DETERMINATION AND REMOVAL OF SELECTED HEAVY METALS IN TREATED WASTEWATER FROM RUAI SEWAGE TREATMENT PLANT FOR POSSIBLE AGRICULTURAL APPLICATIONS

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DECLARATION AND RECOMMENDATION

Declaration

This thesis is my original work and has not been presented for an award of diploma or conferment of degree in this or any other University

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Recommendation

This thesis has been examined, passed and submitted with our approval as University supervisors.

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DEDICATION

I dedicate this work to my husband Andrew Kulumba, my kids Naomi and Faith and to my dear parents Mr. and Mrs. Kakuta.

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ABSTRACT

Fresh water has become scarce and many arid and semi-arid regions in the world suffers from water shortage. Wastewater reuse remains the only reliable and potential source of water. One of the major challenges in recycling of wastewater is the presence of toxic heavy metals which are persistent and non-biodegradable and are known to affect human health. This study sought to synthesize and characterize soda lime and borosilicate waste glass and a composite of Multi-walled Carbon Nanotubes (MWCNTs)/soda lime waste glass adsorbents and utilize them for removal of Pb^{2+} from wastewater. Glass wastes were collected within Chuka University and MWCNTs purchased from Hongwu International Group Ltd. The adsorbents were washed, dried, functionalized with nitric-sulfuric acid mixture and characterized using FTIR. Wastewater samples were collected in Ruai wastewater treatment plant, Kenya using grab method, transferred to 250 ml plastic bottles and were transported to Chuka university for analysis in a cooler box at 4^{o}C. Standard laboratory procedures of determining the physicochemical parameters were employed. Batch adsorption experiments were conducted to study the effect of contact time, pH, temperature, shaking speed, initial adsorbate concentration and adsorbents dosage on removal of lead (II) ions. Residual Pb^{2+} concentration was determined using AAS. The findings were: pH 5.5-7.9, Temperature 22.7^{0}C-26.1^{0}C, Conductivity 526.7- 1209.7µS, turbidity 73-1000 NTU, nitrates 6.66-25.1 mg/l, Phosphorus 1.16-10.30 mg/l, BOD_5 ranged from 10-480 mg/L, COD 90-980 mg/L, TSS 14-422 mg/L, and TDS 244-967 mg/L. pH, temperature, NO_3^-, BOD_5(wet season) results met the WHO and NEMA standards for wastewater reuse in irrigation while EC, turbidity, P, COD, BOD_5(dry season), TDS and TSS did not. The results of heavy metals were Ni 0.02-0.22 mg/L, Zn 0.03-1.67 mg/L, Cu 0.01-0.23 mg/L, Cd 0.01-0.05 mg/L, Fe 0.05-7.24 mg/L, Mn 0.14-2.26 mg/L, and Pb 0.04-0.78 mg/L. The levels of Zn, Cu, and Ni were within WHO and NEMA standards while Cd, Mn, Pb and Fe did not meet the threshold at some sampling points. All the metals studied met the FAO guidelines for reuse of wastewater in irrigation. Characterization of the adsorbents was done using FTIR which displayed the dominant functional groups to be silanols, hydroxyls, carboxylic and carbonyl groups. Adsorption of lead (II) ions was conducted using a composite of soda lime waste glass and multiwalled carbon nanotubes, borosilicate and soda lime waste glass. The composite and borosilicate adsorbents reported 100% adsorption of lead (II) ions while soda lime was average. Adsorption of Pb (II) ions followed Freundlich isotherms for borosilicate and soda lime adsorbents with r^2 of 0.8665 and 0.9257 while Composite had a better fit in Langmuir isotherm with r^2 of 0.9446. Cd (II) and Ni (II) ions did not interfere with adsorption of lead (II), but a stiff competition for the adsorption sites was observed for the case of Mn (II) ions. Regeneration efficiencies of 99.61%, 97.45%, and 99.82% were observed for borosilicate, soda lime, and composite adsorbents. The findings of this study clearly showed that soda lime waste, borosilicate waste glass and composite of soda lime waste glass/MWCNTs are effective for the removal of lead (II) ions from waste water.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic absorption spectrophotometry
ANOVA	Analysis of variance
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
FAO	Food and Agriculture Organization
FTIR	Fourier transform infrared spectrophotometry
ICPMS	Inductively coupled plasma mass spectrophotometry
MWCNTs	Multiwalled carbon nanotubes
NEMA	National Environmental Management Agency
NPK	Nitrogen, Phosphorus and Potassium
Rpm	Revolutions per minute
SAS	Scientific Analysis System
TDS	Total dissolved solids
TSS	Total suspended solids
WHO	World health organization
WSP	wastewater stabilization ponds

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Water is an important natural resource as it supports life development and human activities. In entire planet, fresh water forms only 3% and the remaining 97% is salty. About 70% of the planets freshwater is found in Greenland and icecaps and the rest is found deep underground (Ashraf *et al*., 2018). Nearly one billion population in developing nations do not have access to fresh water (Justo, 2015). According to Meng *et al.* (2016), increased urbanization, socio-economic development and the increasing population in recent years have led to scarcity of fresh water resources to satisfy the daily mankind demands in terms of industrial, urban uses and agricultural purposes. Water scarcity is expected to rise to 15% by 2030, causing water shortages in countries where water is scarce, such as North Africa and Middle East region (Hashem & Qi, 2021). Furthermore, Rizzo *et al.* (2020), stated that by 2025, approximately 1.8 billion people in the world will live in a location with water scarcity.

This water shortage is rapidly increasing in arid and semi -arid areas because of uneven distribution of water resources and high competition for water demand in different sectors. Land irrigation is the largest consumer of freshwater and accounts for about 80% of worldwide freshwater utilization (Calzadilla *et al*., 2011). This increased water scarcity calls for better management schemes of water resources in semi-arid regions through enhancing water usage efficiency or even utilizing the available poor-quality water. In this regard, the escalating volumes of waste and sewage water produced by commercial, domestic, and industrial sources are mostly used for peri-urban and urban agriculture (Seenivasan *et al.,* 2015).

Due to increased unemployment and rapid urbanization in developing nations people are adopting urban farming to fill the gap of the continuous demand of fresh produce (Njuguna *et al.,* 2019). Thus, overwhelming pressure is exerted on these declining water resources. The use of wastewater for cultivation lowers freshwater demands, recycles nutrients such as potassium and phosphorus to the soil, helps in conservation of water and reduces the pollution of surface water (Galal *et al.,* 2018). The presence of large amounts of nutrients in treated wastewater increases crop production, limits the use of fertilizer, boosts soil fertility and minimizes the cost of production (Jeong *et al.,* 2016).

The use of treated wastewater for agricultural applications is encouraged for those nations suffering from water shortages due to large amounts of effluents produced. For example, China is the leading nation in wastewater production with about 68.5 billion tons of wastewater yearly and this water is treated and recycled back for agricultural use. Many low income nations such as Saudi Arabia and Tunisia utilize treated wastewater for farming to curb the water crisis (Jeuland, 2015). In Egypt approximately 5 billion M^3 of sewage effluent is generated annually and this water is recycled back for agricultural purposes (Hashem & Qi, 2021). However, the recycled water, specifically untreated or inadequately treated wastewater, might pose significant health and environmental dangers due to microbial and chemical contaminants present in it (Becerra-Castro *et al.*, 2015).

Heavy metals such as Cu, Mn, Pb, Ni, Fe, Cd, and Zn are present in wastewater; through industrial effluent, urban wastewater, and domestic sewage. Copper (Cu) and zinc (Zn) commonly come from plumbing and metal manufacturing plants while manganese (Mn) from mining and leaching of soils. The risk of Lead (Pb) contamination is noticeable with old piping systems, battery industries, and paint industries (Rai *et al.,* 2019). While Nickel (Ni) may come from electroplating, stainless steel production, and battery casing waste, iron (Fe) may originate from corrosion and erosion, mining, and decreased steel production. Cadmium (Cd) is frequently emitted from batteries, plastics, and electroplating industries. Altogether, these metals are hazardous to both marine life and human beings when they are released in high levels in the wastewater (Paul *et al.,* 2012).

These heavy metals are non-biodegradable, and have a long half-life, thus able to remain in the body for a long time posing health risks to the organism (Mitra *et al.,* 2022). The utilization of wastewater for irrigation introduces these toxic elements into the soil and they enter the food chain through consumption of crops irrigated with wastewater or direct inhalation of dust from soils contaminated with heavy metals (Mehmood *et al.,* 2019). For example, a study conducted by Chaoua *et al.,* (2019), in

Marrakech region of Morocco on the levels of heavy metals in soil and crops irrigated with wastewater, showed that the daily intake of Pb and Cd was above the permissible levels thus posing a potential health risk to both humans and animals.

Cu, Mn, Pb, Ni, Fe, Cd and Zn are high-risk health metals that are dangerous when ingested or inhaled at high concentrations. Lead (Pb) is the most toxic heavy metal that effects neurotoxicity, developmental disorders and renal toxicity particularly in children (WHO, 2023). Cadmium (Cd) is acknowledged to be nephrotoxic, causing bone abnormalities, as well as a human carcinogen (Nordberg & Fowler, 2015). Nickel (Ni) can cause skin allergy, respiratory problems, and lung cancer in case of long-term exposure (Genchi *et al.*, 2020). Copper and Iron are micro nutrients that can cause harm to the body when taken in large quantities; they cause gastrointestinal discomfort and harm to the liver and kidneys (Silva *et al.*, 2019). Too much Zinc (Zn) can lead to vomiting and nausea and inhibit the assimilation of other nutrients in the body. Neurological effects have been associated with manganese, with symptoms similar to those of Parkinson's disease being exhibited in workers exposed to high levels of this metal (Bartzatt, 2017).

Apart from heavy metals pollution, water is contaminated by high levels of organic materials. The organic material contamination in wastewater is assessed by the ratio of Chemical oxygen demand to biological oxygen demand levels which indicates the extent of pollution of wastewater. COD to BOD levels are monitored for both influent and effluent wastewaters, to ensure environmental protection and assess the effectiveness of a treatment plant (Alam, 2015). If the proportion of BOD to COD is 0.5 and higher the wastewater is considered to be treatable by biological ways such as aerobic, and anaerobic processes (Alsaqqar *et al.*, 2014). High levels of organic matter in wastewater decomposes in soil by biological means to produce carbon dioxide, water and nutrients. Carbon dioxide dissolves in water to form carbonic acid which acts as cation in leaching of organic matter in soil. Large amounts of carbon dioxide in soil increases the number of fungi, which decomposes the organic wastes and regulates nutrients in soil (Fazi *et al.*, 2019). If the ratio of BOD to COD is lower than 0.3 the wastewater is considered to have toxic components that inhibits degradation (Abdalla & Hammam, 2014). Presence of toxic components in wastewater has significant effects on the proportion of BOD to COD depending on the concentration and nature of the toxicant. Large quantities of toxic heavy metals decrease the biodegradation of organic matter by impacting both ecology and physiology of the microorganisms that degrades organic wastes. The proportion of BOD to COD levels can be elevated by reducing the concentration of heavy metals in the wastewater (Andrio *et al.,* 2019).

Ruai sewage treatment plant is the largest in Kenya, and processes 80,000m^3/day of wastewater produced in Nairobi city using the wastewater stabilization ponds (WSP). The WSP systems is one of the potential lower-cost treatment systems utilized extensively in mid-income nations (Maina *et al.,* 2020). It has the ability to create effluent that fulfills the WHO guidelines for wastewater reuse in irrigation purposes. Ruai sewage treatment plant releases its effluent into Nairobi river and the communities around utilize this effluent directly or indirectly in unregulated ways for sustaining their livelihoods without considering its quality status (Maina *et al*., 2020).

A recent study conducted by Maina *et al,* (2020) showed that the levels of Cd, Cu, Ni, Fe, Cr, and Mn were within the NEMAs permissible limits while lead was very high with a concentration of 0.158mg/l as compared to 0.1 mg/l NEMA standard. The levels of lead thus restrict the use of this effluent in agricultural purposes due to its toxicity. The levels of phosphates, chlorides and total solids were within the standards except for nitrates 42.0 mg/l, BOD 80 mg/l and COD 278 mg/l as compared to 10.0 mg/l, 30 mg/l, and 50 mg/l respectively recommended by NEMA (Maina *et al.,* 2020). Crops require macro-nutrients like phosphorus, potassium, and nitrogen in large amounts for their healthy growth. However, the exceedingly high amounts of these macronutrients lead to decreased growth. Other elements like zinc, copper, iron, chlorine, molybdenum and boron are required in small amount by crops. The surplus amounts of these micro-nutrients lead to premature leaf falls, uneven distribution of chlorophyll and can be toxic to the plants. The deficiencies of these micronutrients results in leaf discoloration and necrosis (Toor *et al.,* 2021).

In another study conducted by Uzel (2015), on the levels of heavy metals on vegetables irrigated with effluent from Ruai showed a high concentration of lead (2.8-5.1 ppm) while the concentration of other heavy metals were insignificant. A study carried out by Mbugua (2015), at Ruai sewage treatment plant showed that the concentration of Zn (1582.82 mg/l), Cu (1319.9 mg/l), Cd (8.92 mg/l), and Ni (116.8 mg/l) in the anaerobic ponds were within the limits recommended by European Union while lead showed a high concentration of 3464.3 mg/l as compared to the 1200mg/l EU standard. All the current studies show that the levels of lead in the plant are above the NEMA, EU and WHO limits which is a rising concern and it restricts the use of the waste waters for use in agricultural purposes. This calls for research on the appropriate and cost -effective method for the remediation of heavy metals in the wastewater.

Many nations have enacted more stringent measures to combat water contamination (Tortajada & Joshi, 2014). The efficient removal of heavy metal ions from wastewater has become a major concern nowadays (Zhao *et al.*, 2016). For the elimination of toxic metals from water, precipitation succeeded by coagulation has been widely used (Vidu *et al.*, 2020). This method, however, frequently results in enormous quantities of sludge containing only minor concentrations of heavy metals (Qasem *et al.*, 2021). Membrane filtration is a well-established method for removing metal ions, but its expensive cost prevents it from being widely used (Cevallos-Mendoza *et al.*, 2022). Adsorption is a good way to get tracer components out of water and the mostly used adsorbent is activated carbon, which is made by carbonizing organic materials. Metal ion adsorption capacities have been demonstrated by activated carbon but the high expense of the activation process, on the other hand, restricts its application in wastewater treatment (Salam *et al.*, 2011).

Recent studies have concentrated on developing of a low-cost method of remediating heavy metals through adsorption using the widely available raw materials. Some of these raw materials are rice husks which has shown great efficiency in removal of Cd (II), Cu (II), Cr (VI), Pb (II), Zn (II) and As (III) with adsorption capacities between 72.80 and 99.12 percent (Barrero-Moreno *et al.*, 2021). Fern (Joseph *et al.*, 2019), sugarcane bagasse (Iwuozor *et al.*, 2021), maize bran (Thaçi & Gashi, 2019), grape stem waste (Schwantes *et al.*, 2018), modified egg shell (Alamillo-López *et al.*, 2020) have also been used in heavy metal removal. Tea waste showed ability to remediate copper (77%) and lead (94%) and the percent removal increased with increase in adsorbent dose (Thakur & Parmar, 2013). A study carried out by Meez *et al.* (2021), showed that saw dust has ability to remediate Pb (76%), Ni (73%), Cr (68%), and Cu (65%), however the increase in adsorbent dose and contact time led to a maximum adsorption 96%, 94%, 89% and 97% respectively. In a study conducted by Ibrahim *et al.,* (2012), recycled waste glass (RWG) was effective in remediation of Cd (6.29ppm), Cu (6.68ppm), and Pb (11.68ppm). Recycled Waste Glass modified with sodium hydroxide was used as adsorbent in removing Cr, Pb, Cu, Zn, Ni, and Cd and the efficiencies were 81%, 53%, 37%, 52%, 47% and 89% respectively at a pH range of 4.5-6.2 (Catalfamo *et al.,* 2006).

In most industrialized nations, reusing huge volumes of discarded glass from municipal solid waste (MSW) sorting facilities is an issue and has led to accumulation of glass wastes (Abdel-Shafy & Mansour, 2018). Glass is a versatile material because of its safe and long-lasting usage, and it may be recycled for the same purpose or others if few alterations are made to it. Despite this, glass is still thrown in landfills, resulting in long-term buildup in the environment because of its bio-refractory and chemical inertia (USEPA, 2018). Recycling of glass help to minimize wastes and increase interest in recovery operations, as required by current legislation (Petrella *et al.,* 2012).

Some of the common approaches to the elimination of heavy metals from wastewater involve chemical precipitation, adsorption, ion exchange, coagulation/flocculation, and membranes. The chemical precipitation is one of the most used methods, which involves precipitation of metals as insoluble compounds by the help of agents like lime or sulfides. Its main advantage is that it is relatively simple and inexpensive to operate for handling a massive amount of wastewater. But it produces a large volume of sludge, which has to be treated and disposed of, and this leads to environmental issues (Fu & Wang, 2011). Adsorption, for example, by using activated carbon or biochar is suitable for removing low concentrations of metals and is relatively cheap. However, its disadvantage is that it only adverts the adsorbent material to its saturation level where regeneration or replacement is necessary and the efficiency of the process highly depends on the type of adsorbent material that is used (Kırbıyık *et al.,* 2016).

Another method is ion exchange whereby salts containing heavy metals are exchanged with harmless ions by passing through resins. It is useful in large volumes of wastewaters with high removal efficiency but poses limitations such as the expense of resins and the difficulty in regenerating them. Methods like reverse osmosis or nanofiltration can effectively filter out heavy metals and other impurities from the water. Its main strength includes the capability for attaining a high level of separation of metals wherein the negative factors include high energy consumption problems like membrane fouling, and frequent need for repair and renewal (Barakat, 2011). On balance, even those traditional techniques that are efficient, many of them involve a compromise between costs, energy, and environmental concerns.

Conventional adsorbents are used to remove the heavy metals from wastewater but their low efficiencies and sorption capacities limit their use (Kumar, 2021). Currently, nanomaterials are being used as the new adsorbents for toxic metals from wastewaters to overcome the challenge of using conventional adsorbents (Sadegh *et al.,* 2017). Carbon based nanomaterials having graphene oxide, fullerenes and carbon nanotubes have been widely used for removal of heavy metals from wastewater because of their non-toxic nature and high sorption capacity (Kumar, 2021). The use of carbon nanotubes (CNTs) have become the main focus of research in nanotechnology due to their unique physicochemical properties (Griger *et al.,* 2022). CNTs have large surface area between 150-1500m^2/g and they can be functionalized to improve their adsorption capacity for heavy metals (Baby *et al.*, 2019). The adsorption of heavy metals on carbon nanotubes depends on the electrochemical potential, surface feature and ion exchange capacity (Yang *et al.,* 2019). Acidified functionalized Multiwalled carbon nanotubes with a large surface area of 194m^2g^{-1} were used to remove copper, cadmium, lead and nickel and the efficiencies were 78%, 15%, 93% and 83% respectively (Farghali *et al.,* 2017). In this study adsorption of heavy metals on modified glass wastes and a composite will be studied.

1.2 Statement of the Problem

Nairobi is a fast-growing city in terms of industrialization. The increased number of production industries, textile, paints, and iron industries, garages and petroleum depots have elevated the environmental and water pollution. The industrial effluents and by-products from these industries are channeled to the sewer systems and water bodies. The recent studies have shown presence of heavy metals in Ruai wastewater treatment plant effluent. The plant utilizes wastewater stabilization ponds (WSP) method in wastewater treatment which removes pathogens and reduces organic matter, but do not remove the heavy metals implying that they are able to go through all the treatment cycles and find their way into the environment. This plant processes 90% of Nairobi wastewater and this treated wastewater is released to Nairobi River as a waste. The area surrounding the treatment facility is a semi-arid region, and farmers in the lower part of the plant have inadequate water for farming and they utilize this water released from the plant for irrigation of food crops and herders graze their cattle in the plant vicinity. Determination of heavy metals present in Ruai sewage treatment plant is necessary because the water is being used for irrigation purposes and if the micro pollutants are present, they might find their way through food chain into living beings if left to accumulate. This might cause serious problems since some of them if present are hazardous even at minute amounts.

1.3 Objectives

1.3.1 General Objectives

To determine and remove selected heavy metals in treated wastewater from Ruai sewage treatment plant for possible agricultural applications

1.3.2 Specific Objectives

i. To determine the levels of Pb, Cd, Mn, Ni, Fe, Cu, Zn and physicochemical parameters in Ruai wastewater treatment plant.
ii. To synthesize and characterize modified waste glass and waste glass/MWCNTs composite.
iii. To determine the adsorption parameters and interference of the selected heavy metals on the modified waste glass and waste glass/MWCNTs composite.
iv. To determine the regeneration ability of the adsorbents.

1.4 Hypotheses

$H0_1$: There is no statistical significant difference in the levels of Pb, Cd, Mn, Ni, Fe, Cu, Zn and physicochemical parameters in treated wastewater of Ruai wastewater treatment plant.

$H0_2$: There is no significance difference on the functional groups of the synthesized and characterized modified waste glass and waste glass/MWCNTs composite.

$H0_3$: There is no significance difference in the adsorption parameters and interference of the selected heavy metals on the modified waste glass and waste glass/MWCNTs composite.

$H0_4$: There is no statistical significant difference in the regeneration ability of the modified waste glass and a composite of waste glass/MWCNTs.

1.5 Significance of the Study

This study will provide information on the levels of heavy metals in Ruai waste water treatment plant. It also seeks to provide information on the efficiency of heavy metals remediation by adsorption technique using waste glass and a composite of glass wastes and MWCNTs. The data obtained will be essential to the government as it can employ this remediation technique to minimize the heavy metals accumulation in water and environment. Since fertilizers have become expensive the remediated treated sewage wastewater will be of much benefit to farmers because it recycles the nutrients into the soil.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Human anthropogenic activities and technological advancement has resulted to increased production of new chemicals which are released to the surrounding. These chemicals enter the water cycle through industrial discharge, wastewater treatment facilities or diffuse sources like runoff of agricultural waste, fertilizers, and sea and railway accidents involving huge amounts of oil carriers (Geissen *et al.,* 2015). Recently, wastewaters from industries, agriculture and homes have been observed to have emerging pollutants which have the potential to harm the environment and human health (Ahmed *et al.,* 2021). Emerging contaminants are synthetic and natural chemicals that have been detected at trace levels in water. Growth disorders, immune dysfunction and endocrine disruption are some of the effects of acute and chronic exposure caused by these chemicals (Janna, 2011). Emerging contaminants have been classified into three; pharmaceuticals and personal care products, disinfection by-products and persistent organics and inorganics (Richardson & Kimura, 2016; Pontoni, 2016).

Heavy metals, and pesticides are the priority contaminants although they are largely regulated in developed countries and well known, they are emerging because their evolution is not known even at small amounts once released into the environment (Pontoni, 2016). Inorganic pesticides are mostly used as rodenticides, insecticides and fungicides, they find their way into the treatment facilities through rain runoffs. These pesticides are non-biodegradable unlike organic pesticides thus they increase the inorganic pollutants in wastewater (Hassan, 2019). ECs shows up in distinct matrices depending on their qualities and the receptor body features. Pollutants of diffuse sources reaches the receptor body based on their physico-chemical features and the matrix properties with which they interact (Durães *et al.,* 2018). As a result, generalizing their environmental behavior and their love for roots and soils is not possible. Furthermore, because of the evident changes in operating conditions and loads the concentration level would probably vary from one treatment facility to the next. Different kinds of soils have shown wide variation in their affinity for pollutants, making it difficult to assess potential risks associated with the discharge of such contaminants into the environment, and in particular, the reuse of wastewater in cultivation, is a hard task that necessitates a thorough understanding of water/soil adsorption and release equilibria (Janna, 2011).

On the other hand, because the concentrations of these pollutants are usually very low, down to ultra-trace, and trace levels, simple monitoring of these pollutants needs advanced, and sometimes expensive analytical procedures (Komolafe *et al.,* 2021). Atomic absorption spectrometry is the most widely used technique in elemental analysis, but its precision is low as compared to inductively coupled plasma techniques and graphite furnace atomic absorption spectrophotometry. Inductively coupled plasma mass spectrometry (ICPMS) has higher detection limit as compared to other elemental analysis techniques and can be used in multielemental analysis (Balcaen *et al.,* 2015). The results of a comparison study of ICPMS and AAS on detection of mercury, lead and cadmium on blood samples showed that ICPMS has higher detection limit with 0.05, 0.09, 0.17 $\mu g dl^{-1}$ for Pb, Cd and Hg respectively with a dilution factor of 50, while for AAS the following concentrations were obtained 1, 0.54, and 0.6 $\mu g dl^{-1}$ for Pb, Cd and Hg respectively (Palmer *et al.,* 2006). Use of a low precision technique might lead to false inference that some contaminants are not present in water bodies. ICPMS will be used in determination of the levels of heavy metals in this study since some of them might not be detected using AAS.

2.2 Wastewater Components

2.2.1 Heavy Metal Pollutants

Heavy metals pollution are of primary concern in treatment facilities since they can build up in crops and soils irrigated with wastewater and have significant effect to living things (Chaoua *et al.,* 2019). These elements have variety of features in soil, in terms of their bioavailability, leaching losses, mobility and uptake by plants and build up in the soil over the period the wastewater is used for irrigation (Lone *et al*., 2013). Some of the heavy metals that are mainly present in industrial wastewaters are chromium, lead, arsenic, nickel and cadmium and others such as zinc, and copper are important to humans as they maintain body metabolism but at higher levels, they become toxic. Lead induces serious bone marrow dysfunction and damages liver and kidneys, neurological system, circulatory system, as well as other organs (Assi *et al.,* 2016). It has also shown substantial inhibitory effect on root elongation, transpiration, seed germination, chlorophyll production, plant growth, and seedling development (Pourrut *et al.*, 2011). The health effects linked to chromium(VI) are liver and kidney damage, ulcers, respiratory issues, impaired immune systems, genetic material alteration, lung cancer, dermatitis, irritation, and death (Achmad & Auerkari, 2017). High levels of Cd in human body increases risk of cancer in lungs, breast, prostate and kidney (Mbugua, 2015). Long term exposure to nickel and its compounds in the body has been linked to a number of negative health effects in humans, including cancer of the respiratory tract, and cardiovascular illness, lung fibrosis and kidney (Das *et al.*, 2019).

Heavy metals removal is largely considered in the recycling of treated urban wastewaters. Many wastewater treatment plants are not designed to remove these elements because the removal method of heavy metals should be specific to certain industrial wastewater (Fu & Wang, 2011b). Several research investigations have addressed the distribution of heavy metals in conventional biological wastewater treatment. Shikuku and Achieng (2017), studied the distribution and removal heavy metals by conventional activated sludge at a treatment plant in Kisumu and found that the levels of Cu, Zn, Pb, Fe, Mn and Mg were higher in the influent and lower in the treated effluent, but the sludge sediments had higher levels of the metal ions.

The metal ions dissolution and biosorption in the sludge decreased their concentration in the wastewater. A study conducted in Thessaloniki, Greece on metal fraction in different phases of activated sludge plant revealed Mn and Ni were present in the dissolved phase of wastewater while Pb, Zn, Cr, Cu and Cd were associated with the particulate phase and removed in primary sedimentation. The individual heavy metals distribution in the sludge and treated effluent revealed that about 70% of Cu and Mn accumulated in the sludge while 47-63% of Cr, Fe, Zn, Pb, Ni and Cd remained in the treated wastewater (Sharifuzzaman *et al.,* 2016). Complete removal of heavy metals requires advanced tertiary treatment, which is scarcely applicable in large scale and even less in developing nations (Shikuku &Achieng, 2017).

2.2.2 Oxygen Demanding Wastes

Organic compounds are made up of carbon-based compounds, which are the fundamental building blocks of all living organisms and can be found in almost any environment. Paper goods, detergents, Humans wastes, agricultural products and cosmetics all contain organic materials that come from animals, manufactured organic compounds and plants (Zheng *et al.,* 2013). Receiving waterways can be harmed by too much organic debris in wastewater. High levels of biodegradable substances are harmful to water bodies because organisms utilize the DO in water to break-down the wastes. This limits or depletes the oxygen supply in the water that aquatic life need, leading to death of fish, smells, and decrease in water quality (Chen *et al.,* 2010).

2.2.2.1 Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD)

Chemical Oxygen Demand is a helpful measure of water quality as it determines the quantity of organic contaminants contained in surface water as well as wastewater. COD is frequently used as a quick indication of organic contaminants in water and provides information of the treatment process's effectiveness. COD levels are assessed in both the effluent and influent water (Alam, 2015). BOD is the quantity of dissolved oxygen required by aerobic biological organisms in a water body to break down the organic matter present in a given water sample at a particular temperature during a certain time period. The BOD test determines the biodegradable component of wastewater by tracking the absorption of organic material by aerobic microorganisms for 5 days under highly regulated circumstances (Khan *et al.,* 2011). BOD: COD ratio is a good indicator of the quantity of biodegradable organic compounds in wastewater (Abdalla & Hammam, 2014). Based on the water being tested, the ratio ranges from 1:1.25 to 1:2.50 and it rises with each level of biochemical treatment as biodegradable matter is eaten while non-biodegradable organic matter persists and gets oxidized in the COD. The association is generally constant for particular wastes; however, it is substantially less when the COD levels are 100mg O_2/l (Kasima, 2014).

2.2.3 Nutrients

High levels of nitrogen, and phosphorus, in the form of nitrate and phosphate, are frequently found in wastewater, both of which encourage plant development. There is an oversupply of accessible nutrients in treated wastewater after biological treatment (Tymchuk *et al.,* 2020). Excess nitrogen and phosphorus can cause eutrophication, which is the nutrient enrichment of water bodies that cause enormous aquatic plant growth (Kim *et al.,* 2008).

2.2.3.1 Phosphorus

Phosphorus can be found in a variety of forms in wastewaters, including the soluble orthophosphate ion (PO_4^{3-}), various phosphorus-oxygen complexes and organically bound phosphate. Excreta and foods residue account for the majority of the organically bound phosphate in wastewater. Phosphorus related to non-biodegradable fraction of algal cells remains immobilized in the sediments as organic phosphate precipitates as algal biomass. Hence, increasing the number of facultative ponds in WSP is one strategy to boost phosphorus removal (Walsh *et al.*, 2012). Phosphorus in all living tissue, including vegetable and animal, is eventually oxidized to phosphates. The phosphorus removal mechanism takes place in maturation ponds. Anaerobic treatment, on the other hand, maintains more nutrients (NPK) in the effluent, meaning that it has a greater potential for irrigation (Kasima, 2014).

2.2.3.2 Nitrogen

Ammonium (NH_4^+), organic nitrogen, nitrogen gas, nitrate (NO_3^-), and nitrite (NO_2), are all major nitrogen types in wastewater (N_2). Biochemically, all of these types are interchangeable. Presence of nitrites in wastewater increases the disinfection costs because they are oxidized by chlorine as a result increasing the chlorine dosage in water (Rezvani *et al.*, 2017). Nitrate is readily available to plants and is the limiting nutrient for primary productivity in saline waters. Since nitrates is a negative ion in solution, it does not bond to negatively charged soils thus nitrate flows through the soil and into groundwater. The primary sources of high levels of nitrates in water bodies are industrial discharges, runoff from animal manure storage areas, Surface runoff from fertilized lawns and farmland which has received too much nitrate fertilizer, and sewage treatment plants (Lwiza, 2016). The permissible limit for nitrates in effluents of wastewater treatment plants is 30 mg/L. The use of treated wastewater in crop irrigation recycles nitrates back to the soil (Hyánková *et al.*, 2021).

2.2.4 Solid Wastes

The primary sources of solid wastes are household trash and rain run-off, forming sludge deposits that cause siltation of water reservoirs and regular treatment plant blockages. Since toxic metals as well as other micro pollutants frequently adsorb onto suspended particles, they tend to build in the sludge (Ouko, 2020).

2.2.4.1 Total Suspended Solids (TSS)

Total Suspended Solids (TSS) are solids suspended in water that are able to be filtered out. TSS can be made up of a wide range of materials, including silt, decomposing plant and animal debris, sewage and industrial waste. Suspended particles absorb heat from the sun, high TSS can induce an increase in surface water temperature. This can result in even lower dissolved oxygen levels (since warmer waters can store less dissolved oxygen) and in turn increase the quantity of organic matter in the wastewater (Miruka, 2016). TSS levels beyond a certain threshold can indicate greater levels of microorganisms, metal ions, or pesticides in the water (Zhang *et al.*, 2017). These contaminants may bind to sediment particles on the ground and be transferred into bodies of water by storm water. Contaminants may be discharged from the sediment or transported further downstream in the water. Because the solids may block or scour pipes and machinery, high TSS can pose difficulties in treatment and plant industrial settings. NEMA specifies 30 mg/L and 250 mg/L as the maximum permitted limits for TSS release into the environment and public wastewater systems, respectively (Kariunga, 2019) .

2.2.4.2 Total Dissolved Solids (TDS)

Total Dissolved Solids is a measurement of the quantity of material dissolved in water. Chloride, magnesium, sulphate, nitrate, phosphate, calcium, and other ions are examples of this substance. Aquatic life requires a particular amount of these ions in the water. Because the density of the water regulates the passage of water into and out of an organism's cells, changes in TDS levels can be hazardous. TDS concentrations that are too big or too small, on the other hand, might inhibit the growth of very many aquatic organisms, and mortality can result. High TDS levels, affects water visibility and contributes to a reduction in photosynthesis. The highest permissible limit for TDS release into the environment and public sewer is 1200 mg/L and 2000 mg/L, respectively, according to NEMA (Kasima, 2014).

2.2.5 Temperature and pH

Temperature of wastewater is essential in biological processes and chemical reactions. Biological treatments decreases in low temperatures and increases in warm temperatures (Alisawi, 2020). At temperatures below 2^oC the biological organisms are denatured and when temperatures increases above 50ºC nitrification and anaerobic digestion stops (Kasima, 2014a). pH has a significant effect on the distribution and migration of metal ions in water. Cadmium speciation varies with change in pH and Cd content of Fe-Mn oxides and carbonates increases with increase in pH from 4.5-9.5 (Zhang *et al.,* 2018). pH affects the adsorption of heavy metals by controlling the solubility of hydroxides, phosphates and carbonates (Caporale & Violante, 2016).

2.3 Use of Carbon Nanotubes as Adsorbents

Carbon has an atomic number of 6 with electronic configuration $1S^2$, $2S^2$, and $2P^2$. Carbon can hybridize in three different forms: sp^3, sp^2 and Sp. Carbon has the capacity to connect in a variety of ways in the sp^2 hybridization, resulting in fascinating structures with unique features. Carbon nanotubes (CNTs) are type of allotropes of carbon with an aromatic surface rounded up to make cylindrical shape that were initially discovered in 1991 (Suliman, 2017). CNTs are classified depending on the number of cylindrical layers present. If a CNT is made of one shell it's referred to as single walled CNT (SWCNTs) and if there are several shells it's termed as multi-walled CNT (MWCNTs). Carbon nanotubes varies in length from 10nm to 10mm, for SWCNTs the diameter varies from 0.7-2.5nm while for MWCNTs it ranges from 4-150nm. CNTs have large surface area, pore diameter and pore size which determines their adsorption capacity.

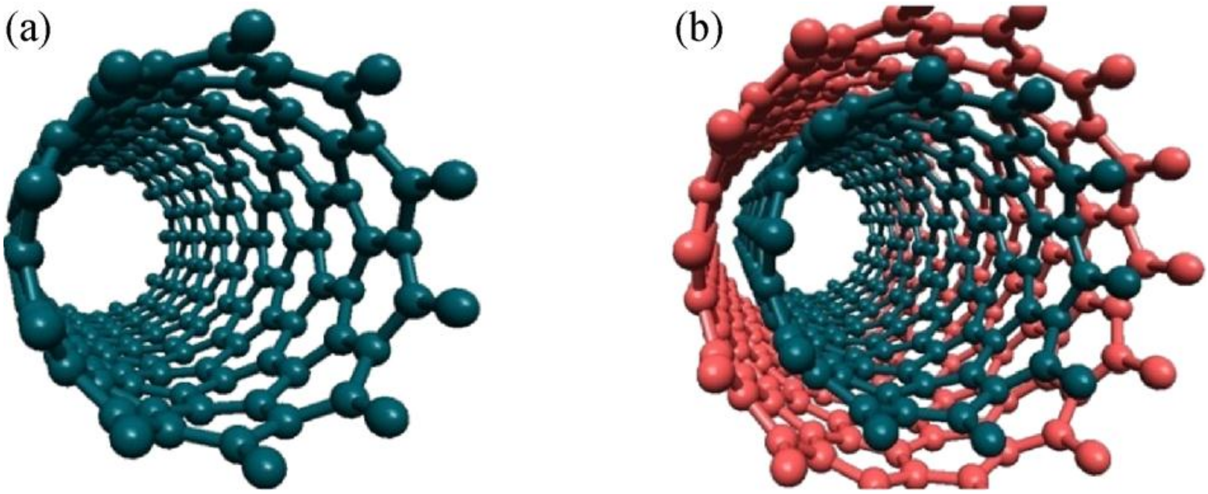

Figure 1(a) SWCNT (b) MWCNT (Ouni et al., 2019)

2.3.1 Synthesis of Carbon Nanotubes

There are many methods that have developed for the production of both SWCNTs and MWCNTs since their discovery. The common ones are laser vaporization, electric arc discharge and chemical vapor deposition.

2.3.1.1 Electric Arc Discharge

In this method a large current of 80-100A is passed between two opposing high purity graphite electrodes with diameter of 6mm-12mm which are separated by an inert gas (helium or argon) maintained at 500-600torr. Helium is mostly used because it gives the greatest results, owing to its high ionization potential (Suliman, 2017). In the process of arcing, molecules of carbon evaporate from the anode and they solidify at the cathode in form of CNTs at a speed of 1mm/min. The arc is a reliable and simple way to generate the huge temperatures ($< 3000^0$C) required to evaporate the carbon atoms into plasma. The production of carbon nanotubes is determined by plasma stability yielded between the electrodes, inert gas pressure, cooling of electrodes and chamber and current density. The arc chamber and well-cooled electrodes help to increase the nanotube production in the process of arc growth (Mubarak *et al.*, 2014). This method is commonly used in the synthesis of MWCNTs which does not require the use of catalyst. The synthesis of SWCNTs requires a metallic catalyst like nickel, cobalt or iron and the final product is purified. This method yields carbon nanotubes of high quality and fewer structural defects as compared to others (Prasek *et al.*, 2011). In this study the electric arc discharge method will be employed in the synthesis of the MWCNTs.

2.3.1.2 Laser ablation

Laser vaporization or laser ablation is the exposure of a graphite target containing a metal catalyst to a high-powered laser in an inert gas environment. This was first done in 1995 by Smalley and collaborates using a process in which high purity, defect free and with the diameter of the nanotube determined by the metal catalyst and laser intensity CNTs were prepared. However, laser vaporization is costly and not very efficient and thus is more useful when it comes to producing pure samples for analytical purposes rather than for commercial purposes (Mubarak *et al.*, 2014).

2.3.1.3 Chemical vapor deposition

chemical vapor deposition (CVD) is widely used because of its applicability, scalability and flexibility in producing Single Walled Carbon Nanotubes (SWCNT) and Multi Walled Carbon Nanotubes (MWCNT). In the CVD process, substrates on which metal catalysts have been deposited are put into a high temperature reaction chamber where hydrocarbon gases undergo decomposition to release carbon atoms that then diffuse to the catalyst particles to form CNTs. CVD is cheap and can be applied at industries for large scale production because it is highly scalable in nature (Prasek *et al.*, 2011). The impurity levels as well as structural defects in CVD synthesis are higher compared to laser vaporization synthesis (Mubarak *et al.,* 2014). The selection of CVD or laser vaporization is based on the requirements of the specific application; laser vaporization can be used for synthesis of high purity targets while CVD is best suited for large-scale production of thin films (Suliman, 2017).

2.3.1.4 Functionalization of Carbon Nanotubes

Carbon nanotubes are mostly used in aqueous environments. CNTs don't have affinity for water and they usually aggregate in aqueous solution because of their high Van der Waals interaction forces along the outer tube. Due to this they are not dispersible in water. Nevertheless, the dispersion of CNTs in aqueous solutions is improved by functionalization such as addition surfactant or surface oxidation. Functionalization of CNTs increases their adsorption ability and their interaction with the pollutants (Bassyouni *et al.,* 2020). Surface of a CNT can be modified by covalent or non-covalent method. Non-covalent method is dependent on Van der Waal's forces, hydrophobic and pi-pi interactions. The functional groups are physically attached to the surface; this method causes only few defects on the surface structure of CNT. Examples of non-covalent modification are adsorption of surfactants on nanotube surface and wrapping of polymer chains around CNT (Ibrahim, 2013). In a study conducted by Oliveira *et al.* (2021), MWCNTs modified with surfactant showed high efficiency in removal of lead, copper, zinc and nickel. In covalent method, a functional group is permanently bound to the surface of the carbon nanotube and interferes with the surface structure of the nanotube and its original physical properties. Some of the chemical groups used in modification are carboxylic, fluorine, p-amino benzoic acid which are bound at the ends or the surface of CNTs. Chemical functionalization creates more attractive sites on the surface and ends of CNT which are helpful in binding of nanotubes with the pollutants (Mittal, 2011). Rodríguez *et al.* (2020), carried a study on the removal of Cu, Zn and Mn in wastewater using MWCNTs oxidized with nitric acid and it showed high efficiency under column experiment.

2.4 Treatment of Wastewater

Wastewater treatment is a method of cleaning up wastewater and it's mainly done to remove the contaminants that are difficult to handle once they are discharged to the environment from the point source. There are three stages of wastewater treatment; primary, secondary and tertiary treatment. These treatment stages rely on the characteristics of wastewater released, and the potential hazard it can cause and also the cost effectiveness of treatment (Saravanan *et al.*, 2021). For water to be recycled again after pollution it must treated with several purification and filtration methods. This is because there is no one purification or filtration technique that can be employed for all kinds of water pollution. As a result, it's critical to treat toxic metals discharged from industrial effluents using approaches that are both inexpensive and technically possible. This necessitates the investigation of cost-effective, simple, and efficient eradication methods (Juma, 2014).

2.4.1 Primary Treatment of Wastewater

Primary treatment of wastewater removes the large solid particles and coarse solids from the raw sewage that have come from different non-point and point sources. The essence of this treatment is to remove the large suspended solids that can settle down at the bottom of the tanks by gravitational force and also the floatable materials. Grit and coarse solids are eliminated through screens which involves gravity sedimentation of screened sewage water to eliminate all solids that have settled. Primary treatment removes 30% of BOD and 60% of TSS (Mbugua, 2015).

2.4.2 Secondary Treatment of Wastewater

At this level the 70% of BOD of organic matter that has remained after primary treatment is biologically broken down by microorganisms (Asthana *et al.,* 2017). The microorganisms consume the suspended and dissolved organic matter, generating CO_2 and some other by products. Secondary treatment reduces the pathogens in wastewater but does not remove the heavy metals that are being released from industrial activities (Mbugua, 2015).

2.4.3 Tertiary Treatment of Wastewater

This is the last treatment stage. At this stage disinfectant like chlorine, ultraviolet radiation and ozonation are utilized to treat the wastewater. In most of developed nations, like Thailand the treatment of wastewater polluted by heavy metals is carried out using chemical precipitation, in China coagulation followed by flocculation is employed, Greece and united states of America flotation is used. Italy and Spain use ion exchange and membrane filtration is used in South Korea and Taiwan for wastewater treatment (Asthana *et al.,* 2017).

2.4.3.1 Adsorption

Adsorption is extensively applied in removal of toxic metal ions in effluents because it's inexpensive and produces minimal wastes and high-quality treated wastewater. This method is environmentally friendly because it does not any produce toxic pollutants (Hussain *et al.,* 2021). The choice of adsorbent is highly dependent on its surface area, porosity, cost-effectiveness and the polarity and distribution of functional groups (Ali *et al.,* 2016). Carbon based adsorbents, and zeolites are the commonly utilized adsorbents due to their large surface, easy chemical modification and porosity. These adsorbents have excellent adsorption efficiency however, they are expensive, difficult to regenerate and not economical (Duan *et al.,* 2020). Current research has been directed to use of non-convectional low-cost adsorbents which are inexpensive, available and environmentally friendly for the removal of pollutants in effluents. Agricultural wastes and industrial by-products have been studied extensively for removal of heavy metals in wastewater (Crini *et al.,* 2019).

2.4.3.2 Glass Wastes as Adsorbent for Heavy Metal Adsorption

Recycled waste glass (RWG) has 69.506 percent SiO_2, 10.69 percent CaO, and a tiny quantity of alumina, totaling 0.668 percent Al_2O_3. The utilization of waste glass in construction industry is critical for improving environmental sustainability since glass is a bio permanent material that would otherwise be landfilled (Ogundairo *et al.,* 2019). Furthermore, recycling is a significant duty since it requires less energy than the energy necessary to manufacture glass from sand, soda, and lime. However, glass could be easily recycled without affecting its unique properties; as a result, interest in the potential reuse of this novel material has recently increased, as this material is distinguished by durability, abrasion resistance, safety, excellent hardness, and negligible water absorption (Petrella *et al.*, 2018). Glass is a green adsorbent that is being developed for heavy metal adsorption. Heavy metal adsorption on waste glass occurs through cation exchange. Coleman (2011), studied the adsorption of lead and cadmium on soda-lime –silica glass containers. Sessile batch adsorption experiments were carried out at a pH of 5.5 and 6.2 for Pb^{2+} and Cd^{2+}respectively for a period of 24hrs. The metal adsorption on the glass surface occurred through cation exchange.

A study conducted by Sodeinde *et al.* (2021), waste glass showed a high efficiency in removal of cadmium (97.5%), and lead (94%) from wastewater at 70^0C. A composite of glass wastes and activated carbon was studied for heavy metal removal and maximum adsorption was achieved at a ratio of 2:1 (Activated carbon to waste glass). The composite showed high efficiency (99-100%) in removal of Cu, Fe, Pb, Zn and Cd at a contact time of 45mins, room temperature and neutral pH (Rashed *et al.,* 2019). Recycled Waste Glass modified with sodium hydroxide was used as adsorbent in removing Cr, Pb, Cu, Zn, Ni, and Cd and the efficiencies were 81%, 53%, 37%, 52%, 47% and 89% respectively at a pH range of 4.5-6.2 (Catalfamo *et al.,* 2006). A novel composite of Fe/ waste glass was used in adsorption of arsenic (V) and showed 97% removal efficacy from 1mg/l As (V) spiked synthetic water (Ying *et al.*, 2009).

2.4.3.3 Removal of Heavy Metals in Wastewater Using Multiwalled Carbon Nanotubes

Carbon nanotubes have been used recently, in removal of heavy metals from wastewater. In most of the studies a functional group is introduced and its effect on the nanotube behavior studied. Vuković *et al.* (2011), modified MWCNTs with amino acids to study individual and competitive adsorption characteristics of cadmium and lead ions. The study revealed that the adsorption of Pb^{2+} and Cd^{2+} on MWCNTs is highly depended on the pH, the maximum adsorption was achieved at a pH of 6.2. The results of this study were similar to a study conducted by (Tehrani *et al*., 2013a), on the adsorption of lead on MWCNTs functionalized with tris (2-aminoethyl) amine which showed that the adsorption of lead is largely dependent on the pH. Pristine

MWCNTs was studied by (Salam *et al.,* 2012), in this study intra-particle diffusion model was used to show the interaction of the heavy metals with the MWCNTs surface. A competition for active binding sites on the MWCNT was observed amongst the metal ions in the following series; Cu (II) >Zn (II) >Pb (II) >Cd (II). Li *et al.,* (2011), studied the adsorption of lead on the presence of surfactants using oxidized MWCNTs. Sodium dodecyl benzene sulfonate increased the lead adsorption on MWCNTs from 17-80% when the concentration of the surfactant (SDBS) was increased to 2mmol/L. Further, the removal of Pb was lowered to 45% when the concentration of SDBS was increased to 4mmol/L. Addition of octyl-phenolethoxylate (TX-100) elevated the removal of lead by 4%. Adsorption of As^{3+} and Cd^{2+} on carboxylated MWCNTs was modified with 5-amino-3-(2-thienyl) pyrazole in a study conducted by (Alimohammady *et al.,* 2018). The presence of sulfur and nitrogen groups on p-MWCNTs increased the adsorption of As^{3+} and Cd^{2+} as compared to c-MWCNTs.

2.5 Adsorption kinetic models

Pseudo first and second kinetic models describes the rate of adsorption processes, especially in the adsorption of solutes from aqueous solutions onto solid adsorbents. These models are used to predict and understand the mechanism of adsorption process.

2.5.1 Pseudo first order

The pseudo first order kinetic models assumes that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites (Mmbaga, 2018). It’s expressed by equation 2.1:

$$\ln(qe - qt) = \ln qe - \frac{k_1}{2.303} t \qquad \text{Equation 2.1}$$

Where *qt* is amount of adsorbate adsorbed (mg/g) at time (t), *qe* -amount of adsorbate adsorbed at equilibrium (mg/g) and k_1 is rate constant for pseudo-first-order. The values of k_1 and *qe* and are calculated by plotting a graph of ln (*qe*-*qt*) against time (t).

2.5.2 Pseudo second order

The pseudo second order model assumes that the rate of adsorption is proportional to the square of the number of unoccupied sites (Mmbaga, 2018). It's expressed by equation 2.2:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{...Equation 2.2}$$

Where k_2: pseudo-second-order rate constant. The value of qe and k_2 are calculated by plotting *t/qt* against time (t).

2.6 Adsorption isotherms

Adsorption isotherms describes the interaction of adsorbates with adsorbents, and gives insights about the affinity and capacity of adsorbents. The most commonly used models are Langmuir and Freundlich isotherms (Chung *et al.*, 2015).

2.6.1 Langmuir isotherm

This isotherm assumes a monolayer adsorption on a uniform surface with a finite number of identical sites, where each site can hold only one adsorbate molecule. It assumes that once a site has been filled, no further adsorption can occur in the same site (Chung *et al.*, 2015). Equation 2.3 describes the model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad \text{.. Equation 2.3}$$

Where;

C_e-is the concentration of adsorbate in the solution at equilibrium (mg L^{-1}),

q_e-is the amount of adsorbate adsorbed on the adsorbent at equilibrium (mg g^{-1}),

q_{max}-is the monolayer adsorption capacity of adsorbent (mg g^{-1})

K_L-is the Langmuir adsorption constant (L mg^{-1}).

The plot of $1/q_e$ against $1/C_e$ should give a straight line with a slope $1/q_o$ and an intercept of $1/q_{max}.K_L$.

2.6.2 Freundlich isotherm

This is an empirical model that describes adsorption on heterogeneous surfaces with sites of varying affinities. Its best suited for multilayer adsorption and does not predict a saturation point (Chung *et al.,* 2015). Equation 2.4 describes the model.

$log\, qe = \frac{1}{n} log\, Ce + log\, K_F$ ……………........…………………………. Equation 2.4

Where: q_e- is the amount adsorbed at equilibrium (mg g^{-1}),

C_e-the equilibrium concentration of the adsorbate at equilibrium (mg g^{-1}),

K_F-is the Freundlich constant related to adsorption capacity

n-is the constant related to intensity of adsorption associated with heterogeneity factor. The plots of log q_e against log C_e should give a linear graph where the values of n and K_F can be obtained from the slope and intercept of the graph, respectively. A higher value of n (or a smaller value of 1/n) indicates a stronger bond between the adsorbate and the adsorbent (Mmbaga, 2018).

2.7 Regeneration of Adsorbents

The success of an adsorption method is highly dependent on the ability of the adsorbent to desorb the contaminant for its reuse. Adsorbents are pretreated with selected conditioning agents such as bases, surfactants and acids to facilitate desorption of already adsorbed ions and also elevate the affinity for solute of interest. Regeneration helps to substitute the surface cations with more exchange friendly cations such as Na^+, NH_4^+ and K^+ during the adsorption process (Mmbaga, 2018).

2.8 Spectroscopic Techniques

2.8.1 UV-visible Spectroscopy (UV-Vis)

UV-V is spectrophotometer is a crucial physical tool that exploits light in ultraviolet and visible region of electromagnetic spectrum. This technique is used to determine the concentration of absorbers, when path length is fixed. It utilizes Beer-Lamberts law to determine the relationship between absorbance, concentration of absorbing species in solution and path length. A light beam having certain wavelength and energy is focused onto the sample and it absorbs some energy of the incident wave. Energy of the transmitted light coming from the sample is measured by a photodetector and absorbance recorded. The concentration of the analyte is determined using Beer-Lamberts law $A = \varepsilon.c.d$. Where; A-absorbance, ε - extinction coefficient, c-sample concentration, d- path length (Akash & Rehman, 2020).

2.8.2 Scanning Electron Microscopy (SEM)

SEM is used to determine the surface morphology of compounds, and chemical composition of elements and compounds in the surface and their relative ratios. In Scanning electron microscope, a beam of electrons from an electron gun is accelerated towards the sample surface using a positive electrical potential. The metal apertures and magnetic lenses are used to confine and focus the electron beam into a thin and focused monochromatic beam. Electrons in the monochromatic beam interact with the sample atoms, to produce signals that have information about the surface topography, composition and electrical properties. The interactions of the electron beam and sample atoms are detected, and transformed into an image (Kannan, 2018).

2.8.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a powerful and sensitive technique for analysis of any varying signal to its constituent frequency components in a single operation. IR is used in structure elucidation and can be used to analyze micro samples of up to nanogram level (Jaggi & Vij, 2006). IR originates from an aperture which regulates the amount of radiation. The regulated radiation beam is encoded spectrally by an interferometer before being focused to the sample. The sample is exposed to a single pulse radiation of wavelength range 400-4000cm^{-1} resulting in partial absorption and transmittance. The quantity of radiation transmitted or absorbed by the sample determines the amount of analyte of interest in the sample and the resulting beam from the sample is detected and an infrared spectrum is obtained (Mmbaga, 2018). Different materials have different vibrations and produce distinct infrared spectra and a certain molecule can be identified. A nonlinear molecule with N atoms exhibits 3N-6 fundamental vibrations. Only those molecular vibrations which are IR active appear in the infrared spectrum. For a vibration to be IR active it must induce a change in the dipole moments of the vibrating molecule thus symmetric vibrations do not appear in the IR spectrum (Zampieri, 2021).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study area

The study was conducted in Ruai sub location Embakasi sub county Nairobi east. The samples were collected in Ruai sewage treatment plant located east of the City Center, on the way to Kangundo on the latitudes of 1^0 14'S and 1^0 28' S, and the longitudes of 36^0 56'E and 37^0 6' E. The Ruai area map is shown in figure 2 (Maina *et al.*, 2020).

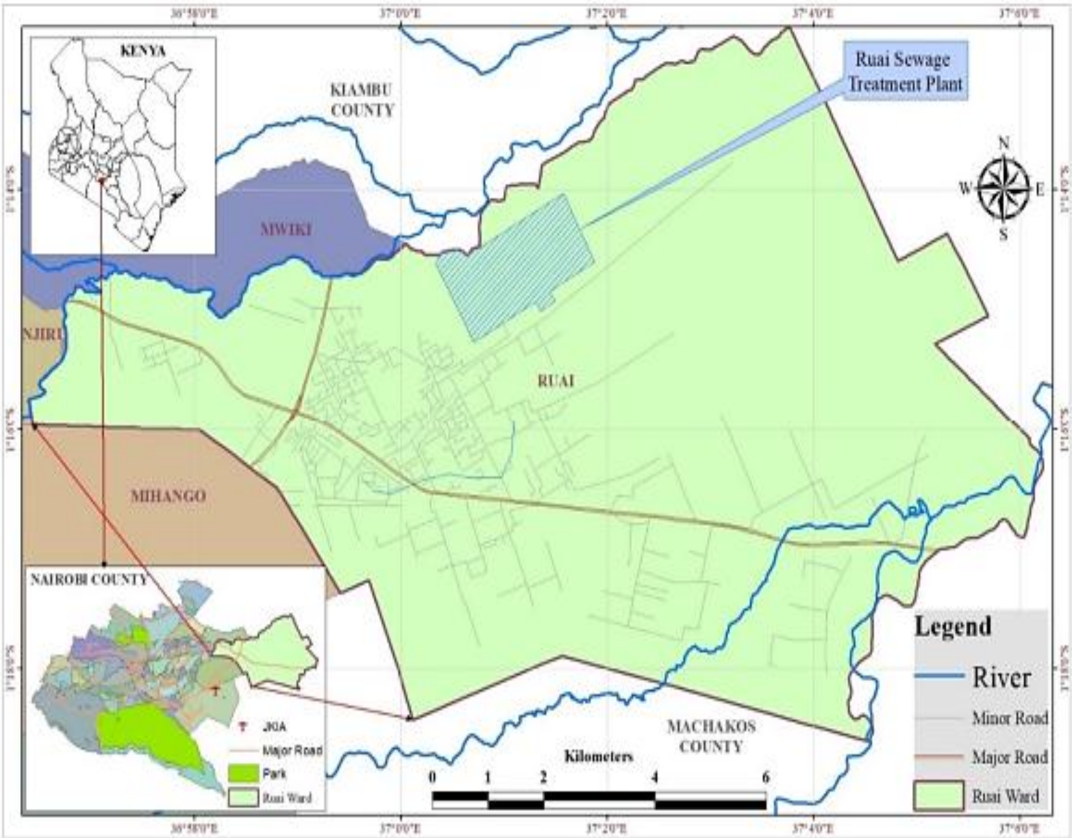

Figure 2: Ruai area map

Maina et al., 2020

The Ruai Wastewater Treatment Plant manages about 80,000 cubic meters of wastewater daily having expanded from the initial capacity due to growth within Nairobi. The plant also uses wastewater stabilization ponds whereby the stabilization ponds are constituted of natural biological treatment ponds. In these ponds, sedimentation takes place and oxidation and reduction of organic pollutants takes place by way of microorganisms. This method is suitable when the treatment of the organic matter and selected nutrients is necessary but may not be so good in the removal of heavy metals from the water.

Heavy metals such as lead, nickel, zinc, copper, manganese, and cadmium are a big area of concern at the Ruai plant mainly resulted from industrial effluent. These metals can deposit on the sludge and if not handled well may end up in the environment through discharge. Untreated or poorly treated wastewater from Ruai wastewater treatment plant is discharged into Nairobi River. This causes eutrophication, affect aquatic life and water sources used by people and for irrigation downstream of the river. This calls for further advancement in treatment methods of the wastewater to ensure safer wastewater management.

3.2 Reagents and Materials

All glass wares used were purchased from Sigma Aldrich chemicals ltd. Concentrated sulphuric acid 98% pure from sigma Aldrich, 69% nitric acid, dilute hydrochloric acid, sodium hydroxide, Multiwalled carbon nanotubes were purchased from Hongwu International Group Ltd. Portable pH, DO/Temperature 903P.16 super clean TM LC-8-meter was used to measure pH and temperature. Conductivity was measured using EC 215 and turbidity meter LP2000 from Hanna instruments. Nitrates and phosphates were determined using Shimadzu 1800 UV-vis spectrophotometer and heavy metals using PG-990 Atomic Absorption Spectrophotometer at Chuka University.

3.3 Sample Collection

3.3.1 Collection of wastewater samples

Ruai sewage treatment plant has wastewater treatment ponds which are divided into three i.e. anaerobic ponds which receives the raw sewage, facultative ponds which receives the waste water from anaerobic ponds and lastly the maturation ponds which receives the waste water from facultative ponds. There are eight anaerobic ponds in the plant and each is subdivided into three. A total of 42 samples were collected in both wet season (Oct-Nov 2021) and dry season (Feb-Mar, 2022) using grab method. Prior to use, the sampling plastic bottles and the grabbing bottle were soaked overnight with 10% nitric acid and rinsed with distilled water to avoid sample contamination (Nzeve, 2015). The sample bottles were rinsed with the treated wastewater at each sampling point before transferring the sample into the bottle. The samples were collected at the outlet of anaerobic, facultative and maturation ponds 2, 5 and 8 which were active during the sampling periods. Raw sewage samples were collected at three sampling points at the entrance of the wastewater, after the first sieve and the last sieve. Three sampling points were identified in the upper stream of Nairobi River, making a total of 21 samples at each sampling. The samples were labelled and transported in a cooler box at 4°C to Chuka University laboratory, where the analysis was carried out. The flow diagram in figure 3 shows the sampling points. ANR-Anaerobic Pond, F-facultative pond, M- Maturation Pond.

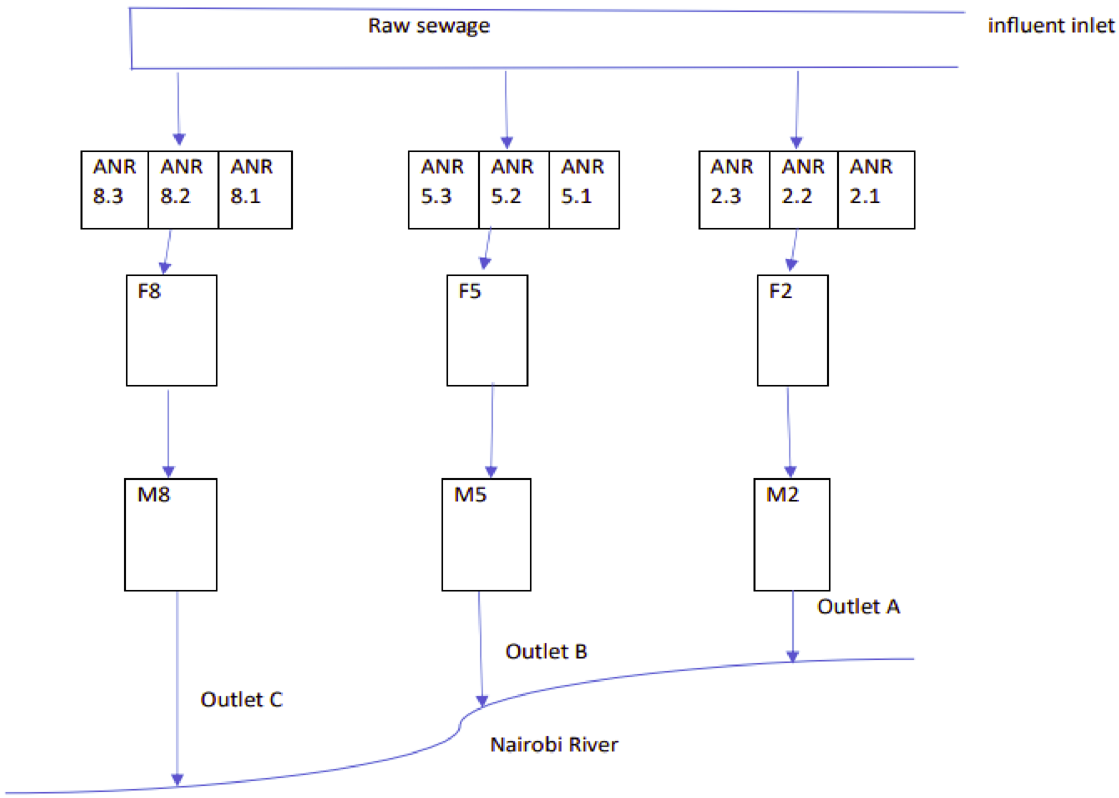

Figure 3: Sample collection points at Ruai wastewater treatment plant

3.3.2 Sample Preparation

3.3.2.1 Determination of heavy Metals

A volume of 90 ml of each wastewater sample and a blank was measured and put in labelled 100 ml beakers. Ten (10) ml of nitric acid was added to each sample and digested in a hotplate to 10ml. The digested samples were filtered using 0.42µm Whatman filter papers onto 50 ml volumetric flasks and topped up to the 50 ml mark using distilled water. The salt of each metal ion was used to prepare the standards in the range of 5 ppm, 10 ppm and 20 ppm. The levels of Cu, Pb, Ni, Zn, Mn, Cd and Fe were determined using a *PG-990* AAS at Chuka University (Rice *et al*., 2012).

3.3.2.2 Determination of nitrates

A fixed volume of 100ml of each wastewater sample was measured and put in a 250 ml beaker and 1 ml of HCl added. Nitrate stock solution was prepared by weighing 1.6306g of KNO_3 using analytical balance and put in a 100 ml beaker, distilled water was added to dissolve the solid and the solution transferred into 1000 ml volumetric flask and topped up to the mark. Dilute standard solutions of 1 ppm, 2 ppm and 3 ppm were prepared from it and 1 ml of HCl added to each. The concentration of nitrates in each sample was determined at 220nm using Shimadzu 1800 UV-Vis spectrophotometer at Chuka University (Rice *et al.*, 2012).

3.3.2.3 Determination of phosphates

A fixed volume of 100 ml of each wastewater sample was measured and put into 250 ml beaker and 1 ml of Sulphuric acid followed by 5 ml of nitric acid were added. The samples were digested in a hot plate to 10 ml and 2 drops of phenolphthalein indicator was added followed by stepwise addition of NaOH to control the pH. Ten (10) ml of this solution was transferred into a beaker and 10ml of ammonium molybdovanadate added and allowed to settle for 5 mins to allow formation of phosphomolybdovanadate complex and 25 ml of distilled water was added. The solutions were transferred to 100 ml volumetric flask and topped up to 100 ml mark using distilled water. Analytical balance was used to weigh 4.390g of potassium dihydrogen phosphate and transferred into 100 ml beaker, distilled water was added to dissolve it and the solution was transferred into 1000 ml volumetric flask and distilled water added up to the mark. From this stock solution of phosphorus 100 ppm, 10 ppm and 1 ppm standards were prepared and the concentration of each sample was determined at a wavelength of 830nm using Shimadzu 1800 UV-Vis spectrophotometer at Chuka University chemistry laboratory (Rice *et al.*, 2012).

3.3.2.4 Determination of Total Suspended Solids (TSS)

Twenty-one (21) filter papers were labelled and weighed using analytical balance and the mass recorded. A volume of 50 ml of each wastewater sample was measured and filtered on the weighed filter paper. The filter papers were dried on an oven at a temperature of 105^oC and remeasured. The difference between the weight of filter paper after filtration and drying and the initial weight before filtration gave the total suspended solids (Rice *et al.*, 2012)

3.3.2.5 Determination of Total Dissolved Solids (TDS)

Twenty-one (21) clean empty beakers were labelled and weighed on analytical balance and the weight recorded. A volume of 50 ml of each wastewater sample was measured and put on the weighed beakers. The samples were dried on oven at a temperature of 105°C. The beakers were allowed to cool and then remeasured. The difference between the mass of the empty beaker and the dried solids minus the mass of empty beaker gave the total dissolved solids (Rice *et al.*, 2012)

3.3.2.6 Determination of Biological Oxygen Demand and Chemical Oxygen Demand

The titrimetric technique was applied in closed reflux to determine the amount of COD. The sample was refluxed with sulfuric acid and potassium dichromate in the presence of silver sulfate, which served as a catalyst and counteracted the effects of the chloride. The amount of oxidizable organic matter in the wastewater sample directly correlated with the amount of potassium dichromate used (Rice *et al.*, 2012). The COD was obtained using the equation 3.1 and 3.2 shown below.

$$Molarity\ of\ (dichromate) = \frac{\text{volume of } 0.01667\text{K}_2\text{CrO}_7 \text{ solution titrated mL} \times 0.1000}{\text{volume of dichromate used in titration mL}} \text{……Equation 3.1}$$

$$COD(mgO_2/L) = \frac{(A-B)\times M \times 8000}{mL\ sample} \text{…………………… Equation 3.2}$$

A= mL dichromate used for blank, B= mL dichromate used for sample, 8000= milliequivalent weight of oxygen×1000mL/L, M= molarity of dichromate

The difference between the oxygen concentration of a diluted sample before and after 5 days incubation at 20°C was used to determine the BOD_5 using the following equation 3.3 (Rice *et al.*, 2012).

$$BOD_5(mgO_2/L) = \frac{D_1 - D_2}{P} \text{………………… Equation 3.3}$$

Where D_1=DO of diluted sample immediately after preparation, D_2= DO of diluted sample after 5 days' incubation at 20°C, P= Decimal volumetric fraction of sample

3.3.2.7 Determination of pH, Conductivity, Temperature and Turbidity

The pH and temperature of the samples were determined using a pH meter and thermometer at each sampling point. Turbidity and conductivity were determined using a turbidity and conductivity meter at Chuka University laboratory (Rice *et al.,* 2012).

3.3.3 Heavy Metals Adsorption

3.3.3.1 Oxidation of Multiwalled Carbon Nanotubes

MWCNTs were purchased from Hongwu International Group Ltd. Analytical balance was used to weigh 500mg of MWCNTs and they were put in a 250 ml round bottomed flask, and 100 ml of 32% concentrated HCl added to remove impurities. The suspension was stirred for 2 hours, filtered and the MWCNTs washed with distilled water until the solution was neutral. The tubes were dried in vacuum oven at 80^{o}C overnight. The MWCNTs were functionalized using a mixture of 6 M H_2SO_4 and 6 M HNO_3 in a ratio of 1:3 at 80^{o}C for 19 hours and sonicated for 4 hours at 70^{o}C. The mixture was filtered using glass microfilters with a pore size of 0.45μm, washed till a neutral pH and dried overnight at 80^{o}C. The functionalized tubes were stored in glass vials.

3.3.3.2 Dispersion of Multiwalled Carbon Nanotubes

A volume of 50 ml distilled water was added to Raw and oxidized MWCNTs and the suspensions were dispersed using an ultrasonic bath for 30 mins at 70^{o}C. The samples were allowed to decant for 24 hours and filtered (Rodríguez *et al.,* 2020).

3.3.3.3 Collection of Waste glass

Soda lime waste glass samples were collected in residential areas around Chuka University and borosilicate glasses in the University laboratory. The glasses were thoroughly cleaned using tap water and rinsed with distilled water. The glasses were labeled, dried, and transferred to polyethylene bags. The samples were crushed using a hammer and sieved. The powder samples were stored in sample holder bags and stored in a desiccator.

3.3.3.4 Surface Functionalization of the waste glass adsorbents

Ten grams (10g) of borosilicate and soda lime waste glass samples were each treated with 500 ml of 0.5 M nitric acid and the mixtures were shaken for 12hours at 160 rpm.

The suspensions were filtered with whatman-542 filter papers and washed with distilled water until the pH became neutral (Rashed *et al.,* 2019). The samples were oven dried at 105^oC overnight and the adsorbents were stored in glass vials.

3.3.3.5 Soda lime waste glass/Multiwalled Carbon Nanotubes Composite

Modified soda lime waste glass sample and oxidized MWCNTs were mixed in the ratio of 3:1 (1.5g:0.5g) and ground in an agate mortar. The powder was functionalized using a mixture of 6M H_2SO_4 and 6M HNO_3 in a ratio of 3:1 at 80^oC for 19 hours and sonicated for 4 hours at 70^oC. The mixture was filtered using glass microfilters with a pore size of 0.45μm, washed till a neutral pH and dried overnight at 80^oC. The functionalized composite was stored in glass vials and kept in a desiccator (Rodriguez *et al.,* 2020).

3.3.3.6 Characterization of the Adsorbents

A sample of both raw and oxidized MWCNTs, soda lime and borosilicate glass samples (modified and unmodified), and modified soda lime glass sample/MWCNTs composite each was mixed with KBr in the ratio of 100:1. The samples were ground and a pellet prepared using press pellet technique. The pellets were analyzed using an FTIR (Shimadzu 1S) at a frequency range of 4000-400cm^{-1} (Cheng *et al.,* 2011).

3.3.4 Adsorption Experiments for Pb^{2+} ions

3.3.4.1 Effect of pH on adsorption of lead (II) ions

A fixed mass of 200mg borosilicate, soda lime and soda lime/MWCNTs composite adsorbents were weighed onto 200 ml labelled beaker, 100 ml of 10 ppm Pb^{2+} metal solution was added to each adsorbent and the pH of each solution adjusted to 2. The solutions were shaken on an orbital shaker for 30mins operated at 200 rpm at room temperature. The suspensions were filtered in a vacuum pump using 45μm glass microfilters and transferred into 150 ml polypropylene bottles. The procedure was repeated at a pH of 4, 6 and 8 and the amount of Pb^{2+} adsorbed at each pH determined using AAS (Suliman, 2017; Rashed *et al.,* 2019).

3.3.4.2 Effect of contact time on adsorption of lead (II) ions

A fixed mass of 200mg soda lime, borosilicate and soda lime/MWCNTs composite adsorbents were weighed on analytical balance, and put on 200 ml beakers. 100 ml of 10 ppm Pb^{2+} solution was added to each adsorbent and the pH adjusted to 6, these solutions were shaken on an orbital shaker operated at 200 rpm at room temperature for 30mins. The suspensions were filtered in a vacuum pump using 45μm glass microfilters and transferred into 150 ml polypropylene bottles. The amount of Pb^{2+} adsorbed was determined using AAs and the procedure was repeated at 15, 45 and 60 mins.

3.3.4.3 Effect of shaking speed on adsorption of lead (II) ions

A fixed mass of 200mg of each adsorbent was weighed onto 250 ml beaker, 100 ml of 10 ppm Pb^{2+} solution was added to each adsorbent and pH adjusted to 6. The solutions were shaken for 30 mins at room temperature at a speed of 150 rpm. The suspensions were filtered in a vacuum pump using 45μm glass microfilters and transferred into 150 ml polypropylene bottles. The procedure was repeated at 200, 300 and 350 rpm, and the amount of lead (II) ions adsorbed at each speed determined using AAS.

3.3.4.4 Effect of adsorbent dose on adsorption of lead (II) ions

A mass of 50mg of each adsorbent was weighed on an analytical balance and transferred to 250 ml beakers. 100 ml of 10 ppm pb^{2+} solution was measured and put onto each adsorbent and pH adjusted to 6. These solutions were shaken on an orbital shaker at 200 rpm for 30 mins at room temperature. The suspensions were filtered in a vacuum pump using 45μm glass microfilters and transferred into 150 ml polypropylene bottles. The amount of Pb^{2+} adsorbed was determined using AAS and the procedure was repeated with 100, 150 and 200 mg of each adsorbent.

3.3.4.5 Effect of temperature on adsorption of lead (II) ions

A fixed mass of 200mg of borosilicate, soda lime and soda lime/MWCNTs composite adsorbents were weighed on an analytical balance and transferred onto 250 ml beakers. Onto each adsorbent 100 ml of 10 ppm Pb^{2+} solution was added and the pH adjusted to 6, the mixtures were shaken at 200 rpm for 30 mins at 25^{o}C. The suspensions were filtered in a vacuum pump using 45μm glass microfilters and transferred into 150 ml polypropylene bottles. The procedure was repeated at 30, 35 and 40^{0}C and the amount of Pb^{2+} adsorbed at each experiment determined using AAS.

3.3.4.6 Effect of initial metal concentration on adsorption

A fixed mass of 200 mg of each adsorbent was weighed in an analytical balance and transferred onto 250 ml beakers. A 100 ml of 5ppm Pb^{2+} solution was added to each adsorbent and pH adjusted to 6, the solutions were shaken at 200 rpm for 30 mins at 25^{o}C. The suspensions were filtered in a vacuum pump using 45μm glass microfilters and transferred into 150ml polypropylene bottles. The procedure was repeated with 10, 15 and 20 ppm Pb^{2+} solutions and the amount of lead (II) ions adsorbed at each experiment determined using AAS.

3.3.5 Interference studies on Pb^{2+} adsorption

Stock solutions of 100 ppm lead, cadmium, manganese and nickel were prepared from lead (II) nitrate, cadmium (II) chloride, manganese (II) chloride and nickel (II) nitrate respectively. A fixed volume of 80 ml 0.4ppm dilute solution of lead (II) ions was prepared from the stock and transferred to a beaker containing 200 mg of composite, its pH was adjusted to 6 and labelled sample A. Sample B contained 20 ml of 0.1ppm Cd^{2+}, sample C 20 ml of 0.2 ppm of $Cd^{2+,}$ sample D 20 ml of 0.1 ppm $Ni^{2+,}$ sample E had 20 ml of 0.2ppm $Ni^{2+,}$ sample F contained 20 ml of 0.1 ppm Mn^{2+} and sample G had 20 ml of 0.2 ppm Mn^{2+} onto each of these samples 80 ml of 0.4ppm Pb^{2+} was added. These solutions were transferred to labelled beakers containing 200mg of soda lime/MWCNTs composite and the suspensions pH adjusted to 6. The samples were shaken for 30 mins in an orbital shaker operated at 200 rpm in room temperature and then filtered in a vacuum pump using 45μm glass microfilters and transferred to 150 ml polypropylene bottles. The amount of Pb^{2+} adsorbed in each sample was determined using AAS (Karimi *et al.,* 2015).

3.3.6 Regeneration of the Adsorbents

3.3.6.1 Desorption of Pb^{2+} from adsorbents surface

A fixed volume of 100 ml of 0.1 M HCl was measured and transferred to three labeled beakers and 0.2g of borosilicate, soda lime and the composite adsorbents used in adsorbing Pb^{2+} were added to the beakers. The pH of the suspension was adjusted to 2 and shaken for 30 mins at 350 rpm and room temperature. The adsorbent was filtered in a vacuum pump using 45μm glass microfilters and the filtrate was transferred to 150 ml polypropylene bottles. The amount of Pb^{2+} desorbed was determined using AAS and the procedure was repeated twice (Kosa *et al.,* 2012).

3.4 Data Analysis

Data obtained from the levels of physico-chemical parameters of Ruai wastewater treatment plant was tabulated using excel. The data was analyzed using excel in order to calculate the mean values and standard deviation between the two seasons. Student's t-test was performed at 5% probability level confidence interval in order to determine the seasonal variation of the physico-chemical parameters of wastewater in the two seasons. The mean levels were compared to WHO (2006), NEMA (2006), and FAO (1992) standards to ascertain suitability of the wastewater for agricultural use. The significant difference in heavy metal concentration was separated using least significance difference at $p<0.05$. The equilibrium adsorption isotherms data were fitted to Langmuir and Freundlich models and constants of isotherm equations was determined. Adsorption models were used to determine the quantity of lead (II) ions adsorbed on the surface of borosilicate and soda lime waste glass, and composite of MWCNTs/ soda lime waste glass adsorbent. Adsorption kinetics of lead (II) ions removal was analyzed using pseudo-first order and pseudo-second order kinetic models.

3.5 Ethical Considerations

This study was conducted in line with Chuka University guidelines. The researcher got an introductory letter from Chuka University ethics committee and obtained a research permit from National Commission for Science, Technology and Innovation (NACOSTI) to carry out the study at Ruai wastewater treatment plant (appendix XII). Standard laboratory procedures were employed in carrying out all the analysis and no harm was caused to the staff and environment. Any sourced information was properly referenced and cited to avoid plagiarism. The findings of this study will be shared with NEMA and Nairobi sewerage company for necessary measures.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Physicochemical parameters in Ruai wastewater treatment plant during wet and dry season

4.1.1 Physical parameters of the wastewater

The pH in this study ranged from 6.8-7.9 during the wet season as shown in table 4.1.

Table 1: Physicochemical parameters of Ruai wastewater treatment plant during the wet season

REF: CODE	pH/Temp. ^oC	Conductivity In µS	Turbidity NTU	NO_3 mg/L	P mg/L	BOD mg/L	COD mg/L	TDS mg/L	TSS mg/L
ANR 2.1	7.0/23.0	972	464	9.33	1.28	200	142	791	90
ANR 2.2	6.8/23.0	983.3	156.7	8.92	4.42	198	138	711	89
ANR 2.3	6.8/22.7	989.3	186.7	11.3	4.39	204	144	738	136
ANR 5.1	6.8/23.3	966	129.7	16.9	4.18	140	158	708	178
ANR 5.2	6.8/23.4	947	102.7	18.4	4.15	136	162	741	102
ANR 5.3	7.2/22.7	1209.7	73	9.38	7.35	144	156	852	25
ANR 8.1	6.8/24.0	1058.3	132	14.9	10.3	220	221	824	113
ANR 8.2	6.9/24.1	1012.3	115.7	12.0	4.37	218	211	783	72
ANR 8.3	6.8/24.3	1084.3	95	14.1	5.22	224	233	827	88
F8	7.7/25.1	980	87.3	8.94	3.2	80	196	825	87
F5	7.8/23.4	959	183	14.6	3.1	60	164	656	91
F2	7.8/24.1	1023.7	146.3	11.1	5.31	60	117	743	58
M2	25.4/7.8	1061.7	120	25.1	3.36	30	92	967	58
M5	7.9/25.7	964.3	167.7	9.91	3.31	40	139	707	59
M8	7.8/25.1	1011	74.3	11.1	3.15	40	133	734	68
RS1	7.2/23.7	970.3	967	16.3	5.96	480	964	931	378
RS2	7.3/23.9	984	965.7	21.3	5.99	472	960	902	422
RS3	7.3/23.3	1000.3	1000	14.9	5.32	490	970	930	344
NR1	7.5/24.0	540.7	562	7.59	1.21	-	-	472	378
NR2	7.4/23.9	526.7	428.3	6.66	1.16	-	-	470	422
NR3	7.4/24.3	536	449.7	10.0	1.30	-	-	469	344
FAO guidelines	6.5-8.4/20-35^{0}C	700-3000	-	5	2.0	-	-	450-2000	-
WHO standards	6.5-8.4/20-35^{0}C	1000	5	50	5.0	50	70	750	50
NEMA limits	6.5-8.4/20-35^{0}C	1000	50	10	2	30	50	1200	30

pH is an essential parameter which indicates the extent of pollution of water. Changes in temperature, respiratory activities, exposure to air and source of wastewater that is industrial, domestic, agricultural activities, or surface runoff greatly affects pH (Hussain *et al.,* 2021; Manasa and Mehta, 2020). The basic pH values during the wet season was attributed to dilution of sewage by runoff water. The results of Olabode *et al.* (2020), in Cape Town and Sewe (2013), in Ruai Kenya, correlated with this study with pH ranges of 5.85-7.85 and 6.71-8.06 (dry season) respectively. The similarity was attributed to high amounts of domestic and industrial influents into the treatment facilities. Sarkinnoma *et al.* (2013), reported pH of 8.11-8.40 in municipal wastewater in Nigeria, which is higher compared to this study. The pH difference was due to excessive algae growth in Nigeria WWTP which consumed the CO_2 from water for cell growth, thus raising the pH of the wastewater. During the wet season the pH values ranged from 6.8- 7.9 (table 4.1). The samples from Nairobi River (NR1, NR2 and NR3) and raw sewage (RS1, RS2 and RS3) had a pH range of 7.2-7.5 which was attributed to high water input from rains which lead to dilution of the sewage.

Anaerobic ponds contain anaerobic bacteria which break down the organic matter in the effluent into CO_2 and methane thus suspended solids, BOD_5 and COD are primarily removed in these ponds (Quiroga, 2013). In this study high loads of TSS, BOD_5 and COD were observed during the wet season which led to lower pH of 6.8-7.2 in anaerobic pond 2, 5 and 8. The facultative and maturation ponds recorded the highest pH values 7.7-7.9 due to the reaction of bicarbonate and carbonates of calcium and magnesium which decomposed to produce carbon dioxide for algae and hydroxyl ions. The high pH values in maturation ponds was confirmed in a study by Sewe (2013). During the dry season there is reduction in flow of wastewater into the WWTP which leads to lesser dilution of the pollutants, thus increasing the contaminant loads in the plant because the waste load remains the same but the volume of water flowing reduces (Hughes *et al.*, 2021). pH values recorded on this season were slightly acidic 5.5-6.8 (table 4.2) due to formation of carbonic acid which results from release of free CO_2 from decomposition of organic waste and respiration of microbial organisms in the wastewater because of high temperatures (Fouad *et al.*, 2022).

Table 2: Physicochemical parameters of Ruai wastewater treatment plant during the dry season

REF: CODE	pH/Temp. oC	Conductivity (In µS)	Turbidity NTU	NO3 mg/L	P mg/L	BOD mg/L	COD mg/L	TDS mg/L	TSS mg/L
ANR 2.1	6.0/24	1114	447.3	13.93	6.12	160	320	295	40
ANR 2.2	5.9/24.0	1097	248.3	11.96	5.75	154	312	304	32
ANR 2.3	6.2/24.6	1110	208.7	13.33	5.44	168	332	302	40
ANR 5.1	5.8/24.4	1144	185.7	14.18	5.04	140	253	272	37
ANR 5.2	5.7/25.4	1139	187	14.48	5.35	133	258	278	48
ANR 5.3	5.7/26.2	1122	142	17.19	7.17	152	249	269	35
ANR 8.1	5.5/24.4	1113	208	12.13	6.25	200	259	260	29
ANR 8.2	5.5/24.4	1089	223	15.06	5.91	197	244	290	41
ANR 8.3	5.6/24.2	1125	217	15.41	4.97	205	269	273	32
F8	6.2/24.1	1075	147.7	19.34	4.84	40	192	319	63
F5	6.4/24.2	1049	311.7	11.71	5.09	50	246	341	199
F2	6.4/23.9	1059	250	14.54	6.56	40	262	322	93
M2	6.4/24.3	958	406.3	20.94	2.86	10	310	422	87
M5	6.8/24.2	1030	391	11.04	5.90	75	195	351	117
M8	6.7/25.0	1068	182.3	9.67	5.41	80	90	319	16
RS1	6.6/24.9	1184	959	19.51	6.04	440	976	320	14
RS2	6.4/24.0	1176	1000	18.05	7.27	458	964	301	55
RS3	6.2/24.2	1160	1000	19.34	7.27	426	980	304	28
NR1	6.5/26.1	852	161.3	9.72	1.86			274	24
NR2	6.4/25.8	839	178.3	12.16	2.39			244	20
NR3	6.4/25.3	853	176.3	13.65	1.88			275	33
FAO guidelines	6.5-8.4/20-350C	700-3000	-	5	2.0	-	-	450-2000	-
WHO standards	6.5-8.4/20-350C	1000	5	50	5.0	50	70	750	50
NEMA limits	6.5-8.4/20-350C	1000	50	10	2	30	50	1200	30

A statistically significant difference between the sampling points for both wet and dry seasons was reported with a p-value of 0.000 and this might be due to different amounts of pollutants in the sampling pods which led to slight pH changes. The value of t-calculated was 8.975 while t-tabulated 2.021 at 95% confidence level this showed there is a significant difference between the results of wet and dry seasons (appendix I and II). The factors that might have contributed are discussed above. The final treated wastewater released into Nairobi River downstream (from maturation pods) had a pH of 6.6-7.8 which met the Food and agriculture organization FAO (1992), guideline pH of 6.5-8.4 for reuse in agricultural purposes.

Performance of WWTPs is greatly influenced by temperature changes. Biological reactions usually occur faster at warm temperatures and this enhances the conversion processes of the effluents, and improves the removal efficacy of the pollutants (Tolkou & Zouboulis, 2016). Temperature ranged from 22.7^{0}C to 26.1^{0}C (table 4.1 and 4.2) which was higher as compared to 16.01-18.32^{0}C reported by Hussain *et al.* (2021), in India which was attributed climatic changes and geolocation of the treatment plant. Study carried out by Lokhande *et al.* (2011), in Taloja industrial effluents India, reported higher temperatures of 27.7-37.1^{0}C as compared to results of this study. The difference in temperatures was due to the source of wastewater, where Taloja effluents were from a textile industry which manufactures dyes. The results of Sewe (2013), in Ruai WWTP for dry and wet season were within 23.10^{0}C-27.27^{0}C which tallied with findings of this study. The lower temperatures on wet season were attributed to climate change Gadhia *et al.* (2012), and the slightly higher temperatures recorded on dry season were due to heat, which raised temperature of the wastewater. A statistically significant difference between the sampling pods was detected with a p-value of 0.004 at 95% confidence limit, which might be due to different sampling time and composition of pollutants in the pods (appendix I and II). The wastewater temperature met the water quality regulations, Kenya (2006) and FAO (1992), of 20-35^{0}C for discharge into the environment.

Electrical conductivity indicates the amount of dissolved salts in a solution and is utilized in monitoring of wastewater treatment processes which causes change in salt concentration for example anaerobic biological treatment (Khengaoui *et al.,* 2015).

Conductivity ranged from 526.7 to 1209.7 for this study which was higher than 91.41 - 115 observed by Hussain *et al.* (2021) and correlates with results of (Hamaidi-Chergui & Brahim Errahmani, (2019); Odjadjare & Okoh, (2010)). Results of Sewe (2013),in Ruai WWTP reported conductivity values 1503-1977 µS/cm for wet and dry seasons which indicates high amounts of dissolved salts in the effluent and also poor conversion of organic wastes by anaerobic bacteria. During the wet season the EC ranged from 526.7 to 1209.7µS (table 4.1). The lowest values were observed in Nairobi River samples (526.7-540.7µS) while ANR 5.3, ANR 8, F2, M2 and M8 EC was higher than 1000 µS recommended by WHO and NEMA standards for wastewater.

During the dry season conductivity was high for all the samples except M2 and Nairobi River samples (table 4.2). This high electrical conductivity was due to the large amounts of dissolved salts in the wastewater and high temperatures (Vepsäläinen & Sillanpää, 2020). Conductivity increases with increase in temperature due to fast mobility of charged ions in the water which increases overall conductivity (Dewangan *et al.*, 2023). A research conducted by Wyasu (2020), in Nigeria had conductivity values ranging between $1022.17 \pm 12.32\mu S/cm$ -$1532.21 \pm 12.43\mu S/cm$ which was attributed to high dissolved salts from domestic and industrial effluents. A statistically significant difference in conductivity between the seasons was reported with a p-value of 0.014 at 95% confidence level and this is due to different temperatures during the seasons. There was a significant difference in conductivity amongst the sampling pods with a p-value of 0.010 at 95% confidence limit which might be due to different amounts of dissolved solids /salts in the pods (appendix I and II). The results of this study met the FAO guidelines (1992) of 700-3000 $\mu S/cm$ for discharge into the environment but surpasses the WHO and NEMA standards (2006) of $1000\mu S/cm$ in some sampling points.

Turbidity is the measure of clarity of water and it indicates the kind of colloidal matter involved either of mineral or organic origin (silt, microorganisms, clay). During the wet season turbidity ranged from 73to 1000 NTU which was very high and might be due to runoff water during the rains and sediment disruption. During the dry season the values were between 142-1000 NTU which was higher as compared to wet season and this was due to excessive growth of algae in the sampling pods (Mandal, 2014). The raw sewage samples had the highest turbidity for both seasons due to large amounts of unsettled suspended particles, clay and silt in the incoming effluents. Turbidity results obtained from this study differs with the results of Ngoulou *et al.* (2019); Iram *et al.* (2013) and Adewumi and Ajibade, (2019), of 161-453NTU, 272.8-487.05NTU and 238-371NTU respectively. A statistically significant difference between the seasons was observed with a p-value of 0.000 and this is due to the reasons listed above. There was no statistical significant difference amongst the sampling points since the p-value was 0.748 at 95% confidence level. All the values for both seasons were higher than WHO and NEMA standards, of 5 NTU and 50 NTU respectively.

Total suspended solids are composed of silt particles, inorganic and organic compounds, fine clay and microorganisms while total dissolved solids give the quantity of organic and inorganic substances in water. TSS and TDS are highly influenced by pH change which causes precipitation of some solutes and solubility of suspended matter (Gadhia *et al.*, 2012). The TDS varied from 25 mg/L to 422 mg/L in this study which are higher as compared to Edori and Nna, (2018), study which reported TDS of 7.31mg/l and 26.97mg/l TSS in effluents in port Harcourt, Nigeria. The difference might be due to high concentration of inorganic and organic matter reported in this study. Research conducted by Maina *et al.* (2020), in Ruai treatment wastewater showed total solids of 1230mg/l which is high as compared to findings of this study. The difference is attributed to improved decomposition of organic matter by the bacteria and also desludging of the pods.

Raw sewage had the highest values of dissolved solids was observed during the wet season (902-3090mg/l) due to runoff from farms, industries, presence of leached wastes, and water treatment chemicals (table 4.1). Anaerobic pods 2.1, 5.3, and 8, F8, and M2 exceeded the WHO and NEMA limit of 750mg/l. High TDS values recorded in these were attributed to runoff of dissolved organic and inorganic matter during the rains. During the dry season a significant reduction in TDS values was observed which met the WHO and NEMA limit in all the sampling points (Table 4.2). TSS were high during the wet season except for ANR 5.3 these values indicate high amounts of silt particles in the runoff water during the rains (Table 4.1). On dry season the TSS were high in F2, F5, F8, M2, M5 and RS2 (Table 4.2). These higher values of TSS might be due to high BOD loading caused by bacteria deficiency and solids accumulation in the pods (Ersahin *et al.*, 2011). There is a statistically significant difference between the sampling pods since the p-values were 0.000 and 0.001 for TDS and TSS at 95% confidence level (appendix I and II). The results of TDS for this study met the FAO guidelines (1992), guidelines for reuse in agriculture.

4.1.2 Chemical parameters of the wastewater

The levels of nitrates in this study ranged from 6.66- 25.1mg/l which is high compared to results of Edori and Nna (2018); Odjadjare and Okoh (2010), which are 0.32-0.51mg/l and 0.32 to 6.6mg/L respectively. Nitrate result of Maina *et al.* (2020) and Adewumi and Ajibade (2019), of 38.0-50.8mg/L and 35.0 to 58.2mg/L were higher. During wet season a range of 6.66- 25.1 mg/l (table 4.1) nitrate concentration was observed and this may be due to runoff of leached wastes from fertilized lawns and animal manure storage areas within the plant (Ombaka *et al.*, 2012). Discharge of nitrogen containing compounds into the environment has a significant effect on human health, and causes eutrophication of rivers at higher levels (Wyasu, 2020). According to Bazeli *et al.* (2022), high nitrate concentration in drinking water causes methemoglobinemia in infants. Dry season reported higher nitrate levels of 9.67-20.94mg/L (table 4.2) because of high amount of organic matter in the pods due to large quantity of BOD and COD in the wastewater and also industrial discharges that contain corrosion inhibitors such as nitrate could have contributed to this (Sastri, 2012).

The wet season results of this study are lower compared to the same season outcome of a study conducted by Sewe (2013), in Ruai Sewage treatment plant and this might be due to reduction in improper use of nitrate fertilizers and desludging of the pods. A statistically significant difference between the wet and dry season was observed with a p-value of 0.011 at 95% confidence level due to reasons stated above. No significant difference was observed between the sampling pods because the p-value was 0.196 (appendix I and II). The nitrate levels for this study were below WHO and NEMA limit of 50mg/L but higher than FAO (1992) guideline of 5mg/L for reuse in irrigation.

Phosphorus is an important element in plants and plays a major role in physiological processes like division of cells, synthesis of DNA and energy metabolism, however excessive amount of phosphorus in water bodies causes eutrophication (Carrillo *et al.*, 2020). In this study phosphorus ranged from 1.16-10.30 mg/L which is higher compared to 0.29-0.54mg/L results of Odjadjare and Okoh (2010), but lower than 21.1 to 43.4mg/L obtained by Adewumi and Ajibade, (2019) and 28.43- 32.45mg/L of Kihila et al. (2014). Olabode *et al.* (2020), study had phosphate range of 0.10-11.32mg/L which correlated with results of this study. During the wet season P ranged between 1.16-10.30 mg/L with ANR 5.3, ANR 8.1, ANR 8.3, F2 and raw sewage having higher values compared to WHO limit of 5 mg/L (table 4.1). These slightly high amounts of phosphorus in these pods were attributed to excessive use of phosphate fertilizers within the area.

Samples collected during the dry season were high in phosphorus except M2, NR1, NR2 and NR3 (table 4.2). The high levels might be due to large amount of grey water from households (detergents, toothpastes, hair shampoos and conditioners, presence of phosphates and elemental phosphorus in mineral and multi-vitamin supplements) (Comber *et al.*, 2015). Phosphate is used in coating surfaces before painting and also to reduce corrosion, this increases its levels in construction wastes (Comber *et al.*, 2013). A study conducted by Sewe (2013), in Ruai WWTP the concentration of phosphorus in wet and dry season ranged from 32.20 -82.56mg/l. The difference in results obtained in Ruai that period and results of this study could be due to quantity of the influent, improved cleaning of industrial waste discharged into the plant and improved desludging of the pods. There was a statistically significant difference between the two seasons since the p-value was 0.003 at 95% confidence level. No statistical significance difference was reported amongst the sampling points because the p-value was 0.098 (appendix I and II). The results of phosphorus in most of the sampling points exceeded the FAO, (1992) and NEMA limit of 2.0mg/L and WHO standard of 5mg/l for reuse in agriculture.

The results of BOD_5 ranged from 10-480mg/L which is lower compared to 535.80 to 604.80mg/L reported by Lokhande *et al.* (2011), but higher than 3.7 to 14mg/L results of Agoro *et al.* (2018), for municipal effluent in cape town. During the wet season the levels of BOD were above the WHO and NEMA limit (50mg/L) in all sampling points except M2, M5, M8 (table 4.1). The raw sewage reported the highest value 480mg/L and this was due to excess runoff of nutrients from agricultural lawns, domestic wastes, decaying vegetation and large amounts of organic pollutants from industrial areas into the treatment plant during the rains (Paltahe *et al.*, 2018). The anaerobic pods 2, 5 and 8 reported lower BOD values of 224-136mg/L compared to raw sewage due to depletion of the organic wastes by anaerobic bacteria which reduced the wastes loads in the influent. In facultative and maturation pods the organic waste was converted into water, CO_2 and new bacteria and algae cells (Dasgupta & Yildiz, 2016). The photosynthetic algae grow in these pods and releases excess oxygen which is used by the bacteria to disintegrate the organic matter in the sewage thus low BOD is achieved (Sewe, 2013). During the dry season the BOD5 values reduced slightly compared to wet season this might be due to reduction in organic waste pollution load (Table 4.2).

The COD values in this study were between 90-980mg/L for both seasons which correlated with 270 to 900mg/L reported in Rwanda by Nikuze *et al.* (2020), and 23.70-898.58mg/L results of (Olabode *et al.*, 2020). Gadhia *et al.* (2012), and Ma *et al.* (2020), studies reported lower COD values of 72.00mg/l in Tapi estuary and 165.25mg/l Bilaspur treatment facility in India, respectively. The lower values were attributed to decreased discharge of chemicals and clean-up of wastes by industries before release into sewer lines. Raw sewage had the highest COD values for both season with a range of 960-980 mg/l as illustrated in table 4.1, due to increased levels of soluble organic compounds, dying bacterial cells responsible for decomposition of wastes and piled solid and food wastes (Ayilara *et al.*, 2020). In general, all the pods had higher COD values than WHO recommended standard of 70mg/l which indicates poor treatment of the wastewater and possibility of more organic pollutants during the season.

During the dry season the COD values slightly accelerated compared to wet season, and this might be due to excessive wastes from food, construction and chemical industries and also domestic wastes (table 4.2). The results of this season surpassed the WHO limit. Wolfgang *et al.* (2013), reported high BOD_5 and COD load of 14500-18500mg/l and 36000-41800mg/l respectively. The high amount of organic substances and solid wastes in the wastewater contributed to this. A statistically significant difference between the seasons was reported for both COD and BOD_5 with a p-value of 0.000 at 95% confidence limit. No significant difference was reported for BOD_5 and COD in the sampling pods since the p-values were 0.874 and 0.588 respectively at 95%

confidence level (appendix I and II). The levels of BOD_5 at the final effluent during the wet season met the WHO guidelines for reuse in agriculture while COD did not meet the threshold for all seasons.

4.1.3 Levels of inorganic elements in Ruai wastewater treatment plant during wet and dry season

The inorganic elements tested in this study were found to be present though some were in minute concentrations. Iron levels were within the WHO, NEMA and FAO limits for all the seasons except for NR1, NR2 and NR3 wet season (table 4.3).

Table 3: Levels of Fe, Mn and Cd in Ruai wastewater treatment plant during wet and dry season

REF:	Fe (mg/l)		Mn (mg/l)		Cd (mg/l)	
CODE	Wet	Dry	Wet	Dry	Wet	Dry
ANR 2.1	0.49±0.01	0.34±0.00	0.39±0.02	1.08±0.01	0.01±0.00	ND
ANR 2.2	1.15±0.01	1.00±0.04	0.38±0.04	0.87±0.00	0.01±0.00	ND
ANR 2.3	2.66±0.03	0.73±0.01	0.31±0.01	1.09±0.01	0.02±0.00	ND
ANR 5.1	2.93±0.01	0.68±0.01	0.32±0.02	1.46±0.01	0.01±0.00	ND
ANR 5.2	1.49±0.05	1.01±0.01	0.35±0.01	1.34±0.01	ND	0.01±0.00
ANR 5.3	0.68±0.02	ND	0.43±0.01	1.18±0.01	ND	0.01±0.00
ANR 8.1	1.53±0.02	0.40±0.01	0.55±0.02	1.06±0.01	ND	ND
ANR 8.2	0.91±0.01	0.65±0.01	0.38±0.02	1.06±0.02	0.01±0.00	ND
ANR 8.3	0.86±0.02	0.56±0.00	0.44±0.01	1.05±0.03	0.01±0.00	0.01±0.00
F8	0.31±0.01	ND	0.25±0.00	0.95±0.01	0.01±0.00	ND
F5	0.17±0.01	ND	0.23±0.01	1.05±0.01	ND	ND
F2	0.26±0.01	ND	0.25±0.02	0.14±0.01	ND	ND
M2	0.05±0.01	ND	0.27±0.01	0.72±0.01	ND	ND
M5	0.23±0.01	ND	0.31±0.05	0.48±0.01	ND	ND
M8	0.07±0.01	ND	0.57±0.01	0.72±0.01	0.05±0.00	ND
RS1	2.29±0.10	1.34±0.02	1.23±0.04	0.96±0.00	ND	ND
RS2	2.78±0.08	1.00±0.01	1.31±0.03	0.99±0.02	ND	ND
RS3	1.93±0.03	1.51±0.02	1.19±0.02	1.11±0.01	ND	0.01±0.00
NR1	4.78±0.11	1.93±0.06	0.46±0.01	0.95±0.02	0.01±0.00	ND
NR2	7.24±0.07	1.75±0.03	0.54±0.01	2.26±0.02	0.01±0.00	ND
NR3	7.24±0.03	2.28±0.02	0.31±0.009	1.83±0.009	0.02±0.0	ND
WHO standards	0.3		0.1		0.03	
NEMA limits	1.5		1.0		0.01	
FAO guidelines	5.0		0.2		0.01	

This can result from corrosion of water pipes, iron sheets and runoff water from plating industries into the stream thus exceeding WHO limit 3.5mg/l. The concentration of Mn during the wet season were within the WHO limit (1mg/l) except RS1, RS2 and RS3.

During the dry season the Mn level was high in ANR 5and 8, F5, RS3 and NR2 (table 4.3). This indicates high concentration of Mn in the incoming industrial wastes, especially from chemical and construction industries within Ruiru. High levels of cadmium were reported on wet season at ANR 2.2, 2.3 and 5.1, F8, M8, raw sewage and in Nairobi River (table 4.4). On dry season only ANR 2.1 and 2.2 exceeded the WHO limit of 0.01mg/l. The major source of Cd is attributed to water draining from landfills, industrial wastes having NiCd batteries, plastics, plating and pigments. The concentration of zinc, copper and nickel were found to be within the WHO and NEMA limits of 2mg/l, 0.5mg/l and 0.5mg/l respectively for both seasons.

Table 4: Levels of Ni, Zn and Cu in Ruai wastewater treatment plant during wet and dry season

REF: CODE	Ni (mg/l) Wet	Dry	Zn (mg/l) Wet	dry	Cu (mg/l) wet	Dry
ANR 2.1	0.03±0.01	ND	0.17±0.01	0.20±0.01	ND	0.07± 0.00
ANR 2.2	0.08±0.01	ND	0.18±0.01	0.29±0.00	0.01±0.01	0.11± 0.01
ANR 2.3	ND	0.06± 0.02	0.37±0.01	0.19±0.00	0.06±0.00	ND
ANR 5.1	ND	ND	0.46±0.00	0.28±0.01	0.07±0.01	ND
ANR 5.2	ND	ND	0.19±0.02	0.21±0.01	0.05±0.02	ND
ANR 5.3	0.04±0.01	ND	0.33±0.01	0.05±0.01	0.07±0.01	0.01± 0.004
ANR 8.1	0.07±0.02	0.02± 0.01	0.31±0.01	0.63±0.01	0.23±0.02	ND
ANR 8.2	0.02±0.01	0.11±0.012	0.17±0.00	0.20±0.00	0.11±0.09	ND
ANR 8.3	ND	ND	0.12±0.02	0.15±0.01	0.01±0.01	ND
F8	0.12±0.00	ND	0.06±0.00	0.05±0.00	0.02±0.00	ND
F5	0.06±0.00	N D	0.06±0.00	0.12±0.01	0.02±0.00	ND
F2	0.02±0.01	ND	0.04±0.01	0.08±0.00	0.02±0.00	ND
M2	0.18±0.01	ND	0.11±0.00	ND	0.05±0.01	ND
M5	0.14±0.01	0.17± 0.01	0.11±0.00	0.03±0.01	0.06±0.01	ND
M8	0.01±0.01	ND	0.33±0.01	ND	ND	ND
RS1	0.22±0.03	ND	1.02±0.01	0.23±0.00	0.10±0.01	ND
RS2	0.04±0.01	ND	0.49±0.01	0.19±0.00	0.12±0.00	ND
RS3	0.02±0.00	ND	0.31±0.00	0.31±0.00	0.07±0.01	ND
NR1	0.08±0.01	ND	1.67±0.02	0.16±0.00	0.03±0.01	ND
NR2	0.13±0.00	ND	0.34±0.03	0.20±0.00	0.04±0.01	ND
NR3	0.19±0.01	ND	0.68±0.01	0.13±0.01	0.04±0.01	ND
WHO standards	0.02		5.0		2.0	
NEMA limits	0.3		2.0		1.0	
FAO guideline	0.2		2.0		0.2	

The findings of Maina *et al.* (2020) on zinc, copper and nickel in Ruai treated wastewater were within the WHO and NEMA standard which correlated with results of this study. Mathenge *et al*. (2018), study on heavy metals showed the concentration of Cd, Fe, Mn and Pb in upper and lower Ruai wastewater were above the WHO limit while zinc and Cu were within the limit (table 4.3 and 4.4). The results of Kasima (2014b), on concentration of lead in Kipevu wastewater ranged from 0.11-0.18mg/l and zinc 0.05-0.07mg/l which are higher compared to this study, while cadmium and chromium were not detected. Study conducted by Bahiru (2020), in eastern industrial zone wastewater, Ethiopia showed high concentration of Cr (1.04mg/l), Pb (3.11mg/l) and Cd (0.08mg/l) while Zn, Fe and Cu were within the limit. A statistical significant difference was reported amongst the sampling points with p-values of 0.021, 0.000, 0.027, 0.006,0.046 and 0.001 for Fe, Mn, Cd, Ni, Zn, and Cu respectively at 95% confidence level (appendix I and II). The difference might be due to excessive inflow of wastes containing these elements during the rains. The concentration of heavy metals studied met FAO (1992), guidelines for irrigation apart from Manganese and cadmium in M8 wet season for the final effluents released into Nairobi River.

4.1.4 Levels of lead (II) ions in Ruai wastewater treatment plant during wet and dry season

The levels of Pb were high in RS3, NR1 and NR2 during the wet season and ANR5.2, 5.3, 8.1 and M5 during the dry season as compared to 0.1mg/l WHO limit (table 4.5). The elevated levels of Pb might be due to improper disposal of metallurgy in the environment which might have led to runoff into the WWTP. A mean concentration of 0.1106 mg/l was reported in sugar industry wastewater which was attributed to pollution from metal processing (Dande *et al.*, 2019).

A study conducted by Sewe (2013), in Ruai WWTP showed high concentrations of lead as compared to findings of this study. The difference in results is attributed to desludging of the pods and also controlled lead pollution from point sources. A statistically significant difference amongst the sampling points for both seasons was reported with a p-value of 0.011 at 95% confidence limit (appendix I and II). The results of lead met the FAO (1992), guideline for reuse in agriculture practices.

Table 5:Levels of Pb in Ruai wastewater treatment plant during wet and dry season

REF: CODE	Pb (mg/l)	
	wet	Dry
ANR 2.1	0.08 ± 0.036	ND
ANR 2.2	0.08 ± 0.007	ND
ANR 2.3	0.06 ± 0.006	ND
ANR 5.1	0.23 ± 0.008	ND
ANR 5.2	0.29 ± 0.010	0.18 ± 0.082
ANR 5.3	0.26 ± 0.018	0.78 ± 0.120
ANR 8.1	0.30 ± 0.003	0.13 ± 0.057
ANR 8.2	0.19 ± 0.016	ND
ANR 8.3	0.18 ± 0.004	ND
F8	0.27 ± 0.016	ND
F5	0.26 ± 0.021	ND
F2	0.23 ± 0.016	ND
M2	0.35 ± 0.008	ND
M5	0.18 ± 0.010	0.18 ± 0.078
M8	0.41 ± 0.003	ND
RS1	0.24 ± 0.021	ND
RS2	0.12 ± 0.001	ND
RS3	0.08 ± 0.013	ND
NR1	0.04 ± 0.005	ND
NR2	0.06 ± 0.008	ND
NR3	0.09 ± 0.022	ND
WHO standard	0.01	
NEMA limit	0.01	
FAO guideline	5.0	

4.2 Adsorbents characterization

4.2.1 FTIR spectrum of borosilicate waste glass adsorbent

The FTIR spectrum of borosilicate waste glass is shown in figure 4. The peak at 432cm^{-1} corresponds to Si-O-Si bending vibrations. The broad band observed at 682 cm^{-1} was assigned to bending vibrations of bridging oxygen between trigonal BO_3 (Rao *et al.,* 2013). Symmetric stretching vibration of O-Si-O and Si-O-B are confirmed by a band at 774cm^{-1} and 907.55cm^{-1} respectively. Presence of tri-, tetra- groups belonging to BO_3 and BO_4 and asymmetric stretching of Si-O-Si bonds were confirmed by broad bands observed at 1037cm^{-1} and 1090cm^{-1} (Zhong *et al.,* 2014). The peaks at 1385cm^{-1} and 1468cm^{-1} were assigned to symmetric stretching relaxation of B-O bond of BO_3 units (Shao *et al.,* 2015). The broad peaks at 3268cm^{-1} and 3341cm^{-1} are assigned to -OH group from silanol (Si-OH) (Sodeinde *et al.,* 2021). These functional groups played an essential role in adsorption of lead (II) ions at the waste glass surface through electrostatic interactions.

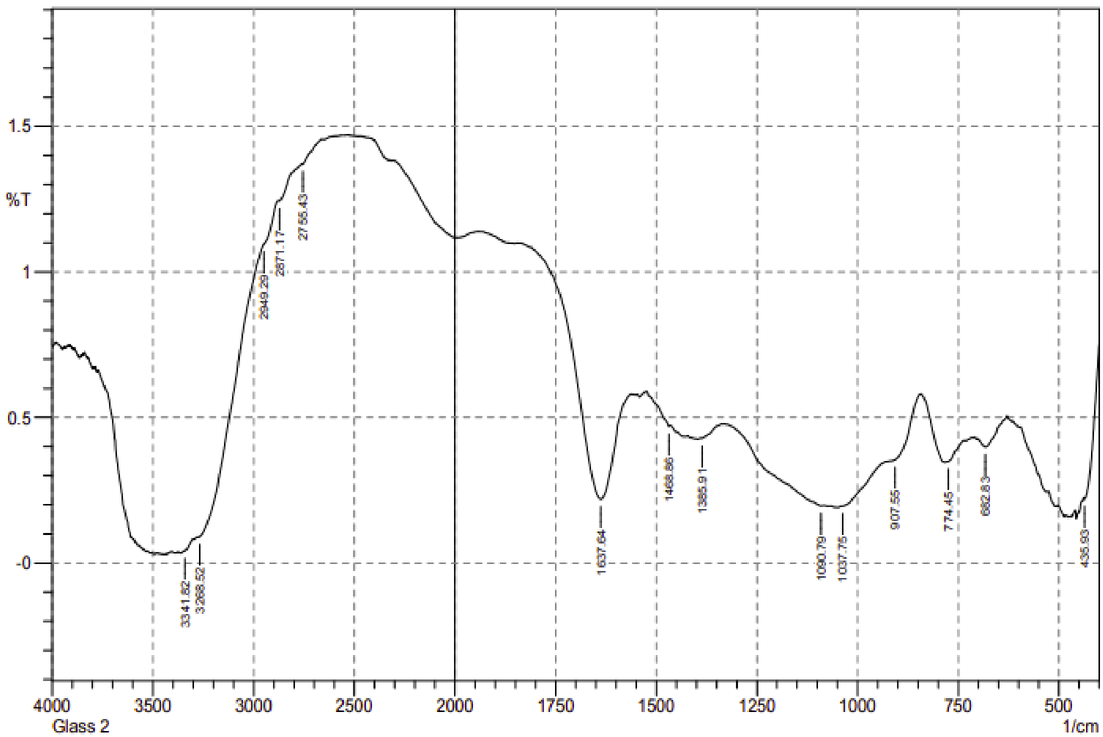

Figure 4: FTIR spectrum of modified borosilicate waste glass adsorbent

4.2.2 FTIR spectrum of soda lime waste glass adsorbent

The FTIR spectrum of soda lime waste glass is shown in figure 5. The peaks observed at 431cm^{-1} and 498cm^{-1} were assigned to bending vibrations of Si-O-Si and stretching vibrations of O-Si-O respectively. The broad peak at 776cm^{-1} was attributed to stretching vibration of Si-O-Al while the peak at 933cm^{-1} indicates stretching of metal oxides (M-O) in the glass structure (Hussain *et al.,* 2020). The peaks at 3215 and 3351cm^{-1} indicates -OH group from the silanol or trapped water molecule adsorbed within the silicate structure of the soda lime waste glass (Sodeinde *et al.,* 2021).

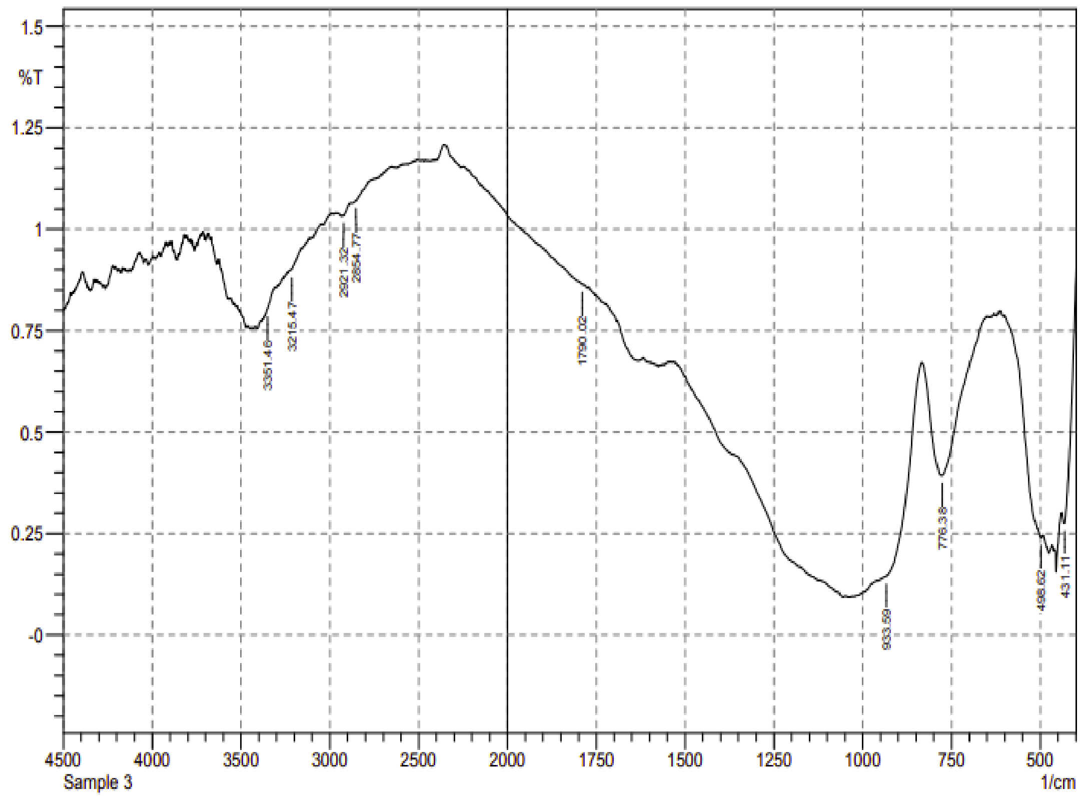

Figure 5: FTIR spectrum of soda lime waste glass adsorbent

4.2.3 FTIR spectrum of MWCNTs/Soda lime waste glass composite

FTIR spectrum of the composite is shown in figure 6. The peak at 487cm^{-1} was ascribed to asymmetric vibration of Si-O-Si while the broad peak at 778cm^{-1} was attributed to symmetric vibration of Si-O-Al (Hussain *et al.*, 2020). The peak at 1087cm^{-1} was assigned to C-O stretching while the signal at 1398cm^{-1} was associated with O-H bending deformation of the carboxylic group on the MWCNTs surface (Ahmed *et al.*, 2013). C=C stretching of MWCNTs was confirmed by a peak at 1631cm^{-1} while a peak at 2930cm^{-1} indicated C-H stretching (Abuilaiwi *et al.*, 2010). The broad peaks observed at 3436 and 3558cm^{-1} were assigned to O-H stretching of the carboxyl groups (O=C-OH and C-OH), and silanol (Si-OH) within the glass surface (Jirakittidul *et al.*, 2019).

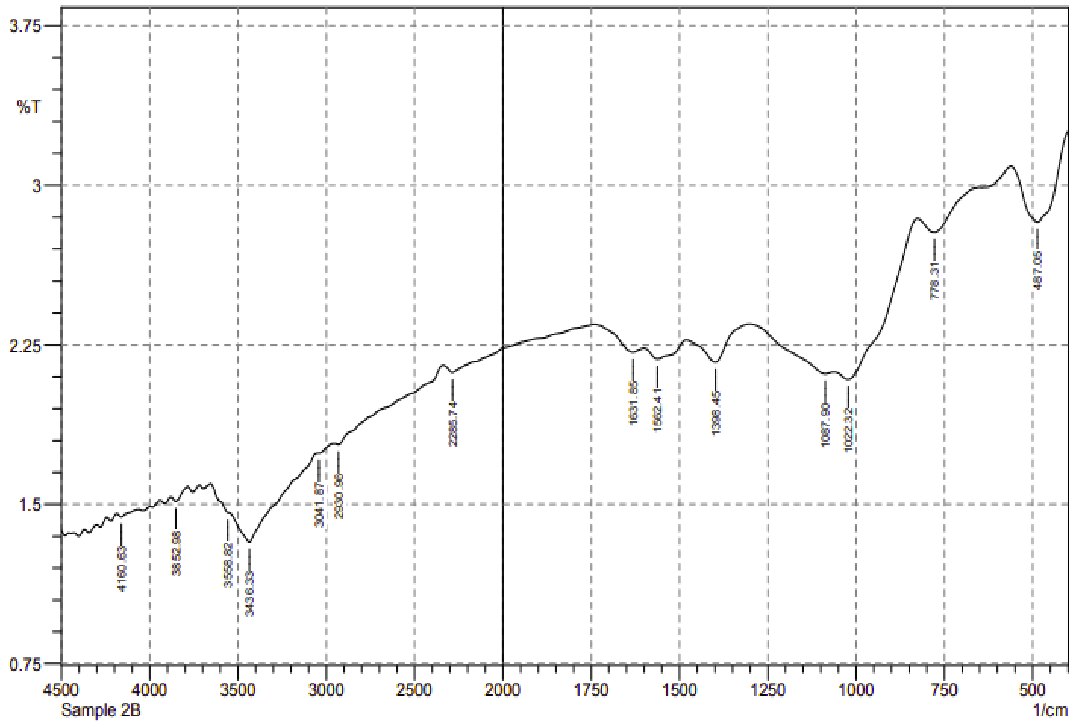

Figure 6: FTIR spectrum of MWCNTs/Sodalime waste glass composite

4.3 Adsorption experiments for lead (II) ions

4.3.1 Effect of pH on adsorption of lead (II) ions

The measure of alkalinity or acidity in a medium plays a major role in the process of adsorption by facilitating sorption and precipitation of ions through repulsion and attraction of charges between the adsorbate and adsorbent surfaces. The percentage adsorption for all the adsorbents increased with an increase in pH with maximum adsorption at pH 6 as shown in figure 7. Due to acidity of the medium at pH 2 low Pb^{2+} removal was reported because of the competition with H_3O^+. Soda lime waste glass reported the lowest adsorption at pH 2 which increased gradually with increase in pH and the maximum adsorption was recorded at pH 6. As the pH increased Si-OH group on the glass surface dissociated and acquired a negative charge density which led to increase in electrostatic attractions between Pb^{2+} and electronegative surface. Maximum adsorption was reported at pH 6 due to high Pb^{2+} precipitation, further increase in pH to 8 led to decrease in adsorption due to supersaturation of adsorption sites. For borosilicate waste glass higher adsorption efficiencies were reported (20,77,94 and 91%), as compared to soda lime (6, 22, 45 and 43%) as indicated in figure 7 and appendix III. This was due to presence of more adsorption sites on the glass surface as boron is unreactive on the alkaline medium it was substituted by lead which can precipitate in form of oxide and hydroxides. Increase of pH in the composite medium led to increased adsorption due to increase in negative charge density (-OH groups) on the soda lime glass and MWCNTs surface.

The nanotubes have large surface area which increased the ion exchange capacity thus maximum adsorptions (24,79,97 and 95%) were reported for the composite. Sodeinde *et al.* (2021), reported an increase in % adsorption of Pb (II), Cd (II) and CV dye by a porous soda lime waste glass adsorbent with increasing pH and a maximum efficiency was attained at pH 6. A composite of glass waste and activated carbon proved to be effective in adsorption of copper, cadmium, lead, iron and zinc at pH 7 with efficiencies of 90.7%, 90%, 90%, 90.5% and 91.2% respectively (Rashed *et al.*, 2019). Rashed *et al.* (2018), investigated the adsorption of Zn^{2+}, Pb^{2+}, Fe^{2+}, Cd^{2+} and Cu^{2+} using waste glass adsorbent and the results revealed maximum adsorptions at pH 5-7, due to increased negative charge density on the glass surface as a result of deprotonation of the positively charged groups. Results of Ibrahim *et al.* (2012), on adsorption of Pb(II), Cu(II) and Cd(II) using recycled waste glass showed maximum sorption capacity at pH 6.

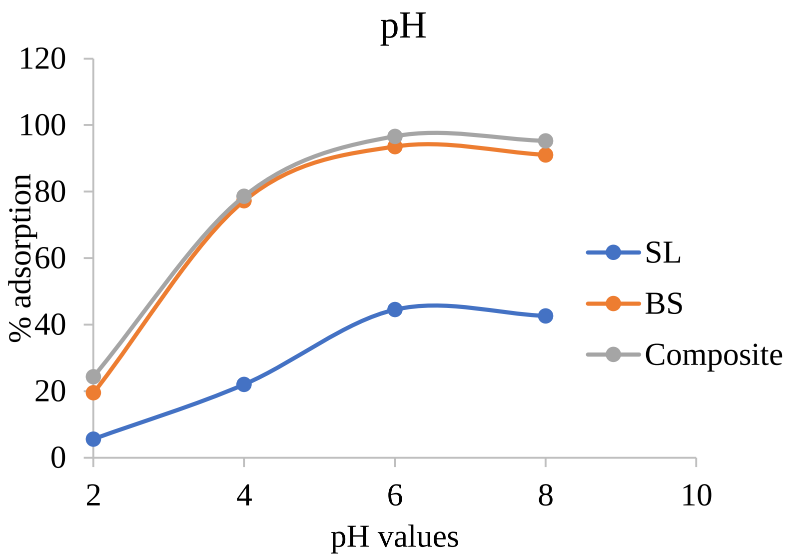

Figure 7: Effect of pH on the adsorption of lead (II) ions

4.3.2 Effect of contact time on adsorption of lead (II) ions

Effectiveness of adsorption process is determined by how long the adsorbents take to adsorb maximum sorbents. Soda lime waste glass adsorbent reported maximum adsorption at 30 mins, as the contact time increased the adsorption decreased and slightly increased at 60 mins (figure 8, appendix IV). The decrease was due to occupation of all active sites by the sorbent and the slight increase observed after 60 mins was attributed to dissociation of some Si-OH groups on glass surface as the shaking continued thus creating more sorption sites. Borosilicate adsorbent reported almost the same values at 30 mins and 60 mins, the slight decrease at 45 mins was due to competition of the H_3O^+ ions in the medium with the Pb^{2+} ions for active sites. Presence of initially active sites which have not been occupied could have led to the slight increase from 87.54% to 87.88% at 60 mins. Due to large surface area and many sorption sites in the composite higher adsorption was reported (87.86%, 90.65% and 90.34%). The equilibrium was achieved at 45 mins and started decreasing at 60mins due to super saturation of adsorption sites.

Maximum lead adsorption of 88% was achieved at 45minutes using a composite of glass waste and activated carbon (Rashed *et al.*, 2019). The results of borosilicate waste glass tallied with findings of Rashed *et al.* (2018), where maximum adsorption of lead was achieved at 45minutes using waste glass adsorbent. Adsorption of lead (II) ions using soda lime waste glass attained equilibrium at 30mins in a study conducted by Sodeinde *et al.* (2021), which resonated with results of soda lime waste glass in this study. Removal of Pb^{2+} using multiwalled carbon nanotubes was achieved at 45minutes with 96% efficacy (Tehrani *et al.*, 2013).

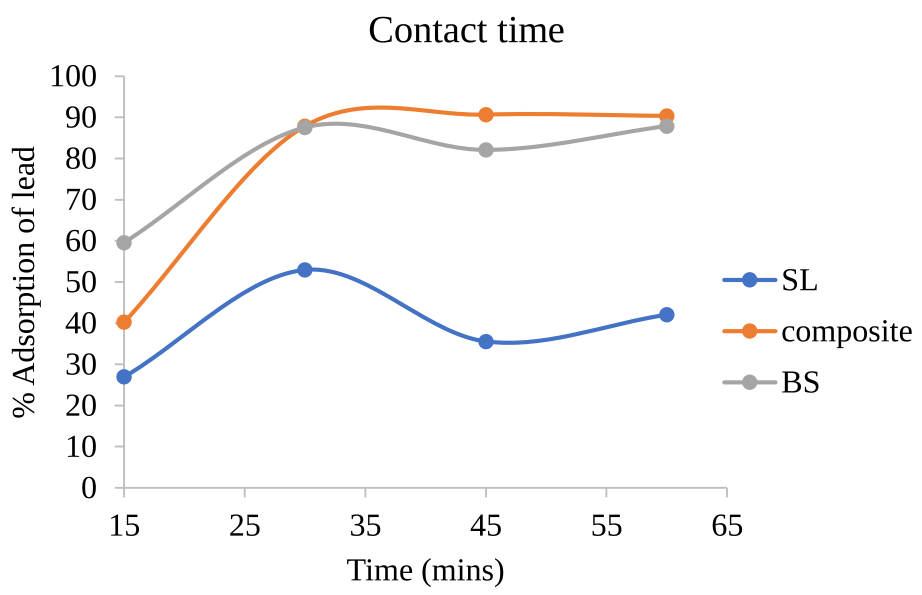

Figure 8: Effect of contact time on the adsorption of lead (II) ions

4.3.3 Effect of shaking speed on adsorption of lead (II) ions

The agitation speed determines the frequency of collisions between the adsorbate (Pb^{2+}) and the adsorbent surfaces (soda lime waste glass, borosilicate waste glass and soda lime/MWCNTs composite). Percentage adsorption increased with increase in shaking speed for all the adsorbents due to better mass transfer of Pb^{2+} from the bulk solution to the adsorbent surface because of the reduction in boundary layer thickness around the adsorbents thus decreasing the equilibrium time (figure 9, appendix V). Maximum adsorption was attained at 200 rpm; beyond this speed a reduction in % adsorption was observed. Increase in kinetic energy reduced the contact time for both physical and chemical bond formation and the newly formed bonds between the adsorbate and adsorbent surfaces were broken which led to decrease in adsorption (Ngugi, 2015).

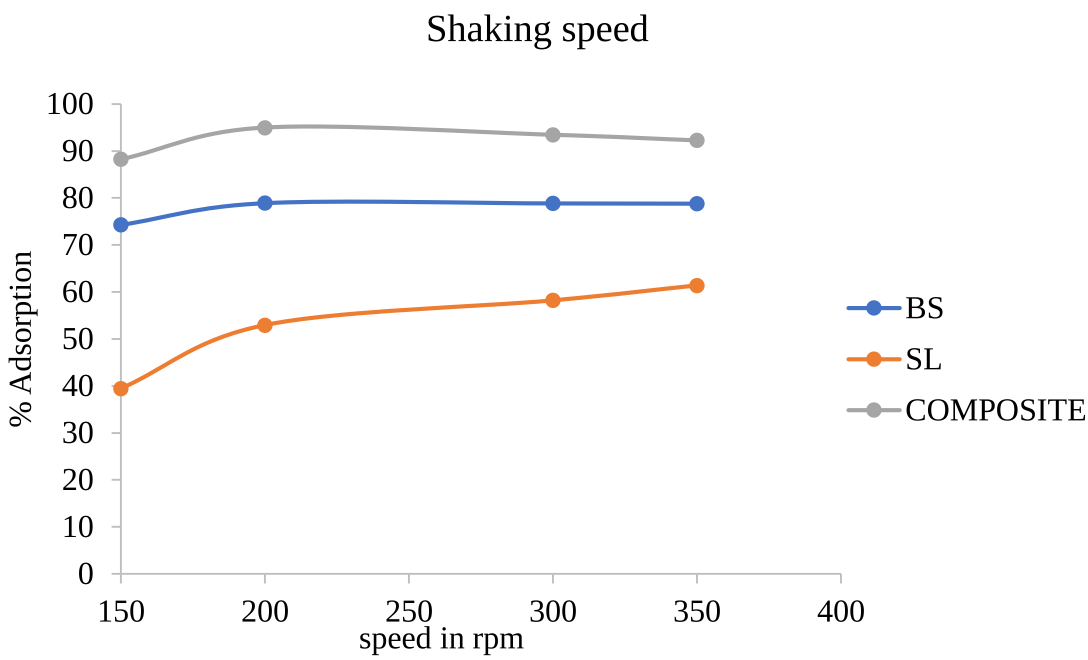

Figure 9: Effect of shaking speed on the adsorption of lead (II) ions

4.3.4 Effect of adsorbent dose on adsorption of lead (II) ions

The results for adsorbents dosage are shown in figure 10 and experimental data presented in appendix VI. The dose was varied from 50-200mg under these conditions (pH 6, initial metal concentration 10ppm, 200rpm speed, room temperature and 30mins contact time). For all the adsorbents increase in adsorbent dose led to higher % adsorption because of availability of more adsorption sites for the adsorbate ions (Pb^{2+}). The maximum adsorption efficiencies of 87.3%, 66.89% and 58.59% were recorded for composite, borosilicate and soda lime respectively. Adsorption of lead (II) ions on a composite of sugarcane bagasse and MWCNTs increased with increase in adsorbent dose from 1g to 10g (Hamza *et al.*, 2013). Variation of MWCNTs dose from 5-35mg increased the adsorption of lead (II) ions with maximum adsorption at 10mg. A plateau was observed at higher doses indicating all the ions had been adsorbed at 10mg dosage (Tehrani *et al.*, 2013). Increase in sorbent amount from 0.5-1.5g increased the adsorption of lead (II) ions to 92% using a composite of waste glass and activated carbon (Rashed *et al.*, 2019).

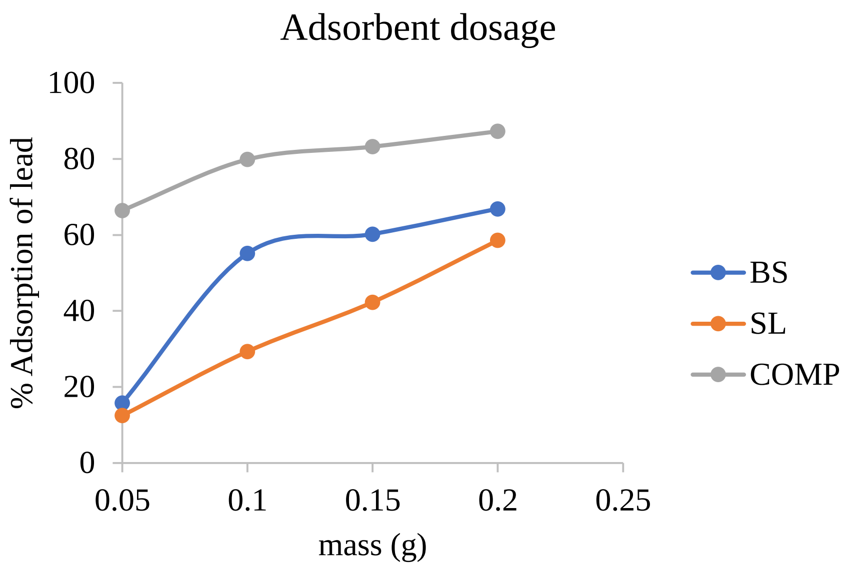

Figure 10: Effect of adsorbent dose on the adsorption of lead (II) ions

4.3.5 Effect of temperature on adsorption of lead (II) ions

Increase in temperature decreases the solution viscosity which enables the adsorbate molecules to diffuse faster around the external boundary layer (Rashed *et al.*, 2019). Increase in temperature from 25^0C -40^0C led to higher adsorption percentage of 81.53% to 93.05% (figure 11) for the composite adsorbent due to increased mobility of ions around the boundary layer as a result of dissociation of functional groups on the adsorbent surface, thus creating more adsorption sites (Ngugi, 2015). For borosilicate and soda lime waste glass maximum adsorption was attained at 25^0C, further increase in temperature led to decrease in % adsorption indicating that the reaction is exothermic. Gradual decrease in % adsorption was recorded from 81.75% -77.95% for borosilicate and 65.58-39.08% soda lime at 40^0C, experimental data presented in appendix VIII. As the temperatures increased the adsorbents were unable to adsorb more adsorbates due to deactivation of active sites on the glass surfaces and the bonds binding the Pb^{2+} on the glass surface might have been weakened (Siwi *et al.*, 2018).

The results of the composite in this study agrees with Rashed *et al.* (2019), where increase in temperature from 25-45^{0}C led to higher adsorption of Cu, Pb, Fe, Cd and Zn using a composite of activated carbon and waste glass. Adsorption of crystal violet dye, lead (II) ions and cadmium (II) ions increased with increase in temperature from 30-70^{0}C. Increase in temperature from 22-45^{0}C decreased the adsorption of lead (II) ions on sugarcane bagasse. The decrease in adsorption was attributed to the exothermic nature of the reaction (Hamza *et al.*, 2013).

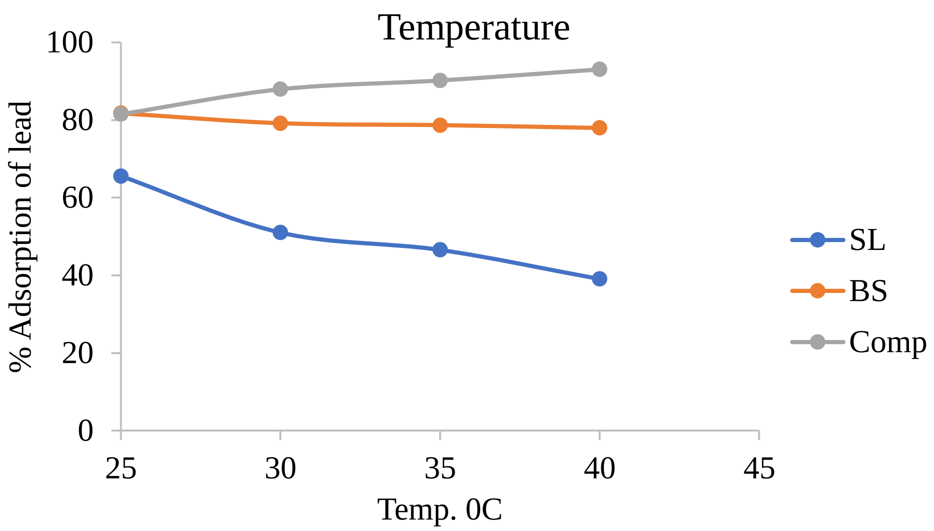

Figure 11: Effect of temperature on the adsorption of lead (II) ions

4.3.6 Effect of initial lead (II) ions concentration on adsorption capacity

Initial metal concentration was studied at a range of 5-20 ppm with an adsorbent dose of 200 mg, temperature of 25°C, pH 6, speed of 200 rpm for 30 minutes. The results of both borosilicate and soda lime adsorbents showed an increase in percentage adsorption as the adsorbate concentration (Pb^{2+}) increased (figure 12). This was attributed to large surface area of the adsorbents, increase in mass transfer driving force and effective trapping of adsorbate ions on the adsorbent small pore sizes. At 10ppm maximum adsorption was attained due to saturation of active sites on the glass surfaces and a gradual decrease in % adsorption was observed beyond this concentration due to supersaturation of the adsorbent surfaces with the Pb^{2+} (Hummadi, 2021; Sodeinde *et al.*, 2021).

Increase in metal concentration led to a decrease in % adsorption for the MWCNTs/ soda lime composite adsorbent. Highest adsorption efficiency of 73.04% was reported at 5ppm Pb^{2+} concentration due to presence of more active sites on the adsorbent surface, which decreased to 58.1% at 10ppm of Pb^{2+} as a result of saturation of binding sites in the surface of the composite (figure 12), experimental data presented in appendix VII. A slight increase in percent adsorption was observed at 20ppm of Pb^{2+} concentration and this was attributed to soda lime adsorbent character which adsorbed more at high metal concentration as a result of high mass transfer across the boundary layer and also the presence of initially unoccupied active sites on the adsorbent might contribute to the increase in adsorption efficiency. Increase in metal ion concentration from 8mg/l to 25mg/l led to decrease of Pb^{2+} and Cd^{2+} adsorption on activated Carbon (Kamau, 2022). Rashed *et al.* (2019), studied the effect of initial metal concentration on adsorption of iron, zinc, copper, lead and cadmium using a composite of activated carbon and waste glass. Decrease in Pb^{2+} adsorption was observed when lead concentration was increased from 50mg/l to 300mg/l using activated carbon adsorbent (Yarkandi, 2014).

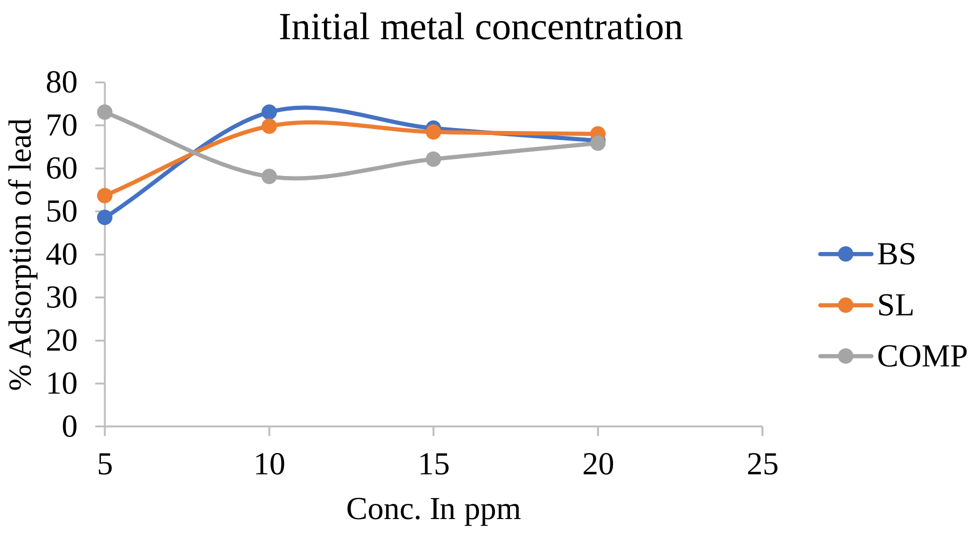

Figure 12: Effect of initial lead (II) ions concentration on adsorption efficacy

4.3.7 Adsorption of Pb2+ from raw wastewater samples

The samples collected in Ruai wastewater treatment plant on wet season were used to prepare composite samples from ANR 5, Facultative pods, maturation pods, raw sewage and Nairobi River. The concentration of lead (II) ions in these samples was determined before adsorption and after adsorption. The three adsorbents (borosilicate waste glass, soda lime waste glass and a composite of MWCNTs/ soda lime waste glass) were used to remove the Pb^{2+} from the wastewater samples under these conditions (pH 6, speed 200rpm, contact time 30mins,200mg dose and room temperature) and the results presented in table 4.6 and 4.7. Borosilicate and composite adsorbents recorded 100% Pb^{2+} removal while soda lime adsorbed the Pb^{2+} in NR and M samples but was unable to adsorb the adsorbate in ANR and F samples. The low adsorption efficiency of soda lime waste glass and high multielemental concentration in these pods led to low adsorption due to competition of sorption sites by different pollutants. The results of Pb (II) ions obtained after adsorption meets the WHO recommended value of less than 0.01mg/l concentration for wastewater reuse in agriculture.

Table 6:Concentration of lead (II) ions in raw wastewater samples

Raw sample.no	Actual concentration
BLK	0
RS	0.000
ANR	0.111
F	0.033
M	0.111
NR	0.554

Table 7:Concentration of lead (II) ions in raw wastewater samples after adsorption

Pb SAMPLES ADSORPTION				
Sample	Absorbance	Actual conc.	Final conc.	% Adsorption
BLK	0.002	0.000	0.346	ND
RS BS	0	0.000	0	ND
ANR BS	0	0.176	0	100
F BS	0	0.292	0	100
M BS	0.001	0.235	0	100
NR BS	0.002	0.346	0	100
RS SL	0.002	0.000	0	ND
ANR SL	0.003	0.457	0.111	0
F SL	0.004	0.568	0.222	-572.7
M SL	0.001	0.235	0	100
NR SL	-0.001	0.013	0	100
RS comp	0	0.000	0	ND
ANR Comp	0.001	0.235	0	100
F comp	0.002	0.346	0	100
M comp	0.002	0.346	0	100
NR Comp	0.002	0.346	0	100

4.4 Adsorption isotherms

4.4.1 Langmuir and Freundlich isotherms of borosilicate waste glass adsorbent

The adsorption of lead (II) ions using borosilicate waste glass was evaluated using the Langmuir and Freundlich models. Langmuir isotherm model, had maximum adsorption capacity Q max =-30.7503mg/g, KL of -0.0402 and (R^2) of 0. 78422 (figure 13, table 4.8). The negative values indicate that the model cannot be used to describe the system. On the contrary, the adsorption on a heterogeneous surface using the Freundlich isotherm model provided a Freundlich constant kF of 0.8670 and a Freundlich exponent n of 0.9508 with an R^2 = 0.87654 (figure 14, table 4.8). The Freundlich model of adsorption had a higher value of R^2 which indicates that the model is a better fit for the system than the Langmuir model. This result indicates that the adsorption of lead (II) ions on borosilicate waste glass follows the Freundlich isotherm model, indicating surface heterogeneity and multi-layer adsorption, experimental data presented in appendix IX. The Freundlich model constants also indicate favored adsorption when the value of n is between 0 and 1, implying that the adsorption process is efficient (Mmbaga, 2018).

Table 8:Langmuir and Freundlich constants for borosilicate waste glass adsorbent

Adsorbent	Langmuir			Freundlich		
borosilicate	Qmax	KL	R^2	n	KF	R^2
waste glass	-30.75	-0.04	0.78	0.9508	0.867	0.877

The Langmuir isotherm of borosilicate waste glass adsorbent is shown in figure 13.

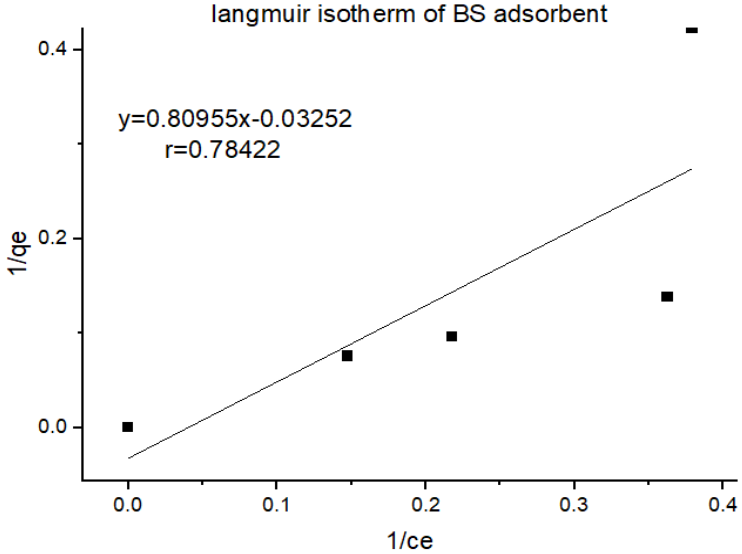

Figure 13: Langmuir isotherm of borosilicate waste glass adsorbent

The Langmuir isotherm of borosilicate waste glass is shown in figure 14 below.

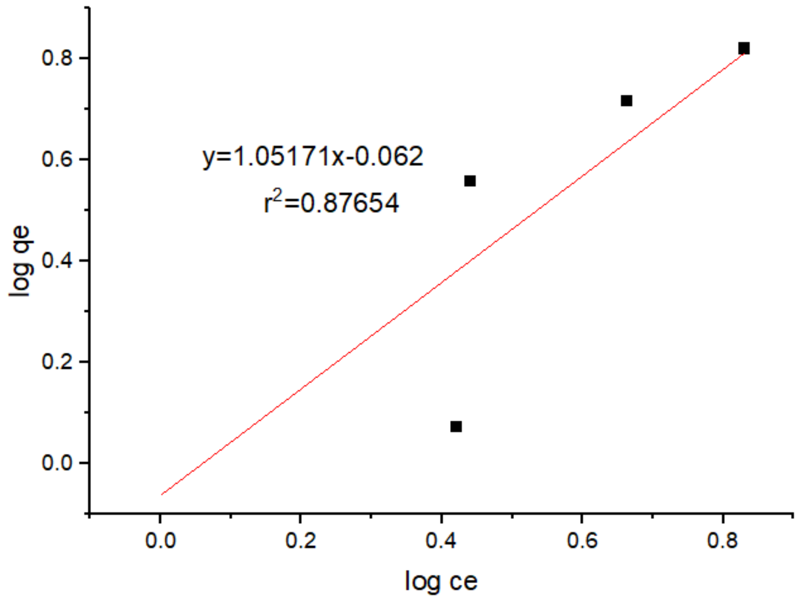

Figure 14: Freundlich isotherm of soda lime waste glass adsorbent

4.4.2 Langmuir and Freundlich isotherms of soda lime waste glass adsorbent

The Langmuir and Freundlich isotherms have been employed to study the adsorption of lead (II) ions on soda lime waste glass. The Qmax obtained from the Langmuir constants is -5. 8459 mg/g while the KL value is -0. 1268 with R^2 of 0. 89712 (figure 15, table 4.9, appendix IX). These negative values imply that the parameters are nonphysical, which means that the Langmuir model cannot be used to describe this adsorption process. The Freundlich isotherm, had a KF of 0. 6616 and n= 0. 5977, and a better R^2 value of 0.92571 (figure 16, table 4.9, appendix IX). The higher R^2 value in the Freundlich model suggest that the adsorption of lead (II) ions on soda lime waste glass occurs on a heterogeneous surface having sites with different adsorption energies. The fact that the exponent n is less than 1 indicates that the adsorption process is more favorable and effective at low concentrations of the adsorbate molecules. The Freundlich isotherm is more suitable and realistic to describe the adsorption process in the given system in comparison to the Langmuir isotherm. The adsorption of Cd, Fe, Zn, Cu and Pb using waste glass fitted best in freundlich isotherms compared to Langmuir (Rashed *et al.*, 2018).

Table 9:Langmuir and Freundlich constants for soda lime waste glass adsorbent

Adsorbent	Langmuir			Freundlich		
soda lime waste glass	Qmax -5.8459	KL -0.1268	R^2 0.89712	n 0.5977	KF 0.6616	R^2 0.92571

The Langmuir isotherm model of soda lime waste glass is shown in figure 15 below.

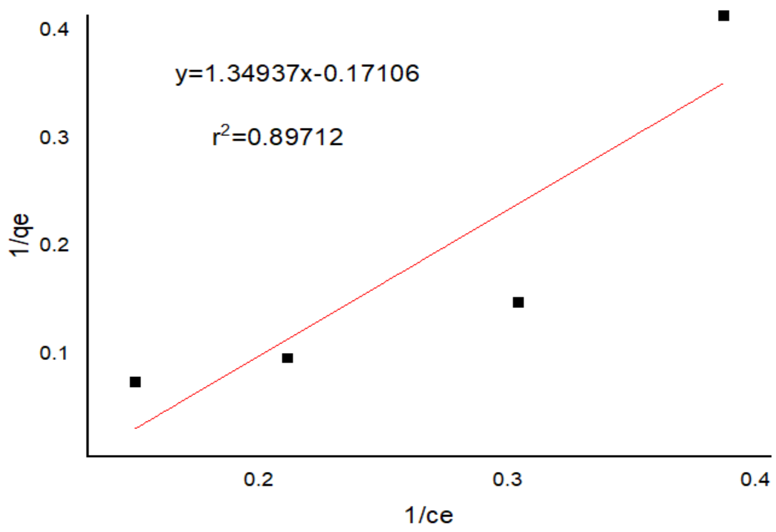

Figure 15: Langmuir isotherm of soda lime waste glass adsorbent

The Freundlich isotherm of soda lime waste glass is presented in figure 16.

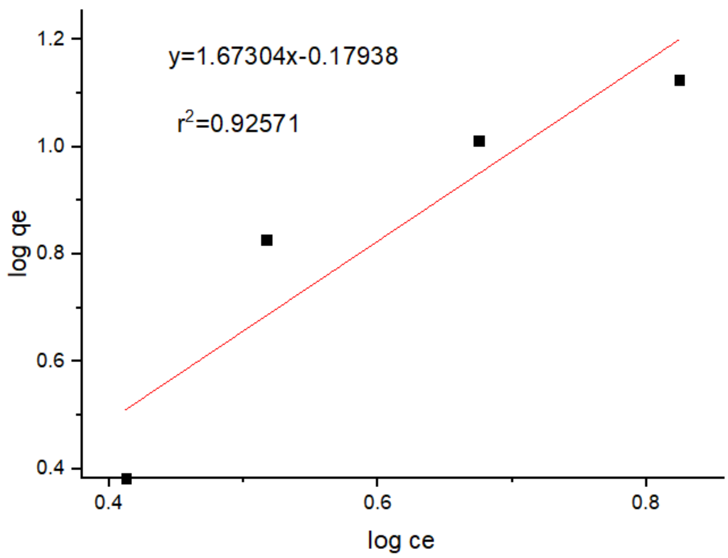

Figure 16: Freundlich isotherm of soda lime waste glass adsorbent

4.4.3 Langmuir and Freundlich isotherms of composite of MWCNTs/soda lime waste glass

The adsorption of Pb (II) ions from aqueous solution by composite of soda lime waste glass and oxidized multi-walled carbon nanotubes was studied by employing the Langmuir and Freundlich isotherm models. The data supports the Langmuir isotherm model with Qmax and KL parameters of 16.8379 mg/g and 0.1926, respectively, and $R^2 = 0.94458$ (figure 17, table 4.10, appendix IX), suggesting monolayer adsorption on a homogeneous surface. The Freundlich isotherm model yields a Freundlich constant (KF) of 2.6263, an exponent (n) of 1.3615 with an R^2 value of 0.9358 (figure 18, table 4.10, appendix IX). The high R^2 value for the Freundlich model validates that the model has a good fit with the data and this indicates that adsorption takes place at a heterogeneous surface. The values of the exponent n greater than one indicate that the adsorption is favorable and that there is a good interaction between the adsorbent and the adsorbate (Mmbaga, 2018). The high value of R^2 of Freundlich model indicates that one cannot deny the surface heterogeneity or multilayer adsorption completely. Even though both models were able to provide satisfactory regression to the data set, the Langmuir model is a better model for the current adsorption study for monolayer adsorption.

Table 10: Langmuir and Freundlich constants for composite of MWCNTs/soda lime waste glass adsorbent

Adsorbent	Langmuir			Freundlich		
	Qmax	KL	R^2	n	KF	R^2
Composite of soda lime/oxidized MWCNTs	16.8379	0.1926	0.94458	1.3615	2.6263	0.9358

The Langmuir isotherm of composite of MWCNTs/soda lime waste glass is shown in Figure 17.

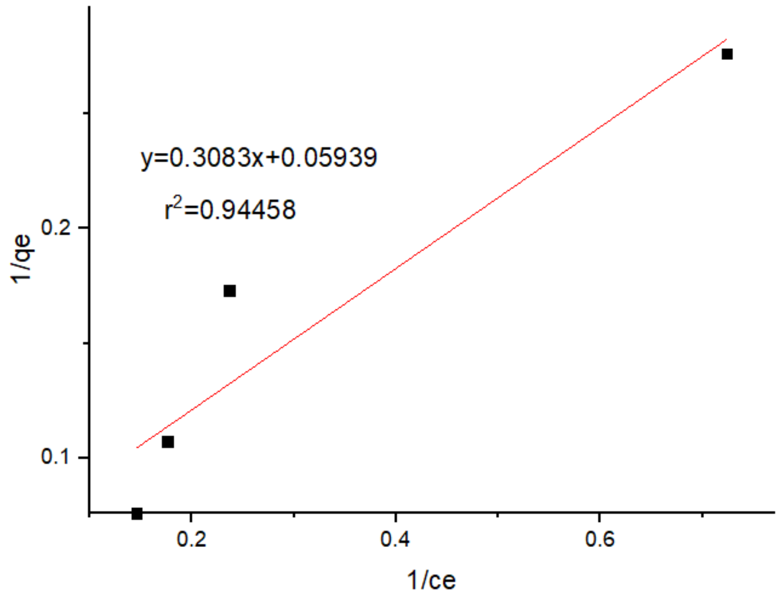

Figure 17: Langmuir isotherm of the composite of MWCNTs/soda lime waste glass

The Freundlich isotherm of composite of MWCNTs/soda lime waste glass adsorbent is shown in figure 18 below.

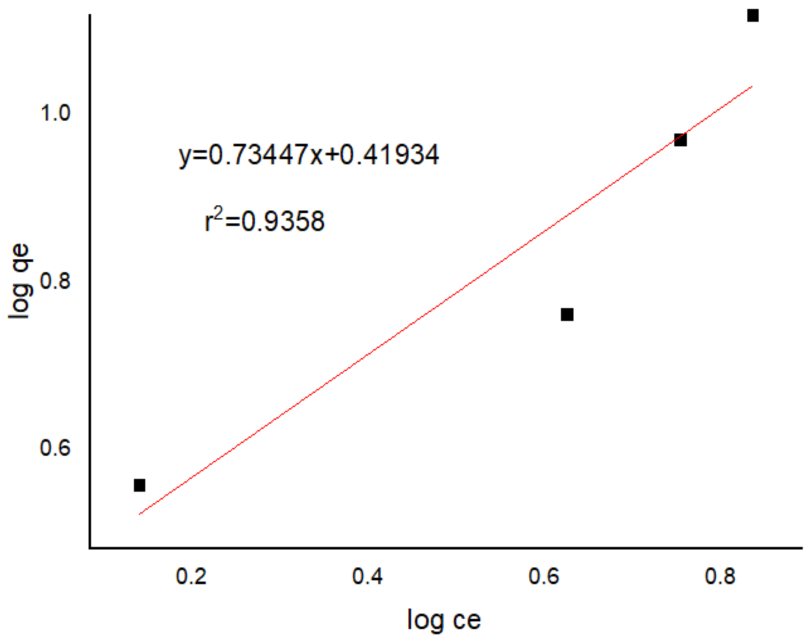

Figure 18: Freundlich isotherm of the composite of MWCNTs/soda lime waste glass

4.5 Kinetic studies

4.5.1 Pseudo 1st and 2nd order kinetics of borosilicate waste glass adsorbent

The pseudo first order had a rate constant K_1 of 0.168 and the equilibrium adsorption capacity (qe) of 4.517mg/g, $R^2 = 1$, (figure 19, table 4.11). This suggests best fit of the data to the pseudo-first-order model of adsorption, which shows that the adsorption process might be mainly through physisorption. However, the pseudo second order model with rate constant K_2 of 0.0304 and the equilibrium adsorption capacity qe of 9.5356mg/g had R^2 of 0.99019 (figure 20, table 4.11), which although very close to 1, is still satisfactory, experimental data presented in appendix X. The higher qe for the pseudo-second-order model indicates that, the adsorption process might have involved chemisorption since this model occasionally predicts the adsorption of heavy metals by valency forces through sharing or exchange of electrons between the adsorbent and adsorbate (Nizam *et al.*, 2024). Due to the high qe, of pseudo-second-order model it indicates that the adsorption process follows pseudo second order kinetics which supports the contribution of the chemical step in the overall adsorption process. The adsorption of metals on waste glass adsorbent follows a pseudo second order kinetic model which tends to have higher qe according to (Rashed *et al.*, 2021, Rashed *et al.*, 2018).

Table 11:Pseudo first and second order constants of borosilicate waste glass

Adsorbent	Pseudo first order			Pseudo second order		
Borosilicate	K_1	qe	R^2	K_2	qe	R^2
waste glass	0.168	4.517mg/g	1	0.0304	9.5356mg/g	0.99019

The pseudo first order kinetics of borosilicate waste glass is shown in figure 19 below.

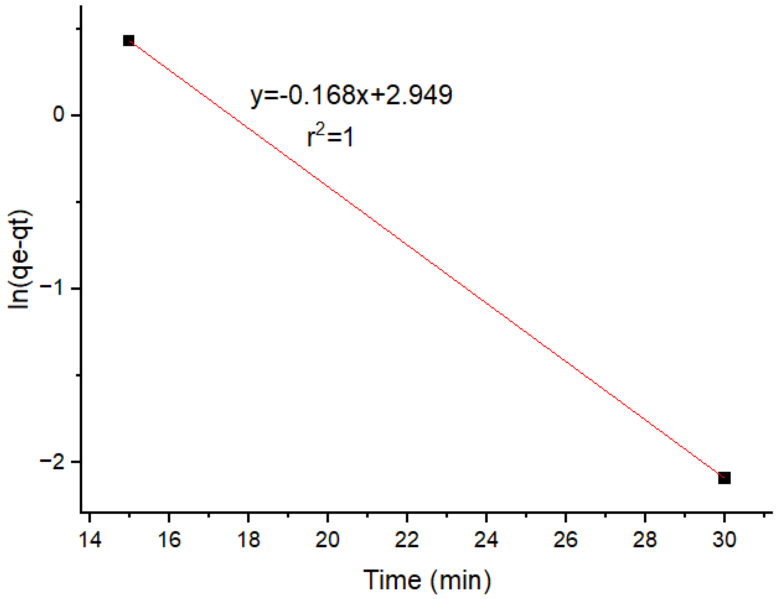

Figure 19: Pseudo first order kinetics of borosilicate waste glass adsorbent

The pseudo second order kinetics of borosilicate waste glass adsorbent is shown in figure 20 below.

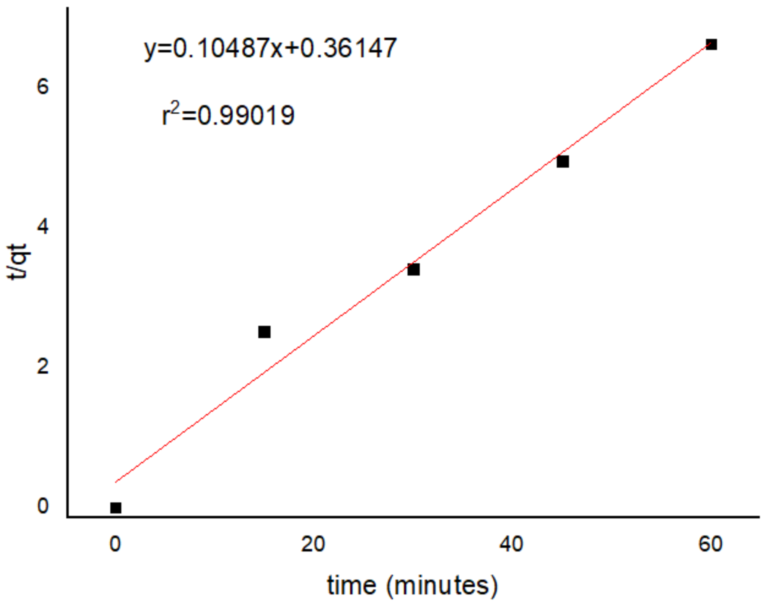

Figure 20: Pseudo second order kinetics of borosilicate waste glass adsorbent

4.5.2 Pseudo 1st and 2nd order kinetics of soda lime waste glass adsorbent

The adsorption kinetics of Pb (II) ions on soda lime waste glass has been analyzed with pseudo first and second order equations. For the pseudo-first-order model, K_1= 0.02821, qe= 2.102 mg/g and the R^2 = 1 (figure 21, table 4.12) which demonstrate a perfect straight-line fit and suggest that the mechanism of adsorption may be mainly through physisorption. In the pseudo-second-order model, the calculated rate constant K_2 =0.1118 and the adsorption capacity at equilibrium, qe= 4.2101mg/g with R^2 of 0.96754 (figure 22, table 4.12), experimental data presented in appendix X. In this case, the fit is slightly lower compared with the pseudo-first-order model but still acceptable. The higher qe in the pseudo-second-order model indicates that chemisorption played a vital role in the adsorption process, where there is a formation of chemical bond between the adsorbent and adsorbate.

A study conducted by Sodeinde *et al.* (2021), shows that waste glass had higher fit to pseudo first order model compared to pseudo second order which means the adsorption process of lead, cadmium and CV dye occurred through physisorption. Even though the result obtained from the fitting of pseudo-first-order model in this study is satisfactory, the higher value of qe and reasonably good fitting of the pseudo second order model support the probability of chemical interaction in the adsorption of lead (II) ions on soda lime waste glass. The adsorption of Cu(II), Cd(II), and Pb(II) ions using recycled waste glass fitted best in pseudo second order model with r^2=0.999 (Ibrahim *et al.,* 2012).

Table 12:Pseudo first and second order constants of soda lime waste glass adsorbent

Adsorbent	Pseudo first order			Pseudo second order		
soda lime waste glass	K_1 0.028	qe 2.102mg/g	R^2 1	K_2 0.1118	qe 4.21mg/g	R^2 0.968

Pseudo first order kinetic of soda lime waste glass is shown in figure 21 below.

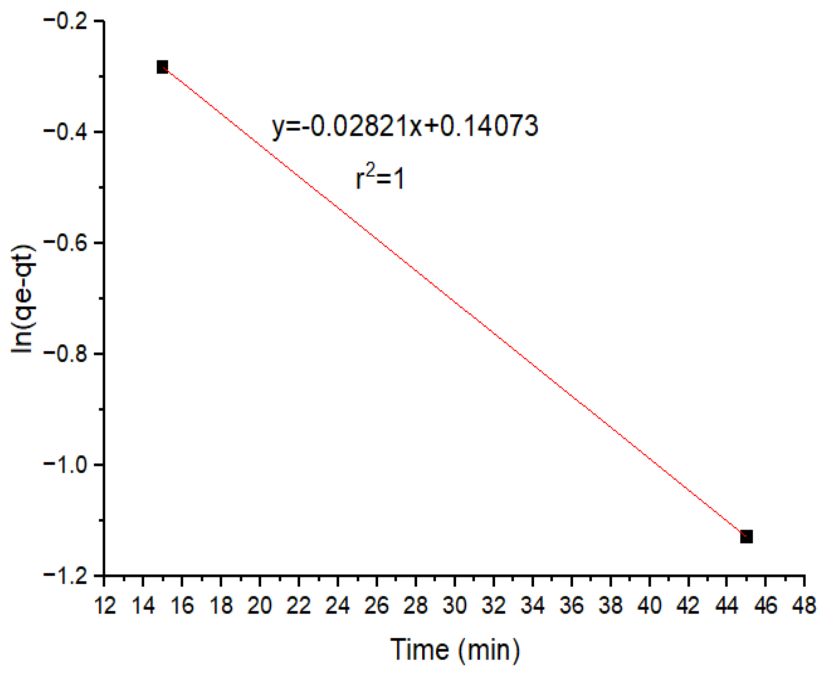

Figure 21: Pseudo first order kinetics of soda lime waste glass adsorbent

The pseudo second order kinetic of soda lime waste glass is shown in figure 22 below.

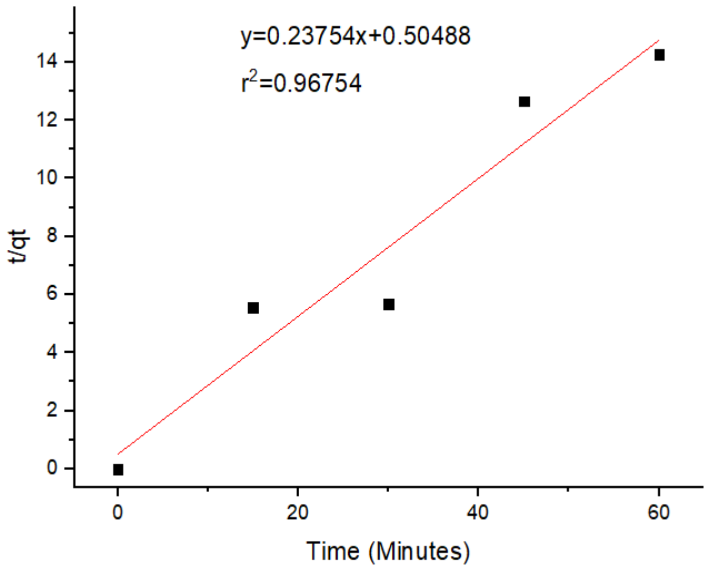

Figure 22: Pseudo second order kinetics of soda lime waste glass adsorbent

4.5.3 Pseudo 1st and 2nd order kinetics of composite of MWCNTs/soda lime waste glass

The adsorption of Pb (II) ions using composite of soda lime waste glass and oxidized multi-walled carbon nanotubes (MWCNTs) was investigated through the application of pseudo-first-order and pseudo-second-order kinetic models. For the pseudo-first-order model, the rate constant K_1=0.07019 whereas the equilibrium adsorption capacity qe was 4.394mg/g and the coefficient of determination R^2 was 0.99877 (figure 23, table 4.13) which represents a perfect fit. This suggests that the adsorption process was characterized by physisorption. In contrast, the pseudo-second-order model had a rate constant K_2 of 0.0130 and a higher adsorption capacity at equilibrium qe of 9.7333 mg/g, with an R^2 of 0.946 (figure 24, table 4.13), experimental data presented in appendix X. The qe value obtained using the pseudo-second-order model is much higher compared with that of the pseudo-first-order model, suggesting that chemisorption has a large proportion; thus, there were chemical interactions between lead (II) ions and the composite material during the adsorption process. A very good fit of the pseudo-first order model suggests that primary adsorption mechanism was physisorption while the higher qe value of the pseudo-second order model supports chemisorption meaning that the adsorption process was a combination of both and involved more than one rate- limiting steps (Revellame *et al.*, 2020). Due to the high qe in pseudo 2nd order the adsorption followed the pseudo second order model.

Table 13: Pseudo first and second order constants for composite of MWCNTs/soda lime waste glass adsorbent

Adsorbent	Pseudo first order			Pseudo second order		
composite of soda lime / oxidized MWCNTs	K_1	qe	R^2	K_2	qe	R^2
	0.07	4.39mg/g	0.999	0.013	9.7333mg/g	0.95

The pseudo first order kinetic of composite of MWCNTs/soda lime waste glass adsorbent is shown in figure 23 below.

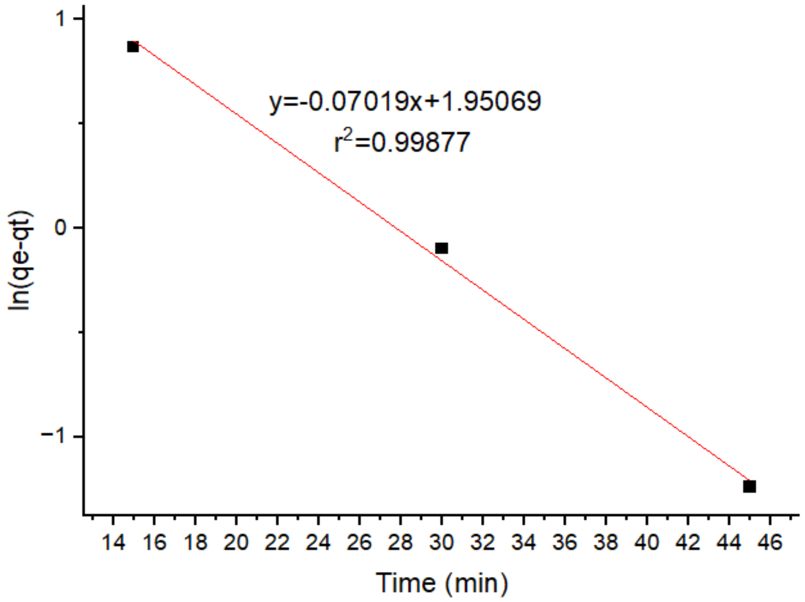

Figure 23: Pseudo first order kinetics of a composite of MWCNTs/soda lime waste glass

The pseudo second order kinetic of composite of MWCNTs/soda lime waste glass adsorbent is shown in figure 24 below.

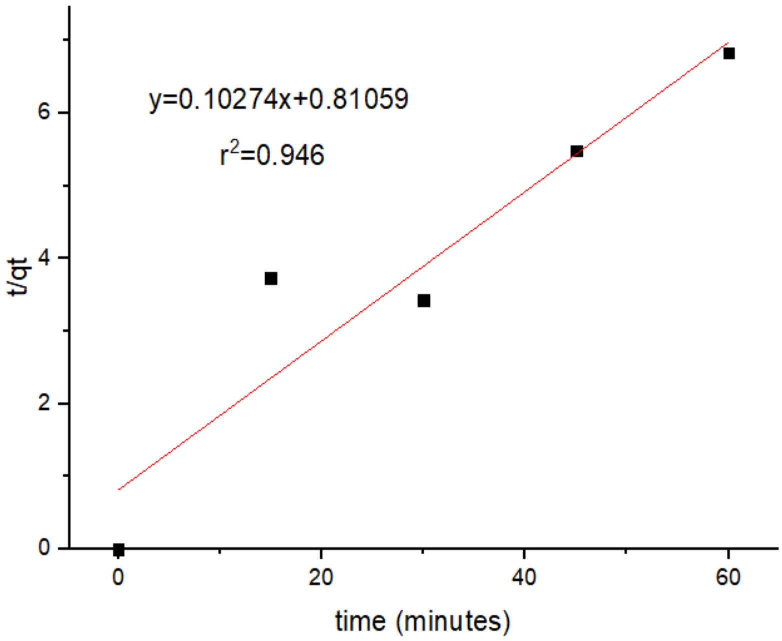

Figure 24: Pseudo second order kinetics of a composite of MWCNTs/soda lime waste glass

4.6 Interference studies

4.6.1 Cation interference on adsorption of Pb^{2+}

The interference of cadmium, manganese and nickel in the adsorption of lead (II) ions was studied at different concentrations using the composite of soda lime waste glass/MWCNTs adsorbent. 0.1ppm of Cd^{2+} showed no effect on adsorption of lead while a slight decrease in Pb^{2+} binding was observed at 0.2ppm Cd^{2+} concentration. 0.2 and 0.3ppm manganese (II) ions concentration decreased the binding of lead (II) ions onto the adsorbent surface to 56.75% and 25.5% respectively (figure 25). Nickel recorded a slight decrease in Pb^{2+} binding (88%) but increase in concentration did not affect the binding ability of the sorbate. From the results, it's clear that lead can adsorb onto the composite selectively in presence of Cd (II) and Ni (II) while a stiff competition for the adsorption sites is observed for the case of Mn (II) ions.

A study conducted by Nassar (2010), showed that addition of Ni^{2+}, Co^{2+}, Ca^{2+} and Cd^{2+} at 100mg/l had no remarkable effect on binding of Pb^{2+} on Fe_2O_3 nano sorbent. MWCNTs adsorbed lead (II) ions selectively in presence of Co (II) and Zn (II) while Copper (II), Nickel (II) and manganese (II) showed adsorptions of 47%, 6% and 20% respectively in presence of lead (II) ions (Tehrani *et al.*, 2013).

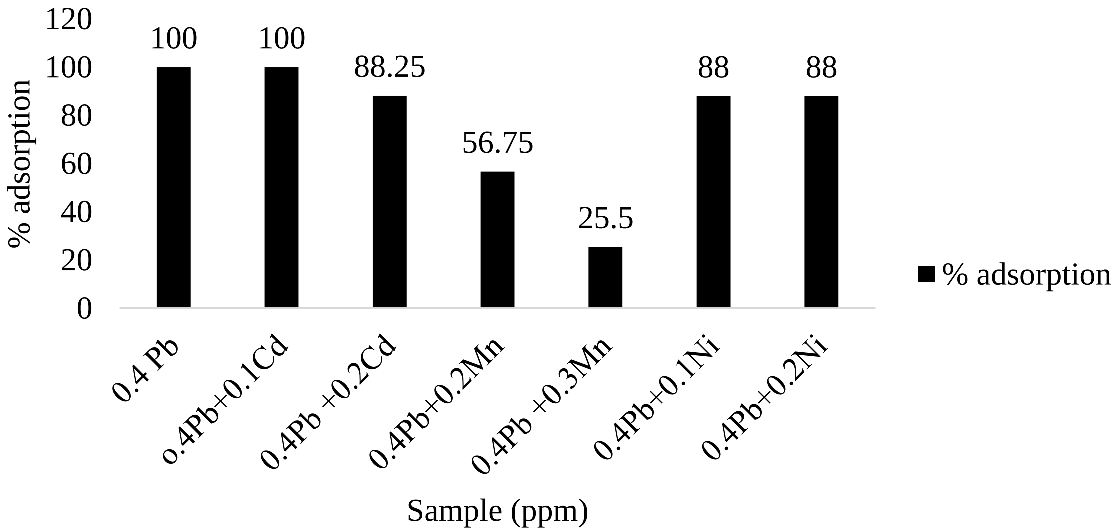

Figure 25: Cation interference on adsorption of Pb^{2+}

4.7 Regeneration of the adsorbents

The ability of an adsorbent to desorb the adsorbate is important in adsorption process and makes the process cost effective. In this study 0.1M HCl was used to desorb the Pb^{2+} in three consecutive cycles, the results for % desorption are presented in figure 11 and 12. A steady decrease in regeneration efficiency was observed over the three cycles as a result of desorption of the lead (II) ions from the adsorbents surface. The large pore size and surface area of the adsorbents led to a faster desorption of the sorbate with regeneration efficiencies of 99.61%, 97.45%, and 99.82% for borosilicate, soda lime, and composite adsorbent respectively, experimental data presented in appendix XI.

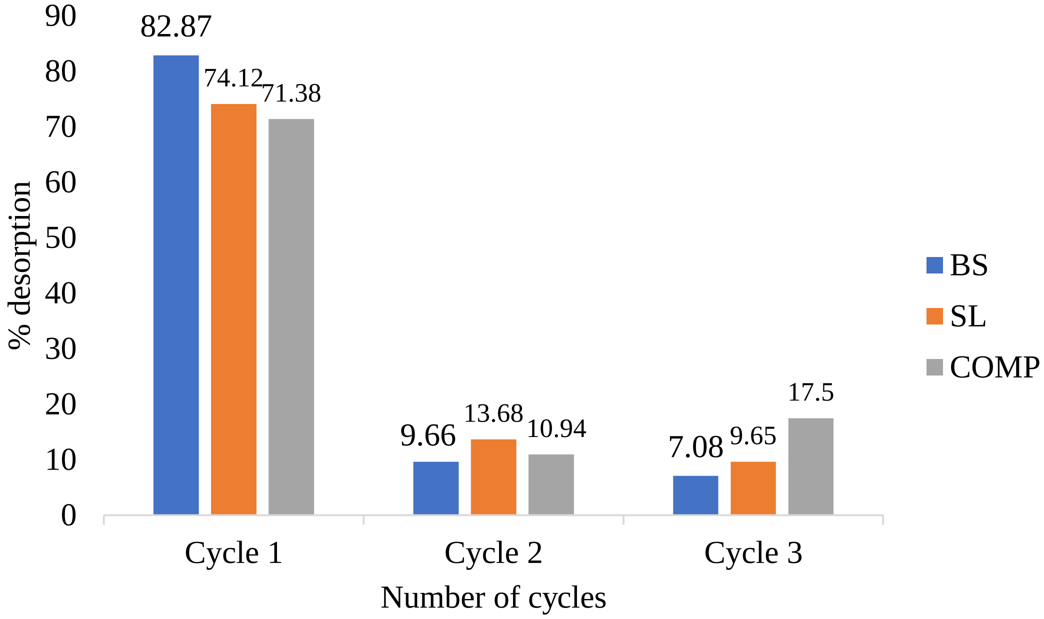

Figure 26: Regeneration ability of the adsorbents

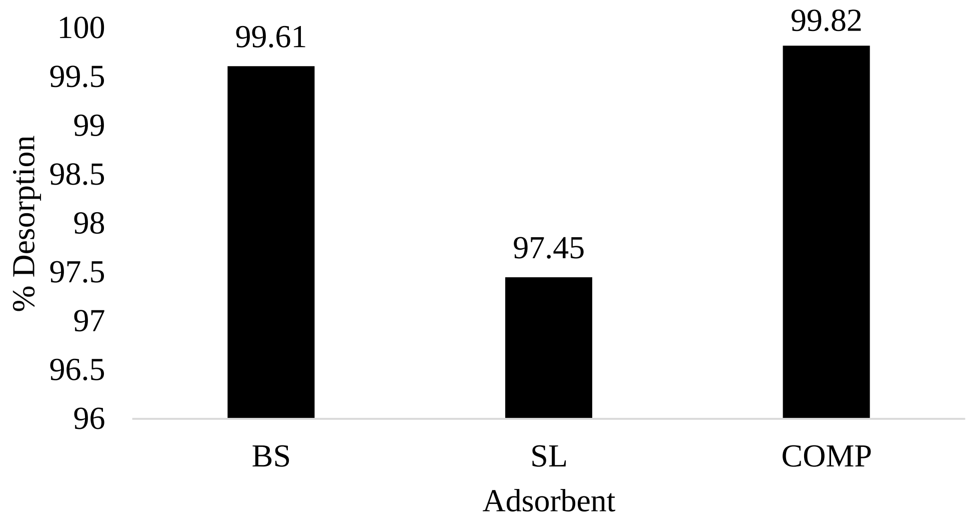

Figure 27: Percentage regeneration ability of the adsorbents

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

Use of conventional methods of water treatment has led to accumulation of pollutants in the environment and water bodies due to inefficiency of the techniques to effectively remove the pollutants in wastewater treatment systems. The poorly treated wastewater ends up in water reservoirs, and land irrigation schemes which possess significant impact to both humans and plants. Several techniques are being developed in all fields to enhance the efficiency of treatment process. This study focused on development of an effective adsorption system using borosilicate waste glass, soda lime waste glass and a composite of soda lime waste glass and multi walled carbon nanotubes for removal of lead (II) ions from wastewater. The prepared adsorbents were characterized and evaluated for their influence in experimental conditions, regeneration and desorption properties using lead (II) ions as model pollutant in aqueous solution.

5.1.1 Physico-chemical properties of Ruai wastewater during wet and dry season

The pH and temperature of the wastewater samples ranged between 5.5 to 7.9 and 22.0-26.1^{o}C which were within WHO and NEMA standards of for wastewater discharge from the sewer system to the environment. Electrical conductivity and turbidity were high during the dry season. The high levels of dissolved inorganic pollutants that increase EC should be removed before reuse of wastewater for irrigation purposes. The nitrates and phosphates were higher during the wet season because of inflow from agricultural lawns. Nitrate concentration in the wastewater met the WHO and NEMA limits for reuse in agriculture. The phosphorus level was slightly above the WHO limit for discharge into streams but fit for agricultural irrigation due to nutrient recycling into the soils. High levels of BOD (480 mg/L) and COD (980 mg/L) were recorded for both seasons which indicated high amounts of organic matter in the wastewater. TDS increased from 422 mg/L during the dry season to 931 mg/L during wet season, reflecting more solids in rainy season. TSS were higher in wet season 422 mg/L compared to 199 mg/L during dry seasons which shows excessive suspended materials during rainy periods. Excess dissolved and suspended materials would lead to contamination of farms if the wastewater is used for irrigation.

5.1.2 Inorganic elements in Ruai wastewater treatment plant during wet and dry season

The levels of zinc, copper, and nickel met the WHO and NEMA standards for wastewater discharge to the environment. Nairobi River samples had a higher concentration of iron (7.24 mg/L) which exceeded the WHO limit. The levels of manganese, cadmium, and lead were high in raw sewage and NR samples. The concentration of cadmium and manganese inhibits the reuse of wastewater for irrigation. A statistical significance difference amongst the heavy metals and physicochemical parameters analyzed was observed.

5.1.3 Characterization of the Adsorbents

Characterization of the adsorbents using FTIR showed these functional groups; Si-OH, -OH, C=O, and C-O. The adsorbents displayed different functional groups on their surface thus the null hypothesis was disqualified.

5.1.4 Adsorption studies of lead (II) ions

The removal of lead (II) ions from the wastewater was achieved at a pH of 6, 25^0C, 200mg adsorbent dose, 30mins contact time, and 200 rpm shaking speed for borosilicate and soda lime adsorbents. The composite had maximum adsorption at 40^0C, pH 6, 200 mg dose, shaking speed of 200rpm, and 45minutes contact time. The adsorption parameters varied from one another in terms of adsorption capacity, thus the null hypothesis did not hold. Composite and borosilicate waste glass adsorbents had 100% adsorption of lead (II) ions while sodalime had an average value. The experimental data for the three adsorbents was subjected to pseudo first and second order kinetic models to determine the interaction of adsorbent and adsorbate during the adsorption process. The adsorption of lead (II) ions obeyed the pseudo second order model for all adsorbents and fitted best in freundlich isotherm for borosilicate and soda lime waste glass while the composite had better fit in Langmuir model. The interference of cations in adsorption of lead (II) ions was studies using manganese (II), cadmium (II) and nickel (II) ions at different concentrations. An increase in manganese (II) ions concentration showed increased interference in the adsorption of lead (II) ions. Cadmium (II) and nickel (II) ions showed a slight interference in adsorption of lead (II) ions which means Pb^{2+} can be adsorbed selectively in the presence of these cations. The null hypothesis holds since the heavy metals studied showed ability to interfere with lead (II) ions adsorption. Desorption of the adsorbate using 0.1M hydrochloric acid in three consecutive cycles was effective. Regeneration efficacies of 99.61%, 97.45%, and 99.82% were achieved for borosilicate, soda lime, and composite adsorbents respectively. The adsorbents displayed different regeneration abilities thus the null hypothesis holds.

5.2 Conclusion

pH and temperature of the wastewater met the WHO and NEMA limits for discharge into the environment. Conductivity and turbidity exceeded the WHO and NEMA limits during the dry season due to lesser dilution of wastes and excess accumulation of solid wastes in the treatment plant. Phosphates and nitrates were high during the wet season due to runoff from agricultural lawns. High amounts of BOD_5 and COD were observed during both wet and dry seasons as a result of increased inflow of organic from industries, residence areas and farms. TSS and TDS were higher during the wet season compared to dry season due to accumulation of suspended and dissolved materials in the wastewater from runoff during the rains. The levels of zinc, copper, and nickel met the WHO and NEMA standards for wastewater discharge to the environment. Nairobi River samples had a higher concentration of iron (7.24 mg/L) which exceeded the WHO limit. The levels of manganese, cadmium, and lead were high in some sampling points. The concentration of cadmium and manganese inhibits the reuse of wastewater for irrigation.

Characterization of the adsorbents using FTIR showed these functional groups; Si-OH, -OH, C=O, and C-O. The removal of lead (II) ions from the wastewater was achieved at a pH of 6, 25^0C, 200mg adsorbent dose, 30mins contact time, and 200 rpm shaking speed for borosilicate and soda lime adsorbents. The composite had maximum adsorption at 40^0C, pH 6, 200 mg dose, shaking speed of 200rpm, and 45minutes contact time. The adsorption of lead (II) ions obeyed the pseudo second order model for all adsorbents and fitted best in freundlich isotherm for borosilicate and soda lime waste glass while the composite had better fit in Langmuir model.

The interference of cations to Pb^{2+} removal was studied using Mn (II), Cd (II) and Ni (II) ions at different concentrations. An increase in manganese (II) ions concentration showed increased interference in the adsorption of lead (II) ions. Cadmium (II) and nickel (II) ions showed a slight interference in adsorption of lead (II) ions which means Pb^{2+} can be adsorbed selectively in the presence of these cations. Desorption of Pb^{2+} ions was carried out in three consecutive cycles and the regeneration efficacies of 99.61%, 97.45%, and 99.82% were achieved for borosilicate, soda lime, and composite adsorbents respectively.

5.3 Recommendations from the Study

Lead is an essential element because its widely used in crystal glasses, batteries and production of electronics. Due to rapid economic growth lead consumption has increased because of the demand for cars and power assisted bicycles. Lead toxicity affects plant growth, photosynthesis and decreases nutrient absorption efficiency. It also causes brain damage in humans, and interferes with development and cognitive functions in young ones. From this study, it is evident that borosilicate waste glass, soda lime waste glass and composite of MWCNTs/soda lime waste glass adsorbents are effective in removal of lead (II) ions from polluted wastewater. It is therefore recommended that:

i. Borosilicate waste glass, soda lime waste glass and composite of MWCNTs/soda lime waste glass adsorbents can be used in removal of lead (II) ions from wastewater.
ii. Desludging of the pods should be done regularly to reduce the heavy metals concentration in the wastewater. Inorganic pollutants tend to settle on the bottom of the pods, thus removing the sludge will decrease their concentration in the wastewater.
iii. Strict regulations should be reinforced for industries that release their wastewater into the Ruai wastewater treatment plant. NEMA should provide clear guidelines for the levels of pollutants to be released into the plant, such that each industry treats its wastes to a considerable level before disposal into the facility. This will increase the performance of the treatment plant.

5.4 Recommendation for further Studies

i. The levels of other heavy metals like chromium and arsenic in the Ruai wastewater treatment plant should be studied.

ii. Studies should be conducted on the ability of borosilicate and soda lime waste glass adsorbents to remove other heavy metals.

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APPENDICES

Appendix I:Samples seasonal ANOVA

Seasonal ANOVA						
		Sum of Squares	df	Mean Square	F	Sig.
Conductivity In µS	Between Groups	735961.551	20	36798.078	2.692	0.014
	Within Groups	287042.485	21	13668.690		
	Total	1023004.036	41			
Turbidity in NTU	Between Groups	3279189.385	20	163959.469	12.997	0.000
	Within Groups	264919.445	21	12615.212		
	Total	3544108.830	41			
NO3	Between Groups	501.561	20	25.078	2.811	0.011
	Within Groups	187.349	21	8.921		
	Total	688.911	41			
P	Between Groups	124.320	20	6.216	3.465	0.003
	Within Groups	37.671	21	1.794		
	Total	161.991	41			
BOD	Between Groups	489161.905	20	24458.095	115.097	0.000
	Within Groups	4462.500	21	212.500		
	Total	493624.405	41			
COD	Between Groups	1879006.619	20	93950.331	32.193	0.000
	Within Groups	61285.500	21	2918.357		
	Total	1940292.119	41			

Appendix II: Sampling points ANOVA

Sampling points ANOVA						
		Sum of Squares	df	Mean Square	F	Sig.
Conductivity In µS	Between Groups	158006.934	1	158006.934	7.307	0.010
	Within Groups	864997.103	40	21624.928		
	Total	1023004.036	41			
Turbidity in NTU	Between Groups	9273.829	1	9273.829	0.105	0.748
	Within Groups	3534835.001	40	88370.875		
	Total	3544108.830	41			
NO3	Between Groups	28.520	1	28.520	1.727	0.196
	Within Groups	660.391	40	16.510		
	Total	688.911	41			
P	Between Groups	10.843	1	10.843	2.869	0.098
	Within Groups	151.148	40	3.779		
	Total	161.991	41			
BOD	Between Groups	314.881	1	314.881	0.026	0.874
	Within Groups	493309.524	40	12332.738		
	Total	493624.405	41			
COD	Between Groups	14374.500	1	14374.500	0.299	0.588
	Within Groups	1925917.619	40	48147.940		
	Total	1940292.119	41			
pH	Between Groups	13.149	1	13.149	80.550	0.000
	Within Groups	6.530	40	0.163		
	Total	19.678	41			
Temp. oC	Between Groups	5.869	1	5.869	9.629	0.004
	Within Groups	24.381	40	0.610		
	Total	30.250	41			
Fe	Between Groups	14.727	1	14.727	5.765	0.021

	Within Groups	102.183	40	2.555		
	Total	116.909	41			
Mn	Between Groups	3.360	1	3.360	22.714	0.000
	Within Groups	5.918	40	0.148		
	Total	9.278	41			
Pb	Between Groups	0.157	1	0.157	7.068	0.011
	Within Groups	0.890	40	0.022		
	Total	1.047	41			
Cd	Between Groups	0.000	1	0.000	5.281	0.027
	Within Groups	0.003	40	0.000		
	Total	0.003	41			
Ni	Between Groups	0.028	1	0.028	8.494	0.006
	Within Groups	0.133	40	0.003		
	Total	0.161	41			
Zn	Between Groups	0.347	1	0.347	4.248	0.046
	Within Groups	3.271	40	0.082		
	Total	3.619	41			
Cu	Between Groups	0.023	1	0.023	13.170	0.001
	Within Groups	0.071	40	0.002		
	Total	0.094	41			
TDS	Between Groups	2121752.381	1	2121752.381	191.832	0.000
	Within Groups	442419.905	40	11060.498		
	Total	2564172.286	41			
TSS	Between Groups	151080.024	1	151080.024	14.021	0.001
	Within Groups	431008.381	40	10775.210		
	Total	582088.405	41			

Appendix III: Effect of pH on Pb2+ adsorption

Adsorbent (10ppm Pb^{2+}, 200mg adsorbent)	pH 2		pH 4		pH 6		pH 8	
	Average	STD	average	STD	Average	STD	Average	STD
BS	9.971	0.07	7.809	0.32	0.650	0.02	5.74	0.01
SL	9.909	0.12	8.529	0.08	5.648	0.08	0.90	0.03
COMP	8.116	0.13	2.080	0.08	0.341	0.04	0.48	0.19

Appendix IV: Effect of contact time on Pb2+ adsorption

Adsorbent (10ppm Pb^{2+}, 200mg adsorbent)	15 mins		30 mins		45 mins		60 mins	
	Average	STD	Average	STD	average	STD	Average	STD
BS	5.959	0.02	1.214	0.16	0.935	0.02	0.966	0.02
SL	2.696	0.04	4.708	0.09	6.444	0.22	5.796	0.21
COMP	4.025	0.01	1.246	0.02	1.792	0.01	1.212	0.08

Appendix V: Effect of shaking speed on Pb2+ adsorption

Adsorbent (10ppm Pb^{2+}, 200mg adsorbent)	150rpm		200rpm		300rpm		350rpm	
	Average	STD	average	STD	average	STD	Average	STD
BS	2.572	0.06	2.759	0.03	2.115	0.06	2.176	0.02
SL	6.054	0.06	5.355	0.07	4.18	0.01	3.927	0.08
COMP	1.174	0.02	1.153	0.01	0.656	0.01	0.841	0.04

Appendix VI: Effect of adsorbent dose on Pb2+ adsorption.

Adsorbent (10ppm Pb^{2+})	50mg		100mg		150mg		200mg	
	Average	STD	average	STD	Average	STD	Average	STD
BS	8.486	0.06	4.553	0.05	3.979	0.00	3.378	0.12
SL	9.019	0.05	7.333	0.05	5.767	0.14	4.409	0.00
COMP	3.388	0.07	2.046	0.06	1.675	0.32	1.304	0.02

Appendix VII: Effect of initial metal concentration on Pb2+ adsorption

Adsorbent (200mg adsorbent)	5ppm		10ppm		15ppm		20ppm	
	Average	STD	average	STD	Average	STD	Average	STD
BS	2.638	0.07	2.759	0.03	4.599	0.04	6.775	0.17
SL	2.585	0.06	3.288	0.03	4.7325	0.09	6.673	0.03
COMP	1.382	0.06	4.224	0.05	5.676	0.01	6.861	0.02

Appendix VIII: Effect of temperature on Pb2+ adsorption

Adsorbent (10ppm Pb^{2+}, 200mg adsorbent)	25^0C		30^0C		35^0C		40^0C	
	Average	STD	average	STD	Average	STD	Average	STD
BS	2.093	0.07	2.350	0.02	5.343	0.004	2.473	0.04
SL	3.509	0.10	4.964	0.06	2.131	0.02	6.159	0.11
COMP	1.881	0.05	1.239	0.03	0.979	0.06	0.729	0.05

Appendix IX: Langmuir and Freundlich isotherms data

ADSORBENT	ce	qe	log qe	log ce	1/ce	1/qe
Borosilicate waste glass adsorbent	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	2.6380	1.1810	0.0722	0.4213	0.3791	0.8467
	2.7590	3.6205	0.5588	0.4408	0.3625	0.2762
	4.5990	5.2005	0.7160	0.6627	0.2174	0.1923
	6.7750	6.6125	0.8204	0.8309	0.1476	0.1512
Soda lime waste glass adsorbent	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	2.5850	1.2075	0.0819	0.4110	0.3868	0.8282
	3.2880	3.3560	0.5258	0.5174	0.3041	0.2980
	4.7325	5.1338	0.7104	0.6746	0.2113	0.1948
	6.6730	6.6635	0.8237	0.8244	0.1499	0.1501
Composite of soda lime waste glass/ oxidized MWCNTs	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	1.3820	1.8090	0.2574	0.1409	0.7236	0.5528
	4.2240	2.8880	0.4606	0.6253	0.2367	0.3463
	5.6760	4.6620	0.6686	0.7536	0.1762	0.2145
	6.8610	6.5695	0.8175	0.8365	0.1458	0.1522

Appendix X: Regeneration of adsorbents

Adsorbent	1st cycle	2nd cycle	3rd cycle	% regeneration
BS	14.278	1.665	1.22	99.61
SL	7.776	1.435	1.012	97.45
Comp	13.48	2.065	3.305	99.82

Appendix XI: Pseudo first and second order data

Adsorbent	initial. conc	ce	T	qe	qt	qe-qt	ln(qe-qt)	t/qt
Borosilicate waste glass adsorbent	10	0	0	4.517	5	-0.483	#NUM!	0
	10	4.041	15	4.517	2.9795	1.5375	0.430158	5.034402
	10	1.214	30	4.517	4.393	0.124	-2.08747	6.829046
	10	0.935	45	4.517	4.5325	-0.0155	#NUM!	9.928296
	10	0.966	60	4.517	4.517	0	#NUM!	13.28315
	10	0	0	2.102	5	-2.898	#NUM!	0
	10	7.304	15	2.102	1.348	0.754	-0.28236	11.1276

Soda lime waste glass adsorbent	10	4.708	30	2.102	2.646	-0.544	#NUM!	11.33787
	10	6.443	45	2.102	1.7785	0.3235	-1.12856	25.30222
	10	5.796	60	2.102	2.102	0	#NUM!	28.54424
Composite of soda lime waste glass/ oxidized MWCNTs	10	0	0	4.394	5	-0.606	#NUM!	0
	10	5.975	15	4.394	2.0125	2.3815	0.867731	7.453416
	10	1.246	30	4.394	5.3036	0.9096	-0.09475	5.656535
	10	1.792	45	4.394	4.104	0.29	-1.23787	10.96491
	10	1.212	60	4.394	4.394	0	#NUM!	13.65498

BS- borosilicate waste glass adsorbent, **SL**- soda lime waste glass adsorbent, **Comp-** composite of MWCNTs/ soda lime waste glass

Appendix XII: NACOSTI Permit

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