# ADSORPTION OF MANGANESE AND NICKEL IONS FROM AQUEOUS SOLUTION USING PALM KERNEL SHELL ACTIVATED CARBON

BY

| | |
|---|---|
| Hidayat Anakobe | SE/12/59184 |
| Ismaila Ibrahim Suleiman | SE/12/34574 |
| Nasir Baba Mohammed | SE/12/65059 |
| Hauwa'u Muhammed | SE/12/65369 |
| Rabi Ibrahim Musa | SE/12/59261 |
| Khadijat Danjuma Isah | SE/12/59262 |

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**HIDAYAT ANAKOBE**

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**ISMAILA IBRAHIM SULEIMAN**

**SE/12/64574**

**NASIR BABA MOHAMMED**

**SE/12/65059**

**HAUWA'U MUHAMMED**

**SE/12/65369**

**RABI IBRAHIM MUSA**

**SE/12/59261**

**KHADIJAH DANJUMA ISAH**

**SE/12/59262**

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**AUGUST, 2015.**

# CERTIFICATION

This is to certify that this project was carried out by: ANAKOBE Hidayat, IBRAHIM Suleiman Ismaila, NASIR Baba Mohammed, MUHAMMED Hauwa'u, IBRAHIM Musa Rabi, DANJUMA Isah Khadijah of the Department of Chemistry, Niger State College of Education, Minna.

12/10/15

Mr. Musa Monday
Project Supervisor

Signature & Date

12/10/15

Mallama Yerima Habiba
Head, Chemistry department

Signature & Date

# DEDICATION

This project is dedicated to Almighty God and to our parents who were there for us throughout our academic pursuit.

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Our immeasurable gratitude goes to Almighty God for His mercies, grace and favour upon our lives. He's been a great God.

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# ABSTRACT

This research work entails the effects of high concentration of manganese and nickel in our environment and the need to reduce/remove them from the environment using activated carbon derived from palm kernel shell. The ability of the activated carbon before and after interaction with the adsorbates was ascertained. The results obtained indicate that with increase in the adsorbent (activated carbon) mass, the percentage removal of the ions increased and with increase in the contact time the percentage removal of the adsorbent also increased. For instance, the nickel ions percentage removal was 64.71, 68.63, 78.43, 80.40 and 80.40% when the adsorbent mass used was 0.2, 0.4, 0.6, 0.8 and 1.0g respectively. At a constant contact time of 60min, manganese ions had its highest percentage removal (77.50%) when an adsorbent mass of 0.6 and 1.0g were used and had its lowest percentage removal (59.20%) when an adsorbent mass of 0.2g was used. When a constant adsorbent mass of 0.2g was used at different contact time, it was observed that with increase in the contact time (30, 60, 90, 120, and 150min), the percentage removal of the manganese ions increased (70.42, 79.00, 82.00, 83.10 and 83.10%). However, considering the manganese ions, the percentage removal of the ions appeared to be stable as the contact time increased to 150min. This denotes saturation of the adsorbent mass used. The nickel ions percentage removal using a constant adsorbent mass of 0.2g and different contact time of 30, 60, 90, 120, and 150min was 69.00, 77.00, 82.40, 82.40 and 84.31% respectively. Finally, the experiment carried out showed that activated carbon derived from palm kernel shell can be used as an adsorbent for the removal of manganese and nickel ions.

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# CHAPTER ONE

# 1.0 INTRODUCTION

## 1.1 Background Study

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries such as metal plating, mining operations, tanneries and smelting.

Studies on the treatment of effluent have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent. In recent years, the need for more viable and safe methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the efficacy of activated carbon generated from agricultural wastes in removing various types of heavy metals which are toxic to the environment. Agricultural wastes such as rice husk, sugarcane bagasse, coconut husk e.t.c can be termed 'low cost adsorbents' as they require little processing and are abundant in nature (Aliyah, 2012). However, these low cost adsorbents as cheap as they may appear are not yet satisfactorily scientifically proven to be highly effective at removing most of these heavy metals compared to the well known efficacy of carbon which is already been used industrially. Yes, their source might be cheaper but its handling would be cumbersome as the industrial and technological inputs required to make them more amenable adsorbents are yet to be developed. Moreover, they are seasonal products which are likely not to be available when out of season. So, carbon which is readily available remains the most viable option as an adsorbent.

Activated carbon is a well known adsorbent that has been used effectively for the removal of a broad spectrum of pollutants from air, soil and liquids. Adsorption onto activated carbon has been found to be superior to other techniques because of its capability of adsorbing a broad range of different types of adsorbates efficiently and its simplicity of design. Activated carbon adsorption process is used in environmental engineering practice for removal of colour, taste and odour-producing substances from natural water. The process of activation is a physical change in which the adsorptive property of the primary carbon is greatly increased and improved. It has been reported that activated carbon as adsorbent has many applications due to its nature and properties. A large number of materials have been used in the preparation of activated carbon, many carbonaceous materials of animal, vegetable or mineral origin can be converted into activated carbon if properly treated (Okeola *etal.,* 2012).

## 1.2 Definition of Terms

### 1.2.1 Adsorption

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid.

### 1.2.2 Adsorbate

These are the substances (or the heavy metals, manganese and nickel ions as with this research) which are adsorbed on another surface (activated carbon which is the adsorbent) in a solution.

### 1.2.3 Adsorbent

This is the substance on which the adsorbates attach themselves. They are usually physically porous. The porosity of the adsorbent enables it to perform better as an adsorbent. In this study, the adsorbent implored is carbon obtained from tree leaves.

## 1.3 Agricultural Adsorbent

At present, a number of technologies can be used to remove heavy metals from contaminated waste water such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation and electro remediation methods. However, most of this method might not be efficient in removing heavy metals at very low concentrations, and could be relatively expensive. These methods are also not effective due to their secondary effluent impact on the recipient environment. For this reason, the uses of some low-cost materials for sorbent/adsorbent of metals from contaminated wastewater have been popular. In recent years, more attentions have been gained by the biomaterials which are byproducts or the wastes of large-scale industrial processes and agricultural waste materials. A range of adsorbents such as orange peel, grass, leaf, rice husk, saw dust etc have been reported to be used to remove or recover heavy metals from aqueous solutions (Aliyah, 2012). Carbon which can be derived from, leaves, wood, etc has been regarded over the years as a good adsorbent in the treatment/purification of water. Effective use of biomass wastes (like tree leaves, barks, wood, rice husks, palm kernel shells etc) has become one of the promising fields of the treatment of heavy metals due to the low cost as well as their environmentally friendly nature (Shao *etal.,* 2011). (Wong *etal.,* 2003) investigated these agricultural wastes which were extensively used for the removal of heavy metals due to their abundance in nature. Besides that, it has been used for adsorbing metal ions due to their characteristic functional groups (Tarley *etal.,* 2004). These promising agricultural material (i.e tree leaves, palm kernel shells, barks, rice husk, bagasse etc which are been converted to carbon) can be used in the removal of several heavy metal ions after some physical and chemical modification. In fact, many studies have shown that the adsorption capacity of these adsorbents may be increased by their treatment with chemical reagents (Tarley *etal.*, 2004). Agricultural wastes which are mostly available in rural areas are collected, dried and ground. Its then sieved & washed with distilled water repeatly for dirt and other particulate matter removal, then dried in hot oven at a specified temperature over a period of time, then either directly used as an adsorbent or treated with acid or alkaline solution and then washed again with distilled water for removing acidity. After the washing for acid removal, the carbon is dried and collected in air tight plastic bags and then used as an adsorbent.

## 1.4 Problem Statement

Heavy metals released into the environment due to industrialization and urbanization has become a huge problem. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. So, heavy metals can give bad effect to human body and the environment itself. Many researchers have done the research and found that adsorption is the most effective technique to remove heavy metals. The common adsorbent that has been used before to remove heavy metals from wastewater is the commercially available carbon due to its high efficacy at removing most of these heavy metals. So, this research is to ascertain the efficacy of carbon (when activated with an alkaline solution) as an adsorbent generated from agricultural wastes (palm kernel shell) for the removal of manganese and nickel ions from an aqueous solution.

### 1.5 Justification of study

The dire need to remove toxic metals released into the environment as a result of industrialization can not be overstated. Identifying cheaper means of deriving activated carbon as a substitute to the commercially available ones which are reckoned to be suitable for the removal of wide range of heavy metal ions would be a welcome development. Hence, the quest to convert agricultural wastes like palm kernel shells into carbon to be used as adsorbents which would be easier and cheaper to acquire compared to the costly conventional carbon. If the efficacy of the chemically (using alkaline solution) modified carbon obtained from palm kernel shells as an adsorbent in removing manganese and nickel ions from aqueous solution is ascertained by the end of this study, that gives us an economically viable option in getting rid of various heavy metals from our environment as carbon has already been proven to be effective adsorbent for the removal of various heavy metals. This also helps in getting rid of these agricultural wastes from our environment. Also, carbon which can be obtained from plants would then be of great use to man in various ways including the provision of job opportunities for our youth.

## 1.6 Aim and Objectives

### 1.6.1 Aim

The aim of this study is to investigate the effectiveness of a less expensive activated material (carbon) derived from agricultural waste (palm kernel shells) and chemically modified with alkaline solution as an adsorbent for the removal of manganese and nickel ions from aqueous solutions.

### 1.6.2 Objectives of Study

This research is focusing on the following objectives:

1) Conversion of palm kernel shells into carbon

2) The chemical modification of carbon using alkaline solution to enhance the adsorption capacity.

3) To get or prepare aqueous solutions in the laboratory containing manganese and nickel ions.

4) To study the efficacy of the adsorbent with respect to the adsorption parameters like contact time and mass of the adsorbent.

5) Batch experiments in laboratory scale to be carried out to obtain all data in this study using a spectrophotometer.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

Adsorption is one of the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions. Adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a by product of waste material. Plant materials are inexpensive as they have no or very low economic value. Industries carry out operations like electroplating, metal/surface finishing and solid-state water processing which generate wastewater contaminated with hazardous heavy metals. The concentrations of some of the toxic metals like Cu, Ni, Mn and Zn etc are higher than permissible discharge levels in these effluents. It, therefore, becomes necessary to remove these heavy metals from these wastewaters by an appropriate treatment before releasing them into the environment.

### 2.1 Heavy Metals

With rapid development in agriculture, industry, commerce, hospital and health-care facilities, many activities are consuming significant quantities of toxic chemicals and generating a large amount of hazardous waste. Currently, there are about 110 000 types of toxic chemicals commercially available. Each year, another 1 000 new chemicals are added into the market for industrial and other uses. One of the most hazardous pollutants in environment is heavy metals(Sud etal., 2008). Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Fu and Wang, 2011). Heavy metals generally refer to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Mn (manganese), Pb (lead), Fe (ferum), Zn (zinc) etc which are commonly associated with pollution and toxicity problems. Heavy metals occur naturally in rock formation and ore minerals and so a range of normal background concentration is associated with each of these elements in soils, sediments, water and living organisms. These heavy metals are of specific concern due to their toxicity, bio-accumulation tendency and persistency in nature. Several past disasters due to the contamination of heavy metals in aquatic streams are Minamata tragedy in Japan due to methyl mercury contamination and 'Itai-Itai due to contamination of cadmium in Jintsu river of Japan (Sud etal., 2008).

In small quantities, certain heavy metals are nutritionally essential for healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, mining, refining ores, fertilizers industries, paper industries and so forth.

Many of these products are in our homes and actually add to our quality of life when properly used. However, high concentrations of heavy metals are known to produce a range of toxic effect and also have a potentially damaging effect on human physiology and other biological systems. Heavy metals such as Cd, Cu, Mn, Zn, Ni, Cr, and metalloids like As in drinking water have adverse impacts on human health. The above mentioned heavy metals and metalloids target the liver, kidneys, lungs, brain and bones once absorbed through various path ways. For the purpose of this research, nickel and manganese are reviewed below.

### 2.1.1 Nickel Ions

Nickel is a naturally occurring, lustrous, silvery-white metallic element. It is the fifth most common element on earth and occurs extensively in the earth's crust. However, most of the nickel is inaccessible in the core of the earth. Reflecting these characteristics, nickel is widely used in over 300,000 products for consumer, industrial, military, transport, aerospace, marine and architectural applications. The biggest use is in alloying - particularly with chromium and other metals to produce stainless and heat-resisting steels. These are used for pots and pans, kitchen sinks as well in buildings, food processing equipment, medical equipment and chemical plants. Although nickel is a nutrient needed in human body, but high dose will cause serious health problem.

Nickel is generally considered to be one of the most toxic metals found in environment, ones it enters the food chain progressively, larger accumulation of nickel compounds takes place in humans and animals. Ni (II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries. Higher concentration of nickel causes cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness (Mukesh and Lokendra, 2013).

#### 2.1.1.1 Health Hazard of Nickel

In small quantities nickel is essential but when the uptake is too high it can be a danger to human health. Large dosage of nickel in the body will increase chances of development of lung cancer,larynx cancer, and prostate cancer cause dizziness, lung embolism, respiratory failure, birth defects, heart disorder, asthma and all chronic bronchitis (Lenntech, 2011).

Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may also result in the development of dermatitis known as "nickel itch" in sensitized individual (Lenntech, 2011).

### 2.1.2 Manganese Ions

In the last century, the massive production of manganese-containing compounds (metallurgic and chemical products, municipal wastewater discharges, sewage sludge, alloys, steel, iron, ceramics, fungicide products) has attracted the attention of scientists who investigated manganese as a potential emerging contaminant in the environment, especially in the marine environment (CICAD 63, 2004). In humans, manganese excess is renowned for its role in neurotoxicity, associated with a characteristic syndrome called 'manganese madness' or 'Parkinson-like' diseases (Perl and Olanow, 2007). This neurodegenerative disorder is due to the accumulation of manganese inside intracellular compartments, such as the Golgi apparatus and mitochondria. In mammals, prenatal and postnatal exposure to manganese is associated with embryo-toxicity, fetal-toxicity, and decreased postnatal growth (Sanchez *et al.*, 1993; Colomina *et al.*, 1996). Manganese is one of the most abundant and widely distributed metals in nature. In fact it is typically found in rocks, soils and waters. The Earth's crust consists of 0.1% of manganese. As constituent of the soil, its concentrations range from 40 - 900 mgkg$^{-1}$. Pure manganese is a silver-stained metal; however, it does not occur in the environment in a pure form. Rather, it occurs in manganese-compounds, combined with other elements such as oxygen, sulphur, carbon, silicon and chlorine. These forms of manganese are solid and some of them can dissolve in water or be suspended in the air as small particles. The small dust particles in the air usually settle at the bottom within a few days, depending on their size, weight, density and weather conditions. Manganese can exist in eleven (11) oxidation states, ranging from –3 to +7, but the most common ones are: +2 (e.g., $MnCl_2$) and +4 (e.g., $MnO_2$). In marine organisms some studies showed that an excessive amount of manganese causes toxicity, although the cause-effect evidence is not extensive.

Manganese is an oligo-element necessary for human survival but becomes toxic when the concentration becomes too high in the human body. According to World Health Organisation (WHO), the maximum concentration of manganese admissible in drinking water is 0.05 mg/L (WHO, 2011). Excess manganese in portable water can cause problems in the nervous system and in the respiratory system and hinders the intellectual development and normal growth of infants. Manganese cans also cause the illness such as pulmonary disorder and bronchitis. The exposure of humans to manganese for a long period can render him impotent (ATSDR, 2000; Barceloux, 1999; Collipp *et al.,* 1983). While manganese is abundant and widely distributed in nature, it is required only in trace amounts in the organisms during their life span, where it guides normal development and body function. In fact, it plays essential roles in many metabolic and non-metabolic regulatory functions, such as: bone mineralization, connective tissue formation, energetic metabolism, enzyme activation, immunological and nervous system activities, reproductive hormone regulation, cellular defence, amino acid, lipid, protein, and carbohydrate metabolisms, glycosaminoglycans formation, blood clotting e.t.c (ATSDR, 2008; Santamaria, 2008). Manganese works as a constituent of metallo-enzymes or as an enzyme activator. Examples of manganese-containing enzymes include: arginase, the cytosolic enzyme responsible for the urea formation; pyruvate carboxylase, the enzyme that catalyses the first step of the carbohydrate synthesis from pyruvate; and manganese superoxide dismutase, the enzyme that catalyzes the dismutation of superoxide into oxygen and hydrogen peroxide (Wedler, 1994; Crowley *et al.*, 2000). In contrast to the relatively few manganese metallo-enzymes, there are a large number of manganese-activated enzymes, including the hydrolases, the kinases, the decarboxylases, the DNA and RNA polymerases and the transferases (Missiaen *et al.*, 2004; Au *et al.*, 2008). Some of these transporters are localized within specific intracellular compartments, but none of them are manganese specific transporters (Culotta *et al.*, 2005).

#### 2.1.2.1 Health Hazards of Manganese Ions

Manganese is considered an emerging contaminant because it is a perceived or real threat to the human health and the environment. Manganese exposure occurs at different levels and through a wide variety of industrial sources such as mining, alloy production, goods processing, iron-manganese operations, welding, agrochemical production and other anthropogenic activities. Manganese products can be discharged into the sea and become an unforeseen toxic metal in the marine environment. As manganese bioavailability increases, its uptake into living organisms occurs predominately through the water. The manganese rates of accumulation, as well as its elimination, are relatively fast-regulated processes. The exposure to high levels of manganese causes toxicity and decreases the fitness of the organisms (Roth, 2006). In humans, the neurological damage induced by excessive manganese exposure has been well documented for over a century (Cooper, 1837; Mena *et al.*, 1967; Normandin and Hazel, 2002; Takeda, 2003; Ketcha *et al.*, 2009; Shin and Lee 2006).

Also, considering their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritised as major contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics.

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system. The metals are mineralised by microorganisms, which in turn are taken up by plankton and further by the aquatic organisms. Finally, the metals by now, several times biomagnified is taken up by man when he consumes fish from the contaminated water. Slightly elevated metal levels in natural waters may cause the following sublethal effects in aquatic organisms: histological or morphological change in tissues, changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation, change in biochemistry, such as enzyme activity and blood chemistry, change in behaviour and changes in reproduction (Mukesh and Lokendra Singh, 2013).

Metals are one of the most abundant classes of contaminants generated by human activities and represent an actual hazard for marine ecosystems and organisms' health. In fact, although metals are terrestrially produced, they flow into the sea through effluent and sewage or are directly discharged from industries placed on the sea water front. Marine organisms can take up from the sea and from their diet these metals, which may consist of particles in suspension or might be deposited in the sediment. A great number of factors may influence dose-effect and dose-response relationships between metals and organisms; their tolerance to and use of trace metals reflect sea water concentrations. Marine invertebrates accumulate and bio-concentrate metals more than higher organisms; thus, their peculiar position in the marine trophic chain, where pelagic larvae are part of the diet of several planktonic and benthic organisms (bio-magnification), increases the interest of many researchers. Trace essential metals are of environmental interest both as limiting nutrients (Fe, Zn, Mn, Cu, Co, Mo and Ni), playing important roles in metal-requiring and metal-activated enzyme systems, and as toxicants when present at high concentrations. On the contrary, non-essential heavy metals as Cd, Hg, Ag, Pb, Sn and Cr, are toxic for living organisms even at low concentrations.

The effects of several metals on echinoderm embryos have been studied for many years. The response of sea urchin embryos to metal exposure involves selective sets of defence "macromolecules". The type of defence response elicited greatly depends on the different sensitivity of the organisms to the different metal used. Metal toxicity can trigger several biochemical and cellular events that include: the induction of a set of highly conserved proteins, such as the heat-shock proteins and the metallothioneins; the efflux transporters; the activation of anti-oxidative enzymes; autophagy and apoptosis. In this chapter it was reported that manganese-exposed embryos do not activate a fast defence response, but activate or repress signalling pathways and transcriptional activities involved in the regulation/preservation of development. This surprising behaviour is probably due to the fact that a moderate manganese increase is not recognized by the cell as stressful event. In fact, low manganese concentrations stimulate embryos growth (not shown), probably as a consequence of their role in the metabolic-enzymatic reactions. On the contrary, non-essential heavy metals, such as cadmium, activate several cellular defence strategies aimed at permitting embryo survival. In fact, Paracentrotus lividus embryos showed an elevated tolerance to manganese, due to the increased HSC levels, did not activate the synthesis of the HSPs inducible forms and did not enter into the apoptotic program. However, manganese interferes with calcium uptake and it's internalization into embryos, suggesting that skeletal growth is highly dependent on calcium signalling. The use of manganese-exposed embryos as a new model to study signalling pathways involved in skeletogenesis provides new insights into the mechanisms involved in manganese embryotoxicity and emphasizes the role of calcium trafficking, recruitment and storage in the biomineralization process. Also, in echinoderm immune cells, manganese acts as a trigger for the proliferation of coelothelial cells and thus increases the number of circulating coelomocytes. Studies on the effects of manganese on the activation of putative progenitor cells, including their proliferation and differentiation, should make an important contribution to our understanding of the operating mechanisms, and to the identification of those genes expressed before their release into the coelom.

## 2.2 Activated Carbon

Activated carbon is a microcrystalline, non-graphitic form of carbon with porous structure that has been processed to develop its internal porosity. The physical and chemical properties of activated carbon depend on pore size, pore distribution and number of surface oxygen groups. The pore size and pore volume can be controlled during the activation process such as activation time, activation agent and temperature. The surface oxygen also can be manipulated by using suitable oxidizing agents and thermal treatment in order to get the surface functional groups such as carboxyl, phenolic and lactonic group attached to carbon (Toles *et al.,* 1999; Park and Jang 2002). These groups can improve the adsorption capacity and selectivity on a certain adsorbate in the gaseous or liquid phase. The use of commercial activated carbon is well-known adsorbent for the removal of heavy metals from water and wastewater. However, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence it is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several researchers used different low-cost adsorbents from agricultural wastes such as coconut shells, tree leaves, palm kernel shells, barks, saw dust, rice husk, banana peels, cotton seed hulls, apple wastes, sugarcane bagasse etc for the removal of heavy metals from water and wastewater.

It is well known that several treatment technologies have been developed to remove heavy metals from water and waste water. Common methods include chemical precipitation, ion exchange, membrane separation, ultrafiltration, filtration, solvent extraction, sedimentation, reverse osmosis, electrodialysis, adsorption and filtration, evaporation, flocculation etc. Reduction and chemical precipitation has traditionally been the most used method. The most often used precipitation processes include hydroxide, sulphide, carbonate and phosphate precipitation techniques. The disadvantage of precipitation technique is the production of sludge. This process suffers from draw backs like incomplete removal, requirement of sizable quantities of treatment chemicals and production of voluminous toxic sludge. It constitutes a solid waste disposal problem. Thus, a variety of other treatment technologies were considered and evaluated. Techniques like ion exchange and adsorption with products obtained from naturally occurring materials like activated carbon were considered as better alternatives. The exorbitant cost involved with ion exchange makes it prohibitive for wide application. Therefore, adsorption using activated carbon derived from agricultural wastes seems a viable means for heavy metal removal. Activated carbon can be produced from various biomass materials. With the increasing ecological and economical significance of environmental protection, the use of waste biomass as feedstock material for the production of activated carbons is attracting increasing interest (Uwadiae *etal.,* 2010).

### 2.2.1 Agricultural Wastes (converted into carbon) as Adsorbent

Sharma & Bhattacharya (2005) studied adsorption of cadmium using neem leaf powder. The kinetics of the interactions was tested with pseudo-first-order Lagergren equation, simple second order kinetics, Elovich equation, liquid film diffusion model and intra-particle diffusion mechanism. The leaves of olive tree (Olea europaea) were proposed (Hamdaoui, 2009) as a novel low-cost non-conventional adsorbent for the removal of cadmium from solutions with and without the assistance of ultrasound and by associating simultaneously ultrasonic irradiation and stirring. It was reported that adsorption was significantly increased in the presence of ultra sound. A batch adsorption study of Cd(II) ions from aqueous solution by Hevea Brasiliensis (HB) leaf powder has also been reported (Hanafiah *et al.,* 2006). The cadmium removing capacity of a biosorbent Calotropis procera (Pandey *et al.,* 2008), a perennial wild plant, was investigated. The FTIR analysis indicated the involvement of hydroxyl (–OH), alkanes (–CH), nitrite (–NO2), and carboxyl group (–COO) chelates in metal binding. The complete desorption of the cadmium was achieved by 0.1 M $H_2SO_4$ and 0.1 M

HCl. Mengistie *etal.* (2012) stated that the adsorption of manganese (II) onto activated carbon derived from the leaf of an indigenous Ethiopian plant, namely Birbira (Militia ferruginea), was investigated using flame atomic absorption spectrometer. The effects of contact time, adsorbent dose, Mn (II) initial concentration, pH and temperature were investigated. The maximum adsorption occurred after 2hrs. There was 95.8% of $Mn^{2+}$ adsorption at pH of 4.0. The positive value of $\Delta H$ shows that the adsorption of manganese ions on the adsorbent is an endothermic process. The values of free energy ($\Delta G$) were negative. The decrease in $\Delta G$ value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The calculated value of $\Delta H$ is 16.05 $kJmol^{-1}$ and $\Delta S$ is 99.13$JK^{-1}mol^{-1}$. The results showed that activated carbon prepared from Birbira (Militia ferruginea) leaves can be used for the removal of Mn (II) from wastewater.

## 2.3 Factors affecting Adsorption Capacity:

There are various factors affecting the adsorption capacity of adsorbents. These factors include pH, temperature, contact time, agitation speed, adsorbent mass etc. For the purpose of this work, adsorbent mass and contact time are reviewed below.

### 2.3.1 Contact time

Mukesh and Lokendra, (2013) Studied the effect of contact time on the adsorption of Zn onto tea floor waste (TFW), Initially the removal was very rapid in first 25 minutes, then adsorption rate gradually decreases and removal reaches equilibrium in around 30 minutes. The time required to reach equilibrium was dependent on initial concentration of zinc. For the same concentration the percentage removal of zinc increases with increase in contact time till equilibrium attained in 30 minutes. It is observed that in all cases the percentage removal is comparatively lower for 24 hr contact time, with increasing removal efficiencies at higher contact time. In case of Ni(II) and Cd(II) ions rise sharp rise in percentage removal with increasing contact time. On other hand, percentage removal of Mn(II), Zn(II) and Cu (II) increases gradually with contact time, reaching nearly 100% removal only at around 72 hr. It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with carbon aerogel was.experimentally found to be about 48 hrs. The effects of the contact time on the amount of $Cu^{2+}$ and $Ni^{2+}$ adsorbed per unit of adsorbent at three different temperatures (30, 45, and 60 .C). For $Cu^{2+}$ and $Ni^{2+}$, a gradual increase in adsorption occurred upon increasing the contact time up to 120, 240 min, at which point the maximum values of adsorption were attained.

### 2.3.2 Effect of Adsorbent Mass

It is apparent that the percentage removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions. It is observed that there is a sharp increase in percentage removal with adsorbent dose for Ni (II) ions (Mukesh and Lokendra Singh, 2013).

# CHAPTER THREE

## 3.0 MATERIAL AND METHOD

### 3.1 APPARATUS

a. Oven and Crucible

b. Pestle and Mortar

c. Volumetric Flask

d. Beakers

e. Filter paper and Spatula

f. Wash bottle

g. Conical flask

h. Measuring cylinder

i. Funnel

j. Sample Bottles

k. Aluminium foil

## 3.2 MATERIALS AND CHEMICALS

a. Activated carbon (palm kernel shells)

b. Distilled water

c. Manganese Nitrate $(MnNO_3)_2$

d. Nickel Nitrate $(NiNO_3)_2.6H_2O$

## 3.3 PREPARATION OF ACTIVATED CARBON

About 3g of the pre-carbonized sample was mixed with $3cm^3$ each of 1M KOH. The sample was allowed to stand for 2hours and then introduced into a furnace and heated at 800°*C* for 5minutes. The activated sample was allowed to cool in ice-cold water and excess water was drained and the sample was allowed to dry at room temperature (Gimba *etal.,* 2004; Turoti *etal.,* 2007). Washing with 0.1M HCL was done after activation to remove surface ash, with hot water to remove excess acid until pH of between 6 and 8 was obtained (Turoti *etal.,* 2007). The sample was dried in an oven at 110°C over night and grounded, followed by Sieving using 2mm sieve (Rahman *etal.,* 2005) and stored in air tight container. The process used in preparing the sample (activated carbon is called "Two step"process).

## 3.4 PREPARATION OF STANDARD SOLUTION

### 3.4.1 Preparation of $Ni(NO_3)_2.6H_2O$ solution

Computations

Molar Mass of Nickel(Ni) = 58.78g/mol

Molar Mass of Nitrogen(N) = 14g/mol

Molar Mass of Oxygen (O) = 16g/mol

Molar Mass of Hydrogen = 1g/mol

Molar Mass of Nickel Nitrate$[Ni(NO_3)_2].6H_2O$

$$= 58.7 + (14\times2 + 16\times12) + 12\times1$$

$$= 58.7 + 28 + 192 + 12$$

$$= 290.7\text{g/mol}$$

%by mass of Ni $= (NiNO_3)_2 / Ni$

$$= 290.7 / 58.7$$

$$= 4.9522\text{g}$$

Since 4.9522 =1000ppm

Therefore dissolve 1.2381g of $Ni(NO_3)_2.6H_2O$ in $250cm^3$ of distilled water.

Applying the dilution factor.

$C_1V_1= C_2V_2$

Where $C_1$ =initial concentration

$V_1$ =initial volume of solution to be determined.

$C_2$ = final concentration of solution required

$V_2$ = final volume of solution

DATA

$C_1 = 1000ppm$

$V_1 = ?$

$C_2 = 20ppm$

$V_2 = 250cm^3$

$C_1V_1 = C_2V_2$

$V_1 \quad = C_2V_2/C_1$

$V_1 \quad = 20 \times 250/1000$

$V_1 = 5000/1000$

$V_1 = 5cm^3$

This simply means to prepare $1000cm^3$ of 1.2381 $Ni(NO_3)_2$ solution, $5cm^3$ should be measured using a dry measuring cylinder and added to distilled water in a $1000cm^3$ $1dm^3$ volumetric flask made up to the mark with enough distilled water.

### 3.4.2 Preparation of $[MnNO_3]_2$ solution

Molar mass of Manganese (Mn) = 54.93g/mol

Molar mass of Nitrogen (N) = 14g/mol

Molar mass of Oxygen (O) = 16g/mol

Molar mass of Manganese Nitrate ($Mn[NO_3]_2$)

$(Mn[NO_3]_2) = 54.93 + (14+16 \times 3)_2$

$= 54.93 + (14+48) \times 2$

$= 54.93 + 124$

$= 178.93g/m$

% by mass of Mn = $(Mn[NO_3]_2 / Mn = 178.93 / 54.93$

$= 3.2574$

Since $3.2574 = 1000\text{ppm}$

Therefore dissolve 0.8144 of $Mn(N0_3)_2$ in $250\text{cm}^2$ of distilled water

Applying the dilution factor

$C_1V_1 = C_2V_2$

Where $C_1$ = initial concentration

$V_1$ = initial volume of solution to be determined

$C_2$ = final concentration of solution required

$V_2$ = final volume of solution

Data

$C_1 = 1000\text{ppm}$

$V_1 = ?$

$C_2 = 20\text{ppm}$

$V_2 = 250\text{cm}^3$

$C_1V_1 = C_2V_2$

$V_1 = C_2V_2/C_1$

$V_1 = 20 \times 250/1000$

$V_1 = 5000/1000$

$V_1 = 5cm^3$

This simply means to prepare $1000cm^3$ of 0.8144 $Mn(NO_3)_2$ solution. $5cm^3$ should be measured using a dry measuring cylinder and added to distilled water in a $1000cm^3$ $1dm^3$ volumetric flask made up to the mark with enough distilled water.

## 3.5 BATCH ADSORPTION STUDIES

### 3.5.1 BATCH ADSORPTION AT DIFFERENT CONTACT TIME WHEN THE ADSORBENT MASS IS CONSTANT

The batch adsorption method was used to determine the percentage removal of the metal ions. This was done by using different contact time and a particular adsorbent mass for the different time intervals implored. Activated carbon (0.2g) was weighed into five different beakers containing 20ml of the solution in a covered beaker. Each of the beakers was labelled accordingly with the various contact time implored. The various beakers containing the solution and the adsorbent mixture was swirled periodically until its contact time (30, 60, 90, 120and 150 mins) elapsed. Using a filter paper, each mixture was filtered separately as its contact time elapsed. The filtrate was collected using a sample bottle labelled same with the beaker while the residues were discarded.

### 3.5.2 BATCH ADSORPTION USING DIFFERENT ADSORBENT MASS AND A CONSTANT CONTACT TIME

The batch adsorption experiment was performed using different mass of activated carbon (0.2g, 0.4g, 0.6g, 0.8g and 1.0g) at a constant contact time of 60mins before filtering. Activated carbon (0.2g, 0.4g, 0.6g, 0.8g and 1.0g) was weighed into five different beakers containing 20ml of the solution in a covered beaker. About 10mins interval was allowed between each of the adsorbent mass introduced into the beakers containing the solution. This was done to give room for immediate filtration for each of the experimental set up when the 60mins elapsed. Each of the beakers was labelled accordingly with the adsorbent mass introduced into it. The various beakers containing the solution and the adsorbent mixture were swirled periodically until the 60mins elapsed. Each of the beakers containing the solution and the adsorbent mixture were filtered immediately its contact time elapsed. The filtrate was collected using a sample bottle labelled same with the beaker while the residue was discarded. The concentrations of $Mn^{2+}$ and $Ni^{2+}$ before and after interaction were determined using atomic absorption spectrophotometer (AAS). Percentage adsorption was calculated using the expression below (Erden *et al.*, 2004) separately as its contact time elapsed. The filtrate was collected using a sample bottle labelled same with the beaker while the residues were discarded.

## 3.5.2 BATCH ADSORPTION USING DIFFERENT ADSORBENT MASS AND A CONSTANT CONTACT TIME

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$$\%RE = \frac{C_i - C_f \times 100}{C_i}$$

Where

$C_i$ = initial concentration of heavy metal

$C_f$ = final concentration of heavy metal

%RE = Percentage Removal of heavy metal.

The concentration are all measured in milligram per litre (mg/L)

# CHAPTER FOUR

## 4.0 RESULTS AND DISCUSSION

### 4.1 RESULTS

The results of analysis carried out are presented in the tables and figures below:

Table 4.1: Percentage Adsorption of $Mn^{2+}$ at different Mass

| Mass (g) | Time (min) | Initial (mg/L) | Final (mg/L) | %RE |
|---|---|---|---|---|
| 0.2 | 60 | 0.071 | 0.029 | 59.20 |
| 0.4 | 60 | 0.071 | 0.024 | 66.20 |
| 0.6 | 60 | 0.071 | 0.016 | 77.50 |
| 0.8 | 60 | 0.071 | 0.017 | 76.10 |
| 1.0 | 60 | 0.071 | 0.016 | 77.50 |

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| 0.8 | 60 | 0.071 | 0.017 | 76.10 |
| 1.0 | 60 | 0.071 | 0.016 | 77.50 |

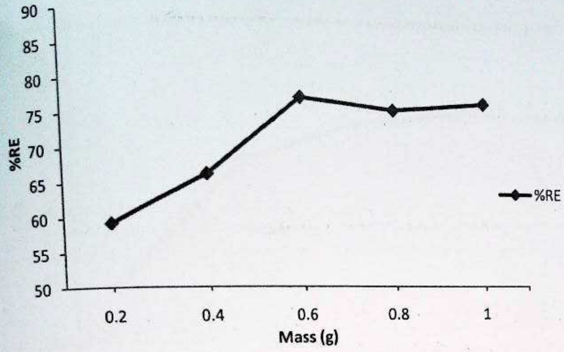

Figure 4.1: Plot of %RE of $Mn^{2+}$ versus different Adsorbent mass (g)

**TABLE 4.2:** Percentage Absorption of $Mn^{2+}$ at different Time interval

| Mass (g) | Time (min) | Initial (mg/L) | Final (mg/L) | %RE |
|---|---|---|---|---|
| 0.2 | 30 | 0.071 | 0.021 | 70.42 |
| 0.2 | 60 | 0.071 | 0.015 | 79.00 |
| 0.2 | 90 | 0.071 | 0.013 | 82.00 |
| 0.2 | 120 | 0.071 | 0.012 | 83.10 |
| 0.2 | 150 | 0.071 | 0.012 | 83.10 |

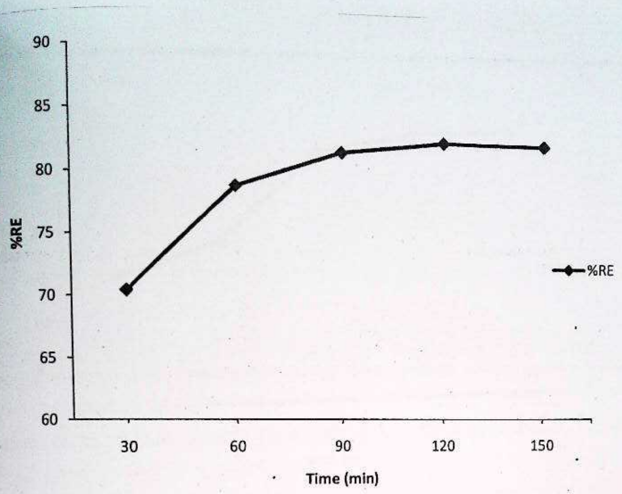

Figure 4.2: Plot of %RE of $Mn^{2+}$ versus different Time Interval.

**Table 3:** Percentage Absorption of $Ni^{2+}$ at different Mass

| Mass (g) | Time (min) | Initial (mg/L) | Final (mg/L) | %RE |
|---|---|---|---|---|
| 0.2 | 60 | 0.051 | 0.018 | 64.71 |
| 0.4 | 60 | 0.051 | 0.016 | 68.63 |
| 0.6 | 60 | 0.051 | 0.011 | 78.43 |
| 0.8 | 60 | 0.051 | 0.010 | 80.40 |
| 1.0 | 60 | 0.051 | 0.010 | 80.40 |

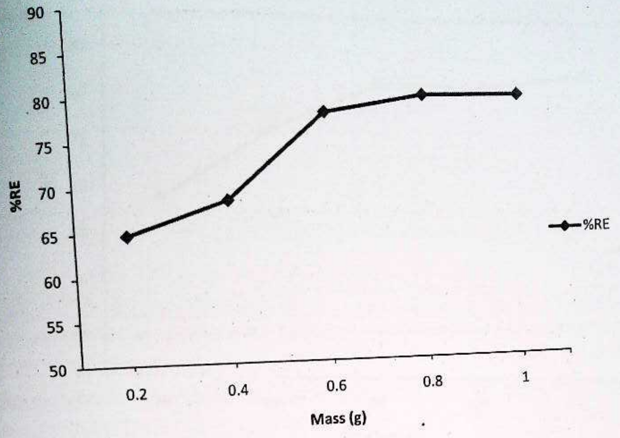

Figure 4.3: Plot of %RE of $Ni^{2+}$ versus different Adsorbent Mass (g)

**Table 4.4:** Percentage Absorption of $Ni^{2+}$ at different Time Interval

| Mass (g) | Time (min) | Initial (mg/L) | Final (mg/L) | %RE |
|---|---|---|---|---|
| 0.2 | 30 | 0.051 | 0.016 | 69.00 |
| 0.2 | 60 | 0.051 | 0.012 | 77.00 |
| 0.2 | 90 | 0.051 | 0.009 | 82.40 |
| 0.2 | 120 | 0.051 | 0.009 | 82.40 |
| 0.2 | 150 | 0.051 | 0.008 | 84.31 |

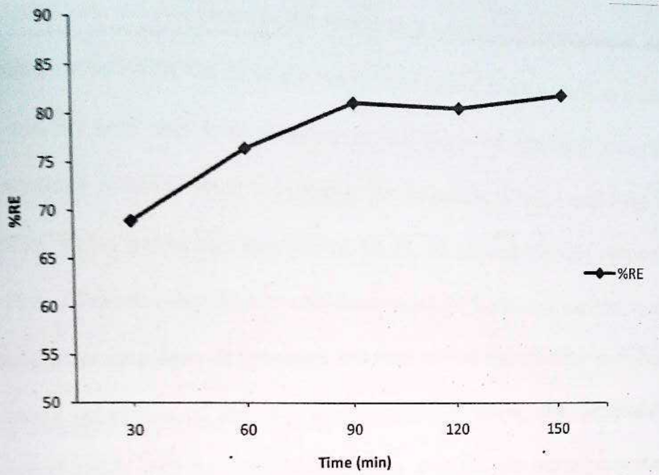

Figure 4.4: Plot of %RE of $Ni^{2+}$ versus different Time Interval

## 4.2 DISCUSSION

Table 4.1 showing the various adsorption results obtained for manganese ions on the activated carbon using different mass values (0.2, 0.4, 0.6, 0.8 and 1g) at a constant time (1min). Table 4.1 shows that the highest percentage of adsorption (77.50%) within 1min occurred with the 0.6 and 1g mass of the activated carbon while the lowest percentage of adsorption (59.20%) occurred with the 0.2g of activated carbon. This shows that higher mass value of the activated carbon adsorbs more of the manganese ion within the shortest possible time compared to a smaller quantity of the activated carbon used at the same time. Figure 4.1 helps us to appreciate the difference in the percentage removal of manganese ions from the aqueous solution by the different mass of activated carbon used at a constant time. It can be seen that with increase in the mass of activated carbon used, the percentage removal tends to increase. For instance, 0.2, 0.4 and 0.6g of activated carbon had a percentage removal of 59.20, 66.20 and 77.50% respectively. This further illustrates that higher adsorbent mass of activated carbon removes more manganese ions from the aqueous solution within the shortest possible time than smaller quantities of the activated carbon. However, the percentage removal seemed stable with the 1g adsorbent mass as it had the same percentage removal with the 0.6g adsorbent mass. This is likely to be that the 1g adsorbent mass could not adsorb more manganese ions within the specified contact time. The 0.8g of activated carbon had a lesser percentage removal than the 0.6g and the 1g which had the same percentage removal with the 0.6g of activated carbon. This slack in the normal progression of the results obtained could be due to some experimental factors like agitation speed implored within the 60min interval. In this case, the agitation speed refers to the periodic swirling adopted for the mixture within the duration of the contact time.

Table 4.2 shows the percentage removal at different contact time (30, 60, 90, 120 and 150mins) when a constant adsorbent mass (0.2g) was used. The highest percentage removal (83.10%) of the manganese ions occurred after 120 and 150mins while the lowest percentage removal (70.42%) occurred after 30mins. This shows that with adsorbent mass (0.2g) used, percentage removal tends to increase with increase in contact time. The percentage removal after a contact time of 120mins was the same after 150mins. Figure 4.2 illustrates that fact better. It shows that the percentage removal increased with increase in contact time and appeared stable after 120 and 150mins. This could be as a result of the adsorbent mass saturation. A situation whereby the manganese ions where no longer attracted to the activated carbon probably due to the unavailability of valence electron that can attract the manganese ions.

Table 4.3 shows the percentage removal of nickel ions when various adsorbent mass (0.2, 0.4, 0.6, 0.8 and 1g) was used at a constant time of 60mins. As with the percentage removal of manganese ions, the percentage removal of the nickel ions increased with increase in the adsorbent mass used. The highest percentage removal occurred with the 0.8 and 1g while the lowest percentage removal occurred with the 0.2g adsorbent mass. The pattern of increment can be seen clearly from Figure 4.3, where the percentage removal increased from the 0.2g to 0.6g. The increment continued with the 0.8g adsorbent mass but appeared stable with the 1g adsorbent mass as the percentage removal with the 0.8g adsorbent ass was the same with the 1g adsorbent mass. This could probably be as result of e contact time adopted not being enough for further adsorption of the nickel ions sing higher adsorbent mass.

The batch adsorption of nickel ions using a specific adsorbent mass (0.2g) at different contact time (30, 60, 90, 120 and 150min) is shown in Table 4.4 and Figure 4.4. The percentage removal of nickel ion increased with increase in contact time as with the adsorption of manganese ions. Table 4.4 shows that the lowest percentage removal (69%) occurred after 30min while the highest percentage removal (84.31%) occurred after 150min. This shows that contact time adopted could play a big role in determining the percentage removal of nickel ions using activated carbon. As Figure 4.4 shows clearly that with increase in contact time (30, 60, 90, 120 and 150min), the percentage removal of the nickel ions increased. The results show that the percentage removal increased across the contact time adopted of which 30min was the lowest and 150min the highest contact time adopted. The percentage removal after 90 and 120min was the same (82.40%). This could be as a result of the rate of agitation of the mixture as the contact time of 120min elapsed. Probably, the mixture was not properly agitated to enable more nickel ions to attach themselves to the available valence electrons in the activated carbon as in the case of the mixture that stayed for 150mins.

Comparing Table 4.1 and 4.3, it can be deduced that the percentage removal of nickel ions was more than the percentage removal of the manganese ions by the same various adsorbent mass (0.2, 0.4, 0.6, 0.8 and 1.0g) of the activated carbon used and at the same contact time (60min) adopted. This shows that the nickel ions seem more excited and attracted to the valence electrons present in the activated carbon made available by the increment in the adsorbent mass. Considering the above comparison, the nickel ions have more affinity to the activated carbon than the manganese ions.

A comparison of Table 4.2 and 4.3 didn't show much difference in the percentage removal of the manganese ions and nickel ions by the adsorbent (activated carbon) mass (0.2g) used and the various contact time (30, 60, 90, 120 and 150min) adopted.. Taking the average percentage removal of all the contact time adopted, the percentage removal of manganese ions by the adsorbent (activated carbon) mass used was insignificantly higher than the percentage removal of nickel ions.

# CHAPTER FIVE

## 5.0 SUMMARY, CONCLUSION AND RECOMMENDATION

### 5.1 SUMMARY

This research work entails the benefits and hazardous effects heavy metals pose to the environment. Due to its non-biogradability attributes, heavy metals excessive concentrations in our environment are highly unwanted in our environment. Thus, the need to determine a viable means to get rid of them from the environment using an agricultural adsorbent (i.e. palm kernel shells which was converted into carbon and chemically modified) in place of the mostly used commercial carbon was highlighted. Activated carbon's wide range ability to remove or reduce the concentration of various heavy metals (including manganese and nickel ions) from the environment compared to other adsorbents was reviewed with regards to the literature reports used in this work. Finally, the efficacy of the palm kernel shells which were converted into carbon and was chemically modified using alkaline solution was ascertained.

### 5.2 CONCLUSION

From this experiment, activated carbon derived from palm kernel shells has good ability to remove manganese and nickel ions from aqueous solutions. It was observed that a specific mass (0.2g) of the activated carbon attained its highest percentage removal for each of the heavy metals for a period of time and gets saturated after a certain contact time. This is a situation whereby the adsorbent stops adsorbing the ions after a specified contact time and might probably desorb the ions if left longer than necessary in the mixture. Also, it was observed that with increase in the mass of the activated carbon (0.2, 0.4, 0.6 and 0.8g), the percentage removal of the ions tend to increase within the contact time adopted (60min). However, it got to a stage where further increment in the mass of the activated carbon (1.0g) yielded no increment in the percentage removal at the adopted specified contact time (60min). Rather, the same percentage removal obtained for the adsorbent mass of 0.8g was obtained for adsorbent mass of 1.0g. This was mostly observed with the nickel ions. In this case, the activated carbon probably requires additional time to adsorb more ions due to its increased mass or that the agitation rate for the mixture was not good enough.

## 5.3 RECOMMENDATION

1. To achieve a better experimental result, a mechanical shaker is recommended for the purpose of agitation of the mixture to enable equal agitation speed for all the experimental setup used.
2. More adsorbent (activated carbon) mass above 1.0g (like 1.2, 1.5g e.t.c) is recommended the same contact time (60min) and volume of solution (20ml)

used to ascertain the actual point at which the activated carbon is saturated and probably leads to a decline in the percentage removal.

3. Also, contact time can be extended above 150min (like 180, 210min e.t.c) with the same adsorbent dosage (0.2g) and volume of solution (20ml) used to ascertain the actual point at which the activated carbon is saturated and probably leads to a decline in the percentage removal.
4. Awareness should be created on the use of activated carbon and other similar agricultural waste or wood finishing products on the removal of heavy or toxic metals from polluted water.

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