 – 3.4.12.4 for each metal ion strictly followed in order to avoid interferences. The molar absorptivity coefficient of each metal ion was also considered at each measurement to cater for any interference due to bands overlap.

3.6.1 Preparation of model solutions containing heavy metal ions.

A stock solution of 1000 ppm containing Zn^{2+}, Cu^{2+}, Fe^{2+}, and Mn^{2+} ions was prepared by from their respective salts. The stock solution was prepared by dissolving 2.3217g, 1.9005g, 2.4882g, and 1.5968g of $Zn(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $FeSO_4.7H_2O$ and $MnSO_4.H_2O$ respectively in 500 ml volumetric flask and solution made to the mark. The masses were calculated basing on the formula; $\text{mass(g)} = \frac{\text{M.wt}}{\text{At.wt}} \times \frac{100}{\%\ \text{purity}} \times \frac{\text{V}}{1000} \times \frac{\text{C}}{1000}$ where,

M.wt = molecular weight of the compound

At.wt = atomic weight of the element to be determined

V = volume to be prepared (depends on the volumetric flask to be used)

C = expected concentration to be prepared in ppm

Using the relationship $C_1V_1 = C_2 V_2$ 25 ppm and 5 ppm for both single and mixed metal ions was prepared as follows; for 25 ppm single metal ions of each metal ion, 2.5 ml of stock solution was made to 100 ml in volumetric flask and transferred to 100 ml beaker prior to introduction of the arrowroots. For 25 ppm mixed metal ions, 2.5 ml of each stock solution of each metal ion was put in 100 ml container and the total solution made to 100 ml, for the mixed metal ions; five replicates was prepared so that each heavy metal could be determined at a time. To evaluate efficiency of biosorption at low concentration, 5 ppm was prepared that contained the metal ions singly and when they are mixed. For single metal ions 0.5 ml of 1000 ppm of each solution was diluted to 100ml in separate beakers. For mixed metal ions, 0.5 ml from 100 ml solution of each metal ion solution was put in the same container and the solution diluted to 100ml; five replicates was prepared so that each heavy metal was determined at a time.

3.7 Pollutant removal efficiency levels from municipal wastewater using live arrowroots

Pollutant removal efficiency levels from wastewater using live arrowroots was carried out by setting up a model constructed wetland where arrowroots were planted in raw influent and effluent of wastewater obtained at a waste water treatment plant at a quarry in Eldoret. Twenty litre buckets were modified so as to be used in the experiment. The buckets were fitted with a valve socket which was plugged from inside, a few centimeters from the bottom and the steel cap was used to close the socket. 10 arrowroot plants were planted in six buckets, three containing 10 litres of the influent and the other three, 10 litres of the effluent. Two controls of the influent and effluent with no arrowroots planted were also set up. The models were then set up under a roof to avoid dilution. The concentration levels of both influent and effluent determined after a retention time of 7 days and loading of both influent and effluent done again. Pollutant removal efficiency of both treated and untreated wastewater was compared by using the RTEI (relative treatment efficiency index) technique as suggested by Marchand *et al* (2010) in addition to statistical parameter, paired t- test at 5 percent significant level.

For RTEI, the efficiency of the metal removal with or without arrowroot plants and the differences in retention times, were derived from the differences in metal removal between the influent and effluent for the treatment (T %) with arrowroots and compared with the control (C %), which was wastewater without the arrowroots. Since treatment in the presence of arrowroots plants compared to unplanted control may increase metal removal, thus providing benefits (where benefits were defined as Δta, where, 0% <Δt_a<100%) but could also be a source of disadvantage by decreasing the retention time because of the displacement of the volume by the biomass (where disadvantages were defined as Δt_b where $0 < \Delta t_b < C$). The assumption was that both phenomena were independent and have additive and antagonistic effects on metal removal. Hence, $T = C + \Delta t_a - \Delta t_b$ and the final removal rate of the system was assigned the actual value Δt_{ab} so that $\Delta t_{ab} = \Delta t_a - \Delta t_b$. Since this was relative and non – dimensional, then a RTEI was used. Where $\mathrm{RTEI} = \frac{\Delta \mathrm{ta} + (-\Delta \mathrm{tb})}{((\Delta \mathrm{ta} + \mathrm{C}) + -(\Delta \mathrm{tb} + \mathrm{C}))}$ or $\mathrm{RTEI} = \frac{\Delta \mathrm{tab}}{(\Delta \mathrm{tab} + 2\mathrm{C})}$. The simplified equation; RTEI= $\frac{\mathrm{T}-\mathrm{C}}{\mathrm{T}+\mathrm{C}}$ was used and ranged between -1 to 1. Values of RTEI approaching 1 indicated strong benefits in terms of removal efficiency of metal removal while values around 0 indicated no effect of the treatment when arrowroots were used, while values approaching -1 indicated strong inhibition of the metal removal (Marchand *et al.*, 2010). The effluent of the planted and the unplanted treated wastewater were also compared.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 The level of pollutants in Malakisi River

The pollution level in Malakisi river was investigated by analyzing levels of heavy metals, nutrients, sulphates, fluoride, faecal coliforms and physical- chemical parameters in the river during both dry and wet seasons. The dry season comprised of; January, February and March whereas the wet season comprised of; April, May and June. Tables 4.1-4.3 show the established concentrations for respective parameters.

Table 4.1: Range of levels of metal ions in the river (mg/l) during wet and dry seasons

	Zn		Cu		Mn		Fe	
Sampling stations	Dry	Wet	Dry	Wet	Dry	Wet	dry	Wet
S1	0.240 - 0.258	0.200 - 0.266	0.015 - 0.040	0.045 - 0.061	0.130 - 0.300	0.196 - 0.260	0.690 - 0.730	0.750 - 0.860
S2	0.161 - 0.169	0.192 - 0.200	0.040 - 0.076	0.059 - 0.093	0.234 - 0.291	0.300 - 0.340	0.330 - 0.426	0.357 - 0.434
S3	0.460 - 0.490	0.517 - 0.621	0.071 - 0.083	0.084 - 0.100	0.211 - 0.276	0.300 - 0.342	0.861 - 1.000	0.968 - 1.121
S4	0.200 - 0.240	0.245 - 0.251	0.082 - 0.123	0.106 - 0.133	0.237 - 0.242	0.300 - 0.348	0.289 - 0.300	0.268 - 0.310
WHO Max. limits	1.5		0.05		0.1		0.3	

From Table 4.1, the concentration values for Zn during dry season at the four sampling stations ranged between 0.161 mg/l – 0.490 mg/l and 0.200 mg/l – 0.621 mg/l during wet season. High values of Zn were observed upstream at sampling station S1 but reduced downwards at sampling station S2 and then increased drastically at sampling station S3 and then reduced at S4. Reduction of Zn concentration at S2 could be due to the rivers self dilution (Ajibade, 2004). Sampling station S3 is where Ndakaru river meets Malakisi river and hence higher values could from Ndakaru river. Reduction of Zn levels at S4 again could be due to dilution of the river downstream. There were slightly higher Zn levels during wet season compared to dry season. The levels of Zn at all the sampling stations were, however, within the WHO recommended limits but slightly higher than those reported by Enuneka *et al*. (2013), with Zn levels of 0.10 – 0.13 mg/l.

High levels of Mn, greater than the WHO maximum limit of 0.1 mg/l were noted at all the sampling stations. The levels ranged between 0.130 – 0.348 mg/l during both dry and wet seasons at the four sampling stations. Higher levels were also observed during wet season. This could be as a result of erosion from agrochemicals. Sampling stationS4 had partially highest Mn levels compared to other sampling stations. This could be due to tobacco farming which is the main cash crop at the catchment area S4 where Mn ethylene bisdithiocabamate is highly used as the main insecticide among the tobacco farmers (NBI, 2011).

Higher values of Mn greater than WHO maximum limits at all the sampling stations during both seasons could be as a result of fertilizer application and runoff. Although Mn levels at all the sampling stations of the Malakisi river were higher than WHO maximum limits, studies done on other rivers show even higher Mn levels. For instance, a study done on Kikwe river in Zimbabwe to assess the impact of effluent from iron and steel company on the physical-chemical quality of the river established Mn levels of 125.21 mg/l (Jonathan, 2010), while in Nairobi river at stations Museum and Dandora, Ngong river (Embakasi), Kasarani river (Kasarani) and Kamiti river

(Kamiti), had Mn levels of 1.6 mg/l, 2.5 mg/l, 1.65 mg/l, 2.1 mg/l and 2.8 mg/l, respectively (Mulei, 2012), probably due to industrial effluents. Mn levels of 0.01 – 4.08 mg/l during dry season, 0.01 – 0.98 mg/l during wet season were observed in another study done to establish the pollution levels of Sasumua river in Kenya (Gathenya *et al*., 2009), while Mn levels of 0.33 mg/l, 0.44 mg/l, 1.71 mg/l and 0.19 mg/l were established in rivers; Nzoia, Yala, Kisati and Nyando respectively (Mutuku *et al*., 2014).

Although slightly higher Mn levels above WHO maximum limit were established in Malakisi river water, these levels were very low compared to those in rivers within Nairobi city which has many industries. Thus Mn pollution in Malakisi river could be mainly from agricultural insecticide application with higher values observed during the wet planting season. The Mn levels in water samples at stations S2, S3 and S4 were all found to be above 0.3 mg/l, while slightly low values were established upstream at sampling station S1. This could be due to tobacco farming at sampling stations S2, S3 and S4 where the main pesticide dithane M-45 or Mancozeb (dithane) fungicide is the main pesticide and fungicide frequently used. Mancozeb is a product of Zn ion and Mn ethylene bisdithiocabamate with % compositions of 7.4 % Mn^{2+} and 0.9 % Zn^{2+} (Dara, 2004). This could also be the reason for high Zn levels at sampling stations S3 and S4.

The levels for Fe and Cu were higher than the maximum WHO limits of 0.3 mg/l and 0.05 mg/l, respectively. The values of Fe at the sampling stations ranged between 0.330 - 1.121 mg/l, with very high values being observed at S1 (0.690- 0.860 mg/l) and S3 (0.861- 1.121 mg/l). High values at S3 could also be due to geological origin of Ndakaru river whose water is always brown in colour and which joins Malakisi river at this point, while higher values at S1 could be because of both geological origin and runoff during wet season. This augment is supported by Davies (1996), Kritzberg and Ekstrum (2012) where it was observed that most surface waters in Western Kenya are coloured as a result of high concentrations of Fe and Mn.

The level of Fe at all the sampling stations was higher than WHO maximum limit of 0.3 mg/l. According to WHO (2008), the median Fe concentration in surface waters has been reported to be 0.7 mg/l. Similar studies to establish the levels of Fe in rivers Nairobi and Ngong both showed Fe concentrations of 1.99 mg/l and 1.30 mg/l, respectively which are slightly higher but close to those of Malakisi river (Mulei, 2012). Fe concentration range of 0.08 – 1.84 mg/l was established in Sasumua reservoir and contributing rivers during wet season and 0.17 – 18.46 mg/l during dry season. In Owan river, Nigeria, the levels of Fe were 1.16 -1.49 mg/l (Enuneka *et al*., 2013), while Fe level of 7.61 mg/l was established in river Kikwe in Zimbabwe (Jonathan, 2010). Cu levels in the same Sasumua river was; 0.01 - 0.02 mg/l during wet season and 0.01 -0.31 mg/l during dry season. Malakisi river had lower Cu levels than Sasumua river ranging from 0.01 – 0.13 mg/l which were also slightly lower than what was established in the rivers Nairobi (0.01 – 0.20 mg/l) and Ngong (0.15 mg/l) (Mulei, 2012; Gathenya *et al*., 2009). However, these levels were slightly higher than those established in natural waters of Kerio Valley (Mn < 0.2 mg/l, Cu; 0.03 mg/l, Fe; 0.1 – 0.4 mg/l), in river Gucha (Mn; 0 mg/l, Cu; 0.04 mg/l, Fe; 0.4 mg l) and in Nzoia river(Fe; 0.2 – 0.4 mg/l, Cu; 0.01 – 0.20 mg/l), but lower than those in natural waters in Thika area (Fe 0.883 mg /l, Mn 0.442 mg/l, Zn; 0.01 – 2.996 mg/l) and Nyando river (Mn; 1.5 mg/l, Fe; 4.4 mg/l) (Davies, 1996). High levels of Mn and Zn in Malakisi river compared to water from Kerio valley could be due to more farming activities within Malakisi river catchment area that involve use of fertilizers and pesticides, while alot of industrial effluents into rivers within Thika and pollutants from tributaries that join river Nyando in addition to agricultural activities could have contributed to higher levels of Mn and Zn compared to Malakisi river.

Table 4.2: levels of anionic pollutants (NO_3^- , PO_4^{3-}, SO_4^{2-} and F^-) in Malakisi river water

	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	WHO max. limit
NO_3^- (mg/l)	0.090	0.200	0.100	0.400	0.070	0.300	0.095	1.000	10
PO_4^{3-} (mg/l)	0.136	1.442	0.065	0.351	0.124	0.548	0.096	0.653	5.0
SO_4^{2-} (mg/l)	0.100	0.600	0.090	0.400	0.456	1.000	0.628	1.100	400
F^- (mg/l)	0.20	0.23	0.49	0.46	0.673	0.64	0.240	0.280	1.5

From Table 4.2, the levels of nitrates, phosphates and sulphates at all the sampling stations during dry and wet seasons ranged between, NO_3^- (0.07- 1.0 mg/l), PO_4^{3-} (0.065 – 1.442 mg/l), SO_4^{2-} (0.09 – 1.1mg/l) which were all very low compared to WHO maximum limits. The NO_3^- and PO_4^{3-} were, however, slightly higher than those established in Nzoia river; NO_3^- (0.01 - 0.13 mg/l), PO_4^{3-} (0.01 -0.43 mg/l)). Nzoia river, however, had higher SO_4^{2-} levels (29.9 - 66.7 mg/l) probably due to discharge of effluents from pan paper industry in Webuye compared to Malakisi river (Mulei, 2012). These values were also low compared to nutrient levels of some rivers. A study done by Gathenya *et al*. (2009), to establish the nutrient concentrations in Sasumua reservoir and contributing rivers showed NO_3^- levels ranged from 17.16 – 477.38 mg/l during wet season, 6.88 -8.90 mg/l in dry season, PO_4^{3-} levels of 0.21- 0.96 mg/l during wet season, 0.25 – 9.69 mg/l during dry season and SO_4^{2-} levelsof8.45 – 71.83 mg/l during wet season and 7.21 – 71.50 mg/l during dry season. A similar study on Mara river showed PO_4^{3-} levels of 1.21 – 1.15 mg/l (Mulei, 2012; Gathenya *et al*., 2009). Sulphate levels in the river ranged between 0.09 – 1.1 mg/l which were very low compared to WHO maximum required limit. According to Davies (1996) surface waters of East Africa contain low levels of SO_4^{2-}.

Table 4.3 shows concentration levels of faecal Coliforms (Cfu/100 ml), COD (mg/l) and BOD (mg/l) obtained in Malakisi river during dry and wet seasons

Table 4.3: Concentration levels of faecal Coliforms (Cfu/100 ml), COD (mg/l) and BOD (mg/l)

	S1		S2		S3		S4		WHO max. limits
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	
Coliforms	28	35	36	42	42	39	34	46	Nil
COD(mg/l)	24.00	20.00	18.00	15.00	33.00	25.00	40.00	33.00	50
BOD(mg/l)	11.00	9.00	9.00	7.00	17.00	12.00	21.00	15.00	20

Water from all the four sampling stations in table 4.3 had high levels of coliforms above WHO maximum limit during both dry and wet seasons which ranged from 28 – 46 cfu/100 ml. Malakisi river is the main source of both domestic and drinking water for animals mainly cows and donkeys. Thus, the presence of faecal coliforms in the water could be due to direct input by the animals. Runoff into the river during wet season could have contributed to slightly higher coliform levels. Although the Malakisi river is polluted due to presence of coliforms hence requiring treatment before drinking, these levels are low compared to those of other rivers. A study done by Dulo (2008) to determine the levels of physical chemical parameters of the Nairobi river showed a value of 35000 cfu/100 ml faecal coliforms.

In Table 4.3, the COD and BOD levels of the river water were found to within the range of: 15- 40 mg/l and 9 -21 mg/l respectively. These levels were low compared to WHO maximum limit and indicated low organic pollution of the river water. The BOD level during dry season at S4 was slightly above WHO limit probably due to dispose of rejected tobacco leaves from tobacco buying companies and some tobacco farmers. These levels were, however, similar to those established in natural waters of Kerio Valley (BOD: 9 mg/l, COD: 14 mg/l) and Gucha river (BOD: 26.3 mg/l) (Davies, 1996). The BOD and COD levels of river Malakisi were found to be lower than those for rivers in urban areas or within the industrial set up. For instance, Githurai river, Nairobi river, rivers within Thika and Nzoia river were found to have higher BOD and COD (Dulo, 2008, Davies, 1996, Kaluli *et al*., 2006). High BOD levels of 475 mg/l were also established in river Sabarmati in India (Bhardwaj & Scientist, 2005), while BOD levels of 333.2 – 524.2 mg/l were established in river Owo in Nigeria (Kuforiji & Ayandiran, 2013). Although the BOD levels in Malakisi river were slightly below the WHO maximum limit, all the values were above 3 mg/l, implying possibility to affect coagulation and rapid sand- filtration process in conventional water treatment and thus requiring expensive advanced water treatment (UNEP, 2006). Malakisi river is also regarded as grossly polluted since all its BOD values were above 6 mg/l (Bhardwaj & Scientist, 2005).

Table 4.4 shows the levels of physical-chemical parameters and fluorides established in river water during dry and wet seasons.

Table 4.4: Levels of Total Hardness, Turbidity, Conductivity and pH in the river

	S1		S2		S3		S4		WHO max. limit
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	
Total hardness (mg/l)	2.34	2.35	2.36	2.37	2.29	2.27	2.22	2.19	100
Conductivity (µs/cm)	166.0	164.0	170.0	169.0	291.0	289.0	191.0	188.0	1500
Turbidity (NTU)	54.00	60.00	59.00	61.50	238.00	248.0	134.0	139.0	5.0
pH	7.00	7.20	6.90	7.10	7.10	7.3	6.8	7.10	6.5-8.5

Total hardness and conductivity levels ranged between 2.19 -2.37 mg/l and 164 – 291 mg/l respectively. The levels were below WHO maximum limits of 100 mg/l and 1500 mg/l. The low total hardness implied that the water was soft while low conductivity levels could be due to low ionic strength of the river water. The conductivity levels were however slightly higher than that in natural waters of Kerio Valley (conductivity: 141 us/cm^3), Gucha river (conductivity: 119 us/cm^3) and Mara river (conductivity: 50 us/cm^3) (Davies, 1996), but lower than that of Nzoia river, Githurai river, Nairobi river, rivers within Thika (Dulo, 2008, Davies, 1996, Kaluli *et al.*, 2006).

Turbidity levels of the water at all the sampling stations during dry and wet seasons ranged between 54 - 238 and 60 – 248 NTU, respectively. The turbidity of Malakisi river alone before joining the Ndakaru river had values ranging from 54 – 61.5 NTU. The levels increased drastically after joining with the Ndakaru river where the turbidity values ranged between 238 – 248 NTU. Water from all the sampling stations in Table 4.3 had high turbidity levels which were much above the WHO maximum limit of 5.0 NTU, with water from the sampling station S3 having the highest values. Wet season had high turbidity levels compared to dry season.

In Kenya, many of the streams have been established to be turbid, due to largely soil erosion which is especially high in the rainy season (Davies, 1996). The turbidity levels of the river water were found to be similar to those of Nzoia river (7 – 66 NTU), but lower than natural waters of Kerio Valley (5 – 620 NTU) and Mara river (7.1 – 1999 NTU) and higher than those of the Nairobi river (8 – 57 NTU) (Dulo, 2008; Davies, 1996). However, very high turbidity levels have been noted in Mesopotamia plain in Iraq (Younus &Enaam, 2014). The pH levels ranged between 6.8 -7.3which was within the WHO maximum limit of 6.5 – 8.5.

4.2 The optimum pH and time for maximum adsorption of the metal ions from river water using arrowroots

The removal efficiency of metal ions in river water by the arrowroots was monitored at different pH values while the effect of contact time was monitored at the constant pH. The optimum pH and time for maximum adsorption of the heavy metals by the arrowroots was then established. Data showing variation of residual metal ion concentrations in river water at different contact time were fitted to both Langmuir and Freundlich isotherms models which were compared to establish the adsorption capacity of the arrowroots for the metal ions. Figures 4.1- 4.3 show the adsorptions at different pH values, contact time and residual metal ion concentrations at different contact times with constant pH.

Figure 4.1 shows the percent metal ions removal efficiency (y-axis) by arrowroots at different pH values (x-axis)

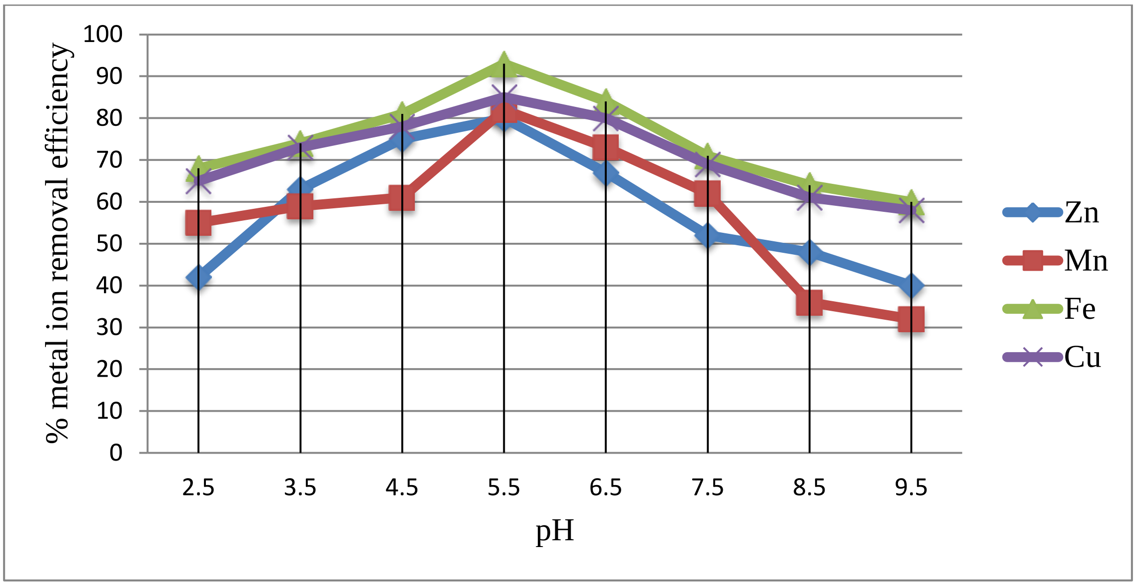

Figure 4.1: Percent metal ions removal efficiency in river water using arrowroots at different pH values

Figure 4.1 shows that arrowroots adsorbed metal ions effectively at pH of 5.5. The percent removal efficiency of the four metal ions was low at low pH but increased steadily up to pH 5.5. This could be because at low pH, there were more hydrogen ions that competed for active sites on the adsorbent surface. This was similar to what was established by Sevil and Bilge (2007) and Mousa *et al.*, (2013) using natural clay and rice straw biosorbents respectively. Higher % removal efficiency was noted at pH 5.5 where the trend in % removal efficiency was in the order of Fe> Cu > Mn > Zn. A similar trend was established by Agbozu and Emoruwa (2014), where the corresponding removal efficiencies of Cu and Fe at pH = 6 using coconut husk were: Cu 75 – 98.5 % and Fe 84 -97.0 %. The results were similar with those reported by Jenny (2006), where Cu^{2+} was effectively removed at pH = 5 and Zn^{2+} at pH= 5.5 using peat. It was also noted that the metal uptake decreased at pH above 7.0. This could be because at high pH, the hydroxide ions competed with metallic ions for active sites on the biosorbent surface and other metal ions were precipitated as metal hydroxides. Similar results were noted by El – Sayed *et al*., (2011) using maize stalks, and Agbozu and Emoruwa (2014). According to their findings, Zn, Cu and Mn adsorption increases with increasing pH from 2 to 7 and above that pH, the adsorption decreases due to precipitation of the metal hydroxides. In these findings, high uptake of Zn (63%) was noted at pH = 6 and Mn (38 % at pH = 7.0). pH influences metal species present in solution as well as the corresponding ionic charge where in another study, adsorption of metals like Cu and Zn have been found to be more effective at pH 5.6 and 7.0, respectively using peat and water hyacinth (Jenny, 2006; Achanai *et al*., 2012b).

Figure 4.2 shows the percent metal ions removal efficiency at different contact times when 0.3 g of dry arrowroots was placed in 100 ml river water and percent absorption calculated by evaluating changes in concentrations at various times with respect to changes based on maximum biosorption in equation 2.1.

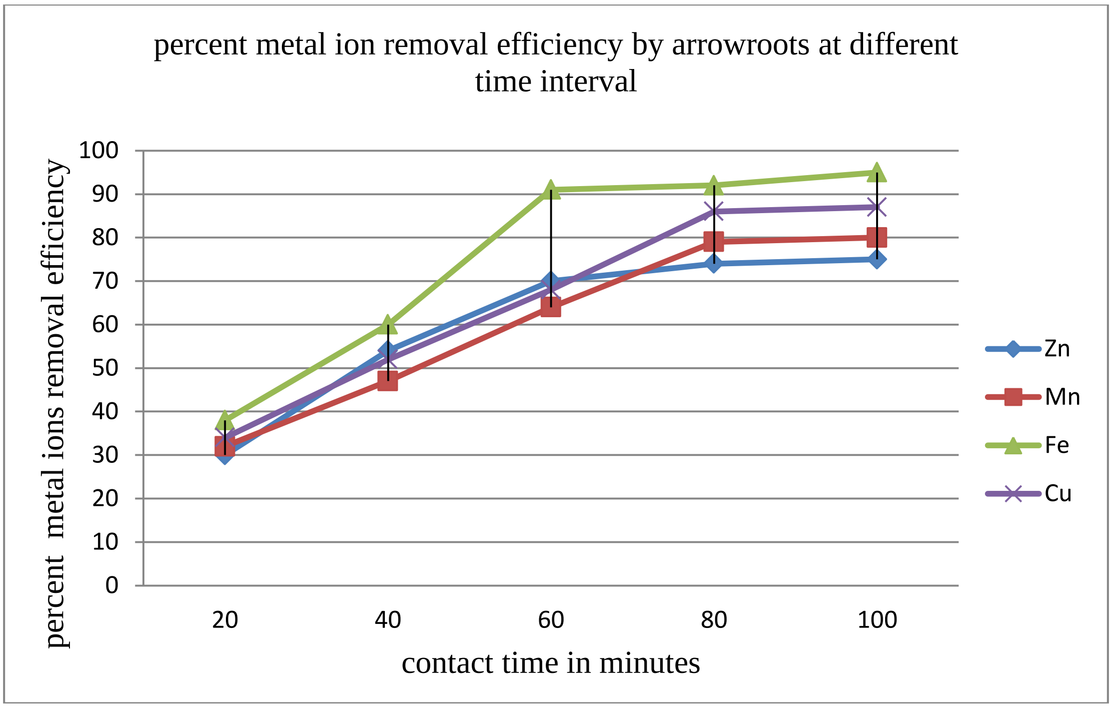

Figure 4.2: Percentage removal efficiency at different contact times- in river water

Figure 4.3 shows the residual metal ion levels in river water at different time intervals with dry arrowroots biosorbent.

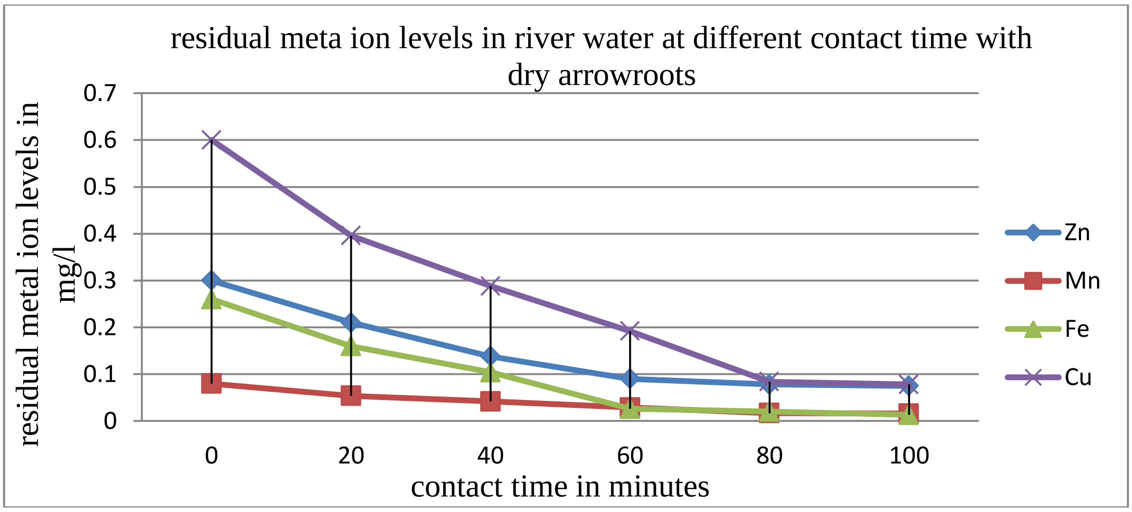

Figure 4.3: Residual metal ion concentrations against contact time- in river water

Figures 4.2 and 4.3 showed % metal ion uptake and the residual metal ion levels, respectively in the solution after the adsorption at the same time intervals. In Figure 4.2, there was a gradual increase in the % metal uptake from 20 minutes up to around 60 minutes followed by a slow rise in % metal uptake which remained almost constant after about 80 minutes. A complementary trend was observed in Figure 4.3 where the residual metal ion levels gradually decreased with increase in time and remained constant after 80 minutes, as a result of gradual increase in % metal uptake. The initial rapid phase in both Figures 4.2 and 4.3 could be due to the presence of a large number of vacant sites on the adsorbent, leading to increase in concentration gradient between the adsorbate solution and adsorbent surface (Zhanming *et al*., 2009). As time elapsed, the initial concentration was reduced due to accumulation of metal ions on the vacant sites leading to decrease in adsorption gradient. At optimum time of 80 minutes, the % removal efficiency was generally in the order of Fe > Cu > Mn > Zn. These results were close to those reported by Mousa *et al*. (2013), using rice straw. The trend was, however, different from that observed by Agbozu and Emoruwa (2014), using coconut husk biosorbent, implying that different biosorbents show different favourability trends for various metal ions probably due different active sites on the biosorbents. Removal favourability trend of Cu > Fe at 60 minutes was also noted by Jenny (2006), using peat as the biosorbent. Different optimum time was also established by El- Sayed *et al*. (2011), where optimum contact time of 30 minutes was established for Zn and Mn using maize stalks. Different biosorbents, therefore have different optimum contact times.

4.3 The arrowroot biomass metal ion uptake capacities and the adsorption isotherms using river water

The metal uptake capacities from river water using arrowroot biomass was calculated from the relevant metal ion levels in water and the experimental data for biosorption were fitted in the linear form of Langmuir isotherm using equation 2.5 and Freundlich isotherms models equation 2.8 and the adsorption process described.

Table 4.5 and table 4.6 show the values for Zn that were fitted into the linear forms of Langmuir and Freundlich isotherms and the constants a and b for Langmuir and n and k for Freundlich isotherms obtained from the linearized Langmuir and Freundlich plots.

Table 4.5: Values for Langmuir equation terms for Zn – river water

M	Y	C	M/Y	1/C
0.3	0.09	0.21	3.33	4.76
0.3	0.162	0.138	1.85	7.24
0.3	0.21	0.09	1.42	11.11
0.3	0.222	0.078	1.35	12.82
0.3	0.225	0.075	1.33	13.33

The Langmuir equation was; $\frac{M}{Y} = \frac{1}{ab} X \frac{1}{C} + \frac{I}{b}$. The constants a and b were obtained by plotting $\frac{M}{Y}$ against $\frac{I}{C}$

Where,

Y = concentration of contaminant adsorbed in mg/l

M = adsorbent concentration in g

C = equilibrium concentration of contaminant in mg/l

a = constant related to energy of adsorption

b = constant, adsorption capacity (amount of adsorbate per weight of adsorbent)

Table 4.6: Values for Freundlich equation terms for Zn – river water

C	x/m	Log C	Log x/m
0.21	0.3	-0.68	-0.52
0.138	0.54	-0.86	-0.27
0.09	0.7	-1.05	-0.15
0.078	0.74	-1.11	-0.13
0.075	0.75	-1.12	-0.12

The Freundlich equation was; $\text{Log}\left(\frac{\mathrm{x}}{\mathrm{m}}\right) = \log K + \frac{1}{n}\log C$

Where,

x = mass of the adsorbate adsorbed in mg/l

m = mass of adsorbent in g

C = equilibrium concentration of adsorbate in mg/l

K = constant, adsorption capacity

n = constant, degree of favourability of adsorption

The Freundlich constants k and n were obtained from the linearized plot of log x/m against log C. The linearised Langmuir and Freundlich terms and plots for the other metal ions were obtained in the same way as for Zn and from the plots, the Langmuir and Freundlich constants for all the metal ions were obtained and recorded in Table 4.7.

Table 4.7: Constants for linearized Langmuir and Freundlich models- in river water

Metal ion	Langmuir constants- river water			Freundlich Constants – river water		
	a	b	R^2	n	k	R^2
Zn^{2+}	0.788	0.258	0.808	1.155	4.217	0.951
Cu^{2+}	0.048	0.758	0.674	1.634	58.070	0.898
Fe^{2+}	0.001	0.346	0.796	1.938	2.013	0.858
Mn^{2+}	0.010	0.084	0.753	2.77	5.272	0.893

From Table 4.7, the constant b represents the adsorption capacity. Thus, according to Langmuir and using river water, the arrowroots had higher adsorption towards Cu^{2+}while Mn^{2+} was the least. Thus the trend in terms of adsorption capacity was: Cu^{2+} > Fe^{2+} > Zn^{2+} >Mn^{2+}. The constant, b denotes the maximum value of adsorbate metal ion that can be obtained at equilibrium concentrations. The other constant a, represents the energy associated with adsorption, and increases as the strength of the adsorption bond increases, where in this case the trend was; Zn^{2+} > Cu^{2+} > Mn^{2+} >.Fe^{2+}. The trend of adsorption basing on R^2 of Langmuir was Zn^{2+} > Fe^{2+} > Mn^{2+} > Cu^{2+}. This trend was similar to what was reported by Shahmahammadi *et al*., (2011), Zhanming *et al*. (2009), Agbozu and Emoruwa (2014), Jenny (2006), El-Sayed *et al*.(2011)and Achanai *et al*. (2012a). The adsorption of the metal ions in river water by the arrowroots was best fitted for the Freundlich isotherm.

From the Freundlich values in Table 4.7, there was high favourability of adsorption for Mn^{2+}due to its high value of n, followed by Fe^{2+} while least favourability for adsorption was observed with Zn^{2+}. The trend of biosorption basing on n was Mn^{2+} > Fe^{2+} > Cu^{2+} > Zn^{2+}. The trend of adsorption basing on R^2 of Freundlich was, however, Zn^{2+} > Cu^{2+} > Mn^{2+} > Fe^{2+}. This trend was similar to what was reported by Mustaqeen *et al*. (2014), Achanai *et al*., (2012a) and Jenny (2006). This trend could be because of the charge and the hydrated ionic size, where Zn^{2+} and Cu^{2+} have higher affinity for the adsorbent and hence are the most successful metal in terms of competitive sorption where the ions compete faster for exchange sites than others. Basing on R^2 for both Langmuir and Freundlich, all the metal ions were best fitted for Freundlich isotherm. The value of n for all metal ions was below 10, indicating favourable adsorption (Shahmohammadi *et al*., 2011). However, the results were in agreement with both isotherms, where the R^2 values for all cases were close to unity, although the metal ions were adsorbed more through hetero layer mechanism.

4.4 The adsorption capacity of metal ions by the arrowroots in model solutions of different concentrations

The results of Tables 4.8 - 4.11 were obtained after evaluating the ability of dry arrowroots corresponding with the removal of dissolved metal ions from wastewater. Model batch experiments were conducted using metal ions at both high and low concentrations both when single and when mixed at the optimum pH of 5.5. The results were then subjected to both Langmuir and Freundlich isotherms where constants were obtained using equations 2.3 and 2.6 respectively. Tables 4.8 and 4.9 shows the Langmuir and Freundlich equation terms for Zn at single low and mixed high concentrations that were subjected to both Langmuir and Freundlich equations. The equation terms for Zn at different concentrations and for the other metal ions were obtained using the same procedure. Langmuir and Freundlich constants were obtained from the respective Langmuir and Freundlich graphs for all the metal ions and recorded in tables 4.10 and 4.11.

Table 4.8 shows the Langmuir equation terms for Zn ions when single at low initial concentration of 2.42 ppm and change in concentration was measured after every 10 minutes after adding 0.5 g of the biosorbent while table 4.9 shows the Freundlich equation terms at mixed high initial concentrations.

Table 4.8: Langmuir equation terms for Zn (single low concentration)

C_e	q_e	$q_e/m=q_m$	c_e/q_m	c_e/q_e
2.00	0.42	0.84	2.38	4.762
1.70	0.72	1.44	1.12	2.36
1.51	0.91	1.82	0.83	1.66
1.38	1.04	2.08	0.66	1.327
1.36	1.06	2.12	0.642	1.28
1.36	1.06	2.12	0.642	1.28
1.36	1.06	2.12	0.642	1.28

The Langmuir equation; $C_e/q_e = 1/q_m k_L + C_e/q_m$ was used.

Where,

q_e = amount adsorbed in mg/l

k_L = Langmuir constant related to the energy of adsorption

q_m = maximum amount of adsorbed metal per unit mass of sorbent corresponding to complete coverage of the adsorptive sites. The Langmuir constants were obtained by plotting graphs of c_e/q_e against c_e/q_m for all the metal ions where the constants (q_{max}, b and a) were obtained from the respective values of 1/slope, 1/y-intercept and slope/ y intercept.

Table 4.9: Freundlich terms for Zn (mixed high initial concentration)

c_e	q_e	log c_e	log q_e
15.03	3.64	1.18	0.56
14.52	4.15	1.16	0.618
13.98	4.69	1.15	0.671
12.97	5.70	1.11	0.756
12.26	6.41	1.08	0.807
10.20	8.46	1	0.928

The Freundlich equation used was; $q_e = K_fC_e^{(1/n)}$ or log q_e = log k_f + 1/n log C_e. The Freundlich constants k_f and n were obtained from the respective plots of log q_e against log C_e for all the metal ions.

Where,

$q_e =$ adsorption capacity (metal concentration on adsorbing material, mg/g),

$K_f =$ constant linked to adsorption capacity,

$C_e =$ equilibrium concentration of the contaminant and

n = empirical parameter linked to sorption intensity, where high 1/n show preference for sorption of the metal while high K imply greater adsorption tendency towards the adsorbent.

Tables 4.10 and 4.11 show the Langmuir and Freundlich constants obtained after monitoring the adsorption of all metal ions from model solutions of different concentrations using arrowroots. Low concentrations were those between 2 – 5 ppm while high concentrations were those between 15 – 25 ppm as model solutions in a given industrial effluent. In this work, low concentrations for Zn, Cu, Mn and Fe before adsorption were 2.42, 2.34, 2.21, and 2.40 ppm respectively when single but 4.81, 4.26, 4.39 and 4.31 ppm respectively for mixed solutions. Concentrations of

18.12, 16.45, 18.45 and 17.07 ppm single high and 18.67, 16.36, 18.34 and 19.28 ppm represented high levels of the Zn, Cu, Mn and Fe ions when single and when mixed before adsorption. These levels were measured immediately before adsorption using dry arrowroot biomass.

Table 4.10: Constants for linearized Langmuir model of metal ions at different concentrations

Metal	Single low			Single high			Mixed low			Mixed high		
	q_{max}	b	R^2	q_{max}	b	R^2	q_{max}	b	R^2	q_{max}	b	R^2
Zn	0.499	-667	1.00	0.496	-111	0.999	0.50	-1000	1.000	0.48	-20.57	0.990
Cu	0.50	-2.00	0.999	0.50	-286	1.000	0.504	132	1.000	0.49	-1000	1.000
Mn	0.63	-0.11	0.998	0.501	332	1.000	0.499	2.001	1.000	0.50	332.7	0.999
Fe	0.502	-199.0	1.000	0.50	-1999	1.000	0.498	-669	0.999	0.50	-2000	0.999

Results of q_{max} Langmuir constants of Table 4.10 show that the trend of biosorption for single metal ions at low concentrations was: Mn > Fe > Zn > Cu. Which while the trend at high initial concentration, was: Mn > Fe > Cu > Zn. The atomic sizes of Cu, atomic radius = 0.128 nm and Zn, atomic radius = 0.137 nm are very close and most probably they compete for the negative surface of the biosorbent equally or interchangeably depending on the amount of surface present (Abdel & Elchaghaby, 2007). Values of q_{max} for mixed metal ions at low initial concentration followed the trend Cu > Zn > Mn > Fe with very close q_{max} values probably due to their close initial concentration. This trend could also be due to ionic potential where removal of metals from solutions is sequential according to the ionic potential in terms of charge – to – radius ratio. The strongest bond should be formed by the metal with the greatest charge - to – radius ratio and hence Cu with the high charge and smaller hydrated radius had higher affinity for adsorption onto the adsorbent where greater polarization facilited electrostatic ion exchange. Similar trend was observed by Agbozu and Emoruwa (2014).

For mixed metal ions at higher initial concentration, the trend of adsorption in terms of q_{max} was, Mn = Fe > Cu > Zn, which could be again as a result of electrostatic interactions based on charge density and hydrated radius and ionic potential, where in a mixed ionic atmosphere, metals with lower ionic radius have lower charge density and lower electrostatic attractions that limit interaction of the metal ion with the adsorption sites and metals with high electronegativity adsorb more readily. Except for Mn where its q_{max} at low initial concentration when single differed greatly with other concentrations. q_{max} for other metal ions were not influenced by change in concentrations both mixed and single, indicating that the mechanism of adsorption was second order. It was also noted that, the R^2 values for all the systems at different concentrations in table 4.10 remained the same and were all close to unity, indicating little effect of change in concentration on adsorption capacity although the adsorption mechanism could still best be described by the Langmuir model.

Table 4.11: Constants for Linearized Freundlich model of metal ions at different concentrations

Metal ion	Freundlich parameters											
	Single Low			Single High			Mixed low			Mixed high		
	K_f	n	R^2	K_f	n	R^2	K_f	n	R^2	K_f	n	R^2
Zn	2.20	0.44	0.966	74	1.28	0.999	25.00	0.40	0.969	885	0.5	0.967
Cu	1.67	0.55	0.990	182.8	0.762	0.835	17.42	0.40	0.898	173	0.695	0.999
Mn	1.22.	0.89	0.999	83.0	1.08	0.877	7.62	0.63	0.965	100	0.874	0.950
Fe	2.83	0.37	0.995	88.0	0.951	0.805	2163	0.141	0.449	467.8	0.580	0.996

Comparing values of n, the preference for sorption of the metal ions low concentration was Fe > Zn > Cu > Mn (single), Fe > Cu > Zn > Mn (mixed) while high concentration followed the trend Cu > Fe > Mn > Zn (single) and Zn > Fe > Cu > Mn (mixed). The constant n is an empirical parameter linked to sorption intensity, where high 1/n (low n) shows preference for sorption of the metal ion (Shahmohammadi et al., 2011). The R^2 for the four systems in table 4.11 were all close to unity, indicating that the mechanism of adsorption could also be hetero layer apart from Fe^{2+} when mixed low where its R^2 value was very low probably due to desorption (Zhanming *et al*., 2009). Comparing R^2 for both Langmuir and Freundlich, the biosorption of the metal ions in the model solutions at different concentrations were best described by the Langmuir model, indicating that the mechanism of adsorption was on the surface.

4.5 Pseudo first and second –order adsorption kinetics and intra – particle diffusion models

Tables 4.12 – 4.14 show the values obtained when the experimental data were fitted to pseudo first and second order and inter – particle diffusion model equations 2.9, 2.11 and 2.12 respectively. For first and second order kinetic equations;

$\log q_t = -K_1t/2.303 + \log q_o$ and $1/q_t = k_2t + 1/q_o$, values investigated were:

q_o = initial concentration at time t = 0

q_t = equilibrium concentration at time t = 60 minutes

q_e = maximum amount of the metal ion adsorbed after 60 minutes

K_1 = pseudo first order rate constant

K_2 = pseudo second order rate constant

Both experimental values such as q_o exp. for single metal ions high (S.H.) or low (S.L.) levels or mixed metal ions at high (M.H.) or low (M.L.) levels were compared with those calculated using the first and second order adsorption model equations, q_o cal.

Table 4.12: Pseudo first order adsorption constants

Metal ion		Pseudo first order kinetics							
		q_o exp.	q_o cal.	q_t exp.	q_t cal.	q_e exp.	q_e cal.	K_1	R^2
Cu^{2+}	S.H	16.45	19.10	4.00	6.41	12.45	12.67	-0.0184	0.723
	S.L.	2.34	1.93	1.30	1.27	1.04	0.66	-0.007	0.731
	M.H.	16.36	13.84	9.85	9.09	6.51	4.75	-0.007	0.652
	M.L.	4.26	4.11	2.25	2.36	2.01	1.75	-0.0092	0.955
Zn^{2+}	S.H	18.12	21.67	3.16	7.18	14.96	14.46	-0.0184	0.558
	S.L.	2.42	2.18	1.36	1.26	1.06	0.923	-0.0092	0.888
	M.H.	18.67	17.66	10.20	5.10	8.47	12.56	-0.0210	0.923
	M.L.	4.81	4.52	2.63	2.60	2.18	1.92	-0.0092	0.957
Mn^{2+}	S.H	18.45	26.00	2.18	3.77	16.27	22.23	-0.0322	0.746
	S.L.	2.21	1.60	1.01	1.56	1.20	0.015	-0.0092	0.705
	M.H.	18.34	16.60	6.35	5.50	11.99	11.10	-0.0184	0.940
	M.L.	4.39	3.88	2.06	1.95	2.33	1.93	-0.0115	0.926
Fe^{2+}	S.H	17.07	23.07	2.50	2.91	14.57	20.16	-0.0345	0.871
	S.L.	2.40	7.03	1.23	4.05	1.17	2.98	-0.0092	0.943
	M.H.	19.28	15.38	9.87	8.86	9.41	6.52	-0.0092	0.625
	M.L.	4.31	3.51	2.14	2.02	2.17	1.50	-0.0092	0.594

Table 4.13: Pseudo second order adsorption constants

Metal ion		Pseudo second order kinetics							
		q_o exp.	q_o cal.	q_t exp.	q_t cal.	q_e exp.	q_e cal	K_2	R^2
Cu^{2+}	S.H	16.45	31.25	8.89	6.58	7.56	24.67	0.002	0.582
	S.L.	2.34	1.93	1.30	1.22	1.04	0.71	0.005	0.779
	M.H.	16.36	13.89	9.85	7.57	6.51	6.32	0.001	0.680
	M.L.	4.81	4.20	2.25	2.39	2.56	1.81	0.003	0.962
Zn^{2+}	S.H	18.12	58.82	3.16	7.30	14.96	51.52	0.002	0.438
	S.L.	2.42	2.22	1.36	1.33	1.06	0.89	0.005	0.916
	M.H.	18.67	18.87	10.20	8.85	8.47	10.02	0.001	0.941
	M.L.	4.81	4.57	2.63	2.95	2.18	1.62	0.002	0.970
Mn^{2+}	S.H	18.45	47.61	2.18	3.11	16.25	44.49	0.005	0.622
	S.L.	2.21	1.55	1.01	0.89	1.20	0.67	0.008	0.633
	M.H.	18.34	18.18	6.35	8.69	11.99	9.48	0.001	0.964
	M.L.	4.39	3.95	2.06	2.03	2.33	1.92	0.004	0.964
Fe^{2+}	S.H	17.07	83.33	2.50	2.67	14.57	14.38	0.006	0.763
	S.L.	2.40	1.18	1.23	0.83	1.17	0.35	0.006	0.947
	M.H.	19.28	15.38	9.87	8.00	9.41	7.38	0.001	0.705
	M.L.	4.31	4.13	2.14	2.37	2.17	1.76	0.003	0.974

The order of reaction was calculated by comparison of R^2 values obtained for the first and second order reaction. Pseudo - second order at different initial concentrations in tables 4.13 had higher R^2 values than the first order. Therefore, the rate of adsorption could be well described by pseudo- second order and adsorption of the ions onto adsorption sites was proportional to the square of the number of unoccupied sites. Sorption of the metal ions by the arrowroots was thus chemisorption which is the rate controlling step and sorption of the metals involved the metal and the arrowroot biomass. However, the q_e calculated (q_e cal.) for both systems was not equal to the equilibrium uptake (q_e exp.) obtained at the end of the biosorption for all metal ions implying that the adsorption was not entirely first order despite their high R^2 values. This observation was similar to what had been established earlier (Alkpokpodion *et al.,* 2010).

The inter-particle constants in table 4.14 below were obtained by subjecting the experimental values to the inter-particle diffusion equation; Log r = log K_{id} + y log (t)

Where,

r = the percent metal ion adsorbed

t = contact time

y = the intraparticle diffusion rate constant

K_{id} = the rate factor or percent metal ion adsorbed per unit time

Table 4.14: Intra- particle diffusion parameters of Zn, Cu, Mn and Fe during adsorption by the arrowroots

Metal	Single high			Single low			Mixed high			Mixed low		
	y	Log K_{id}	R^2	y	Log K_{id}	R^2	y	Log K_{id}	R^2	y	Log K_{id}	R^2
Zn	0.146	0.993	0.889	0.111	1.794	0.941	0.451	0.782	0.878	0.121	0.993	0.889
Cu	0.109	1.269	0.156	0.6	0.613	0.922	0.371	0.996	0.679	1.273	0.571	0.934
Mn	1.127	0.183	0.846	0.147	1.492	0.739	0.635	0.763	0.901	0.431	0.966	0.987
Fe	1.358	0.448	0.975	0.476	0.832	0.949	0.321	1.172	0.686	0.355	1.074	0.512

The R^2 values in table 4.14 were high for all the metal ions except Fe when mixed at low initial (M.L.) and mixed high concentrations (M.H.), Cu (S.H. & M.H.), and Mn (S.L.) implying that the adsorption also fitted the intra- particle diffusion model. From the table, log K_{id} for Cu at S.H was 1.269, which represents 18.85% uptake of the metal ion by the arrowroot per minute. Higher K_{id} values for Cu (S.H), Zn and Mn (S.L) and Fe (M.H and M.L), illustrate an enhancement in the rate of adsorption and better adsorption mechanism and improved bonding. K_{id} represents the % metal uptake per min by the adsorbent. The rate of uptake reduces at higher concentration for single metal ions of Zn, Mn and Fe compared to when single low concentrations due to desorption after saturation. The rate of uptake increases for Fe and Cu at higher concentration when mixed than at low concentration but decreases for Zn and Mn.

Values of K_{id} show no observable difference in the order of adsorption for low concentrations, but an observable difference in the order of adsorption at higher concentration. This implies influence of other factors on the adsorption rate other than concentration, showing that the mechanism of adsorption is second order. Generally there was a reduction in the relative rate of metal ions uptake when mixed than when single for Cu and Zn for both high and low initial concentrations. This could be due to decrease in the available chances of adsorption on the arrowroots. However, the trend was opposite for Mn and Fe, where higher adsorption rate at higher concentration when mixed than when single could also be due to other factors such as presence of other elements competing for adsorption sites. The high charge density and presence of more oxidation states which provides more sites for adsorption could have also contributed to their higher adsorption rate other than concentration and hence their removal from wastewater can also be described by pseudo - second order adsorption kinetics and intra- particle diffusion model. However, comparing these models in terms of R^2, adsorption of the metal ions by dry arrowroots from model solutions of higher concentration than river water, was best described by Langmuir.

4.6: Percent removal efficiency of metal ions from municipal wastewater with live arrowroots compared to municipal wastewater without arrowroots.

Figure 4.4 shows results of % removal efficiency of metal ions from municipal wastewater with live arrowroots compared to wastewater in maturation ponds without arrowroots and in effluents with arrowroots after passing through the maturation ponds.

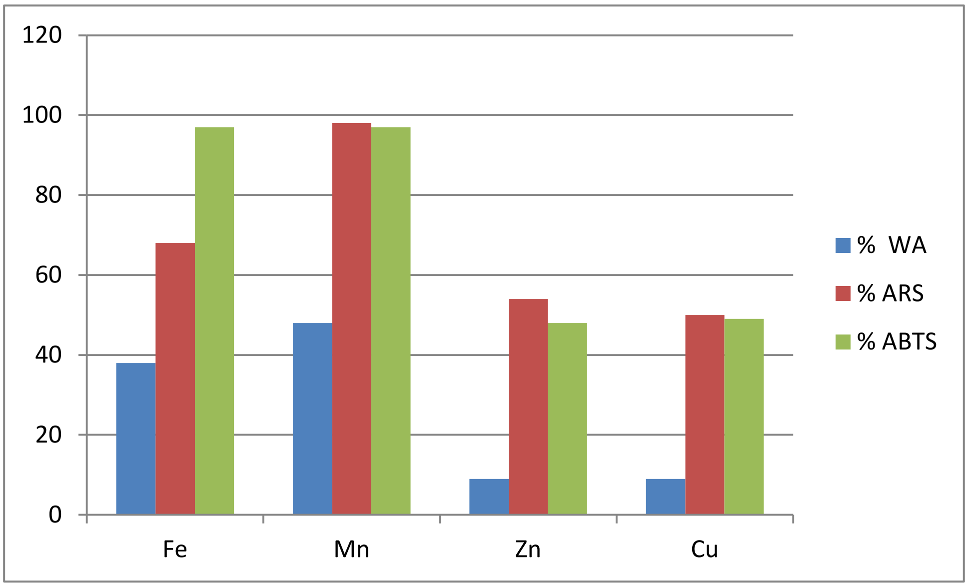

Figure 4.4: Percent removal of metal ions in municipal wastewater without arrowroots (WA) and with arrowroots in the influent of raw municipal wastewater before being passed through the maturation ponds (ARS) and in the effluent of biologically treated wastewater after being passed through the maturation ponds (ABTS).

From Figure 4.4, the % removal values for metal ions from raw municipal wastewater without arrowroots (WA) and after 7 days of allowing natural biological action in the maturation ponds were: Fe (38%), Mn (48 %), Zn (9 %) and Cu (9%). These percentages indicates slight removal of the metal ions probably due to presence of some sulphate reducing bacteria such as desulfovibrio spp. which takes part in the reduction of sulphates and subsequently to sulphides. Then these sulphides react with metals Cu, Zn, Mn and Fe which are precipitated as metal sulphides. However, for the same raw municipal wastewater after introduction of arrowroots in a model constructed wetland environment, the % reduction levels after 7 days were; Fe (68%), Mn (98%), Zn (54%) and Cu (50%) with order of preference of Mn > Fe > Zn > Cu. This trend could have partly been influenced by the initial concentration of the metal ions in the raw sewage and the ionic sizes. Mn, having higher concentration level in raw influent of municipal wastewater was preferentially adsorbed followed by Fe while Cu was the least probably due to its very low levels. This trend was also similar to what had been reported earlier (Marchand *et al*., 2010). This % removal rate using the arrowroots was also found to be comparable with the removal rates of other plant species (Maine *et al*., 2007). The difference in % removal showed that more metal ions could be removed both from the raw influent of municipal wastewater and final effluent of municipal wastewater with arrowroots than in maturation ponds without arrowroots. There was also higher % removal of Mn and Fe by arrowroots in the final biologically treated effluent compared to raw influent of municipal wastewater. This could be because of the low concentration in the final effluent after passing through the maturation ponds.

Figure 4.4 shows a significant difference in the removal of metal ions from waste water using unplanted maturation ponds with those having arrowroots. Further reduction of metal ions in the final effluent after passing through natural unplanted ponds by arrowroots was also noted in the figure. Arrowroots can either be planted in the municipal wastewater or final effluent passed through the planted arrowroots in order to reduce the level of metal ions to recommended levels before being discharged to rivers or streams. In order to test the significance of contribution using live arrowroots in removal of metal ions from municipal waste water, values obtained in this figure were subjected to relative treatment efficiency index (RTEI) and null hypothesis tested using the paired t- test at 5 percent significant level (Kothari, 2011) and values obtained recorded in Table 4.15.

Table 4.15: Values of RTEI of the metal ions using live arrowroots.

Pollutant	C%	T%	RTEI
Fe	38	68	0.28
Mn	48	98	0.34
Zn	9	54	0.71
Cu	9	50	0.65

In Table 4.15, C% represented % removal for the wastewater without arrowroots and represented the control, while T% represented pollutant removal for the treated wastewater with arrowroots. The RTEI in this table was calculated using equation,

RTEI = $\frac{T-C}{T+C}$ (Marchand *et al*., 2010) and null hypothesis (Kothari, 2011).

From Table 4.15, the RTEI was used to express the net metal removal interaction implying the benefits of using arrowroots in terms of efficiency. These values were high for Zn^{2+} and Cu^{2+} ions but slightly low for Fe^{2+} and Mn^{2+}. Since RTEI values were positive, arrowroots were of benefit. However, there was a strong benefit for Zn^{2+} and Cu^{2+} but were lower for Mn^{2+} and Fe^{2+}implying less effect on the treatment of the wastewater with arrowroots. This difference could have been again due to the difference in levels of the ions in raw sewage where high RTEI for Zn and Cu could probably be due to their low levels. This suggests that live arrowroots can be of more significant use if applied further to treat the biologically treated effluent. This can be done by passing the effluent through arrowroot wetlands and also applied as a tertiary wastewater treatment alternative. Thus, arrowroots can effectively be used to remove metal ions from dilute solutions which is in agreement with similar arguments reported earlier (Abdel & Elchaghaby, 2007; Brisson & Chazarenc, 2009). The null hypothesis with results; $t(3) = 2.110$, $p < 0.002$, was rejected implying that arrowroots could significantly adsorb heavy metals from dilute solutions such as river water and model solutions of wastewater containing higher concentrations of metal ions

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The concentration levels of Cu^{2+}, Mn^{2+} and Fe^{2+} heavy metal ions in Malakisi river were found to be higher than WHO maximum required levels while that of Zn^{2+} was within.

The anionic pollutants (phosphates, nitrates, fluorides and sulphates) in Malakisi river water were also within the WHO maximum required levels.

The level of faecal coliforms and turbidity in Malakisi river water were however found to be above the WHO maximum required levels while other physical – chemical parameters (BOD, COD, conductivity, total hardness and pH) were within. The Malakisi river is thus polluted.

The acidity of the media and contact time affected the metal uptake on a biosorbent. Metal ions were effectively removed at pH 5.5 and at an optimum contact time of 80 minutes for Mn^{2+} and Cu^{2+} and 60 minutes for Zn^{2+} and Fe^{2+} ions. According to Langmuir and using river water, the arrowroots had higher adsorption towards Cu^{2+} while Mn^{2+} was the least. Thus the trend in terms of adsorption capacity was: $Cu^{2+} > Fe^{2+} > Zn^{2+} > Mn^{2+}$. In terms of the energy associated with adsorption, with respect to increase in the strength of the adsorption bond, the trend was $Zn^{2+} > Cu^{2+} > Mn^{2+} > Fe^{2+}$, While the trend of adsorption basing on R^2 of Langmuir was; $Zn^{2+} > Fe^{2+} > Mn^{2+} > Cu^{2+}$. The trend of adsorption basing on R^2 of Freundlich was, however, $Zn^{2+} > Cu^{2+} > Mn^{2+} > Fe^{2+}$. Basing on R^2 for both Langmuir and Freundlich, all the metal ions were best fitted for Freundlich isotherm. The value of n for all metal ions was below 10, indicating favourable adsorption. However, the results were in agreement with both isotherms, where the R^2 values for all cases were close to unity, although the metal ions from river water were adsorbed more through hetero layer mechanism.

For model solutions of different concentration for mixed and single ionic atmosphere, results of q_{max} Langmuir constants showed that the trend of biosorption for single metal ions at low concentrations was: Mn > Fe >Zn > Cu. While the trend at high initial concentration, was: Mn > Fe> Cu > Zn. For mixed metal ions at higher initial concentration, the trend of adsorption in terms of q_{max} was, Mn = Fe > Cu > Zn. Comparing values of n, using the Freundlich isotherm, the preference for sorption of the metal ions low concentration was Fe > Zn > Cu > Mn (single), Fe > Cu=Zn >Mn (mixed) while high concentration followed the trend Cu > Fe > Mn > Zn (single) and Zn > Fe > Cu > Mn (high). Their R^2 for the four systems were all close to unity, indicating that the mechanism of adsorption could also be hetero layer apart from Fe^{2+} when mixed low where its R^2 value was very low probably due to desorption. Comparing R^2 for Langmuir, Freundlich, pseudo first and second order kinetics and inter-particle diffusion models, the biosorption of the metal ions in the model solutions at different concentrations using dry arrowroots were best described by the Langmuir model, indicating that the mechanism of adsorption was on the surface.

Live arrowroots effectively removed Zn, Cu, Fe and Mn from both raw untreated municipal waste water and from already naturally treated waste water effluents from maturation ponds. The following % removal rates were established. For unplanted ponds, the % removal efficiencies ranged between 9% - 48%. For raw wastewater influent, the % removal efficiencies using arrowroots varied from 50% - 98%. Arrowroots also effectively lowered the levels of the metal ions from the already treated wastewater effluents from maturation ponds to minimal levels recommended for final discharge into surface waters such as rivers and streams over about 50% removal rates, suggesting that arrowroots could be of significant benefit, providing a tertiary wastewater treatment alternative. High RTEI for Zn and Cu implied a strong benefit in terms of removal efficiency of these metal ions while Mn and Fe had lower RTEI implying less benefit or lower removal efficiency with live arrowroots. A paired t- test showed that the alpha level was below 0.05 at 5 % confidence level ($p < 0.002$) and hence rejecting the null hypothesis at 5 % significant level. Thus, arrowroots can significantly be used to remove metal ions from municipal waste waters. Comparing metal removal efficiency using dried arrowroot biomass with live arrowroots, dried arrowroot biomass works well with wastewaters containing high concentration levels of the pollutants such as in the influents of municipal wastewater or industrial effluents containing very high concentration of the metal ions while live arrowroots shows higher removal efficiencies in wastewaters with relatively low levels of the metal pollutants such as final effluents of municipal wastewater or river water.

5.2 Recommendations

1. Treatment of the water from Malakisi river is required before being used for drinking. Coagulation of the river water by adding alum is recommended to remove turbidity followed by chlorination or boiling in order to remove coliforms.
2. Creation of buffer zones along the river systems is recommended to allow growth of river line vegetation such as arrowroots which can take up some of the pollutants and hence reduce water quality degradation and restore quality of the water.

3. Monitoring of the pollution levels in the river should be done continuously in order to follow up properly the pollution parameters so as to enable the right action to be taken at the right time.
4. The farmers within the catchment area of the Malakisi river should be advised on the required amounts of agrochemicals to be applied to their farms so that very little or none of the chemicals find their way into the river by runoff. Education on various methods of preventing soil erosion will also be important.
5. Arrowroots are recommended to be used for reduction of heavy metals in wastewater from industries such as refinery process waste waters, metallurgic waters, sugar, coffee and textile factory process wastewaters, agricultural drainage, animal wastes and municipal waste.
6. Treatment plants such as Eldoret water and sanitation company (Eldowas) that have large parcels of land are recommended to use arrowroots in tertiary ponds of wastewater in addition to natural unplanted biological ponds.
7. Further research should be carried out to study the adsorption efficiency of other metals, organic pollutants, phosphates, nitrates and other pollutants using arrowroots.
8. Further research should be carried out on other plants to study their adsorption efficiency with respect to removal of pollutants from wastewater.

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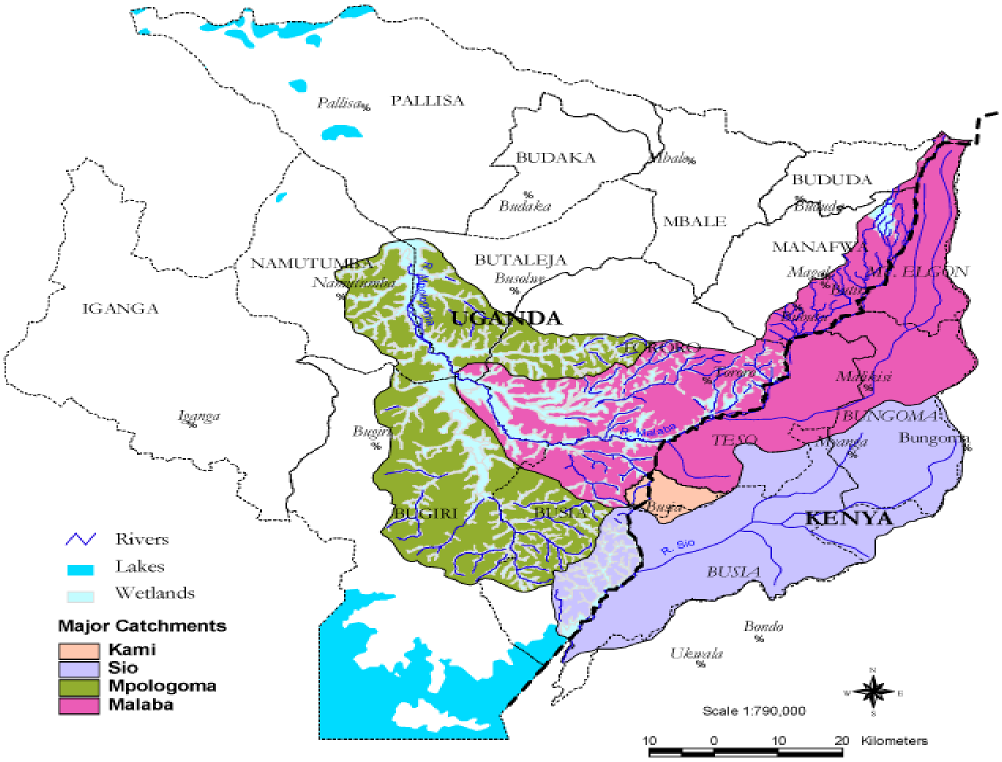
APPENDICES

Appendix I: The Malakisi-Malaba river profile



Source: Author (NBI 2011).

The Malakisi river

Source: Author (2014).

Domestic water use from the Malakisi river

Source: Author (2014).

Domestic and drinking water use from the Malakisi river

Source: Author (2014)

Appendix II: Water sampling and analysis

Sampling water from the Malakisi River in order to establish its quality

Source: Author (2014).

Sampling of municipal wastewater to establish its quality

Source: Author (2014).

Sampling of waste water influent to be treated with arrowroot

Source: Author (2014).

Analyzing levels of pollutants from river, untreated wastewater and treated wastewater using UV Spectrophotometer at Eldowas Company LTD

Source: Author (2014).

Appendix III : The Arrowroots

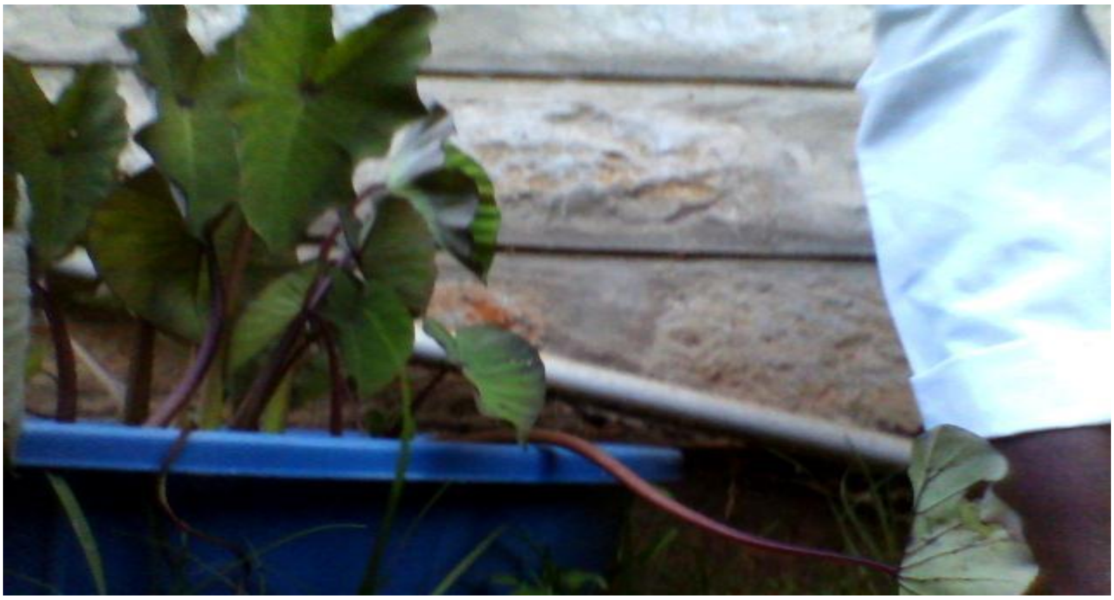
Source: Author (2014).

The mature arrowroots ready for harvest

Source: Author (2014).

Shoots of harvested arrowroots replanted for root formation

Source: Author (2014).



Replanted arrowroot shoots after harvest in distilled water to promote root Formation.

Source: Author (2014).

Arrowroots with large biomass roots

Source: Author (2014).

Influent of raw municipal wastewater treated with arrowroots

Source: Author (2014).

Clean wastewater for final concentration measurement of the pollutants after one week of treatment of raw influent of municipal wastewater with arrowroots

Source: Author (2014).