PEANUT HUSKS FUNCTIONALIZED WITH CITRIC ACID AND ETHYLENE -1, 2-DIAMINE FOR REMOVAL OF LEAD (II) IONS FROM CONTAMINATED WATER

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DECLARATION

I hereby declare that this is my original work and has not been presented for the award of a degree or diploma in any university or other institution.

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We confirm that the work reported in this thesis was carried out by the candidate and submitted with our approval as University supervisors.

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DEDICATION

I dedicate this work to Divine Mercy

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometer
ATSDR	Agency for Toxic Substances and Diseases Registry
CMP	Peanut husks modified with citric acid
DMF	N,N-dimethylformamide
EAC	East African Community
EMP	Peanut husks modified with ethylene-1,2-diamine
FTIR	Fourier Transform Infrared
Pb	Lead metal
PATH	Program for Appropriate Technology in Health
rpm	Revolutions per minute
UMP	Unmodified peanut husks
WHO	World Health Organization
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

ABSTRACT

Consumption of water contaminated with heavy metals poses a major risk. Consequently, safe and effective treatment of contaminated water remains a topic of global concern. Lead is among the most prevalent heavy metal contaminants as it is widely used in metallic form. It is easily absorbed by the body through water intake. In body, lead inhibits the enzymes and induces generation of reactive oxygen species that intensifies oxidative stress. This mechanism makes lead neurotoxic, mutagenic, teratogenic and carcinogenic. Studies reveal that some parts of Tanzania have higher levels of lead than the recommended level by World Health Organization and East African Community of 0.01mg/L in drinking water. Although several water treatment methods are available, adsorption offers an attractive method for the removal of heavy metal in terms of cost of adsorbent production, simplicity of design and operation. Cellulose-carboxylate ion and 6-(2-aminoethylamino)-6-deoxycellulose (or called celen) are thermally stable and can be easily employed for the adsorption of cations from aqueous medium. Hence, this study was aimed at modifying the peanut husks with citric acid and ethylene-1,2-diamine to synthesize cellulose-carboxylate ion and celen respectively to determine the adsorption capacity and efficiency in the removal of Pb(II) ion from contaminated water. Peanut husks were collected from Dodoma region in Tanzania, washed, ground and modified with citric acid and ethylene-1,2-diamine to prepare adsorbents. FTIR confirmed the peanut husks to contain cellulose and that the citric acid and ethylene-1,2-diamine are anchored onto the cellulose. XRF revealed that the peanut husks contained zero percent of Pb metal and XRD proved the amorphous nature of the cellulose present in peanut husks. Batch experiments were carried out to determine the effect of pH, contact time, temperature, initial concentration and adsorbent dose on adsorption process. The experimental data were fitted in Langmuir and Freundlich isotherms and were found to fit best in Langmuir isotherm as it had the highest value of correlation coefficient of 0.998, 0.959 and 0.997 for UMP, CMP and EMP respectively. The maximum monolayer adsorption capacities were 18.8 mg/g for UMP, 11.36mg/g for CMP and 19.23mg/g for EMP. Based on the adsorption capacities, EMP is a better adsorbent than the rest. These results indicate that peanut husks tethered with citric acid and ethylene-1,2-diamine constitute a promising material for the development of an adsorption technology for the removal of Pb(II) ion from aqueous systems.

CHAPTER ONE

INTRODUCTION

1.1 Background

Water is essential for life as it enables and sustains life and human civilization (Falkenmark, 2020). Provision of safe and clean water to the citizenry is a critical concern and urgent priority globally and especially in the developing countries (Ahmed *et al*., 2004). Today, however, life is threatened and endangered by the serious water pollution. The water pollution is the addition of undesirable foreign matter into water that impairs the beneficial uses of water (Owa, 2013). These materials are those which are poisonous and harmful (heavy metals and chemicals) to life or those which either directly or indirectly reduce the dissolved oxygen content of natural water such as phosphates, nitrates and sulphates (Owa, 2013).

Increasing population, urbanization and industrialization have led to the decreased availability of water and deteriorated quality. Anthropogenic sources (industrial and agricultural activities) and other natural resources continue to add a threat to the water sources in both developing and developed countries (Chinnaiya and Wolfgang, 2005). Improper water management especially through treatment and disposal of solids and liquids due to uncontrolled and uncensored urbanization and industrialization has also increased vulnerability of water pollution by heavy metals and thus created increased demand for the little water available. Thus, water remediation is a critical global concern to save life.

Lead is a metal widely used in numerous industrial, domestic, agricultural, medical, technological processes. Lead finds its use in production of batteries, ammunition and

pipes, in x-ray shielding devices, cosmetics and toys, lead based paints, pipes and glazed pottery (Martin and Griswold, 2009). These uses have led to wide distribution of this metal in the environment as contaminants of many environmental systems (Tchounwou *et al.*, 2014). Lead is a systematic toxicant as it induces damage to many organs even when exposed to lower levels especially to the kidney, liver, skin, nose, endocrine and even the reproductive system (Martin and Griswold, 2009). Lead is also a probable human carcinogen (Silbergeld *et al*, 2000; Rousseau *et al*., 2007)

Due to its uses, inadequate handling and improper management and poor disposal methods, lead finds its way into water, contaminates and thus causes health effects to human beings. Most people in Tanzania rely on tap water, well water and unprotected springs for their household drinking water (PATH – Tanzania, 2013). Many studies have indicated the presence of heavy metals at significant levels in some parts of Tanzania. For example, significantly higher levels of Pb were recorded in Mwanza, (4.3±0.55) mg/L (Makokha *et al*., 2011); Ruvuma, 0.078 mg/L (Banzi *et al*., 2015); Dodoma, 0.0197mg/L (Knivsland, 2012) and Dar es Salaam, (0.453±0.276)mg/L (Mwenda, 2014). These are higher than the recommended levels by WHO and EAC which are 0.01 mg/L for Pb.

Peanut husks, like other agricultural by-products, have use in the remediation of heavy metals and other water contaminants (Li *et al*, 2008). Their cellulosic composition helps to bind and draw together the heavy metals from the aqueous medium by pure physio-chemical pathways of uptake (Igwe *et al.*, 2005). Presence of cellulose makes the peanut husks a great potential as an adsorbent in remediation of heavy metals and other contaminants from the aqueous medium. Cellulose contains large amount of

hydroxyl groups that give it hydrophilic properties to the natural fibers. Various chemical modifications bring about bonding of hydroxyl groups to several functional groups which provide covalent bond formation by the interaction of modifier agent and the surface centre (Eyley and Thielemans, 2014). The cellulosic derivatives proved to be more advantageous in removing heavy metals and other contaminants from the aqueous medium.

Conversion and modification of peanut husks and other agricultural products into metal adsorbents increases their values and makes them of great potential in reducing the level of certain metals in industrial and municipal waste water (Wafwoyo *et al.*, 1999). Subsequently, this research aimed at functionalizing peanut husks and creating value products that can effectively remediate contaminated water as a way of addressing and mitigating water problems and water borne diseases in the region and also globally.

1.2 Statement of problem

Majority of world's population resides in regions experiencing scarcity of clean and safe water (Rosegrant *et al*., 2002). The limited resource is threatened by overpopulation, poor management and ecological degradation. Surface and ground water resources in Tanzania are becoming polluted by human activities of agriculture, urbanization, industrialization and mining (Yhdego, 1991).

Among the most dangerously toxic pollutants released into the water bodies are the heavy metals such as arsenic, cadmium, mercury, chromium and lead which can cause serious adverse health effects (Borowska and Brzoska, 2015). Large amounts of lead metal in water have so far become a major and serious global concern due to its health

effects. Lead is non-degradable in the environment and it bioaccumulates. The studies of the toxicity of lead reveal that no blood-lead level appears to be safe to human health especially to young children (Assi *et al*., 2016). WHO estimates that 240 million people are overexposed to lead poisoning (Gottesfeld, 2016); which in 2017 accounted for 1.06 million deaths, with highest report being in lower and middle-income countries (WHO, 2019). This metal is reported to be neurotoxic (Lidsky and Scheider, 2003), mutagenic (Vij, 2009), teratogenic (Bellinger, 2005) and carcinogenic (Silbergeld, *et al*., 2000). Due to these and other serious poisoning effects, WHO has identified lead as one of chemicals of major public health concern that needs action by Member States to protect human health (WHO, 2019).

Studies have indicated the presence of lead metal in various sites at significant levels in some parts of Tanzania (Bitala *et al*., 2009, Makokha *et al*., 2011, Mwenda, 2014). It is therefore necessary to remove it from the waste and contaminated water for the beneficial use of both human beings and other living things. However, there is limited information reported on the removal of lead metal from water in Tanzania and more so on the use of the cellulose-carboxylate ion and celen (6-(2'-aminoethylamino)-6-deoxycellulose) synthesized from peanut husks for the remediation of Pb(II) ions from contaminated water. Thus, this research was aimed at modifying peanut husks with citric acid and ethylene-1,2-diamine to synthesize the cellulose-carboxylate ion and 6-(2'-aminoethylamino)-6-deoxycellulose (celen) respectively from peanut husks for the removal of Pb(II) from aqueous contaminated solution.

1.3 Justification of the study

Despite of the efforts to establish the levels of heavy metals, very little work has been done on how to remediate the water already polluted (Mwakaboko *et al*., 2014). The focus of this work was to develop a new waste water treatment method by using the modified and unmodified peanut husks which available and abundant that would supplement the adsorption treatment method. This research was aimed at coming out with one solution on how to remove the lead metal from the water to save the little water for both human beings and other living things. It was also aimed at improving the accessibility of better health and sanitation for communities in Tanzania and in turn help reduce the financial burden of medical treatment due to the waterborne diseases in the area. The research was further aimed at providing cheap means of water treatment.

1.3 Hypothesis

Functionalizing peanut husks with citric acid and ethylene -1, 2-diamine will enhance their efficiency and capacity to remove Pb(II) from the contaminated water.

1.4 Objectives

1.4.1 General Objective

To assess the potential of peanut husks functionalized with citric acid and ethylene -1, 2-diamine in remediation of water contaminated by Pb(II) ions.

1.4.2 Specific objectives

i.To determine chemical composition and crystalline phase in the raw peanut husks using XRF and XRD respectively.

ii. To functionalize and characterize the adsorbents derived from peanut husks by using citric acid and ethylene-1,2-diamine for adsorption of Pb(II)using FTIR.

iii. To determine the percentage removal of raw and functionalized peanut husks in removing Pb(II)ions from aqueous solution at varying parameters of pH, temperature, initial concentration, contact time and adsorbent dose.

iv. To determine the adsorption capacity of raw and functionalized peanut husks for Pb(II) ions from aqueous solution.

1.5 Scope and limitation

i. The study was restricted to the peanut husks collected from Dodoma region and not from the whole country of Tanzania.

ii. The research focused only on one heavy metal and only on one oxidation state: Pb(II). Other heavy metals or any other oxidation states of Pb were not considered.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metals and their toxicities in human beings

Heavy metals are defined as metals whose density exceeds 5 mg/mL (Jarup, 2003). Lead (Pb), cadmium (Cd), zinc (Zn), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn) are the most common toxic heavy metals in waste water (Daruibe *et al*., 2007). Some are essential micronutrients as they maintain the metabolism of the human body but can become toxic at high concentrations such as copper, manganese, iron and zinc (Fraga, 2005). Other heavy metals such as cadmium, mercury and lead have so far unknown role in living organism and are toxic even at low concentration (Cols *et al*., 2001)

Heavy metals may be released to the environment by natural means in small amount by leaching from rocks, airborne dusts, forest fires and vegetation (Ogoyi *et al*., 2011) or artificial means through the process of industrialization, urbanization and agriculture just to mention a few (Daruibe *et al*., 2007). Unlike many other pollutants in the environment, heavy metals are non-biodegradable which means cannot be converted into non-toxic derivatives and are intrinsically persistent in nature (Valls *et al*., 2000). Remediation processes are difficult and expensive. Ingestion and inhalation are the means by which human beings find exposed to these metals. As they are toxic, they damage or reduce functioning of mental and central nervous system. They also reduce energy levels and damage blood composition, kidney, lungs, liver and other vital organs (Simon *et al*., 2016)

2.2 Lead and its toxicity in human beings

Lead occurs in nature as a soft bluish-grey metal which turns into dark grey in air. It is found in the earth's crust in small amounts as lead compound in combination with other elements. It has atomic number of 82, atomic weight of 207.2 and density of 11.34 g/cm^3.Lead rarely occurs in its elemental state but rather in its +2 oxidation state (Pb^{2+}) in various ores as found in the environment throughout the earth (Sanders *et al*, 2009). Lead can be found both in inorganic form (such as compounds of carbonate, nitrate, chromate, tetraoxides) and in organic form such as tetraethyl and tetramethyl lead (Assi *et al*, 2016).

Anthropogenic activities that release high concentration of lead are fossil fuel burning, mining and manufacturing. Lead is an important metal which is used in manufacturing lead-acid batteries, ammunitions, metal production and shield x-ray devices, manufacture of paints, glass, pigment and other chemicals (Qaiser *et al*, 2007).

Lead finds its way into the human body mainly through inhalation, ingestion and dermal absorption (ATSDR, 2020). The adsorption of lead through the gastrointestinal means takes place in the duodenum by saturable mechanism. The adsorption depends on the physiological state of the individual and on the physicochemical characteristics of medium ingested. Adsorption is thus higher in children than in adults. Adsorption is affected by the nutritional iron status (Bannon *et al*., 2003) and dietary calcium. The absorbed lead is rapidly distributed from blood plasma simultaneously into erythrocytes, soft tissues, and bone (Vaziri, 2008).

It is worth noting that long time exposure to this metal affects the nervous system (leading to headache, poor attention span, irritability, loss of memory), digestive system (abdominal pain, loss of appetite and constipation), hematopoietic system, cardiovascular system (hypertension, cardiac attack, and atherosclerosis) endocrine system and reproductive system (Martine and Griswold, 2009). Acutely chronic exposure causes brain damage and could lead to death (Simeonov *et al*,. 2011). The major and direct effects associated with Pb poisoning are as follows:

2.2.1 Neurotoxic effects of Pb

A neurotoxin is a naturally occurring or synthetic chemical agent that can cause a functional or structural change in the nervous systemis (Harris and Blain, 2004). In that sense, a neurotoxin brings about inhibition, damage, destruction or impairment to the developing and mature tissue of nervous system (Spencer and Lein, 2014). Brain is the mainly sensitive part to the lead.

Lead neurotoxicity has both morphological and pharmacological effects. The former alters the development of nervous system from prenatal period through childhood. It disrupts key molecules during neuronal migration and differentiation (Silbergeld, 1992), interferes with synapse formation (Bressler and Goldstein, 1991) and glial cells get prematurely differentiated (Cookman *et al*., 1987). The latter results from the fact that lead substitutes for calcium and zinc and thus triggers the different processes such as interference of neurotransmitter release, disruption of dopaminergic and cholinergic systems

This effects lead to obvious effects within the brain (prefrontal celebral cortex, hippocampus and cerebellum) leading to brain damage, mental retardation, and behaviour problems. It can also lead nerve damage possibly causing Alzheimer's disease, Parkinson's disease, and schizophrenia (ATSDR, 2000).

2.2.2 Mutagenic and carcinogenic effects of Pb

A mutagen is a substance or agent that causes DNA impairment that results in the alteration of the DNA sequence and a carcinogen is a substance which has potential to induce cancer or increase its incidence to humans under certain condition and for prolonged period of time (Loechler, 2001). The two are related as they both primarily affect the genetic material, DNA.

Lead is considered both as a mutagen (Vij, 2009) and probable carcinogen (Silbergeld *et al*., 2000). The mechanism for both as agents is the direct DNA damage as it generates reactive oxygen and causes the oxidative damage to it. Lead inhibits the DNA synthesis and repair. Lead also replaces zinc in some proteins like protamines reducing its binding to recognition elements. And this brings alteration in gene expression. (Silbergeld *et al*., 2000). The epidemiological studies conducted reveal that cancer occurrence of stomach, lung and bladder has strong association in lead-occupationally exposed people (IARC, 2006)

2.2.3 Teratogenic effect of Pb

A teratogen is defined as a substance that causes birth defects and brings about malformation (Vargesson and Fraga, 2017). It is broadly explained as a chemical or physical agent, metabolic state that produces permanent pathologic or

pathopsychologic alteration in the offspring at exposure or circumstances that commonly affect it (Jamkhande *et al*., 2014). Lead significantly decreases the functioning of male reproductive organs. It also alters the testicular tissues in their histological pattern of testis (Elgawish and Abdelrazek, 2014). Lead exhibits reduction in the motility and density of sperms (spermatogenesis), reduces libido, causes abnormal prostatic function and sperm head, damages chromosomes, changes serum testosterone and bringing infertility (Telsman *et al*., 2000).

In women, lead is believed to cause miscarriages and stillbirths, prevalence of menstrual disturbances, pregnancy hypertension, and infertility (Flora, 2011). Moreover, the young mothers who are exposed to lead, can pass lead on to theirunborn foetuses as has been evidenced by the strong correlation between umbilical cord blood lead levels (Gardella, 2001).

2.2.4 Renal effects of Pb

Epidemiological studies show that most of lead is stored in the kidney and liver (Nakhaee *et al.*, 2019). The exposure to Pb causes biological changes that bring about kidney function alteration which leads to chronic kidney diseases (ATSDR, 2020). The acute Pb poisoning causes generalized deficiet of tubular transport mechanism and degenerate changes in the tubular epithelium (Rastogi, 2008). It also causes glomerular sclerosis, and interstitial fibrosis and proximal tubular nephropathy **(**Longhman-Adham, 1997). The chronic Pb poisoning cause high incidences of renal failure associated with hypertension and hyperuricemia (Rastogi, 2008).

2.2.5 Cardiovascular effects of Pb

Studies reveal that there a sufficient causal relationship between lead poisoning and adverse effects on cardiovascular system (Navas-Acien *et al*., 2007). Pb is proved to promote oxidative stress, limit the availability of and impair signalling of nitric oxide in the body (Vaziri, 2008). It primarily the production of the reactive oxygen species such as peroxides and superoxides that brings the dysfunction and diseases of the cardiovascular system (Vaziri, 2008).

The obvious effects of lead poisoning are the increased systolic and diastolic blood pressure, hypertension, atherosclerosis, altered cardiac conduction, increased risks of heart diseases and the increase in mortality due to cardiovascular diseases. (ATSDR, 2020).

2.3 Peanut husks

Peanuts are important subsistence food crops throughout the tropics. They are mainly grown for the kernel and the edible oil. Their husks are dry pericarp of the mature fibrous pods. As the production of peanuts expands, the problem of disposing the husks has been a challenge to many countries. The common means of handling the disposal has mostly been by incineration or incorporation in the soil land. The former emits smoke and particulate matter causing air pollution, the latter influences physical, biological and chemical properties of soil (Grandawa, 2014). However, many people in different parts of Tanzania just dispose them, creating their availability in large quantities in local markets and posing a disposal challenge as shown in figure 2.1

Accordingly, it is suggested that the transformation of the husks into valuable material, ingredient or products would be a better method to utilize them

Figure 2.1: Peanut husks disposed at Majengo Market in Dodoma City

2.3.1 Composition of peanut husks

Previous studies on characterization of physical and chemical properties of husks revealed that they are composed of cellulose, hemicelluloses and lignin containing polysaccharides, proteins, and lipids (Raju *et al.*, 2012) and thus offering different functional groups such as carboxyl, carbonyl, hydroxyl and amino groups that may be manipulated (Ossman *et al.*, 2014). Elemental composition reveals the presence of elements such as Ca, K, P, S, Mg, Na, Fe depending on the type of soil and the climate (Grandawa, 2014).

2.3.2 Uses of peanut husks

The husks are also used for manure as alternative in curbing agricultural waste problems and reduce waste management cost (Grandawa, 2014). They are used as fuel

in form of pelletized and smokeless briquette (Grandawa, 2014). The peanut husks have also been employed in usage for the dye removal and in removal of colour in vegetable oil (Hassanaein *et al.*, 2011). Largely, the peanut husks are used as adsorbents to remove heavy metals from the aqueous medium (Li *et al*., 2008; Salaam *et al.*, 2011; Ossman *et al.*, 2014).

2.4 The cellulosic material in the peanut husks

Cellulose is a linear biopolymer composed of D-anhydroglucose units $(C_6H_{10}O_5)_n$ linked with β(1-4) glucosidic bond (Wan Ngah *et al*., 2018). The degree of polymerization depends largely of the source cellulose material. Cellulose is mainly found in higher plants, some marine animals, fungi, bacteria and amoeba (Eyley and Thielemans, 2014). Cellulose is the main structural component of the cell wall and is responsible for many of its distinctive traits.

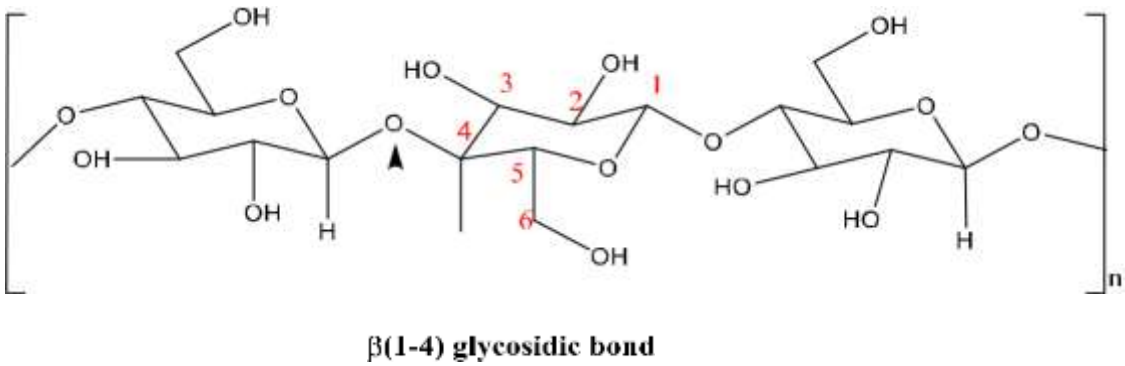

Figure 2.2: Molecular structure of cellulose
(Alcantara-Garcia and Ploeger, 2018)

Structurally, the unit is six membered heterocycle with an anomeric carbon in the chair conformation, where the attached hydroxyl group at C1 is in equatorial position in the β-anomer and in axial position in α-anomer (Eyley and Thielemans, 2014). Cellulose is oriented with -CH_2OH groups alternating above and below the plane of the cellulose molecule thus producing long, unbranched and straight chains (Festucci-Buselli *et al*., 2007). The absence of side chains allows cellulose molecules to lie close together and form rigid structures.

Cellulose has lots of hydroxyl groups. Each glucosyl ring has three active hydroxyl groups at C-2, C-3 and C-6 (Chen, 2014) The hydroxyl groups help in anchoring metal ions tightly onto cellulose fibers via ion−dipole interactions (He, 2003), and can also bond to several functional groups through different means of chemical modifications. Natural cellulose has a porous structure with 10-30 nm width which enhances its interaction with metal ions (Mark and Kroschwitz, 1985).The chemical modifications of cellulose provoke the formation of covalent bond that makes cellulose have advantageous and additional properties from the original form (Bezzera *et al*., 2015). These cellulose derivatives have advantage in removal of different contaminants from aqueous medium.

2.4 Functionalization of Peanut Husks in Relation to Enhanced Adsorption

Peanut husks contain cellulose which has a number of hydroxyl groups that can exchange with metal ions and that can be modified before its use (Li *et al*., 2008). Among the many types of modifications are the following:

2.4.1 Carbon Activation of peanut husks

Peanut husks processed through steam activation followed by air oxidation do produce granular activated carbons. The peanut husks get carbonized by subjecting to a high temperature of above 400C under inert atmosphere and then activated by either physical or chemical means (Ajala and Ali, 2020) These carbons have been found to have the effect of individually binding toxic metal ions that are commonly found in environment similar to the commercial coal-based carbons (Wilson *et al.*, 2006). Activation changes the surface area of peanut husks. The chemical structure of the carbon's surface (ie carbon-oxygen) greatly affects in turn its adsorption capacity (Salaam *et al.*, 2011). Moreover, peanut husks are reported to have been activated by conventional pyrolysis process and microwave irradiation followed by pyrolysis (Georgin *et al.*, 2016). This was modified for the removal of dye. It proved superior in surface area of the texture, volume size of the pore and finally higher adsorption capacity.

2.4.2 Acid-base modification of peanut husks

Acid modification has been reported to increase the carboxyl groups on the surface of the peanut husks thus increasing its adsorption capacity for the positively charged metal ions (Wafwoyo *et al.*, 1999; Chamarthy, 2001). Moreover, the report showed that the base wash increased the effectiveness of acid treated samples in single ion solution because the base increased the net negative charge on the surface of the adsorbent (Chamarthy, 2001).

2.4.3 Magnetic modification of peanut husks

Peanut husks were magnetically modified. This type of modification forms what is known as distinctive-enhanced Fe content whereby the iron takes primarily the form of magnetite (Rozumova *et al.,* 2016). This was used in adsorbing of Cd, Pb and Zn ions from aqueous solution as well as their desorption. Peanut husks are also reported to have been modified by simply contacting with a water-based magnetic fluid (Safarik *et al.,* 2010). The modification performed with perchloric acid stabilized ferrofliud resulted in adsorption of ion oxide nanoparticles into surface for the removal of water soluble dyes, giving relatively high results.

2.5 Modification of peanut husks by citric acid and ethylene-1,2-diamine

2.5.1 Citric acid modification of peanut husks

Citric acid is a tricarboxylic organic acid. This acid has hydroxyl (-OH) and carbonyl (-COOH) groups in its structure which account as very good groups for the metal chelating ability (Liu *et al*., 2018). The hydroxyl and carbonyl groups can also be used as linking groups for anchoring on any macromolecular supporter (Zhang *et al*., 2019). The lone pairs in the linking atoms provide a good metal chelating ability towards metal ions (Liu *et al*., 2018). Due to these properties, citric acid has been employed in many different modifications and functionalization of agricultural material for the adsorption of metal ions.

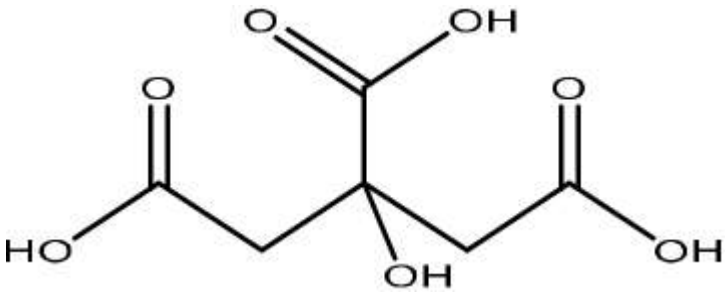

Figure 2.3: Molecular structure of citric acid (Show *et al*., 2015).

Citric acid combines with various cellulosic components of peanut husks and adds carboxyl moieties to the by-product substrate called carboxylate ion which is a hard base having high occupied molecular orbital (HOMO) of lowest energy; it is stable with sufficiently additional negative charges which can be translated into greater metal ion adsorption. Therefore, it can easily interact with both hard and intermediate acids, with higher total ion capacity among adsorbents especially in comparison to the other resins (Marshall *et al.*, 2000). The affinity of hard acids and bases for each other is mainly ionic in nature.

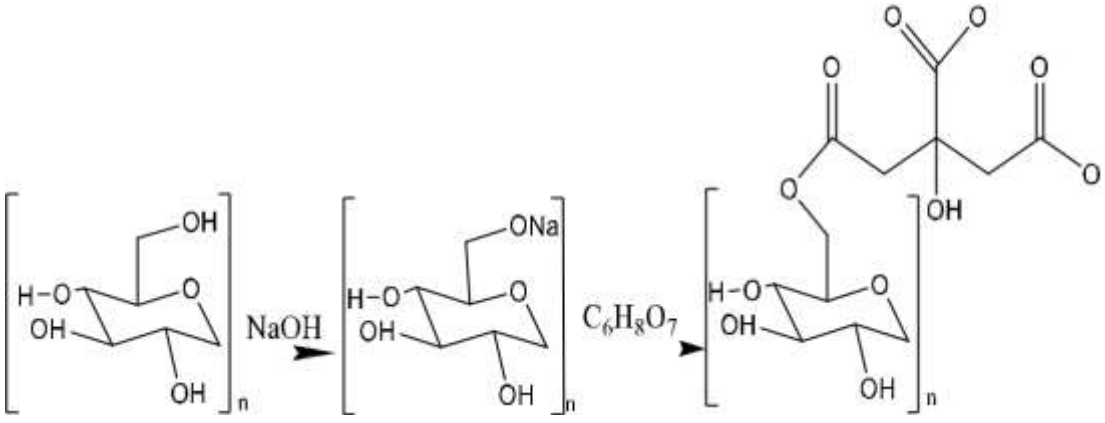

Figure 2.4: Reaction scheme of cellulose with citric acid (Adopted from Bezzera *et al*.,2015)

2.5.2 Ethylene-1, 2-diamine modification of peanut husks

Ethylene-1,2-diamine is an organic compound of low molecular weight with a relative low kinetic diameter. It contains terminal amino group which can easily interact with open metal sites, thus providing the basicity for the free amine group. It is used as chelating agent. Ethylene-1,2-diamine is a molecule in which intramolecular hydrogen bonds form (Xu *et al*,2006). Due to this property, ethylene-1,2-diamine is used as a building block for many chemical compounds

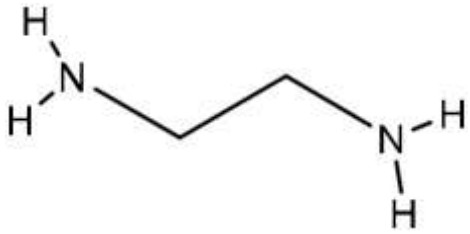

Figure 2.5: Molecular structure of ethylene-1,2-diamine
(www.sigmaaldrich.com).

Molecular merging of ethylene-1, 2-diamine increases the number of carbon in the structure of cellulose, by giving rise to C7and C8 (Eyley and Thielemans, 2014) as seen in Figure 2.6 below. The molecular reactions (inter and intra) found in peanut husks give rise to its organization and the amorphous crystalline arrangement. The celen is also a thermally stable matrix. The advantage over other functionalization is that it leads to formation of large number of basic centres (amine groups) held to the chain, which gives higher adsorption values (Bezerra *et al*., 2015). The present amine groups that covalently get bonded to the cellulose backbone have the capacity to adsorb cations from the aqueous medium because of the compexing nature of the basic centres found at the solid-liquid interface (Bezerra *et al*., 2015).

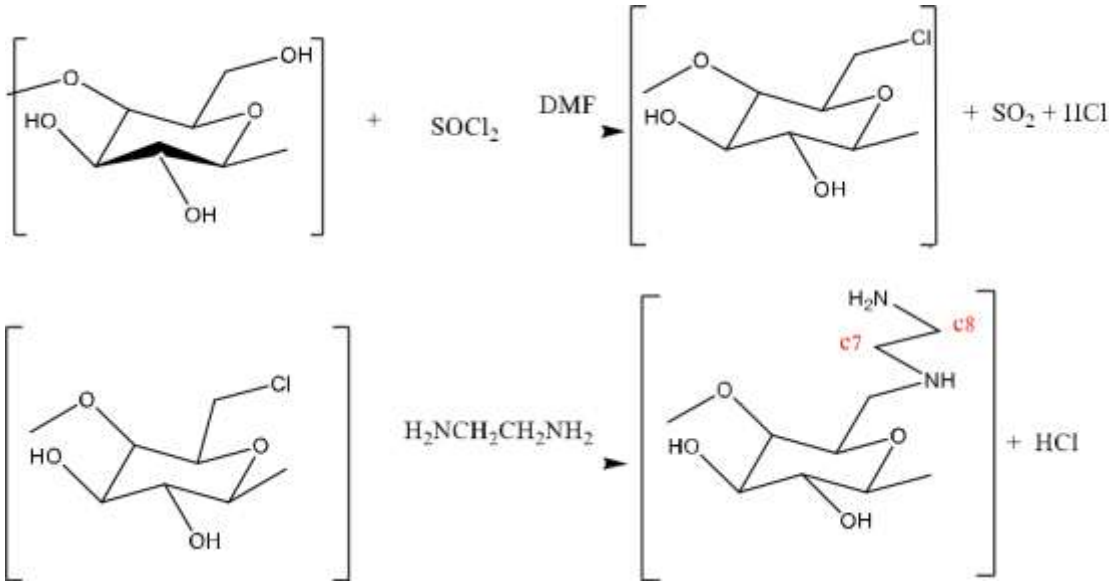

Figure 2.6: Reaction scheme of cellulose with thionyl chlorine and the chlorinated cellulose with enthylene-1,2-diamine
(Bezzera *et al*., 2015)

2.6 Treatment of waste water contaminated by heavy metals

Water treatment has called the attention of the world today as means to combat the challenges of pollution effects and water scarcity. There are several methods that are used in treatment of waste water.

Ion exchange is a method of removing contaminants from water through exchange of another substance which both must be dissolved and having the same type of electrical charge. It is widely used in chemical analysis, purification and separation of radioisotopes and water treatment (Luca *et al*, 2009) due to its advantages of high treatment capacity, high removal efficiency and fast kinetics (Kang *et al*., 2004) Drawbacks of this process include the regeneration of the resin. This must be done because the resin gets exhausted when the ions in it have mostly been replaced by the ions that are being removed from the solution (Kurniawan *et al*., 2006). As such it

produces volumes of regenerant solution which requires to be treated before discharging it (Eizel and Tseng, 1985). It has also a high chemical cost per unit metal

Chemical Precipitation is a process based on to produce insoluble metal precipitation by reacting the dissolved metal in solution and the precipitant. The water treated is decanted and appropriately discharged and re-used. This process is effective since it is simple and inexpensive as widely used in industries (Parma and Thakur, 2013). The precipitants (coagulants and flocculants) are used to increase the particle size by aggregation and removed as sludge. The resulting insoluble precipitates are hydroxides, sulphides, carbonates and phosphates (Ku and Jung, 2001). The mechanism for heavy metal removal is presented in equation 2.1.This process has a number of drawbacks: huge sludge production which requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, large amount of chemicals to reduce the metals to acceptable level of discharge and the long term environmental impact of the sludge disposal (Aziz *et al*., 2004).

$M^{n+}_{(aq)} + n(OH)^{-}_{(aq)} \rightarrow M(OH)_{n(s)}$ .....equation 2.1

Where M^{n+} represents the dissolved metal ion, OH^{-} represents precipitant and $M(OH)_n$ represents the insoluble metal hydroxide.

Reverse osmosis is a process of separation whereby pressure is used to force the solution through a semi-permeable membrane retaining the solute on one side while passing the pure solvent to the other side. Pressure applied to the concentrated solution reverses the natural direction of flow as to force the water across the membrane from concentrated solution into the more dilute solution (Keen *et al.*, 2005)**.** Drawback of

this process is the high cost of running and that it may not remove all the contaminants.

Adsorption is found to be the alternative to the above methods. It is a mass transfer process that involves accumulation of substances at the interface of the two phases. The substances are bound by physical and chemical interactions of solids. Different methods of adsorption have been used in water treatment such as activated carbon, animal by-products (Kar and Misra, 2004; Ajayi *et al*, 2005) and marine microorganisms (Vijayaraghavan *et al*. 2004). But the cellulose based materials have shown good metal ion adsorptive capacity due to the contained cellulose, lignin, carbohydrates etc.

Studies have shown that adsorption especially by agricultural materials has advantages over the other methods of wastewater treatment. Crini (2004) stipulated the advantages as follows:

a. They are low cost material since they are obtained from the natural raw material.
b. They are cost effective due to easy preparation with less expensive reagents.
c. High capacity and rate of adsorption together with high effluency and selectivity in detoxification of concentrated and dilute solutions make them efficient for pollutant removal at different concentrations.
d. The repetitive functional groups provide good chelating and complexing character for wide variety of pollutants (heavy metals, dyes).
e. The various functional groups can be substituted to selectively improve adsorption capacity.

f. They are amphiphilic in character since they are crosslinked. This character makes them so appealing since they are both hydrophilic and hydrophobic.
g. They are environmentally friendly.

2.7 Adsorption Studies

Adsorption is a process in which a molecular, atomic or ionic species of one substance gets accumulated at the surface of another where the concentration of the adsorbed substance is more at the surface than in the hulk (Barakat, 2011). When the two phases come into contact, an interface is created at which the constituent particles of the either of the two phases tend to accumulate. The adsorbent may be a solid or liquid. The solid ones are such as minerals, organic or biological origin, agricultural wastes, industrial by-products, zeolites, biomass and polymeric materials (Crist *et al.*, 1996)

Adsorption is driven by the surface atoms in an adsorbent. The atoms possess unbalanced physical forces and chemical bond forces. These forces come into existence as soon as a solid piece is broken into two to develop two new surfaces. When the new surface is created, some of the forces are left free to attract the gases or solutes and hold them onto the surface.

Factors affecting the adsorption especially on solids are the nature and the adsorbent's surface area, temperature and activation of the adsorbent (Jain, 2005), initial concentration, pH of solution, agitation time, adsorption dosage and shaking speed (Nawar *et al.*, 2013).

2.7.1 Isotherm models

The adsorption isotherm is the equation that describes the molecule distribution between the two phases (liquid and solid) when equilibrium state is reached by the adsorption process (Macharia, 2015). It shows the relationship between the amount of the adsorbate and the extent of absorption at any fixed or given temperature. There are commonly two models that are used especially for the wastewater treatment. These are:

2.7.1.1 Freundlich isotherm

This model is a multi-site isotherm. It deals with the heterogeous adsorbent surface with different adsorption sites (Oubagaranadin *et al*., 2007). The ratio of the amount of solute adsorbed on to a given mass of sorbent to the concentration of the solute in solution is not constant at given concentration.

It is given by the equation $q_e \quad K_f C_n^{\frac{1}{n}}$ **.....** equation 2.2

When in linearization gives $\log q_e \ \log K_f \quad \frac{1}{n} \log C_e$ equation 2.3

Where K_f = adsorption capacity constant, n= intensity and C_e = metal concentration in the equilibrium. Plotting a graph of log q_e versus log C_e gives a straight line which is used in determining K_f and n.

2.7.1.2 Langmuir isotherm

This model takes into assumption and is valid for monolayer coverage, equilibrium model and that all adsorption sites are equally probable and that the sorbent is not transmitted in the plane of the surface even on the adjacent sites (Boukhiar *et al*.,

2008). The sorption occurs on a homogenous surface, at fixed sites and can hold one adsorbate molecule at a time.

It is expressed as $q_e \quad \frac{bQ_{\max}C_{eq}}{1\ bC_{eq}}$ equation 2.4

This equation in linearization becomes $\frac{C_{eq}}{q_{eq}} \quad \frac{1}{KQ_{\max}} \quad \frac{C_{eq}}{Q_{\max}}$ equation 2.5

Where q_e= amount of the metal ion adsorbed per gram of the adsorbent at equilibrium, C_{eq} = solute concentration in aqueous solution at equilibrium,

Q_{max} = adsorption capacity when the surface is fully covered with

ions, b = affinity constant for binding sites.

A plot of $\frac{C_{eq}}{q_{eq}}$ versus C_{eq} gives a straight line where $\frac{1}{KQ_{\max}}$ is line intercept and $\frac{1}{Q_{\max}}$ is the slope.

2.8 Methods of analysis

2.8.1 Fourier Transform Infrared (FTIR)

It is a technique of analysis used in identification of organic materials and/or in some cases inorganic ones. It is the absorption of infrared radiation that is measured by this technique by the sample material versus wavelength. Infrared radiations are of low energy and when they interact with matter they excite the molecules causing them to vibrate or rotate (Park *et al*., 2007).The vibration transitions correspond to their characteristic bonds natural frequencies (Crist *et al*., 1996). The infrared absorption bands identify molecular components and structures.

When infrared radiation illuminates the material, the absorbed IR radiation causes the molecules to get excited into a higher vibrational state. The wavelength of light absorbed by particular molecule is function of energy difference between the at-rest and excited vibrational states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

The FTIR spectrometer uses an interferometer to modulate the wavelength from a broadband infrared source based on Michelson interferometry, which analyses a wide range of radiation wavelength simultaneously (Perkin-Elmer, 1957). The signal produced is processed by a mathematical process called Fourier Transform to produce IR spectrum (Skoog *et al.*, 2007). The kinds of functional groups available can be identified by comparison between the absorptions seen in the experimental spectrum and the literature absorption of the different functional groups and hence figure out a list of possible identities for the present bonds (Feng and Guo, 2009)

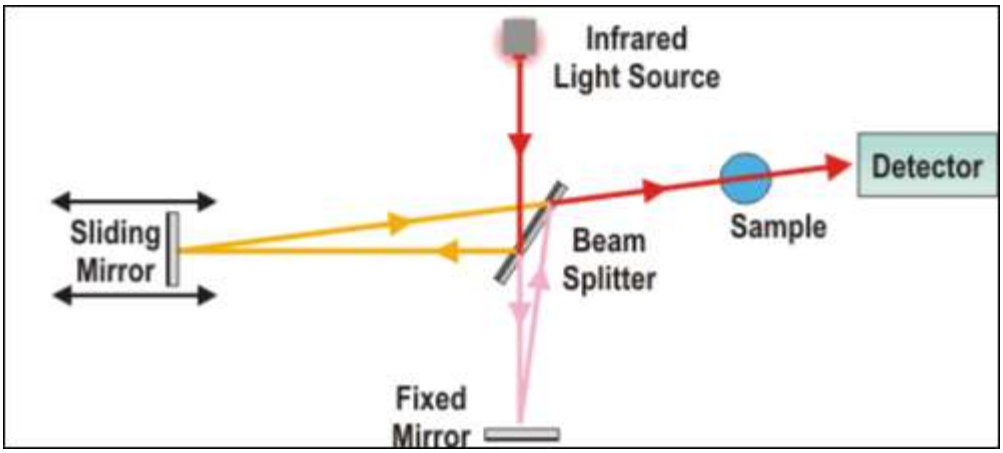

Figure 2.7: Schematic representation of FTRI instrumentation (instrumentatioforum.com)

2.8.2 Atomic Absorption Spectrometer (AAS)

It is an analytical technique which is used to study absorption of electromagnetic radiation in manner in which is associated with molecular structure. This technique measures the concentration of elements in the sample through their light absorption. It is somewhat simple and reliable as it uses visible light radiation by free atoms to figure out the contents of different elements.

AAS works on the fact that a beam of electromagnetic radiation passes through the substance. Following the wavelength of radiation, that radiation may be absorbed or transmitted.

The source of light (hollow cathode or electrodeless discharge lamp) gives a spectrum particularly intended for the element of which is made. This light is then adjusted into the monochromator through the sample cell. There must be electrical adjustment or mechanical shaping of the light source to differentiate this source light from sample cell emission. The monochromator separates the rays of light. Thus, the isolated specific light wavelength then goes to the photomultiplier tube detector. An electrical current gets generated relying on the light intensity and manufactured by the instrument electronics. The electronics determine the amount of light attenuation in the sample cell and change those readings to the actual sample concentration. With single-beam systems, a short warm-up period is required to allow the source lamp to stabilize. The spectrometer is usually placed between the atomizer and the detector to reduce the effect of the emission from the atomizer (Skoog *et al*., 2004).

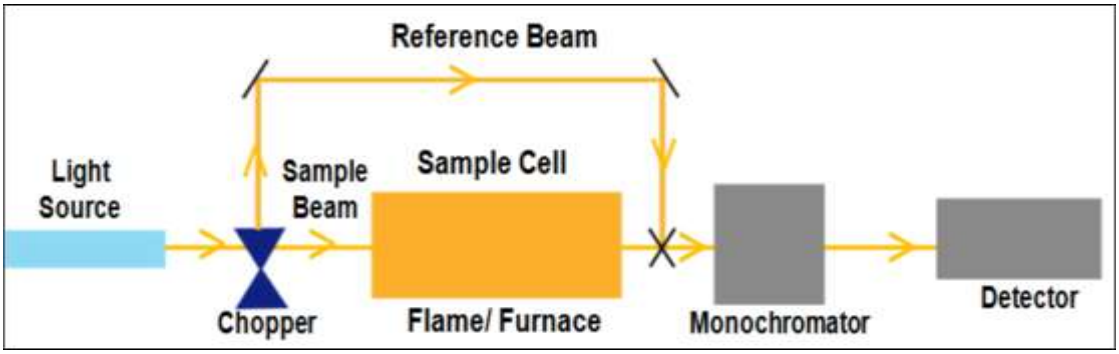

Figure 2.8: Schematic representation of AAS instrumentation
(lab-training.com)

2.8.3 X-Ray Fluorescence (XRF)

XRF is a non-destructive technique of analysis both qualitative and quantitative of chemical elements by measuring wavelength and intensities of their X-ray spectral lines as given by secondary excitation. The important components of XRF are a source, a sample and a detector. As the source illuminates the sample, the detector does measure the fluorescence radiation as given from the sample.

As the element is put in a beam of x-rays, the rays become absorbed by some atoms which become ionized (Young *et al*, 2000). From the higher energy level, the electron falls to a lower energy level left by inner electron and thus gives x-rays characteristic of wavelength (Skoog and Leavy, 1992) by a process known as x-ray fluorescence. The energy of excitation that comes from the inner atom is transferred to one of the outer electrons. This makes it to be given out from the electron. This process is called a competing process.

Presence of many elements in a sample provides the use of wavelength dispersive spectrometer to allow separating the complex emitted x-ray spectrum into different

characteristic wavelengths for each elements present. XRF therefore is used to identify an element by measuring its characteristic x-remission length and energy. This method also gives room for the quantification of an element by first measuring the characteristic line intensity emitted and then relating it to elemental concentration. The peak energy is used to identify the element present (qualitative analysis) and the peak intensity gives the relevant or absolute elemental composition (quantitative analysis) (Fified and Kealy, 1995).

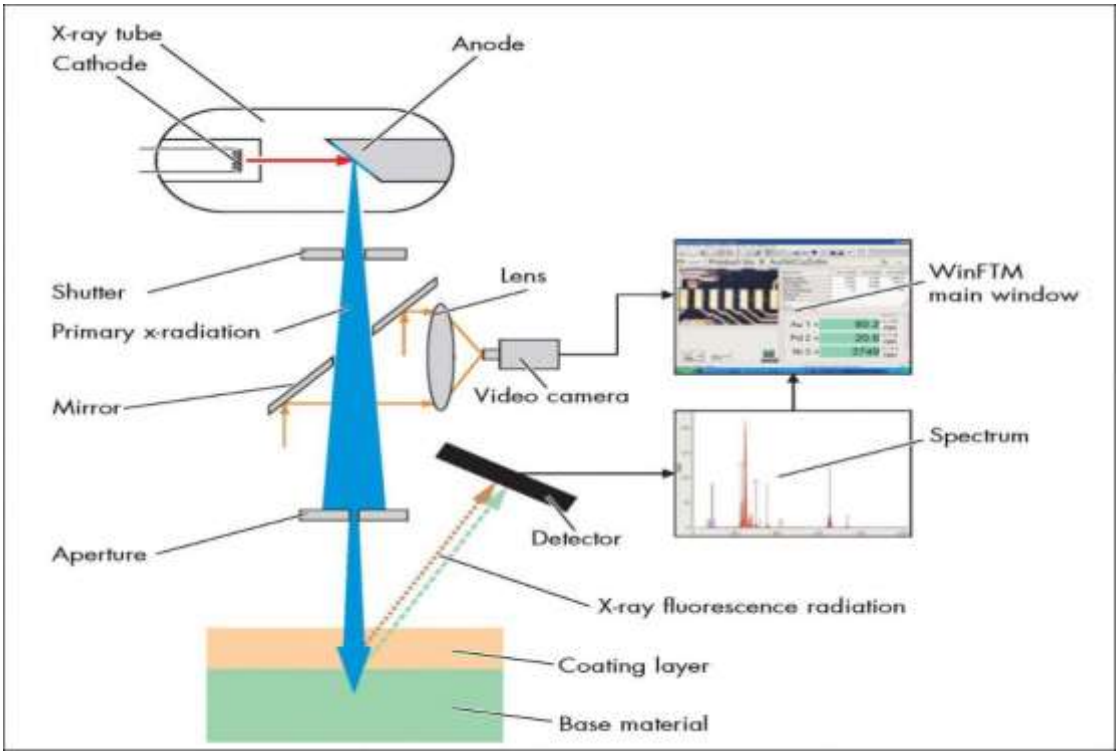

Figure 2.9: Schematic representation of XRF instrumentation (xrf-spectroscopy.com)

2.8.4 X-Ray Diffraction (XRD)

XRD is a method of analysis that is non-destructive. It is use to identify and quantitatively determine various crystalline forms called phases. Comparison of X-ray

diffraction patterns leads to identification of phases. As the radiation enters a crystalline substance and gets scattered, thus the diffraction occurs. Direction and intensity of diffraction are affected by orientation of crystal lattice of radiation.

The X-rays passing through a crystalline material produce patterns that inform about the size and the shape of the unit cell. As the X-rays pass through a crystal, there is always a bending at various angles. This process is called diffraction. Interaction of X-rays with electron in matter brings about scattering of the rays by the electron cloud of atoms. The angles at which this X-rays are diffracted is determined by the distance between the adjacent layers of atoms or ions. The X-rays that come into contact with adjacent layers can add their energies constructively when they are in phase. This gives out dots on a detector. Detection of an X-ray beam diffracted from a lattice plane happens when there is correct orientation of X-ray source, sample and detector which usually gives the Bragg diffraction.

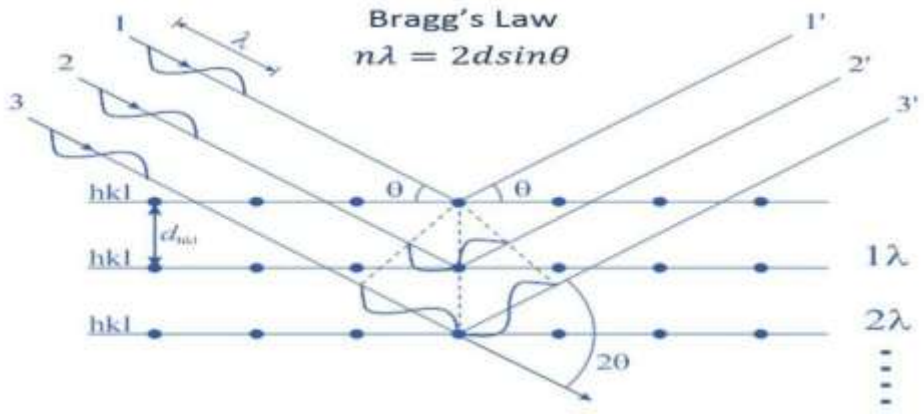

Figure 2.10: Bragg's law
(publish.illinos.com)

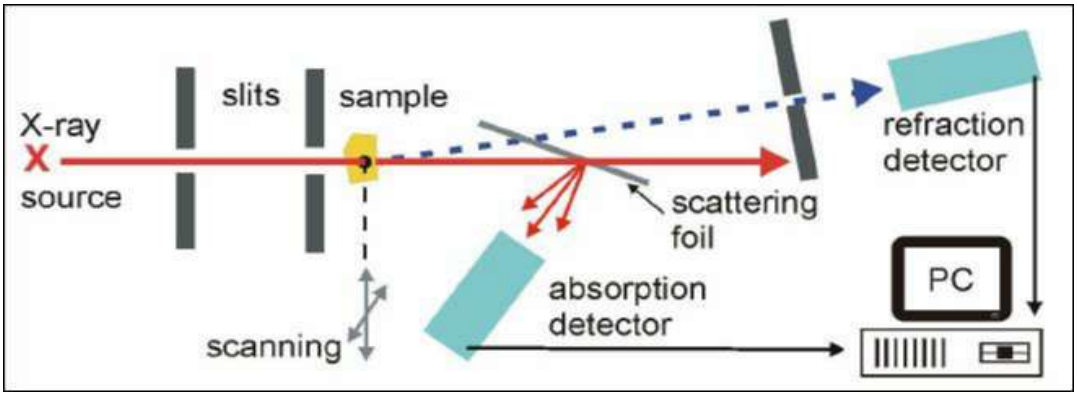

Figure 2.11: Schematic representation of XRD instrumentation
(gpatindia.com)

2.9 Factors affecting adsorption of metal ions

Several factors influence the adsorption efficiencies of adsorbents. A number of adsorption studies have reported pH, contact time, temperature, initial metal ions concentration and adsorbent dose as the main parameters that affect the adsorption capacities of the adsorbents (Nawar *et al.*, 2013).

2.9.1 Effect of pH

The metal ions adsorption is influenced by the pH by determining the adsorbent surface characteristics and pH also influences the metal ion speciation (Singh *et al.*, 2006). The pH dependence occurs when metal ions and protons compete for the adsorbent's adsorptive sites such as carbonyl and amine group on the adsorbent surface (Dönmez and Aksu, 2002).

The decrease in competition between proton and metal cations for the same functional groups explains the basis of increase in metal removal with increase in pH. This relationship between metal removal and pH can also be determined by lower electrostatic repulsion between metal cations and the surface as result of decrease in

positive charge of the adsorbent. At very low pH, there is very high number of H^+ ions which reduces the adsorption of metal ions.

2.9.2 Effect of temperature

The effect of temperature is noted in the stability of metal ion species in solution. As temperature increases, there is usually low viscosity and high versatility of the liquid or solution. This increases the adsorbate diffusion rate across the external pores of the adsorbate particle (Ozer and Ozer, 2003).Owing to fact that chemical process can be either exothermic or endothermic, temperature also determines the equilibrium capacity (Ozer and Ozer, 2003).

2.9.3 Effect of adsorbent dose

There is a directly proportional relationship between the adsorption efficiency and adsorbent dosage. Increase of adsorbent dose increases the adsorption efficiency of adsorbent (Xing *et al*., 2011) because the adsorptions sites are more available. However, the adsorptions density is reduced by unsaturated adsorptions sites and particle interactions caused by high adsorbent concentrations.

2.9.4 Effect of contact time

At the initial stage of adsorption, there is good availability of vacant surface sites and high solute concentration gradient. As time goes there develop repulsive forces between the solute molecules on the solid phase and the bulk liquid phase. This decreases the number of adsorption sites by making it difficult for the remaining vacant surface sites to be occupied (Yang *et al*., 1999).

2.9.5 Effect of initial concentration

The relationship between the adsorption capacity and ion concentration is inversely proportional. Increase in ion concentration decreases the adsorption capacity. This is affected by the saturation of the binding sites, although there is an increase in amount of absorbed ion with increase in initial concentration. Thus, at high concentration many adsorbents are ineffective while at low metal ion concentration they have high efficiency (Gadd, 1990).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Chemicals, apparatus and instruments

3.1.1 Chemicals and reagents

All chemicals and reagents used were of analytical grade purchased from Sigma Aldrich (Germany). They include lead nitrate, citric acid, sodium hydroxide, N-N-dimethylformamide (DMF), thionyl chloride, ethylene-1,2- diamine, ammonium hydroxide and nitric acid.

3.1.2 Apparatus and instrumentations

The apparati for the laboratory experiments were all well cleaned using running tap water and well rinsed with distilled water. The surface functionality of peanut husks was analyzed using FTIR (IRTracer-100 SHIMADZU)from Kenyatta University Chemistry Laboratory and XRD (D2 Phaser Model-Bruker) from Kenya Geological Department and Mining in Nairobi, Kenya. Elemental composition of the (sample) peanut husks was analyzed using XRF (model S1 Titan 800) from Kenya Geological Department and Mining in Nairobi. Batch experiments were done by shaking the samples at constant speeds using an electric shaker (WiseShake SHR-2D model) at Kenyatta University Chemistry Laboratory and the residual metal ions were analyzed and quantified using AAS (AA-6300 SHIMADZU model) from Kenya Geological Department and Mining. Other equipment used include; an electric weighing balance (ATX 224 SHIMADZU), an oven (WTC binder), grinding mill (Retsch SR 200 model), pH meter (OHAUS STARTER 2000 model) and water bath (model KOTTERMANN LABORTECHNIR) from Kenyatta University Chemistry Laboratory.

3.2 Sampling

Peanut husks were collected randomly from the local farms in Dodoma region whose geographical location is Latitude: 6° 9' 46.6524" S and Longitude: 35° 45' 5.7852" E which is found in central Tanzania.

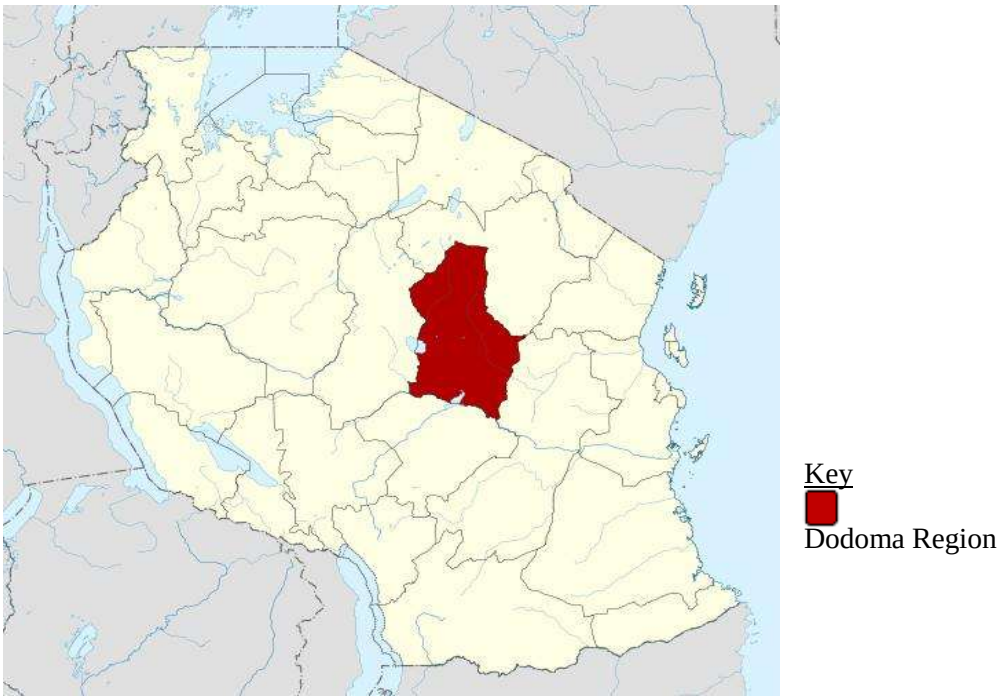

Figure 3.1: The map of Tanzania
(map.svg by Semhur, retrieved on 04/08/2021)

The soil and sand from the peanut husks were removed by washing with clean tap water and rinsed with distilled water. The washed peanut husks were dried at room temperature ground a using laboratory mill, sieved and stored for further use and modification per this study.

Plate 3.1: Picture of unmodified peanut husk (UMP)

3.3 Sample preparation

3.3.1 Modification of peanut husks with citric acid

A sample of 25g of ground peanut husks was placed in a beaker and 40mL of 0.1M of NaOH were added. Base treatment with NaOH is done to break the covalent association that exists between the lignocelluloses components, to hydrolyse hemicelluloses and to polymerize lignin for adsorption enhancement (Fathy *et al*., 2013), and to remove the fats and wax from the surface of the cellulosic material; thereby revealing the reactive functional groups (Ndazi *et al*., 2007). The mixture was stirred for 45 minutes and filtered. The mixture was washed with water for 20 minutes and thereafter rinsed for 30 minutes, filtered using Whatman filter paper and then dried on stainless steel trays in open air. To the resulting material, 150mL of 0.6M citric acid solution was added, well stirred for 30 minutes, filtered using Whatman filter paper and the residue dried. The acid treated peanut husks were washed in hot water until the effluent/filtrate turned no turbid upon mixing it in equal volume with

lead (II) nitrate in buffer solution at pH 4.8 (Wafwoyo *et al*., 1999). The lead (II) nitrate solution is used here to confirm that excess of citric acid was completely removed from the prepared adsorbent (Fathy *et al*., 2013). The mixture was filtered and dried. It was then characterized by FTIR to confirm the anchored functional group.

Plate 3.2: Picture of peanut husk modified with citric acid (CMP)

3.3.2 Modification of peanut husks with ethylene-1,2-diamine

The sample of 35 g of ground peanut husks was activated at 80 ˚C for 12 hours. The resulting material was cooled in a desiccator. After the cooling, the sample was suspended in a 600 mL of N-N-dimethylformamide (DMF). Drop wise addition of 105 mL of thionyl chloride ($SOCl_2$) at 80˚C followed with mechanical stirring (Drake *et al*., 1996). After the mixing is through, stirring was continued at the same temperature for 3 hours. Dilute ammonium hydroxide solution was used to wash the resulting mixture to attain neutral pH.

Since the reaction consists in allogeneic derivative synthesis, chlorine addition is preferably more effective. Thus thionyl chloride, being a very effective reagent, is used for the biopolymer chlorination through nucleophilic attack on the hydroxyl group of the cellulosic material which results in chlorine atom pending in the polymer structure (Bezzera *et al*., 2015). The chlorine atom is more reactive that the original hydroxyl group.

The resulting material was separated by filtration through a sintered glass crucible and dried under vacuum at room temperature (Drake *et al*., 1996).The chlorinated peanut husk biomaterial was refluxed with 175 mL of ethylene-1, 2-diamine (ratio of 1 to 5) for 3 hours. Filtration of this resulting mixture was then done through a sintered glass crucible and the solid material dried in a vacuum at room temperature for 24 hours. The presence of anchored functional groups was confirmed with FTIR (Drake *et al*., 1996).

Plate 3.3: Picture of peanut husk modified with ethylene-1,2-diamine (EMP)

3.4 Characterization of peanut husks

3.4.1 X-Ray Fluorescence (XRF) analysis

The elemental composition of the unmodified peanut husk was analyzed using XRF to ascertain the absence of any trace lead metal that might interfere with the experiment. The sample was put into the holder, then X-rays from the 4 W excitation source set between 6-50 kV and 5-200 mA were allowed to irradiate the sample and thus the sample emitted fluorescent X-rays with discrete energies. The energy intensities were then measured by the detector for the percentage composition of the component.

3.4.2 X-Ray Diffraction (XRD) analysis

The sample (unmodified peanut husks) was analysed for its crystalline and amorphous nature using XRD (D2 Phaser Model-Bruker) with Cu Kα radiations at the operating power of 40 kv and 40 mA with a graphite monochromator (λ=1.54060 À) at a scanning speed of 3º 2 /min within diffractions angle ranging from 15 to 40º.

3.4.3 Fourier Transform Infra-Red (FTIR) analysis

FTIR analysis was used to verify and confirm the functional groups of the sample before and after modification. The sample for the analysis was prepared by mixing the peanut husks and the grade potassium bromide (window material) to form a pellet. The pellet was examined using FTIR spectrophotometer and the FTIR spectra were recorded in the mid-infrared range of 350 cm^{-1} - 4600 cm^{-1} (Naja *et al*., 2005).

3.5 Preparation of stock solution, working solution and calibration standards

Preparation of standard stock solution of lead (II) was done by dissolving 1.6 g of lead (II) nitrate in distilled water in 1000 mL volumetric flask. The solution was made up to the mark. Preparation of the working solution was then done from the stock

solution by placing 100mL of the stock into 1000 mL volumetric flask and adding it with distilled water to the mark.

3.6 Batch adsorption experiments

Adsorbent dose, pH, contact time, temperature and initial concentration were the parameters considered in carrying batch experiments to investigate their influence and check the possible maximum metal ions removal.

3.6.1 Optimization of dosage

In determining the optimum dosage for Pb (II) ions removal at equilibrium, the adsorbent dose was varied from 0.02 g, 0.05 g, 0.1 g, 0.15 g to 0.3 g. This experiment was carried out at 25^{o}C, 5.5 pH and 150 rpm shaken for 1 hour. It was then filtered and analyzed for the metal ion adsorption.

3.6.2 Optimization of pH

Different pH values of 2, 4 7, 9 and 12 were used in carrying the adsorption experiments while maintaining the temperature at 25^{o}C and initial concentration of 100 mg/L. The adjustment of pH was done by adding 0.1M nitric acid and 0.1M sodium hydroxide solutions. 0.2 g of peanut husks was put into the polythene screw cap bottles, agitated for one hour at 150 rpm, filtered and analyzed for the metal ions.

3.6.3 Optimization of contact time

Determining of contact time was done by carrying the adsorption experiments by mixing 0.2 g of adsorbent with 50 mL of the metal solution at 100 mg/L. The mixture was allowed to equilibrate at time of 5, 15, 30, 60, 90 minutes at 150 rpm for 1 hour. The filtrate was analyzed for the metal ion remaining.

3.6.4 Optimization of temperature

A sample of 0.2 g of peanut husks was added to the 50 mL of Pb (II) ion solution at concentration of 100 mg/L and pH of 5.5. The shaking speed was adjusted to 150 rpm. Different temperatures of 20, 30, 40, 50 and 60^{o}C were used in carrying out the adsorption experiment. The resulting mixtures were collected, filtered and analyzed for the remaining ions.

3.6.5 Optimization of initial concentration

Investigation of effect of initial concentration on adsorbent of metal was done by agitating 50 mL of Pb (II) solution of 60, 70, 80, 90 and 100 mg/L with 0.2 g of adsorbents in a water bath shaker at 25^{o}C. The shaking speed was set at 150 rpm and the pH at 5.5. The samples were run for 1 hour, filtered and then analyzed for the percentage removal.

3.7 Data analysis

The data was collected as an average of the three replicates so as to calculate the standard deviation which was used as error bars to discriminate differences among isotherms. This was done to produce reasonable estimate of the true value for the sample to account for measurement variability. The variances were analyzed by calculating the P- value associated with one way ANOVA test with post hoc comparison (Bonferron test) using software Stata Special Edition 2013 package and Microsoft Excel. They were then fitted into Freundlich and Langmuir isotherms to determine adsorptions capacities of the UMP, CMP and EMP. The results are presented in chapter four.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Elemental analysis of peanut husks

The elemental composition of the peanut husks was determined using XRF and given in table 4.1.

Table 4.1: The elemental composition of the peanut husks

Component	% Composition
MgO	34.153 ± 1.897
Al_2O_3	3.749 ± 0.254
SiO_2	7.098 ± 0.162
P_2O_5	0.000 ± 0.056
S	4.211 ± 0.045
Cl	0.250 ± 0.002
K_2O	14.670 ± 0.034
CaO	31.134 ± 0.042
Ti	0.493 ± 0.012
Cr	0.012 ± 0.006
Fe	3.666 ± 0.015
Cu	0.046 ± 0.001
Zn	0.147 ± 0.001
Sr	0.066 ± 0.001
Pb	ND

From the table 4.1, it is clear that the elemental composition of peanut husks is varied. The peanut husks contain transition metals, alkali metals and alkaline earth metals. Of interest is that lead was not detected in the peanut husks. This was necessary to confirm so that it does not interfere with the experiment.

4.2 Characterization of peanut husks by XRD

Characterization and phase analysis of peanut husks was done using x-ray diffraction with counts of diffracted x-ray plotted against angle 2 . The X-ray diffraction pattern of peanut husks is represented by figure 4.1.

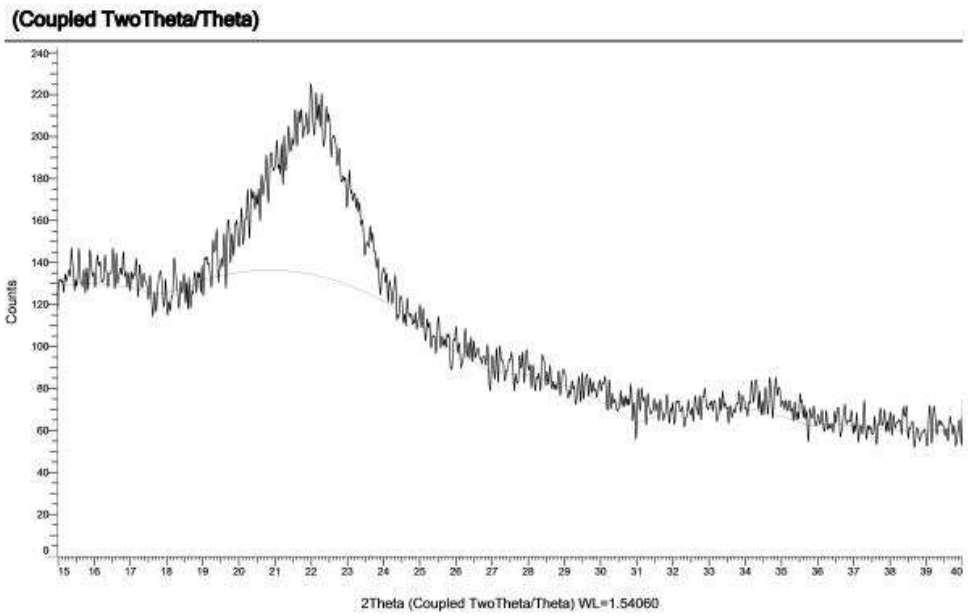

Figure 4.1: The XRD patterns of peanut husks

Interactions between solid cellulosic materials with other reactive or adsorptive substances occur first in the non-crystalline domains (Cialacu *et al*, 2011). Sharp narrow high peaks are for crystalline phases while broad small peaks are for amorphous phases (Cullity, 1956). The amorphous part in the cellulose is represented by broader and less clearly refined features in the diffraction pattern. From the pattern, the 2θ for the highest point is 21.975^0, 225 counts and interspacing of 4.03908. This fits well because according to Park *et al* (2010), the amorphous peak maximum is limited to between 18^0 and 22^0. Moreover, the diffractograms clearly indicate an amorphous structure as this character is demonstrated by the absence or strong reduction of peaks to planes to values of the Bragg angle characteristic to cellulose (Ciolacu *et al*, 2011).

4.3 Characterization of UMP, CMP and EMP by FTIR

UMP, CMP and EMP were characterized by using FTIR and the spectra recorded in the range of 350 to 4600 cm^{-1} as given in figures 4.2, 4.3 and 4.5 respectively.

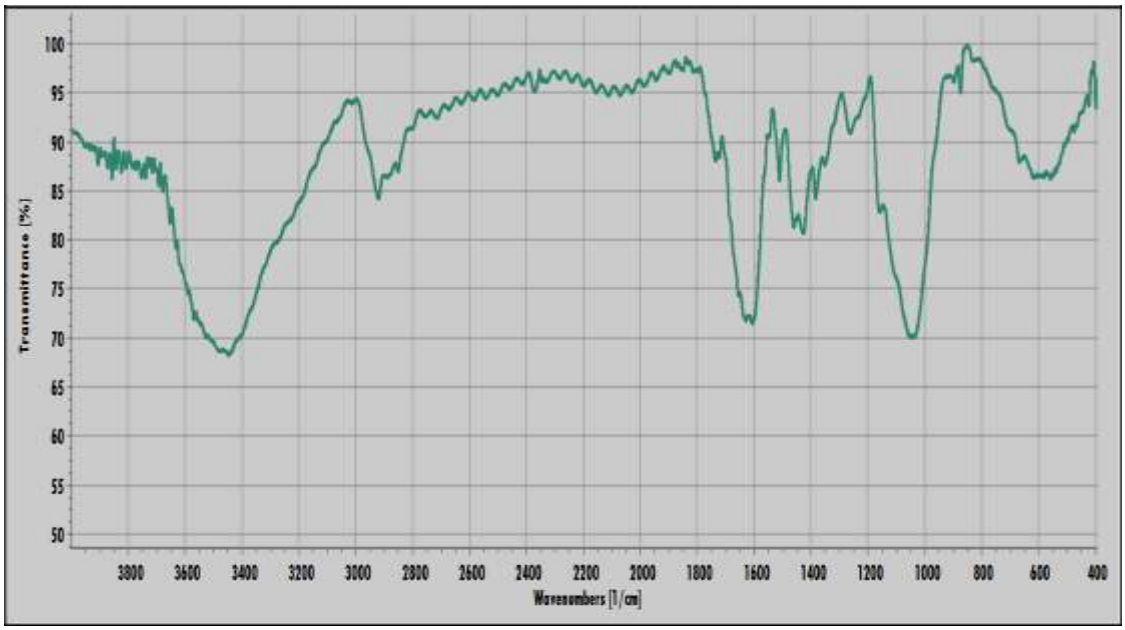

Figure 4.2: FTIR spectrum of UMP

The FTIR spectrum of UMP shows absorption bands at different wave numbers. The bands observed around ~ 3447 cm^{-1} is attributed to –OH stretching vibration and at ~ 1607 cm^{-1} is attributed to –OH bending vibration of absorbed water (Pandey, 1999). The band around ~ 2920 cm^{-1} is attributed to C-H stretching and that around ~ 1426 cm^{-1} is attributed to HCH and OCH in plane bending vibration. That around ~ 1263 cm is attributed to glucose ring stretching and around ~ 1063 is attributed to C-C, C-OH, CH ring and side group vibration, while the band at around ~ 874 cm^{-1} is attributed to CCH, COC and CCO deformation and stretching (Hospodarova *et al.*, 2018). This shows that the peanut husks contain the cellulosic material.

Figure 4.3: FTIR spectrum of CMP

Cellulosic hydroxyl group combines with citric acid anhydride to form an ester linkage and thus introduces carboxyl group to the adsorbent material. It can be seen therefore that there is a strong characteristic stretching absorption band of a free carboxyl group (COOH) around ~ 1735 cm^{-1} in spectrum of citric modified peanut husk sample (Baranauskas *et al*., 2002). The peak observed at ~ 1511 cm^{-1} region is due to the asymmetric stretching vibration of –COO- groups (Hon *et al*., 2002). Moreover, the broad absorption peaks around 3403.45 cm^{-1} and 2919.31 cm^{-1} also confirm the existence of carboxylate O-H group (2500-3500 cm^{-1}) after citric acid modification.

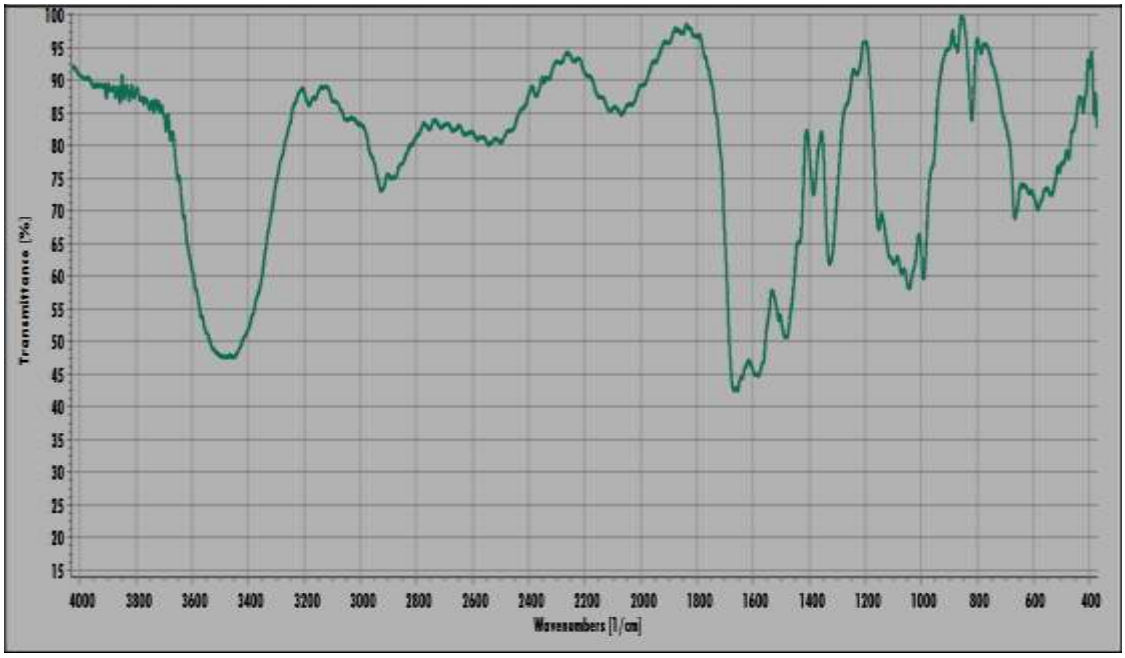

Figure 4.4: FTIR spectrum of EMP

The spectrum shows several different peaks of bands. The strong band around ~3474 cm^{-1} which was a result of an amine group appears as two bands (Avisha *et al*., 2012). The broad band at ~3474 cm^{-1} region after modification and the appearance of the band at 1581 $cm^{-1}$is due to the angular deformation of the N-H (amine group) which is an indicator of EDA immobilization of the adsorbent (Pavia *et al*., 1996). The band around ~1326 cm^{-1} is attributed to N-H group (Khazael *et al*., 2007).

4.4 Adsorption studies of peanut husk adsorbent

4.4.1 Effect of adsorbent dosage on removal of Pb (II) ions

The impact of dosage on Pb(II) ion removal was investigated by using UMP, CMP and EMP adsorbent material at different adsorbent dose value of 20 mg to 200 mg/50 mL, temperature of 25 ºC, contact time of 90 minutes and shaking speed of 150 rpm. The results are displayed in figure 4.5.

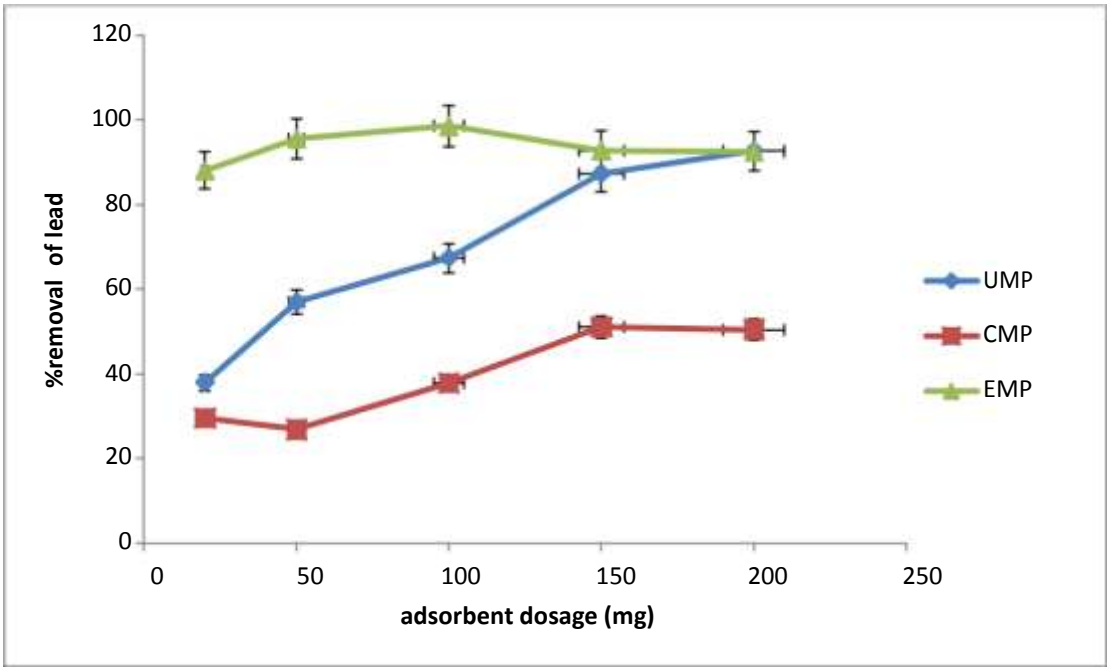

Figure 4.5: Effect of adsorbent dose on removal of Pb (II) ion using UMP, CMP and EMP

Percentage of removal of Pb(II) ions by UMP increased gradually from 37.9±0.87% to 87.3±1.87% and attained optimum at dose of 200 mg with 92.6±2.19%. Percentage removal by CMP ranged from 26.5±0.75% to 51.0±1.99% with optimum at 150 mg/50 mL while that of EMP ranged from 88.0±1.64% to 98.5±1.4% with optimum percentage at 100 mg/50 mL.

From the figure 4.5, it is notable that for UMP the percentage removal increased almost linearly to the optimum with increase in the dose of the adsorbent as compared to CMP and EMP adsorbents that demonstrates an increase with dosage and followed by a drop in percentage removal. The increasing dosage increases surface range and active destinations accessible for adsorptions of lead ions. This increment in adsorptions with dosage can be ascribed to expanded surface zone and the accessibility of more binding destinations for adsorptions (Vasudevan and Lakshmi, 2011). The increase can also be due to the increase in the available binding sites in

adsorbent because of the progressive increase in the electrostatic interaction between the metal ion and the adsorbent (Rotimi and Okeaghene, 2014). The percentage removal decreased at optimum adsorbent dosage for CMP and EMP at 150 mg/50 mL and 100 mg/50 mL respectively because of the overlapping/aggregation of vacant adsorptive sites due to overcrowding of adsorbent particles (Garg *et al*., 2003). High dosage could also impose a screening effect of the dense outer layer of the cells; thus shielding the binding sites from the metal ions (Ponse and Fuste, 1993).

4.4.2 Effect of contact time on removal of Pb (II) ions

Figure 4.5 shows the variation of percentage removal of Pb(II) ions as the contact time was varied from 5 to 90 minutes, at pH of 5.5, temperature of 25 ºC, shaking speed of 150 rpm and initial concentration of 0.2g/50mL for UMP, CMP and EMP adsorbents.

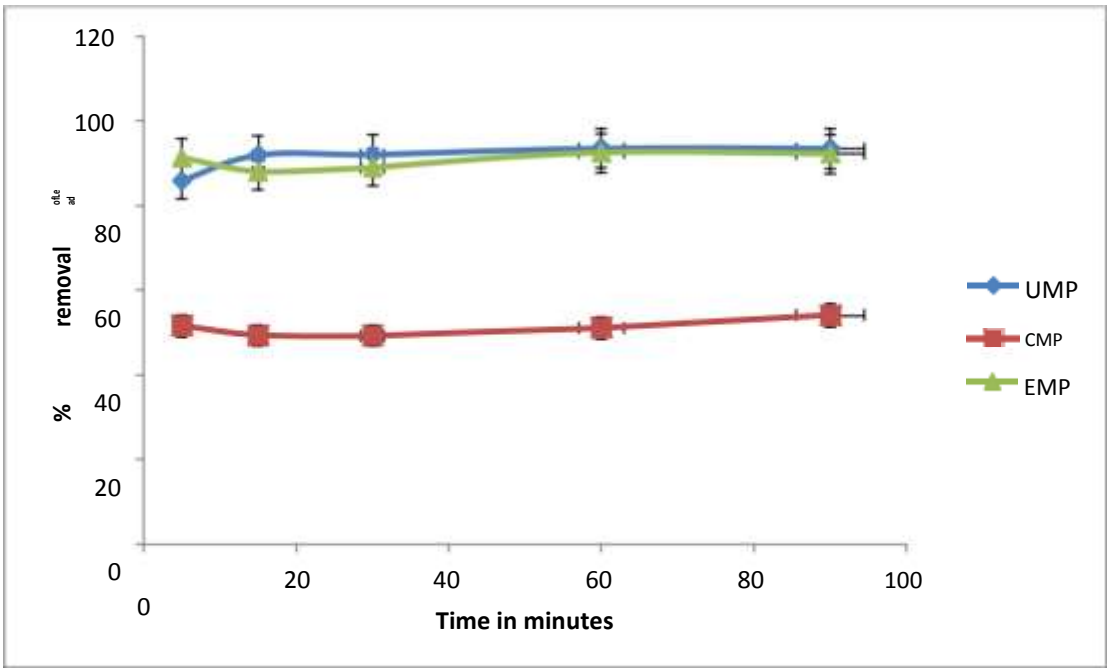

Figure 4.6: Effect of contact time on removal of Pb (II) ion using UMP, CMP and EMP

The percentage removal of Pb(II) ion increased from 85.8±1.83% to 93.5±1.39% for UMP, 49.2±1.57% to 54.0±1.47% for CMP and 88.0±2.19% to 92.4±1.30% for EMP. This shows that beyond 60 minutes, most of lead ions are adsorbed and that the contact time has little effect on percentage removal in contaminated water.

The percentage adsorption increased during the initial stage and then became slower at the later contact time until the equilibrium was attained (Krika *et al*., 2016). For CMP and EMP adsorbents, the percentage removal for Pb(II) ions was high within the first 5 minutes of contact then dropped with 15 minutes and then increased progressively. This high percentage at the start is probably due to the larger surface area of the adsorbent being available for the adsorption of the metal ions. This fast adsorption can be attributed to the initial concentration gradient between the adsorbate in solution and the number of the vacant sites available on the surface for both adsorbents, there is a progressive increase in percentage removal and thereafter attaining equilibrium after 60 minutes. This equilibrium is due to the limited external binding sites of the adsorbent (Acksu, 2001)

4.4.3 Effect of pH on removal of Pb (II) ions

The percentage removal of Pb (II) ion was investigated using varied pH of 2 to 11. The temperature was maintained at 25ºC, shaking speed at 150 rpm and the concentration of 0.2 g/50 mL. The results are presented in the figure 4.6.

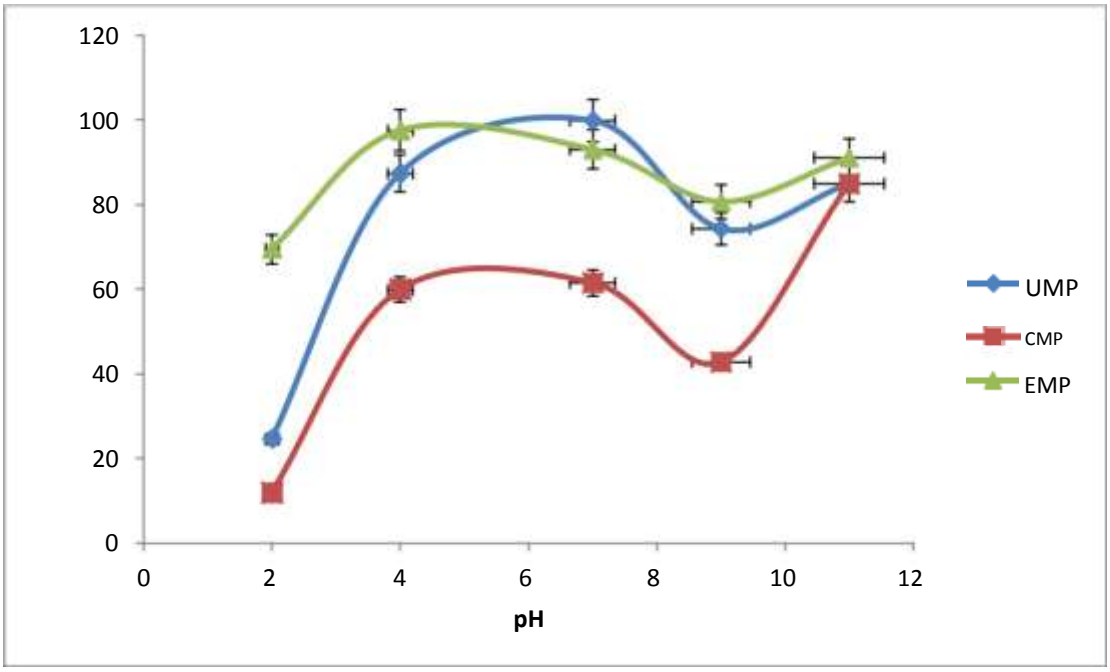

Figure 4.7: Effect of pH on removal of Pb (II) ion using UMP, CMP, EMP

Metal adsorption is dependent on pH. As shown in figure 4.7, the percentage removal by UMP increased from 24.6±0.36% to 99.8±0.10%, by CMP varied from 11.9±1.18% to 84.9±0.61% while that by EMP ranged between 69.4±0.85% and 97.5±0.87%. Both UMP and CMP recorded optimum percentage removal at pH of 7 and 11 with 99.8±0.10% and 84.9±0.61% respectively, whereas the EMP recorded the maximum adsorption at pH of 4 with 97.5±0.87%.

At lower pH of 2, the adsorption is low due to the overall positive charge on the adsorbent surface caused by the protonation (H^+/H_3O^+) that hinders metal access to the ligands of the adsorbent due to the repulsive forces. (Hameed and Ahmad, 2009). The low adsorption can also result from the competition between protons, H^+ and the metal ions (Sari *et al*., 2007).

At pH of 4 to 7, the adsorbent is relatively more negatively charged in comparison to the solution. This contributes to a high adsorption of metal ion in the solution (Singh *et al*, 2006). But beyond the pH of 7, metal hydrolysis forms that leads to precipitation due to the formation of hydroxyl metal ions which leads to lower solubility (Sen Gupta and Bhattacharyya, 2008). This proves that removal is not only by adsorption (Wang and Qin, 2005).

Lead is amphoteric; and at high pH than 8, the lead ions are reported to form hydrocomplexes (Anna and Rafael, 2011). Complex formation leads to the dissolution of the previously formed precipitate and thus allows for high adsorption.

4.4.4 Effect of initial concentration on removal of Pb (II) ions

In this study, the initial concentration was varied from 60 mL to 100 mL while the adsorbent dose was maintained at 0.2 mg/50 mL. The temperature was at 25 ºC, pH of 5.5, shaking speed of 150 rpm and running time of 150 minutes. The data on the percentage removal was reported in the figure 4:8.

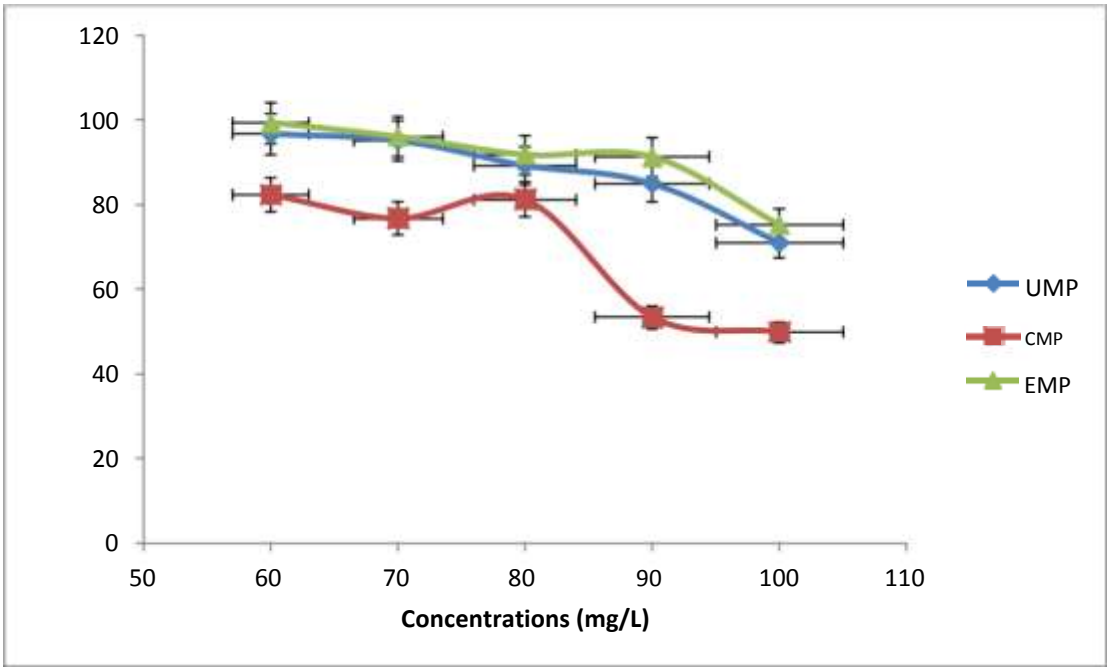

Figure 4.8: Effect of initial concentration on removal of Pb (II) ion using UMP, CMP and EMP

From the results, the initial concentration has effect on the removal of the Pb (II) ion from the contaminated water. In UMP, percentage removal ranged from 96.6±1.73% to 70.9±0.98%, in CMP it ranged from 82.3±1.35% to 49.8±0.96% and in EMP it ranged from 99.2±0.26% to 75.2±1.66%.In all the adsorbents, the optimum uptake was recorded at 60mg/L, and thereafter there was subsequent drop in percentage removal in all adsorbent giving a similar trend for removal of divalent metal ions by biosorbents (Brown *et al*, 2001).

Accordingly, the peanut husks have a higher adsorption at a lower concentration for the Pb (II) ion. The capacity reduced as the concentration increased due to decreasing number of adsorptive sites because of saturation (Fourest and Roux, 1992).

The number of moles of Pb (II) ions is small at lower concentration relative to the available adsorption sites on the adsorbent, hence giving high rate of the adsorption

(Jnr and Spiff, 2005). Increase of the metal ion concentration causes competition that locks inlet channel of the surface as adsorption occurs on the surface only (Al-Anber and Al-Anber, 2008). High concentration means a high amount of number of moles per given volume. In this situation, ionic mobility is strongly affected due to the viscous solvent that results from the high amount of ions per given volume.

4.4.5 Effect of temperature on removal of Pb (II) ions

The adsorption studies were done at different temperature (293, 303, 313, 323 to 333K) using adsorbent material of UMP, CMP and EMP of 0.2g/50mL, shaking speed of 150 rpm, contact time of 90 minutes and pH of 5.5. The results are illustrated in the figure 4.8:

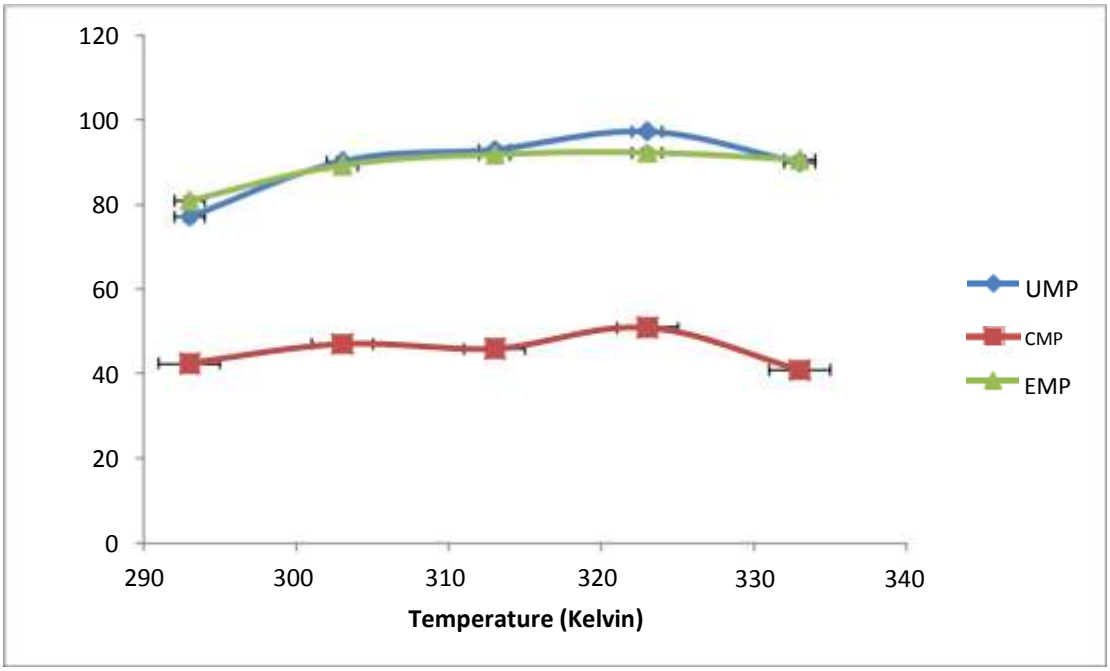

Figure 4.9: Effect of temperature on removal of Pb (II) ions using UMP, CMP and EMP

Temperature influences the adsorptions rate by adjusting the molecular connections and the solubility of the adsorbate (Singh *et al*., 2001). In all adsorbents, there is a

slight increase in percentage removal from 293 K to 323 K and a slight drop at 333 K. UMP records a rise from 77.0±1.14% to 97.2±1.07% and drop to 89.9±2.26%. CMP records 42.4±1.15% increasing to 50.9±0.72% and dropping to 40.9±1.78%, while EMP has an increase from 80.9±1.08% to 92.2±1.35% and decrease to 90.6±1.39%.

From 293 K to 323 K, there is constant increase in adsorption of Pb (II) ions. This can be attributed to the fact that amount of heat energy required to push ions to the sorbent surface nearly equals heat of desorption from the monolayer. The slight drop in percent removal of lead ions at 333 K indicates that a high temperature works against the removal of Pb (II) ions (Zubeyde *et al*., 2009) because the thickness of the boundary layer decreases due to increased tendency of the metal ions to escape from most of the adsorbent's surface to the bulk of solution (Aksu and Kutsal, 1991).

The decrease in percentage adsorption could also be due to a distortion of some sites of the adsorbent surface available for metal adsorption (Kapoor and Viraraghavan, 1997). Another reason for the decrease is the desorption which is an endothermic process. This process involves the breakdown of the covalent bonds or attractive forces and hence causes the release of the adsorbed substance from the surface. This shows that the adsorption of lead ion on the three adsorbents is an exothermic process (Zang *et al*., 2020).

4.5 Adsorption isotherms

Langmuir and Freundlich isotherm models were used in this work to describe the adsorption isotherms. Equilibrium data obtained were fitted in Langmuir and

Freundlich isotherms and the data of Pb (II) ion adsorptions using UMP, CMP and EMP are presented in tables 4.2 and 4.3.

Table 4.2: Langmuir adsorption isotherm for Pb (II) ion using UMP, CMP and EMP

Ion	Adsorbent	Q_{max}(mg/g)	b(dmg^3/g)	R^2
Pb^{2+}	UMP	18.18	9.17	0.998
	CMP	11.36	0.8	0.959
	EMP	19.23	4.33	0.997

Qmax= adsorption capacity of Langmuir, b= Langmuir equilibrium constant associated with energy of adsorption and R^2=Correlation coefficient

Table 4.3: Freundlich adsorption isotherm for Pb (II) ion using UMP, CMP and EMP

Ion	Adsorbent	$\frac{1}{n}$	Kf (mg/g)	R^2
Pb^{2+}	UMP	0.06	15.03	0.837
	CMP	-0.083	15.849	0.074
	EMP	0.081	15.205	0.730

1/n = heterogeneity parameter, K_f = adsorption capacity of Freundlich and R^2=Correlation coefficient

The adsorption data of Pb (II) ions for UMP, CMP and EMP fit best on the Langmuir isotherm model based on the R^2 values of 0.998, 0.959 and 0.997 respectively. This indicates that the adsorption of Pb (II) ion on these adsorbents is monolayer. The adsorption capacities on UMP, CMP and EMP are 18.8, 11.36 and 19.23 mg/g respectively.

The adsorption capacities value for UMP and EMP are higher than those of adsorbents reported in the table 4.6. The lower capacity value of CMP may be attributed to steric

hindrance of citric acid during anchoring which reduces accessibility of cellulosic hydroxyl groups; thus, reducing the amount of crosslinked product (Rojas and Azevedo, 2011)

Table 4.6: Comparison of monolayer adsorption of Pb (II) ion onto UMP, CMP and EMP with other various adsorbents

Adsorbate	Adsorbent	Q_{max}(mg/g)	Reference
Pb^{2+}	Kaolin	4.73	Jiang *et al* (2009)
	Bentonite	16.70	Eren *et al* (2009)
	Raw laterite soil	1.053	Chansuvarn and Jainae (2015)
	Activated carbon from cane sugar bagasse	13.70	Giraldo and Moreno-Pirajan (2008)
	UMP	18.80	Current work
	CMP	11.36	Current work
	EMP	19.23	Current work

Q_{max} stands for maximum monolayer adsorption capacity

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study was carried out to investigate the suitability of peanut husks in carboxylate and celen synthesis for the adsorption application and whether modifying with citric acid and ethylene-1,2-diamine would enhance the adsorption efficiencies. The results were as follows:

i. XRF analysis indicated absence of Pb metal in chemical composition of the peanut husks collected from Dodoma region in Tanzania and XRD analysis indicated presence of amorphous phase between 18 – 24 (2θ).

ii. The peanut husks were the potential raw material for modification as the FTIR indicated presence of –OH stretching vibration and –OH bending vibration in the raw/unmodified peanut husks (Pandey, 1999).The FTIR confirmed that functionalization of peanut husks with citric acid and ethylene-1,2-diamine was achieved as indicated by the presence of strong characteristic stretching absorption band (Baranauskas *et al*., 2002) and of the asymmetric stretching vibration (Hon *et al*., 2002) of a free carboxyl group ($-COO^{-}$)and of strong band of NH_2^{-} which appears as two bands (Avisha *et al*., 2012).

iii. Maximum percentage removal for UMP and CMP is 99.8±0.10% and 84.9±0.61% at pH of 7 and 11 respectively, dosage of 0.2g/50mL; and 98.5±1.4% for EMP at pH of 5.5, dosage of 0.1g/50mL. Thus UMP, CMP

and EMP are efficiently good adsorbents based on their percentage removal of Pb (II) ions registered at different batch parameters.

The UMP has a maximum percentage removal. This could be due to the derivatization of the functional groups such as carbonyl and hydroxyl groups which have literally high affinity for lead metal ion in the unmodified adsorbent (Koch *et al*, 1970).

CMP records the lowest percentage removal. This could possibly result from reality that when reaction temperature is sufficiently high or the reaction time is long enough, all the three carboxyl groups of the citric acid can form crosslink with the raw material (McSweeny, *et al*., 2006). This reduces the ion exchange capacity of the adsorbent.

iv. Experimental data was fitted in Langmuir and Freundlich isotherm models. Based on their correlation coefficients, the equilibrium data best fitted Langmuir isotherm model with R^2 values of 0.998, 0.959 and 0.997. The model was further used to predict the adsorption capacities and found that the maximum monolayer adsorption capacities were 18.8 mg/g for UMP, 11.36 mg/g for CMP and 19.23 mg/g for EMP. Hence, the EMP is recommended.

v. The present investigation shows that the peanut husks can be employed as potentially effective adsorbent for the removal of Pb(II) ion from

contaminated water. The adsorption was found to greatly depend on the pH, contact time, temperature, initial concentration and adsorbent dosage.

5.2 Recommendations

5.2.1 Recommendations from this work

i. The use of peanut husks be enhanced for the adsorption application in solving the problem of presence of lead metal in our water systems.

ii. Industries that use lead metal as raw material or those produce products with lead metal be encouraged to embrace peanut husk filters before letting the industrial effluents into the water systems.

iii. The Ministries for Water, Health and Environment be sensitized to educate people on the health effects of lead metal and on the use of peanut husks, modified and unmodified, to treat water for the beneficial use.

5.2.2 Recommendations for further studies

i. Further studies to be conducted to determine whether peanut husks can be applied in purification of waste water in local sewerage plants and at local house hold levels.

ii. Studies on the synthesis of zeolite material from peanut husks be done for the determination of efficiency in removal of non-metallic ions such as nitrates and fluorides which are also water pollutants

iii. Studies be conducted on regeneration and reuse of the peanut husk adsorbent.

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APPENDICES

Appendix 1: Effect of contact time on percentage removal of lead (II) ion by using adsorbents UMP, CMP and EMP

Contact time (min)	% Lead ion removal by UMP	% Lead ion removal by CMP	% Lead ion removal by EMP
5	85.8 ± 1.83^{a}	51.6 ± 2.78^{a}	91.2 ± 0.90^{a}
15	91.8 ± 1.14^{b}	49.3 ± 1.39^{c}	88.0 ± 2.19^{b}
30	92.0 ± 3.92^{a}	49.2 ± 1.57^{e}	89.0 ± 1.31^{a}
60	93.5 ± 1.39^{f}	51.1 ± 1.30^{g}	92.4 ± 1.30^{f}
90	93.4 ± 0.79^{h}	54.0 ± 1.47^{i}	92.2 ± 1.01^{h}

Mean percentages with the same letter in the same row differ ($P < 0.05$) as analyzed by one-way ANOVA.

Appendix 2: Effect of adsorbent dose on percentage removal of lead (II) ion by using adsorbents UMP, CMP and EMP.

Adsorbent dose (mg)	% Lead ion removal by UMP	% Lead ion removal by CMP	% Lead ion removal by EMP
20	37.9 ± 0.87^{a}	29.5 ± 0.75^{a}	88.0 ± 1.64^{a}
50	56.9 ± 1.21^{b}	26.8 ± 1.78^{b}	95.8 ± 2.27^{b}
100	67.3 ± 1.51^{c}	37.8 ± 1.39^{c}	98.5 ± 1.40^{c}
150	87.3 ± 1.87^{a}	51.0 ± 1.99^{a}	92.8 ± 4.84^{a}
300	92.6 ± 2.19^{e}	56.4 ± 0.56^{f}	92.5 ± 2.50^{e}

Mean percentages with the same letter in the same row differ ($P < 0.05$) as analyzed by one-way ANOVA.

Appendix 3: Effect of pH on the percentage removal of lead (II) ion by using adsorbents UMP, CMP and EMP.

pH	% Lead ion removal by UMP	% Lead ion removal by CMP	% Lead ion removal by EMP
2	24.6 ± 0.36^{a}	11.9 ± 1.18^{a}	69.4 ± 0.85^{a}
4	87.3 ± 0.46^{b}	59.9 ± 1.39^{b}	97.5 ± 0.87^{b}
7	99.8 ± 0.10^{c}	61.5 ± 0.79^{c}	93.0 ± 0.95^{c}
9	74.2 ± 1.40^{a}	42.7 ± 0.92^{a}	80.6 ± 0.66^{a}
11	84.9 ± 1.39^{e}	84.9 ± 0.61^{e}	91.0 ± 1.57^{f}

Mean percentages with the same letter in the same row differ ($P < 0.05$) as analyzed by one-way ANOVA.

Appendix 4: Effect of initial concentration on the percentage removal of lead (II) ion by using adsorbents UMP, CMP and EMP.

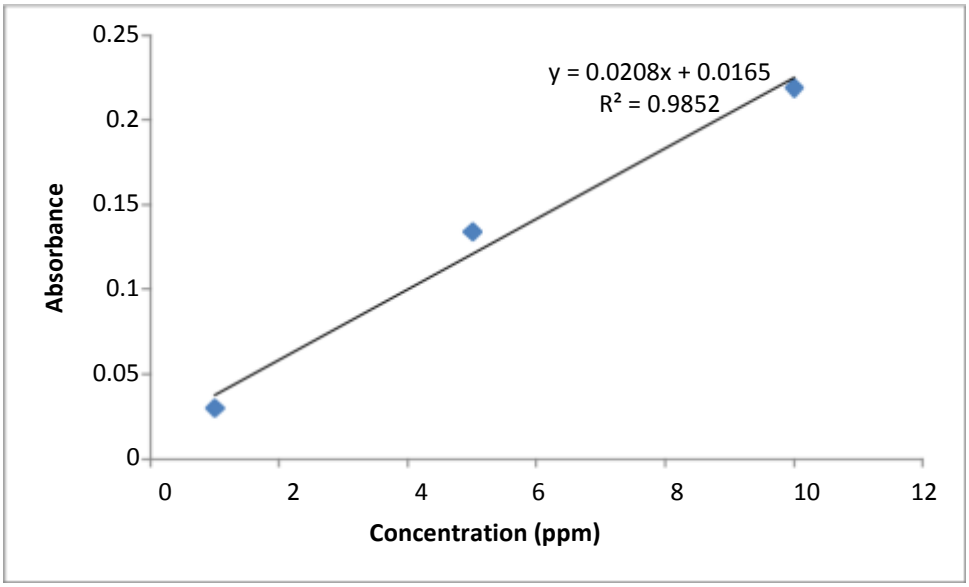
Concentration (ppm)	% Lead ion removal by UMP	% Lead ion removal by CMP	% Lead ion removal by EMP
60	96.6±1.73^{a}	82.3±1.35^{a}	99.2±0.26^{a}
70	95.1±2.91^{b}	76.7±1.91^{z}	96.0±1.30^{b}
80	89.2±1.14^{c}	81.2±0.78^{k}	91.7±0.52^{c}
90	84.9±0.56^{d}	53.3±1.13^{d}	91.2±0.36^{d}
100	70.9±0.98^{e}	49.8±0.96^{e}	75.2±1.66^{e}

Mean percentages with the same letter in the same row differ ($P < 0.05$) as analyzed by one-way ANOVA.

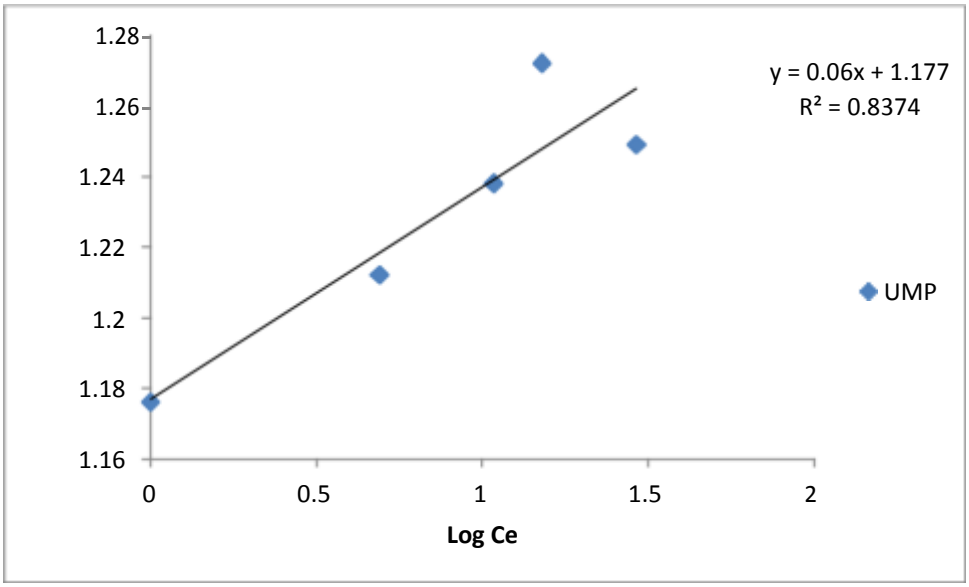
Appendix 5: Effect of temperature on the percentage removal of lead (II) ion by using adsorbents UMP, CMP and EMP.

Temperature (^{0}C)	% Lead ion removal by UMP	% Lead ion removal by CMP	% Lead ion removal by EMP
20	77.0 ± 1.14^{a}	42.4± 1.15^{a}	80.9± 1.08^{a}
30	90.2± 1.11^{b}	47.0 ± 1.05^{c}	89.2± 1.22^{b}
40	92.9± 2.50^{d}	45.9± 1.05^{e}	91.7± 1.85^{d}
50	97.2± 1.07^{f}	50.9± 0.72^{f}	92.2± 1.35^{f}
60	89.9± 2.26^{g}	40.9± 1.78^{h}	90.6± 1.39^{g}

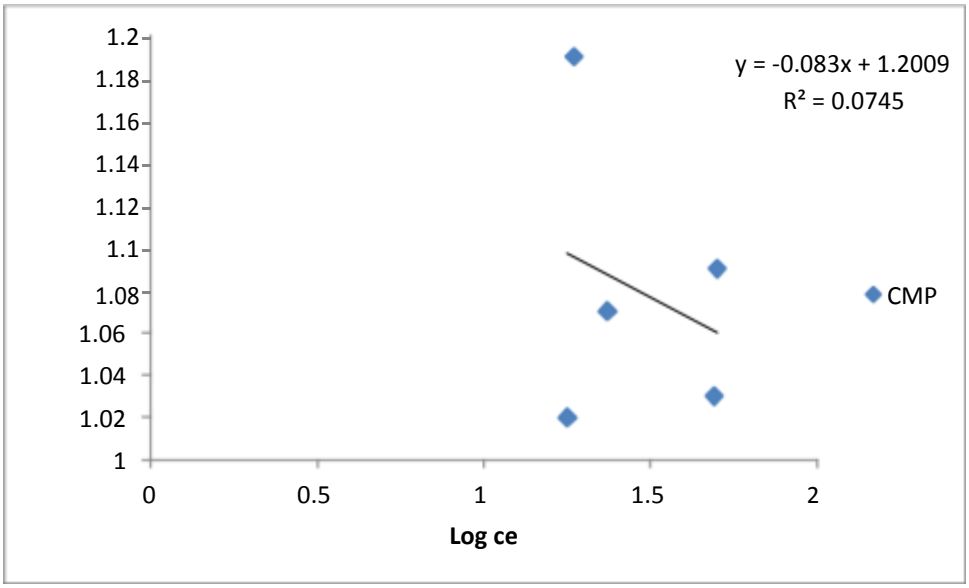
Mean percentages with the same letter in the same row differ ($P < 0.05$) as analyzed by one-way ANOVA.



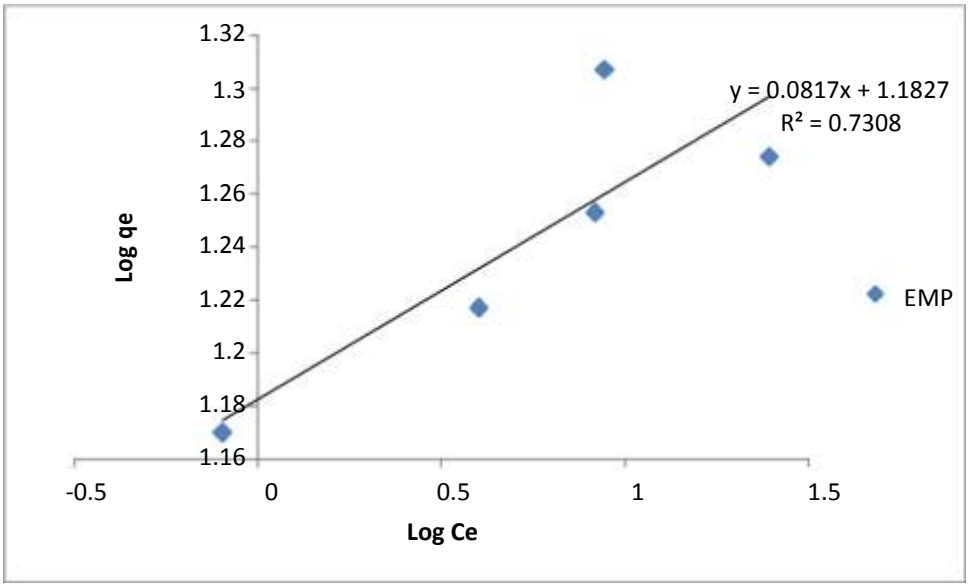
Appendix 6: Calibration curve for lead



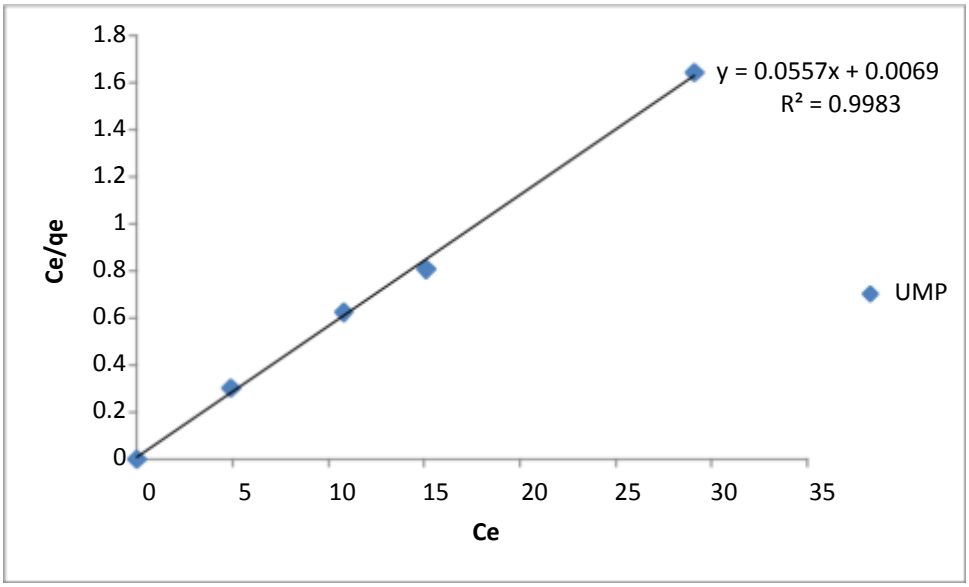
Appendix 7: Freundlich adsorption isotherm for the adsorption of Pb (II) ion using UMP



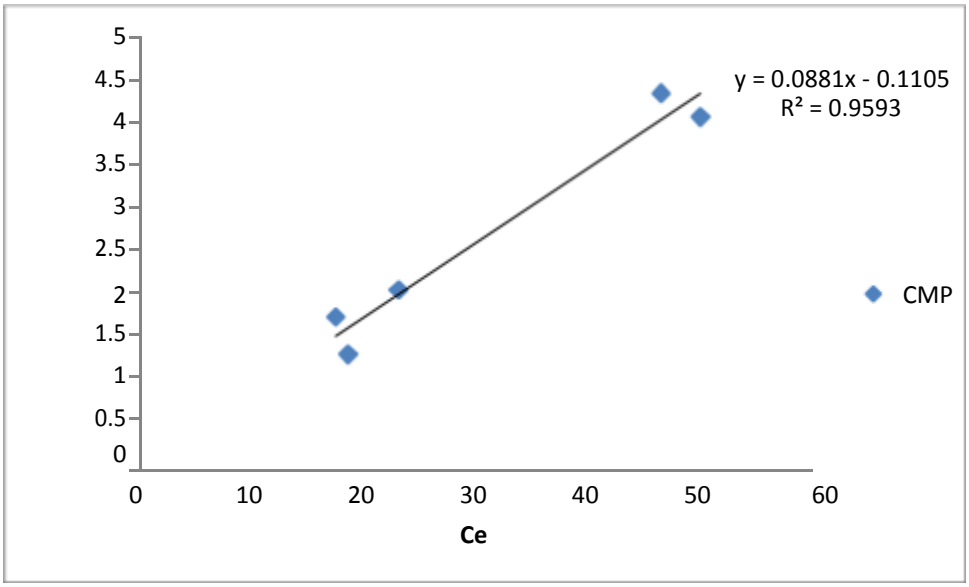
Appendix 8: Freundlich adsorption isotherm for the adsorption of Pb (II) ion using CMP.



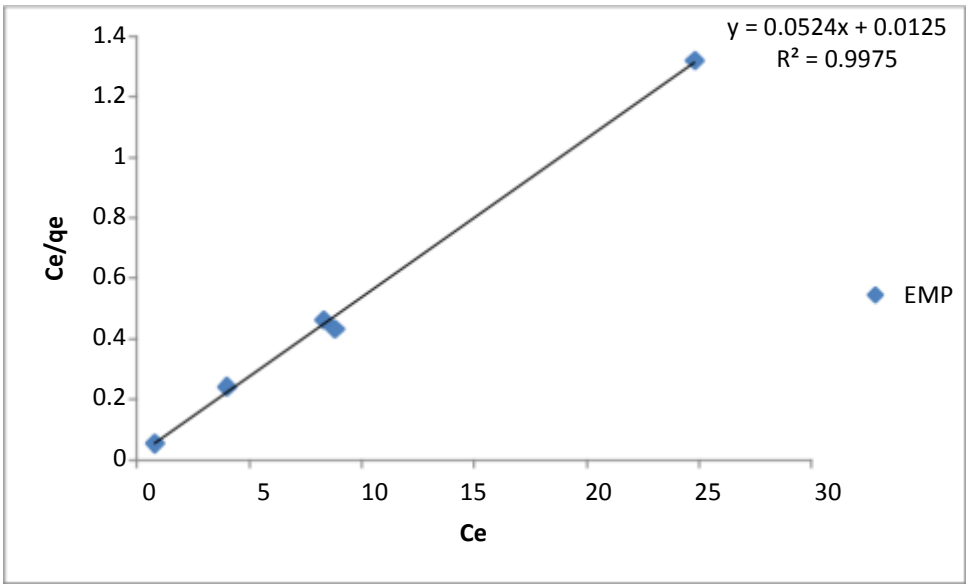
Appendix 9: Freundlich adsorption isotherm for the adsorption of Pb (II) ion using EMP



Appendix 10: Langmuir adsorption isotherm for the adsorption of Pb (II) ion using UMP



Appendix 11: Langmuir adsorption isotherm for the adsorption of Pb (II) ion using CMP



Appendix 12: Langmuir adsorption isotherm for the adsorption of Pb (II) ion using EMP