ADSORPTION OF SELECTED HEAVY METALS ON ACTIVATED CARBON PREPARED FROM PLANTAIN *(Musa paradisiaca*L.**) PEEL**

BY

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY

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DECLARATION

I hereby declare that the work in this thesis entitled "ADSORPTION OF SELECTED HEAVY METALS ON ACTIVATED CARBON PREPARED FROM PLANTAIN *(Musa paradisiaca*L.) PEEL**"** has been performed by me in the Department of Chemistry under the supervision team of Prof. (Mrs.) E.B. Agbaji and Dr. S.O. Idris. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university or institution.

_____	_____	_____
Name of Student	Signature	Date

CERTIFICATION

This thesis titled **"**ADSORPTION OF SELECTED HEAVY METALS ON ACTIVATED CARBON PREPARED FROM PLANTAIN *(Musa parasidiaca*L.) PEEL**",** by Idowu Elijah AGBELE meets the regulations governing the award of the degree of Master of Science of the Ahmadu Bello University, Zaria and is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

This thesis is dedicated to the Almighty God, the Creator of Heaven and Earth

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ABSTRACT

Activated carbon prepared from plantain peel is used to adsorb selected heavy metals such as copper, cadmium and chromium. Heavy metals are toxic and may be found in both surface and underground water. Plantain peel which is an agricultural wastes comprising mostly of cellulose materials was activated with three activating agents (0.10M H_3PO_4, 0.10M NaOH and 0.10M $ZnCl_2$), then latter used for the removal of these toxic metals from their aqueous solutions. Activation of plantain peel with 0.10M H_3PO_4 and 0.10M NaOH solutions resulted to a two-fold increase in the amounts of adsorbed Cd^{2+}, Cr^{6+} and Cu^{2+} compared to activation with 0.10M $ZnCl_2$.The effects of varying the particle sizes, the type of activating agents as modifiers, adsorbent dosage, agitation time, agitation speed, pH as well as initial concentration of the metal ions on the adsorption capacity of the activated carbons were determined. The linearization of equilibrium isotherms data for Langmuir and Freundlich models were obeyed over the entire range of the concentration studied, while the metal sorption closely followed Langmuir model and Freundlich model. The Langmuir isotherm has R^2 values of 0.9557 for Cd^{2+}, 0.9924 for Cr^{2+} and 0.9954 for Cu^{2+} which indicated that the adsorption behaviour was homogenously distributed. The R_L value indicated favorability of adsorption capacity by adsorbent since R_L value fall within 0 to 1.The characterization by FTIR showed absorbance peaks of aldehyde, amide, alkyl, hydroxyl and carboxylic functional group. Hence, these functional groups are responsible for the adsorption and activation process has an enhanced factor on the adsorption of the selected metals. The optimum conditions for the adsorption of Cd^{2+}, Cr^{6+} and Cu^{2+} onto the activated carbon are 2.5 g of the adsorbent dosage of particle size 75 µm, 20.0 mg/dm^3 of the adsorbate concentration at 60 min agitation time carried out at 150 rpm agitation speeds. At the optimum conditions the highest percentage of the metal ions adsorbed were Cr^{6+} (97.2%), followed by Cu^{2+} (90.2%) and the least was Cd^{2+} (53.9%).

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LIST OF ABBREVIATION

FTIR	Fourier Transform Infra – Red
NAA	Neutron Activation Analysis
AA	Activating Agents
PP	Plantain Peel
EDCs	Endocrine Disrupting Compounds
PEI	Polyethylenimine
SA	Salt Activated Carbon
BA	Base Activated Carbon
CC	Carbonized Carbon
CV	Commercial Activated Carbon
K_f	Freundlich Constant (dm^3/g)
b	Langmuir Constant (dm^3/g)
q_{max}	Maximum Adsorption Capacity (mg/g)
q_e	Calculated Adsorption Capacity (mg/g)

CHAPTER ONE

1.0 Introduction

1.1 Background to the Study

Heavy metals are environmental pollutants that can be derived from various sources including lead in petrol, industrial effluents, purification of metals, smelting of ores, preparation of nuclear fuels and electroplating (Al-Omair and El-Sharkawy, 2001; Shikurrullah*et al.,* 2006). These metals are any elements in the d-block of the periodic table, usually referred to as transition metal (Ahmad *et al.,* 2006). Some are known to be harmful to both human and other living forms, with their accumulation over period of time causing damage to kidney, liver, lung, and reproductive system (Anwar, *et al.,* 2010; James *et al.,* 2007; Gimba*et al.,* 2004). They percolate into soil, underground water and surface water. Unlike organic pollutants, heavy metals are not biodegradable and are thus considered a challenge for remediation.

Many nations including Nigeria have set up bodies concerned with the protection of the environment from degradation. In Nigeria for instance, we have the National Environmental Standards and Regulation Enforcement Agency (NESREA). Its duties range from enactment of laws granted to them by empowering body, to the implementation of these laws. It also ensure that wastes from industries are treated to remove the hazardous chemicals before they are introduced into environment and water bodies such as rivers, lakes etc. (Mayflor, 2009). Accordingly, many studies have been carried out on removal of heavy metals using ion exchange, reverse osmosis, chemical precipitation, electro-dialysis, electrolytic extraction and coagulation techniques. However, a number of these are too expensive or incapable of meeting treatment objectives. Adsorption on the other hand, has been shown to be potentially viable alternative with adsorption using activated carbon is the most common method.

1.2 Activated Carbon

Activated carbon is an amorphous form of carbon in which a high degree of porosity has been developed during manufacturing or treatment. This high degree of porosity and associated large surface area make it an excellent adsorbent for a wide variety of heavy metals in both liquid and gaseous phases (Abram, 1973).The use of "carbon" dates back to ancient Egypt (1500BC) where it was employed for medicinal purposes. Later in ancient Greece, wood chars were used to treat host of ailments (Yehaskel, 1978). In the 18th century, an application was found for the removal of foul odors from gangrene (Al-Omair and El- Sharkawy, 2001). Subsequently, the application of charcoal was used mainly as a decolorizing agent for sugar (Sun and Xu 1997). A wide variety of agricultural by-products and agricultural wastes comprising mostly cellulose matrix were tried by different workers for removal of heavy metals from their aqueous solutions. These include pine bark (Al-Ashe*het al.,* 2000), saw dust (Argun*et al.,* 2007), cotton (Ozsoy and Kumbur, 2006), fibre (James *et al.*, 2007) biomass of fungi and yeast (Kumud and Emilia, 2007), *Carica papaya* seed (Omeiza*et al.*, 2011), etc. The preparations of activated carbon from agricultural wastes is motivated by cost considerations (relatively cheaper), local generation in developing countries and effectiveness in the removal of heavy metals (Loo, 1974 and Madukasi*et al.,* 2001). This research investigated the efficiency of activated carbon produced from plantain peel in the adsorption of three selected heavy metals (cadmium, copper and chromium) from their aqueous solutions under variable factors such as: agitation speed, agitation time, particle sizes, pH, initial concentration of the adsorbate and different chemical activation among others.

1.3 Plantain Peel

Plantain is an important staple food in many developing countries, especially in Africa. It provides food security and income for small-scale farmers who represent the majority of producers (Akyeampong, 1999). Only about 15% of the global plantain production is involved in international trade; most production is consumed domestically FAO (2005). Plantains, like banana, are believed to have originated in Southeast Asia, having been cultivated in south India by 500 BC. From here, ancient trade routes distributed it to Africa through Madagascar. By 1000 AD, plantains had spread eastward to Japan and Samoa. It arrived in the Caribbean and Latin America by 1500 AD. Since then, it has spread widely throughout the tropics Oladele and Aina (2007). The scientific names of most cultivated bananas are *Musa acuminate* and *Musa balbisiana*, depending on their genomic constitution. The plantain peel principally consists of cellulose, pectin, pigment and proteins (Microsoft Encarta, 2009; Fortier *et al*., 1953).

1.4 Justification for the Research

The hazardous and adverse effects caused by heavy metals present in waste waters which are released onto the environment from different industries are of significant environmental concern. Heavy metals are non-biodegradable and bio- accumulates in living organisms thereby causing various damages, diseases and disorder. Hence, attention is currently on the use of cost effective adsorbent which studies have shown to exhibit high adsorption capacity of unwanted pollutants (Ahalya*et al.*, 2003). The need to search for new technique for removing of heavy metals from waste waters have directed attention to adsorption based on the metal binding capacities of different agricultural waste like cassava husk, tree bark, ground nut husk, saw dust among others (Volesky and Holan, 1995). The adsorption of heavy metals is an effective method for treatment

of effluents mainly because of following advantage features: cheaper cost, regeneration of adsorbent, high metal binding efficiency, high efficiency in dilute effluents, no additional nutrient requirement, readily available raw material and minimal usage of chemicals among others (Pattabhi*et al.*, 2008).

1.5 Aim and Objectives

The aim of this research was to prepare activated carbon from plantain peel by using various activating agents and application for the adsorption of some selected heavy metals. The above aim would be achieved by the following objectives

1 Determination of the elemental composition of plantain peel.

2 Preparation of activated carbon from plantain peel by chemical activation method using $ZnCl_2$, H_3PO_4 and NaOH as activating agents.

3 Evaluation some physicochemical properties of the adsorbent.

4 Studying the effects of contact time, adsorbent dosage, agitation time, agitation speed, pH and initial concentration on the adsorption efficiency in order to ascertain the optimum conditions as well as nature of the adsorption process of the selected heavy metals (Cu^{2+}, Cr^{6+} and Cd^{2+}) on the activated plantain peel.

5 Investigation of the adsorption efficiency of activated carbon prepared from plantain peel with variable particle sizes on adsorption of selected heavy metals.

6 Examination of the adsorption efficiency using adsorption isotherm models.

7 Determination of adsorption efficiency using R_L value.

CHAPTER TWO

2.0 Literature Review

Several studies have shown that it is imperative to monitor, control and clean up environmental pollution caused by some heavy metals (Austin, 1987; Diets, 1990; Ekanem, 1996). Heavy metal ions are reported as prioritized pollutants, due to their mobility in natural water ecosystems and due to their toxicity (Volesky and Holan, 1995; Min *et al*., 2004).

The enormous available environmental pollution in the present age is due to urbanization and industrialization, which have added significant amount of heavy metals into natural aquatic and terrestrial ecosystem. These heavy metals are not biodegradable and their presence in streams and lakes lead to bioaccumulation in living organisms causing health problems in plants, animals and human beings (Shetty and Rajkumar, 2009). Several methods such as ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption have been proposed for the treatment of waste water polluted with heavy metals (Gupta and Babu, 2004). Hence, adsorption process by using activated carbon is being widely used to remove heavy metals pollutants from waste waters. (Okuo and Ozioka, 2001)

Among the several chemical and physical methods, adsorption onto activated carbon has been found to be superior to other techniques in water-re-use methodology, because of its capability for adsorbing a wide range of different types of adsorbates (pollutants) efficiently and its simplicity of design (Ahmad *et al.,* 2006).

2.1 Other Uses of Activated Carbon in Metals Adsorption

I. Medicinal applications

First and foremost use of activated carbon is seen in treatment of poisonings and overdoses following oral ingestion. To be specific, overdoses and poisoning following oral ingestion are cured using activated carbon (Yehaskel, 1978). It has become the treatment of choice for many poisonings, and other decontamination. In addition to this, activated carbon is used to reduce blood alcohol content; it is ingested before consumption of ethanol. It is also apparently helpful in detoxification of the body and is a common constituent of colon cleanse products.

II. Industry and Environment Applications

Carbon adsorption has numerous applications in removing pollutants from air or water streams, both in the field and in industrial processes such as: Spill cleanup, Groundwater remediation, Drinking water filtration, Wastewater treatment, Air purification, Volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes (Yenkie and Natarajan, 1993; Rao*et al.*, 1993).

III. Gas Purification

In chemical industry, activated carbon has an important role to play. For instance, activated carbon air filters are used for purification of compressed air and gas (Houghton and Wildman 1971). This helps removal of oil vapors, hydrocarbons and odor from it. These filters are also used to retain radioactive gases from a nuclear boiling water reactor turbine condenser. When it comes to purification, activated carbon is helpful for purifying sodium acetate, a non-dangerous homemade chemical (Ekanem, 1996).

IV Storage of Fuel

The fuel storage is another area where researchers see a lot of potential in activated carbon on

account of its adsorption qualities. In fact, the prospect of storing gas in activated carbon seems very feasible and practical as the gas can be stored in low mass, lower pressure and low volume environment (Yang and Chen 2008; Faller, 2009).

V. Agriculture

As far as agriculture is concerned; the uses of activated carbon are significant. Fundamentally it is used to detoxify the soil or water when growing plants. Another good part about this form of carbon is that it helps plants get rid of pesticides, fertilizers or herbicides applied to the soil (Ahmedna*et al.*, 2000).

2.2 Carbonization and Activation Processes

This is the process in which the starting materials are converted into chars. It involves heating the sample at an appropriate temperature (usually 500 to 750^{o}C), in an atmosphere of limited supply of oxygen. Here, most of the volatile components are burned out leaving the char the weight loss is usually 60-70% (Sun and Xu, 1997; Diet, 1990; Dobrowolski*et al.*, 1986; Crusberg 1998).

Activation is done to increase and enhance the adsorptive capacity of the carbonized materials. It involves heating the "chars" with activating agents at high temperatures and cooling as fast as possible. The aim of activation is to widen the pores of the charcoal to be used, hence increasing the effective site for adsorption. In chemical activation, the char is impregnated with an activating agent and fired to high temperatures (usually 500^{o}C to 1000^{o}C). The activating agent corrodes the carbon to form the pore structure (Missbah*et al.*, 1996; Mozammel*et al*., 2002).

2.3 Elemental Analysis Using Neutron Activation Technique

Neutron Activation Analysis is based on two physical (as opposed to chemical) procedures. The first step entails the neutron irradiation of small amounts of the materials to be analyzed. Secondly, the neutron irradiation causes a fraction of some stable isotopes in the samples to be transformed or 'activated' into radioactive isotopes. Most of these isotopes emit gamma rays of very specific energies as part of their radioactive decay. By detecting and quantifying the emitted gamma rays, the elemental concentration of the samples can be determined (Raghavaro*et al.*, 2009).

2.4 Earlier Studies on the Use of Activated Carbon from Agricultural Wastes

Adsorbents prepared in the form of activated carbon from low cost and readily available materials have previous been used to adsorbed heavy metals from aqueous solutions. Previous studies have shown that activated carbon has many individual applications due to its nature and properties (Gupta and Ali, 2004; Bansode*et al.*, 2003; Diets, 1990). The adsorption of ions are effected by surface charge of the particles of the activated carbon, pH of experimental condition, particle sizes of the activated carbon, activating agents among others. Some specific interaction between particular kinds of surface groups and ions exist such as in the case of adsorption of multivalent cations (Dobrowolski*et al*., 1986).

However, commercially available activated carbons are still considered expensive (Ceribas*et al.*, 2001). Consequently, many researchers have studied using locally made carbon as cheaper substitutes, which are relatively inexpensive and are at same time endowed with reasonable adsorptive capacity. Hence, various types of activated carbon are produced from carbonaceous materials of either animal or mineral origin as well as from agricultural waste (Austin, 1987).

Okiemen and Onyenkpa (1989) used melon seed for production of adsorbent. Another researcher used rice seed husk for sorption of Cd (II), Pb (II), Ni (II) and Cu (II) from aqueous solution adsorption mechanism is an ion exchange process (Brewer, 1998). Also, adsorbent was prepared using thiolated maize (*Zeamais*) cob powder for the removal of Hg(II), and Cr(II) ions from aqueous solution (Mcpherson and Rowley, 1990). Okieimen*et al*., (1991) used rubber seed shell as adsorbent which was very effective for the removal of Hg(II) and Cr(III) from aqueous solution, the same rubber is modified with EDTA for sorption of Cd(II) and Pb(II) ions from aqueous medium. Previous studies have shown that thiolated beans (*Vignaunguiculata*) seed husk was used for sorption of As (III), and Cr (III) ions from aqueous solution, and chemically treated periwinkle shell was also used for the sorption of Pb(II) and Hg(II) from aqueous solution (Ashiegbu, 1995, Okuo and Ozioka, 2001). *Carica papaya* activated carbon has also been used in removing malachite green commonly found in textile industry (Omeiza*et al*., 2011).

A large number of activated carbon has been prepared from different raw materials such as coconut shell, rice husks, nut shell (Pollard *et al*., 1992), cow dung (Kagbu and Ekanem, 2004) with each having its own limitations and applications.

Ahmad *et al*. (2006) reported that most pollutants indicators are mobile and they are easily leached through to the underground waters. Experimental reports show that the use of biomass to alleviate the menace caused by indiscriminate discharge of heavy metals into the environment by industries has been extensively studied (Rao, *et al*., 1993, Alderhold*et al*., 1996, Okuo and Ozioka, 2001, Hammaini, 2003, Okolo and Okuo, 2004, Okuo*et al*., 2006; Raghavaro*et al*., 2009).

Ekanem, (1996) used cow dung to decolorize textile effluents and reported that the use of this adsorbent is highly effective. Many treatment methods have been developed for the removal of toxic compounds; these treatment processes involve adsorption by activated carbon, chemical sludge prepared from carbon, chemical coagulation, sedimentation, filtration, chemical Oxidation, and convectional biological treatments also known as activated sludge etc. (Chirwa and Wang, 1997; Crusberg, 1998; Khan *et al*., 2000). The extent to which this occurs differs between systems and places; and will have impact on the amount of these metals leached from the soil to water body.

2.5 Theory of Adsorption Isotherms

Adsorption isotherm is the relationship at a given temperature between the amount of substance adsorbed and its concentration in the solution. Weber and Morris (1964) presented three models based on the work of Langmuir and Freundlich models

In the Langmuir model the degree of adsorption of solute from an effluent or aqueous solution of a heavy metal onto adsorbent is taken as defining the distribution of a solute in the effluent between the adsorbent and the liquid phase. This distribution is a measure of the degree of equilibrium in the adsorption process which depends on the concentration of the solute in the effluent, the concentration and nature of adsorbents

Weber and Morris (1964) described it as

$$\frac{1}{\text{qe}} = \frac{1}{q_{max}} + \frac{1}{b\ q_{max}\ c_e} \quad \text{.....(2.1)}$$

Where C_e is the equilibrium concentration (mg/l).

q_e is the amount adsorbed at equilibrium time mgg^{-1}

q_m and b are Langmuir constants which relate adsorption capacity and the energy of adsorption respectively. q_m and b can be obtained from the slope and intercept of the graph C_e/Q_e against $C_{e..}$

The Langmuir adsorption isotherm is applicable to monolayer adsorption onto a surface having homogeneously distributed identical binding sites over the surface sorbent.

Langmuir adsorption made the following assumptions:

i. The adsorption is an equilibrium process
ii. Adsorption cannot proceed beyond monolayer coverage
iii. Each adsorption site is equivalent in terms of energy of adsorption and uniform i.e. the surface is perfectly flat on a microscopic scale and all sites are equivalent.
iv. There is no interaction between adjacent adsorbate molecules.
v. The surface containing the adsorbing sites is perfectly flat plane with no corrugations (assume the surface is homogeneous).

The Freundlich model, three assumptions were made

i. That maximum adsorption corresponds to a saturated monolayer of solute on the adsorbent surface.
ii. That there is no transmigratory activity of the adsorbent molecule on the plane of the surface.
iii. That the energy of adsorption is constant.

Equation 2.1 could be reduced to Freundlich isotherm, it can be expressed as:

$Q_e=KC_e^{1/n}$…….. (2.2)

and has been widely used for many years (Atkins, 1999). In the equation 2.2,

Q_e is similarly defined as that in the Langmuir isotherm, C_e is the equilibrium concentration, and K is a constant. The above can also be written as:

$$Log_{10}Q_e = \log_{10}K_F + \frac{1}{n}\log_{10} C_e \quad \text{(2.3)}$$

A plot of $Log_{10}Q_e$ against $\log_{10}C_e$ gives a straight line graph for dilute solution. $\log_{10}K$ is the intercept and 1/n is the slope. K and n are Freundlich constants, n gives an indication of how favorable the adsorption capacity of the adsorbent and capacity of adsorbent-adsorbate system which is the magnitude of adsorption capacity, and it decrease with temperature (Igwe*et al.*, 2007; Atkins, 1999; Uchimiya*et al., 2011*).

2.6 Heavy Metals as a Source of Pollution

Some heavy metals – such as cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc are essential to health in trace amounts. Others are non-essential and can be harmful to health in excessive amounts. These include cadmium, antimony, chromium, mercury, lead, and arsenic. There are two types of heavy metal toxicity: acute and chronic. In many cases, the symptoms brought on by metal toxicity are often misdiagnosed for chronic conditions such as autism, chronic fatigue syndrome, depression and multiple sclerosis. (Cowi, 2003; Romero-Gonzalez *et al.*, 2001).

Heavy metals are defined as those metals whose density is above $5g/cm^3$ (Pattabhi*et al.*, 2008). High degrees of their concentration in the environment are harmful and detrimental to plants, animals and all living organism systems. The harmful effect of heavy metals are due to their ability to bind to oxygen, nitrogen and sulfur groups in proteins, resulting in alterations of

enzymatic activity. The organ systems affected by heavy metals and the severity of the harmfulness vary with the particular heavy metal involved, the extent of exposure, the age of individual and the chronicity. The main sources of heavy metals pollution include urban industrial aerosols, solid wastes from mining activities, agricultural chemical among others (Bong *et al.,* 2004; Shetty and Rajkumar, 2009)

Nevertheless, there is great concerned by government on the effects of heavy metals and an attempt to protect public health has increased leading to upsurge researches in development of advanced technologies to remove heavy metals from wastewaters (Shinomiya and Yahaskel, 1978, Malik, 2003 and Resmi, *et al.,* 2010).

2.6.1 Sources and Toxicity of Some Selected Heavy Metals

2.6.1.1 Cadmium

Cadmium in its elemental form is a soft, silver-white metal. It is not usually present in the environment as a pure metal, but is most often present as complex oxides, sulphides, and carbonates in zinc, lead, and copper ores. Report has shown that cadmium does not have any recognizable odor (James *et al.,* 2007; Faller, 2009). Cadmium sulphate and cadmium chloride are quite soluble in water, whereas elemental cadmium, cadmium oxide and cadmium sulphide are almost insoluble. Cadmium (Cd) is one of the heavy metals considered to be toxic to humans and aquatic life. Over the last two decades there has been a sharp rise in the global use of Cd for batteries and a steady decline in its use for other applications, such as pigments, polyvinyl chloride stabilizers and plating. This trend in the case of Cd products and compounds has inspired a number of international agreements to manage and control the release of Cd to the environment and limit human and environmental exposure (Cowi, 2003). Chronic exposure to

Cd can cause kidney damage in mammals and humans (Wartelle and Marshell, 2011; Gaballah and Kibertus, 1998; Romero – Gonzalez *et al*., 2001). One of the major sources of surface water contamination by heavy metals, such as Cd, is urban and agricultural storm water runoff. There is a great need for new and cost effective processes for preventing excess concentration of toxins from accumulating in streams, Ponds and lakes (Gimba*et al.*, 2008; Hannafiah*et al.*, 2006).

2.6.1.2 Copper

Copper is a light reddish-brown metallic element with the symbol "Cu" and atomic number 29 on the periodic table of the elements. Naturally occurring pure copper is called "native copper." Copper is also found in nature mixed with other elements in a number of compounds, many distinguished by their blue-green color. Turquoise, malachite, and azurite are three brilliantly colored copper compounds used as gemstones (Atkins, 1999). Copper sulfate and copper oxide are two important copper compounds used in industry and agriculture. Copper can be mixed with other metals to form alloys, such as bronze (copper and tin) and brass (copper and zinc). Geological, meteorological, and biological processes disperse copper into the air, soil, and water. Human activity accounts for much of the copper found today in air, soil, and water. Industrial operations such as smelters, foundries, power stations, incinerators and other combustion sources emit copper into the atmosphere, where it can return to the earth in precipitation. Smelters and other copper production facilities emit high copper concentrations to surrounding air and soil (Micheal, *et al.*, 2005). Copper mines can be a significant source of pollution. Copper and other minerals present in the tailings; the waste left over after ore has been extracted from rock -makes their way into soil and waterways. Water can be polluted by a number of other copper sources as well, including agricultural runoff from farms using copper-based pesticides (James *et al*., 2007).

Some people who drink water with high copper levels may experience nausea, vomiting, abdominal pain, and diarrhea. (Igwe*et al.,* 2007; Gimba*et al.,* 2009)

2.6.1.3 Chromium

Hexavalent chromium is known for its negative health and environmental impact, and its extreme toxicity. It causes allergic and asthmatic reactions, is carcinogenic and is 1000 times as toxic as trivalent chromium. Health effects related to hexavalent chromium exposure include diarrhea, stomach and intestinal bleedings, cramps, liver and kidney damage (Deepa, *et al.,* 2006). The distinctive chemical property of chromium oxidation state, which can change from as low as +2 to as high as +6. Most often, in the natural environment, it occurs at an oxidation state of +2, +3 and +6. Chromium is a metal that rarely occurs in nature, the main mineral containing this element is chromate $FeCr_2O_4$, which contains up to 70% of pure Cr_2O_3.(Bong *et al.,* 2004). Chromium deficits are very rare and chromium feed supplements are not often applied. Chromium (III) toxicity is unlikely, at least when it is taken up through food and drinking water. Hexavalent chromium is mutagenic. Toxic effects may be passed on to children through placenta. Chromium (VI) oxide is a strong oxidant. Upon dissolution chromium acid is formed, which corrodes the organs. It may cause cramps and paralysis. The lethal dose is approximately 1-2g. A professional illness in chromium industries is chromium sores upon skin contact with chromates. Chromium trioxide dust uptake in the workplace may cause cancer, and damage the respiration tract (Allen, *et al.,* 1997; Csuros and Csuro, 2002).

2.7 Treatment of Industrial Effluents with Activated Carbon

Reports showed that adsorption of selected heavy metals using activated carbon from plant, fungi, biomass and other animal parts as adsorbent sources can be used to eradicate the pollution.

2.7.1 Adsorbent from Plants for Treatment of Effluents

Biosorption involves the use of biological material to concentrate, recover and eliminate pollutants from aqueous solutions. Various workers have investigated the adsorption of many heavy metal pollutants from waste waters (Tsezos and Bell, 1989; Fu and Viranaghovan., 2001). Reports also showed that sorption studies of materials such as heavy metals are controlled by the amount of organic matter (Deepa*et al.*, 2006).

Gaballah and Kibertus (1998) suggested that the uptake of copper by wood takes place by several mechanisms of reaction between Cu(II) species and surface carboxyl groups (RCOOH), hydrogen bonding of cuprate. Cu $(H_2O)_6^{2+}$ ion cellulose and formation of complexes with surface hydroxyl groups of ligand. Activated carbon used for the removal of toxic materials from effluents have been prepared from sun flower stalks (Sun and Xu, 1997); coir pith (Namasivayam and Kadinvelu, 2009); orange peel (Aram *et al.*, 2005); eucalyptus bark (Morais*et al.*, 1999); wheat straw (Nigam *et al*., 2003); Gant duck weed (Waranusantiqul*et al*., 2003); linseed cake (Liversidge*et al*., 1997); rice husk (Malik, 2003); cornelian cherry apricot and almond shell (Demirbas*et al*., 2004).Also, low cost cellulosic materials such bamboo pulp and saw dust have been used to remove Cu^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Zn^{2+} and Ni^{2+} from their aqueous solution, the mechanism of adsorption was ion exchange process (Shinomiya and Yahaskel, 1978). In the studies of the mechanism of adsorption Asku and Donmez (2003) suggested that the change in pH of the solution may indicate anion or exchange mechanism. pH factor has been found to favors adsorption of heavy metals, and also cellulosic non-reducing carbohydrate polysaccharides found in plant, such as cassava have also been used as cheap adsorbent for removal of dye from effluents (Horsefall*et al*., 2003).Carbonaceous materials such as coal, lignite, wood, peat etc. are used in the production of activated carbon commercially for the

removal of heavy metals from effluent because of the abundance and availability of agricultural wastes (Bansode*et al*., 2003).

2.7.2 Adsorbent from Fungi and Biomass for Treatment of Effluents

Recently the biosorption process has been studied extensively using filamenteous fungi as biosorbents to remove harmful substances because of their ease of cultivation and lack of pathogenicity on human and animals (Bras *et al*., 1992). It has been pointed out that adsorption of dyes and metal ions from effluents to make them harmless can be achieved by using fungal mycelia pellets (Ceribasi and Yetis, 2001; Fu and Viraraghavan, 2001; Sadhasivam*et al*., 2005; Deepa*et al*., 2006). Polyethylenimine-modified fungal biomass as a high-capacity biosorbent for Cr (VI) anions. Sorption capacity and uptake mechanisms, the sorption kinetics indicated that redox reaction occurred on the biomass surface, and whether the converted Cr(III) ions were released to solution or adsorbed on the biomass depended on the solution pH. Sorption mechanisms including electrostatic interaction, chelation, and precipitation were found to be involved in the complex sorption of chromium on the PEI-modified biomass.

Adsorption of heavy metals by salvinia biomass and agricultural residues, the investigations revealed that agricultural residues such as rice straw and wheat straw along with Salvinia biomass can serve as low-cost alternative for removal of heavy metals from wastewaters, the sorption of heavy metals was ion exchange mechanism, (Dhir and Kumar, 2010). The wide applicability of adsorbents such as activated carbon is generally attributed to their large surface area and porosity, making them potent adsorbents capable of removing most organic chemicals from effluents (Ahmedna*et al*., 2000). According to Koshima and Onishi (1993), activated

carbon can be used for the preparation of biological products such as medicaments; also it can be used for adsorption of trace quantities of metals from mine tailings, such as gold mine.

Allen (1974) classified treatment process into five conventional methods (e.g. screening, neutralization, sedimentation biological and coagulation), adsorption (using activated carbon), chemicals (e.g. oxidation), polishing (e.g. micro training, lagooning and others ion exchange, reverse Osmosis) with processes based on primary and secondary effluent treatment.

2.8 Preparation of Activated Carbon

Several methods are available for the preparation of activated carbon (Cookson, 1980). The most widely employed method involves treatment of the carbon material with activating agents and the carbonization of raw material in the presence of the modifiers (activating agents).

The various types of activation methods are given below:

(i) Impregnation method (IPM)

The carbonized sample is mixed with the activating agent prior to the use. This is then dried at room temperature and stored in air tight polythene bags (Gimba*et al.*, 2009)

(ii) Microwave method (MWM)

The carbonized sample is mixed with the activating agent and microwaved for 5 minutes.

(iii) One step Method (OSM)

The raw material and reagent are mixed into a paste, dried and carbonized in a rotary furnace at 600^{o}C for five (5) minutes. The activated product is washed with water and dried.

(iv)Two – step Method (TSM)

Different carbonized samples would be mixed separately with different activating agents. The mixture activated at 800^0C for five (5) minutes after which the activated products are washed with water and allowed to dry at room temperature.

2.9 Activating Agents

A wide range of chemical substance can be used as activating agents, these include acids, inorganic salts, organic salts and bases. Others are boric acid, calcium hydroxide, calcium phosphate, chlorine, cyanides, dolomite, ferric chloride, magnesium chloride, phosphoric acid, nitric acid, potassium trioxocarbonate(v) acid, magnesium sulphate, potassium sulphide, potassium thiocyanate, sodium hydroxide, sodium phosphate, sodium sulphate, sulphur, sulphurdioxide ,sulfuric acid and Zinc chloride (Yehaskel, 1978). Recently others used ethylenediamine tetra acetic acid, ferric monosodium salt, ferrous oxalate salt, cobalt sulphate, and cupric nitrate salt (Yang and Chen 2008; Faller, 2009)

2.10 Definitions and Processes of Adsorption

Cheremisinoff and Ellerbusch (1978) defined adsorptions as a reversible process in which liquid or gaseous molecules are concentrated on the surface by chemical or physical forces or both. The two major processes of adsorption are:

I. Chemisorption: This is a term used for chemical adsorption; it is also known as specific adsorption. It is limited to monolayer coverage of the substrate and a covalent bond is formed between the adsorbate and adsorbent. The bonding force associated is much stronger and the heat liberated during the process is much larger than that in physisorption. The enthalpy of chemisorption is within the region of 200kJ /mol (Atkins, 1999). Chemisorption is an irreversible

process; on desorption the chemical nature undergoes a chemical change (Bhatia, 2006). The energy required for the chemisorbed molecule to react with the molecular species may be considerably less than the energy required when the two species react directly in the gas phase.

II. Physisorption: It is also known as non-specific adsorption. It is a result of long range weak vander-waal's forces between adsorbates and adsorbents. The energy released when a particle is physisorbed is of the same order of magnitude as the enthalpy of condensation. The enthalpy of physisorption can be measured by monitoring the rise in temperature of a sample of known heat capacity. Typical values are in the region of 20kJ/mol (Atkins, 1999). The adsorption process is exothermic and liberates heat depending on the magnitude of the attractive force. Physisorption is usually directly proportional to the amount of solid surface available and the adsorption process is reversible.

2.11 Factors that affect the extent of adsorption

There are many factors that affect adsorption capacity of the adsorbent, these are listed below:

i. The nature of the adsorbate.

ii. The nature of the carbon.

iii. The concentration of the adsorbate.

iv. Effects of interfering substances.

v. The physical and chemical characteristics of the adsorbent such as surface area, pore size, chemical composition (Wartell*et al.*, 2001; Wing *et al.,* 1997; Uchiminiya *et al.*, 2011).

CHAPTER THREE

3.0 Materials and Methods

3.1 Sample Collection, Identification and Treatment

Samples of plantain peel were collected from SabonGari Central Market in Zaria, Kaduna State. Plantain peels were washed thoroughly with tap water and then with distilled water to remove all trace of impurities, oil, dirt, dust and salts. The samples were sundried and then dried in an oven at 100^{o}C for 24 hours. The dried PP were cut and pulverized into smaller particle sizes with a mortar and pestle; then sieved into different particle sizes such as 75 µm, 150 µm, 355 µm, 425 µm and 835µm. The plantain peel family is known as *musaceae*and was identified as *Musa paradisiaca*L. in Department of Biological Sciences Ahmadu Bello University, Zaria.

3.2 Reagents

The chemicals used were of analytical grade except where stated otherwise.

3.3 Carbonization Process

Carbonization process is achieved by weighing 2.00 g fresh batch of sample in clean silica crucibles and heating in an air – tight oven at 500^{o}C for 5hours. (Gimba and Bahago, 2004; Omeiza*et al*., 2011). The equation for the process is shown below:

$$\text{Raw plantain peel} \xrightarrow{500^{o}\text{C, 5 minutes}} C + CO_2 \quad \text{(carbonization)} \ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

3.4 Activation

Exactly, 2.00 g each of the carbonized plantain peel were weighed into three crucibles and mixed separately with 2 cm^3 of 0.1M NaOH, H_3PO_4 and $ZnCl_2$. Each crucible with its content was heated at 750 ± 5^{0}C for a period of five minutes. Each activated sample was allowed to cool

to the ambient temperature; the samples were washed with de-ionized water several times until pH 6-7, filtered with Whatman No. 1 filter paper and then dried in the oven at 110^{o}C for 8 hours. Activated carbon of same type and treatment were pooled together for adsorption studies. The equation for the process is shown below.

$$\text{Carbonized-plantain peel} \xrightarrow{750^{o}\text{C, AA, 5minutes}} \text{AC} + CO_2\,(\text{Activation}) \qquad 3.2$$

AA is the activating agent and AC is the activated charcoal.

3.5 Characterization Studies

3.5.1 Moisture and Dry Mater Content Determination

Clean crucibles were dried and 2.00 g of the raw plantain peel was placed in the crucible and weighed. This was dried in an oven at 105ºC for 3 hrs after which they were cooled in a desiccator and then weighed (Allen *et al.,* 1997)

$$\text{Moisture [\%]} = \frac{\text{Loss in weight on drying (g)}}{\text{Initial sample weight (g)}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.3)$$

$$\text{Dry matter [\%]} = \frac{\text{Oven dry weight (g)}}{\text{Initial sample weight (g)}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.4)$$

3.5.2 Ash Content Determination

Crucibles were heated in a furnace at about 500ºC, cooled in a desiccators, then 2.00g of plantain peel sample were weighed in them. The crucibles containing the dry sample were placed in a furnace, then the temperature raised to 700ºC. After 3 hrs the crucibles were removed and

allowed to cool in desiccators, after which they were weighed and the content of plantain peel was evaluated (Ocholi, 2006; Pattabhi*et al.*, 2008; Shetty and Rajkumar, 2009).

$$\text{Ash [\%]} = \frac{\text{Ash weight (g)}}{\text{Oven dry weight (g)}} \times 100 \quad \ldots\ldots\ldots(3.5)$$

3.5.3 pH Determination

Solution of the activated sample of plantain peel 1% (w/v) was prepared using mixture of the sample in deionized water. pH of the supernatant was obtained after 2hrs by using crisson pH meter (Faller, 2009).

3.5.4 Bulk density

This was determined by measuring the volume of water displaced when a known weight(2.00 g) of sample of activated carbon were dropped into a graduated measuring cylinder with tapping until the carbon occupied a initial volume (Bhatia, 2006)

Procedure

A 100 cm^3 calibrated measuring cylinders was washed and dried. 50 cm^3 of the water was added to the measuring cylinder and was noted. 2 grams of the sample was transferred into the measuring cylinder and volume of the increased water level was recorded. Care was taken to ensure there were no air bubbles before taking volume measurements

Calculation

Volume of water displaced (cm^3) = Final volume – Initial volume

Bulk density (g/cm^3) = $\frac{\text{Mass of samples}}{\text{Volume of water displaced}}$ ……. (3.6)

3.5.5 Elemental Analysis

The elemental analysis was carried out on both the raw and carbonized plantain peel samples using Neutron Activation Analysis (NAA) at the Centre for Energy Research and Training A.B.U. Zaria. Adoptions (employment) of both short and long radiation energy for neutron activation analysis were allowed, mainly to known all the probable elements present in the plantain peel.

3.5.6 FTIR Analysis

This was carried out on both the raw and carbonized peel (Ocholi, 2006; Omeiza*et al.*, 2011). This technique was used to determine the functional groups in the adsorbent which are responsible for adsorption of the selected metals. The FTIR was in the range 4000 - 400 cm^{-1} region with resolution of 4 cm^{-1}. For this analysis 0.20 g of granulated sample of plantain peel was encapsulated in 200 mg of KBr (sigma). The FTIR was recorded on a Shimatzu Fourier Transform Spectrometer at the National Research Institute for Chemical Technology (NARICT) Zaria. The scans were collected in the spectral range specified above (Cruros and Cruros, 2002).

3.5.7 Density of Carbonized Material

The oven dried plantain peel of a known weight Wa (2.0 g) was put into a measuring cylinder, was tapper gently and volume of the plantain peel recorded as Va. A known volume of distilled water was added slowly through the side of the cylinder to soak the sample thoroughly. The final volume containing plantain peel and distilled water was recorded as Vb.

The particle density is calculated as:

$$P\ (g/cm^3) = \frac{Wa}{Vb - Va} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3.7)$$

Procedure

A 100 cm^3 calibrated measuring cylinders was washed and dried. 20 cm^3 of the water was added to the measuring cylinder and was noted. 4.0 grams of the carbonized was transferred into the measuring cylinder and volume of the increased water level was recorded. Measurement was taken to ensured there were no air bubbles before taking volume measurements

Calculation

Volume of water displaced (cm^3) = Final volume – Initial volume (Vb-Va)

$$\text{Bulk density } (g/cm^3) = \frac{\text{Mass of carbonized}}{\text{Volume of water displaced}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3.8)$$

3.5.8 Determination of Surface Area

The surface area of various particle sizes were determined using the iodine adsorption method, the amount of aqueous solution was estimated by titrating a blank with standard thiosulphate solutions and compared with titrated values against iodine containing sample.

$$\text{Iodine value} = \frac{(B - S) \times M \times 126.91)}{B \times W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.9)$$

B and S are the volumes of thiosulphate solution required for blank and sample titrations respectively. W, the mass of activated plantain husk sample and M, the concentration of (mol/l) of iodine solute and 126.91, atomic mass of iodine .The iodine number is used to determine the surface area of different particle sizes of the activated carbon, by measure of the

microporecontent of the activated carbon on adsorption of iodine from solution. This is equivalent to surface area of activated carbon (Drake *et al*., 1996).

3.6 Preparation of Standard solutions of Cu^{2+}, $Cd^{2+}$and Cr^{6+}

3.6.1 Chromium stock solution (1000 mg/dm³)

Potassium dichromate ($K_2Cr_2O_7$) of 1.4675 g was dissolved in 100 cm^3 deionized water. This was then transferred into a 500 cm^3 volumetric and made up to mark with deionized water.

3.6.2 Cadmium stock solution (1000 mg/dm³)

Cadmium nitrate $Cd(NO_3)_2$ of 1.0516 g was dissolved in 100 cm^3deionized water. This was then transferred into a 500 cm^3 volumetric and made up to mark with deionized water.

3.6.3 Copper stock solution (1000 mg/dm³)

Copper nitrate $Cu(NO_3)_2.3H_2O$ of 1.8990 g was dissolved in 100 cm^3deionized water. This was then transferred into a 500 cm^3 volumetric and made up to mark with deionized water.

3.6.4 Working Solution of Cd^{2+}, Cr^{6+} and Cu^{2+}

The working solutions concentration of 50, 100, 200, 250, 300, 400 and 500 mg/dm^3were prepared from 1000 mg/dm^3 of stock by serial dilution (Al-Ashehe*t al*., 2000).

3.6.5 1M H_3PO_4

Exactly 67.80 $cm^3$of phosphoric acid (specific gravity of 1.7 g/cm^3) was measured into 1000 cm^3 volumetric flask and made up to the mark with de-ionized water.

3.6.6 0.1M NaOH

Exactly 4.0 g of sodium hydroxide pellets was dissolved in de-ionized water into 1000 cm^3 volumetric flask and made up to the mark with distilled de-ionized water.

3.6.7 0.1M $ZnCl_2$

Exactly 136.1 g zinc chloride was dissolved in de-ionized water into 1000 cm^3 volumetric flask and made up to the mark with distilled de-ionized water, (Atkins and De-paula 2003; Juang*et al.*, 1996*;* Fortier *et al.*,1953).

3.7 Adsorption Experiments

The experiments were carried out using the method of Argun*et al.,* (2007). Exactly 50.0cm^3 of working solution was measured into polythene bottles and 0.5g adsorbent was transferred into these bottles. The mixtures in polythene bottles were agitated at the same time with a basic reciprocating shaker at 200rpm for 3hours and left undisturbed on the desk for 24hours to allow the system to equilibrate. After 24 hours, the mixture was filtered through a whatman filter paper into another 100cm^3 polyethylene bottle. (Okiemen and Okiemen, 2001). The concentration of the residual or remaining metal ion in the filtrate after adsorption process was determined using AAS. The amount of the metal adsorbed was calculated using the equation

$$q_e = \frac{V(\mathrm{Co} - \mathrm{Ce})}{1000\,m} \qquad \text{.......} \qquad (3.10)$$

q_e is the amount of adsorbate ion adsorbed in milligram per gram of the adsorbent.

C_o is the initial concentration of the metal ion before the adsorption process, while

C_e is the equilibrium concentration of the metal ion in the filtrate after adsorption process,

m is the mass of the adsorbent and

V is the volume of the solution in cm^3.

The equation that gives percentage of metal ion removal by the plantain peel adsorbent is given by:

$$\% \text{ Adsorbed} = \frac{(Co - Ce)}{Co} \times 100 \quad \ldots\ldots (3.11)$$

C_o is the initial concentration of the metal ion before the adsorption process

C_e is the equilibrium concentration of the metal ion in the filtrate after adsorption process

3.7.1 Effect of Initial Concentrations on Cd^{2+}, Cr^{6+} and Cu^{2+} on the Adsorption

The adsorption experiment was by batch method. The experiment was carried out at ambient temperature (27±2^{o}C) with a basic reciprocating shaker using 100 cm^3 polythene bottle as a reactor. The working concentrations in mg/dm^3 for all metal were 20, 40, 60, 80, 100 and 120 mg/dm^3.

3.7.2 Effect of Adsorbent Dosage on the Removal of Heavy Metals (Cd^{2+}, Cr^{6+} and Cu^{2+})

Adsorbent dosage of 0.5, 1.0, 1.5, 2.2, 2.5, 3.0, 3.2 3.5 and 4.0 g were used to determine the adsorption efficiency of activated carbon of plantain peel on these selected metals. Each of the pre-weighed adsorbents were mixed with 100 mg/dm^3 of selected heavy metals, agitated for predetermined time of 60 minutes in a Griffin shaker at 27±2^{o}C. The adsorbent and adsorbate solution were separated by filtration using whatman filter paper. The concentrations of un-adsorbed heavy metals were determined using AAS technique of MUSRL/ABU Zaria (Ahalya*et al.*, 2005; Krishnakumar*et al.*, 2007)

3.7.3 Effect of Agitation Time on the Removal of Heavy Metals (Cd^{2+}, Cr^{6+} and Cu^{2+})

Exactly 0.50 g of activated carbon sample was used as constant adsorbent dose and 10 cm^3 working solution of 100mg/dm^3. The effect of agitation time is important in order to determine the time for maximum adsorption. The mixtures of adsorbent and metal ions solutions were shaken together at allowed agitation times of 10, 20, 30, 40, 50, 60, 120, 150 and 180 minutes. The final concentration of filtered supernatant filtrate was determined by spectrometer.

3.7.4 Effect of Particle Sizes on the Adsorption of Cu^{2+}, Cd^{2+} and Cr^{6+}

The adsorption capacities of various selected metals were determined using variable particle sizes. The employed particle sizes were 75, 150, 300, 425, 600 and 835 µm, with constant mass of adsorbent 0.5 g. The effect of particle sizes is very important as its give account of relative surface area, degree of porosity, filterability and density needed for the adsorption of selected heavy metals.

3.7.5 Effect of Activating Agents on the Adsorption Rate of Selected Metals

The strength of adsorption on activated carbon prepared from plantain peel was determined using different activating agents, these ranges from acid, base, salt to carbonized samples. The effect of chemical activation on the adsorption of metals ions (Cr^{6+}, Cu^{2+} and Cd^{2+}) are cogent, because chemical activation had significant effect on the iodine number and invariably increased the micropores and macropores of the activated carbons produced from plantain peel (Rao*et a*l., 2008 and Pattabhi*et al.*, 2008).

3.7.6 Effect of Agitation speed on the Adsorption Efficiency of Heavy Metals

The agitation speed on adsorption of selected metals were determined, the employed agitation speeds were 30, 60, 90, 120, 150, 180, 210, 270 and 320 rpm. The agitation speed give the measurement of frequency of rotation per minute, the degree of agitation speed improves the

diffusion of metal ions towards the surface of the adsorbent. This also implies that there is a shaking speed that is sufficient to ensure that all surface binding sites were made readily available for metal uptake in adsorption process.

3.8 Atomic Absorption Spectrometry

The concentration of the residual / remaining metal ion in the filtrates after adsorption process was determined using the Schimadzu Scientific Absorption Spectroscopy machine with model number VGP 240. Air- acetylene flame was used for all the determination.

3.9 Adsorption Modeling of Heavy Metal ions

Equilibrium adsorption experiments have been carried out to evaluate the adsorption capacity of the adsorbent. The batch equilibrium for the adsorption was performed in a set of Erlenmeyer flask (250 ml) where solutions of metal ions (50 ml) with different initial concentration (20-120 mg/dm^3) were placed in these flasks. Equal mass (0.5 g) of particle size 325µm activated carbon was added to each metal solution. The pH was adjusted to 7 by adding either few drops of diluted hydrochloric acid or sodium hydroxide, operation temperature was ambient temperature (27 ± 2^oC). Thereafter, the different supernatants were filtered and the concentration remaining in the filtrates were determined using spectrophotometer.

The rates of adsorption of the various samples were determined from the uptake level of the selected heavy metals in their aqueous solution. The degree of adsorption was determined using Langmuir model and Freundlich model.

3.9.1 Langmuir Isotherm model

The essential characteristics of Langmuir isotherm model can be expressed by a dimensional constant called equilibrium parameter, R_L (Pattabhi*et al.,* 2008) which is defined by equation below

$$R_L = \frac{1}{1+bC_e} \quad \text{.....3.12}$$

Where b is Langmuir constant at m^3/kg

C_e is initial concentration in mg/dm^3

The Langmuir isotherm modeling equation is given below

$$q_e = \frac{q_{max}\, b C_e}{1+bC_e} \quad \text{... ..... (3.13)}$$

Analytical isotherm equation such as Langmuir isotherm is widely used for modeling adsorption data.

$$\frac{1}{qe} = \frac{1}{q_{max}} + \frac{1}{b\ q_{max}\ c_e} \quad \text{.....(3.14)}$$

Where $q_e$is the amount of adsorbate adsorbed per gram of dried absorbent at equilibrium (mg ion bound per g of adsorbent for a monolayer adsorption capability, b is Langmuir constant or adsorption coefficient or the adsorption affinity (dm^3/mg) for binding of adsorbate concentration in solution after adsorption (mg/dm^3). The values of q_{max} and b can be calculated from the intercept ($\frac{1}{q_{max}}$) and slope ($\frac{1}{q_{max}\ b}$) of the plot of ($\frac{1}{q_e}$) against ($\frac{1}{c_e}$) (Limousin*et al*., 2007).q_{max} signifies whether the entity of the adsorbent in the adsorption of the selected metals is monolayer and b is adsorption constant related to the affinity of binding site and the lower the value of b, indicate the particle radius of adsorbents are small toward adsorption (Alderhold*et al.,* 1996; Asku and Donmez, 2003; Hanafiah*et al.,* 2006).

3.9.2 Freundlich Isotherm Modeling

A fairly satisfactory empirical isotherm, which can be applied to adsorption of gases with considerable success but has been used principally for adsorption from solution, has been discussed by Freundlich.

The Freundlich equation has general formula: $q_e = K_F C_e^{1/n}$ ……3.15

$Log_{10} q_e = Log_{10} K_F + (\frac{1}{n}) \log_{10} C_e$ ……3.16

Where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent, K_F is Freundlich constant measuring adsorption capacity, C_e is the equilibrium concentration of the adsorbate in solution, n is a constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent.

The Freundlich equation is basically empirical but is often useful as a means for data description. This is because the equation is adequate to describe non-linear adsorption in a narrow range of adsorbate concentration. The mathematical simplicity of the equation enables it to be used easily. It describes the adsorption processes on adsorption sites that are energetically heterogeneous. However, theoretically, the amount of absorbed solute may become infinite as bulk solute concentration increases and this is a disadvantage.

Taking the logarithm of equation (3.15), we obtained equation (3.16).

A plot of log q_e against log C_e gives a straight line with a slope 1/n and intercept of log K_f. The K_F value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The numerical value of n is a useful index of the adsorption capacity or efficiency and is related to the energy of adsorption intensity. The adsorption isotherm is useful for predicting the capacity that an adsorbent has for adsorbing adsorbate. The steeper the isotherm, the more effective is the

adsorbent. As the concentration increases, the higher will be the effective capacity at the concentration level desired for adsorption (Ceribasi and Yeti, 2001).

The Langmuir and Freundlich equations provide mathematical description of the experimentally observed dependence of capacity on concentration. The adsorption isotherm relates to an equilibrium condition. However, the practical retention times used in many water treatment applications do not provide sufficient time for true equilibrium to be obtained (Okuo*et al.,* 2006; Atkins, 2003; Zhou and Banks, 1993).

CHAPTER FOUR

4.0 Results

4.1 Physicochemical Properties

The results of determinations on plantain peel are presented in Table 4.1.

Table 4.1: Physicochemical Properties of Plantain Peel

Parameter	Mean ± Standard deviation
pH of 1% solution of raw plantain peel	6.8±0.3
pH of 1% solution carbonized plantain peel	7.3±0.12
Surface area (m^2g^{-1})	46.12±6.20
Bulk density (g/cm^3)	0.68±0.12
Density of Carbonized Material (g/cm^3)	1.68±0.09
Moisture Content (%)	6.70±0.11
Ash Content (%)	2.01±0.01
Dry matter (%)	93.3.0±2.11

4.2 Characterization of the Adsorbent

4.2.1 Fourier Transform Infrared Analysis

The FTIR spectra obtained for the raw and carbonized plantain peel samples are shown in Figs 4.1 and 4.2 respectively.

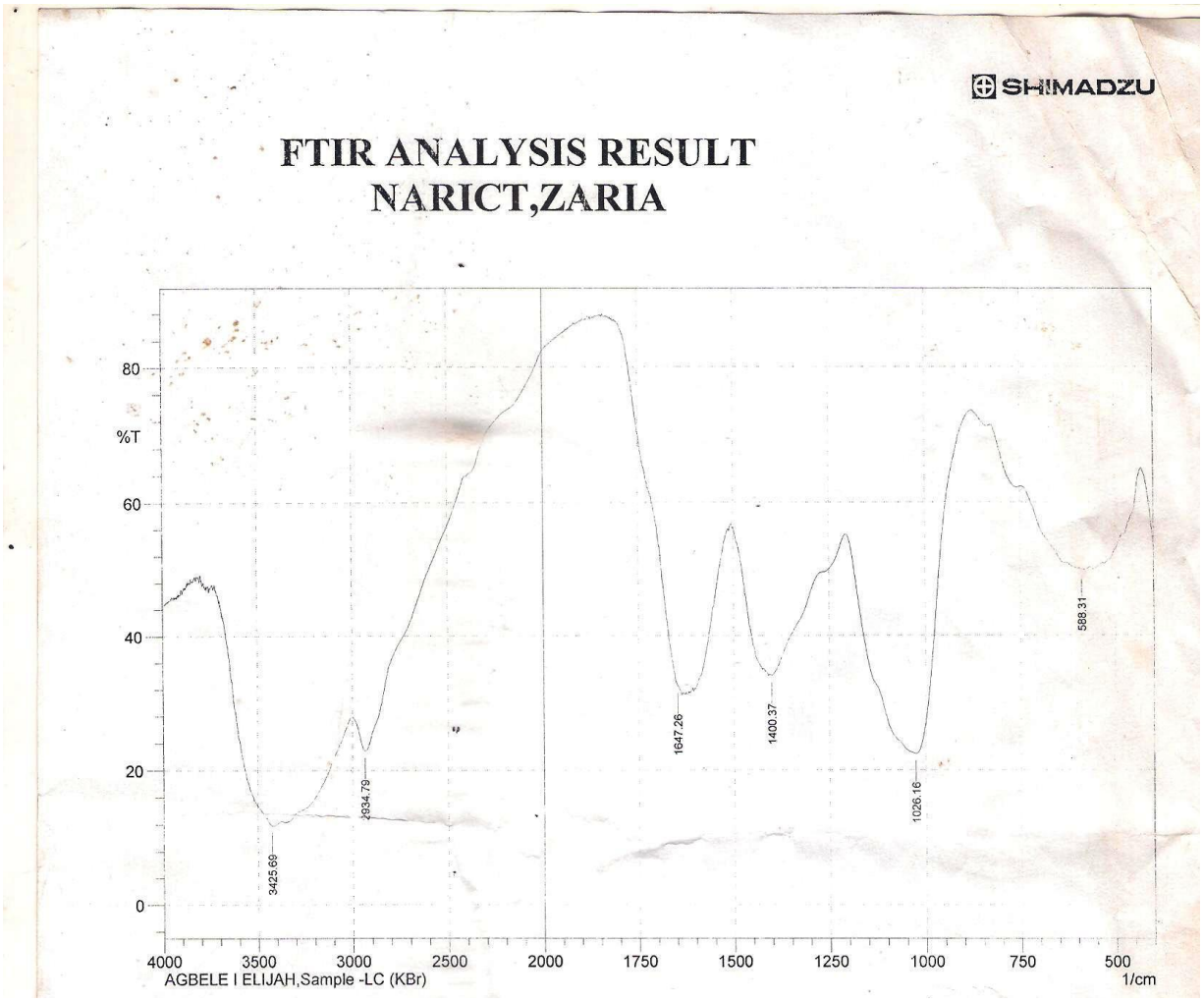


Figure 4.1: FTIR Spectra of Raw Plantain Peel Waste

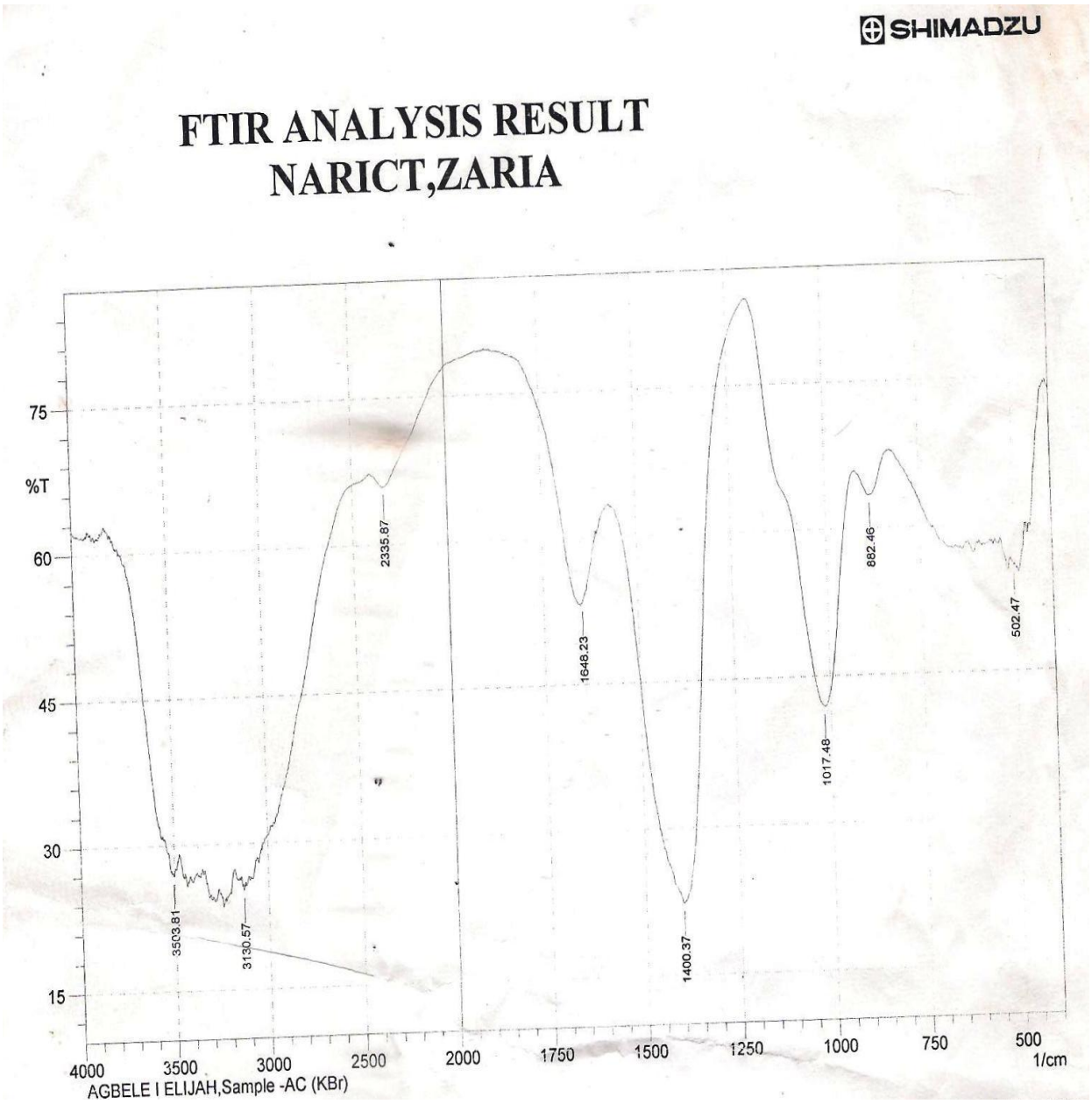


Figure 4.2: FTIR Spectra of Carbonized Plantain Peel Waste

Table 4.2 FTIR showing the different bonds present in the raw plantain peel

Wave number /cm^{-1}	**Intensity**	**Assignment**
588.31	Very sharp	N-H and C-H rocking
1026.16	Very sharp	O-H bending and secondary cyclic alcohols
1400.37	Sharp	-CH_2- and N-H bending, C=C, C=N
1647.26	Sharp	Amide, non-conjugated – C-C-H_3, C=O and C=N
2934.79	Sharp, very broad band	C-H stretching.
3425.69	Sharp	O-H stretching, intra-molecular H bonds and (free N-H), =C-H_2

Table 4.3 FTIR showing the different bonds present in the carbonized plantain peel

Wave number/cm^{-1}	**Intensity**	**Assignment**
502.47	Strong	N-H and C-H rocking
882.46	Strong	C=CH_2bending
1017.48	Strong	Secondary cyclic alcohol, C=C, C=N
1400.37	Weak	CH_3, C=O, C=N
1648.23	Strong	N-H bending
2335.87	Strong	O-H stretching
3130.57	Weak	O-H stretching chelate Compound
3503. 31	Sharp	O-H hydrogen bond

4.4 Elemental Composition of Plantain Peel by NAA

Table 4.4: Detected Element in Plantain Peel under Radiation by NAA

Elements	Concentration/ ppm
K	161.1
Mg	2057±272
Fe	268±39
Al	186±4
Cl	1929±33
P	2559±187
Sr	86.7±0.4
La	0.44±0.02
Zn	27±3
Br	20.7±0.1
Rb	66±22

4.3 Adsorption Experiments

4.3.1 Effect of Agitation Time on the Adsorption of Selected Metal.

The effect of contact time on cadmium, chromium and copper are shown in Figure 4.3.The Erlenmeyers were shaken at constant concentration of 20.0 mg/dm^3 with 120 rpm and 2.5 g adsorbent dosage at room temperature.

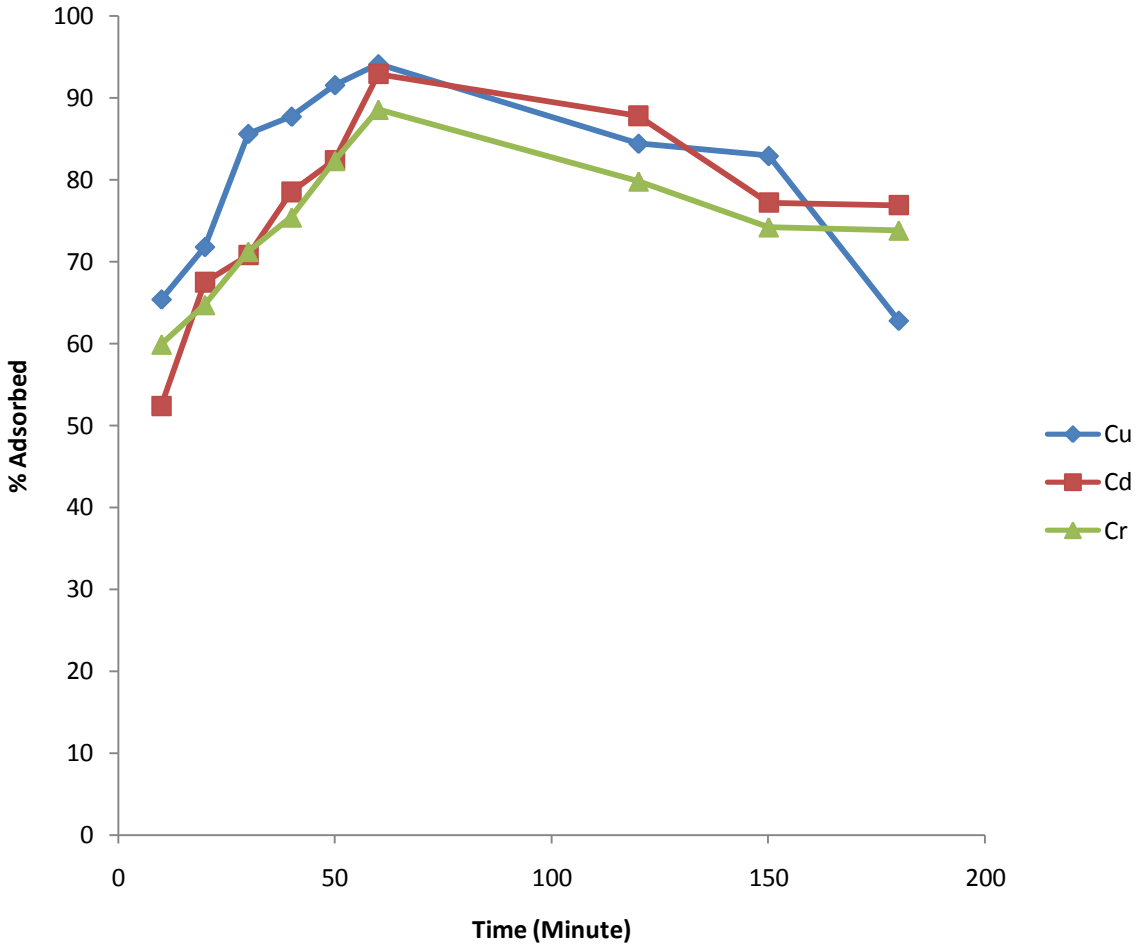


Figure 4.3: The Effect of Agitation Time on Adsorption of Cd^{2+}, Cr^{6+} and Cu^{2+} at pH of 6.5 and Particle Size 75 µm using Acid Activated Plantain Peel

4.3.2 Effect of Adsorbent Dosage on the Adsorption of Selected Metal

The effect of doses was investigated with two copper concentration (10 and 20 mg/l) at constant time 1 hour, 2.5 g adsorbent dosage, 150 rpm at ambient temperature and the results are plotted in Figure 4.4.

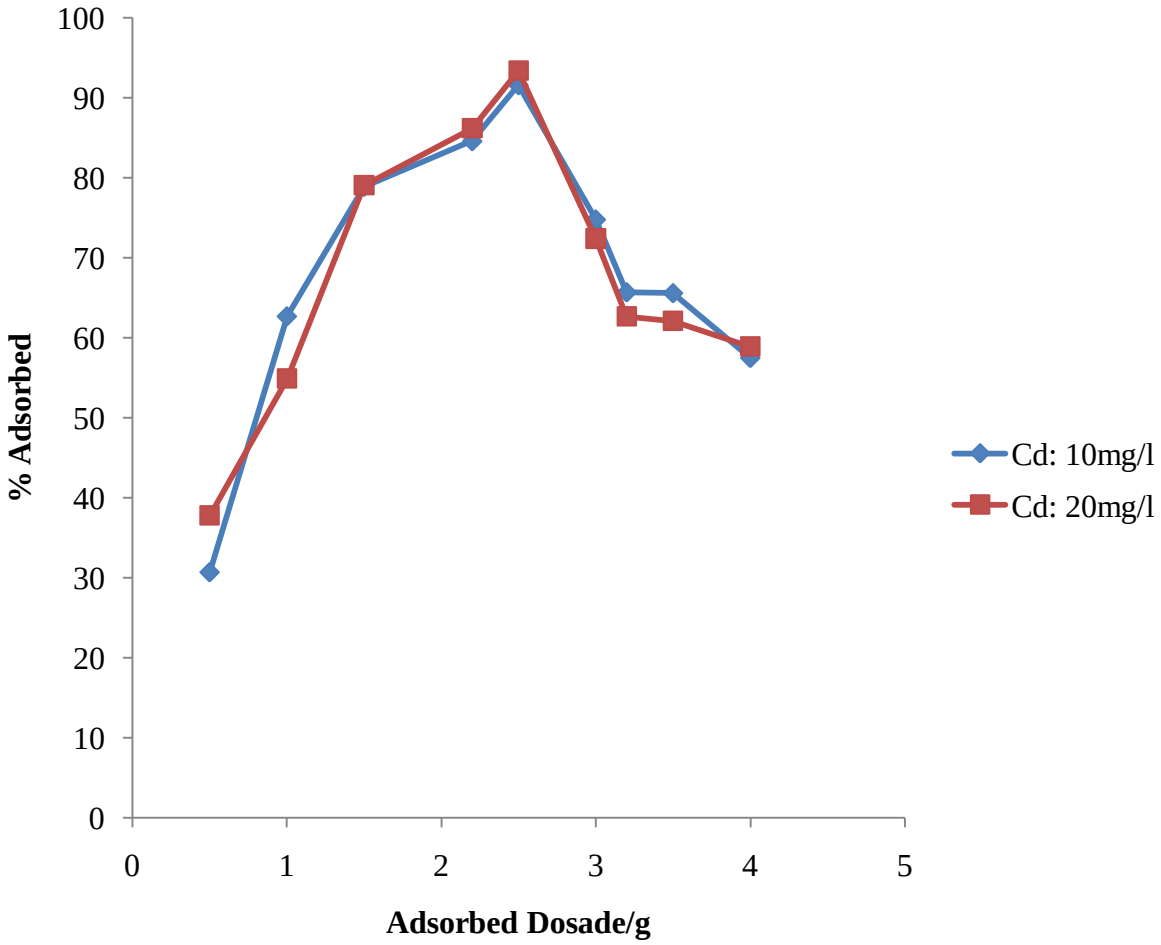


Figure 4.4: Effect of Adsorbent Dosage on the Adsorption of Cd^{2+} at pH of 6.5 and Particle Size 75 µm using Acid Activated Plantain Peel

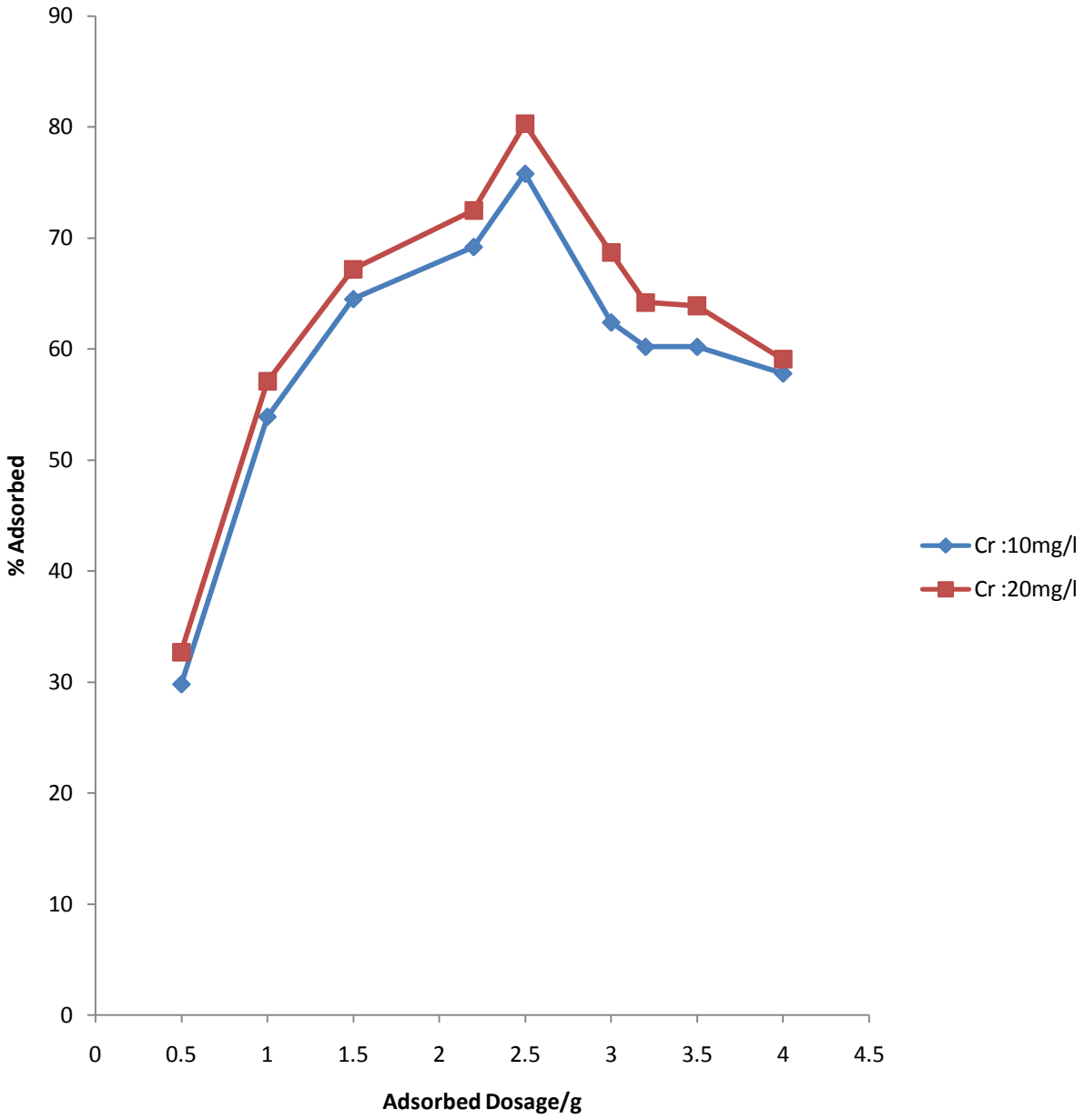


Figure 4.5: Effect of Adsorbent Dosage on the Adsorption of Cr^{6+} at pH of 6.5 and Particle Size 75 µm using Acid Activated Plantain Peel

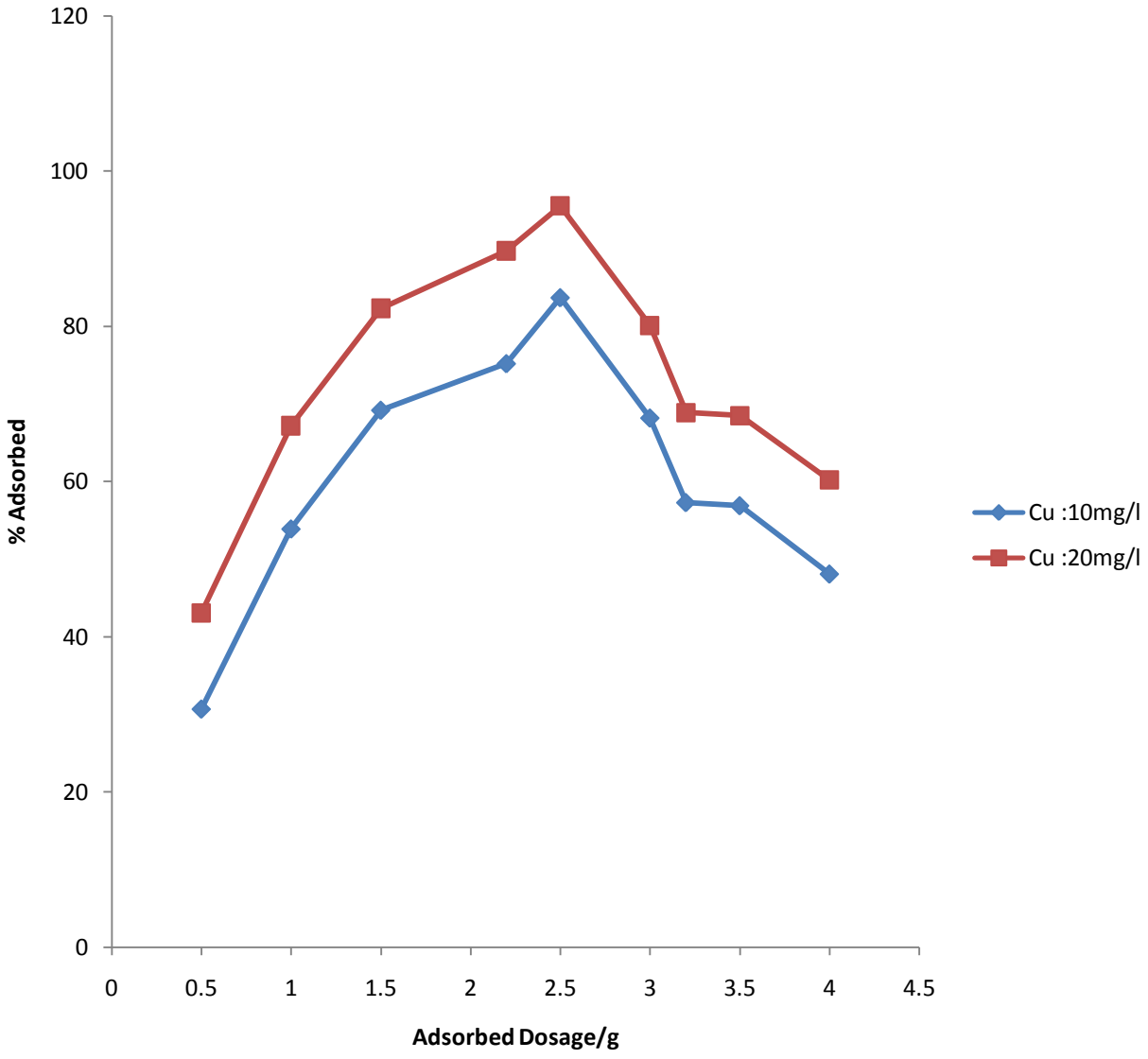


Figure 4.6: Effect of Adsorbent Dosage on the Adsorption of Cu^{2+} at pH of 6.5 and Particle Size 75 µm using Acid Activated Plantain Peel

4.3.3 Effect of Particle Sizes on Removal of Selected Metals Cd^{2+}, Cr^{6+} and Cu^{2+}

The effect of particle sizes was plotted in Figure 4.7. The Erlenmeyers were shaken for 60minutes at 150 rpm at room temperature when adsorbent dosage was 2.5 g with metal ions concentration 20.0 mg/dm^3

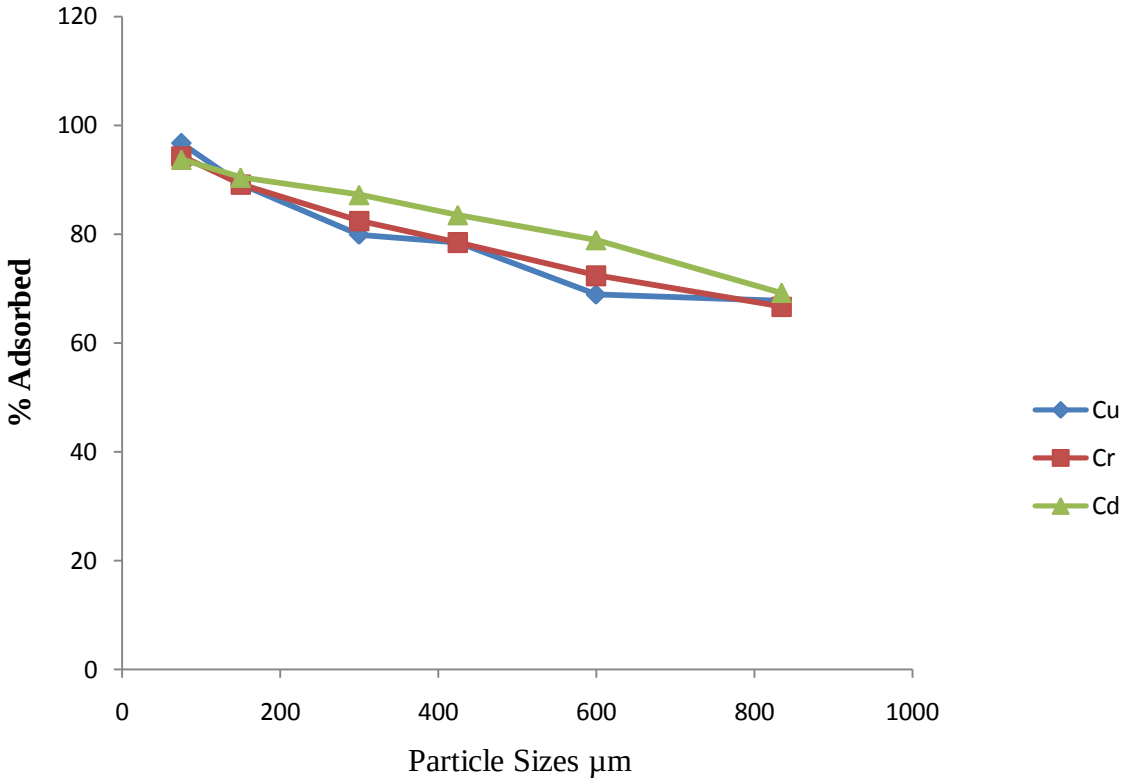


Figure 4.7: Effect of Adsorbent Particle Sizes on the Adsorption Efficiency of Cd^{2+}, Cr^{6+} and Cu^{2+} at pH of 6.5using Acid Activated Plantain Peel

4.3.4 Effect of Agitation Speed on the Adsorption Selected Metals

The effect of shaking speed on adsorption of selected metals were studied over the range of 30-320 rpm for 1h at concentration of 20.0 mg/dm^3 at ambient temperature with particle size of 75 µm and the results are plotted in Fig 4.8.

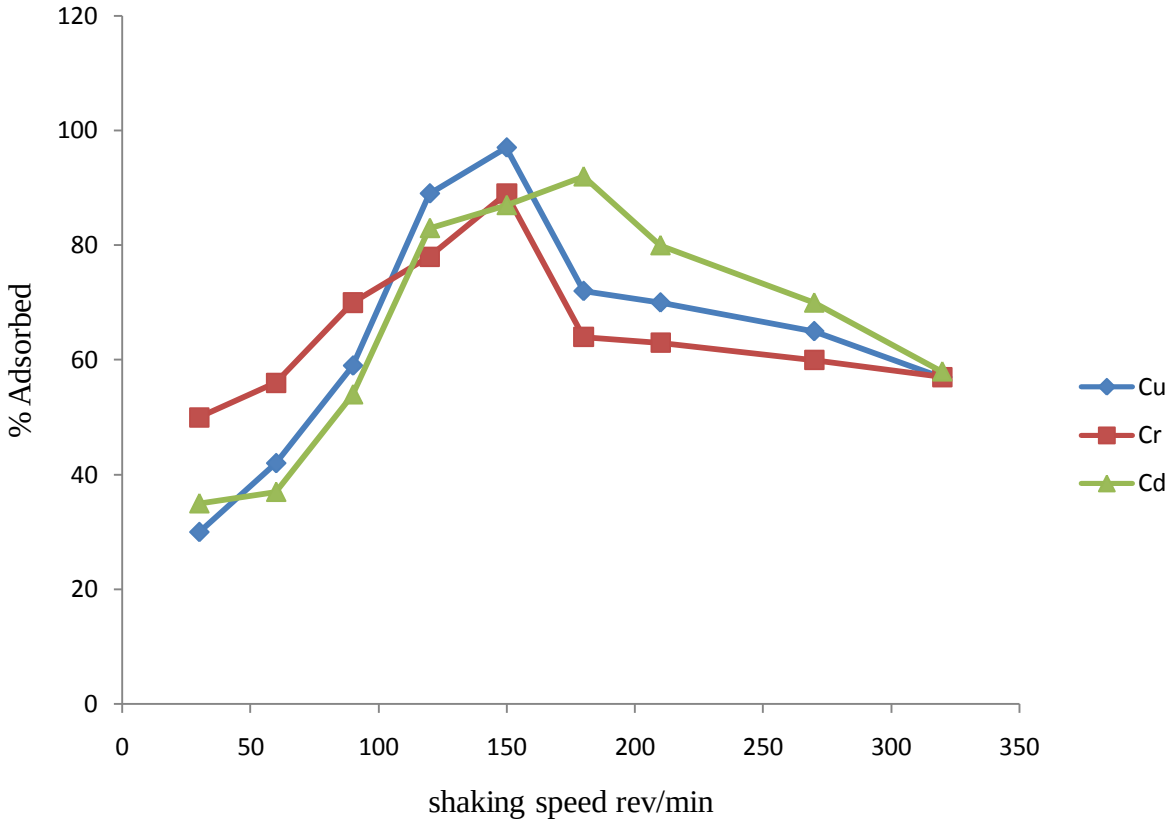


Figure 4.8: Adsorption Efficiency of Cd^{2+}, Cr^{6+} and Cu^{2+} uptake upon Variable Agitation Speed at pH 6.5 of 2.5 g adsorbent dosage using Acid Activated Plantain Peel Carbon

4.3.5 Effects of pH on the Removal of Heavy Metals of Cd^{2+}, Cr^{6+} and Cu^{2+}

The effect of pH on adsorption of heavy metals adsorption by adsorbent is shown in Fig 4.9. The Erlenmeyers were shaken for 1hour with 150 rpm at room temperature at concentration of 20.0 mg/dm^3.

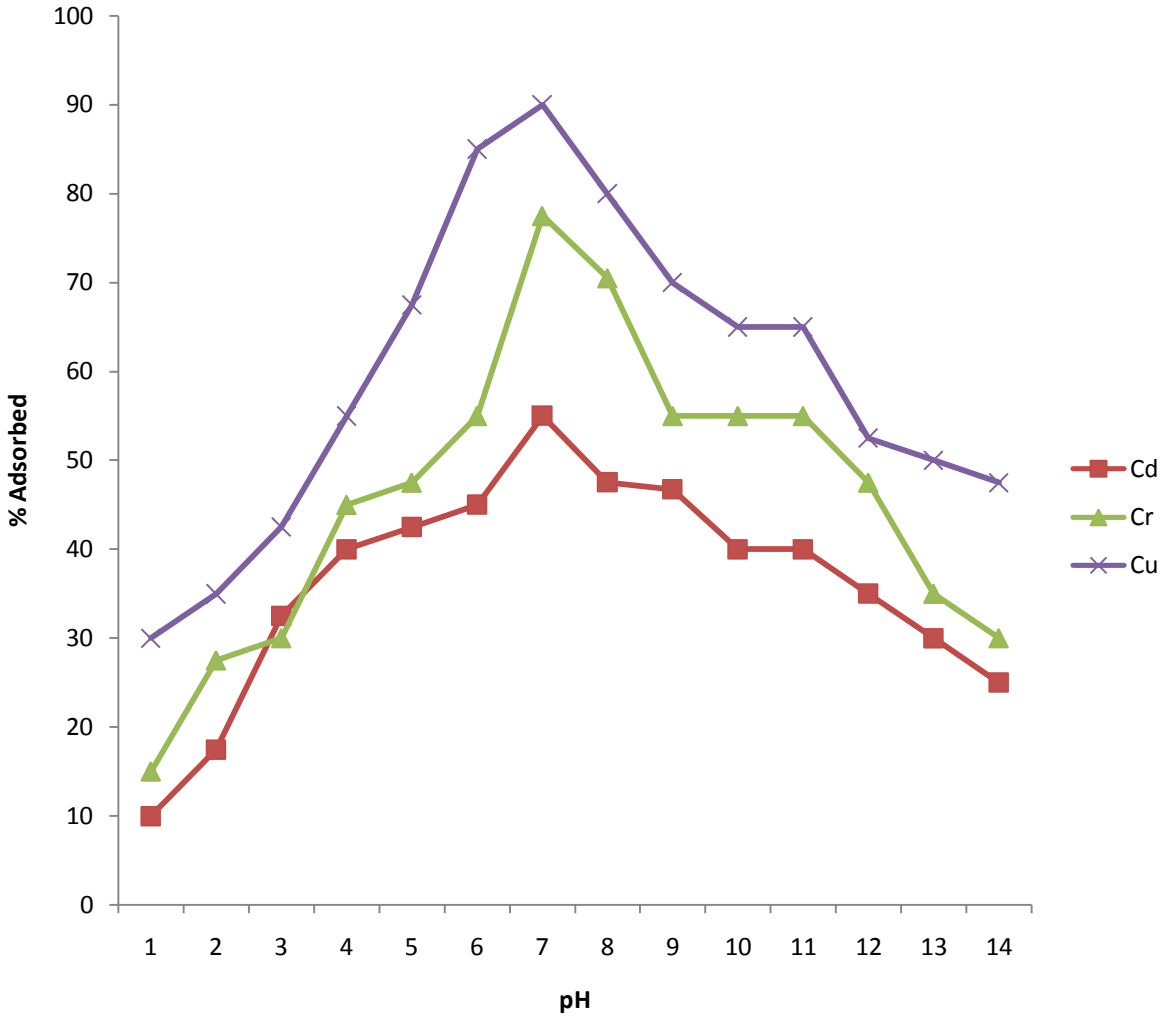


Figure 4.9: Effects of pH on the Removal of Heavy Metals at Adsorbent Particle size 75 µm using Acid Activated Plantain Peel Carbon

4.3.6 Effect of Activating Agents on the Adsorption of Selected Metals

The effect of activating agents on the adsorption of selected heavy metals at 150 rpm in 2.5 g adsorbent dosage of pH 6.5 as shown in figure 4.10

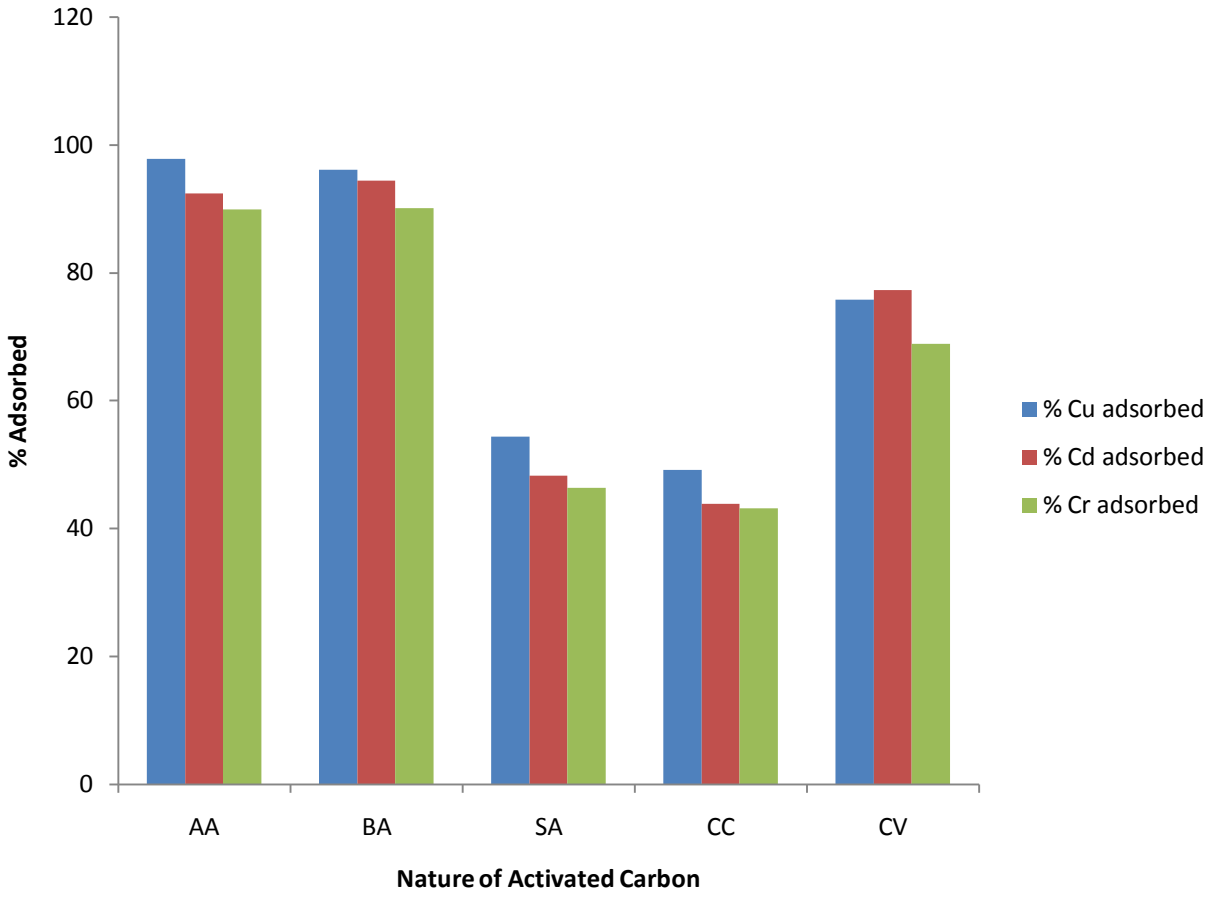


Figure 4.10: Effect of Activating Agents on the Adsorption of Selected Metals in 60min at ambient temperature with metal ions concentration 20.0 mg/dm^3

AA – Acid Activated (H_3PO_3)

BA – Base Activated (NaOH) SA – Salt Activated. ($ZnCl_2$)

CC –Un-activated Carbon CV – Commercial Activated Carbon

4.3.7 Effect of Initial Concentration on Cu^{2+}, Cd^{2+} and Cr^{6+} Adsorption

The effect of initial concentration on the adsorption of selected metals as shown in Figure 4.11 when the agitation time is 1h,adsorbent dosage 2.5 g at 150 rpm with pH of 6.5

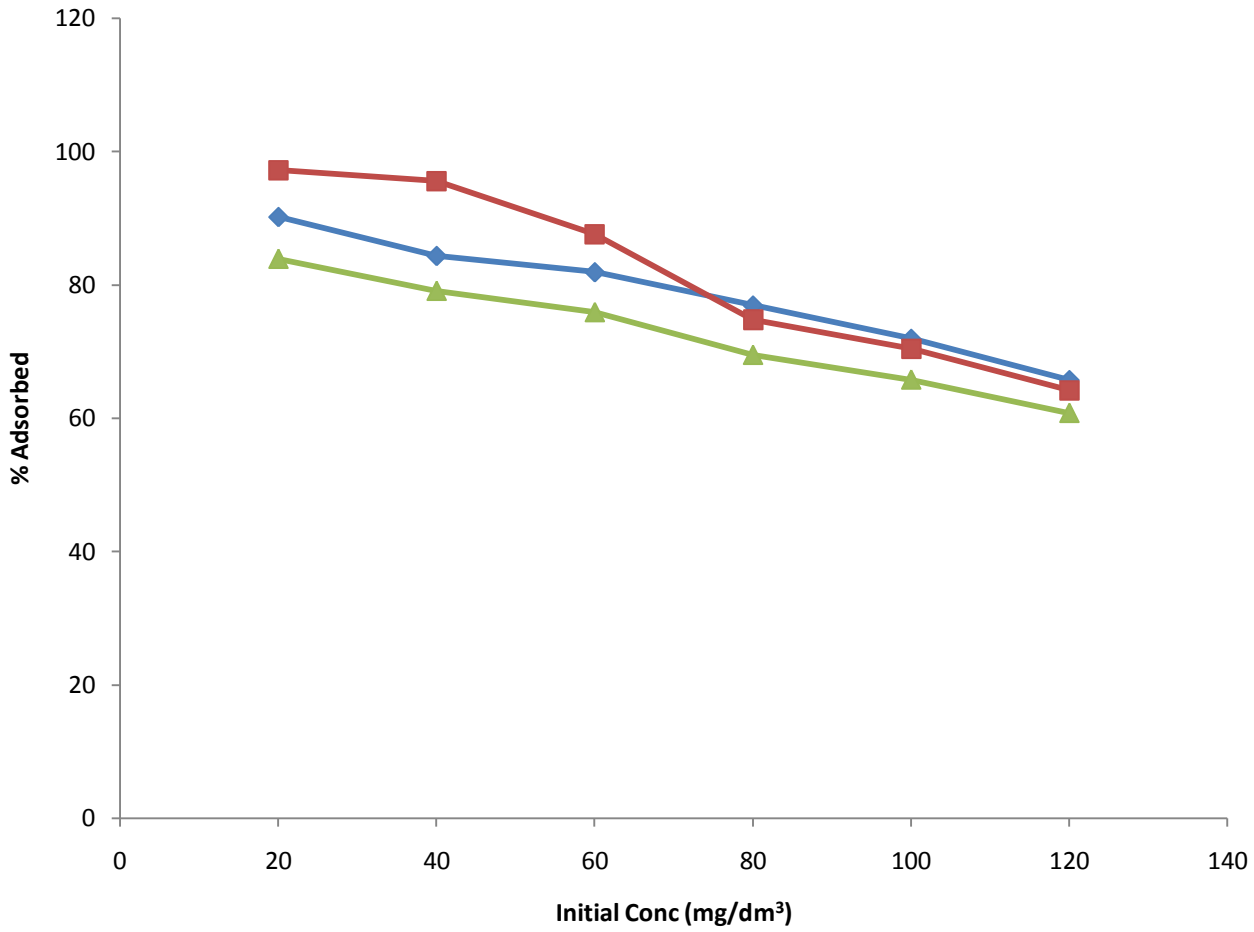


Figure 4.11: Effect of Initial Concentration on Cu^{2+}, Cd^{2+} and Cr^{6+} Adsorption at Adsorbent Particle size 75 µm using Acid Activated Plantain Peel Carbon

Table 4.5: Equilibrium Data on Initial Metal Ion Concentration for Estimation of Adsorption Effectiveness

Table 4.5 present equilibrium data that showed the effect of initial metal ion concentration of Cd^{2+}, Cr^{6+} and Cu^{2+}on adsorption revealed the percentage metals adsorbed and concentration of adsorption capacity at equilibrium.

Initial Conc (mg/dm^3)	Copper		Cadmium		Chromium	
	q_e(mg/g)	% Adsorbed	q_e(mg/g)	% Adsorbed	q_e(mg/g)	% Adsorbed
20	2.82	90.2	3.42	83.9	3.14	97.2
40	3.91	84.35	4.19	79.1	5.16	95.6
60	5.27	81.9	7.13	75.9	7.42	87.6
80	8.82	76.9	10.61	69.5	9.31	74.8
100	10.3	71.9	14.3	65.8	14.55	70.4
120	13.71	65.7	15.1	60.8	23.29	64.2

4.3.8 The Langmuir and Freundlich Isotherms Modeling for Metals Uptake

The extent of adsorption capacity of selected metal ions were determined using Langmuir and Freundlich Isotherms Modeling as shown in Figure 4.12 to 4.17 respectively

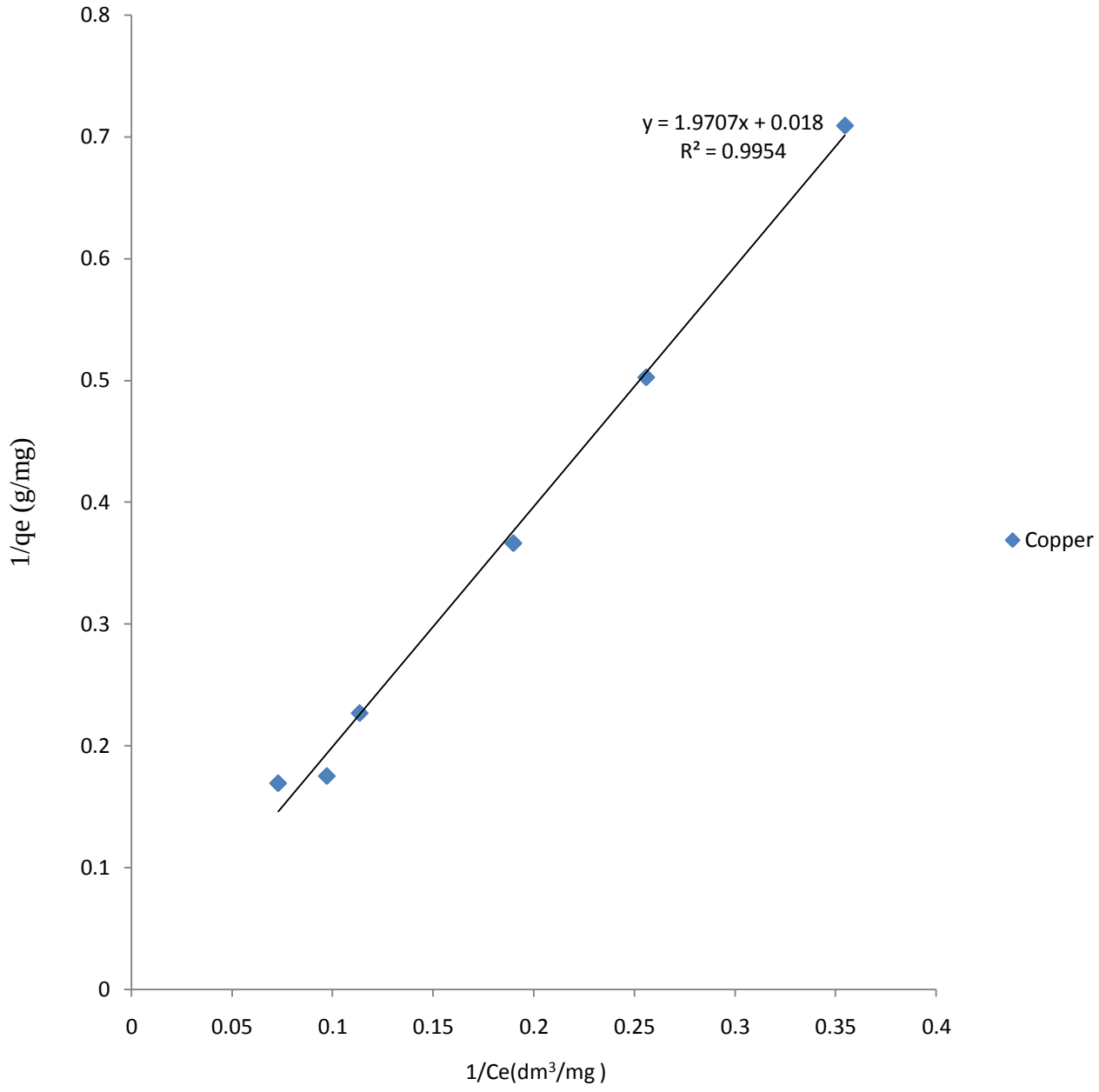


Figure 4.12: Langmuir Adsorption Isotherm for Cu^{2+} Adsorption

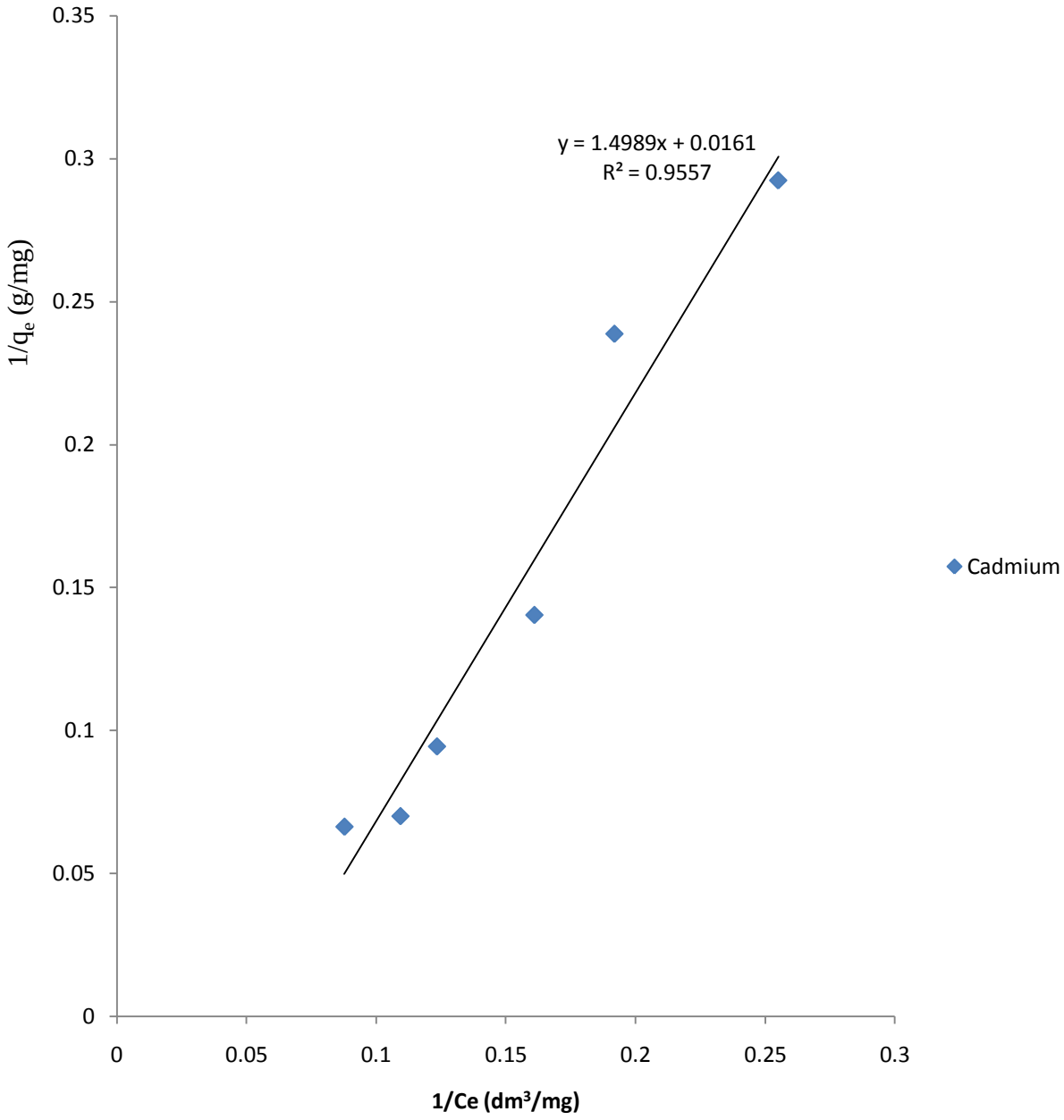


Figure 4.13: Langmuir Adsorption Isotherms for Cd^{2+} Adsorption

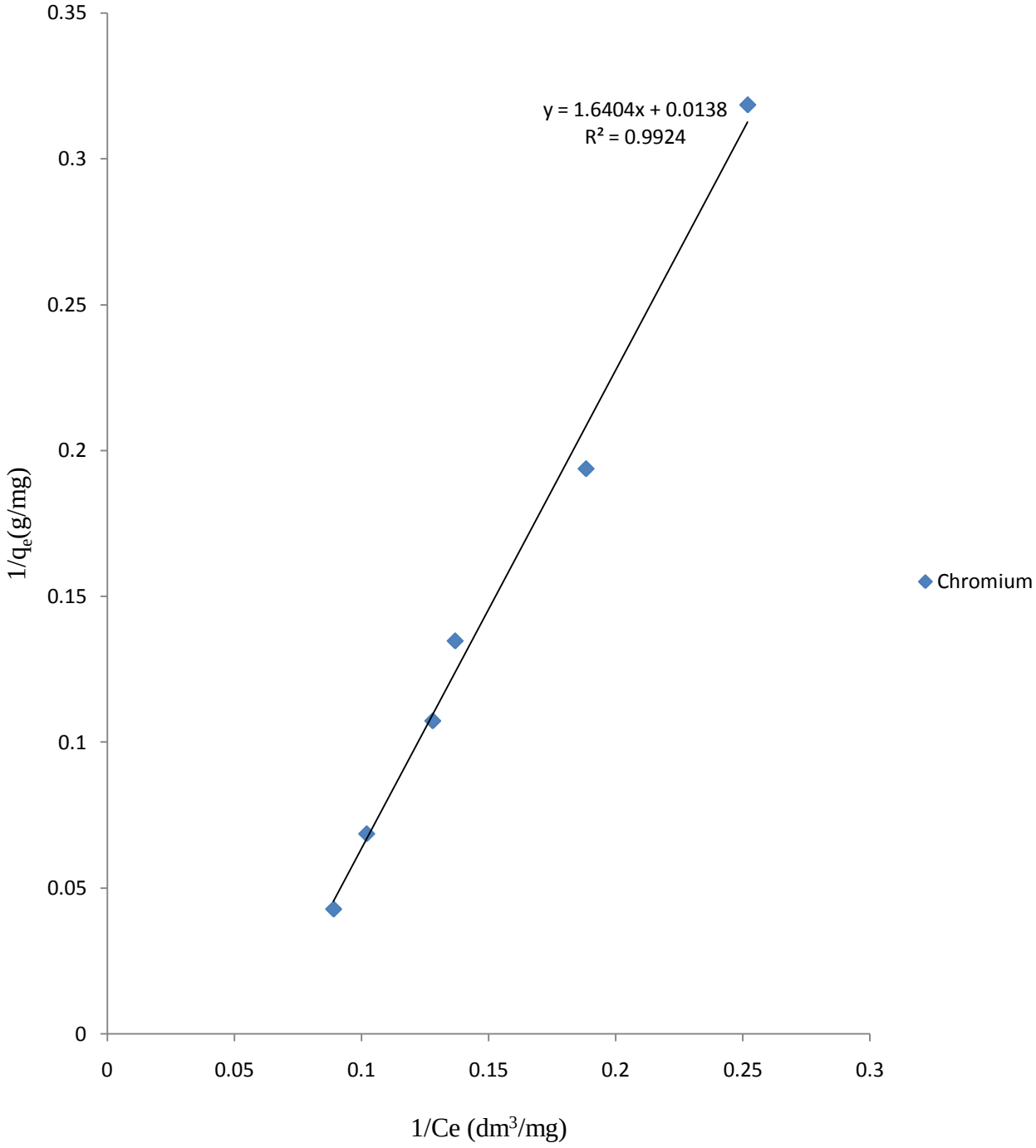


Figure 4.14: Langmuir Adsorption Isotherm for Cr^{6+} Adsorption

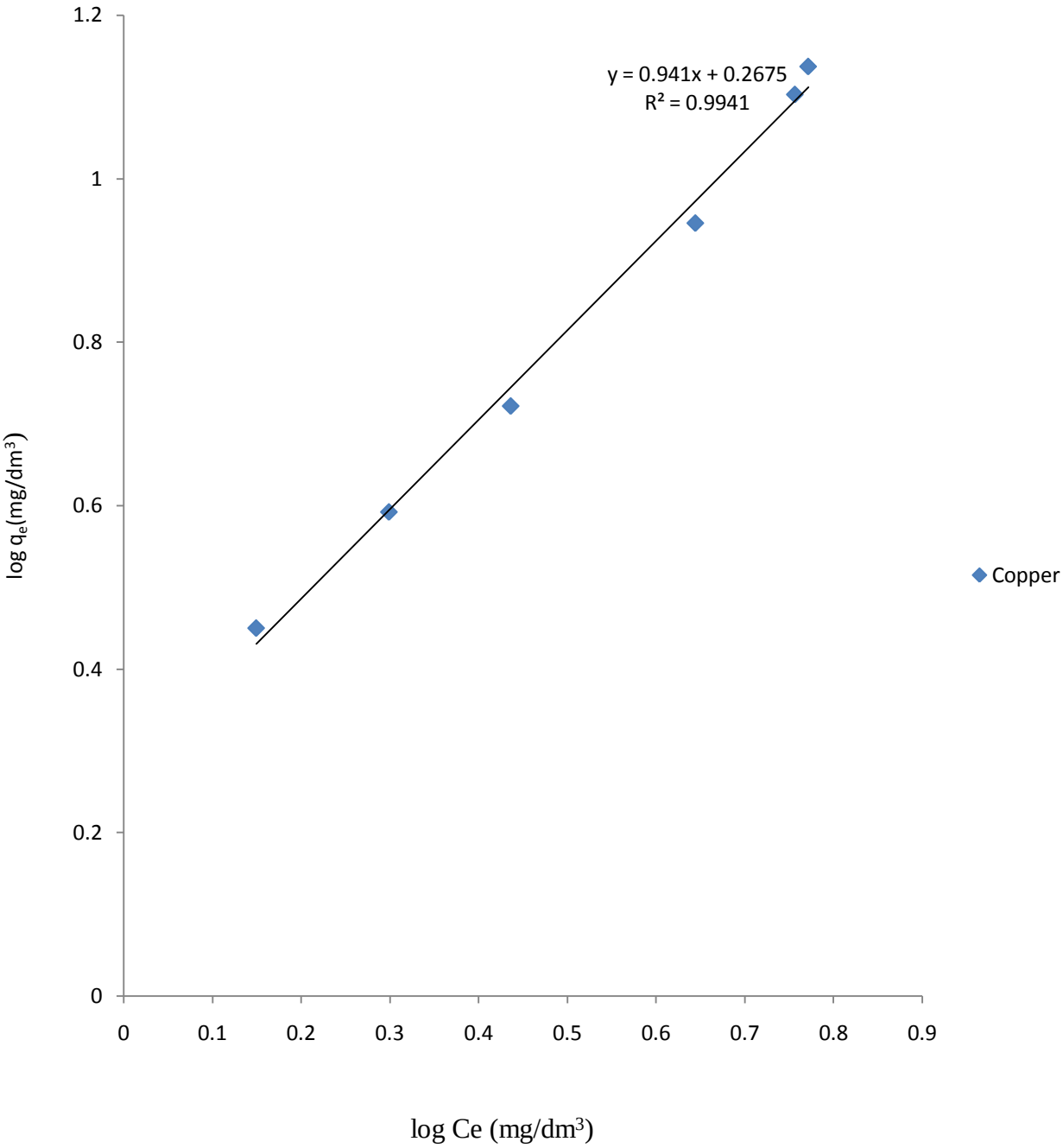


Figure 4.15: Freundlich Adsorption Isotherm for Cu^{2+} Adsorption

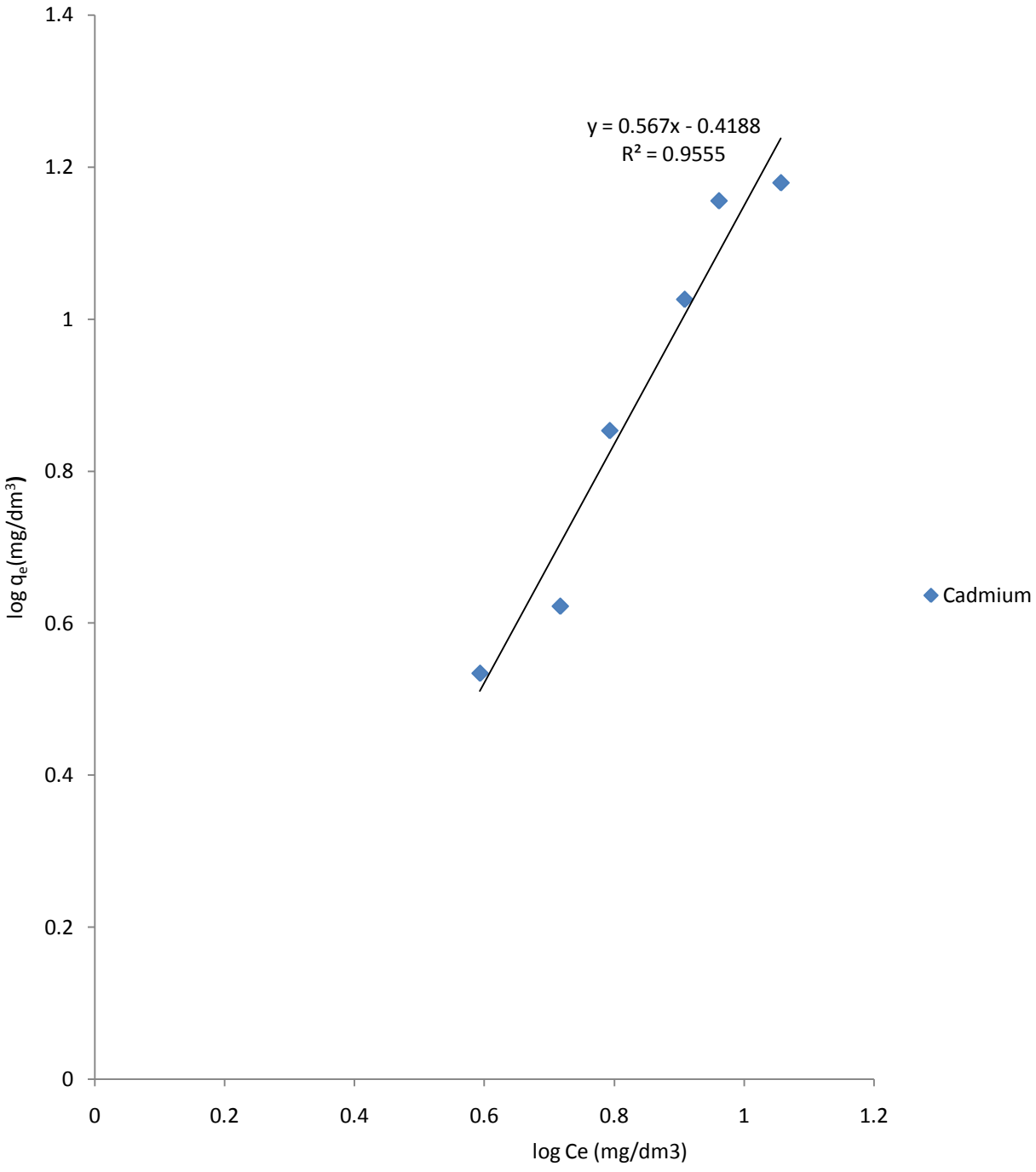


Figure 4.16: Freundlich Adsorption Isotherm for Cd^{2+} Adsorption

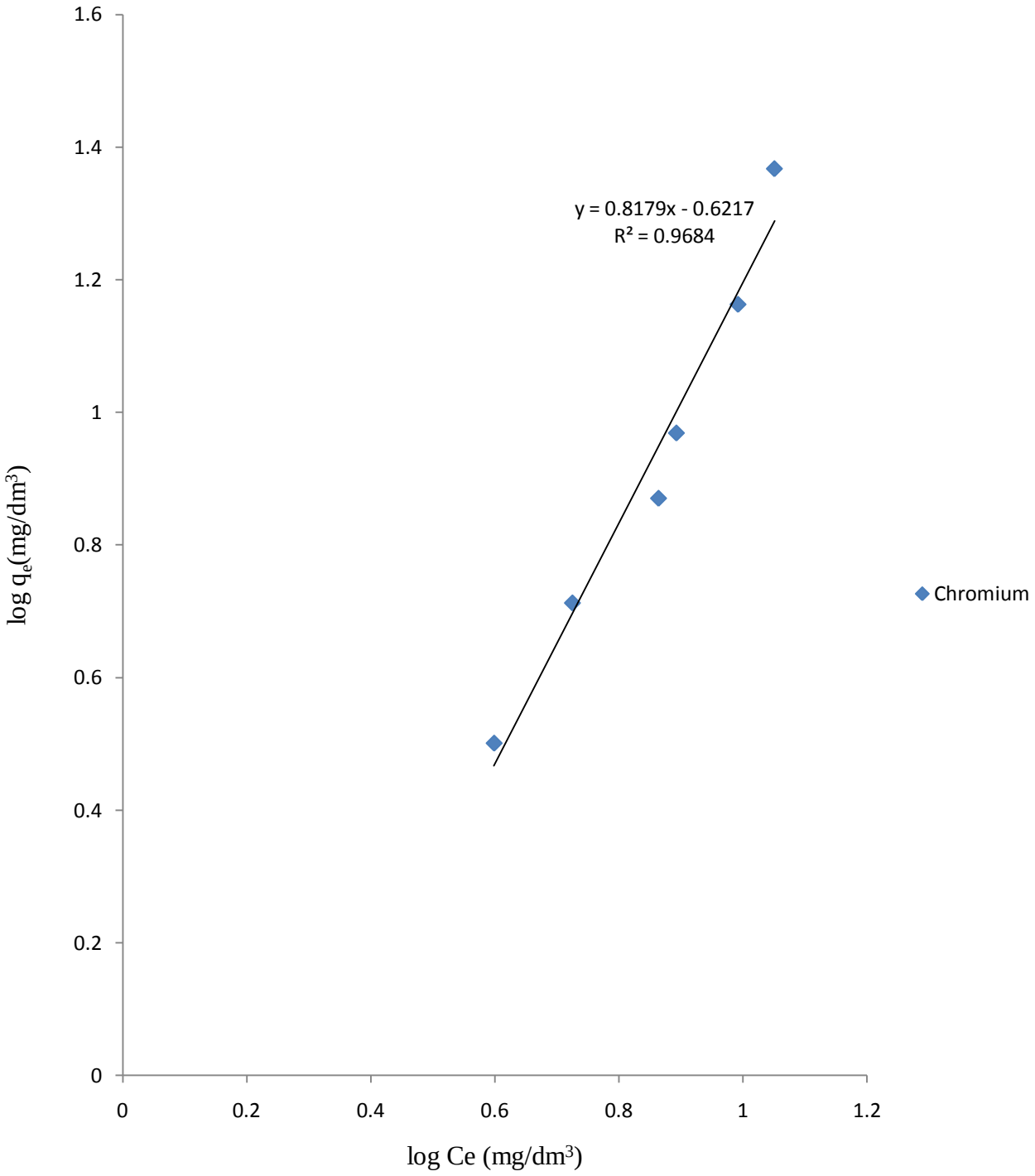


Figure 4.17: Freundlich Adsorption Isotherm for Cr^{6+} Adsorption

Table 4.6: Langmuir and Freundlich Isotherms Constants for the Adsorption of all selected Metals on Activated carbon Prepared from Plantain Peel.

Metals	Langmuir Constant			Freundlich Constant		
	q_{max}(mg/g)	b(dm^3/mg)	R^2	1/n	K_F (dm^3/mg)	R^2
Cadmium	62.11	0.0107	0.956	0.567	0.381	0.955
Copper	55.56	0.0091	0.995	0.941	1.851	0.995
Chromium	72.46	0.0084	0.992	0.817	0.239	0.968

Table 4.7: The $R_{L,}$ Separation Factor of Adsorption of Cu^{2+} on Plantain Peel Activated Carbon

q_{max}	$q_{max}b(m^3/kg)$	Initial Conc(mg/dm^3)	R_L
		20	0.0895
		40	0.0468
43.48	0.5087	60	0.0317
		80	0.0240
		100	0.0193
		120	0.0161

Table 4.8: The R_L, Separation Factor of Adsorption of Cd^{2+} on Plantain Peel Activated Carbon

q_{max}	$q_m b (m^3/kg)$	Initial Conc(mg/dm^3)	R_L
		20	0.0699
		40	0.0362
62.11	0.665	60	0.0244
		80	0.0185
		100	0.0148
		120	0.0124

Table 4.9: The R_L, Separation Factor of Adsorption of Cr^{6+} on Plantain Peel Activated Carbon

q_{max}	$q_m b (m^3/kg)$	Initial Conc(mg/dm^3)	R_L
		20	0.0758
		40	0.0394
72.46	0.609	60	0.0274
		80	0.0201
		100	0.0162
		120	0.0135

CHAPTER FIVE

5.0 Discussion

5.1.1 Dry Matter and Moisture Content of the Plantain Peel

The laboratory results of the moisture content and dry matter content were determined to be 6.7% and 93.3% respectively as shown in Table 4.1. The moisture content of a sample refers to the percentage of water content of the sample. These gave a tangible and substantial amount of organic matter needed for conversion to carbon by carbonization process. Hence, the results obtained for PP samples were good since the yield and quantity of the activated carbon produced can be enhanced by removal of moisture (Shakirullah*et al*., 2006). The percent moisture was higher than 4.18% for walnut shell reported by Abechi (2006) while lower than 7.21% reported by Erhan*et al.*, (2004) for almond shell. According to Abram (1973), the moisture content should be taken into account when evaluating the relative capacities of different carbon materials for the adsorption of a wide range of adsorbates (Roles *et al*., 1997).

5.1.2 Ash Content of the plantain peels Sample.

The percentage of ash content for PP sample was found to be 2.01% as shown in Table 4.1. The ash content of a sample is the inorganic residue left after the organic matter has been burnt off; also the ash content depends on the types of plant and carbon source (FAO, 2005; Akyeampong, 1999). The obtained value for plantain peel was favorable because the ash content serves as interference during the adsorption (Khan *et al.,* 2009). The ash content of plant origins have reported value ranging from < 2- 25% for rice husks. The lower the ash content the better the starting material (Lin and Wu 2001). The result obtained for plantain peel was consistent with Abechi (2006) reported 1.47% for walnut shell; Romero Gonzalez *et al.*, (2001) reported ash

content of 2.0%, 2.21% and 2.14% for cornelian cherry, apricot stone and almond shells respectively.

5.1.3 pH of Raw and Carbonized Samples

The pH of raw PP was determined to be 6.8 while the pH of the carbonized PP was 7.3 as shown in Table 4.1. The pH parameter is a factor affecting adsorption capacity of heavy metals. It is well known that pH could affect the protonation of functional group on plantain peel as well as metal chemistry (Tsezos and Bell, 1989). In general, a decrease in metal ions uptake at acidic pH is due to an increase of competition between hydrogen ions and metal ions for the same adsorption sites. However, an increase in alkalinity enhance metal adsorption rate, due to the predominant presence of hydrated species of heavy metals, changes in surface charge and the precipitation of the appropriate salt. Therefore, there is an optimum pH in which the competition of hydrogen ions is minimized and metal ions precipitation is avoided thus, enhancing metal adsorption (Wartelle*et al*., 2001). Both values were in agreement with the finding of Cheremisinoff and Ellerbusch (1978) that the pH of either raw or carbonized agricultural materials in water suspension can vary between 4 and 12. The value obtained for carbonized raw sample is slightly alkaline, because any activated carbon from plant origin source has alkaline surface which enhance adsorption capacity of heavy metals (Parkhurst*et al*., 2004). This result was consistent with pH of 7.5 obtained by Gimba*et al.,* (2008), and pH of 7.4 as reported by Abechi (2006).

5.1.4 Carbonized Samples and Bulk Densities of Plantain Peel

The carbonized samples and bulk densities of plantain peel were 1.68 g/cm^3 and 0.68 g/cm^3 respectively as shown in Table 1.Density is an important physical parameter especially when an adsorbent is to be investigated for it filterability (Ayoola and Akinbami, 2011). Higher density

provides greater volume activity and normally indicates high quality adsorbent. The obtained values for plantain peels were favorable because it revealed that it was good adsorbent in terms of volume activity, since adsorption is a surface process (Kundu and Gupta 2006). The result was in agreement with Ocholi (2006) reported 0.563 g/cm^3 for *Delonixregia*pods; Gimba*et al.*, (2009) reported 0.81 g/cm^3 for *Khayasenegalensis*fruits and Shakirullah*et al.*, (2006) reported 1.26 g/cm^3 for sawdust of *Dalbergiasissoo*Abechi (2006) reported 1.1034g/cm^3 for walnut shell.

5.1.5 Surface Area of the Plantain Peel

The surface area is a key quality parameter of adsorbent (Abram, 1973). Plant adsorbents are typically porous material with surface areas in the range between 10^2 to 10^3 m^2/g, also their porosity allows the realization of such large surfaces area constituted by the pore walls (Nahm*et al*., 1977; Jeppu*et al.*,2010)

5.2 Fourier Transform Infrared Analysis

Several chemical functional groups such as alkane, alkene, alkyne, amide, amine, carboxylic, alkanoate, alkanol and ether are responsible for binding metallic ions to an adsorbent as presented in tables 4.2 and 4.3 (Role *et al.*, 1997). The relative difference in two spectra may be associated with differences in concentration of respective functional groups in the raw and carbonized samples; the carbonization process had an overall enhancing effect on carbonized plantain peel (Abechi, 2006). The FTIR spectra showed the presence of ionisable functional groups that are able to interact with proton or metal ions in the adsorption process, we observed OH in the range of 3000-3700cm^{-1}, from 600-1400cm^{-1} in the fingerprint range C=C, C=O and C=N bonds were suspected. All the hetero-atoms (functional groups) are able to involve in adsorption process via ion exchange mechanism or complexation mechanism.

5.3 Elemental Composition of Plantain Peel by Neutron Activation Analysis(NAA).

The elemental composition of plantain peels using neutron activation analysis are shown in Table 4.4. It revealed that the plantain peel was multi-elementals moiety, since the followings elements were observed: K, Mg, Fe, Al, Cl, P, Sr, La, Zn, Br, and Rb. Using neutron activation Omeiza*et al.*, (2011) found potassium K, sodium Na, magnesium Mg, iron Fe, calcium Ca, chromium Cr, arsenic Ar, aluminum Al and phosphorus P all were observed within the detection limit (Al-Ashe*et al.*, 2000).

5.4 Effect of Agitation Time on the Adsorption of Selected Metal.

The figure 4.3 showed the effect of contact time on the adsorption of cadmium, chromium and copper. The rate of cadmium adsorption was very rapid during first 60min with percent adsorption increasing from 52.4 – 92.9 %. Thereafter the rate of cadmium removal decreased as the time increased from 60 to 120min (92.9 – 87.8%). From 120 to 150min the rate of cadmium removal has little or no change. The effect of time on chromium and copper followed the same trend as for cadmium. The rates of chromium and copper removal were very rapid within the first 60minutes, with the following percent adsorption ranging from 59.87 to 88.56% and 65.4 to 94.1% respectively. Therefore, 60 min is taken as the optimum time for the adsorption of these three selected metals. The patterns of the curve established that the adsorption is time dependent in which adsorption capacity was proportionally related to the time (Volesky and Holan 1995). This is in agreement with the adsorption kinetic theory which stated that the higher the time, the more the amount of fluid is adsorbed on the adsorbent. Initially, there were large number of vacant active binding sites available at the first phase of experiment and large amount of metal

ions were bound rapidly on activated carbon at a faster adsorption rate (Drake *et al., 1996*). The binding site shortly became limited and the remaining vacant surface sites were difficult to be occupied by metal ions due to the formation of repulsive forces between the metal ions on the solid surface and the liquid phase (Anwar *et al*., 2010; Okuo and Ozioka 2001).

5.5 Effect of Adsorbent Dosage on the Adsorption of Selected Metals

The percent removals of metal ions were found to increase with an increase in the mass of adsorbent. Highest cadmium, chromium and copper removals were 91.6 and 93.4 %, 75.8 and 80.3% and 83.7 and 95.5% for the initial copper concentration of 10 and 20 mg/l respectively at the adsorbent dose of 2.5 g/l**.** Thereafter, the removal of the selected metal ions started to decline with increasing in mass of adsorbent for all the two concentrations (10 and 20 mg/l). Furthermore, significant changes in value of adsorbent dosage (from 3.0 to 4.0g) yield little or no change in percentage adsorption of the metal ions as shown in figures 4.4 to 4.6. Also, due to insufficient of active binding site, lower removals were obtained at low adsorbent doses (Yenki and Natarajan, 1993 and Ahmed *et al.,* 2006). Thus, 2.5 g (0.25 g/100ml) of plantain peel activated carbon and 20 mg/l of metals (copper, cadmium and chromium) ion concentrations were chosen as optimum conditions for this experiment (Shakirullah*et al.,* 2006).

5.6 Effect of Particle Sizes on the Removal of Selected Metals Cd^{2+}, Cr^{6+} and Cu^{2+}

Batch experiments for the effect of particle sizes on adsorption were conducted for six particle sizes (75 μm to 835 μm) at room temperature and pH of 6-6.5 (without adjustment). It was found that particle sizes had a significant effect on the adsorption efficiency of activated carbon. Particle size of 75 μm has the greatest adsorption capacity among the six particle sizes studied as

shown in Figure 4.7. It can be seen from the figure mentioned here that the removal of metal ions decreased with increasing particle sizes of activated carbon. The percent adsorption increased from 69.2 to 93.7%, 66.7 to 94.3% and 67.7 to 96.7% for Cd^{2+}, Cr^{6+} and Cu^{2+} respectively, as decreasing particle sizes from 600 μm to 75 μm. This behavior can be attributed to the increase in effective surface area as the particle size decreased, which led to increase in metals adsorption (Volesky and Holan, 1995). The higher rate of metal removals in smaller particles can be due to greater accessibility to pores and greater surface area for bulk adsorption per unit weight of the adsorbent (Oladele and Aina 2007). Weber and Morris, (1963) have stated that the breaking up of larger particles to form smaller ones opens some tiny sealed channels that will be available for adsorption and therefore the rate of uptake by smaller particles would be higher than that of larger particle. The result obtained is in agreement with these of (Yenki and Natarajan, 1993; Uchimiya, *et al*., 2011; Ceribasi and Yeti (2001).

5.7 Effect of Agitation Speed on the Adsorption of Selected Metal Ions

The Figure 4.8 showed that the percent adsorbed increased with increase of shaking speed, giving a maximum adsorption at near 150 rpm for Cd^{2+}, Cr^{6+} and Cu^{2+} with corresponding percent adsorption of 87, 89 and 97% respectively. Lower speed could not spread the particles properly in the mixture for providing active binding sites for adsorption of selected metal ions; this resulted in an accumulation of adsorbent at the bottom of vessel with the active binding sites buried (Dobrowolski*et al.,* 1986). On the other hand, the higher speed (above 150 rpm) vigorously spread the particles of adsorbent in the vessel and did not allow sufficient time to bind with metal ions (Anwar *et al.,* 2010). It can be deduced that agitation speed improves the diffusion of metal ions towards the surface of the adsorbent. This also implies that there is a

shaking speed that is sufficient (near 150 rev/min) to ensure that all surface binding sites were made readily available for metal uptake in adsorption process (Sadhasivan*et al.,* 2005; Gupta and Ali, 2004).

5.8 Effects of pH on the Removal of Heavy Metals

.The pH dependent experiments were conducted and the results were shown in Fig.4.9.The pH is a controlling factor for many kinds of metal adsorption process from aqueous solution (Igwe*et al.,* 2007; Kagbu and Ekanem 2002). The surface properties of adsorbents, ionic state of functional groups and species of metals are dependent on pH condition**.** The copper adsorption was found to increase with an increase in pH from 1 to 6.5 and attained a maximum value (55%) at pH 6.5 (which was slightly acidic). Later the copper adsorption capacity was declined. A study carried out by Sadhasivan*et al.,* (2005) showed that Cu^{2+} is the dominant free species below pH 6 .5. The H_3O^+ ions compete with Cu^{2+} for binding on adsorbent sites and it may be responsible for lower adsorption capacity below pH 6.5 (Gaballah and Kibertus 1998; Demirbas*et al.,* 2009). At higher pH, the removal was also low compared to the optimum condition. This may be due to the binding site not being activated in basic condition (Gang and Weixing 1998). Above pH 6.5, the copper precipitate as $Cu(OH)^{2+}$, therefore the removal was not completely by adsorption (Sun and Xu 1997 and Anwar *et al*., 2010). Both chromium and cadmium followed same trend as explained for Cu^{2+}. There was an increase in adsorption with an increase in pH from 1 to 6.5 and attained a maximum value (77.5%) at pH of 6.5 for Cr^{6+} and (90%) at pH of 6.5 for Cd^{2+} respectively (which was slightly acidic). Both metals (cadmium and copper) followed the same trend as explained for Cu^{2+}.Therefore; optimum condition in course of this research was taken to be 6.5.

5.9 Effect of Activating Agents on the Adsorption of Selected Metals

A series of activated carbons were prepared from plantain peel by impregnating with different chemical agents namely H_3PO_4, NaOH and $ZnCl_2$. Those activated carbons from plantain peel which were activated different and non-activated carbonized carbon as well as commercially available activated carbon were all used for adsorption of all the selected metals ions as shown in Figure 4.10. The comparative study of the figure mentioned here revealed that the commercial available activated carbon has a relatively higher adsorption capacity than carbonized(un-activated) carbon prepared from plantain peel while in turn lower than the two chemically (NaOH and H_3PO_4) activated carbon (Gimba*et al.,* 2009; Ocholi, 2006).

The differences in the adsorption of the activated carbon types were not affected by the physical geometry of the plantain peel, but by the chemical composition of the plantain peel and type of activating agent used (Al-Omair and El-Sharkawy, 2001). Adsorptions of selected metals were found to be more of chemisorption than ordinary physical adsorption (Giancarlo and Elisabette, 2004). The activated carbon from plantain peel (with the best activators H_3PO_4 and NaOH found to adsorbed metal ions better than a commercial activated carbon. Generally, the chemical activation enhanced the porosity of the adsorbent and therefore resulted in a pronounced increase of total pore volume and specific surface area (Anwar *et al*., 2010). This may be explained on the basis of different activation mechanism. Firstly, the pyrolysis of the raw materials enhanced the cross-linking and hence creates a highly porous material. (Roles *et al.,* 1997) and others showed that the activation with metal halide($ZnCl_2$) produced a tar-free texture by forming HX (Gang and Weixing 1998; Shakirullah*et al.,* 2006). On the other hand activation with phosphoric acid leads to elimination of water and therefore destruction of the cellulosic structure (Jaung*et al.,*

1996) which would leads to great adsorption capacity. Sodium hydroxide activated carbon, Zinc chloride-activated carbon and Phosphoric-activated carbon have higher adsorption capacities for heavy metals compared with un-activated(carbonized) carbons ones. This behavior may be interpreted in term of higher porosity and therefore facilitate the diffusion of metal ions.

5.10 Effect of Initial Concentrations on the Adsorption of Selected Metals

The efficiency of metals uptake by an adsorbent is highly dependent on the initial metal ion concentration of the solution Gimba*et al.,* (2009). Figure 4.11 is graphical representation of effect of initial metal ion concentration of selected metals adsorption. It can be seen that the amount of metal ion adsorbed onto the activated carbon decreased as the initial metal ion concentration increased. The reason for the decrease in adsorption efficiency can due to the relatively smaller numbers of active sites available on adsorbent. The decrease in percentage removal can also be explained by the fact that as the concentration of the adsorbate increases so does the metal loading on the adsorbent (Madukasi*et al.*, 2001). For instance, a concentration of 100mg/dm^3 will have higher surface loading compared to concentration of 20 or 40mg/dm^3. While on the other hand the number of adsorbing sites available for the adsorption is constant for all concentration. So, when the concentration is higher, more ions will be competing for the same adsorption sites and will go through without being adsorbed (Cheremisinoff and Ellerbusch, 1978; Al-Omair and El- Sharkawy, 2001; Ahalya*et al.*, 2003).

5.11 The Langmuir and Freundlich Isotherms Modeling for Metals Uptake.

The adsorption isotherms were used in this adsorption process. The evaluation of the adsorption capacity of the activated carbon was further carried out by analyzing the isotherm data using Langmuir and Freundlich adsorption isotherms modeling. The Freundlich model was used to evaluate the adsorption efficiency and intensity of heavy metal ions uptake by the activated

plantain peel, while the Langmuir model was used to estimate maximum adsorption capacity of activated carbon. Figures 4.12 to 4.14 and 4.15 to 4.17 showed graphical presentation of Langmuir and Freundlich equilibrium data for adsorption isotherm respectively. It was observed that the linearization forms of the isotherms (Langmuir and Freundlich) were obeyed over the wide range studied and the metal sorption closely followed both Langmuir and Freundlich models of sorption. Meaning, the equilibrium data are well represented by Langmuir and Freundlich models, since both isotherm have high correlation coefficient (Gupta, 2008; Limousin*et al*., 2007; Jeppu*et al.*, 2010; Kundu and Gupta, 2006).

The Langmuir isotherm has R^2 values of 0.9557 for Cd^{2+} , 0.9924 for Cr^{6+} and 0.9954 for Cu^{2+} which indicated adsorption behavior was homogenous distributed (Horsefall*et al.*, 2003).Cr^{6+} has the highest (72.46%) maximum adsorption capacity, while Cu^{2+} has the lowest (55.56%) maximum adsorption capacity as shown in Table 4.5 , hence the results shows that the order of sorption is Cr > Cd > Cu, this can be attributed to many factors ranging from types of adsorbent, available binding sites, different cationic sizes, binding sites affinity to the metals to be adsorbed among others (Nahm*et al.*, 1997). The Langmuir and Freundlich adsorption isotherm constants are presented in Table 4.6. The values of all $\frac{1}{n}$ in falls within 0 to 1 (0.567 as in cadmium, 0.817 as in chromium and 0.941 as in copper) which implied favorable adsorption metal ions by the adsorbent (Tsezos and Bell, 1989, Sun and Xu, 1997). The values of $q_{max}$for cadmium at 62.11, chromium at 72.46 and copper at 55.56 mg/g respectively signifies the entity monolayer of the adsorbent in the adsorption of the selected metal ions (Cookson, 1980; Crusberg, 1998; Deepa*et al.*, 2006). The value of b (dm^3/mg) were 0.0107 in cadmium, 0.0084 in chromium and 0.0091 in copper indicated that activated carbon prepared from plantain peel has high affinity of binding sites to adsorbed the selected metal ions (Micheal*et al.*, 2005). Also, lower value of b (dm^3/mg)

indicated that the particle radius of plantain peel activated carbons were small toward adsorption which foster adsorption capacity of selected metal ions (Argun*et al.,* 2007; Atkin and De-Paulla 2003; Raghavaro*et al.,* 2009).

5.12 Separation Factor R_L

Table 4.7 to 4.9 showed that the separation factor for adsorption of the three selected metals onto activated PP over the range of the concentration (20 to 120 mg/dm^3) studied. It was observed that the initial metal ion concentration increased as the separation factor decreased. The essential characteristics of the Langmuir model can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L. The shape of Langmuir can be used to predict whether the adsorption system is favorable or unfavorable in the batch process (Chirwa and Wang 1997). From equation 3.12 where $R_L = \frac{1}{1+bCe}$. The following conditions indicate the shape of the Langmuir isotherm to be either unfavorable or favorable: $R_L > 1$

Linear $R_L = 1$

Favorable $0<R_L<1$

Irreversible $R_L = 0$

Hence, the most effective adsorption concentration was 120 mg/dm^3 for all the selected metals and the adsorption of cadmium was the most effective adsorb since it has the least separation factor 0.0124 (Shakirullah, *et al.,* 2006). Therefore, from Table 4.7 to 4.9, the order of effective adsorption can be deduced as Cd > Cr >Cu while the R_L value 0.0124 < 0.0135 < 0.0161. Since separation factor R_L value fall within $0<R_L<1$ the condition strongly suggest that activated carbon prepared from plantain peel is suitable and favorable for adsorption of metal ion (Uchimiya*et al.,* 2011). However, the q_{max} obtained for Cr (72.46 mg/g) was higher 71.08 mg/g

reported by Gupta and Babu (2005) when tamarind seeds were used as adsorbent (Abdel-ghani*et al.,* 2007).

CHAPTER SIX

6.0 Summary, Conclusion and Recommendation

6.1 Summary

This research showed that activated carbon prepared from plantain peel is an effective and efficient adsorbent for sorption of Cr^{6+}, Cu^{2+} and Cd^{2+}. Physicochemical properties indicated high quality adsorbent and FTIR analysis for plantain peel suggest strongly that there were functional groups capable of adsorbing the selected metals. The removal of the selected heavy metal ions by different particle size of activated carbon showed the removal rate increased as particle size decreased, whereas the strength of adsorptivity increased based on variation of activating agent as follows: carbonized carbon < salt activated carbon < base activated carbon < acid activated carbon. It was also observed, the adsorbent dosage, agitation speed, agitation times, pH and initial concentration of metal ion are factors that have great influence on adsorption effectiveness and efficient. Also, the adsorption isotherms (Langmuir and Freundlich) provided important information about the adsorption of the Cr^{6+}, Cu^{2+} and Cd^{2+} . R_L separation factor give information that the shape of Langmuir which is favorability while the maximum adsorption (q_{max}) the coefficient of correlation gave us clue on linearity.

6.2 Conclusion

From the experimental observation, results and discussion of this research work, it can be inferred that the plantain peel sample used as activated carbon have these:

I. It is a cheap, good alternative source for activated carbon production and the 1 (one) step activation method of preparation with suitable activating agent and agitation time can be employed.

II. It can be used as an adsorbent for the adsorption of the Cu^{2+}, $Cd^{2+}$and Cr^{6+}

III. The adsorption process is highly dependent on particle size, activating agents, agitation time adsorbent dosage, agitation speed, pH and initial concentration.

IV. The adsorption capacity of activated carbon prepared from plantain peel with both acid and base activators have comparable strength adsorption rate which higher than commercial activated carbon.

V. It was observed that the trend of metal affinity for activated PP surface was Cr^{6+}> Cd^{2+}> Cu^{2+}.

VI The adsorption of these metals by activated PP is a monolayer sorption process.

VII. FTIR spectra analysis confirmed the presence of absorbance peaks of carboxyl, alkene, alkanol, amide, aldehyde and alkyl functional groups. Thus, these functional groups are responsible for the adsorption of the selected metals.

6.3 Recommendation for Further Studies

I. Study the adsorption process using other metals like zinc, lead, arsenic among others

II. Use of other activation methods like two –step impregnation and microwave method since the activation determine the efficiency of the adsorption process.

III. Use of other activating agents like H_2SO_4, KOH, HCl among others.

IV. Examine the gas-solid phase adsorption.

VI Ability of this adsorbent to be employed in the treatment of water dispensed for public consumption should be investigated.

VII Research should be carried out on the potential of the adsorbent to adsorb other pollutants such as oil spillage, dyes and other poisonous chemical effluent discharge from textile and food industries.

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APPENDICES

APPENDIX I: The effect of agitation time on the adsorption of selected metals, at constant pH 6.5, adsorbent dosage of 2.5 g and temperature of 29± 2^{o}C

Time (Minute)	Percentage Adsorbed (%) by Cu^{2+}	Percentage Adsorbed (%) by Cd^{2+}	Percentage Adsorbed (%) by Cr^{6+}
10	65.40	52.40	59.87
20	71.80	67.50	64.70
30	85.60	70.80	71.20
40	87.70	78.50	75.40
50	91.55	82.40	82.30
60	94.10	92.90	88.56
120	84.40	87.80	79.80
150	84.90	77.20	74.20
180	62.80	76.90	73.80

APPENDIX II: The Effect of Adsorbent Dosage on Adsorption of Selected Metals at pH 6.5, 27^{o}C and 60 min

II-A: Effect of adsorbent dosage on adsorption of Cu^{2+}

Adsorbent dosage (g)	Percentage Adsorbed (%) at 10m/l	Percentage Adsorbed (%) At 20m/l
0.5	30.70	43.10
1.0	53.90	67.20
1.5	69.20	82.30
2.2	75.20	89.70
2.5	83.70	95.50
3.0	68.2	80.10
3.2	57.30	68.90
3.5	56.90	68.50
4.0	48.10	60.20

II-B: Effect of adsorbent dosage on adsorption of Cr^{6+}

Adsorbent dosage (g)	Percentage Adsorbed (%) at 10m/l	Percentage Adsorbed (%) At 20m/l
0.5	29.80	32.70
1.0	53.90	57.10
1.5	64.50	67.20
2.2	69.20	72.50
2.5	75.80	80.30
3.0	62.40	68.70
3.2	60.20	64.20
3.5	60.20	63.90
4.0	57.80	59.10

II-C: Effect of adsorbent dosage on adsorption of Cd^{2+}

Adsorbent dosage (g)	Percentage Adsorbed (%) at 10m/l	Percentage Adsorbed (%) At 20m/l
0.5	30.70	37.80
1.0	62.70	84.90
1.5	78.90	79.10
2.2	84.60	86.20
2.5	91.60	93.40
3.0	74.80	72.4
3.2	65.70	62.70
3.5	65.60	62.10
4.0	57.50	58.90

APPENDIX III: Effect of Particle Sizes on Adsorption of Selected Metals, at 20 mg/l, pH 6.5, 27^{o}C and 60 min

Particle Sizes (µm)	Percentage Adsorbed Cu^{2+}	Percentage Adsorbed Cr^{6+}	Percentage Adsorbed Cd^{2+}
< 75	96.70	94.30	93.70
150	89.10	89.10	90.40
300	79.90	82.40	87.20
425	78.40	78.50	83.50
600	68.90	72.40	78.90
835	67.70	66.70	69.20

APPENDIX IV: Agitation Speed on Adsorption of Selected Metals at 20 mg/l, pH 6.5, 27°C and 60 min

Agitation Speed (rev/min)	Percentage Adsorbed Cu^{2+}	Percentage Adsorbed Cr^{6+}	Percentage Adsorbed Cd^{2+}
30	30	50	35
60	42	56	37
90	59	70	54
120	89	78	83
150	97	89	87
180	72	64	92
210	70	63	80
270	65	60	70
320	57	57	58

APPENDIX V: The Effect of pH on the adsorption Metals at 20 mg/l, 2.5 g adsorbent, 27°C and 60 min

pH	Concentration Adsorbed Cu^{2+}	Concentration Adsorbed Cr^{6+}	Concentration Adsorbed Cd^{2+}
1.0	0.40	0.6	1.2
2.0	0.70	1.1	1.4
3.0	1.30	1.2	1.7
4.0	1.60	1.8	2.2
5.0	1.70	1.9	2.7
6.0	1.80	2.2	3.4
6.5	2.20	3.1	3.6
7.0	1.90	2.8	3.2
7.5	1.87	2.2	2.8
8.0	1.60	2.2	2.6
9.0	1.60	2.2	2.6
10.0	1.40	1.9	2.1
12.0	1.20	1.4	2.0
13.5	1.00	1.2	1.9

APPENDIX VI: The Effect of Activating Agent on Adsorption of Selected Metals at 20.0 mg/l, pH 6.5, 27^{o}C and 60 min

Nature of Activated Agent	Percentage Adsorbed Cu^{2+}	Percentage Adsorbed Cr^{6+}	Percentage Adsorbed Cd^{2+}
AC	97.80	92.40	89.90
BA	96.10	94.40	90.10
SA	54.30	48.20	46.30
CC	49.10	93.80	43.10
CV	75.80	77.30	68.90

AA – Acid Activated (H_3PO_3)

BA – Base Activated (NaOH)

SA – Salt Activated. ($ZnCl_2$)

CC –Un-activated Carbon

CV – Commercial Activated Carbon

APPENDIX VII: The Effect of Initial Concentration on Adsorption of Selected Metals at 20.0 mg/l, pH 6.5, 27^{o}C and 60 min

Initial Conc. Mg/dm^3	Concentration Adsorbed Cu^{2+} (mg/g)	Percentage Adsorbed	Concentration Adsorbed Cr^{6+} (mg/g)	Percentage Adsorbed	Concentration Adsorbed Cd^{2+}(mg/g)	Percentage Adsorbed
20	2.82	70.20	3.14	86.60	3.42	79.80
40	3.91	69.35	5.16	84.15	4.19	75.40
60	5.27	72.27	7.42	85.14	7.13	73.70
80	8.82	65.80	9.31	87.25	10.61	79.40
100	10.30	63.70	14.55	88.4	14.30	75.40
120	13.71	65.70	17.29	90.60	15.10	79.30

APPENDIX VIII: Experimental Data obtained on Adsorption of Selected Metals at 20.0 mg/l, pH 6.5, 27°C and 60 min

Initial Conc. mg/dm^3	1/qe Cu^{2+}	1/Ce Cu^{2+}	1/qe Cr^{6+}	1/Ce Cr^{6+}	1/qe Cd^{2+}	1/Ce Cd^{2+}
20	0.3546	0.7092	0.3185	0.5076	0.2924	0.5208
40	0.2558	0.5025	0.1938	0.4329	0.2387	0.3115
60	0.1898	0.3663	0.1348	0.2309	0.1403	0.2375
80	0.1134	0.2268	0.1074	0.1751	0.0943	0.1639
100	0.0971	0.1751	0.0687	0.1466	0.0699	0.1399
120	0.0729	0.1692	0.0429	0.1213	0.0662	0.1064