UNIVERSITY OF NAIROBI

COLLEGE OF BIOLOGICAL AND PHYSICAL SCIENCES
SCHOOL OF PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY

CHARACTERISATION AND ADSORPTION OF HEAVY METALS IN INDUSTRIAL EFFLUENT FROM PAINT AND COATING INDUSTRIES IN NAIROBI, KENYA

BY

AHENDA STEPHEN OUMA
I56/81948/2015

A Thesis submitted for Examination in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science in Environmental Chemistry of the University of Nairobi.

2019

DECLARTION

I declare that this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other people's work or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

Signature **…………………………** Date**……………………………..**

Ahenda Stephen Ouma
I56/81948/2015
Department of Chemistry
School of Physical Sciences
University of Nairobi

This proposal is submitted for examination with our approval as research supervisors:

	Signature	Date
Dr. Joyce G. N. Kithure Department of Chemistry University of Nairobi P.O Box 30197-00100 Nairobi Kenya jkithure@uonbi.ac.ke	…………………….	……………………..
Prof. Hellen Njenga Department of Chemistry University of Nairobi P.O Box 30197-00100 Nairobi Kenya hnnjenga@uonbi.ac.ke	……………………….	………………………

DEDICATION

This thesis is dedicated to my lovely family who has always instilled in me the value of hard work and perseverance.

ACKNOWLEDGEMENT

My sincere gratitude goes first to the Almighty God for giving me good health, wisdom and humility. Secondly, I acknowledge my supervisors Dr. Joyce Kithure and Professor Hellen Njenga for their great support, guidance and cooperation during my proposal development, research and writing of this thesis. Special thanks go to the entire staff of Kenya Plant Health Inspectorate Service (KEPHIS), Analytical Chemistry Laboratory, Inorganic and Food Safety Section for their moral support and technical assistance granted in the entire period of laboratory analysis. I cannot forget the staff and students of the Department of Chemistry, University of Nairobi, for their friendly and caring spirit which created the right environment for my studies. Many thanks go to my family for their emotional, academical and financial support. May the almighty God bless you all.

ABSTRACT

In the recent past, the environment in both developing and developed countries have witnessed environmental degradation due to persistent metal ion pollutants among other pollutants. In this respect, a study was conducted to estimate status of physico-chemical characteristics of effluents emanating from three paint factories in the main industrial area of Nairobi County. The effluents were analysed for temperature, conductivity, pH, oil and grease, total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD), total phosphorus, total nitrogen, total sulphur and heavy metal ions of Cadmium, Lead and Chromium. The results were as follows: pH 6.48±0.14 - 6.89±0.04, temperature 28.07±0.12-28.30±0.12 ^{o}C, electrical conductivity 837.33±6.66-881.33±8.62 μS/cm, COD 916.77±28.15 -1881.20±24.82 mg/L, BOD 149.00±1.41 - 183.00±1.41 mg/L, total phosphorus 145.00±3.61-149.32±1.22 mg/L, TSS 6382.3±658.013-7395.33±364.23 mg/L, oil and grease 3525.00±17.52-6374.33±23.03 mg/L, total sulphur 72.62±3.11-73.41±1.71 mg/L, total nitrogen 1586.67±29.14-4442.67±70.47 mg/L. Heavy metal concentrations were 3.03±0.83-4.18±0.09 mg/L, 2.07±0.66-3.04±0.83 mg/L and 5.38±1.41-17.21±1.67 mg/L respectively for cadmium, chromium and lead. Adsorbent was made from waste rubber tyres by soaking chopped tyres in 1M potassium hydroxide solution for 3 hours and consequently pyrrolizing at 700 °C for two hours. The prepared activated carbon was washed with dilute hydrochloric acid and distilled water. The adsorbent was then tested for its suitability in removing three heavy metal ions namely cadmium, lead and chromium from the effluent samples. The optimum adsorption conditions for the uptake of these ions were investigated by varying adsorbent dosage, pH and contact time. The results indicated that metal adsorption was dependent on these factors. The optimum conditions were: pH of 4-6, adsorbent dosage 0.5-0.6 % (w/v) and adsorption time of 90-105 minutes. The adsorption isotherms studies indicated that Langmuir model fitted well with analytical values obtained for cadmium, lead and chromium metal ions adsorption better than Friedrich isotherm.

Table of Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND ACRONYMS

% (w/v)	Percentage weight per volume
A.C	Activated carbon
AAS	Atomic absorption spectroscopy
ACL	Analytical Chemistry Laboratory
BOD	Biological Oxygen demand
COD HR	Chemical Oxygen Demand High Range reagent
COD	Chemical Oxygen Demand
CRM	Certified reference material
DO	Dissolved oxygen
E.C	Electrical conductivity
EAC	Extruded activated carbon
EMCA	Environmental Management and Coordination Act
g	gram
GAC	Granular activated carbon
KEPHIS	Kenya Plant Health Inspectorate Service
log	logarithm
M	molarity
Mg/L	milligram per litre
ml	milliliter
N	Normality
NEMA	National Environmental Management Authority
nm	Nanometer
NTU	Nephelometric Turbidity Unit
O & G	Oil and Grease
PAC	Powdered activated carbon
ppm	parts per million
rpm	Revolution per minute
SD	Standard deviation
Temp.	Temperature

T-N	Total Nitrogen
T-P	Total phosphorus
T-S	Total Sulphur
TSA	Thermal Swing Adsorption
TSS	Total suspended solids
UV/VIS	Ultraviolet/ Visible

CHAPTER ONE

INTRODUCTION

1.1 Background

Industrial and population growth in developing countries have led to environmental degradation due to discharge of polluted wastewater loaded with organic, inorganic and biological contaminants directly to the environment without any or adequate treatment (Kabbaj *et* al., 2014). In Kenya, **v**arious factories within Nairobi's industrial area discharge effluents directly into the surrounding ecosystem particularly into Nairobi River thus posing environmental and health hazards to the inhabitants of Nairobi and its surrounding (Odhiambo *et al*, 2016). Due to, upsurge in investments in transport and real estate industry recently in developing countries including Kenya has led to high demand for automotive and decorative paints hence growth of paint industries. This in turn has led to escalated discharges of huge volumes of sources of physical, chemical and heavy metal ion contaminants by these paint and coating industries into Ngong and Nairobi Rivers' (Ogilo *et al*, 2017). This is in addition to oil and grease and petrochemical wastes as shown in Figure1.2 (a) and (b), from "Juakali' sectors (Mathenge *et al*, 2018). The nature of a particular paint and attributes of the waste produced in its manufacture is dictated by constituents in the blend (Körbahti and Tanyolac¸ 2009), which normally emanate from washing of implements, floors and packaging materials (Jesionowski and Ciesielczyk, 2013).

The Environmental integrity is an important component in Kenya's mission of achieving sustainable development goals. Although the legislation dictates that the industries must treat their effluent before discharging to the environment, some of these industries do improper treatments which ultimately cause some of the contaminants to be drained into surrounding land and water bodies (EMCA, 2006). Therefore, there is need for proper treatment of wastewater to mitigate against release of heavy metals and related pollutants (Odhiambo *et al*, 2016). Removal of these pollutants from the natural ecosystem is essential because accumulation of pollutants such as heavy metals in human physiology and other biological systems above certain levels cause numerous diseases and disorders (Ogilo *et al*, 2017).

In the recent past, efforts have been employed by researchers to employ cheap and readily available industrial solid waste products including coconut shells, cereals husks and waste tyres in the preparation of activated carbon due to their fitness in the implementation as adsorbents (Barakat, 2011; Acevedo, 2015). Due to high cost of production of commercial adsorbents, it has pushed down mass production and accessibility of activated carbon (Chan *et a*l., 2012). This in turn has necessitated the use of industrial and domestic wastes in the preparation of activated carbon (Benard *et a*l., 2013). Waste tyres is another precursor of activated carbon. It is favoured for preparation of adsorbent due to its high carbon content (Gupta *et a*l., 2014). About 3% of waste emanates from tyre wastes (Chan *et a*l., 2012). In third world countries, Kenya included, waste tyres have become a menace as a result of environmental pollution they create due to improper management (Vinod *et al*., 2012). Waste tyres transformation to carbonaceous medium to be employed as adsorbent for up taking of harmful trace contaminants from industrial and domestic effluents is therefore beneficial (Belgacem *et al*., 2013).

Figure 1.1: Industrial discharges of oil and grease (a) and petrochemical wastes (b) into Nairobi River (Herzog *et al*, 2008)

1.2 Statement of the problem

Industrial development in Kenya especially in transport and real estate industry recently has escalated demand for paint products hence growth of paint industries. The paint industry in turn has continually churned out huge volumes of effluents which are sources of physical, chemical and heavy metal contamination into land and water bodies. However, there is .

1.3 General objective

The general objective of this study was to determine the levels of contaminants in wastewater from paint manufacturing industries in Nairobi's industrial area and the use of waste tyre adsorbent in metal pollution reduction.

1.3.1 Specific objectives

The specific objectives of this study were to:

i. Determine physical, chemical and heavy metal characteristics of untreated waste water from some local paint industries.
ii. Investigate the extent of pollution reduction by coagulation and flocculation.
iii. Establish the potential of using an adsorbent prepared from used tyres in removal of metal ion contaminants from paint manufacturing wastewater.
iv. Determine optimum adsorption conditions for the removal of metal contaminants.

1.4 Justification and Significance of the Study

This study sought to document levels of heavy metal contaminants being discharged from paint manufacturing industries into the environment. In addition, the research sought to establish whether an adsorbent prepared from waste tyres as a way of managing waste tyres in the environment, could be used to reduce levels of heavy metal levels in paint factory effluents to levels that are safe for release to the natural environment. Such information is useful to authorities charged with environmental protection and management for policy formulation.

CHAPTER TWO

LITERATURE REVIEW

2.1 Paint industry in Kenya

Kenya has for long been perceived to be economically strong in East Africa, with residential and industrial construction boosting consumption of paints and coatings. Upsurge in urbanization, infrastructure expansion, public and private development; construction of low cost and middle-class housing units, office buildings in major city centers and county headquarters have heightened demand for paints, pigments, varnishes and other architectural coatings (Kigotho, 2017). Most industries are located in major towns due to availability of labour, well established infrastructure and high demand for the finished products. Apart from major players in paint manufacturing industry which include Sadolin Paints, Crown Berger Ltd, Basco Paints and Solai Paints Ltd, there are small scale players employing less than 20 people having a limited product line whose market is within a small geographical region. These companies produce paint allied products like varnishes, industrial and architectural coatings (Wurm, 2016).

2.2 Paint manufacturing process

Paints are a mixture of binders, solvents and other excipients and they are employed as colouring matter and blotters. Paints are categorized as either aqua or oil based (Jesionowski and Ciesielczyk, 2013). Most paint companies use batch process in the manufacture of paints and more often employ a three step process to come up with a finished product as shown in Figure 2.1. The procedure include mixing and milling of raw materials where solid pigments are ground into fine particles in the vehicles system; resins and solvents. Tinting and thinning then follows immediately, where pigments and a fraction of the binder and wetting media are mixed into a consistent paste of a required specifications which is then loaded in a high speed mixer that dissipate the pigments. The end product is packed in different sizes and volumes (Talbert, 2008).

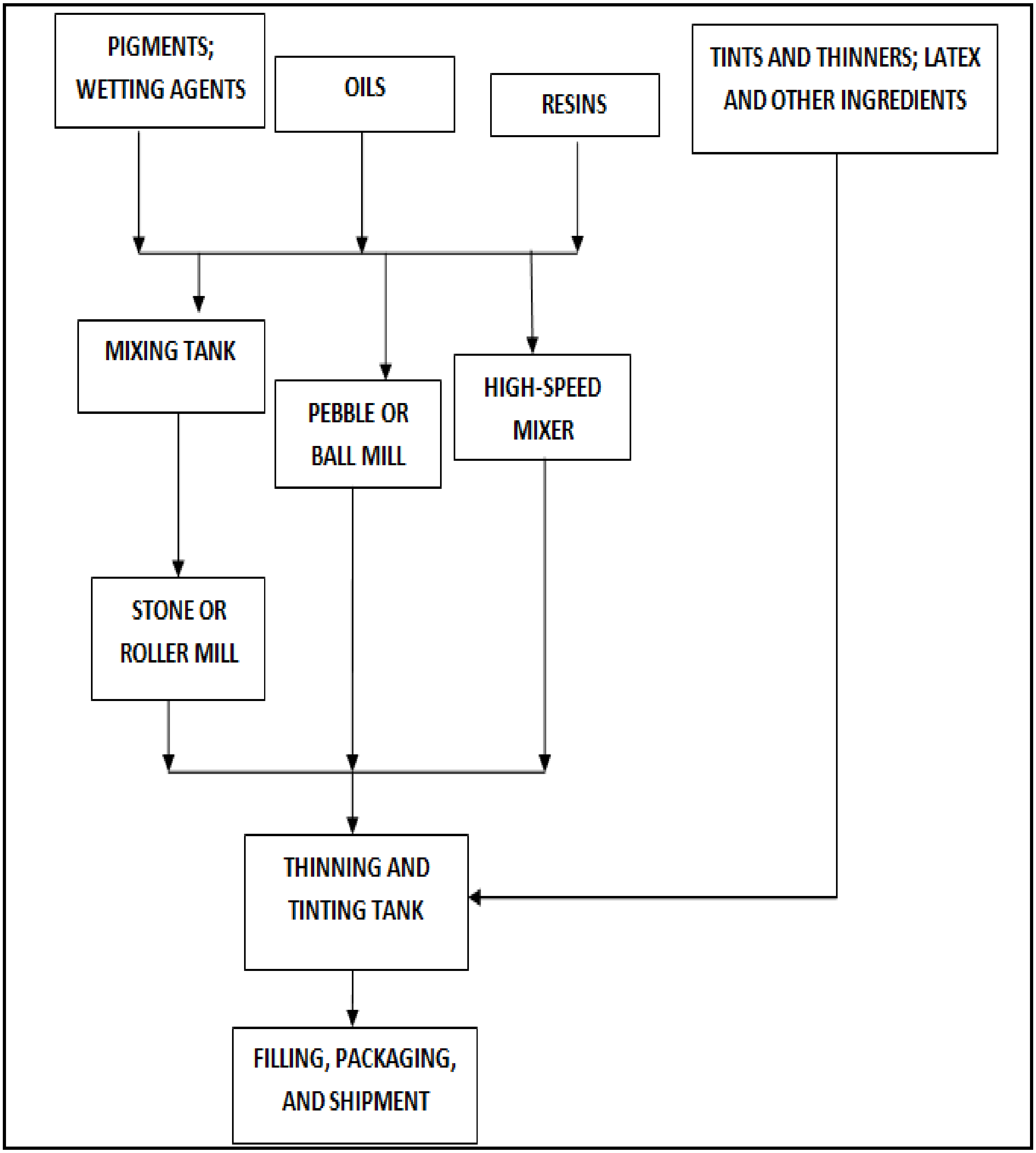

Figure 2.1: Flow diagram of industrial paint manufacturing process (Talbert, 2008).

2.3 Paint components

Paint can be described as a distinctive homogenous formulation of four components namely binder, pigment, solvent and additives that produce a specific end product having a unique properties. When applied to a substrate, it gives an essential characteristic of adhesion, elasticity and durability when the paint dries (Talbert, 2008).

2.3.1 Pigment

Pigment refers to particulate solids that are insoluble in solvents and are majorly used for optical provision of colour, opacity and gloss. It also gives protection to the substrate with regards to paint underlying surface and binder from UV destruction. Pigment are normally less than 1μm in thickness, a property that qualifies them to refract light (Talbert, 2008). Pigments can be broadly categorized as either organic or inorganic.

2.3.1.1 Organic pigment

Organic pigments have functional groups known as chromophores that absorb light and transmit a complimentary colour of the one absorbed and vice versa depending on the conjugation of the functional groups (Talbert, 2008). Major examples of organic pigments include; *Azo* and *Anthraquinone* derivatives.

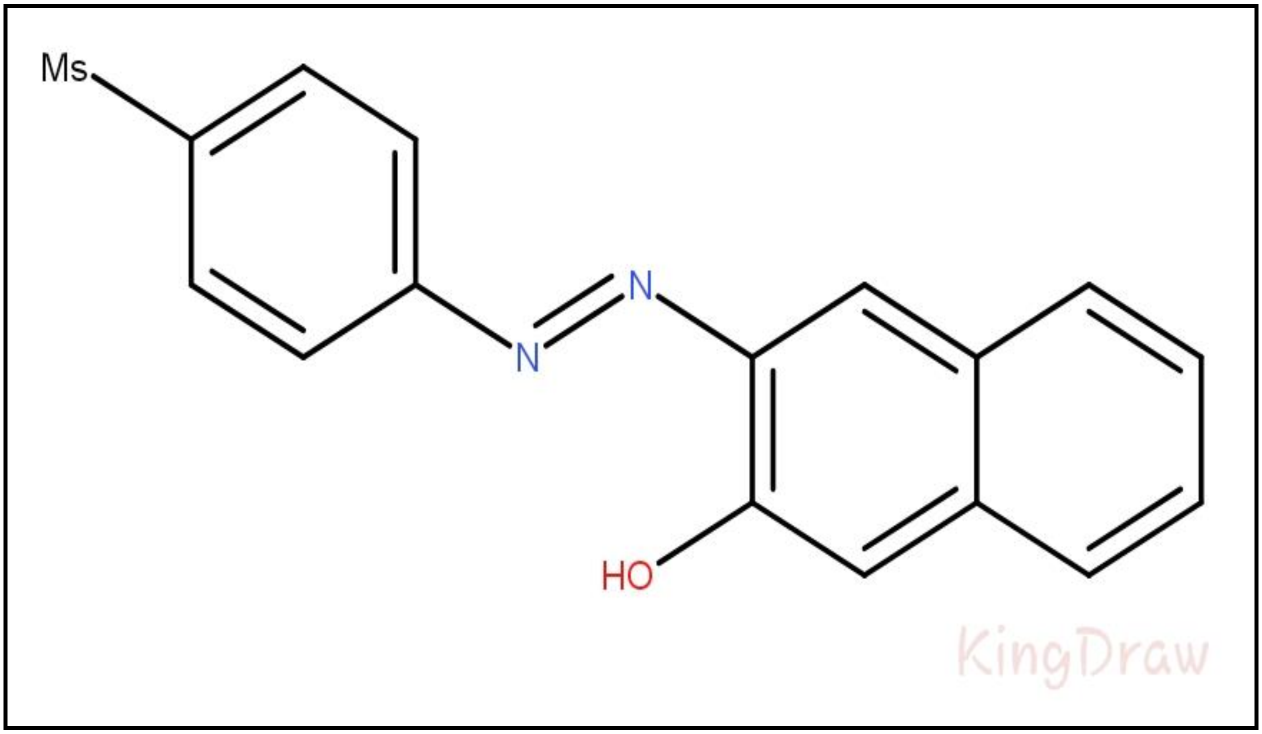

Figure 2.2: Azo (King Draw chemical structure editor v2.1.3)

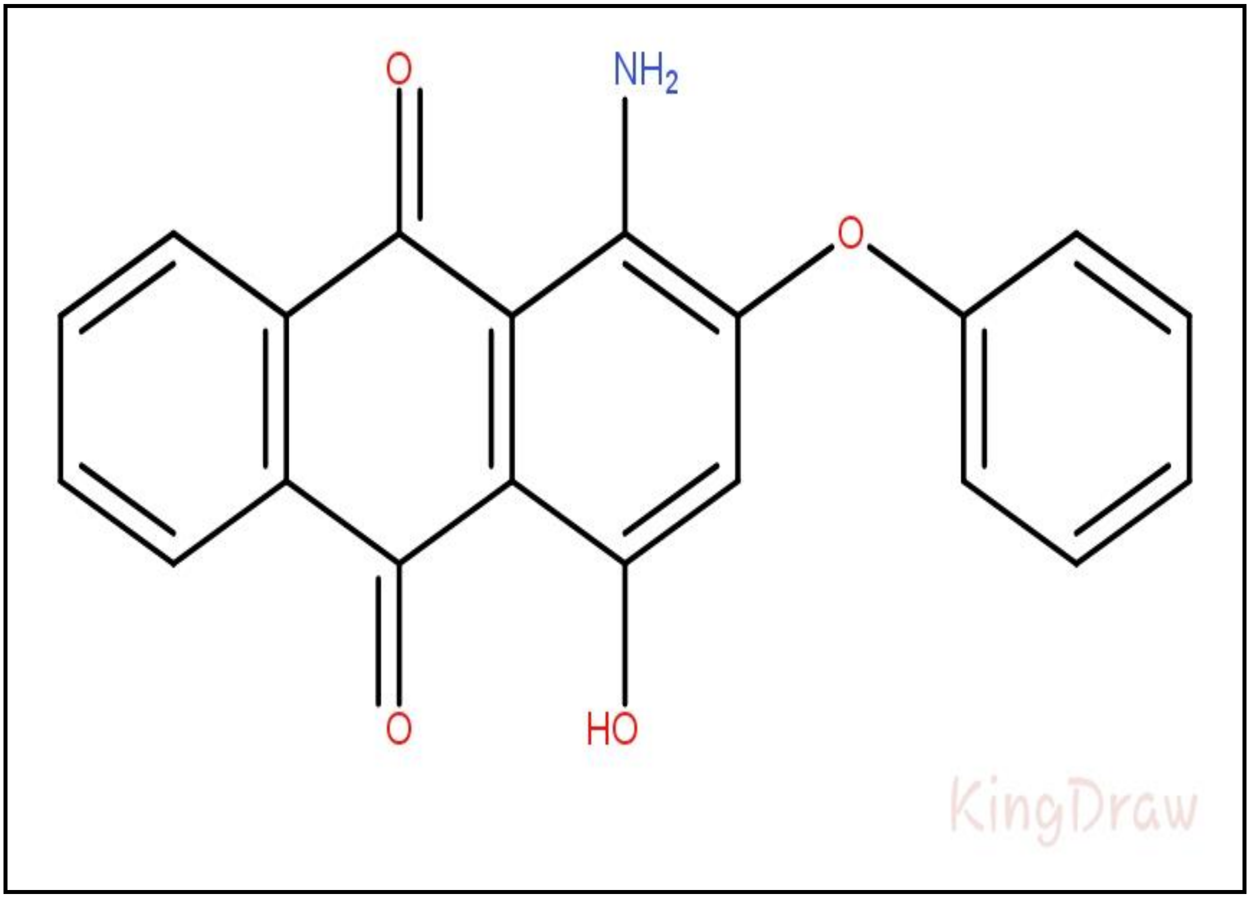

Figure 2.3: Anthraquinone (King Draw chemical structure editor v2.1.3)

2.3.1.2 Inorganic pigment

Most inorganic pigments are made from minerals or products of their respective combustion materials. They can also be produced from a combination of both organic dyes and mineral base (Jesionowski and Ciesielczyk, 2013). Major examples include *white lead* ($2PbCO_3.Pb(OH)_2$), *lead chromates* ($PbCrO_4$), *cadmium yellow* (CdS) and *zinc chromates* ($ZnCrO_4$).

2.3.2 Binder

Binder is the component of paints which forms a continuous coat on the surface of the substrate hence responsible for good adhesion of the film to the surface. It can be either a resin or oil which holds the pigment particles throughout the coating. The binder can be dispersed in a solvent either in molecular or colloidal form to form emulsions or sols (Talbert, 2008). Good examples of binders include acrylic, alkyd and epoxy polymers.

2.3.3 Solvent

This refers to liquid either in pure or mixed form that is essential for even mixing of the paint components in molecular or colloidal form and enhance application. Solvents may be categorised into hydrocarbon, oxygenated and water (Talbert, 2008). Hydrocarbon solvents are majorly used in carrying the resin and pigment. Hydrocarbon can further be classified into aromatic (xylene, toluene), aliphatic (mineral spirits) and naphthenic .The oxygenated solvents are mostly used to dissolve synthetic binders. They include ketones, alcohols, esters (Jesionowski and Ciesielczyk, 2013). Most emulsion paints contain water as a major ingredient of the liquid phase. Water can be used alone or mixed with other hydrocarbon solvents; alcohols or ethers, to disperse water-soluble binders (Mannari and Patel, 2015).

2.3.4 Additives

These are substances added to paint in small amounts in order to enhance or modify certain characteristics of the end paint product in its production, storage, transport processes or application (Lambourne and Strivens, 2014). Additives provide the mechanical and optical properties to the substrate, determine the rheological attributes of paint (viscosity), prevent pigments settlement and also accelerate chemical reaction in the process of film-formation on the substrate (Mannari and Patel, 2015). Examples include silica (SiO_2), talc (hydrated magnesium silicate), whiting ($CaCO_3$) and barytes ($BaSO_4$).

2.4 Characteristics of effluent from paint manufacturing industries

Typical constituents of paint effluent can be categorized into physical, chemical and biological attributes.

2.4.1 pH

This manifests activity of hydrogen ions (H^+) in water. Typical pure water pH is around 7.0 but deviation can be attributed to domestic or industrial discharges which results in either lower or higher pH values. Low pH favours release of metal ions from sediments and rocks into water bodies thereby affecting vegetation and aquatic life (Ben-Chioma *et al*, 2015).

2.4.2 Temperature

Temperature directly affects biological activities and chemical reactions of the receiving water bodies. Hot water generated by many manufacturing processes if discharged in large quantities can elevate the temperature of receiving streams and thus interfere with the natural aquatic life equilibrium (Noorjahan, 2015).

2.4.3 Electrical conductivity

Electrical conductivity (EC) is the ability of aqueous solution to convey electric current and is dependent on the dissolved salts in solution. Most industrial effluents contain high levels of EC attributed to dissolved inorganic compounds which are good conductors of electricity (Mihir *et al*, 2015).

2.4.4 Turbidity

Turbidity refers to optical attribute that makes light to be scattered or absorbed instead of being transmitted in a liquid due to presence of suspended and colloidal matter such as clay, silt and micro-organisms. This causes elevation of water temperature which in turn affects the dissolution of oxygen in water and a decline in photosynthetic activities of aquatic plants (Iheoma *et al*, 2015).

2.4.5 Chemical oxygen demand (COD)

COD measures levels of pollutants in effluents and natural waters by evaluating the amount of oxygen that can oxidize organic matter present in wastewater. COD dictates the level of dissolved oxygen (DO) which is an essential pollution determinant of the waste water sinks (Vinod and Chopra, 2012). Dissolved oxygen has a direct effect on metabolism of living organisms in aquatic ecology as well as aerobic biochemical reactions (Noorjahan, 2015).

2.4.6 Biochemical Oxygen Demand (BOD)

This refers to the quantity of dissolved oxygen required by aquatic living organisms or matter to breakdown. The higher the presence of decomposable matter, the more the dissolved oxygen needed, consequently, the higher the BOD_5 which could negatively affect the quality of the receiving water bodies (Vinod and Chopra, 2012).

2.4.7 Oil and Grease (O & G)

Oil and grease encompass fats, lubricants, waxes and other similar components found in waste water. They are discharged domestically and industrially and form a layer on the water surface thus interfering with light transmission and gaseous exchange through water. This results in decreased concentration of dissolved oxygen and generation of odorous gases through anaerobic reactions. This may have a detrimental effect on aquatic life (Facchin, 2013). Improper check on oil and grease may cause serious damage to surface of ground soil, water and air leading to death of flora and fauna (Abd El-Gawad, 2014).

2.4.8 Total Suspended Solids (TSS)

This refers to sum total of suspended and undissolved particles that cannot pass through a filter. Suspended matter elevates temperature of water by absorbing heat from the sun's rays. This in turn decreases dissolved oxygen concentration in water which could have a detrimental effect on aquatic ecosystem (Oluseyi, 2011).

2.4.9 Phosphorus

In industrial and domestic effluents, phosphorus exists as phosphates, its primary source being detergents and animal excreta (Yamashita and Ikemoto, 2014). Phosphate is vital for plants and animal's development; nonetheless, excess of it leads to eutrophication of water bodies. Eutrophication accelerates growth of algae which diminishes dissolved oxygen in the water when they decompose consequently contributing to death of rivers and lakes (Vinod and Chopra, 2012).

2.4.10 Total nitrogen

Total nitrogen corresponds to sum total of organic and inorganic nitrogen compounds. Nitrogen is an essential nutrient for plant growth, development and reproduction. It is a major component of chlorophyll, the compound responsible for photosynthesis and amino acids which are the building blocks of proteins (Moreno *et al*, 2014). In the soil and wastewater, it exists majorly in the form NH_4^+ and NO_3^-. When nitrogen is in excess in soil, it creates nutritional imbalance which results into depletion of essential minerals such as calcium and magnesium which in turn causes the escalation of toxic elements such as aluminum which are harmful to plants and fish in water bodies (Yamashita and Ikemoto, 2014). Additionally, nitrogen in rivers and streams intensifies growth of algae which when decomposed increase levels of organic matter in water consequently decreasing the concentration of dissolved oxygen (Vinod and Chopra, 2012).

2.4.11 Sulphur

Many natural compounds and pollutants contain sulphur in different forms. Sulphates and hydrogen sulphide are major sulphur-containing compounds that pollute the environment. Hydrogen sulphide when present in high concentrations (1-2 ppm) can give water a rotten egg smell (Leip et al, 2015). Sulphate minerals cause the building up of scales in water pipes. Additionally, it can lead to dehydration of babies due to its laxative outcome (Leip et al, 2015).

2.4.12 Heavy metals

A heavy metal is any metal possessing a high relative atomic weight and is equally harmful at trace levels. Their specific gravity vary from 3.4 to 13.0 g/ml (Rajaswaria and Sailaja, 2014). Heavy metals include and are not limited to lead, chromium and cadmium. In the environment, heavy metals possess low mobility hence a solitary contamination could lead to a chronic exposure to flora and fauna (Adeleken and Abegunde, 2011). Anthropogenic activities have continued to escalate the discharge of heavy metals into the environment. Major problems related to the release of heavy metals in effluents is the immediate pollution experienced by the receiving sinks. These poisonous contaminants get into the environment, then into the human system through nutritional hierarchy and since they are not biodegradable, they cause grievous bodily harm including permanent impairment of essential biosystems (Oluyemi *et al*., 2008). All heavy metals have different effects to human and environment depending on the path, quantity and length of subjection (Fu and Wang, 2011).

2.4.12.1 Cadmium

Cadmium is mostly found in lead and copper sulphide ores and its compounds have been utilized in the production of polyvinyl chloride (PVC), fertilizers, paints and other coatings (Sharma *et al,* 2015). Cadmium is not necessary for growth of both plants and animals as it is very toxic to human tissues on bioaccumulation (Johri *et al,* 2010). Exposure may cause kidney damage, nervous and renal disorder, coma and death (Gerspacher, 2009). Cadmium (II) ion interacts with calcium metabolism in animals. This may lead to hypocalcaemia, especially in fish, due to inhibition of calcium uptake from the water (Monisha *et al.,* 2014).

2.4.12.2 Lead

Lead pollution majorly comes from anthropogenic activities such as minerals extraction, combustion of fossil fuels and manufacturing industries especially those that produce paints and coatings (Simeonov *et al*., 2010). It has applications in battery manufacture, x-ray devices, ammunition and pipes. Lead exposure may lead to miscarriage and still births in expectant mothers and it also affects intellectual growth of children (Pichery *et al*, 2011). Lead does not play any biological functions unlike zinc, copper and manganese (Monisha *et al.*, 2014). In human, manifestation of lead toxicity include physical discomfort, anaemia, kidney damage and mental health deterioration (Pichery *et al*, 2011).

2.4.12.3 Chromium

Chromium concentration has of late been steadily increasing in the environment due to upsurge of metal coating, paint manufacturing and other chemicals and allied industries (Homagain *et al*, 2010). Chromium (III) is essential in animal diet and its inadequacy leads to glucose and lipid reactions disturbance, However, hexavalent chromium (Cr^{6+}) which is mostly breathed in or ingested from polluted environment is toxic and carcinogenic (Pichery *et al*, 2011). Due to its carcinogenic nature, long term exposure may escalate chances of cancer of the respiratory, urinary, dermal and digestion systems (Adeleken and Abegunde, 2011).

2.5 National Environmental Management Authority (NEMA)-Kenya

EMCA was established under the Environmental Management and Coordination Act (EMCA) 1999 for the purpose of giving supervisory role and coordination of environmental related matters. Third Schedule of this act gives guidelines for the effluent discharge into the environment while Fifth Schedule guides on the wastewater discharge levels into public sewers as shown in Tables 2.1 and 2.2

Table 2.1: Effluent discharge Standards into Environment by NEMA

Parameters	**Maximum levels permissible**
Biochemical Oxygen Demand (BOD_5) mg/l	30
Temperature °C	Ambient Temperature ±3
pH	6.5-8.5
Oil and grease (mg/l)	nil
Total suspended solids (mg/l)	30

Chemical Oxygen Demand (COD)(mg/l)	50
Total Nitrogen (mg/l)	10.5
Total Phosphorus (mg/l)	2.0
Sulphide (mg/l)	0.1
Total Lead (mg/l)	0.1
Total Chromium (mg/l)	2.0
Cadmium (mg/l)	0.1

Source: Environmental Management and Co-Ordination (Water Quality) Regulations, 2006

Table 2.2: Effluent discharge Standards into Public sewers by NEMA.

Parameters	**Maximum levels permissible**
Biochemical Oxygen Demand (BOD_5) mg/l	500
Temperature °C	20-35
pH	6-9
Oil and grease (mg/l)-where conventional treatment applied	10
Total suspended solids (mg/l)	250
Chemical Oxygen Demand (COD)(mg/l)	1000
Total Nitrogen (mg/l)	40.0
Phosphates (mg/l)	30.0
Lead (mg/l)	1.0
Chromium (Total) (mg/l)	2.0
Cadmium (mg/l)	0.5

Source: Environmental Management and Co-Ordination (Water Quality) Regulations, 2006

2.6 Paint waste treatment technologies

Many conventional methods employed in the treatment of domestic and industrial effluents include and are not limited to coagulation, ion exchange, electro-coagulation, membrane filtration, reverse osmosis and adsorption

2.6.1 Coagulation

Coagulation is a chemically assisted sedimentation which involves addition of certain chemicals to the wastewater to produce ions of right electrical charge that neutralize the oppositely charged colloidal particles (Kushwaha *et al.,* 2010). This brings about the particles' aggregation or precipitation of some insoluble metal salts (Ukiwe *et al.,* 2013). Coagulants are mostly applied in the removal of harmful metal contaminants up to very low levels from waste water. The operation efficiency of coagulating a particular metal ion is affected by high hydrogen ion concentration, type and amount of coagulating agent and the presence of other ions (Ukiwe *et al.*, 2014). Therefore, the process requires incorporation of other reagents, consequently leading to the production of a viscous mud which is costly to dump (Ukiwe *et al.*, 2014, Aziz, 2008).

2.6.2 Ion exchange

Ion exchange entails interchanging of ions from neighbouring medium. This activity concurrently, can be employed to remove to low level of contaminants and manage a comparatively sizable quantity (Nirali *et al.,* 2016). Major matrices used include synthetic organic ion exchange resins. The technology is relatively expensive and cannot handle high levels of metal ion concentrations as the surrounding medium is poisoned by contaminants in waste water. Furthermore, ion exchange does not select ions of concern and greatly responds to any slight change in the degree of hydrogen ion concentration in the medium (Nirali *et al.*, 2016).

2.6.3 Electro coagulation

This is an approach which employs a flow of electric charge to remove contaminants from a mixture or blend. Whenever charged particles in the mixture or blend are counteracted with reverse ions, they become destabilized and hence precipitate out (Nasrullah *et al*., 2012).

2.6.4 Membrane filtration

This technique is mostly used in the reduction of contaminants in mineral-derived effluents because of its ability to remove particulate matter and dissolved impurities such as cations, anions and sometimes radicals. The size of impurity to be screened dictates the category of the filter to be employed (Abdel-shafy, 2017).

2.6.5 Bioremediation/Biosorption

Bio remediation involves use of organisms to remove or neutralize pollutants from contaminated area (Fathy *et al.,* 2015*)*.These organisms consume and break down environmental pollutants in the process of cleaning up of contaminated site or medium (Ojoawo *et al.,* 2015).

The use of above conventional methods in the treatment of effluents have several limitations which include and not limited to poor performance, large expenditure on treatment plant set up, operation and maintenance, production of large volumes of final discharges which do not meet effluent standards (Fu and Wang, 2011, Akunwa *et al.*, 2014).

2.7 Coagulation and flocculation in water and effluent remediation.

Coagulation and flocculation are crucial processes in the removal of dissolved and suspended matter in the treatment of portable and wastewater treatment. Suspended matter originates from different sources which include soil erosion, dissolved minerals, degradation of organic matter, microorganisms and industrial and domestic effluents (Sahurin *et al*., 2013). These suspended matter differ in charge, size, appearance and weight, and it compromises the water quality by enhancing turbidity, infections and toxicity (Sahurin *et al*., 2013). Particles of suspended and dissolved matter can be classified based on their sizes (Renault *et al*., 2009). Suspended matter have a diameter greater than 10^{-3} cm. Particles which are less than 10^{-7}cm are colloids and the ones having diameter less than 10^{-8} cm are categorised as dissolved particles (Ahmed *et al*., 2016). The particle size of a material dictates the settling time in a given system (Nkurunziza *et al*., 2009). By reducing the particle size, the settling time is increased and this may take longer duration for the particles (Renault *et al*., 2009). Therefore, to quicken the time for settling there is need for destabilization through coagulation and flocculation (Yin, 2010). Coagulation is the process which overcomes the factors promoting the balance of a colloidal system while flocculation is the process which agglomerates the destabilized matter for easier separation through gravity or settling (Gottfried *et al*., 2008). Suspended materials are negatively charged in water and have similar exterior charge, therefore, they parry each other whenever they are in close proximity through electrostatic repulsive forces (Pritchard *et al*., 2010). Consequently, a suitable coagulation and flocculation application relies on these traits. Hence, the materials will be suspended and not cluster jointly except if suitable coagulation and flocculation process is employed.

There are two types of coagulants used in the remediation of portable and waste water, namely; inorganic coagulants and polymers (organic coagulants) (Pritchard *et al*., 2010). The inorganic coagulants commonly employed are aluminium based for example aluminium sulphate ($Al_2 (SO_4)_3$) and iron based and these include iron chloride ($FeCl_3$) and ferric sulphate ($Fe_2 (SO_4)_3$). These cations possess charges which are opposite to that of suspended matter such as clay or colour generating organo-substances. In the interaction, the negative charge is neutralized and inorganic hydroxide flocs are formed when lime is used with the coagulant (Lee *et al*., 2015) as shown in equations 2.1 to 2.3.

$$A1_2 (SO_4)_3 + 3\,Ca\,(HCO_3)_2 \longrightarrow 2\,Al\,(OH)_3 + 3CaSO4 + 6\,CO_2 \qquad \text{Equation 2.1}$$

$$Fe_2 (SO_4)_3 + 3\,Ca\,(HCO_3)_2 \longrightarrow 2\,Fe\,(OH)_3 + 3CaSO_4 + 6\,CO_2 \qquad \text{Equation 2.2}$$

$$2\,Fe\,Cl_3 + 3\,Ca\,(HCO_3)_2 \longrightarrow 2\,Fe\,(OH)_3 + 3CaCl_2 + 6CO_2 \qquad \text{Equation 2.3}$$

Polymers are long chain organic chemicals of high molecular weight which can be used with inorganic coagulants to support the process of coagulation (Renault *et al*., 2009). Basically, organic coagulants segregates solids from liquids and also promote sludge formation (Sahurin *et al*., 2013). Cationic polymers on the other hand can be solely applied. These coagulants can successfully be applied over broad pH range compared to inorganic coagulants, can be applied in small doses to achieve desired results and produce less chemical residues as they cannot eliminate medium alkalinity (Ahmed *et al*., 2016). Typical examples include polyamines (polyallyl dimethyl ammonium chloride) and melamine formaldehydes. Polyamines are effectively used in the treatment of effluents and highly turbid untreated water by counteracting the particle charges hence clusteration (Muruganandam *et al*., 2017). Melamine formaldehydes on the other hand, are well suited in the treatment of toxic sludge due to their ability to successfully soak up organic pollutants like oil and grease (Muruganandam *et al*., 2017)

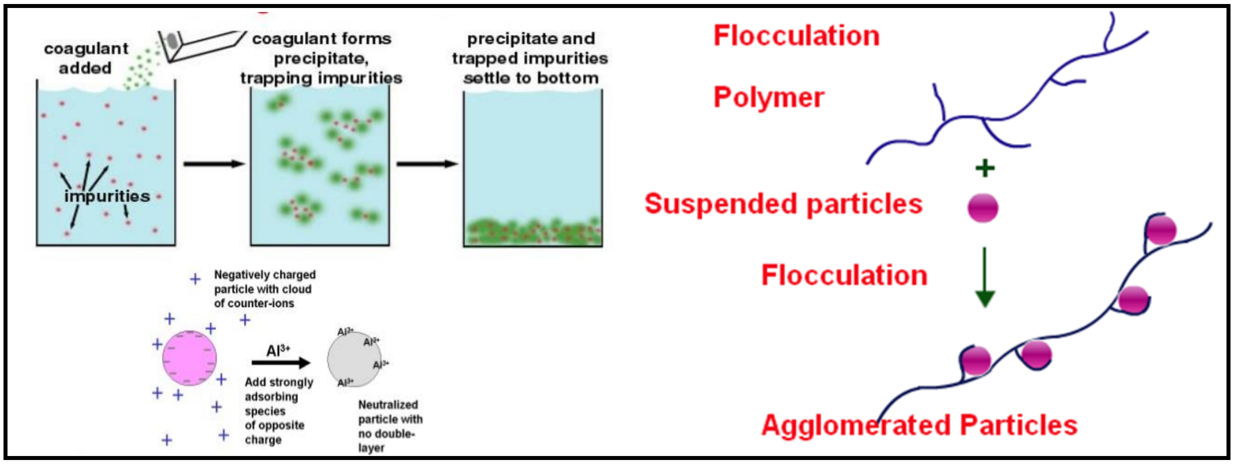

Figure 2.5: Coagulation and flocculation mechanism (Gottfried *et al*., 2008)

2.8 Adsorption process

Adsorption techniques have been employed efficiently in the removal of particulate matter and dissolved impurities especially pigments, dyes, unpleasant smell and biological pollutants from wastewater (Benard *et al*, 2013). The process involves adherence of contaminants from the matrix being transported to the active sites of the adsorbent until equilibrium is achieved (Fu and Wang, 2011). Based on the nature of the involved forces, adsorption process can either be classified as physical or chemical (Danyuo *et a*l., 2014).

2.8.1 Physical Adsorption

In physisorption, weak van der Wall's forces play a major role in attraction between adsorbate and adsorbent which results in the formation of multilayer of adsorbate on adsorbent (Acevedo and Barriocanal, 2015). Due to weak van der wall's forces, physisorption has low values of enthalpy which is mostly around 9-40 KJ/mol (Demirbas, 2008).

2.8.2 Chemical Adsorption

This type of adsorption is characterized by exchange or sharing of electrons between adsorbate and adsorbent forming a strong valence bond of a monolayer of adsorbate on the active sites of the adsorbent (Demirbas, 2008). Chemisorption enthalpies are higher though but the process is slow, since it involves formation of chemical bonds between adsorbate and absorbent (Danyuo *et a*l., 2014).

2.8.3 Factors affecting Adsorption

Several factors impact the uptake of adsorbent which may affect the overall efficacy of adsorption process.

2.8.3.1 Adsorbent dosage

Since adsorption happens on the surface of the adsorbent, the number of active sites available and adsorbent mass influence the number of adsorbate to be adsorbed, consequently the adsorption efficiency (Fu and Wang, 2011). A study done by Abdelkreem, (2013) indicated that with an increase of olive milk waste dosage to 1 g from 0.25 g, there was increase in phenol uptake to 85 % from 52%. Similar findings have been reported by Ghaedi *et al*., 2011.

2.8.3.2 Contact time

The adsorbate and adsorbent contact time affects the adsorption performance. The longer the interaction time, the higher the adsorbate uptake until equilibrium is attained (Bazrafshan *et al.*, 2016). Therefore, sufficient contact time is necessary for optimum adsorption efficiency.

2.8.3.3 pH

The pH of a solution is an essential parameter for assessing the adsorbent adsorption capacity for metal ion as it dictates the adsorbent surface charge, level of ionization and the adsorbate speciation (Adewole *et al.,* 2010). Hydrogen (H^+) and hydroxide ions (OH^-) are adsorbed more strongly than other ions which are affected by the solution pH. Most organic pollutants adsorption increase with decreased pH while heavy metals ions uptake increases with pH escalation (Bazrafshan *et al.*, 2016).

2.8.3.4 Temperature

Physical and chemical adsorption are usually exothermic, therefore, the level of adsorbate uptake normally increases with decrease in temperature (Bazrafshan *et al.*, 2014). At elevated temperatures, heavy metals uptake is usually favoured up to certain levels then gradually drops. Effects of temperature on adsorption equilibrium are not mostly notable over the range of temperature usually encountered in wastewaters. Therefore, small change in temperature do not affect the adsorption process to any significant value (Benard *et al*, 2013).

2.8.3.5 Surface Area

Level of adsorbent uptake is normally proportional to a specific surface area. Specific surface area is that fraction of the total surface area that is present for adsorbate uptake (Tamer *et al.*, 2013). The adsorption is favoured when adsorption accomplished per unit weight of adsorbent is greater, implying the solid is more porous and finely divided and hence more active sites are available (Bazrafshan *et al.*, 2014).

2.8.3.6 Nature of adsorbate and adsorbent

Adsorption decreases with increase in solute solubility due to stronger solute –solvent bond formed which affects adsorption process. Therefore, the higher solubility of the solute in the solvent the lower the adsorption on the adsorbent and vice versa (Tamer *et al.*, 2013). On the other hand, the physiochemical trait of the adsorbent can influence both adsorption capacity and rate due to availability of some of surface functional groups like carbonyl or carboxyl. This can be effected by concentrating the adsorbent surface with suitable functional groups (Aravindhan, *et al.*, 2009).

2.9 Activated Carbon Adsorption systems

There are five broad systems that have been applied in the process of removal of contaminant molecules.

2.9.1 Batch Flow System

In this kind of system amount of adsorbent is continuously mixed with a specified quantity of effluent until the pollutant concentration has been reduced to the required level (Mohammed *et al.,* 2012). The used activated carbon is removed or rejuvenated for application with another effluent batch. When finely powered activated carbon (PAC) is used in this kind of system, segregation of used adsorbent from wastewater may be hard. On the other hand, granulated activated carbon can be removed quickly after exhaustion although needs longer adsorbent-adsorbate contact time prompting for larger tanks for water or effluent retention in the treatment process (Mobasherpour *et al.,* 2014).

2.9.2 Column flow System

In this kind of system, activated carbon is continuously exposed to new wastewater solution (Akpor and Muchie, 2010) hence maintaining the concentration of the solution that is mixed with a given adsorbent layer in a column at any particular time (Chowdhury *et al*., 2013). To enhance the continuous operation of the system, solid granular AC may be added at the column top end and used activated carbon collected at the bottom (Saad *et al*., 2015).

2.9.3 Fixed bed system

The system mostly applied in contacting effluents using granular activated carbon (GAC) and can be designed singly in either parallel or series mode (Unuabonah *et al*., 2010). GAC filters are employed upstream to eliminate the organic pollutants related to suspended solids available in the secondary wastewater. The effluent is injected into the system at the top and collected at the bottom. There is always backwash and outward washing allowance to curb head loss assemblance as a result of elimination of particulate matter within the system (Mohammedin *et al.,* 2009). The downward flow design is preferred more to up flow due to single step uptake of organic adsorbate and filtration of particulate matter. Consequently, accumulation of particulate matter, which would be hard to remove through backwash, at the base of the system is mitigated against (Mohammedin *et al.*, 2009). This in turn, checks on the frequent rejuvenation of used carbon in the system (Karunarathne and Amarasinghe, 2013).

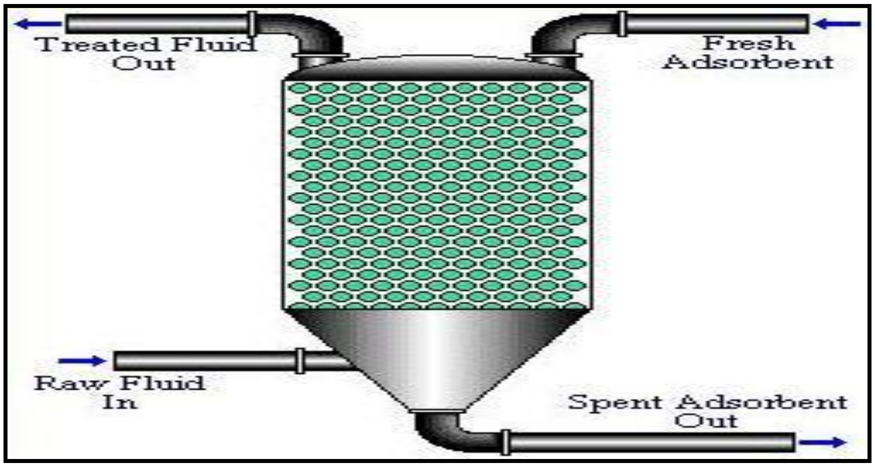

Figure 2.6: fixed bed system (Unuabonah et al., 2010).

2.9.4 Expanded bed system

In expanded system, adsorbate is expanded along with filter base as effluent is launched at the system base during backwash. When activated carbon efficacy is reduced due to clogging of the pores, the bottom part of the adsorbent is separated and equivalent amount of fresh or rejuvenated carbon added at the column summit (Ebrahimpor *et al*., 2009).

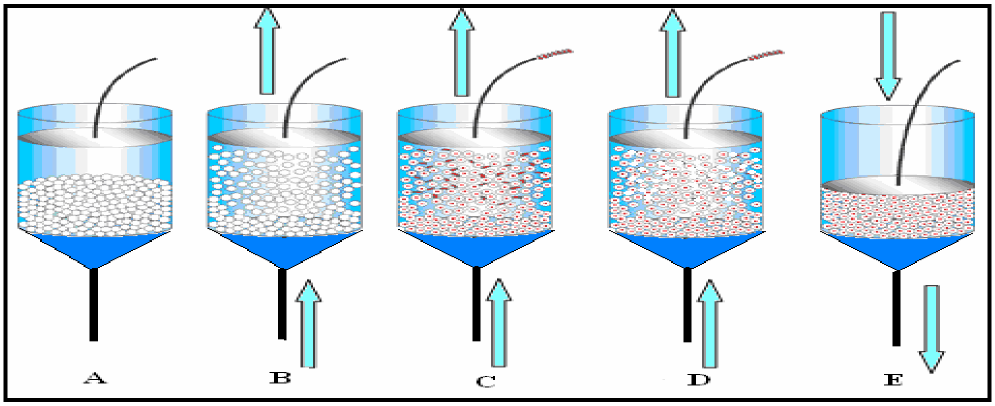

Figure 2.7: Expanded bed system (Ebrahimpor *et al*., 2009).

2.9.5 Fluidized bed system

This system make use of gas or liquid that is passed through GAC at high speed suspending and fluidizing it (Khan *et al.*, 2014). The activated carbon medium in the liquefied base is normally supported by permeable plate called distributor. When the process is started, the solid carbon materials remains static in the current position as the fluid goes through the adsorbent pores. The system attains a stage where the impetus of the fluid on the carbon material balances the load of the adsorbent, as the fluid speed is elevated. The moment the least velocity is exceeded, the contents in the system start to enlarge and swirl around like stirred pot of water creating fluidized bed (Bello *et a*l., 2017).

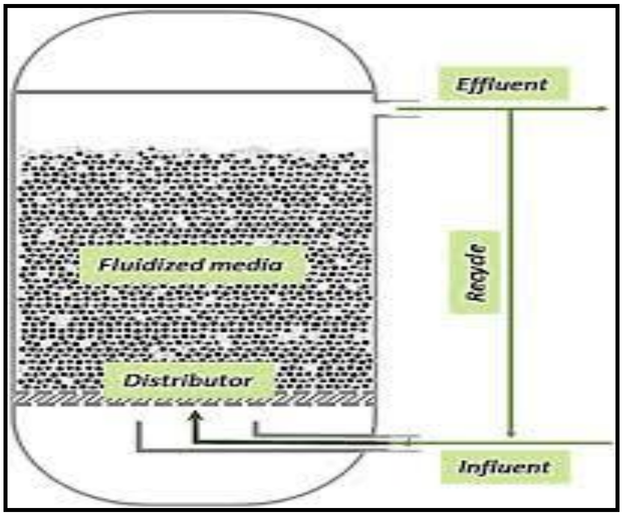

Figure 2.8: Fluidized bed system (Bello *et a*l., 2017)

2.10 Adsorption Isotherms

Adsorption occurs when the solutes dispersed in the solution phase or bulk vapour accumulate at the solid-aqueous or solid-gas interface leading to a local concentration at the interface (Nurulhuda *et al.*, 2009). Adsorption is generally elucidated using various adsorption isotherms which are normally applied to ascertain adsorption capacity of adsorbent, expressed in mg/g or mg/mg. The most commonly applied isotherms for solid-solution adsorption in water purification and waste water treatment are Langmuir and Freundlich models. These models tend to elucidate the adsorption capacity of the adsorbents at the equilibrium for a given initial concentration (Sutherland and Venkobachar, 2010), which was the major aim of the study instead of kinetics of the adsorption.

2.10.1 Langmuir Isotherms

The Langmuir model deduces that adsorbent surface has active sites that adsorb single molecule and the molecule attaches itself to the active sites until it is desorbed. At equilibrium, adsorbate forms a homogenous monomolecular layer during adsorption process, implying no interaction among metal ions adsorbed (Rahimi and Vadi, 2014).

The isotherm equation is expressed as:

$$\mathbf{X_e = Q_m L_c C_a / (1+L_c C_a)} \qquad \text{Equation 2.4}$$

Where:

X_e = Adsorption capacity at equilibrium adsorbate concentration, (mg/g)

$\mathbf{C_a}$= Concentration of adsorbate in solution (mg/L)

$\mathbf{Q_m}$= Maximum adsorption capacity correlating with single layer presentation (mg/g)

$\mathbf{L_c}$= Langmuir constant (L/mg)

The above equation can be linearized to give:

$$\frac{Ca}{Xe} = \frac{1}{QmLc} + \frac{Ca}{Qm} \qquad \text{Equation 2.5}$$

A plot of Ca/X_e against Ca gives a straight line with intercept $\mathbf{{}^1/Q_m L_c}$ and slope of $\mathbf{{}^1/Q_m}$. The plot is used in calculating adsorption capacities, linear regression and Langmuir constants.

2.10.2 Freundlich Isotherm

The Freundlich equation deduces that adsorption of metal ions occurs in heterogeneous surface, implying interaction between metal ions adsorbed on the surface of the adsorbent (Rahimi and Vadi, 2014). The formula is represented by:

$$X_e = K_f C_a^{1/n} \qquad \text{Equation 2.6}$$

In linear form it is given as;

$$\mathbf{\log X_e = \log K_f + {}^1/_n \log C_a} \qquad \text{Equation 2.7}$$

Where: K_f= isotherm constant associated with adsorption capacity

n = isotherm constant associated with adsorption intensity

C_a = Concentration of adsorbate in solution at equilibrium (mg/L)

A plot of log X_e against log C_a gives a straight line with intercept $\mathbf{K_f}$ and slope of $\mathbf{{}^1/n}$

2.11 Activated carbon

Activated carbon refers to a type of carbon which is treated so as to increase its degree of porosity in order to enhance adsorption or chemical reaction (Altenor *et al.*, 2009). The carbonaceous materials which have been employed in the preparation of AC include and not limited to coal, nutshells, coffee and rice husks, peat and waste tyres. In the process of carbonization, non-carbon elements are eradicated through pyrolytic degradation of the precursor material and the residual carbons regroup themselves irregularly giving rise to free interstices which form pores (Cao *et al.*, 2011). The pores developed are further enhanced during activation process either physically or chemically rewarding the end product its enormous surface area. Depending on the pore radius, the adsorption sites created can be grouped as either microporous, mesoporous or macro porous (Vinod *et al.*, 2012). Micropores have diameters that are less than 1.9 nm and make up a large surface area of the AC, thereby influencing the adsorption capacity of the prepared activated carbon (Cao *et al.*, 2011). Mesopores are between 2 and 49 nm in diameter and make up a less surface area of AC while macropores diameters are greater than 50 nm and acts as channel thorough which adsorptive molecules diffuse into micropores and mesopores and are therefore critical in determination of AC adsorption kinetics (Cao *et al.*, 2011). Through these traits, activated carbon isolates among other things, colour and odour forming contaminants from the surrounding medium (Belgacem *et al.*, 2013).

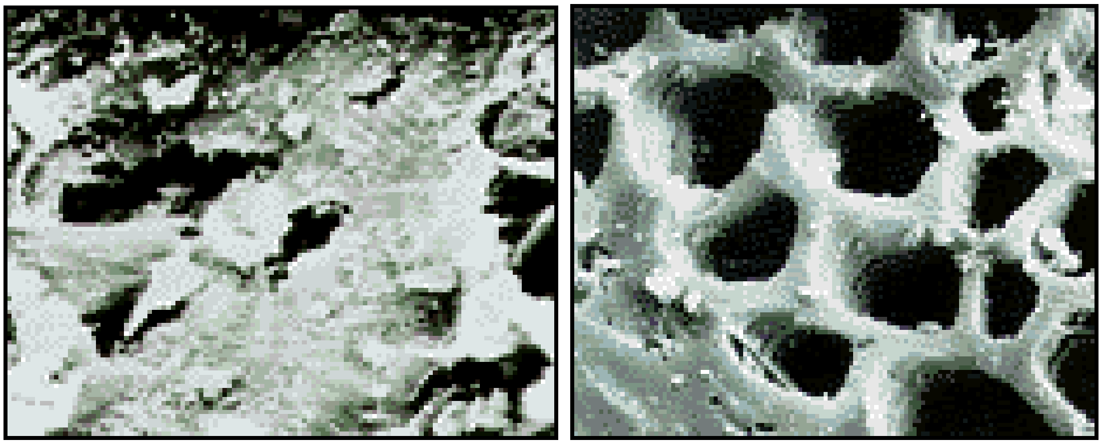

Figure 2.9: Carbonized (a) and activated carbon (b) samples (Betzy and Soney, 2015)

2.11.1 Preparation of activated carbon

Raw materials for activated carbon production are carbo-rich materials sourced from agricultural wastes, industrial by-products wood and other natural materials. The materials are pyrolysed in a low oxygen atmosphere which reduces content of volatile materials and elevating the carbon content (Vinod *et al.*, 2012). This in turn, increases the strength of the precursor material and starting porous structure that is essential for activation step (Belgacem *et al.*, 2013). Activation which is either physical or chemical aims at increasing the adsorption potential as a result of formation of micropores which primarily supports the adsorption process (Cao *et al.*, 2011).

2.11.1.1 Physical activation

Physical activation involves use of gasifying agents like argon or nitrogen on precursors and pyrolysed at temperatures ranging between 550-900 °C and/or exposing carbonized material to oxidizing agents such as oxygen, steam or carbon monoxide, at temperature above 900 °C (Hilber and Bucheli, 2010). The oxidizing conditions catalyzes formation of oxides of carbon which disperse out of carbon further developing AC inner porous structure (Cao *et al.*, 2011).

2.11.1.2 Chemical activation

This can be achieved by impregnating the precursor material with chemicals, usually strong acids, bases or salts. Typical examples of chemicals used include caustic potash, zinc (II) chloride and trihydroxylphosphine oxide. These dehydrating agents extracts the hydrogen and oxygen from the precursor material and modifies the volatile portion in the process of activation (Daud *et al.*, 2010). The impregnated material is carbonized at around 400-800 °C (Hilber and Bucheli, 2010).

2.11.2 Classification of activated carbon (AC)

Based on the general purpose of their physical characteristics and mode of preparation activated carbon can be classified as powder, granular, extruded or pellet.

2.11.2.1 Powdered activated carbon (PAC)

PAC particles are less than 0.01 cm in size with diameter averaging between 150 and 250 μm (Bridgewater, 2012). PAC particles are injected into polluted fluid in dosing systems (batch or continuous) in slurry or powder form and dispersed for a suitable contact time, then removed by sedimentation, flocculation or filtration (Bridgewater, 2012).

Figure 2.10: PAC (Bridgewater, 2012)

2.11.2.2 Granular activated carbon (GAC)

Granular activated carbon is comparatively larger in particle size than powdered activated carbon, therefore possess a relatively smaller outer surface. GAC are normally used in gases and vapours uptake due to gases faster diffusion rate. It has found its application also in water treatment, deodorization in flow system. In loaded bed structure of GAC, fluid circulate through a fixed bed and contaminants get adsorbed from the fluid and their concentration decreases while AC loading increases thereby forming a concentration gradient through the column (Anfruns *et al.,*2009).

Figure 2.11: GAC (Bridgewater, 2012)

2.11.2.3 Extruded activated carbon (EAC)

EAC consists of powder and granular particles of activated carbon that have been fused together and shaped into cylindrical shaped AC masses with particle sizes extending from 800 to 4000 μm in diameter. EAC has been applied in automotive releases control as a result of its low pressure drop, durability and little dust content (Bridgewater, 2012).

Figure 2.12: EAC (Bridgewater, 2012)

2.11.2.4 Impregnated Carbon

This is porous carbon infused with cations of silver, manganese, zinc, iron, calcium, etc. Chemical infusion adds adsorbent functionality which catalyzes chemisorption (Daud *et al.*, 2010). Carbon impregnated with amines and salts has been used in the manufacture of military gas masks. On commercial scale, activated carbon impregnated with potassium iodide or sodium hydroxide has been used in the removal of sulphur (Rivera-Utrilla *et al.*, 2011).

Figure 2.13: $KMnO_4$ impregnated Carbon (Hagemann *et al.*, 2018)

2.11.2 Applications of activated carbon

Activated carbon has found both domestic and industrial applications due to its adsorptive nature which favours contaminant uptake in gaseous and liquid phases.

2.11.2.1 Water treatment

Activated carbon has been employed in the removal of water pollutants which include organic matter and chemical by-products of water remediation. These compounds are sources of infections and are producers of bad taste and smell to water and environment. Synthetic organic matter such as pesticides, dyes, phenols and chloromethanes are some of the byproducts of chemical water treatment. When Powdered activated carbon (PAC) is added in slurry or powder form in dosing system, these contaminants are adsorbed after a suitable contact time then removed by sedimentation, flocculation or filtration (Bridgewater, 2012). GAC is applied when there is persistent odour and taste in the water treatment. Fluid circulate through a fixed bed and contaminants get adsorbed from the fluid (Anfruns *et al.*, 2009). Activated carbon is also used in the remediation of industrial effluents by removing chemicals and biodegradable organic matter prior to reuse or discharge into treatment plants or water bodies, rivers and streams. It is also efficient in elimination of pesticides, heavy metals, aromatic and halogenated organic compounds from urban effluents (Pascal *et al*., 2008).

2.11.2.2 Gas Purification

Activated carbon in granular, powdered or extruded forms have been used in the purification of gases in the chemical industry prior to use and also to mitigate against poisonous gases release to the atmosphere (Kanjana *et al.,* 2013). Biogas is produced through anaerobic digestion of animal wastes and plants to produce methane gas and carbon dioxide in addition to impurities like hydrogen sulphide (H_2S), volatile organic compounds (VOCs) and siloxane. These poisonous, flammable and corrosive impurities are removed by carbon impregnated with hydroxides of potassium and sodium or potassium permanganate salt (Schmidt and Wilson, 2012).

2.11.2.3 Food and beverages industry

Activated carbon is used to remove impurities during industrial processes to enhance quality of finished products. In sugar industry AC is used to decolorize sugar syrup. This in turn improves sugar optical aspect, purity and processing properties; reduced viscosity and improved surface tension of the syrup (Tadda *et al.,* 2016). Consequently, crystallization and separation of sucrose from massecuite is improved. AC eliminates unwanted smell, colour and taste compounds from processed fruit juices. In preparation of rectified alcohol via fractional distillation, fusel oil is removed when passed through bed of activated carbon (Kanjana *et al.,* 2013). This removes obnoxious taste and smell. Other applications include decaffeination of beverages, removal of taste and odour from fats and oils (Mohammed *et al.,* 2014)

2.11.2.4 Medicine

In medicine, activated carbon has been used in the treatment of gastrointestinal decontamination and adsorption of intestinal gases in the treatment of flatulence and intestinal distention (Albertson *et al.,* 2011). In pharmaceutical industry activated carbon is used to eliminate precious metals like palladium and platinum after active component synthesis (Iverlund *et al.,* 2009).

2.11.2.5 Solvent recovery

Most industries involved in manufacturing of paints, petrochemicals and adhesives employ activated carbon in air flows to regain solvent vapors which are recycled and reused in the manufacturing process. Solvents recovered by activated carbon include ethanol, acetone, chlorinated hydrocarbons and ethers (Kanjana *et al.,* 2013).

2.11.3 Activated carbon regeneration

During adsorption process, several organic and inorganic pollutants clog the active sites of the adsorbent thus reducing the efficacy of the activated carbon with time. Therefore, in order to make AC economically viable for pollutants adsorption in major applications, the adsorbent molecules should be removed to equip the system for the next adsorption process (Wen *et al.*, 2011). Regeneration of activated carbon restorers the adsorbent's available surface area and active sites or elimination of adsorbate on AC through desorption or decomposition (Nahm *et al.*, 2012). The regeneration process ensures selective elimination of the accumulated adsorbates on the adsorbent during adsorption process and the repairing of the previous porous structure and potency of the activated carbon (Samonin *et al.,* 2013). Appropriate regeneration employed is dictated by adsorption type, adsorbates nature, cost and processing employed (Kulkarni and Kaware, 2014). Employed techniques can be broadly classified as thermal and chemical regeneration.

2.11.3.1 Thermal regeneration

Thermal regeneration employs high temperature to break the adsorbent-adsorbate bonds created during adsorption (Guo and Du, 2012). Thermal regeneration methods include; thermal swing adsorption (TSA) which is employed in the elimination of gaseous adsorbate at alternating low and high pressures (Eriksson and Kiros, 2014), steaming (Ramalingam, 2012), electro thermal swing adsorption (Johnsen, *et al.,* 2011), microwave regeneration (Ondon, *et al.,* 2014), which require heating procedure to desorb adsorbate pollutants. The process however may be dictated by nature of adsorbent and adsorbate (Irfan *et al.,* 2013). Thermal regeneration is achieved through three steps. Adsorbent is first dried at around 100°C to the desired moisture level. The dried carbon material is then pyrolysed to about 750 °C in inert atmosphere which results in volatilizing 77- 90 % of the adsorbed pollutants, eliminating residual moisture and thermally degrading the remaining stable compounds (Nahm *et al.,* 2012). The last oxidative stage employs controlled steam or carbon dioxide gas into the system to restore the pores of the activated carbon (Taik-Nam and Choong, 2012). During the process of regeneration about 10 % of carbon is lost and therefore it is prudent to replenish with new AC (Kulkarni and Kaware, 2014).

2.11.3.2 Chemical regeneration

In this type of regeneration chemical reagents are employed to the exhausted carbon to desorb or degenerate the adsorbates especially when there is a strong adsorbates-adsorbent bond (Nahm *et al.,* 2012). In most cases, acid and alkali solutions (hydrochloric acid, sulphuric acid, sodium hydroxide, potassium hydroxide) and organic solvents such as ethanol have employed to get rid of adsorbates (Sun *et al.,* 2012). The chemical regeneration system entails changes in pH, chemical response and thermal desorption (Salvador *et al.,* 2015). When sodium hydroxide is used as regenerant, hydroxyl ion alters the pH on the adsorbent surface to be negatively charged thereby weakening the Van der Waals force and chemical bonds formed during adsorption process thus allowing unreactive adsorbates to NaOH to be desorbed (Ghasemzadeh *et al*., 2012, Lu *et al.,* 2011), additionally removing reactive adsorbents through production of soluble and stable compounds (Sun *et al.,* 2012). The formed compounds can be removed through washing with aqueous or organic solvents which extract the water-soluble salts and surplus NaOH solution in the regeneration system (Guo *et al.,* 2011).

2.12 Tyre manufacturing process

Tyre is a flexible and strong circular shaped rubber casing that surrounds the external edge of a wheel made up of rubber. It imparts a firm grasp surface for traction and also cushion the wheels while in motion (Bodziak, 2008). The major roles of tyres include steering the vehicle with accuracy despite the condition of the weather, road surface, carry loads either in motion or at rest, absorption of shock due to friction on the road surface and transmitting drive through vehicles power engine and braking effort (Bounda *et al.,* 2011). Therefore tyres should be designed to withstand transversal forces in order to give optimal and dependable road holding quality (Bounda *et al.,* 2011). Tyres can be broadly categorized as solid or pneumatic (Arslankaya and Çalık, 2016). Solid tyres are produced from solid rubber and plastic materials through molding process and mostly applied in industrial and commercial purposes (Barbosa *et al.,* 2017). Pneumatic tyres are made from rubber (natural and synthetic), wire, fillers (carbon black) and chemicals and majorly applied in transport and agricultural sectors (Bodziak, 2008). Tyre production involves enveloping several layers of specially designed rubber around metallic drum in a tire making device (Barbosa *et al.*, 2017). Processes include mixing, material processing, building of tire, curing and vulcanization as shown in Figure 2.14

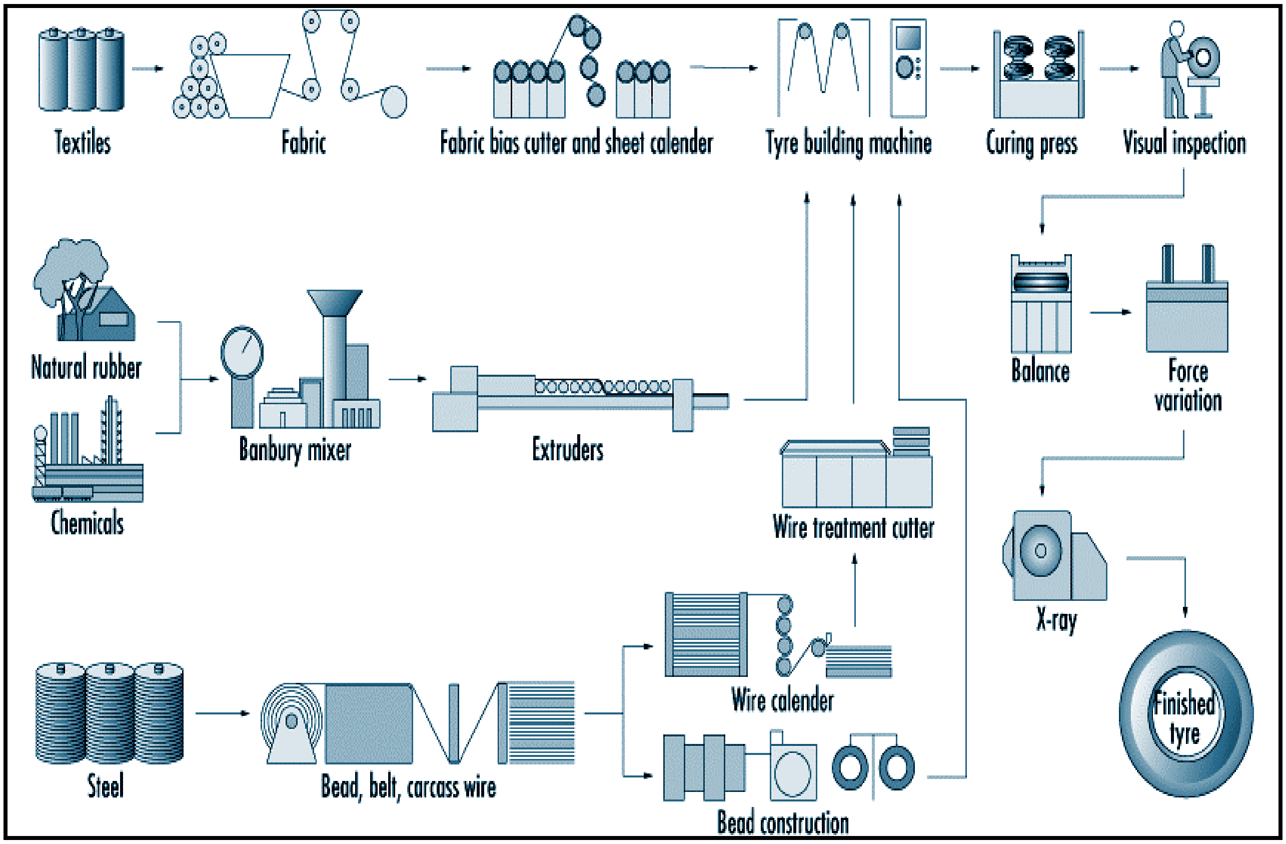

Figure 2.14: Schematic manufacture of tyres (Arslankaya and Çalık, 2016)

2.12.1 Mixing

Major raw materials such as rubber, carbon black, process oil and additional chemical components are mixed at elevated temperatures in a huge mixer to produce a uniform rubber medium (Bodziak, 2008). The produced medium is shaped into long and flat strips when forced through dual set of rolls operating in opposite directions (Bounda *et al.*, 2011).

2.12.2 Material processing

Material processing include extrusion, calendaring and beading (Bounda *et al.*, 2011). Extrusion is the application of heat and pressure on the milled rubber compound to produce tread and sidewall (Bounda *et al.*, 2011). Tread enhance tyre's wear and grip in any condition while sidewall improves abrasion and environmental resistance for the tyre sides (Bodziak, 2008). Calendaring procedure produces thin sheets of rubber of definite breadth and width which envelops fabric layer (Mandar and Pranay, 2015). The calendared sheets of rubber are wound on drums with textile spacers to impede sticking of the sheets (Bounda *et al.,* 2011). Beading process ensures metal wire bunch which enfolds the tyre on the wheel is rubber covered (Bounda *et al.,* 2011).

2.12.3 Tyre building

Material processing output i.e. beads, side walls and treads are assembled and wound onto collapsible drum holding parts of the tyre as per tyre specifications. Building of tyre commences with wrapping of the rubber enveloped fabric layers of the tyre around the device drum joining the end of the layers with adhesive (Bounda *et al.,* 2011). Beads are then added and locked into place adding more layers of rubber sheets on the beads. The tyre rubber plies are then shaped at the edges, extruded for the sidewalls and tread and glued to form the green (assembled) tyre which is then removed from the tyre building device (Mandar and Pranay, 2015).

2.12.4 Curing

Curing is the stage which grants a tyre its shape and tread design by placing green tyres into press loading machine where pressure and heat energy are applied (Arslankaya and Çalık, 2016). Pressure imparts green tyre its eventual shape while heat energy catalyzes the chemical reaction between the rubber components cross linking and additional processing materials (Bounda *et al.,* 2011).

2.12.5 Quality control

Quality control checks begins at raw materials stage as they are supplied (Bounda *et al.,* 2011). During manufacturing process at different stages samples are taken and tested for conformity to set out parameters like tensile strength and degree of compactness (Bodziak, 2008). If the tyre meets the acceptable quality parameters after the final check, they are stored awaiting shipping or sale.

2.13 Tyre components

Tyre consist of several layers made up of assorted raw materials. Layers include inner liner, beads, tread, sidewall, belts and body ply as shown in Figure 2.15

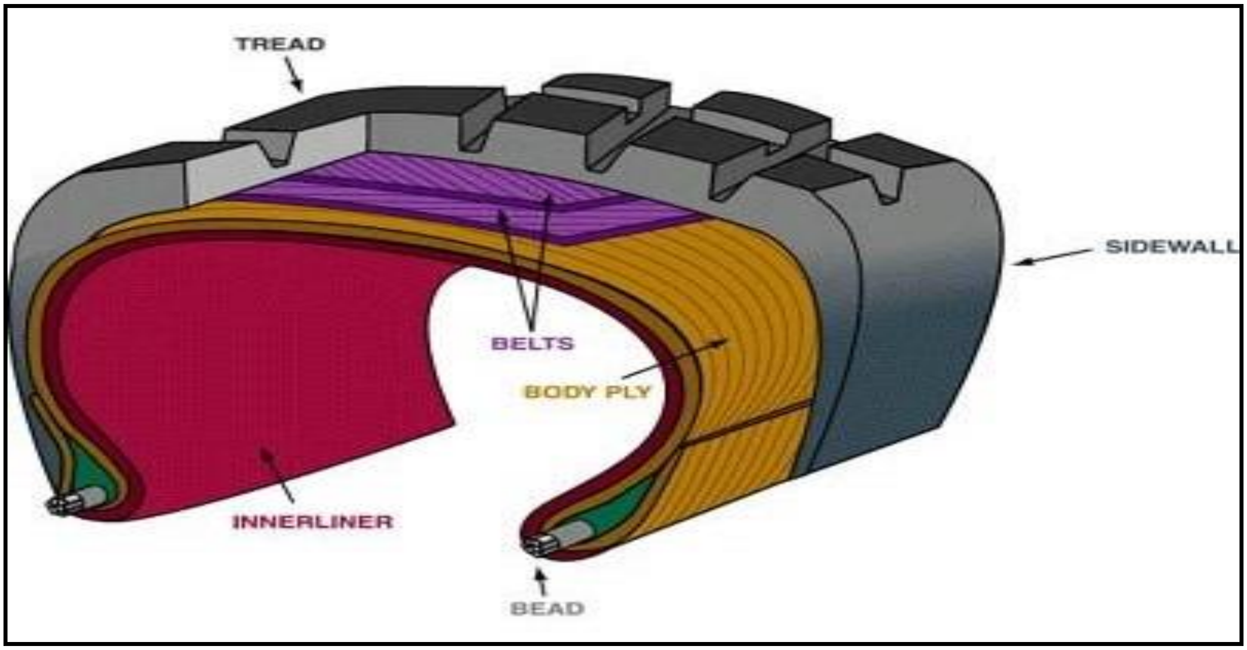

Figure 2.15: Schematic tyre component (Arslankaya and Çalık, 2016)

2.13.1 Inner liner

Refers to extruded elastomer sheet combined with additives giving a low air penetrability (Bounda *et al.,* 2011). It ensures holding of pressurized air by the tyre without air dispersing throughout the rubber system (Barbosa *et al.,* 2017)

2.13.2 Beads

These are straps of high tensile toughness steel wire enclosed in a rubber material. Beads are neither flexible nor elastic hence provide strength mechanically to tyre to be fixed to the wheel (Barbosa *et al.,* 2017).

2.13.3 Sidewall

This is non stiffened extruded outline having additives compounds such as antioxidants and antiozonants which give tyre side’s resistance to wear and harsh environmental conditions (Mandar and Pranay, 2015). It is designed in a way that it provides area on which tyre ornamentation can be done.

2.13.4 Belts

Belts are calendared sheets of rubbers enclosing narrowly spaced steel cords giving tyre its flexibility, strength and depression resistance (Mandar and Pranay, 2015).

2.13.5 Body ply

This denotes two or more calendared sheets of rubber that are mechanically bonded to a fabric to contribute to the tyre structural strength (Bounda *et al.*, 2011).

2.13.6 Tread

The tread is a broad extruded outline that encapsulates the tire carcass and is directly in contact with the road surface. Additives that bestow grip, abrasion and harsh weather resistance constitute tread compounds (Mandar and Pranay, 2015).

2.14 Waste tyre environmental problems

Managing waste tyres has become a global environmental challenge in the recent past. Due to fast population upsurge compounded with high demand for transport of goods and services, it has necessitated production of pneumatic rubber tyres with improper disposal mechanisms. This in turn has led to waste accumulation on the environment (EPA, 2012), consequently contributing further to health and safety concerns (Reschner, 2008).

2.14.1 Human health issue

Waste tyre stacks is a perfect habitat for rodents and insects which transmit diseases to human beings. During rainy seasons, water stagnates in open tyres and become a breeding space for mosquitoes and vermin. Mosquitoes lay eggs in the stagnant water spreading malaria, dengue and yellow fever to human and animals (Reschner, 2008). The tyre components include toxic chemicals such as nickel, dioxins and polynuclear aromatic hydrocarbons which are additional risks to both human and environment health if waste tyres are improperly trashed into the surrounding through combustion (Kar, 2011)

2.14.2 Fire risks

Improper storage of large amounts of waste tyres in piles is a fire hazard and in case of fire outbreak, it may be very hard to control particularly when it involves huge stacks. Tyres can char for long duration of time in the process produce great amount of heat, greasy runoffs and particulate matter which can pollute water bodies, air and soil (Kar, 2011). Exposure to toxic particulate matter also is a health hazard to residents especially the vulnerable group such as those with respiratory diseases in close vicinity and firefighters putting out the fire (Reschner, 2008). Furthermore, waste tyre fires can be expensive financially especially if not controlled (Roy, 2011).

Figure 2.16: Waste tyre fire (Reschner, 2008)

Unchecked tyre fires have several environmental effects. Combustion leads to emission of carbon dioxide, a known greenhouse gas and other volatile organic compounds which are major contributors of air pollution (Kar, 2011). Tyre combustion residues can lead to sudden and long term leaching of toxic byproducts into the soil whose effect can be harmful to plants and animals (Sienkiwicz *et al.*, 2012).

2.15 Waste tyre management technologies

There are numerous ways for managing waste tyres which can be safe and efficient with major aim of recycling, reprocessing or making new products, consequently reducing waste tyre generation. Some of the methods employed include retreading, incineration, pyrolysis, size reduction for various applications and landfilling (Rowhani and Rainey, 2016).

2.15.1 Retreading

This refers to method that replaces tread on repaired and inspected worn out tyres. The method employs non-destructive method like shearography which uses lasers to scan spot damages and embedded foreign matter on the tyre (Bodziak, 2008). In the process, cases in good condition are repaired by buffing away aged tread and replacing with new ones (Rowhani and Rainey, 2016). Tyre retreading is not labour intensive and requires less technology as compared with the initial tyre production process and produces insignificant by products (Patel and Kayasth, 2015).

2.15.2 Pyrolysis

Pyrolysis is the thermal degradation of organic material anaerobically. Waste tyre pyrolysis is one of the alternative method used in the management of rubber wastes. It is environmentally friendly due to absence of greenhouse gases emission compared to open burning (Rombaldo *et al.,* 2008).Additionally, the incineration process produces pyrolysis oil, gaseous constituents and carbon char (Islam *et al.,* 2008). Hydrocarbon gases produced in addition to carbon monoxide and hydrogen sulphide gases are used to fuel the degradation process and the carbon produced can be employed in the production of activated carbon for the adsorption of toxic gases and chemicals (Rombaldo *et al.,* 2008).

2.15.3 Incineration

Incineration refers to combustion of waste tyres which cannot be reused or recycled economically (Orieku *et al.*, 2013). The heat energy released can be used directly in production processes such as cement and steel industries and also to generate steam to drive turbines in electricity production plants (Sienkiwicz *et al.*, 2012). It has also been found that concrete made out of 10 % waste tyre ash possess higher transverse rupture and compression strength in addition to higher resistance to heat compared to conventional mortar (Noor *et al.*, 2015). Whole and shredded tyres can be used as an alternative for fossil fuel in generation of heat and electricity. This ensures preservation of natural resources. Incineration process is conducted under supervised conditions which therefore ensure minimum release of toxic matter (Sienkiwicz *et al.*, 2012).

2.15.4 Size reduction for engineering and construction

Waste tyres and their secondary products can be applied in various civil engineering works. Fragmented tyre waste can be integrated in asphalt production (Najim *et al*., 2010). Rubberized asphalt has less fatigue fracture, good heat and sound proof, low in density, inexpensive and durable than standard asphalt (Orieku *et al.*, 2013). Tyre bale produced by compacting entire tyre and steel tying, can be used as construction block. It is compressed to size of 50 x 55 x 30 inches making it suitable for non-structural and light weight fill applications like gabion baskets and walls for checking soil erosion (Bolden *et al.*, 2013). Additionally, waste rubber tyres can be ground into flakes which can be used to produce mulch which can be employed for sports tracks and children playground (Bolden *et al.*, 2013). Rubber mulch is elastic, minimizes weed development and durable than mulch originating from plant materials (Ferrag, 2016).

2.15.5 Land filling

Landfill is the ultimate step in the waste tyre management order and is one of the conventional methods used in waste tyre management. It is normally applied when solid waste and/or by products cannot be used or processed further (McIssack and Rowe, 2012). Even though the method is convenient and relatively cheap, it still faces many challenges. Tyres utilize landfills space and also buoyant in nature. This makes the tyres to resurface once buried. Upon resurfacing they pose a high fire risk (Petraitis, 2009). Furthermore, vulcanized waste tyre rubber can be degraded after a longer duration through natural mechanical mechanisms. Nonetheless, sanitary landfilling can be employed to cut down on environmental and public health outcomes of solid disposal on the local ecology. Sanitary landfills are specially engineered to contain leachate collectors, multiple liners, cover and hydrogeological system which in totality checks on the water permeation and leaching processes (Johnsen *et al.*, 2011). Wastes are compressed on daily basis and sealed with a layer of dirt to mitigate against smell, risks of fire, vermin and other organism which can spread diseases (Rowe, 2012).

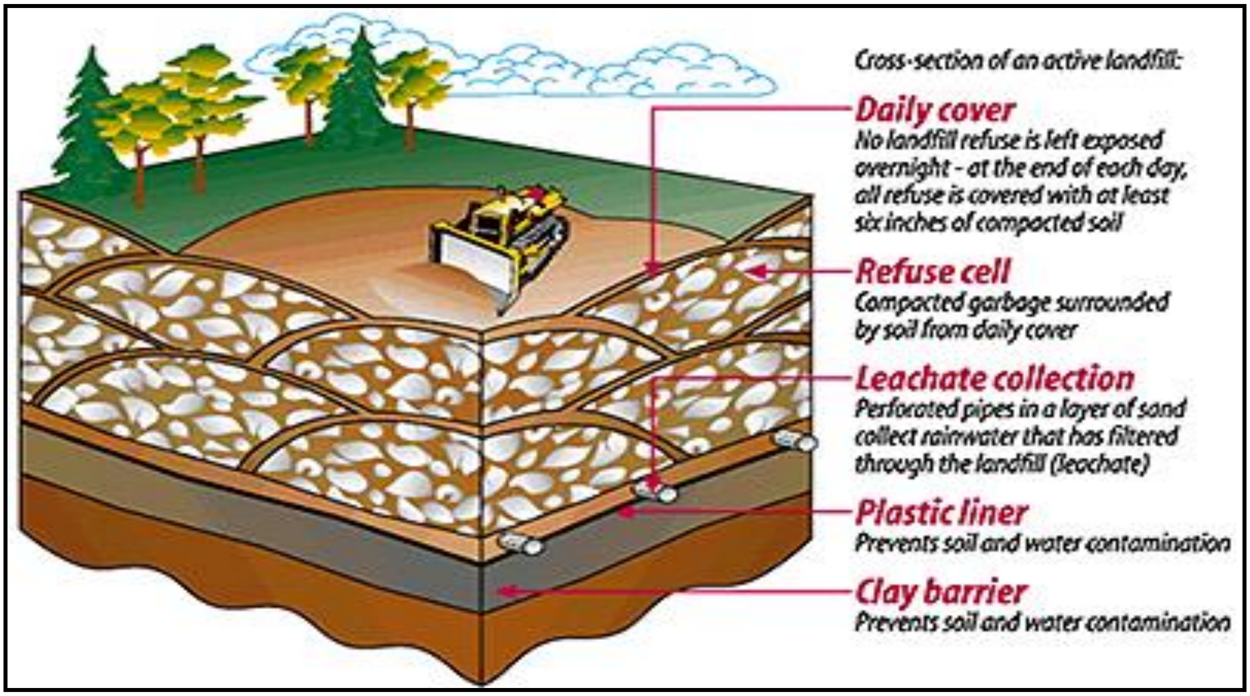

Figure 2.17**: S**chematic cross section of sanitary land landfill (Rowhani and Rainey, 2016)

2.15.6. Other applications

Other applications of waste tyres include stamped products like mats, rubber parts, garden containers and sandals.

Figure 2.18: Tyre sandals

2.19 Atomic Absorption Spectroscopy (AAS)

This is an analytical technique employed in the quantitative determination of elements in a given sample by making use of the absorption of light radiation by free atoms in the gaseous phase.

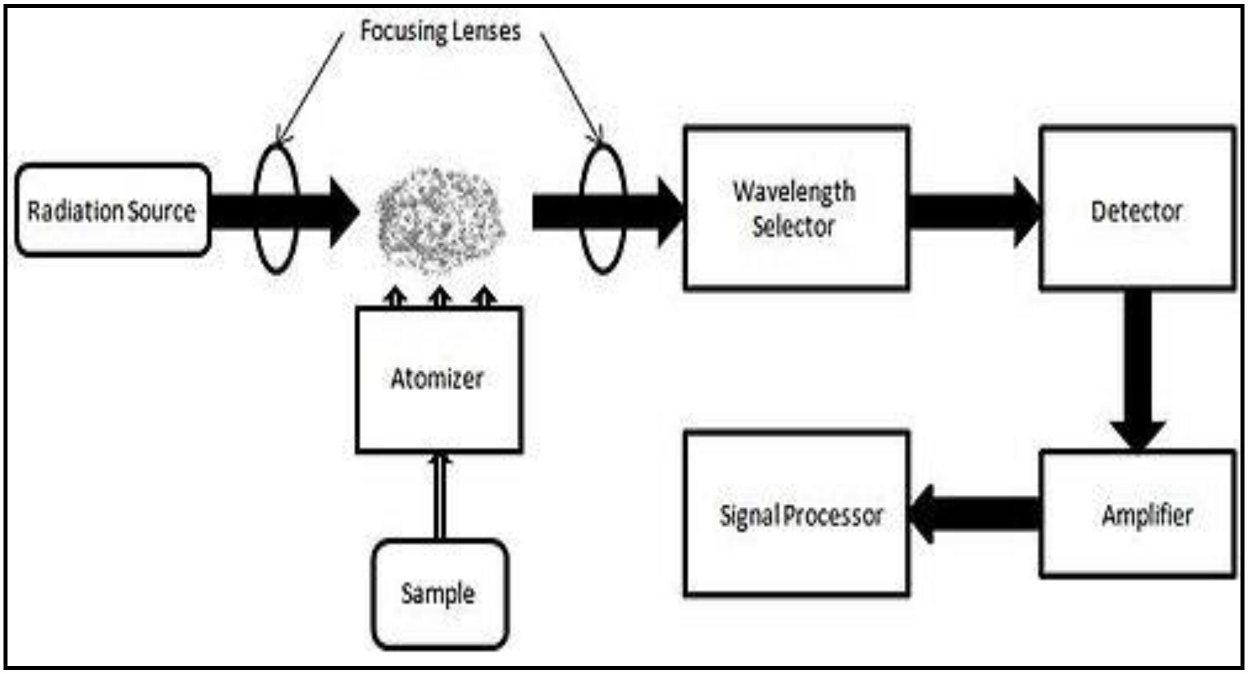

Figure 2.19: AAS schematic diagram (Helaluddin *et al*, 2016)

2.19.1 Principle

AAS technique employs absorption of radiant energy by free atoms of analyte at a specific wavelength that is unique to that element of concern thereby quantifying its respective concentration (Helaluddin *et al*, 2016). During analysis, standard series with known concentrations are used to determine the relationship between the analytes absorbance and the corresponding concentration. In the process of analysis, the sample analyte is atomized and its respective electrons get excited to higher energy states in a short term by absorbing light of specific wavelengths which corresponds to the analyte's electronic transition. The energy from the radiation source travel through monochromater which selects only radiation that is specific to the element of concern. Therefore, the radiation flux in both standards and sample in the flame or electro thermal atomizers is quantified via a detector by converting the absorbance of the analyte to concentration by applying the Beer-Lambert Law (Helaluddin *et al*, 2016).

Beer-Lambert law states that the amount of absorbed light by analyte is directly proportional to its corresponding concentration and the light path length through the analytes solution, given by equation 2.8

$$\mathbf{A = \varepsilon \mathit{lc}} \qquad \text{Equation 2.8}$$

Where; **A** = Absorption

ε =Molar absorption coefficient

l = Path length of light radiation

c = Concentration of the analyte

CHAPTER THREE

MATERIAL AND METHODS

3.1 Study site

The study site was within the City of Nairobi which is in Nairobi County. The county lies in the geographic coordinates of 01°17′10″S 36°49′02″E and altitude of 1600 to 1860 m above sea level. It is the smallest county covering an area of 696 Km^2 besides being the most densely inhabited by approximately 3.9 million people (KNBS, 2015). The county borders Eastern and Rift Valley provinces to the south, Central Province to the north as shown in Figure 3.1. It has a topography that is generally rugged on the western side, flat and lower on the eastside (Tibaijuka, 2007).

The Nairobi industrial area is located towards the southeast part of the main business and commercial area of the city. It is majorly situated between highly populated areas of Mbotela, Kaloleni, Makongeni and Makadara towards the north and Mukuru village, the national park and Mukuru Kayaba to the south. Geographically, it is a flat terrain extending from Athi-Kapiti Plains (Herzog *et al*, 2008).

The Nairobi River Basin shown in Figure 3.1 consists of three major rivers namely Ngong, Nairobi and Mathare. A lot of the City's industrial effluents are discharged into these rivers causing them to be highly polluted (Mbui et al. 2016). These rivers connect on the eastern of Nairobi and join Athi River, which finally flows into the Tana River that cascades into the Indian Ocean. Other feeder rivers include; Kirichwa, Gathara-ini, Karura, Ruiru and Rui-Ruaka, which are mainly narrow are also immensely contaminated with organic and inorganic pollutants (Herzog *et al*, 2008).

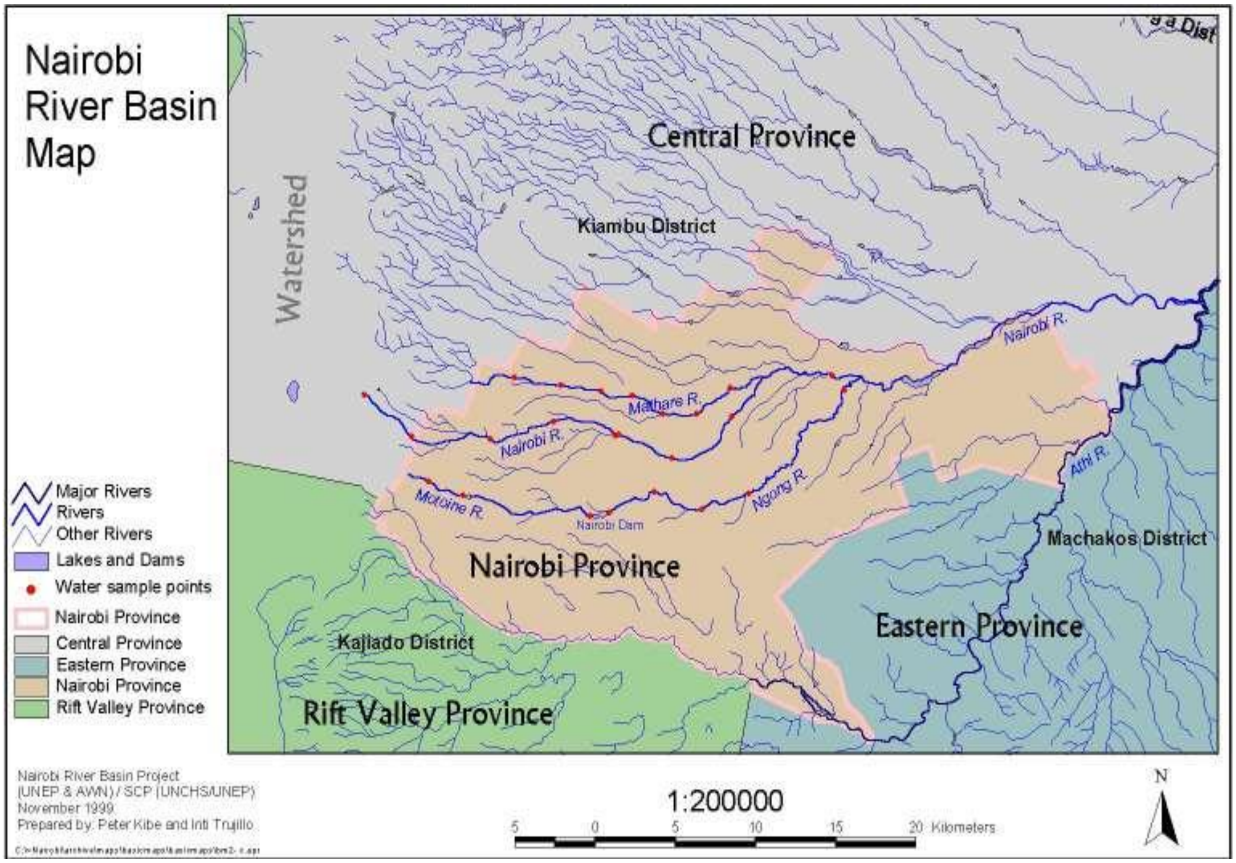

Figure 3.1: Nairobi River basin (Mbui et al. 2016)

Three paint manufacturing companies allowed sampling to be done within their premises on condition that their identity was not disclosed. They were labeled A, B and C respectively. They were situated along Enterprise Road and Outer Ring Road, all within the city. Company A was about 3km from company B and 12.6 km from C. Company B and C were 13 km apart as shown in figure 3.1. The coordinates and altitude of the sampling sites A, B, C and Kariokor market are given in Table 3.1.

Table 3.1: Sampling Sites Coordinates

Sampling Site	**Coordinates**	Altitude
A (EMR)	1^{0}18’00”S, 36^{0}50’23”E	1657 M
B (ESD)	1^{0}18’29”S, 36^{0}50’50”E	1650 M
C (EUP)	1^{0}15’25”S, 36^{0}52’54”E	1614 M
D (Kariokor Market)	1^{o}16’42”S, 36^{o}50’06”E	1660 M

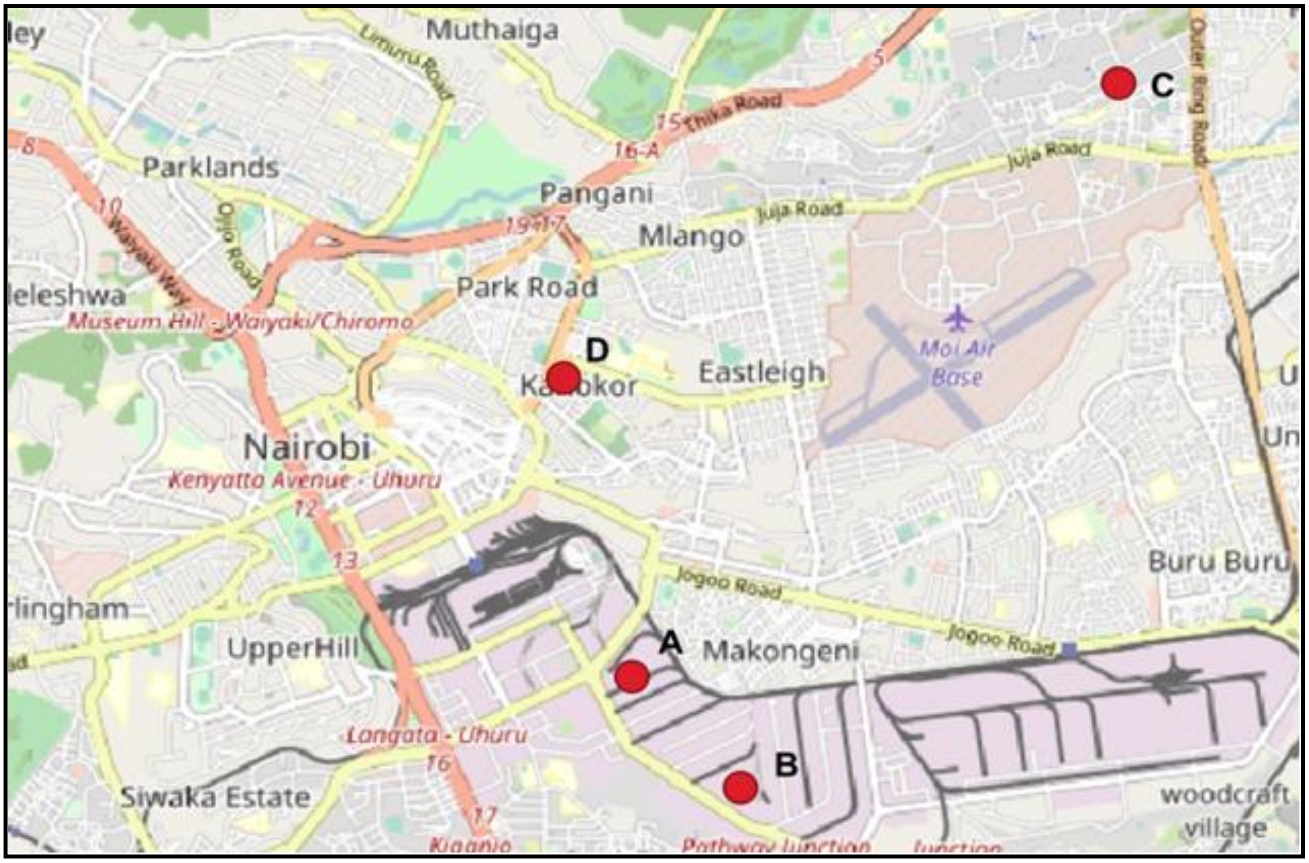

Figure 3.2: Map of Nairobi area showing sampling points for effluents and waste tyres

3.2 Effluent Sampling

The grab samples were drawn using an auto sampler to a depth of about 50 cm from the waste water receiving tanks. The tanks act as meeting points for each of the companies' releases from washings prior to discharge into municipal drainage. The samples were transferred into 2.5L clean amber glass bottles and labelled EMR, ESD and ESP respectively. The samples were then taken to KEPHIS Analytical Chemistry Laboratory (ACL) and stored at 5^{o}C awaiting analysis.

3.3 Waste tyres sampling and pretreatment

Waste tyre material weighing about 5.0 kg was collected from Kariokor open market (site D) of coordinates 1^{o}16'42"S, 36^{o}50'06"E in Nairobi County and packed in a brown manila paper. They were washed with detergent solution and rinsed with 2 litres of distilled water. Washed samples were sun-dried for 3 hours, cut into small pieces about 0.5 to 1.0 cm thick and stored in a sample cabinet at room temperature.

3.4 Reagents and equipment

3.4.1 Reagents

All the reagents used for analyses were of analytical grade and sourced from different manufacturers. They included Aluminium Sulphate, Ammonium Vanadate, Devarda's alloy, Gum Acacia, Barium Chloride, Boric acid, Bromocresol Green, Copper sulphate tablets, Hexane, Magnesium Oxide, Methyl Red, Perchloric acid, Potassium Dihydrogen Phosphate, Potassium Iodide, Ammonium Molybdate ,Nitric acid, Sodium Hydroxide, Potassium Iodide, Potassium Sulphate, Manganese Sulphate, Perchloric acid, Copper sulphate tablets, Potassium Hydroxide, Sodium Azide, Sodium Thiosulphate, Sulphuric acid, high purity standards of Cadmium, Chromium and Lead all manufactured by Sigma Aldrich (USA), while COD HR reagent was sourced from Hannah Instrument (USA)

3.4.2 Equipment

The equipment used for analyses included Flame Atomic Adsorption spectrometer, Thermo Solaar S4 model, RAT2 block digester from JP Selecta, Oxitop BOD incubator, COD reactor and Multiparameter, H839800 model from Hannah Instrument, DT-9 digital pen thermometer, SK-300 Kjeldahl distillation unit, LS-X Lab-Shaker, LH120/12 muffle furnace, Memmert UF 160 Oven, Hannah H1225 pH/Conductivity meter, Thomas scientific 2100Q Turbidimeter, Perkin Elmer Ultraviolet-Visible Spectrophotometer, Lambda 25 model and Sartorius Weighing balance, BA3015 model.

3.5 Physico-chemical parameters determination

3.5.1 Temperature determination

Temperature of the effluent samples were measured at the point of sampling. After drawing the samples, they were allowed to settle in sampling containers and the temperature measured using DT-9 digital pen type thermometer and recorded in triplicate.

3.5.2 pH determination

Measurement of pH was done at site. Hanna H1225 EC/pH meter was first calibrated with 4, 7 and 10 pH buffers. Into 100 ml beaker a 50ml effluent sample was transferred. The pH electrode was immersed in the beaker and after the sample stabilized, readings were taken and recorded. This procedure was repeated for each effluent sample.

3.5.3 Conductivity determination

Hanna H1225 EC/pH meter was calibrated using a calibrating solution of 1413 µS/cm. EC probe was inserted into 100 ml in the beaker and after stabilization, readings were taken. This was done in triplicate for each effluent sample.

3.5.4 Turbidity determination

HACH model 2100Q portable Turbidimeter was first calibrated using 15NTU, 100 NTU and 750 NTU standards. The effluent samples of 15ml were then transferred into tube holder and turbidity readings taken at 855nm.

3.5.5 Oil and grease determination

The liquid-liquid extraction method was used. A sample of 100 ml wastewater was measured and transferred into a 500 ml separating funnel. Then 2 ml of concentrated HCl was added to adjust the pH to 2. To the acidified sample, 30 ml hexane was added, shaken vigorously for 5 minutes and then left to stand to allow organic and aqueous layers to separate. The lower aqueous layer was transferred into a second separating funnel. Extraction was further repeated twice with 20 ml of hexane and the extracts combined with the initial hexane extract. The combined extract was drained through a glass funnel containing anhydrous sodium sulphate into a pre weighed beaker to remove water from the organic extract. The solvent was then evaporated in a water bath and after drying, the weight of the beaker containing dry extract was measured and used determine the oil and grease content in the samples.

3.5.6 Total suspended solid determination

Total suspended solids was determined by filtering into a beaker 100 ml of wastewater in triplicate, through a dry pre weighed Whatman filter paper of 11µm pore size. The paper containing the residue was dried at 105^{o}C for 1 hour in a UF 160 MEMMERT oven. The paper and dry residue were then cooled in a desiccator for 45 minutes and then reweighed

3.5.7 Turbidimetric determination of total sulphur

For each of digest aliquot, blank and sulphur standard solutions of 5, 10, 20, 30 and 40 mg/L, 10 ml was pipetted into a test tube adding 1ml of 0.5 % ($^{w}/_{v}$) gum acacia solution and 1g of barium chloride crystals. The mixtures were gently shaken until the barium chloride crystals completely dissolved. They were left to stand for one hour after which the concentrations of the samples and serial dilutions of the standard were measured using UV-Visible Spectrophotometer (Perkin Elmer lambda 25) at 440 nm wavelength.

3.5.8 Determination of total nitrogen

Total nitrogen was determined using classical Kjeldahl method by adding 5 ml of a sample and copper sulphate tablet into each 100 ml digestion tube and digested in 10 ml concentrated sulphuric acid at 350 ^{o}C for 2 hours. The digests were left to cool and transferred into volumetric flasks and made to 250 ml mark using distilled water. The aliquots were then distilled in 10 ml 1% boric acid, using magnesium oxide and Devarda's alloy (50% Cu, 45 % Al, and 5 % Zn) as catalyst. The distillates were then titrated against 0.01N hydrochloric acid using a mixture of bromo cresol green and methyl red solutions as indicator until a permanent pink colour was achieved.

3.5.9 Total phosphorus determination

Into a 100 ml volumetric flask, 5.0 ml of a previously digested sample, blank, phosphorus certified reference material (CRM) and phosphorus standard solutions 5, 10, 15, 20 and 25 mg/L were pipetted. Then 15 ml of ammonium vanadate-ammonium molybdate solution was added to each standard solution, sample, CRM and blank and made to the mark with distilled water. The resultant solutions were left for 1 hour for colour development and then measured for phosphorous using UV-Visible Spectrophotometer (Perkin Elmer Lambda 25) at a wavelength of 430 nm.

3.5.10 Chemical Oxygen Demand (COD) determination

Into each digestion vials containing 10 ml of HANNA COD HR reagent (Sulphuric acid, mercury sulphate and potassium dichromate), 0.2 ml of blank and effluent samples were pipetted. The contents were mixed gently and digested in COD reactor for 2 hours at 150 ^{o}C where hexavalent chromium (Cr^{6+}) was degraded to trivalent chromium (Cr^{3+}) and cooled. The cool blank mixture was transferred into vial, selecting COD method from HANNA HI 83099 COD and Multi parameter bench photometer form Hannah Instrument (USA) and zeroed. The blank sample was then replaced with samples with effluent mixture samples and the color intensity determined at a wavelength of 610 nm.


Figure 3.3: COD reactor and Multiparameter photometer

3.5.11 Biochemical Oxygen Demand determination

3.5.11.1 Preparation of manganese Sulphate solution

Into 250 ml volumetric flask, 120 g of $MnSO_4.5H_2O$ was weighed and dissolved in 100 ml of distilled water and then diluted to the mark using distilled water.

3.5.11.2 Preparation of alkali-iodide-azide solution

Into 500 ml volumetric flask containing 100 ml of distilled water, 167 g of sodium hydroxide pellets and 45 g of sodium iodide powder were weighed and dissolved. Into a separate beaker, 5 g of sodium azide (NaN_3) was dissolved in distilled water and the solution added to the alkali-iodide solution. The resultant solution was diluted to 500 ml mark using distilled water and allowed to cool to room temperature.

3.5.11.3 Preparation of 0.025 M sodium thiosulphate solution

To prepare 0.025 M sodium thiosulfate solution, 6.2 g sodium thiosulphate pentahydrate ($Na_2S_30_3.5H_2O$) was weighed and dissolved in 100ml of distilled water in a 1000 ml volumetric flask and topped to the mark. The solution was preserved by adding to it 2 ml of chloroform. The solution was standardized using 0.0021 M potassium iodate (KIO_3) solution.

3.5.11.4 Preparation of starch solution

This was prepared by heating 100 ml of distilled water and adding to it 2 g of starch powder while stirring with a glass rod. The resultant mixture was allowed to cool and then stored in a refrigerator at 6 ^oC.

Procedure

Three 10 ml wastewater samples in 200 ml volumetric flasks were diluted with distilled water to the mark. After thorough mixing, the solutions were transferred into 3 labeled BOD bottles and tightly closed. To each of the solutions, 2 ml alkali-iodide- azide solution was added, mixed gently and inverted severally to eliminate air bubbles. The resultant solution was incubated in *Oxitop* BOD incubator at 20^oC for 5 days. To determine dissolved oxygen, about 2 to 3 drops of starch solution was added to the incubated solution which was then titrated using standardized 0.025 M sodium thiosulphate solution until a slight yellow colour was formed and titration proceeded until the blue colour disappears. Titration of a blank solution which had undergone the same treatment as the incubated samples was also carried out.

3.5.12 Determination of metal contaminants before coagulation-flocculation process

3.5.12.1 Preparation of lead standard solution

Lead standard series were prepared by pipetting 10 ml of the 1000 mg/L high purity lead standard solution into 100 volumetric flask, adding distilled water to the mark to make 100 mg/L standard solution. From this standard solution, 1ml, 2ml, 3ml, and 4ml were pipetted and transferred into labelled 50 ml volumetric flasks and topped to the mark using distilled water to make standard series of concentrations 2, 4, 6, and 8 mg/L lead respectively.

3.5.12.2 Preparation of cadmium standard

Cadmium standard solutions were prepared by pipetting 10 ml of the 1000 mg/L high purity cadmium standard solution into a 100 ml volumetric flask, adding distilled water to the mark to make 100 mg/L standard cadmium solution. From the prepared standard solution, 5 ml, 10 ml, 15 ml, and 20 ml were then pipetted and transferred into labelled 100 ml volumetric flasks and topped to the mark using distilled water to make concentrations of 5, 10, 15, and 20 mg/L cadmium respectively.

3.5.12.3 Preparation of chromium standard

Chromium serial standards were prepared by pipetting 1ml of the 1000 mg/L high purity chromium standard solution into 100 volumetric flask. Distilled water was then added to the mark to make 10 mg/L standard solution. From the prepared standard solution, 0.5ml, 1ml, 1.5ml, and 2.0ml were then pipetted and transferred into labelled 100ml volumetric flasks and topped to the mark using distilled water to make concentrations of 50, 100, 150, and 200 µg/L chromium respectively.

3.6 Sample digestion and metal analysis

To each of nine of ten digestion flasks, 5 ml of wastewater samples previously filtered using 11 µm Whatman filter paper was added. Into the remaining tube, 0.5 ml of certified reference material (CRM) of food supplement was pipetted. Then, 10 ml of concentrated nitric acid and 4 ml of chloric (VII) acid were added and the resultant mixture transferred to block digester, RAT2 JP SELECTOR model. The temperature was set at 200°C and the mixture heated for 2 hours. The digests were removed from the block digester and left to cool to room temperature. The cool digest were transferred to 250 ml volumetric flasks and topped up to the mark using deionized water. After calibration using the prepared standard series for cadmium, lead and chromium, the amount of heavy metal contaminants in the samples and CRM were determined using a flame atomic absorption spectrometer (Thermo Electron AAS) at 2170.0 nm, 228.8 nm and 359.4 nm for lead, cadmium and chromium respectively (Nyang'au *et al*., 2017). The results were only valid when the regression value (R^2) was greater than 0.98 and CRM parameters under study were within a deviation of ± 0.5.

3.7 Optimum coagulant determination

3.7.1 Preparation of 1mg/ml Aluminium ion (Al^{3+})

11.6694g of Aluminium hexadecahydrate sulphate ($Al_2(SO_4)_3{\bullet}16H_2O$) crystals was weighed and dissolved in 100 ml of distilled water and transferred to 1000 ml volumetric flask and topped to the mark to make 1000 ppm Al^{3+} and stored at room temperature.

3.7.2 Determination of Optimum amount of coagulant for pollution reduction

To ascertain the optimum coagulant for reduction of pollution load, six clean glass bottles containing 200 ml of effluent samples from the three sampling sites were used adding 2 ml, 4 ml, 6 ml, 8 ml, 10 ml and 12 ml of the prepared 1mg/ml aluminum ion solution into the bottles and swirled rapidly at 250 rpm using *Lab-Shaker LS-X* for 2 minutes. 15 mg of MECCAFLOC-25, anionic electrolyte, was subsequently added to all the bottles and the mixer swirled gently at 90 rpm for 10 minutes. The floc was allowed to settle for 20 minutes and the residual turbidity in each bottle was measured using *ThomasScientic 2100Q* Turbidimeter.

3.8 Preparation of adsorbent from waste tyres

Approximately 500 g of chopped tyres was soaked in 1000 ml of 1M potassium hydroxide solution for 3 hours. The soaked sample was then transferred to a porcelain crucible and placed in Muffle furnace LH 120/12 model and set to gradually attain a temperature of 700 ^{o}C. The set temperature was maintained for 2 hours. The impregnated adsorbent was left to cool to room temperature. After cooling, the final product was washed successively with three 100ml of 0.1 M hydrochloric acid and then filtered to remove excess potassium hydroxide. The acid cleaned sample was then washed severally with distilled water until the filtrate conductivity was less than 15µS/cm. The washed product was then dried in a kiln at 100 ^{o}C for 24 hours and cooled to room temperature. The sample was finally ground to a fine powder and screened with 500 micron sieve and stored in a tightly closed plastic container.

3.9 Determination of Optimum environment for residual metal contaminants adsorption

3.9.1 Optimum dosage determination

Adsorbent weights ranging between 0.1 and 0.7 g were added into seven 150 ml plastic bottles containing 100 ml of previously coagulated-flocculated and decanted wastewater solution. The bottles were closed and sonicated in SK-300 SHAKER for 2 hours at a speed of 180 rotations per minute at room temperature and filtered using 11µm Whatman filter paper. Then 5 ml of the filtrates and 0.5 ml of CRM were pipetted into 100ml digestion tubes. After adding 10 ml and 4ml concentrated nitric acid and perchloric acid respectively, the mixtures were transferred to block digester, RAT2 JP SELECTOR model. The temperature was set at 200 °C and maintained for 2 hours. The digests were removed from the block digester and left to cool to room temperature. The cool digests were transferred into a 250 ml volumetric flask and topped up to the mark using deionized water. After instrumental calibration using the prepared standard series for cadmium, lead and chromium, the residual levels of metal contaminants were quantified using a flame atomic absorption spectrometer (Thermo Electron AAS) at 2170.0 nm, 228.8nm and 359.4 nm for lead, cadmium and chromium respectively. The results were validated when the regression value (R^2) was greater than 0.98 and CRM parameters under study within a deviation of ± 0.5.

3.9.2 Optimum contact time determination

To each of six 150 ml plastic bottles containing 100 ml of coagulated-flocculated and decanted wastewater, 0.5 g of the adsorbent was added. The bottles were closed and sonicated in SK-300 SHAKER at a speed of 180 rpm at room temperature for 30, 45 60, 75,90 , 105 and 120 minutes and then filtered using 11µm Whatman filter paper. For each of the resultant filtrates, 0.5 ml of CRM and 5 ml of samples were pipetted into 100ml digestion tubes followed by addition of 10 ml and 4ml concentrated nitric acid and perchloric acid respectively. The mixtures were then transferred to block digester, RAT2 JP SELECTOR model. The temperature was set at 200°C and maintained for 2 hours. The digests were removed from the block digester and left to cool to room temperature. Each cool digests was transferred into a 250 ml volumetric flask and topped up to the mark using deionized water. After instrumental calibration using the prepared standard series for cadmium, lead and chromium, the residual metal ion levels were quantified using a flame atomic absorption spectrometer (Thermo Electron AAS) at 2170.0 nm, 228.8nm and 359.4 nm for lead, cadmium and chromium respectively. The results were only valid when the regression value (R^2) was greater than 0.98 and CRM parameters under study were within a deviation of ± 0.5.

3.9.3 Optimum pH determination

To each of eight 150 ml plastic bottles, 100 ml of coagulated-flocculated and decanted wastewater was added .The pH of the waste water in the bottles were adjusted to pH 2, 3, 4, 5, 6, 7, 8 and 9 using 0.1 M HCl and 0.1 M NaOH solutions. Then 0.5 g of the adsorbent was added to each sample. The mixtures were sonicated in SK-300 SHAKER for 2hrs hour at a speed of 180 rpm at room temperature, after which the mixtures were filtered using 11µm Whatman filter paper. Then, 5ml of the filtrate was pipetted into 100ml digestion tubes and transferred to block digester, RAT2 JP SELECTOR model, adding 10 ml and 4ml of concentrated nitric acid and perchloric acid respectively. The temperature was set at 200 °C and maintained for 2 hours. The digests were removed from the block digester and left to cool to room temperature. Each cool digest was transferred into a 250 ml volumetric flask and topped up to the mark using deionized water. After instrumental calibration using the prepared standard series for cadmium, lead and chromium, the residual levels of metal contaminants were quantified using a flame atomic absorption spectrometer (Thermo Electron AAS) at 2170.0 nm, 228.8 nm and 359.4 nm for lead, cadmium and chromium respectively. The results were only valid when the regression value (R^2) was greater than 0.98 and CRM parameters under study were within a deviation of ± 0.5.

3.10 Data analysis

The collected data were subjected to Microsoft Excel 2013 package to determine the mean, standard deviation and error bars. Using ANOVA, the means of cadmium, lead and chromium were compared to determine whether they were significantly different.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results of Wastewater physico-chemical from three paint factories

The results of the physicochemical characterization of wastewater from the selected paint factories are summarized in Table 4.1. The mean value are accompanied by standard deviations from triplicate analysis.

4.1.1 pH

The pH of the effluent samples analyzed ranged between 6.48 ± 0.14-6.89 ± 0.04 (Table 4.1) indicating slight acidity. The slight acidity could have been attributed to organic matter from paint components which when broken down by bacteria releases carbon dioxide gas which consequently reduces the pH values (Chidozie and Nwakanma, 2017). The pH values obtained were significantly different in samples ESD, EUP and EMR at 5% significance level ($p<0.05$), (Table 4.1). The values however, complied with NEMA standards of pH 6.5 - 8.5 for environmental and pH 6-9 for public sewers discharges respectively (EMCA, *200*6).

4.1.2 Temperature

The temperatures of the effluents are shown in Table 4.1. There was a significant statistical difference in temperature in the three samples analysed ($p<0.05$), (Table 4.1). When they were compared with the 3rd and 5th Schedules of EMCA regulations of 2006, were found to be compliant (EMCA, *200*6).

4.1.3 Electrical conductivity

Electrical conductivity values shown in Table 4.1 ranged between 837.33±6.66 and 881.33±8.62µS/cm with sample EUP giving the highest value of 881.33±8.62 µS/cm, followed by EMR of 869.67±10.60 and ESD having the lowest value of 837.33±6.66. The p-value obtained, ($p<0.05$) indicated a significant statistical difference in the levels of electrical conductivity in samples ESD, EUP and EMR at 5% significance level (Table 4.1).

4.1.4 Turbidity

Turbidity of the three samples ranged from 183.21 ± 0.78 NTU to 242.47 ± 1.03 NTU, with sample EMR recording the lowest while sample EUP recorded the highest value. There was a significant statistical difference in the levels of turbidity at 5% significance level ($p<0.05$),

(Table 4.1). Turbidity was attributed to high levels of suspended matter originating from paint components during manufacturing process, which consequently produced waste water of high suspended matter (Odhiambo *et al*, 2016)

4.1.5 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) determines the amount of oxygen required for oxidation of oxidisable materials in samples. During the digestion process hexavalent chromium (Cr^{6+}) in the reagent was degraded to trivalent chromium (6) in the presence of mercury sulfate which oxidizes straight aliphatic and aromatic compounds present in the samples (Tesfalem and Abdrie, 2017). There was a significant statistical difference in the levels of COD in the three samples at 5% significance level ($p<0.05$), (Table 4.1). Sample EUP recorded the highest concentration of 1881.20±24.82 mg/L while ESD had the lowest COD value; 916.77 ±28.15 mg/L (Table 4.1). Sample EUP recorded 1163.00 ±17.54 mg/L. This could be attributed to different levels binders, organic solvents, pigments and paint components employed in three different companies during paint production (Tesfalem and Abdrie, 2017). The values of COD obtained were all above NEMA set maximum limit of 50 mg/L for wastewater discharge into the environment. Sample ESD complied with maximum the 1000 mg/L limit for discharge into public sewers. The other two samples did not comply.

4.1.6 Biological Oxygen Demand (BOD)

The BOD levels from the samples obtained had statistically significant difference ($p<0.05$), ranging from 149.00±1.41 to 183.00±1.41 mg/L (Table 4.1) and indicating presence of high organic components in the paint formulation (Tesfalem and Abdrie, 2017). The BOD values obtained were higher than the recommended maximum discharge to the environment value of 30 mg/L, as shown in Table 4.1. However, the values complied with NEMA fifth schedule standard for public sewer discharge.

4.1.7 Oil and grease

Oil and grease concentrations ranged from 3525.00±17.52 to 6374.33±23.03 mg/L (Table 4.1). Sample ESD had the highest oil and grease content of 6374.33±23.03 mg/L, followed by EUP with 3525.00±17.52 mg/L and sample EMR recording the lowest value of 3525.00±17.52 mg/L. The level of oil and grease obtained had a significant statistical difference at 5% significance level ($p<0.05$), (Table 4.1). These values were quite high compared to NEMA third and fifth schedule standards (EMCA, *200*6). These high values were attributed to resins and binders used in the paint manufacturing process (Tesfalem and Abdrie, 2017).

4.1.8 Total suspended solids (TSS)

Sample ESD recorded the highest TSS value of 7395.33±364.23 mg/L while sample EUP had the lowest concentration of 6382.33±658.01mg/L as shown in Table 4.1. Sample EMR's TSS concentration was 7159.00±768.56 mg/L. NEMA limits for total suspended solids in third and fifth schedules are 30mg/L and 250 mg/L for environmental and public sewer discharges respectively (EMCA, *200*6). The p-value obtained indicated a significant statistical difference at 5% significance level ($p<0.05$), (Table 4.1). All the sample concentrations did not meet the set standards by NEMA. The paint components especially binders, additives and pigments were deemed to contribute to the high levels of TSS in the effluent samples (Chidozie and Nwakanma, 2017).

4.1.9 Total phosphorus (TP)

Samples exhibited phosphorus concentrations ranging from 145.00±3.61 to 149.32±1.22 mg/L with sample EMR having the lowest level of 145.00±3.61 mg/L and EUP producing the highest phosphorus concentration of 149.32±1.22 mg/L (Table 4.1). The obtained phosphorus values were higher than recommended by the Water Quality Regulation, 2006 which is 30.0 mg/L (EMCA, 2006). There was no statistical significance difference in the three samples in the levels of total phosphorus ($p>0.05$), (Table 4.1). The high values for phosphorus could have emanated from detergents used during cleaning of equipment and paint components (Chidozie and Nwakanma, 2017).

4.1.10 Total nitrogen (TN)

There was a significant statistical difference in the levels of total nitrogen in the three samples at 5% significance level ($p<0.05$) with sample ESD recording the highest value of 4442.67±70.47 mg/L while EUP recorded the lowest nitrogen level of 1586.67±29.14 mg/L as shown in Table 4.1. Sample EMR had 3042.67±21.39 mg/L. The high nitrogen values are attributed to high employment of organic pigments especially the derivatives of azo, Anthraquinone, phthalocyanine and binders during paint formulations, which had a direct effect on the levels of total nitrogen in the effluent produced (Chidozie and Nwakanma, 2017). However, these values were higher than set limits by the Water Quality Regulation, 2006 of 40.0 mg/L (EMCA, 2006).

4.1.11 Total Sulphur (TS)

There was no statistical significance difference ($p>0.05$) in the concentration of Sulphur across the samples with sample EMR having the lowest level of 72.62±3.11 mg/L and ESD showing highest concentration of 73.41±1.71 mg/L as in Table 4.1. EUP sulphur level was 73.29±3.77 mg/L. The high sulphur levels could be attributed to use of organic pigments especially the azo and phthalocyanine derivatives during paint manufacturing (Chidozie and Nwakanma, 2017). The recommended limit is 2mg/L, clearly indicating the sulphur levels were extremely higher than set limit (EMCA, 2006).

Table 4.1: Physico-chemical parameters in wastewater from three paint factories

Parameter	**ESD** (Mean±SD)	**EUP** (Mean±SD)	**EMR** (Mean±SD)	**P-value**	**NEMA 3rd Schedule (EMCA,2006)**	**NEMA 5th Schedule (EMCA,2006)**
pH	6.48 ± 0.14	6.89 ± 0.04	6.80 ± 0.03	0.002	6.5-8.5	6-9
Temperature (^{0}C)	28.3 ± 0.12	28.13 ± 0.15	28.07 ± 0.12	0.035	Ambient Temp. ±3	20-35
Turbidity (NTU)	195.43 ± 1.12	242.47 ± 1.03	183.21 ± 0.78	<0.0001	-	-
EC (µS/cm)	837.33±6.66	881.33±8.62	869.67±10.60	0.0021	-	-
COD (mg/L)	916.77 ±28.15	1881.20±24.82	1163.00 ±17.54	<0.0001	50	1000
BOD (mg/L)	149.00±1.41	183.00±1.41	165.00±1.41	<0.0001	30	500
Oil &grease (mg/L)	6374.33±23.03	3525.00±17.52	3525.00±17.52	<0.0001	nil	10
TSS (mg/L)	7395.33±364.23	6382.33±658.01	7159.00±768.56	<0.0001	30	250
Total Phosphorus (mg/L)	148.69±2.50	149.32±1.22	145.00±3.61	0.1863	2.0	30.0
Total nitrogen (mg/L)	4442.67±70.47	1586.67±29.14	3042.67±21.39	<0.0001	13.5	40.0
Total sulphur (mg/L)	73.41±1.71	73.29±3.77	72.62±3.11	0.9417	0.1	2.0

Table 4.2: Heavy metals levels in wastewater from paint factories

Parameter	**ESD** (Mean±SD	**EUP** (Mean±SD	**EMR** (Mean±SD	**P-value**	**NEMA 3rd Schedule (EMCA,2006)**	**NEMA 5th Schedule (EMCA,2006)**
Cadmium (Cd)	4.18±0.09	3.03±0.83	3.47±1.04	0.1761	0.1	0.5
Lead (Pb) (mg/L)	12.05±0.41	5.38±1.41	17.21±1.67	<0.0001	0.1	1.0
Chromium (Cr) mg/L	2.07±0.66	2.29±0.24	3.04±0.83	0.2183	2.0	2.0

4.2 Heavy metals

The concentrations of heavy metal contaminants from the three sampling sites are shown in Table 4.2.

4.2.1 Cadmium

The levels of cadmium in the samples ranged from 3.03±0.83 mg/L and 4.18±0.09 mg/L with sample ESD having the highest concentration of 4.18±0.09 mg/L and EUP having the lowest value of 3.03±0.83 mg/L. EMR concentration was 3.47±1.04 mg/L. Tesfalem and Abdrie (2017) observed levels of cadmium ranging from 1.58 mg/L to 69.22 mg/L. The high concentration was attributed to cadmium-containing compounds used as pigments in paint manufacturing (Pravin et al., 2011). The EMCA, 2006 limits for cadmium in the environment and public sewers discharge are 0.1 mg/L and 0.5 mg/L respectively. The values obtained for Cadmium had no statistical significance difference in the three samples analysed ($p>0.05$) and were above the recommended limits by EMCA, 2006 (Table 4.2).

4.2.2 Lead

The levels of lead in the samples ranged between 5.38±1.41 mg/L and 17.21±1.67 mg/L. Sample EMR had the highest concentration of 17.21±1.67 mg/L, ESD 12.05±0.41 mg/L and EUP 5.38 mg/L. There was a significant statistical difference in the levels of lead in the three samples at 5% significance level ($p<0.05$), (Table 4.2). Analytical results for lead in paint industries in Addis Ababa had high levels with the highest value being 53.40mg/L. The high concentration of lead was attributed to high employment of inorganic lead pigment during manufacturing (Pravin et al., 2011) and the use of lead driers. EMCA, 2006 limits for lead in the environment and public sewers discharge are 0.1 mg/L and 1.0 mg/L respectively. Therefore, the values obtained for were not compliant with set limits.

4.2.3 Chromium

Chromium concentration in the samples were found to range from 2.07±0.66 mg/L to 3.04±0.83 mg/L. Sample EMR showed the highest concentration of 3.04±0.83 mg/L while ESD was the lowest at 2.07±0.66 mg/L. EUP concentration was 2.29±0.24 mg/L. These values comparable well with 1.5 to 9.32 mg/L obtained by Tesfalem and Abdrie (2017) in their analysis of five paint industries effluents in Addis Ababa. Chromium-containing inorganic pigments are used in paint manufacture, hence the presence of chromium in the effluents (Pravin et al., 2011). EMCA, 2006 limits discharge of chromium into the environment and public sewers to maximum 2.0 mg/L.

The values obtained for Chromium had no statistical significance difference in the three samples analysed ($p>0.05$) and were above the recommended limits by EMCA, 2006 (Table 4.2).

4.3 Coagulation-Flocculation

The pollution reduction process was achieved by adding 2 ml, 4 ml, 6 ml, 8 ml, 10 ml and 12 ml of 1000 ppm aluminium ion solution to 200 ml of effluent samples. The results are presented in Table 4.3 and Figure 4.1

Table 4.3: Turbidity reduction levels using aluminum sulphate as coagulant

Volume of coagulant (ml)	ESD (NTU)	EUP(NTU)	EMR(NTU)
0	195.43±1.12	242.47±1.03	183.21±0.78
2	193.16±1.01	200.82±0.68	170.47±0.76
4	176.07±0.89	189.11±0.77	150.73±0.49
6	151.42±1.11	132.18±0.91	139.16±0.88
8	102.31±1.04	111.33±0.89	101.37±0.55
10	99.83±1.01	108.48±1.06	99.43±0.88
12	99.14±1.07	107.92±1.01	98.96±0.99

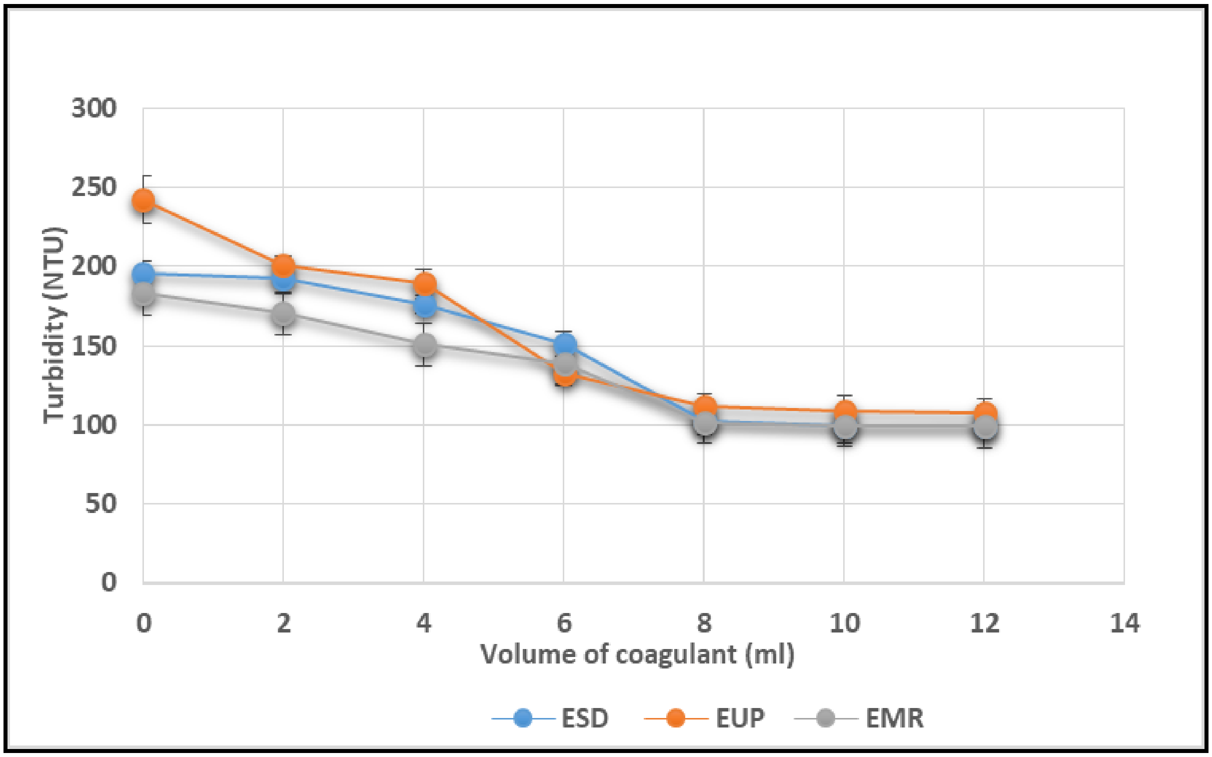

Figure 4.1: Turbidity reduction in wastewater samples using aluminum sulphate as coagulant

The results showed that there was corresponding decrease in turbidity of the wastewater with increase in the coagulant volume. The optimum volume of the coagulant was observed to be between 8ml to 10 ml for all three samples as shown in Figure 4.1. There was a turbidity reduction of 52.18%, 55.26 and 45.73 in samples ESD, EUP and EMR respectively which corresponded to 99.83±1.01 NTU, 108.48±1.06 NTU and 99.43±0.88 NTU respectively.

4.4 Optimization of adsorption conditions for the removal of residual metal contaminants.

The experiment was carried out in batches at different pH, contact time and adsorbent dosage to establish optimum adsorption condition process.

4.4.1 Adsorbent dosage

For each sample, the adsorbent dosage was varied from 0.1 % to 0.7 % (w/v). The results are given in Table A.7 (b) in Appendix A and Figures 4.2 to 4.4. From the results, it was evident that the rate of metal adsorption increased with increase in adsorbent dosage. The increase in adsorption was as a result of increase in exchangeable sites for adsorption in the activated carbon. The trend was observed until the saturation point was attained (Dimpe *et al,* 2017). Saturation point was reached when the available active sites were depleted hence no further significant adsorption could take place. The maximum desorption of cadmium was 84.93 % (ESD), 88.78 % (EUP) and 90.49 % (ESD) at the optimum dosage of 0.5 % (Figure 4.2). The optimum dosage for lead was observed at 0.5% (w/v) with the maximum removal at 79.92%, 78.81% and 83.96 % for ESD, EUP and EMR respectively (Figure 4.3). Chromium was desorbed optimally at 0.6 % (w/v) of adsorbent with 68.60 % (ESD), 77.73% (EUP) and 93.42% (ESD) as shown in Figure 4.4. These results were in agreement with those of Mousavi *et al*, (2010) who observed the optimal lead removal at 99.4 % with the required optimum dose of 2.0 g/L of waste tires ash. Similar work was performed by Dimpe *et al,* (2017) who employed waste tyre-based activated carbon and were able to remove cadmium and chromium by 87.0% and 90.0% respectively from aqueous solution, setting optimum dosage of the adsorbent at 55mg/L.

At these optimum adsorbent dosage, lead and cadmium ions were still way above set limits of 0.1mg/L for discharge into environment for both contaminants (EMCA, 2006). Chromium level at this optimum dosage in all samples complied with set limits of 2.0 mg/L for both environmental discharge and public sewers (EMCA, 2006). NEMA standard for effluent discharge into public sewers is 0.5 mg/L for cadmium (EMCA, 2006). Residual cadmium in samples coded EUP and EMR were within required limit while ESD was above the required limits for discharge into public sewers. With respect to lead, all the treated samples failed to meet the set limit for public sewers discharge of 1.0 mg/L (EMCA, 2006).

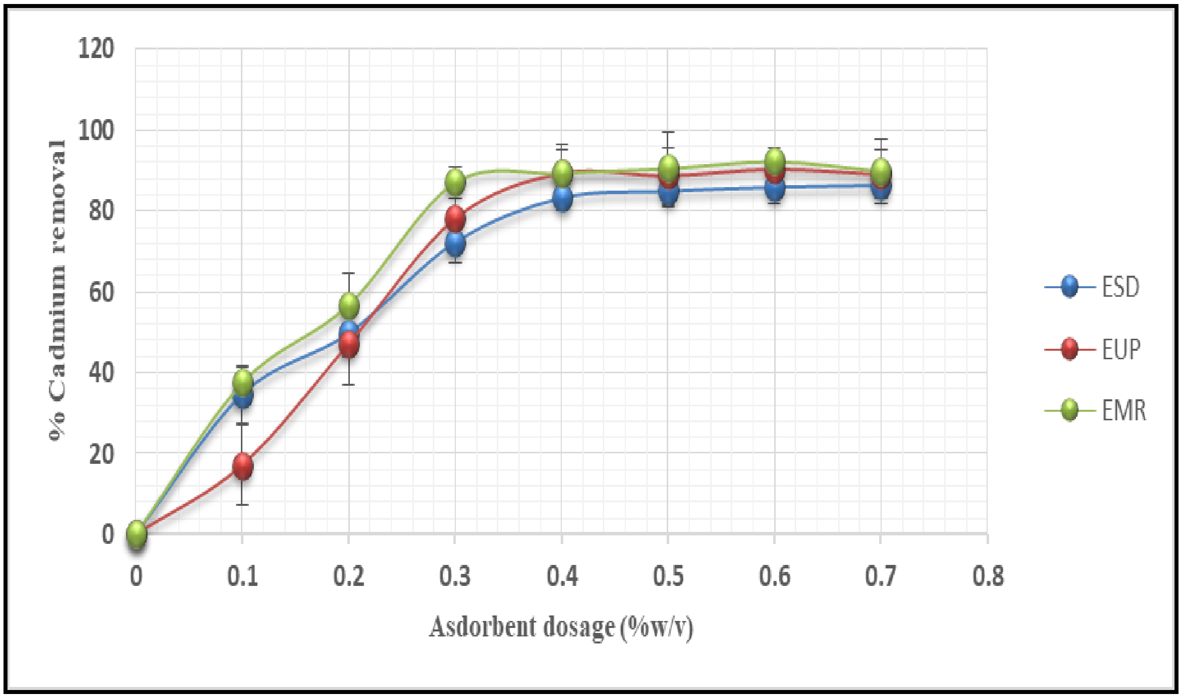

Figure 4.2: Effect of adsorbent dosage on the adsorption of Cadmium (Cd^{2+}) ion by waste tyre activated carbon.

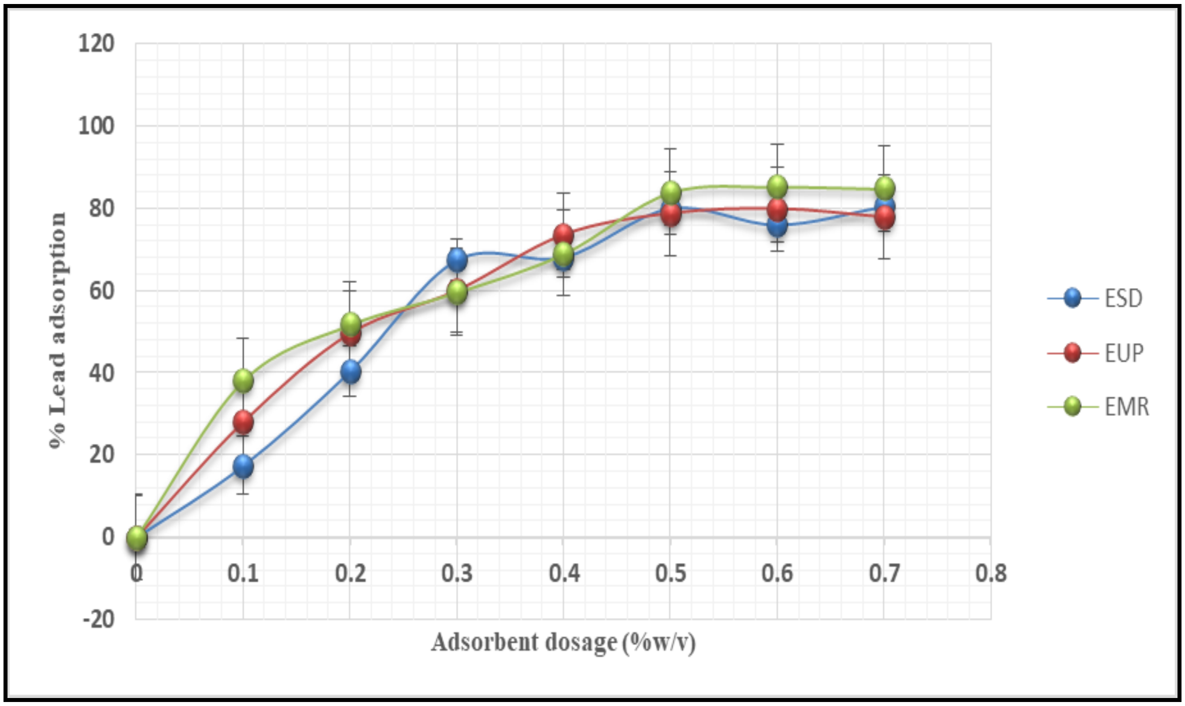

Figure 4.3: Effect of adsorbent dosage on the adsorption of Lead (Pb^{2+}) ion by waste tyre activated carbon.

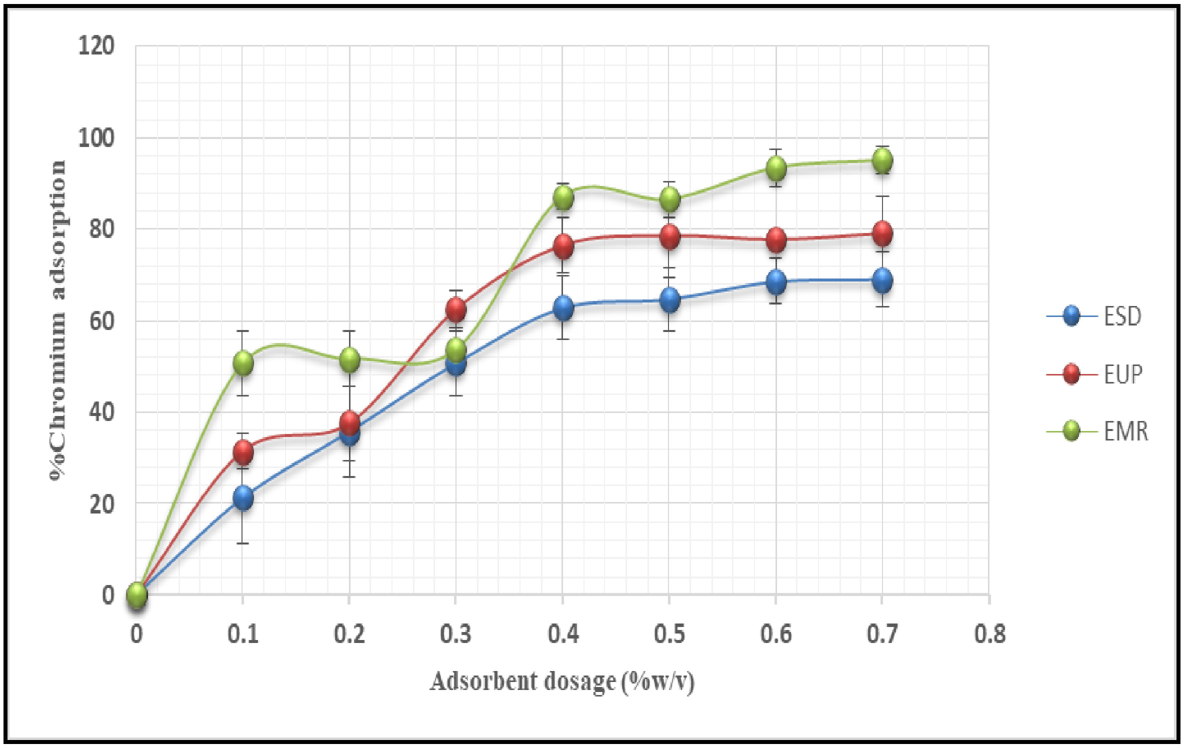

Figure 4.4: Effect of adsorbent dosage on the adsorption of Chromium (Cr^{3+}) ion by waste tyre activated carbon.

4.3.2 Contact time

In this study the contact time was varied between 30 and 120 min. The results obtained are in Table A.8 (b) in Appendix A and Figures 4.5 to 4.7. Analysis was conducted at room temperature, sonication speed being 180 rpm and initial pH of 6.48, 6.89 and 6.80 for sample codes ESD, EUP and EMR respectively. It was noted that the contaminants removal increased with increase in contact time. This was necessitated by the availability of adsorption sites and significant mass transfer driving force, although this is slowed down as the process approaches equilibrium due to increase in the clogging of the active sites which slows down the movement of adsorbate (Nurulhuda *et al.*, 2009). The percentage cadmium uptake from the aqueous solution was observed at 81.60% (ESD), 90.10% EUP and 85.88 % EMR at equilibrium (Figure 4.5). This was up from 44.02 %, 23.76 %and 43.80 % for ESD, EUP and EMR respectively. The optimum contact time was observed at 90 minutes with no significant adsorption of the contaminant. The first 30 minutes of the adsorption process, lead ion removal was 29.46% (ESD), 37.55% (EUP) and 47.24% (EMR). At equilibrium; 105 minutes, it was observed that the percentage uptake increased to 94.52% (ESD), 81.60 % (EUP) and 97.62% (EMR) with no further significant adsorption (Figure 4.6). Maximum adsorption of chromium was noted at 105 minutes representing 64.25 % (ESD), 65.50% (EUP) and 74.67% (EMR) (Figure 4.7). Mousavi *et al*, (2010) conducted similar study noted that equilibrium for lead uptake was at 90 minutes with a corresponding lead removal of 100.0%. Optimum contact time of 60 minutes was noted in Dimpe *et al*, (2017) study. At the observed equilibrium time, cadmium ions uptake was 79.0%. In Onoja *et al*, (2017) study, chromium ion was adsorbed maximumly at 120 minutes to give a percentage removal of 92.45 %.

At the optimum contact time, lead and cadmium ions were above the set limit of 0.1mg/L for discharge into environment for both contaminants in all the samples (EMCA, 2006). Chromium level at the optimum dosage in all samples was within the set limits of 2.0mg/L for both discharge into environmental and public sewers (EMCA, 2006). NEMA effluent discharge standard into public sewers is 0.5 mg/L for cadmium. Residual cadmium in samples obtained in EUP and EMR were within the required limits. Sample ESD did not meet the requirement. Both samples EUP and EMR failed to meet the set limit of 1.0 mg/L for lead, while sample ESD was within the required limit.

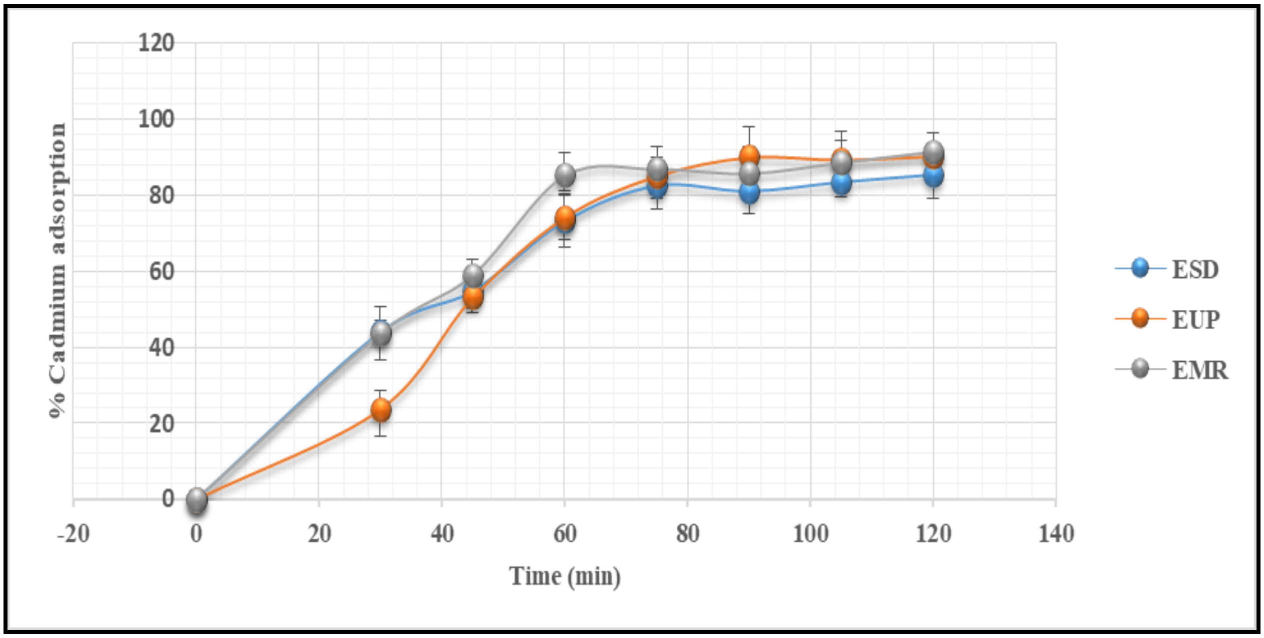

Figure 4.5: Effect of contact time on the adsorption of Cadmium (Cd^{2+}) ion by waste tyre activated carbon.

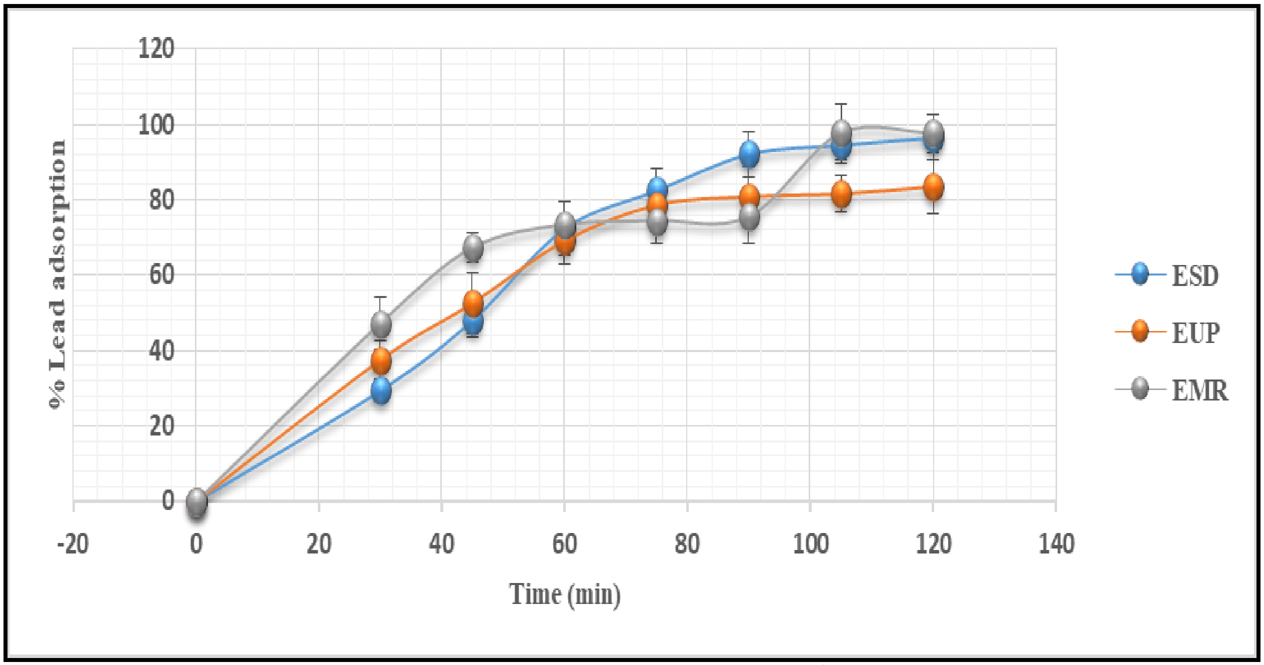

Figure 4.6: Effect of contact time on the adsorption of Lead (Pb^{2+}) ion by waste tyre activated carbon.

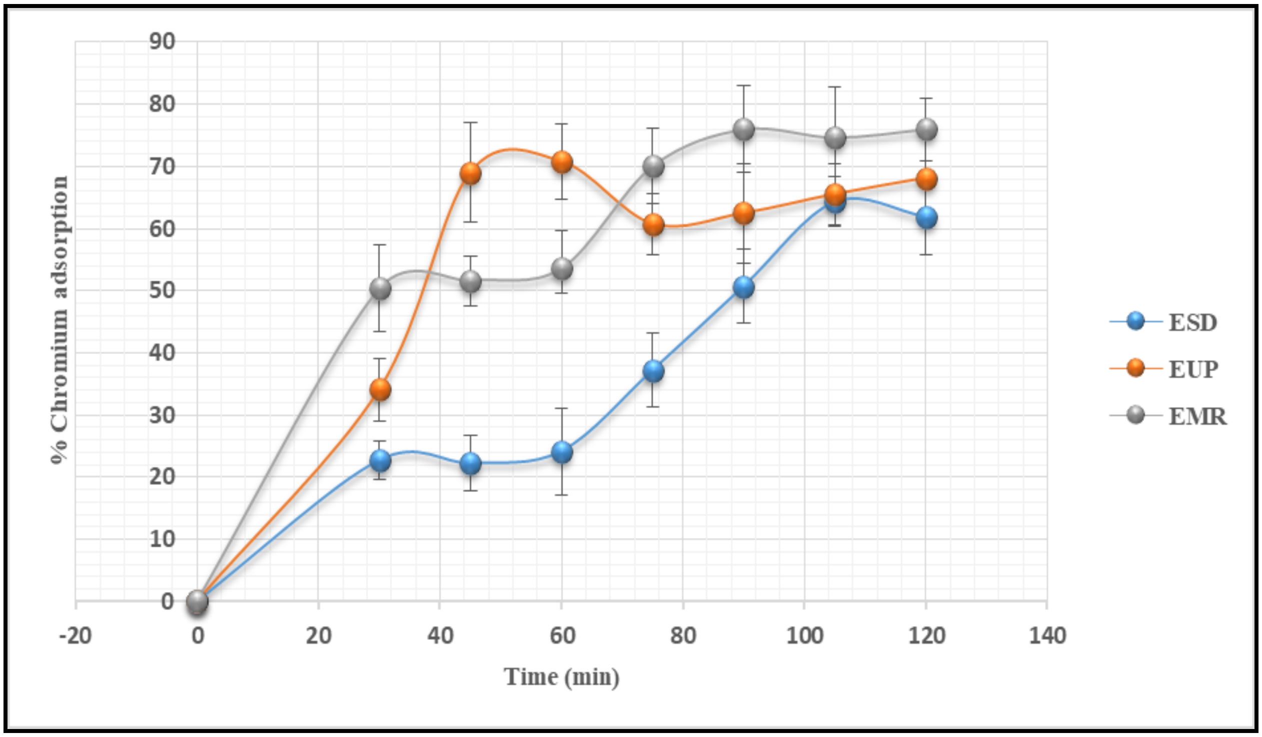

Figure 4.7: Effect of contact time on the adsorption of Chromium (Cr^{3+}) ion by waste tyre activated carbon.

4.3.3 pH range

The study was conducted between pH 2 and 9. The results are shown in Table A.9 (b) in Appendix A and Figures 4.8 to 4.10. From the results, it was noted that metal ions uptake increased as pH increased due to reduction in the net competition between hydronium ion and the metal ion concentration (Onoja *et al*, 2017). The adsorbent surface is deprotonated and hence negatively charged and this escalates electrostatic attraction of the adsorbate (Lohani *et al*., 2008). There was remarkable increase in cadmium (Figure 4.8) and lead (Figure 4.9) removal as the solution pH was increased from 2 to 9. However for chromium, when pH was increased above 6, there was a sudden incline in adsorption (Figure 4.10). This may have been attributed to the fact that the covalent coordination existing between Cr^{3+} ions and functional groups existing on the surface are weak in basic environment (Attia *et al.*, 2010). The weak bond is due to competition for active sites by both chromate and hydroxyl anions hence reduction in the adsorption (Salam *et al.,* 2011). At pH 4, cadmium uptake was observed to be 74.16% (ESD), 81.19 % (EUP) and 86.74% (EMR) and increased to optimum pH of 6 with the corresponding percentage removal being 84.21 %, 89.77% and 90.20 % for ESD, EUP and EMR respectively (Figure 4.8). There was no significant adsorption in pH above 6. It was noted that lead adsorption increased to optimum at pH 5 (Figure 4.9). At this optimum pH, the lead ion removal percentage was 86.64 % (ESD), 79.55% and 80.88% (EMR). Maximum chromium ion adsorption was observed at pH 6, representing 73.91 % (ESD), 91.27% (EUP) and 84.87% (EMR). Desorption was observed thereafter with increased pH beyond 6, because of the formation of metal hydroxides (Figure 4.10). In the work of Mousavi *et al*, (2010), maximum lead removal was observed at pH 6 representing removal percentage of 93.1%. Maximum adsorption for cadmium and chromium was observed at pH 7 in the work of Onoja *et al,* (2017). From their study, it was evident that the metal ions uptake increased steadily in the pH range 3 to 7. At equilibrium pH 7, the maximum adsorption was achieved for cadmium and chromium with a percentage removal of 85.06% and 92.45 % respectively.

At the optimum pH values in this study, lead and cadmium ions did not meet the set limit of 0.1mg/L for discharge into environment for both contaminants in all the samples (EMCA, 2006). Chromium level at this optimum dosage in all samples was within the set limits of 2.0mg/L for both environmental and public sewers discharge. Effluent discharge standard by NEMA into public sewers is 0.5 mg/L for cadmium (Table 4.2). In samples EUP and EMR, cadmium level was within the set limit for discharge. Sample ESD did not meet the required limits. All the three samples did not meet the set limits of 1.0 mg/L for lead.

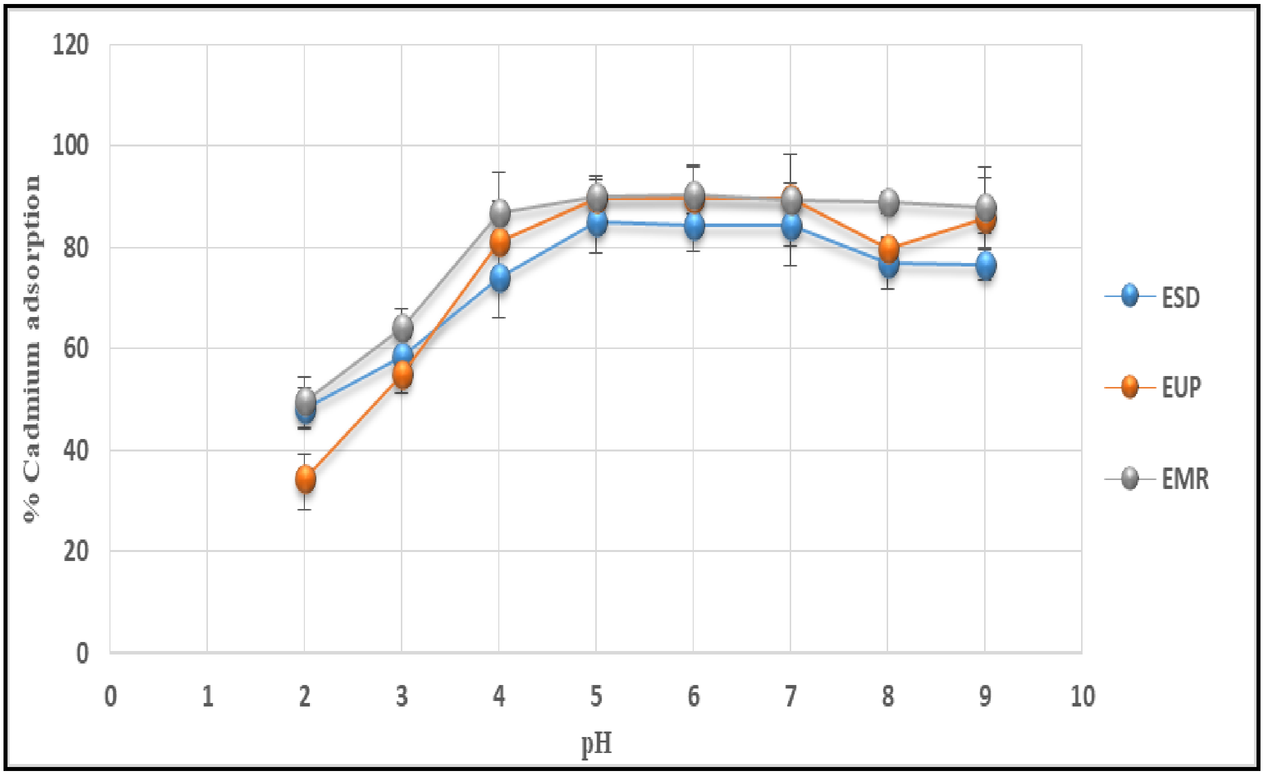

Figure 4.8: Effect of pH on the adsorption of Cadmium (Cd^{2+}) ion by waste tyre activated carbon.

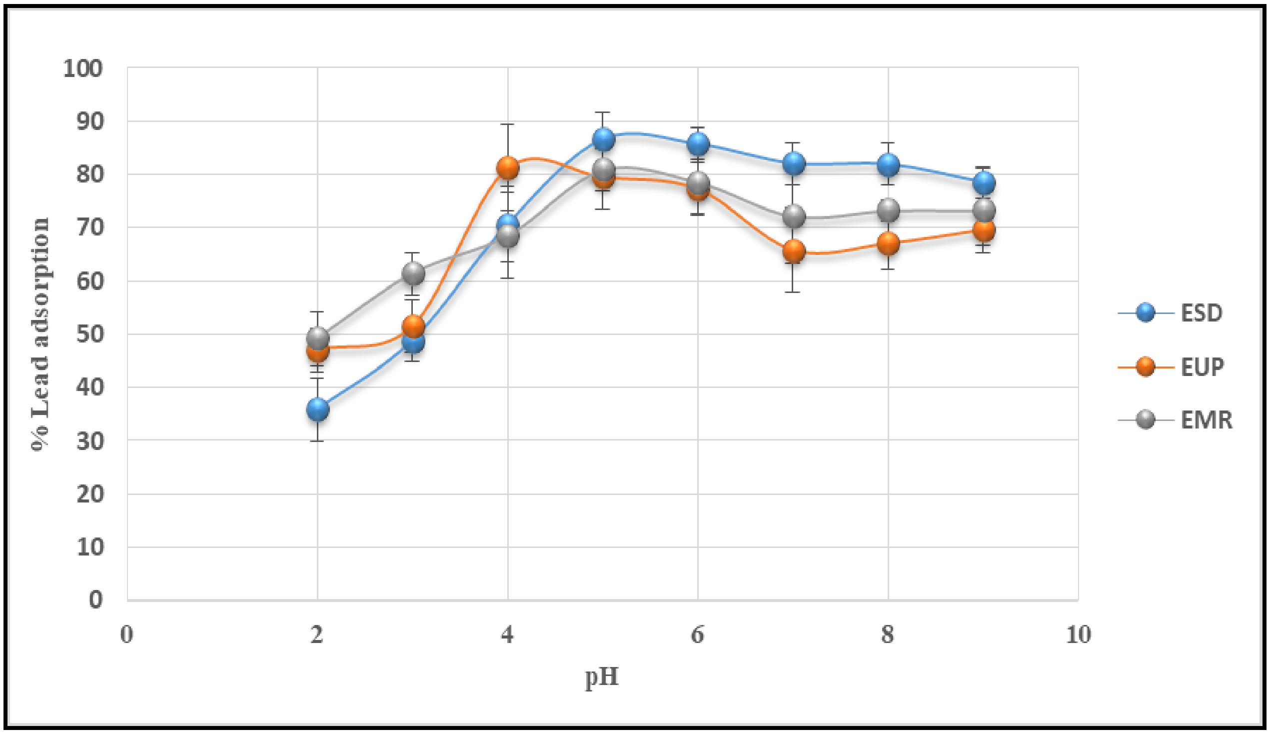

Figure 4.9: Effect of pH on the adsorption of Lead (Pb^{2+}) ion by waste tyre activated carbon.

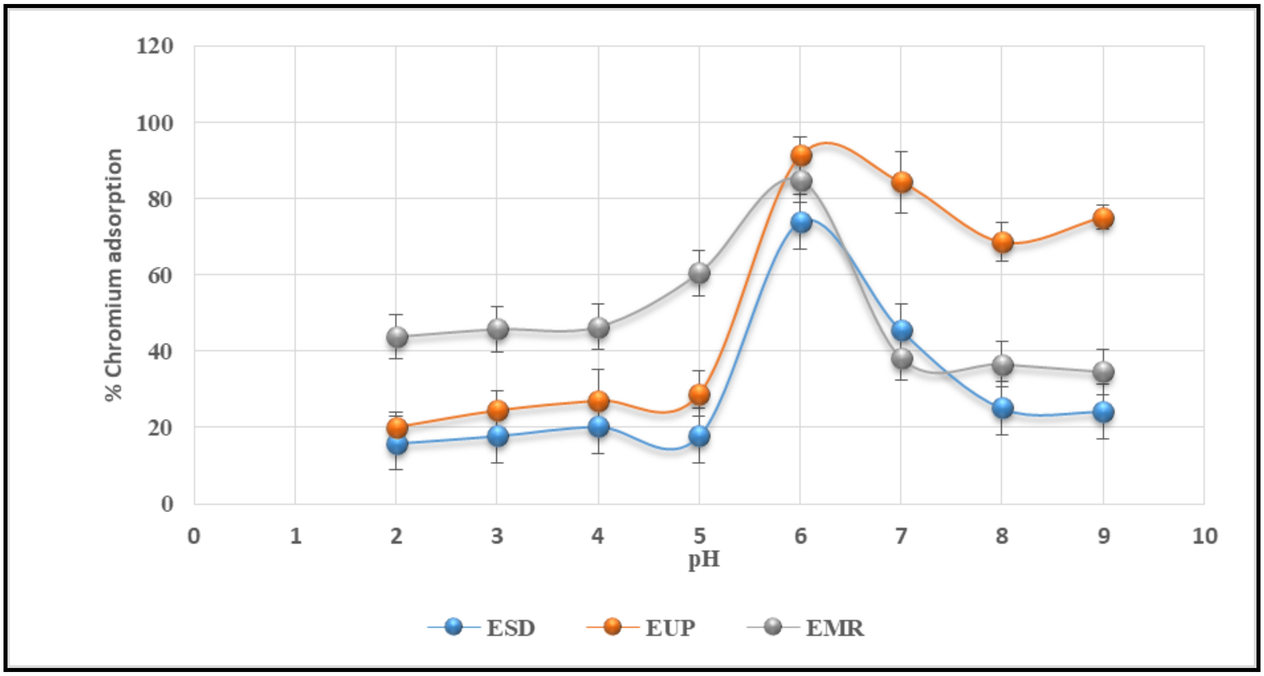

Figure 4.10: Effect of pH on the adsorption of Chromium (Cr^{3+}) ion by waste tyre activated carbon.

4.4 Adsorption Isotherm

In order to understand the adsorption equilibria between adsorbate and the adsorbent, Langmuir and Freundlich isotherms were used.

4.4.1 Langmuir isotherm

The plots of C_a / X_e against C_a gave straight lines with intercept $^1/Q_mL_c$ and slope of $^1/Q_m$ for all the samples as shown in Figures 4.11 to 4.13. Langmuir equations (y = 7.8913x - 2.8213, y = 2.3705x - 0.5434 and y = 0.5216x + 0.6306) in Figure 4.11, (y = 92.609x - 86.333, y = 8.7653x - 16.518 and y = 0.407x + 0.3748) in Figure 4.12 and (y = 34.288x - 12.309, y =15.865x - 2.0621 and y = 1.0325x + 2.028) in Figure 4.13, were used to calculate Langmuir isotherm constants. Adsorption capacity, Q_m, and regression value for the equations are presented in Table 4.4. Sample EMR recorded the highest value of regression R^2 of 0.9621 for cadmium (Figure 4.11) while sample ESD and EUP recorded 0.8607 and 0.8731 respectively (Figure 4.12). The corresponding mono layer adsorption capacities were 1.9172mg/g, 0.1267mg/g and 0.4219mg/g for ESD, EUP and EMR respectively (Table A10). Adsorption capacity for lead ion in the samples were for ESD (0.4914mg/g), EUP (0.0108mg/g) and EMR (0.1141mg/g) with respective regression of 0.9144, 0.9221 and 0.9437. Chromium adsorption recorded the highest adsorption capacity of 0.9685 mg/g with the corresponding lowest regression of 0.6634 for sample ESD. Samples EUP and EMR recorded regression of 0.9724 and 0.9952 with the corresponding adsorption capacities of 0.0292mg/g and 0.063mg/g. The higher regression values for all metal ions at equilibrium demonstrated that the adsorption for the contaminants fitted well into Langmuir isotherm.

Table 4.4: Langmuir isotherm values

Heavy metal contaminant	**Laboratory sample code**	**$1/Q_m$**	**Q_m (mg/g)**	**$1/(Q_m.L_c)$**	**$(Q_m.L_c)$**	**L_c (L/mg)**	**R^2**
Cadmium	**ESD**	0.5216	1.9172	0.6306	1.5858	0.8271	0.8607
	EUP	7.8913	0.1267	-2.8213	-0.3544	-2.7970	0.8731
	EMR	2.3705	0.4219	-0.5434	-1.8403	-4.3623	0.9621
Lead	**ESD**	2.0348	0.4914	1.8738	0.534	1.0859	0.9144
	EUP	92.609	0.0108	-86.333	-0.012	-1.0727	0.9221
	EMR	8.7653	0.1141	-16.518	-0.061	-0.5307	0.9437
Chromium	**ESD**	1.0325	0.9685	2.028	0.4931	0.5091	0.6634
	EUP	34.288	0.0292	-12.309	-0.0812	-2.7856	0.9724
	EMR	15.865	0.0630	2.0621	0.4849	7.6936	0.9952

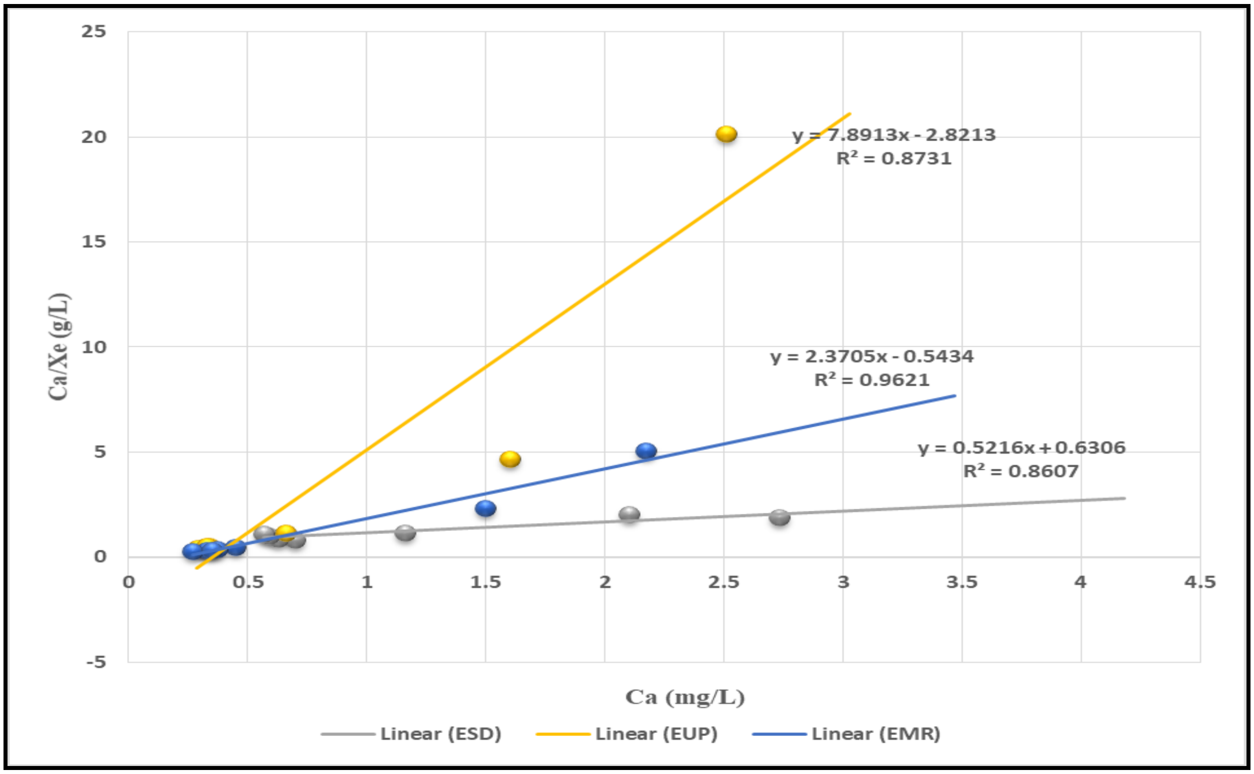

Figure 4.11 :A plot of *Ca /Xe* against *Ca* for Cadmium ion using Langmuir isotherm

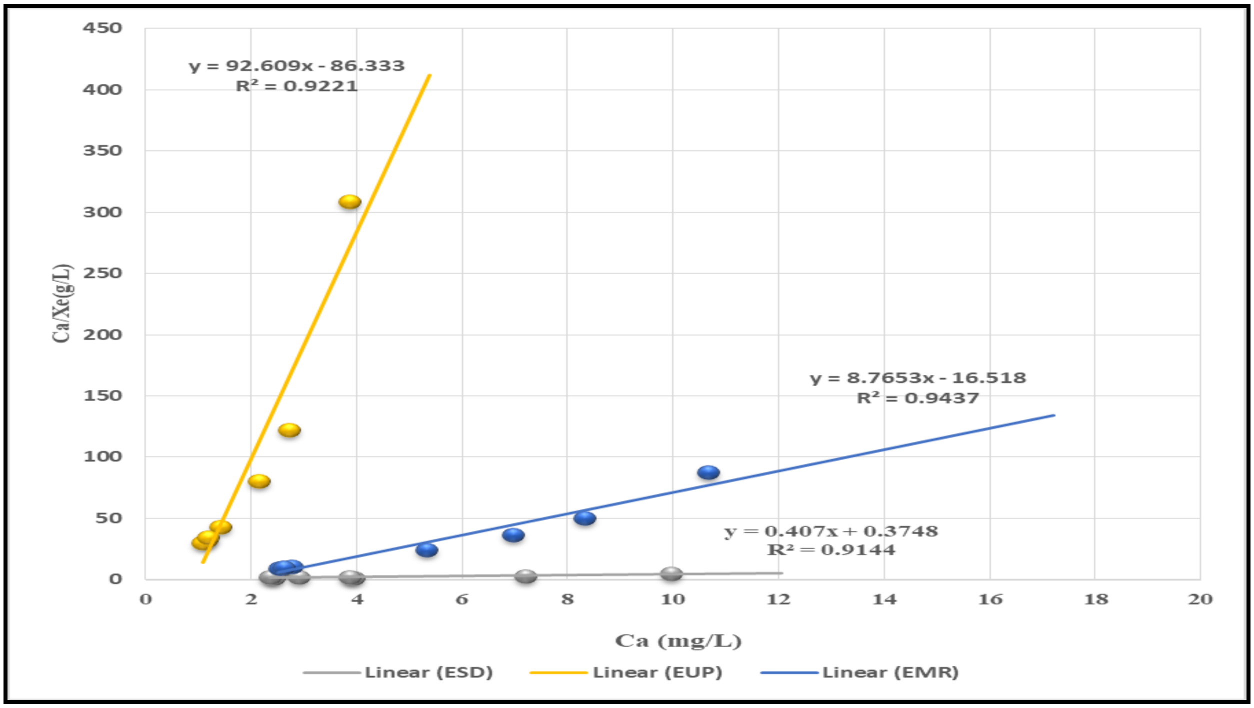

Figure 4.12: A plot of *Ca /Xe* against *Ca* for Lead ion using Langmuir isotherm

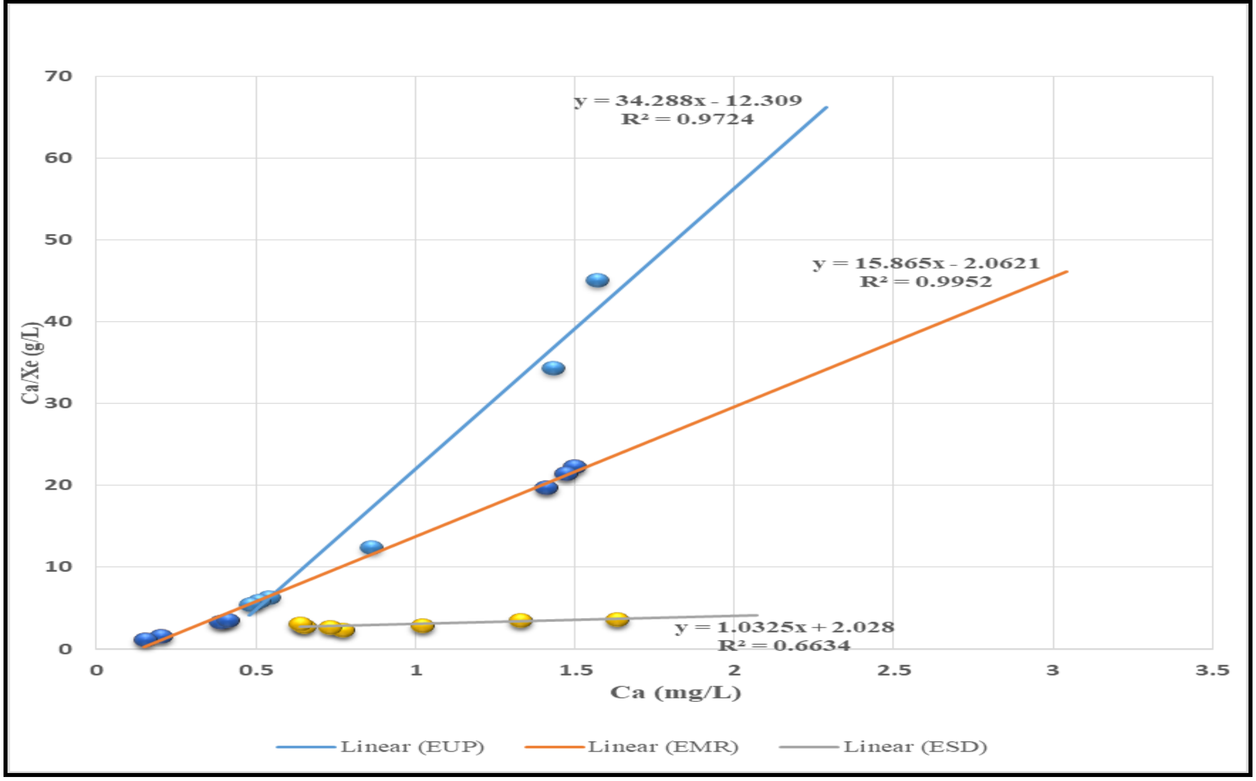

Figure 4.13: A plot of *Ca /Xe* against *Ca* for Chromium ion using Langmuir isotherm

4.4.2 Freundlich isotherm

A graph of log *Xe* against log C_a gave a straight line with slope of $^1/n$ and intercept $K_{f.}$ as shown in Figures 4.14 to 4.16. Freundlich isotherm constants n and K_f which denotes adsorption intensity and capacity respectively were calculated using Freundlich equations (-1.3011x - 3.2655, y = -0.5682x - 0.9426 and y = 1.6496x + 1.7757) in Figure 4.14, (y = -1.2331x - 1.6939, y = 1.8855x - 0.6033 and y = 1.3307x + 0.2158) in Figure 4.15 and (y = -1.3053x - 1.6689, y = -3.1763x - 3.5124 and y = 1.2538x + 0.6075) in Figure 4.16 and presented in Table 4.5. When $1<n<10$, it manifests a remarkable adsorption of adsorbate (Okafor *et al.*, 2015). In addition, as K_f value increases, the intensity of adsorption also increases and vice versa (Moreno-Pirajan and Giraldo, 2012). The results showed that values of n for cadmium ranged from -1.7599 to 0.6062 across the samples while for lead the value ranged from -0.8110 to 0.7515. Chromium adsorption rate was also unremarkable giving n values of between -0.7661 to 0.7976. All the samples showed low K_f values signifying low intensity of heavy metal ion uptake. From the values of n and K_f it was noted that adsorption of cadmium, lead and chromium ions from aqueous phase did not fit into Freundlich model (Figure 4.14, Figure 4.15 and Figure 4.16 respectively)

Table 4.5: Freundlich isotherm values

Heavy metal contaminant	**Laboratory sample code**	**$^1/n$**	**n**	**K_f**	**R^2**
Cadmium	**ESD**	1.6496	0.6062	1.7757	0.8208
	EUP	-1.3011	-0.7686	-3.2655	0.8468
	EMR	-0.5682	-1.7599	-0.9426	0.6694
Lead	**ESD**	1.3307	0.7515	0.2158	0.3339
	EUP	-1.2331	-0.8110	-1.6939	0.9079
	EMR	-1.8855	-0.5304	-0.6033	0.9164
Chromium	**ESD**	1.2538	0.7976	0.6075	0.8462
	EUP	-1.3053	-0.7661	-1.6689	0.9619
	EMR	-3.1763	-0.3148	-3.5124	0.9357

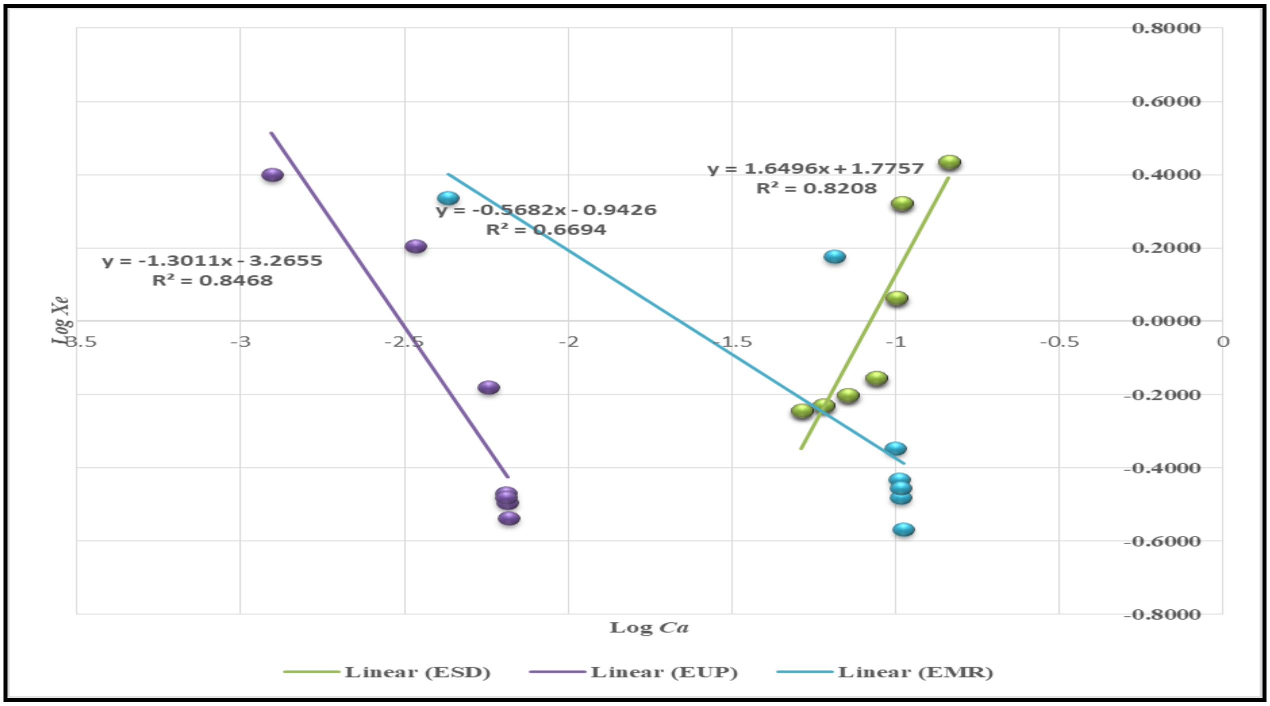

Figure 4.14: A plot of log X_e against log C_a for Cadmium using Freundlich isotherm

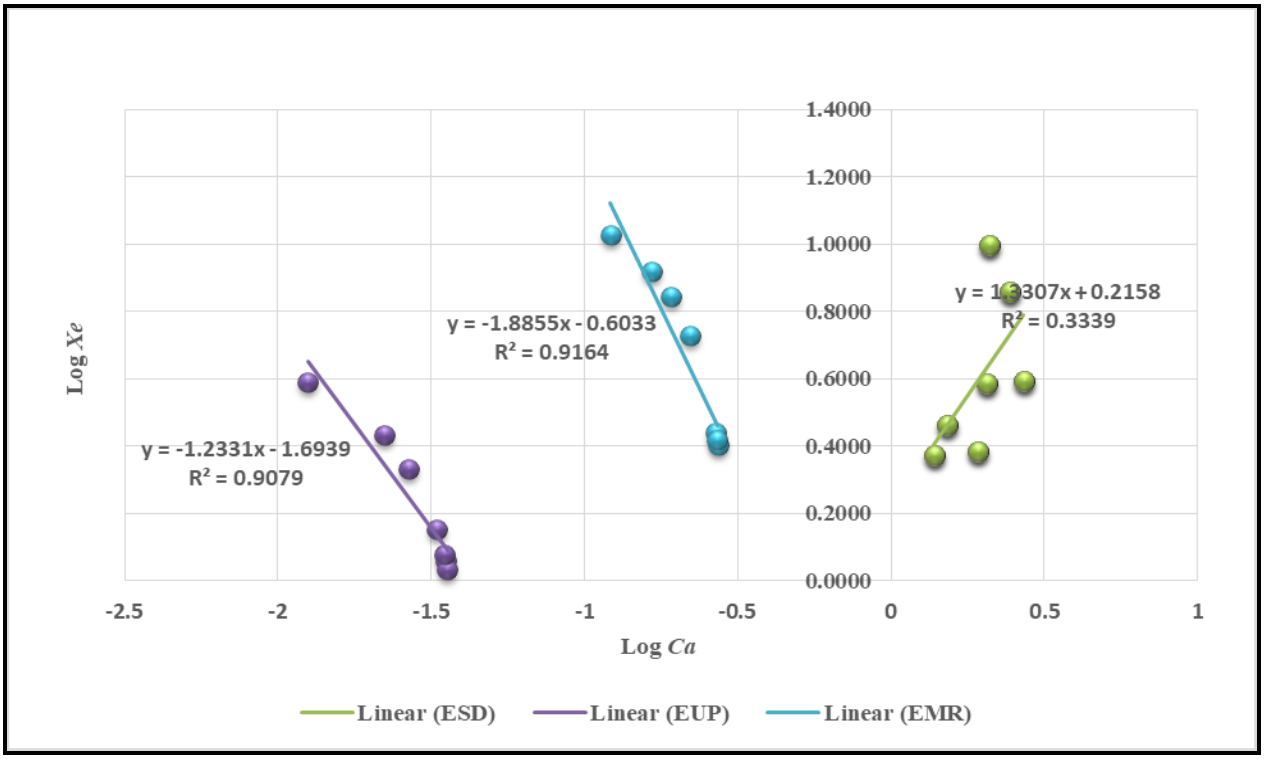

Figure 4.15: A plot of log Xe against log Ca for Lead using Freundlich isotherm

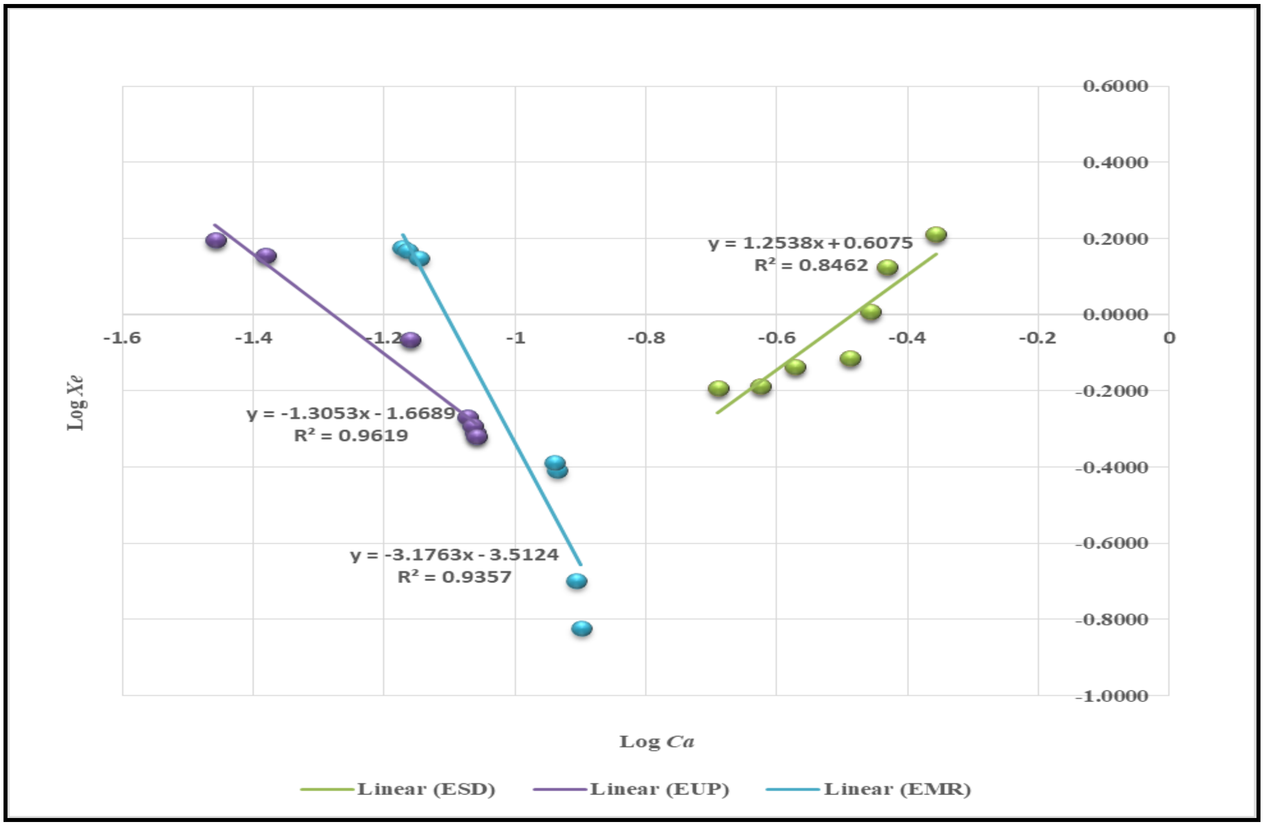

Figure 4:16: A plot of log Xe against log Ca for Chromium using Freundlich isotherm

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the results of physical, chemical and heavy metal analysis, apart from pH and temperature, most of the parameters studied were found to be higher than the maximum recommended limits set by the Environmental Management and Coordination Act of 2006 for discharge into public sewers and the environment (EMCA, 2006). These parameters namely TSS, BOD, COD, Total Nitrogen, Total Phosphorus, oil and grease, Sulphur (Table 4.1) and heavy metals; cadmium, lead and chromium (Table 4.2) were above the permissible limits set by the Act (EMCA, 2006). These high levels of inorganic and organic contaminants in the effluents, are likely to raise the respective levels in the public sewers into which the effluents are drained into, consequently degrading the environment and human health.

There was effective pollution reduction in the coagulation-flocculation process with the use of between 8-10 mg of Al^{3+} ion in 200ml wastewater (Table 4.3). The pollution reduction was manifested in the reduction of turbidity to between 99.43±0.88 and 108.48±1.06 NTU for all three samples representing a reduction of 45.73- 55.26 % (Figure 4.1)

From the batch adsorption study, it was clearly shown that activated carbon made from waste tyres was an effective adsorbent in the removal of Chromium (Figure 4.2), Lead (Figure 4.3) and Cadmium (Figure 4.4) from paint effluent though not to the level that meets the standard set by EMCA act of 2006. Furthermore, it showed that waste tyres which are readily available can be transformed into a useful water and effluent treatment material hence a low cost way of up taking metal ions from industrial effluents.

The batch adsorption experiment was dependent on the contact time, pH and adsorbent dosage. The optimum conditions of adsorption of metal ions was found to be pH range 5-6, adsorbent dosage of 0.5-0.6 % (w/v) and contact time of 90-105 minutes across all the metal ions. The adsorption isotherm studies indicated that Langmuir model fitted well with analytical values obtained for heavy metal ions in this study as manifested by the relatively high regression values (R^2) calculated from Langmuir isotherm equation. Furthermore, Freundlich constants values for n and K_f did not favour the cadmium, lead and chromium metal ion uptake at equilibrium since all the values obtained for n were not in the range of $1<n<10$. The K_f values were quite low signifying less intensity in the adsorption of the adsorbates.

5.2 Recommendation

The recommendations from this study are:

1. More studies should be done to characterize the effluents from treated waste waters from other paint industries within Nairobi and nearby towns such as Thika and Machakos to establish whether they meet NEMA discharge limits. This would help bodies concerned with making and enforcing policy to profile effluents from paint industries.
2. A study should be conducted to characterize and optimize the prepared activated carbon. This will involve determining its specific surface area, pore size and volume, ash content and volatile matter. Other activating methods should be studied to establish the surface features and conditions to be employed to increase the adsorbent efficacy, optimize adsorption capacity for the removal of metallic and organic contaminants from effluents.
3. The feasibility of use of adsorption technology in waste treatment by local industries that discharge metal contaminants in water bodies should be studied. .

REFERENCES

Abd El-Gawad, H. S. (2014). Oil and Grease Removal from Industrial Wastewater Using New Utility Approach. *Journal of advances in Environmental Chemistry,* **204**, 1-6.

Abdelkreem, M. (2013). Adsorption of phenol from industrial wastewater using olive mill waste, *APCBEE Procedia*, **5**, 349-357.

Abdel-Shafy, H., (2017). Membrane Technology for Water and Wastewater Management and Application in Egypt. *Egyptian Journal of Chemistry,* **60** (3), 347-360.

Acevedo, B., and Barriocanal, C., (2015). Texture and surface chemistry of activated carbons obtained from tyre wastes. *Fuel Process Technology,* **134**, 275–283.

Adeleken, B. and Abegunde, K. (2011). Heavy metal contamination of soil and ground water at automobile mechanic village in Ibadan, Nigeria. *International Journal of the Physical Sciences,* **6**, 1045-1058.

Adewole, M.B., Sridhar, M.K.C., and Adeoye, G.O., (2010). Removal of Heavy Metals from Soil polluted with effluents from a Paint Industry Using Helianthus annuus L. and Tithonia diversifolia (Hemsl.) as influenced by fertilizer applications. *Bioremediation Journal,* **14** (4), 169-179.

Ahmed, T., Bhatti, Z.A., Maqbool, F., Mahmood, Q., Faridullah, S., (2016). A comparative study of synthetic and natural coagulants for silver nanoparticles removal from wastewater. *Journal of Desalination and Water Treatment* **57**, 18718-18723.

Akpor, O., and Muchie, M., (2010). Remediation of heavy metals in drinking water and wastewater treatment systems: processes and application .*Journal of Physical Science* **5**, 1807–1817.

Akunwa, N.K., Muhammad, M.N., Akunna, J.C., (2014). Treatment of metal-contaminated wastewater: A comparison of low-cost bio sorbents. *Journal of Environmental Management*, **146,** 517 – 523.

Albertson, T.E., Kelly, P.O., Mark, E. S. and Andrew, L.C., (2011). Gastrointestinal decontamination in the acutely poisoned patient. *International Journal of Emergency Medicine* **4** (1), 65.

Altenor, S., Carene-Melane, B. & Gaspard, S., (2009). Activated carbons from lignocellulosic waste materials for water treatment: a review. *International Journal of Environmental Technology and Management,* **10** (3), 308-326.

Anfruns, A., Canals-Batlle, C., Ros, A., Lillo-Ródenas, M., Linares-Solano, A., (2009). Removal of odour-causing compounds using carbonaceous adsorbents/catalysts prepared from sewage sludge. *Journal of Water Science and Technology*, **59**, 1371–1376.

Aravindhan, R., Rao, J.R. and Nair, B.U., (2009). Application of a chemically modified green macro alga as a biosorbent for phenol removal, *Journal of Environmental Management*, **90**, 1877-1883.

Arslankaya, S., and Çalık, G., (2016). Optimization of the production process of trial tyres at tyre producing company with the simulation technique. *Procedia-Social and Behavioral Sciences*, **229**, 88-95.

Attia, A. A., Khedr, S. A., and Elkholy, S. A., (2010). Adsorption of chromium ion (VI) by acid activated carbon. *Brazilian Journal of Chemical Engineering,* **27,** (01)**,** 183 – 193**.**

Aziz, H.A., Adlan, M.N., and Ariffin, K.S., (2008). Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III) removal from water in Malaysia: post treatment by high quality limestone. *Journal of Bioresource Technology,* **99**, 1578–1583.

Barakat, M.A., (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry* **4**, 361–377.

Barbosa, B., Pereira, M.T., Silva, F. J. G., and Campilho, R. D. S. G., (2017). Solving quality problems in tyre production preparation process: a practical approach. *Procedia Manufacturing,* **11**, 1239 – 1246.

Bazrafshan, E., Amirian, P., Mahvi, A.H., Ansari-Moghaddam, A., (2016). Application of Adsorption process for phenolic compounds removal from aqueous environments: A Systematic Review. *Global NEST Journal*, **18**, (1), 146-163.

Bazrafshan, E., Zarei, A.A., Nadi, H. and Zazouli, M.A. (2014). Adsorptive removal of Methyl Orange and Reactive Red 198 dyes by Moringa peregrine ash. *Indian Journal of Chemical Technology*, **21**, 105-113.

Belgacem, A., Belmedani, M., Rebiai, R., and Hadoun, H., (2013). Characterization, analysis and comparison of activated carbons issued from the cryogenic and ambient grinding of used tyres. *Chemical Engineering Transactions,* **32**, 1705–1710.

Bello, M.M., Raman, A.A., and Purushothaman, M., (2017). Applications of fluidized bed reactors in wastewater treatment -A review of the major design and operational parameters. *Journal of Cleaner Production,* **141**, 1492-1514.

Ben-Chioma, A.E., Jack, A.S., Philip-Okere, G.K., (2015**).** A Comparative Study on the Measurement of pH of Water, Using pH meter and Water Testing Kit (Testube Method) In Port Harcourt, **1** (3),1-5.

Benard, E., Jimoh, A. and Odigure, J.O., (2013) Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell. *Research Journal of Chemical Sciences,* **3** (8), 3- 9.

Betzy, N.T., and Soney, C.G., (2015). Production of Activated Carbon from Natural Sources. *IMed Pub Journals,* **1** (1), 1-7.

Bodziak, W., (2008). Tyre Tread and Tyre Track Evidence: Recovery and Forensic Examination Practical Aspects of criminal and forensic investigations. CRC Press, 90.

Bolden, J., Abu-Labdeh, T., and Fini, E., (2013). Utilization and recycled and waste materials in various construction applications. *American Journal of Environmental Science*, **9** (1), 14-24.

Bounda, A., Kumar, S., Yana, S., and Koyan, F., (2011). Tyre manufacturing process. Seminar report.

Bridgewater, A.V., (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy Journal,* **38**, 68–94.

Cao, X., Ro, K.S., Chappell, M., Li, Y., and Mao, J., (2011). Chemical structures of swine-manure chars produced under different carbonization conditions investigated by advanced solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. *Journal of Energy Fuels*, **25**, 388–397.

Chan, O. S., Cheung, W. H., and McKay, G., (2012). Single and multicomponent acid dye adsorption equilibrium studies on tyre demineralized activated carbon. *Chemical Engineering Journal*, **191**, 162–170.

Chidozie, K., and Nwakanwa, C., (2017). Assessment of Saclux Paint industrial Effluents on Nkoho River in Abia state, Nigeria. *Journal of Ecosystem and Ecography* **7** (2), 1-6.

Chowdhury, Z., Zain, S., Rashid, A., Rafique, R., and Khalid, K., (2013). Breakthrough curve analysis for column dynamics sorption of Mn (II) ions from wastewater by using Mangos tana garcinia peel-based granular-activated carbon. *Journal of Chemistry***,** **3**, 71-79.

Danyuo, Y., Arthur, E.K., Azeko, S.T., Obayemi, J.D and Asuo, I. M., (2014). Design of Locally Produced Activated Carbon Filter from Agricultural Waste for Water Purification. *International Journal of Engineering Research & Technology*, **3** (6), 531-540.

Daud, W.M.A.W., and Houshamand, A.H., (2010). Textural characteristics, surface chemistry and oxidation of activated carbon. *Journal of National Gas Chemistry* **19**, 267–279.

Demirbas, A., (2008). Heavy metal adsorption onto agro-based waste materials: A review. *Journal of Hazardous Materials* **157**, 220-229.

Dimpe, K.M., Ngila, J.K. Nomngongo, P.N., Wei, X. (2017) Application of waste tyre-based activated carbon for the removal of heavy metals in wastewater, *Cogent Engineering*, 4:1

Ebrahimpor, M., Hassan, M., Jahanshahi, S.M., and Najafpour, G. (2009). Nanotechnology in process biotechnology: Recovery and Purification of Nano particulate byproducts using expanded bed adsorption. *Dynamic Biochemistry, Process Biotechnology and Molecular Biology* **3** (2), 57-60.

Environmental Management and Coordination Act, EMCA, (2006). *Kenya Gazette*. Government Printers, Nairobi, Kenya.

Environmental Protection Agency-U.S (EPA)-*Scrap Tires Common Wastes & Materials* (2012). Retrieved May 12, 2018.

Eriksson, T., and Kiros, Y., (2014). Temperature swing adsorption device for Oxygen enriched air. *Journal of Cleaner Production,***76**, 174 -179.

Facchin, S., Alves, P. D. D., Tatiana, J´unia, M.N. V. and Evanguedes, K., (2013) Biodiversity and secretion of enzymes with potential utility in wastewater treatment. *Journal of Ecology* **3** (1), 34–47.

Fathy, N.A., El-Wakeel, S.T., Abd El-Latif, R.R. (2015). Biosorption and desorption studies on chromium (VI) by novel bio sorbents of raw rutin and rutin resin. *Journal of Environmental Chemical Engineering*, **3** (2), 1137 – 1145.

Ferrag, N.M., (2016). Use of waste materials in Architectural application in Egypt. *International journal of Chemical Technology and Research,* **9** (12), 14-27.

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

Gerspacher, C., (2009). The effect of cadmium on brain cells. *International Journal of Science and Research,* **24** (3), 311-318.

Ghaedi, M., Ramazani, S., and Roosta, M., (2011). Gold nanoparticle loaded activated carbon as novel adsorbent for the removal of Congo red. *Indian Journal of Science and Technology*, **4** (10), 1208-1217.

Ghasemzadeh, N., Ghadiri, M., and Behroozsarand, A., (2017). Optimization of chemical regeneration procedures of spent activated carbon. *Journal of Advances in Environmental Technology* **1**, 45-51.

Gottfried, A., Shepard, A., Hardiman, D., and Walsh, M.E., (2008). Impact of recycling filter backwash water on organic removal in coagulation-sedimentation processes. *Journal of Water Resources,* **42**, 4683-91.

Guo, D., Shi, Q., He, B., and Yuan, H. (2011). Different solvents for the regeneration of the exhausted activated carbon used in the treatment of coking wastewater. *Journal of Hazardous Materia*, **86**, 1788–1793.

Guo, Y., and Du, E. (2012). The effects of thermal regeneration conditions and inorganic compounds on the characteristics of activated carbon used in power plant. *Energy procedia*, **17**, 444-449.

Gupta, V. K., Nayak, A., Agarwal, S., and Tyagi, I., (2014). Potential of activated carbon from waste rubber tire for the adsorption of phenolic: Effect of pre-treatment conditions. *Journal of Colloid and Interface Science*, **417,** 420–430.

Hagemann, N., Spokas, K., Hans-Peter, S., Kägi, R., Böhler, M.A., and Bucheli**,** T.D., (2018). Activated Carbon, Biochar and Charcoal: Linkages and Synergies across Pyrogenic Carbon's ABCs. *MPDI-water,* **10** (182), 1-19.

Helaluddin, A.B.M., Khalid, R.S., Alaama, M., and Abbas, S. A., (2016). Main Analytical Techniques Used for Elemental Analysis in Various Matrices. *Tropical Journal of Pharmaceutical Research*, **15** (2), 427-434.

Herzog, J., Meuron, P., Herz, M., Nobre, L. and Rahbaran, S., (2008). Industrial Area Nairobi. ETH Studio, Spitalstrasse 8, Basel, Switzerland.

Hilber, I. and Bucheli, T., (2010). Activated carbon amendment to remediate contaminated sediments and soils: A review. *Global Nest Journal*, **12**, 305–307.

Hill, M. (2010*)*. Understanding environmental pollution. Cambridge, UK: Cambridge University Press, 9-22.

Homagain, P.L., Glimirea, K.N. and Inoveb, K., (2010). Adsorption behavior of heavy metals onto chemical modified sugar cane bagasse. *Journal of Bio resources Technology*, **101,** (6), 2067-2069.

Iheoma, C.C., Chinomso, M.E., Nwanonenyi, S.C., and Ifeoma, C.U., (2015). Adsorption Treatment of Industrial Paint Effluent for the Removal of Pollutants by Local Clays. *International Journal of Scientific & Engineering Research*, **6**, 10.

Irfan, K.S, Pre, P., and Babu, J.A., (2013). Steam Regeneration of Adsorbents: An Experimental and Technical Review. *Journal of Chemical Science Transactions*, **4** (2), 1078-1088.

Islam, M.R., Tushar, M.S.H.K., and Haniu, H., (2008). Production of liquid fuels and chemicals from pyrolysis of Bangladeshi bicycle/rickshaw tire wastes. *Journal of Analytical and Applied Pyrolysis*, **82** (1), 96-109.

Iverlund, N., Parsons, A., and Muller, F., (2009). Carbon cartridges and their use as a purification step in Pharmaceutical API process. *Journal of Chemical engineering, Research and design*, **87** (6), 652-858.

Jesionowski, T., and Ciesielczyk F., (2013). Pigment, Inorganic. In: Luo R. *Encyclopedia of Color Science and Technology*. Springer, New York, NY.

Johnsen, D.L., Mallouk, K.E, and Rood, M.J., (2011). Control of electro thermal heating during regeneration of activated carbon fiber cloth. *Journal of Environmental Science and Technology,* **45**, 738–743.

Johri, N., Jacquillet, G and Unwin, R., (2010). Heavy metal poisoning: the effects of cadmium on the kidney. *Journal of Environmental Research*, **23** (5), 783-792.

Kabbaj, H., El Mai, H., Galindo-Riãno, M. D. and Stitou, M., (2014.) Physicochemical characterization and Analysis of total metal concentration of grease and wastewater samples: Case study for two wastewater treatment plants in the North of Morocco: Tangier and Tetouan. *Journal of Materials and Environmental Science,* **5** (5), 1622-1632.

Kanjana, K., Inoue, K., Ohto, K., Kawakita, H., Kurata, M., Atsumi, K, Fukuda, H. and Alam, S., (2013). Adsorptive Recovery of Palladium (II) and Platinum (IV) on the Chemically Modified Microalgal and Ion Exchange, *Taylor and Francis Online,* **31** (3), 320-334.

Kar, Y., (2011). Catalytic pyrolysis of car tire waste using expanded perlite. *Journal of Waste Management*, **31** (8), 1772–1782.

Karunarathne, H.D.S.S., and. Amarasinghe, B.M.W.P.K., (2013). Fixed Bed Adsorption Column Studies for the Removal of Aqueous Phenol from Activated Carbon Prepared from Sugarcane Bagasse. *Energy Procedia*, **34**, 83 – 90.

Kenya National Bureau of Statistics, KNBS, (2015). Population Distribution by Political Units.

Khan, A. and Ghouri, A. (2011). Environmental pollution: its effects on life and its remedies. *Journal of Arts, Science and Commerce*, **2**: 276-285.

Khan, M.J.H., Hussain, M.A., Mansourpour, Z., Mostoufi, N., Ghasem, N.M.,Abdullah, E.C., (2014). CFD simulation of fluidized bed reactors for polyolefin production e review. *Journal of Industrial and Engineering Chemistry*, **20**, 3919-3946.

Kigotho, K. (2017).Kenya paint market and industry growing into key East African hub in East African coatings congress report.

Körbahti, B.K. and Tanyolac¸ A., (2009). Electrochemical treatment of simulated industrial paint wastewater in a continuous tubular reactor. *Journal of Chemical Engineering,* **148**, 444–451.

Kulkarni, S., and Kaware, J. (2014). Regeneration and recovery in adsorption- a review, *International Journal of Engineering Science and Innovative Technology*, **1**, 61–64.

Kushwaha, J.P Chandra, S.V. Mall, I.D. (2010). Treatment of dairy wastewater by inorganic coagulants: Parametric and disposal studies. *Water Research*, **44**, 5867-5874.

Lambourne, R. and Strivens, T.A., (2014). Paint and Surface Coatings: Theory and Practice. *A volume in Woodhead Publishing Series in Metals and Surface Engineering Book.**2***.Woodhead .Publishing Limited. Cambridge, United Kingdom.

Lee, K.E., Hanafiah, M.M., Halim, A.A., and Mahmud, M.H. (2015). Primary treatment of dye Wastewater using aloe-vera aided aluminum and magnesium hybrid coagulants. *Procedia Environmental Sciences*, **30**, 56-61.

Leip, A., Gilles Billen, B., Garnier, J., Bruna Grizzetti, B., *et al* (2015). Impacts of European livestock production: nitrogen, sulphur, phosphorus and greenhouse gas emissions, land-use, water eutrophication and biodiversity. *Environmental Research Letters*, **10** (11*)*,1-11.

Lohani, M.B., Singh, A., Rupainwar, D.C. and Dhar, D.N., (2008). Studies on efficiency of guava (Psidium guajava) bark as bio adsorbent for removal of Hg (II) from aqueous solutions. *Journal of Hazardous Materials*, **159**, 2-3.

Lu, P.J., Lin, H.C., Yu, W.T., and Chern, J.M. (2011). Chemical Regeneration of activated carbon used for dye adsorption. *Journal of Taiwan Institute of Chemical Engineering* **42**, 305- 311.

Mandar, G and Pranay, L. (2015). Energy Analysis in Tire Manufacturing Industries. *International Journal of Mechanical Engineering and Technology,* **6** (9), 12-119.

Mannari, V and Patel, C.J., (2015). *Paint component*. *Understanding Raw Materials*. Vincentz Network, Hanover, Germany.

Mathenge, S.G., Njoroge, W.G, and Mutuku, O. M., (2018). *Journal of medical Science and clinical research.***6** (8), 743-749.

Mbui, D., Chebet, E., Kamau, G., and Kibet, J. (2016). The State of Water Quality in Nairobi River, Kenya. *Asian journal of Research in Chemistry,* **9** (11*),* 579-586

McIssack, R., and Rowe, R.K. (2008). Effect of filter separators on the clogging of leachate collection systems. *Canadian Geotechnical Journal,* **43**, 674-693.

Mihir, P., Samal, N.R., and Roy, P.K. (2015). Electrical Conductivity of Lake Water as Environmental Monitoring – A Case Study of Rudrasagar Lake. *Journal of Environmental Science, Toxicology and Food Technology,* **9** (3), 2319-2402.

Mobasherpour, I., Salhi, E., and Asjodi, A., (2014). Research on the batch and fixed bed column performance of Red mud adsorbents for Lead removal. *Canadian Chemical Transactions,* **1** (2), 83-96.

Mohammed, F.M., Roberts, E.P.L., Campen, A.K., and Brown, N.W., (2012). Waste water treatment by multistage batch adsorption and electrochemical regeneration. *Journal of Electrochemical Science and Engineering,* **2** (4), 223-236.

Mohammed, M.A., Shitu, A., Tadda, M.A., and Ngabura, M. (2014) .Utilization of various agricultural waste materials in the treatment of industrial wastewater containing heavy metals: a review. *International Research Journal of Environmental Sciences,* **3** (3), 62–71.

Mohammedin, A.T., Hameed, B.H., and Ahmad, A.L. (2009). Batch adsorption of phenol onto physiochemical-activated coconut shell. *Journal of Hazardous Material,* **161,** 1521-1529.

Monisha, J., Tenzin Tseten, N.A., Blessy, B. M. and Krishnamurthy, N. B., (2014). Toxicity, mechanism and health effects of some heavy metals. *Journal of interdisciplinary toxicology*, **7** (2), 60–72.

Moreno, N.F., Barrios, A.N., Leal, R.P., Franco, A.C.G., Rodriguez, A.H. and Hernandez, L.R., (2014). Effect of Nitrogen Deficiency and Toxicity in Two Varieties of Tomatoes (Lycopersicum esculentum L.). *Journal of Agricultural Sciences* **5,** 1361-1368

Moreno-Piraján, J.C and Geraldo, L., (2012). Heavy Metal ions Adsorption from Wastewater Using Activated Carbon, from Orange Peel. *Journal of Chemistry*, **9** (2), 926-937.

Mousavi, H.Z., A. Hosseynifar, A., Jahed,V and Dehghani, S. A. M.(2010). Removal of Lead from Aqueous Solution Using Waste Tire Rubber Ash as an Adsorbent. *Brazilian Journal of Chemical Engineering*, **27** (1), 79-87.

Muruganandam, L., Saravanakumar, M.P., Amarjit, J., Sudiv, G., and Bhagesh, G. (2017). Treatment of waste water by coagulation and flocculation using biomaterials. *IOP Conference series: Material Science and Engineering*, **263**, 1-13.

Nahm, S.W., Shim, W.G., Park, Y.K., and Kim, S.C., (2012). Thermal and chemical regeneration of spent activated carbon and its adsorption property for toluene. *Chemical Engineering Journal*, **210**, 500–509.

Najim, K.B and Hall, M.R. (2010). A review of fresh/hardened properties and applications for plain-(PRC) and self-compacting rubberized concrete (SCRC). *Journal of construction and building material*, **24,** 2043-2051.

Nasrullah, M., Lakhveer, S., and Wahida, Z.A. (2012). Treatment of Sewage by Electrocoagulation and the Effect of High Current Density. *Energy and Environmental Engineering Journal*, **1** (1), 27-31.

Nirali, K., Bhati, L., Narang, M., and Vaishnavi, R. (2016). Wastewater treatment by ion exchange method: a review of past and recent researches. *Environmental Science an Indian Journal*, **12** (4), 143-150.

Nkurunziza, T., Nduwayezu, J., Banadda, E., and Nhapi, I., (2009). The effect of turbidity levels and Moringa Oleifera concentration on the effectiveness of coagulation in water treatment. *Journal of Water Science and Technology*, **59**, 1551-1558.

Noor, N.M., Hamada, H., Sagawa, Y., and Yamamoto, D. (2015). Effect of crumb rubber on concrete on strength and chloride ion penetration resistance. *Jurnal Teknologi*, **77** (32), 171-178.

Noorjahan, C.M., (2015). Physico Chemical Parameters and Identification of Bacteria in Paint Effluent. *International Journal of Scientific Engineering and Technology Research,* **4** (30), 5763-5765.

Nurulhuda, A., Ridzuan Z., and Mohamad Zailani, A.B., (2009). Adsorption of Phenol Using Activated Carbon Adsorbent from Waste Tyres. *Pertanika Journal of Science & Technology,* **17** (2), 371 – 380.

Nyang'au, J., Gatebe, E., Nyagah, C., Njugi, A. and Ahenda, S., (2017). A Comparative Study on the Nutrient Composition of the Biogas Slurry and other Organic Fertilizers used by Small Scale Farmers in Kenya. *International Journal of Scientific Research in Science, Engineering and Technology,* **3** (1), 233-238.

Odhiambo, J., Yusuf, A. and Onyatta, J. (2016). Assessment of Selected Parameters for Industrial Effluents from Some Industrial Sites in Nairobi, Kenya. *Universal Journal of Chemistry,* **4** (2), 65-68.

Ogilo, J. K., Onditi, A. O., Salim, A. M. and Yusuf, A. O. (2017). Assessment of Levels of Heavy Metals in Paints from Interior Walls and Indoor Dust from Residential Houses in Nairobi City County, Kenya. *Chemical Science International Journal,* **21** (1), 1-7.

Ojoawo, S.O., Rao, C.V. and Goveas, L.C., (2015). Bioremediation of Zn, Cu, Mg and Pb in Fresh Domestic Sewage by Brevibacterium sp. *International Journal of Environmental Research,* **10** (1), 139-148.

Okafor, J.O., Agbajelola, D.O. and Shehu, P. (2015). Studies on the Adsorption of Heavy Metals in a Paint industry effluent using Activated Maize Cob. *Journal of Multidisciplinary Engineering Science and Technology,* **2** (2).39-46.

Oluseyi, A. (2011). Perceived Effect of Industrial Water Pollution on the Livelihood of Rural Dwellers in Yewa Area, Ogun State, Nigeria. *European Journal of Social Sciences,* **22** *(1),* 66-75.

Oluyemi, E.A., Feuyit, G., Oyekunle, J.A.O.and Ogunfowokan, O.A., (2008). Seasonal variations in heavy metal concentrations in soil and some selected crops at a landfill in Nigeria. *African Journal of Environmental Science and Technology,* **2**, 89-96.

Ondon, B.S., Sun, B., Yan, Z.Y., Zhu, X.M., and Liu, H. (2014). Effect of microwave heating on the regeneration of modified activated carbons saturated with phenol. *Journal of Applied Water Science*, **4**, 333–339.

Onoja, K.P., Tifwa, P.A., and Idoko, J.O., (2017). Aqueous Phase Removal of Chromium and Cadmium Using Moringa oleifera pod Adsorbents: Equilibrium and Kinetic Modeling. *Journal of Applied Chemistry,* **10** *(9), 33-40.*

Orieku, E.C., Agulanna, C.N., Odenigbo, J., and Nnoruka, N., (2013). Waste to wealth through the incineration of waste tyres and recovery of carbon black. *International journal of multidiscipline and engineering,* **4** (7), 30-36.

Pascal, D., Stijn, V. H., Bjorge, D., W., Audenaert, T.M., (2008*).* Sustainable wastewater treatment of temporary events: The Dranouter Music Festival case study. *Journal of Water Science & Technology,* **58** (8), 1653-7.

Patel, H.V., and Kayasth, B.D. (2015). A Review on design and analysis of Tyre Envelope Expander for tyre retreading process. *International Journal of Engineering Innovation and Scientific Research*, **1** (1), 65-68.

Petraitis, E. (2009). Investigation of Jerubaicial landfill leachate. *Ekologija*, 55, 86-92.

Pichery, C., Bellanger, M., Zmirou-Navier, D., Glorennec P., Hartemann, P., and Grandjean, P. (2011). Childhood lead exposure in France: benefit estimation and partial cost-benefit analysis of lead hazard control*, Journal of Environmental Health*, **10** (1)**,** 1-12.

Pravin, U., Asmita, G. and Ram, S.L., (2011). Water pollution by discharge effluents from Gove Industrial Area of Maharashtra, India: Dispersion of heavy metals and their Toxic effects. *International Journal of Global Environmental Issues,* **11** (1), 28-36.

Pritchard, M., Craven, T., Mkandawire, T., Edmondson, A., and O'neill, J. (2010). A comparison between Moringa Oleifera and chemical coagulants in the purification of drinking water–

An alternative sustainable solution for developing countries. *Journal of Physics and Chemistry of the Earth*, **35**, 798-805.

Rahimi, M. and Vadi, M., (2014). Langmuir, Freundlich and Temkin adsorption isotherms of Propranolol on multi-wall carbon nanotube. *Journal of Modern Drug Discovery and Drug Delivery Research,* **1** (3), 1-2.

Rajaswaria, R., and Sailaja, N. (2014). Impact of Heavy Metals on Environmental Pollution. In National Seminar on Impact of Toxic Metals, Minerals and Solvents leading to Environmental Pollution. *Journal of Chemical and Pharmaceutical Sciences,* **3,** 175

Ramalingam, S.G., Pre´, P., Giraudet, S., LeCloirec, P., Baudouin, O., and De´chelotte, S. (2012). Recovery comparisons—hot nitrogen vs. steam regeneration of toxic dichloromethane from activated carbon beds in oil sands process, *Journal of Hazardous Materia*l, 205–206.

Renault, F., Sancey, B., Badot, P.M., and Crini, G. (2009). Chitosan for coagulation/flocculation processes–an eco-friendly approach. *European Polymer Journal*, **45**, 1337-1348.

Reschner, K. (2008). Scrap Tire Recycling - A Summary of Prevalent Disposal and Recycling Methods, 1-16.

Rivera-Utrilla, J., Sánchez-Polo, M., Gómez-Serrano, V., Alvarez, P., Alvim-Ferraz, M., Dias, J. (2011). Activated carbon modifications to enhance its water treatment applications. An overview. *Journal of Hazardous Material*, **187**, 1–23.

Rombaldo, C.F.S., Lisbôa, A.C.L., Méndez, M.O.A., and Coutinho, A. (2008). Effect of operating conditions on scrap tire pyrolysis. *Journal of Materials Research,* **11** (3), 359-363.

Rowe, R.K. (2012). Short and long term leakage through composite lines. The 7th Arthur Casagrande Lecture. *Canadian Geotechnical Journal*, **49**, 141-169.

Rowhani, A., and Rainey, T.J., (2016). Scrap Tyre Management Pathways and Their Use as a Fuel—A Review. *MDPI-energies*, **9**, 1-26.

Roy, R. (2011). Beneficial Reuses of Waste Tires for Pollution Reduction. *Global Chinese Scientists Environmental Protection Forum*.

Saad, D.M., Cukrowska, E., and Tutu, H. (2015). Column adsorption studies for the removal of U by phosphonated cross-linked polyethylenimine: modelling and optimization. *Applied Water Science journal,* **5**, 57–63.

Sahurin, N., Ahmed, N.F., and Nithyanandam, R. (2013). Wastewater Treatment by using Natural Coagulant. *2nd eureca 2014*, **4**, 213-217.

Salam, O.E.A., Reiad, N.A. and ElShafei, M.M., (2011). A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research,* ***2***, 297–303.

Salvador, F., Martin-Sanchez, N., Sanchez-Hernandez, R., and Sanchez-Montero, M.J. (2015). Regeneration of carbonaceous adsorbents. *Part II: Chemical, microbiological and vacuum regeneration, Microporous Mesoporous Material,* **202**, 277–296.

Samonin, V.V., Podvyaznikov, M.L., Solov'ev, V.N., Kiseleva, V.L., Khrylova, E.D., and Spiridonova, E.A. (2013). Study of the possibility of regeneration of activated carbon spent in water treatment processes using the chemical regeneration and thermal reactivation. Russian. *Journal of Applied Chemistry*, **86**, 1220–1224.

Schmidt, H.P. and Wilson, K. (2012**.** 55 uses of biochar. *Ithaka Journal*, **29**, 286–289.

Sienkiwicz, M., Kucinska, J.K., Janik,H., and Balas , A. (2012). Progress in used tyres management in the European Union. *Waste Management*, **32**, 1742-1751.

Simeonov, L., Kolhubovski, M. and Simeonov, B. (2010). Environmental heavy metal pollution and effects on child mental development. Dordrecht, Netherlands: *Springer,* 114-115.

Sharma, H., Rawal, N., and Mathew, B., (2015). The characteristics, toxicity and effects of cadmium. *International Journal of nanotechnology and nanoscience*,**3**, 1-9.

Sun, K., Jiang, M., and Xu, J. (2012). Chemical regeneration of exhausted granular activated carbon used in citric acid fermentation solution decoloration. *Iran Journal of Chemistry and Chemical Engineering*, **28**, 79-83.

Sutherland, C., and Venkobachar, C., (2010). A diffusion-Chemisorption kinetic model for simulating biosortion using forest macro-fungus, *fomes fasciatus. International Journal of plant Science*, **1** (4), 107-117.

Taik-Nam, K., and Choong, J., (2012). Desorption And Regeneration Characteristics for Previously Adsorbed Indium Ions to Phosphorylated Sawdust. *Journal of Environmental Engineering Research,* **17** (2), 65-67.

Tadda, M.A., Ahsan, A., Shitu, A., ElSergany, M., Arunkumar, T., Bipin Jose, A., and Abdura Razzaque, M. (2016). A review on activated carbon: process, application and prospects**.** *Journal of Advanced Civil Engineering Practice and Research,* **2** *(*1), 7-13.

Talbert, R. (2008). Paint Technology Handbook. CRC Press, New York, 91-93

Tamer, M., A., Abustan, I., Ahmad, M.A., and Ahmad, A.F., (2013). Cadmium removal from aqueous solution using microwaved olive stone activated carbon. *Journal of Environmental Chemical Engineering,* **1** (3), 589-599.

Tesfalem, B.W., Abdrie, S.H. (2017). Toxicity Study of Heavy Metals Pollutants and Physico-Chemical Characterization of Effluents Collected from Different Paint Industries in Addis Ababa, Ethiopia. *Journal of forensic sciences and criminal investigation,* **5** (5), 1-5.

Tibaijuka, A. (2007). Anna Tibaijuka, Executive Director UN-HABITAT and Director General UNON, cited in Nairobi City Development Strategy Top Priority for 21st Century Future of the Kenyan Capital, United Nations Environment Programme.

Ukiwe, L.N., Ibeneme S.I., Duru, C.E., Okolue B.N., Onyedika, G.O. and Nweze, C.A. (2014) Chemical and Electrocoagulation Techniques in Coagulation-Flocculation in Water and Wastewater Treatment- A Review. *Journal of Advances in Chemistry* **9** (3), 1988-1999.

Ukiwe, L.N., Iwu, I.C., Chijioke-Okere, M. (2013) .The role of inorganic metal salts in wastewater clarification. *Journal of Advances in Chemistry*, **4**, 318-322.

Unuabonah, E.I., Olu-Owolabi, B.I., Fasuyi, E.I., and Adebowale, K.O. (2010). Modeling of fixed-bed column studies for the adsorption of cadmium onto novel polymer-clay composite adsorbent. *Journal of Hazardous Material,* **179,** 415-423.

Vinod, K. and Chopra, A.K., (2012). Monitoring of physico-chemical and Microbiological characteristics of Municipal Wastewater at Treatment Plant, Haridwar City (Uttarakhand) India. *Journal of Environmental Science and Technology,* **5** (2), 109-118.

Vinod, K.G., Ganjali, M.R., Nayak, B.A., Agarwal, B.S., (2012). Enhanced heavy metals removal and recovery by mesoporous adsorbent prepared from waste rubber tire. *Chemical Engineering Journal,* **197**, 330–342.

Wen, Q.B., Li, C.T., Cai, Z.H., Zhang, W., Gao, H.L., Chen, L.J., Zeng, G.M. (2011). Study on activated carbon derived from sewage sludge for adsorption of gaseous formaldehyde, *Journal of Bio resource Technology*, **102**, 942–947.

Wurm, D. (2016). The greening of paint: An eco-paint buyer's guide. *Renew: Technology for a Sustainable Future* **136**, 74-78.

Yin, Y. (2010). Emerging usage of plant-based coagulants for water and wastewater treatment. *Process Biochemistry,* **45** (9) 1437-1444.

APPENDIX A

Table A.1: Phosphorus calibration data

Conc.(mg/L)	**Absorbance**
0	-0.002
5	0.2021
10	0.4058
15	0.6106
20	0.7309
25	1.0099

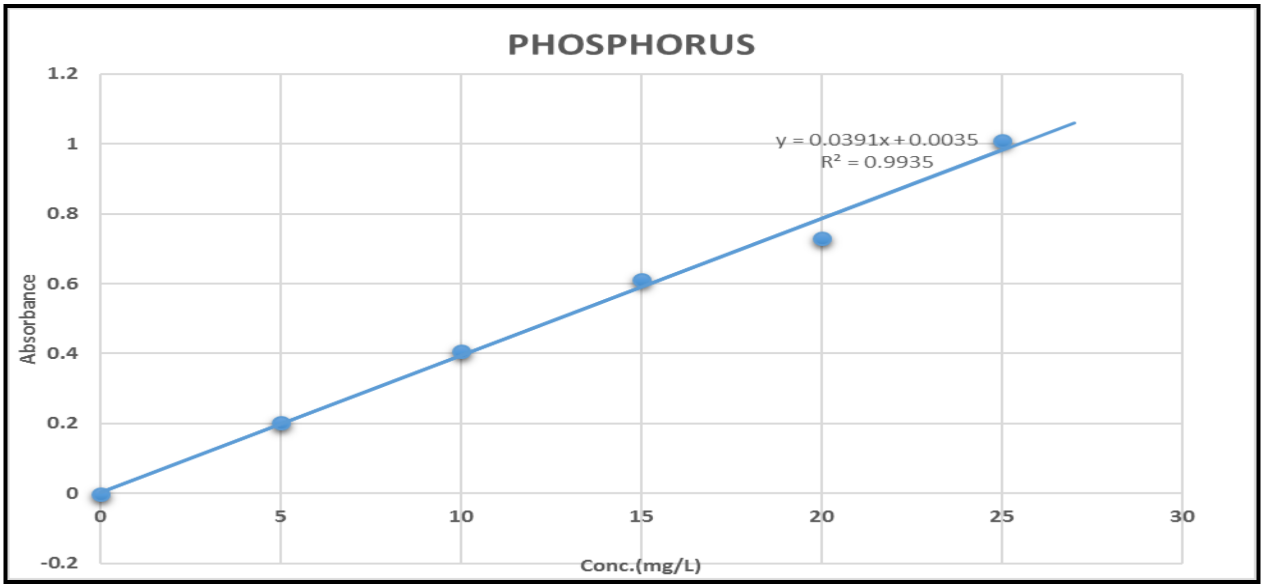

Fig A.1: Phosphorus calibration curve at 430nm

Table A.2: Sulphur calibration data

Conc.(mg/L)	**Absorbance**
0	0.0007
5	0.0682
10	0.1645
20	0.4076
30	0.6264
40	0.9192

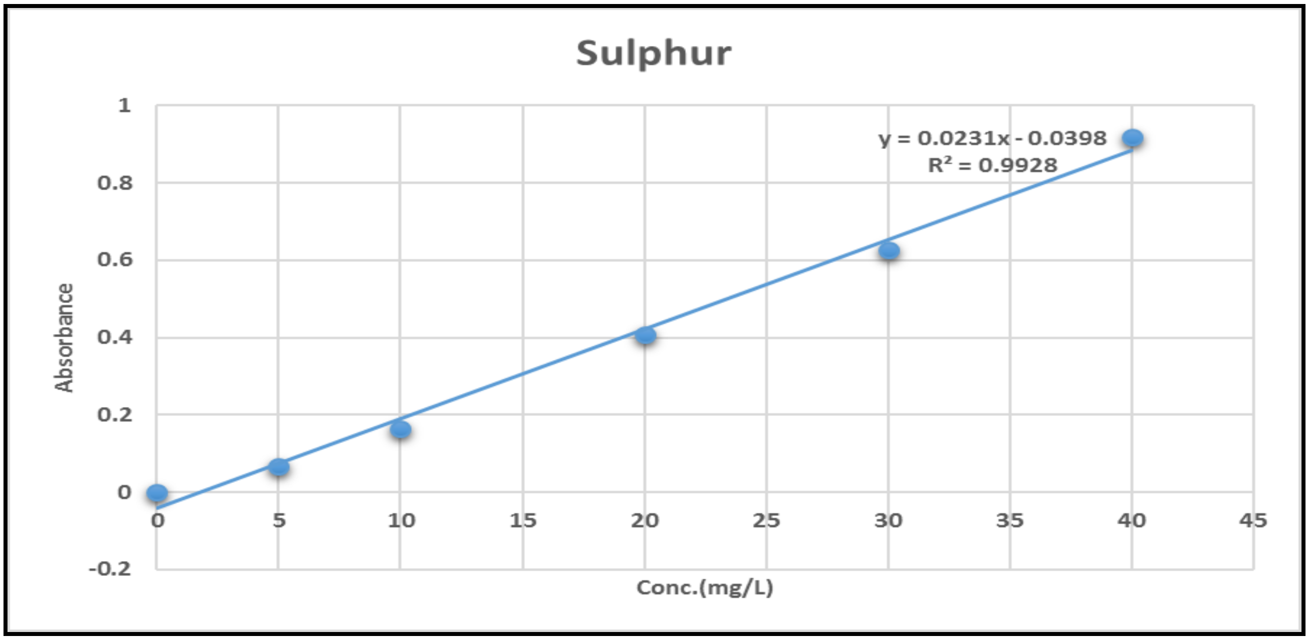

Fig A.2: Sulphur calibration curve at 440 nm

Table A.3: Lead calibration data

Conc.(mg/L)	Absorbance
0	-0.001
2	0.016
4	0.037
6	0.057
8	0.08

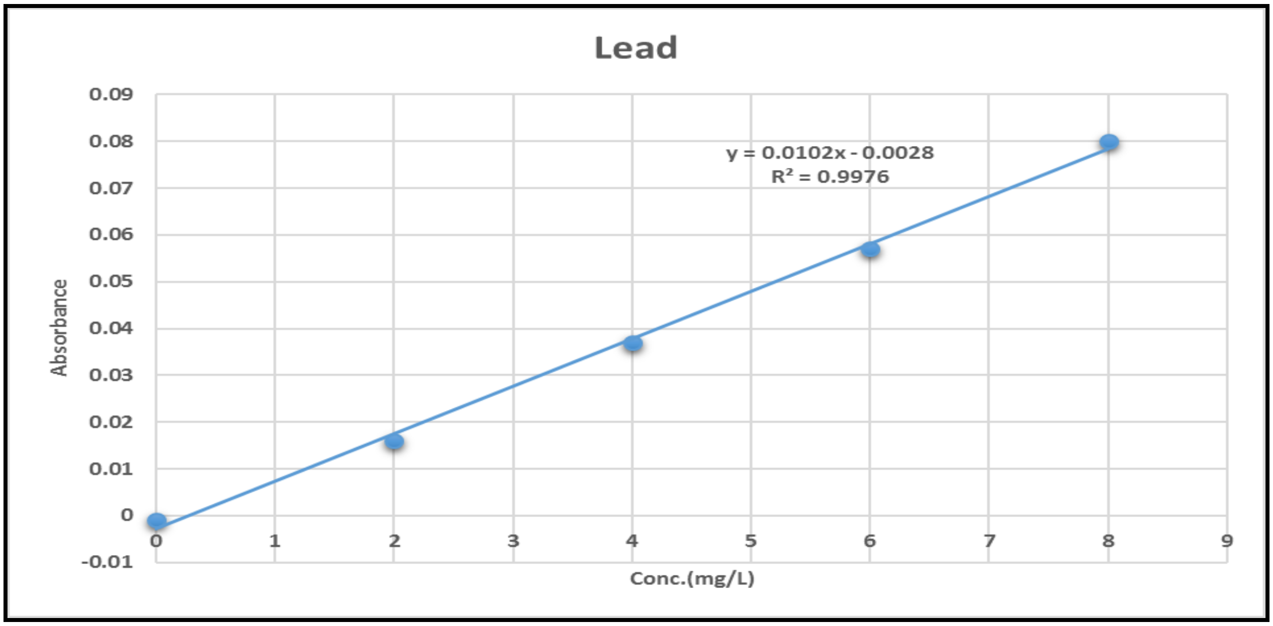

Fig A.3: Lead calibration curve at 217.0nm

Table A.4: Cadmium calibration data

Conc.(mg/L)	Absorbance
0	0
5	0.157
10	0.308
15	0.414
20	0.529

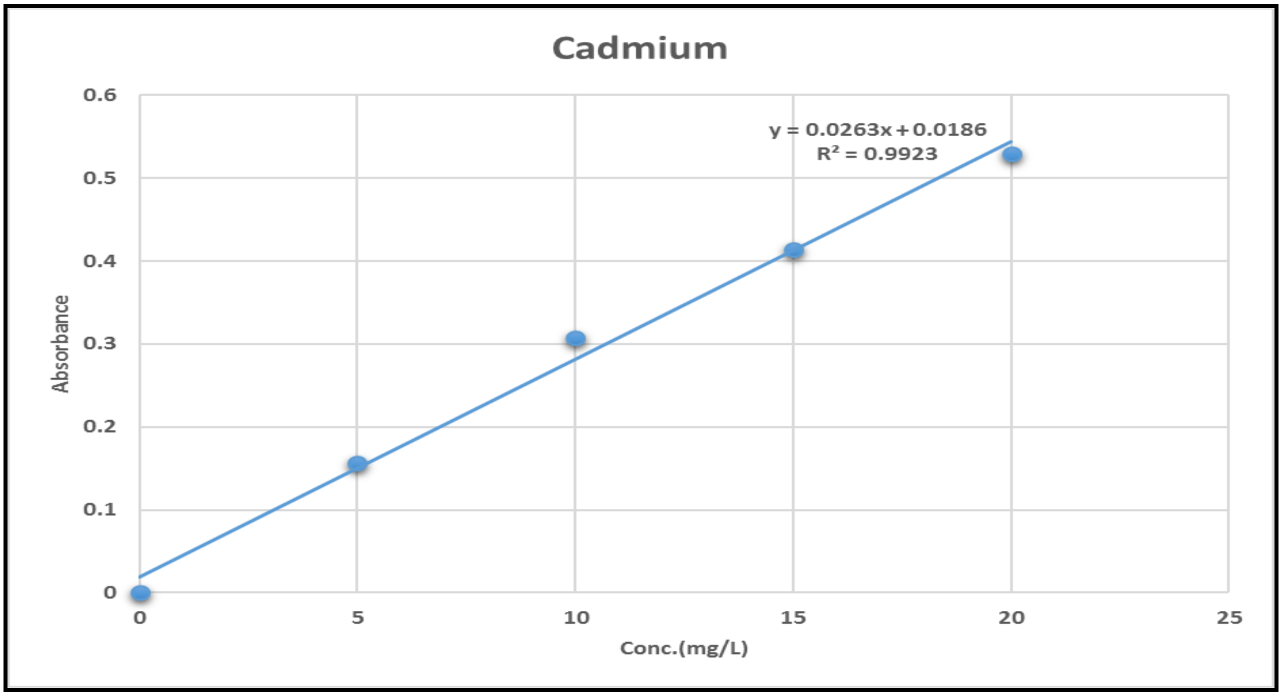

Fig A.4: Cadmium calibration curve at 228.8nm

Table A.5: Chromium calibration data

Conc.(µg/L)	Absorbance
0	0.0603
80	0.7564
120	1.2071
160	1.5134
200	1.6743

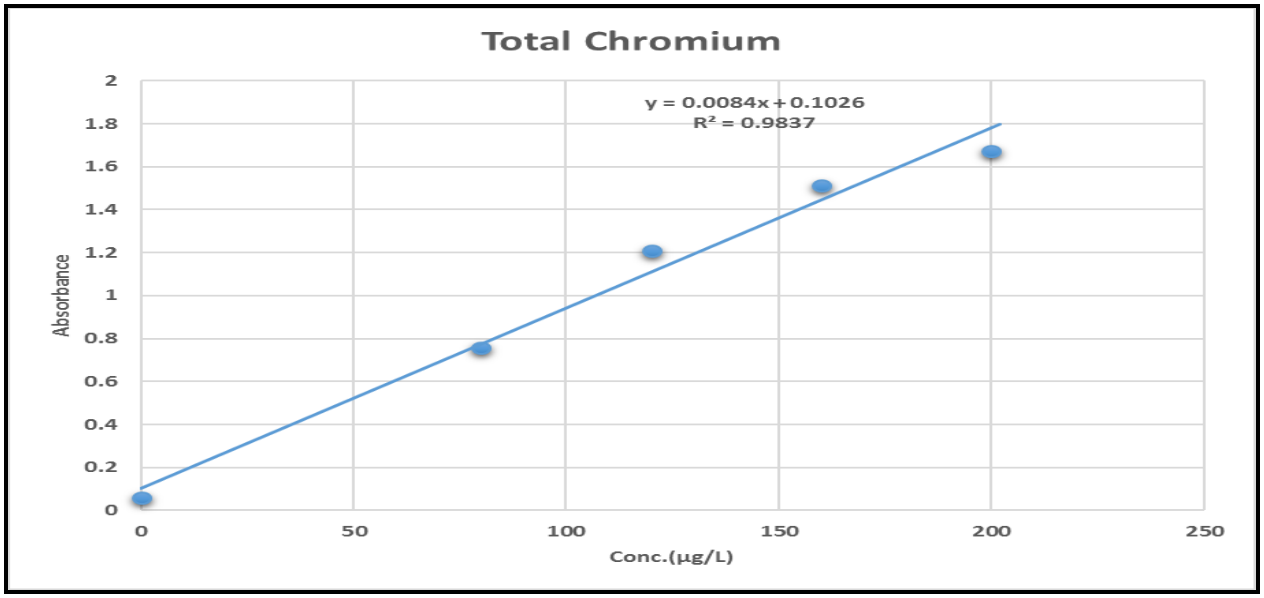

Fig A.5: Chromium calibration curve at 359.4 nm

Table A.6: Biological Oxygen Demand (BOD) values

Trial	Day	Volume taken (ml)	Titrant volume (ml)	Titrant volume$_5$ (ml)	Mean BOD (mg/L)
Blank	0	200	10.1	10.0	2
ESD1	0	200	9.4	1.9	149±1.41
ESD2	0	200	9.4	1.8	
EUP1	0	200	9.8	0.5	183±1.41
EUP2	0	200	9.7	0.7	
EMR1	0	200	9.1	0.7	165±1.41
EMR2	0	200	9.1	0.8	

Table A.7 (a): Effect of adsorbent dosage on the adsorption of Cadmium, Lead and Chromium ions

	Cadmium (mg/L)			**Lead (mg/L)**			**Chromium (mg/L)**		
Wt (g)	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**
0	4.18± 0.09	3.03± 0.83	3.47± 1.04	12.05± 0.41	5.38± 1.41	17.21± 1.67	2.07±0.66	2.29±0.24	3.04±0.83
0.1	2.73± 0.14	2.51± 0.78	2.17± 0.36	9.95± 0.88	3.87± 0.45	10.66± 0.71	1.63± 0.54	1.57± 0.96	1.5± 0.96
0.2	2.1± 0.47	1.6± 0.17	1.5± 0.91	7.19± 0.19	2.71± 0.42	8.31± 0.48	1.33± 0.42	1.43± 0.73	1.47± 0.45
0.3	1.16± 0.04	0.66± 0.82	0.45± 0.42	3.93± 0.14	2.15± 0.77	6.95± 0.56	1.02± 0.29	0.86± 0.12	1.41± 0.47
0.4	0.7± 0.78	0.32± 0.21	0.37± 0.21	3.85± 0.31	1.42± 0.13	5.33± 0.36	0.77± 0.69	0.54± 0.45	0.39± 0.95
0.5	0.63± 0.41	0.34± 0.07	0.33± 0.36	2.42± 0.22	1.14± 0.19	2.76± 0.78	0.73± 0.77	0.49± 0.63	0.41± 0.45
0.6	0.59± 0.72	0.29± 0.89	0.27± 0.41	2.9± 0.08	1.08± 0.84	2.53± 1.04	0.65± 0.45	0.51± 0.45	0.2± 0.97
0.7	0.57± 0.08	0.33± 0.05	0.35± 0.04	2.36± 0.41	1.19± 0.97	2.61± 0.44	0.64± 0.96	0.48± 0.07	0.15± 0.89

Table A.7 (b): Effect of adsorbent dosage on the adsorption rate of Cadmium, Lead and Chromium ions

	Cadmium (%adsorption)			**Lead (%adsorption)**			**Chromium (%adsorption)**		
Wt (g)	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1	34.69	17.16	37.46	17.43	28.07	38.06	21.26	31.44	50.66
0.2	49.76	47.19	56.77	40.33	49.63	51.71	35.75	37.55	51.64
0.3	72.25	78.22	87.03	67.39	60.04	59.62	50.72	62.45	53.62
0.4	83.25	89.44	89.34	68.05	73.61	69.03	62.80	76.42	87.17
0.5	84.93	88.78	90.49	79.92	78.81	83.96	64.73	78.60	86.51
0.6	85.89	90.43	92.22	75.93	79.93	85.30	68.60	77.73	93.42
0.7	86.36	89.11	89.91	80.41	77.88	84.83	69.08	79.04	95.07

Table A.8 (a): Effect of contact time on the adsorption of Cadmium, Lead and Chromium ions

	Cadmium (mg/L)			**Lead (mg/L)**			**Chromium (mg/L)**		
Time(min)	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**
0	4.18± 0.09	3.03± 0.83	3.47± 1.04	12.05± 0.41	5.38± 1.41	17.21± 1.67	2.07±0.66	2.29±0.24	3.04±0.83
30	2.34± 0.95	2.31± 0.42	1.95± 0.92	8.5± 078	3.36± 0.12	9.08± 0.35	1.6± 0.42	1.51± 0.48	1.51± 0.41
45	1.89± 0.13	1.42± 0.85	1.42± 0.83	6.26± 0.45	2.55± 0.63	5.64± 0.74	1.61± 0.86	0.71± 0.13	1.47± 0.74
60	1.12± 0.22	0.78± 0.74	0.51± 0.44	3.33± 0.26	1.66± 0.77	4.58± 0.63	1.57± 0.86	0.67± 0.26	1.41± 0.63
75	0.73± 0.08	0.45± 0.06	0.45± 0.56	2.11± 0.68	1.15± 0.95	4.41± 0.40	1.3± 0.86	0.9± 0.56	0.91± 0.85
90	0.79± 0.04	0.3± 0.32	0.49± 0.47	0.95± 0.88	1.03± 0.83	4.22± 0.78	1.02± 0.78	0.86± 0.74	0.73± 0.75
105	0.69± 0.77	0.32± 0.77	0.39± 0.44	0.66± 0.47	0.99± 0.63	0.41± 0.11	0.74± 0.73	0.79± 0.71	0.77± 0.56
120	0.61± 0.13	0.29± 0.47	0.29± 0.73	0.43± 0.18	0.89± 0.44	0.41± 0.19	0.79± 0.38	0.73± 0.46	0.73± 0.52

Table A.8 (b): Effect of contact time on the adsorption rate of Cadmium, Lead and Chromium ions

	Cadmium (%adsorption)			**Lead (%adsorption)**			**Chromium (%adsorption)**		
Time(min)	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	44.02	23.76	43.80	29.46	37.55	47.24	22.22	34.06	50.33
45	54.78	53.14	59.08	48.05	52.60	67.23	22.71	69.00	51.64
60	73.21	74.26	85.30	72.37	69.14	73.39	24.15	70.74	53.62
75	82.54	85.15	87.03	82.49	78.62	74.38	37.20	60.70	70.07
90	81.10	90.10	85.88	92.12	80.86	75.48	50.72	62.45	75.99
105	83.49	89.44	88.76	94.52	81.60	97.62	64.25	65.50	74.67
120	85.41	90.43	91.64	96.43	83.46	97.62	61.84	68.12	75.99

Table A.9 (a) Effect of pH on the adsorption of Cadmium, Lead and Chromium ions

	Cadmium (mg/L)			**Lead (mg/L)**			**Chromium (mg/L)**		
pH	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**
2	4.18± 0.09	3.03± 0.83	3.47± 1.04	12.05± 0.41	5.38± 1.41	17.21± 1.67	2.07±0.66	2.29±0.24	3.04±0.83
3	2.16± 0.42	1.99± 0.57	1.75± 0.24	7.73± 0.88	2.85± 0.43	8.75± 0.91	1.74± 0.63	1.83± 0.96	1.71± 0.63
4	1.74± 0.36	1.36± 0.52	1.25± 0.36	6.17± 1.03	2.61± 0.11	6.64± 0.89	1.7± 0.46	1.73± 0.78	1.65± 0.52
5	1.08± 0.25	0.57± 0.91	0.46± 0.15	3.54± 1.05	1.01± 0.72	5.42± 0.75	1.65± 0.56	1.67± 0.53	1.63± 0.43
6	0.63± 0.88	0.32± 0.96	0.35± 0.63	1.61± 0.77	1.1± 0.26	3.29± 0.39	1.71± 0.78	1.63± 0.63	1.20± 0.14
7	0.66± 0.89	0.31± 0.78	0.34± 0.96	1.72± 0.78	1.22± 0.63	3.69± 0.83	0.54± 0.46	0.2± 0.88	0.46± 0.63
8	0.65± 0.63	0.32± 0.23	0.37± 0.36	2.16± 0.13	1.84± 0.78	4.79± 0.68	1.13± 0.56	0.36± 0.37	1.88± 0.96
9	0.97± 0.14	0.61± 0.42	0.39± 0.44	2.18± 0.14	1.77± 0.41	4.61± 0.76	1.55± 0.43	0.72± 0.46	1.93± 0.84

Table A.9 (b) Effect of pH on the adsorption rate of Cadmium, Lead and Chromium ions

	Cadmium (%adsorption)			**Lead (%adsorption)**			**Chromium (%adsorption)**		
pH	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**	**ESD**	**EUP**	**EMR**
2	48.33	34.32	49.57	35.85	47.03	49.16	15.94	20.09	43.75
3	58.37	55.12	63.98	48.80	51.49	61.42	17.87	24.45	45.72
4	74.16	81.19	86.74	70.62	81.23	68.51	20.29	27.07	46.38
5	84.93	89.44	89.91	86.64	79.55	80.88	17.87	28.82	60.53
6	84.21	89.77	90.20	85.73	77.32	78.56	73.91	91.27	84.87
7	84.45	89.44	89.34	82.07	65.80	72.17	45.41	84.28	38.16
8	76.79	79.87	88.76	81.91	67.10	73.21	25.12	68.56	36.51
9	79.67	85.81	87.90	78.51	69.70	73.21	24.15	75.11	34.54

Table A.10 (a): Langmuir isotherm values for cadmium (Cd^{2+}) ion

Dosage (g)	Initial ion Conc. (mg/L)			Equilibrium ion Conc. (mg/L) ***Ca***			Mass of Adsorbate Adsorbed (mg),x			**Xe** mg/g			***Ca*/Xe** (g/L)		
	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR
0	4.18	3.03	3.47	4.18	3.03	3.47	0	0	0						
0.1	4.18	3.03	3.47	2.73	2.51	2.17	0.145	0.52	1.3	1.4500	0.1244	0.4290	1.8828	20.1765	5.0578
0.2	4.18	3.03	3.47	2.1	1.6	1.5	0.208	1.43	1.97	1.0400	0.3421	0.6502	2.0192	4.6769	2.3071
0.3	4.18	3.03	3.47	1.16	0.66	0.45	0.302	2.37	3.02	1.0067	0.5670	0.9967	1.1523	1.1641	0.4515
0.4	4.18	3.03	3.47	0.7	0.32	0.37	0.348	2.71	3.1	0.8700	0.6483	1.0231	0.8046	0.4936	0.3616
0.5	4.18	3.03	3.47	0.63	0.34	0.33	0.355	2.69	3.14	0.7100	0.6435	1.0363	0.8873	0.5283	0.3184
0.6	4.18	3.03	3.47	0.59	0.29	0.27	0.359	2.74	3.2	0.5983	0.6555	1.0561	0.9861	0.4424	0.2557
0.7	4.18	3.03	3.47	0.57	0.33	0.35	0.361	2.7	3.12	0.5157	0.6459	1.0297	1.1053	0.5109	0.3399

Table A.10 (b): Langmuir isotherm values for lead (Pb^{2+}) ion

Dosage (g)	Initial ion Conc. (mg/L)			Equilibrium ion Conc. (mg/L) ***Ca***			Mass of Adsorbate Adsorbed (mg),x			**Xe** mg/g			***Ca*/Xe** (g/L)		
	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR
0	12.05	5.38	17.21	12.05	5.38	17.21	0	0	0			0			
0.1	12.05	5.38	17.21	9.95	3.87	10.66	2.1	1.51	6.55	2.1000	0.0125	0.1217	4.7381	308.8311	87.5585
0.2	12.05	5.38	17.21	7.19	2.71	8.31	4.86	2.67	8.9	2.4300	0.0222	0.1654	2.9588	122.3052	50.2335
0.3	12.05	5.38	17.21	3.93	2.15	6.95	8.12	3.23	10.26	2.7067	0.0268	0.1907	1.4520	80.2090	36.4435
0.4	12.05	5.38	17.21	3.85	1.42	5.33	8.2	3.96	11.88	2.0500	0.0329	0.2208	1.8780	43.2096	24.1375
0.5	12.05	5.38	17.21	2.42	1.14	2.76	9.63	4.24	14.45	1.9260	0.0352	0.2686	1.2565	32.3986	10.2760
0.6	12.05	5.38	17.21	2.9	1.08	2.53	9.15	4.3	14.68	1.5250	0.0357	0.2729	1.9016	30.2651	9.2721
0.7	12.05	5.38	17.21	2.36	1.19	2.61	9.69	4.19	14.6	1.3843	0.0348	0.2714	1.7049	34.2232	9.6177

Table A.10 (c): Langmuir isotherm values for chromium (Cr^{3+}) ion

Dosage (g)	Initial ion Conc. (mg/L)			Equilibrium ion Conc. (mg/L) *Ca*			Mass of Adsorbate Adsorbed (mg),x			**Xe** mg/g			***Ca*/Xe** (g/L)		
	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR
0	2.07	2.29	3.04	2.07	2.29	3.04	0	0	0			0			
0.1	2.07	2.29	3.04	1.63	1.57	1.5	0.44	0.72	1.54	0.4400	0.0348	0.0672	3.7045	45.1375	22.3052
0.2	2.07	2.29	3.04	1.33	1.43	1.47	0.74	0.86	1.57	0.3700	0.0415	0.0686	3.5946	34.4198	21.4414
0.3	2.07	2.29	3.04	1.02	0.86	1.41	1.05	1.43	1.63	0.3500	0.0691	0.0712	2.9143	12.4490	19.8092
0.4	2.07	2.29	3.04	0.77	0.54	0.39	1.3	1.75	2.65	0.3250	0.0845	0.1157	2.3692	6.3874	3.3702
0.5	2.07	2.29	3.04	0.73	0.49	0.41	1.34	1.8	2.63	0.2680	0.0870	0.1148	2.7239	5.6350	3.5700
0.6	2.07	2.29	3.04	0.65	0.51	0.2	1.42	1.78	2.84	0.2367	0.0860	0.1240	2.7465	5.9309	1.6127
0.7	2.07	2.29	3.04	0.64	0.48	0.15	1.43	1.81	2.89	0.2043	0.0874	0.1262	3.1329	5.4895	1.1886

Table A.11 (a): Freundlich isotherm values for cadmium (Cd^{2+}) ion

Dosage (g)	Initial ion Conc. (mg/L)			Equlibrium ion Conc. (mg/L) Ca			Mass of Adsorbate Adsorbed (mg),x			Xe mg/g			*logXe*			*log **Ca***		
	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR
0	4.18	3.03	3.47	4.18	3.03	3.47	0	0	0							0.6212	0.4814	0.5403
0.1	4.18	3.03	3.47	2.73	2.51	2.17	0.145	0.052	0.13	0.1450	0.0012	0.0043	-0.8386	-2.9052	-2.3675	0.4362	0.3997	0.3365
0.2	4.18	3.03	3.47	2.1	1.6	1.5	0.208	0.143	1.97	0.1040	0.0034	0.0650	-0.9830	-2.4658	-1.1870	0.3222	0.2041	0.1761
0.3	4.18	3.03	3.47	1.16	0.66	0.45	0.302	0.237	3.02	0.1007	0.0057	0.0997	-0.9971	-2.2464	-1.0014	0.0645	-0.1805	-0.3468
0.4	4.18	3.03	3.47	0.7	0.32	0.37	0.348	0.271	3.1	0.0870	0.0065	0.1023	-1.0605	-2.1882	-0.9901	-0.1549	-0.4949	-0.4318
0.5	4.18	3.03	3.47	0.63	0.34	0.33	0.355	0.269	3.14	0.0710	0.0064	0.1036	-1.1487	-2.1914	-0.9845	-0.2007	-0.4685	-0.4815
0.6	4.18	3.03	3.47	0.59	0.29	0.27	0.359	0.274	3.2	0.0598	0.0066	0.1056	-1.2231	-2.1834	-0.9763	-0.2291	-0.5376	-0.5686
0.7	4.18	3.03	3.47	0.57	0.33	0.35	0.361	0.27	3.12	0.0516	0.0065	0.1030	-1.2876	-2.1898	-0.9873	-0.2441	-0.4815	-0.4559

Table 11.A (b): Freundlich isotherm values for lead (Pb^{2+}) ion

Dosage (g)	Initial ion Conc. (mg/L)			Equlibrium ion Conc. (mg/L) Ca			Mass of Adsorbate Adsorbed (mg),x			***Xe* mg/g**			**logXe**			**logCa**		
	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR
0	12.05	5.38	17.21	12.05	5.38	17.21	0	0	0			0				1.0810	0.7308	1.2358
0.1	12.05	5.38	17.21	9.95	3.87	10.66	0.21	0.151	0.655	2.1000	0.0125	0.1217	0.3222	-1.9020	-0.9145	0.9978	0.5877	1.0278
0.2	12.05	5.38	17.21	7.19	2.71	8.31	0.486	0.267	0.89	2.4300	0.0222	0.1654	0.3856	-1.6545	-0.7814	0.8567	0.4330	0.9196
0.3	12.05	5.38	17.21	3.93	2.15	6.95	0.812	0.323	1.026	2.7067	0.0268	0.1907	0.4324	-1.5718	-0.7196	0.5944	0.3324	0.8420
0.4	12.05	5.38	17.21	3.85	1.42	5.33	0.82	0.396	1.188	2.0500	0.0329	0.2208	0.3118	-1.4833	-0.6560	0.5855	0.1523	0.7267
0.5	12.05	5.38	17.21	2.42	1.14	2.76	0.963	0.424	1.445	1.9260	0.0352	0.2686	0.2847	-1.4536	-0.5709	0.3838	0.0569	0.4409
0.6	12.05	5.38	17.21	2.9	1.08	2.53	0.915	0.43	1.468	1.5250	0.0357	0.2729	0.1833	-1.4475	-0.5641	0.4624	0.0334	0.4031
0.7	12.05	5.38	17.21	2.36	1.19	2.61	0.969	0.419	1.46	1.3843	0.0348	0.2714	0.1412	-1.4588	-0.5664	0.3729	0.0755	0.4166

Table A.11 (c): Freundlich isotherm values for chromium (Cr^{3+}) ion

Dosage (g)	Initial ion Conc. (mg/L)			Equlibrium ion Conc. (mg/L) ***Ca***			Mass of Adsorbate Adsorbed (mg),x			*X* e mg/g			logXe			logCa		
	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR	ESD	EUP	EMR
0	2.07	2.29	3.04	2.07	2.29	3.04	0	0	0			0				0.3160	0.3598	0.4829
0.1	2.07	2.29	3.04	1.63	1.57	1.5	0.44	0.72	1.54	0.4400	0.0348	0.0672	-0.3565	-1.4586	-1.1723	0.2122	0.1959	0.1761
0.2	2.07	2.29	3.04	1.33	1.43	1.47	0.74	0.86	1.57	0.3700	0.0415	0.0686	-0.4318	-1.3815	-1.1639	0.1239	0.1553	0.1673
0.3	2.07	2.29	3.04	1.02	0.86	1.41	1.05	1.43	1.63	0.3500	0.0691	0.0712	-0.4559	-1.1606	-1.1476	0.0086	-0.0655	0.1492
0.4	2.07	2.29	3.04	0.77	0.54	0.39	1.3	1.75	2.65	0.3250	0.0845	0.1157	-0.4881	-1.0729	-0.9366	-0.1135	-0.2676	-0.4089
0.5	2.07	2.29	3.04	0.73	0.49	0.41	1.34	1.8	2.63	0.2680	0.0870	0.1148	-0.5719	-1.0607	-0.9399	-0.1367	-0.3098	-0.3872
0.6	2.07	2.29	3.04	0.65	0.51	0.2	1.42	1.78	2.84	0.2367	0.0860	0.1240	-0.6259	-1.0656	-0.9065	-0.1871	-0.2924	-0.6990
0.7	2.07	2.29	3.04	0.64	0.48	0.15	1.43	1.81	2.89	0.2043	0.0874	0.1262	-0.6898	-1.0583	-0.8989	-0.1938	-0.3188	-0.8239