REMOVAL OF LEAD ION FROM SYNTHETIC WASTE WATER USING BIOMATERIAL

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DECLARATION

I declare that the work in this project report (thesis) entitled REMOVAL OF LEAD ION FROM SYNTHETIC WASTE WATER USING BIOMATERIAL has been performed by me under the supervision of Engineer A. A. Aboje No part of this project report was presented for another degree or diploma elsewhere at any institution to the best of my knowledge.
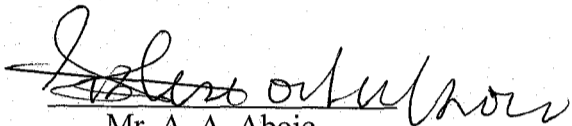

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Date

CERTIFICATION

This is to certify that this report titled REMOVAL OF LEAD ION FROM SYNTHETIC WASTE WATER USING BIOMATERIAL by JAMIU KAZEEM meets the requirements for the partial fulfillment of the award of Bachelor of Engineering (B.Eng) degree in Chemical Engineering, Federal University of Technology, Minna.

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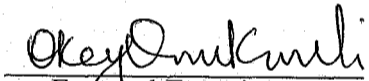Mr. A. A. Aboje   Date

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External Examiner   Date 6/12/10

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Prof. O. D. Onukwuli

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DEDICATION

This report is dedicated to my Parent and the entire family members, who felt that the only way they could express their love and care for me, is to keep my educational pot boiling by giving moral and financial support to me on my career in this institution.

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"Alhamdulillahi" Praise is to Almighty Allah who has been the guardian and Sustainer of my life and success.

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ABSTRACT

This research is an attempt to evaluate the feasibility of neem leave as an inexpensive adsorbent for demonstrating biosorption technology as an alternative for the cost prohibitive Conventional methods in effluents and industrial wastewaters treatment. The influence of various operational parameters such as, contact time, concentration, and particle size on adsorption efficiency was investigated during the batch process. The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (AAS). The results obtained after an optimum contact of 90 min and as the adsorption equilibrium data follows langmuir isotherm, the percentage removal for an unmodified neem leave (UNL) 97 % < the % removal for a 0.5 M modified neem leave (MNL) 98 % with an effective dose of 1.0 g of bioadsorbent (Neem leaves), also the percent removal of lead ion is a function of initial concentration, as the results shows that Pb^{2+} removal efficiency is found to be 98.8 % at 5 mg/l and 97 % up to initial concentration of 20 mg/l but when the concentration increased from 30 to 50 mg/l, there was a decreased in Pb^{2+} removal efficiency to 52.00 % this shows that at lower concentrations, neem leave can be effectively used in the heavy metal removal (lead ion) in industrial wastewater as the equilibrium concentrations were found to be reasonable and within the tolerance levels when matched against SON and UNEP standards for developing countries, hence pose no danger to Soil, man and livestock. Successful application of the adsorption technique demands innovation of cheap, nontoxic, easily and locally available material. Bioadsorbents meet these requirements.

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1.0 INTRODUCTION

Pure water is scarce and is not easily available to all. Deprived sections of the society consume contaminated water and take ill periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents. The increase in usage of heavy metals in industrial activities has caused the existence of them in wastewater. At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health (Kortenkamp et. al. 1996). For example lead which is the wastewater of industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, paper and pulp brewery, pharmaceutical, and so on contains them (Loofa, 2005). The inadequacy of our conventional methods of river dumping was further exposed by the death of fishes and even deforestation of nearby trees on the shore, affecting also, human and animal lives (Porter and Mckay, 2000). Heavy metals are toxic to aquatic organisms even at very low concentration. A number of acute chronic disorders, such as itai-itai disease, renal damage, emphysema, hypertension, testicular atrophy and so on have been reported to be associated with metal ion poisoning. In particular, lead is heavy metal that affects the functioning of the blood, liver, kidney and brains of human being. Most of these minerals were present in our environment only in minute amounts until recent centuries, when the orientation toward industrialization and production brought about our many technological advances. But technology, like medicine, has its side effects. At present, these toxic metals have polluted our atmosphere, our waters, our soil, and food chain. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long-term hazard is encountered. Reviewing all of our vitamins and minerals has shown us; most every substance that is useful can be a toxin or poison, as well. Metals are known primarily and almost exclusively for their potential toxicity in the body, though commercially they may have great advantages. Therefore, the study of the existing effluent disposal methods, facilities, and attitudes is essential in order to make a positive impact on our environmental hygiene as the elimination of metal ions from drinking water or the

elimination of metal ions from drinking water or the removal of metal ion from waste water streams before discharge into receiving bodies of water is a fundamental measure for controlling metallic ion problems (Verwilghen, Guilet, Deydier, Menu, and Dartiguenave, 2004). A conventional method for removing metals from industrial effluents or treatment methods for the removal of metal ions from aqueous solution have been reported, mainly ion exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration, coagulation, electrolysis, membrane separation, and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials (Huang and Wu, 1975). Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Studies on the treatment of effluents bearing heavy metals have revealed Bio-sorption to be highly effective, innovative, versatile, cheap, easy and efficient method among the physicochemical treatment processes. Recent studies have shown that heavy metals can be removed using plant materials such an palm pressed fibers, saw dust, peat moss, sea weed, clay, sugarcane biogases, raw oil palm shell, coal, coconut husk, rice husk, Neem leaves, etc. have been investigated. (Tan, Ooi, and Lee, 1993). Apart from the plant based material wide range of physical and chemical processes is available for the removal of lead (II) from wastewater, such as electro-chemical precipitation, ultrafiltration, ion exchange and reverse osmosis (Rengaraj et al. 2001; Yurlova et al. 2002; Benito and Ruiz, 2002). Chemical modification of various adsorbents, phenol formaldehyde cationic matrices (Singanan, Vinodhini, and Alemayehu, 2006), polyethylonamide modified wood (Swamiappan, and Krishnamoorthy, 1984), sulphur containing modified silica gels and commercial activated charcoals also employed (Verwilghen and Dartiguenave, 2004).

1.1 Aims and Objectives

- The aim of this project is to study the removal of toxic lead ions by using Neem leaves from synthetic waste water.

- The objective is to offer this biosorbent or biomaterial as a local replacement for the pre-existing commercial adsorbent materials.

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1.2 Scope of work

- Preparation of Stock Solutions of Pb (II) (Synthetic Wastewater)

- Chemical Modification of Adsorbent

1.3 Justification for the Study

- Biosorption is a cheap, easy and efficient technology of effluent treatment.

- Reduction of the metallic ions accumulation in the food chain.

- Reduces the dangers pose by industrial waste water pollution.

Chapter Two

2.0 LITERATURE REVIEW

2.1 Introduction to Literature

The contamination of wastewater and soil with toxic heavy metal ions is a complex problem. The removal of this contamination has received much attention in recent years. From an environmental protection point of view, heavy metal ions should be removed at the source in order to avoid pollution of natural waters and subsequent metal accumulation in the food chain. Conventional methods for removal are chemical precipitation, chemical oxidation, chemical reduction, ion exchange, filtration, electrochemical treatment and evaporation (Singanan, Vinodhini, and Alemayehu, 2006). All these procedures have significant disadvantages, which are for instance incomplete removal, high-energy requirements, and production of toxic sludge or waste products that also require disposal. These methods often are very expensive. Alternative methods for heavy metal removal were developed in the last decade. One of them is the biosorption of heavy metal ions on biomass. Microalgae are known to have high capacities and selectivities in the uptake of heavy metals. Although the biosorption process has many advantages compared to conventional techniques, there are only a few established processes up to now. The use of screened microalgae to reduce the heavy metal concentration in wastewater effluents is the main subject.

A new biosorbent material, based on different microalgae with high metal capacities or selectivities, was obtained by a new immobilization process. Batch experiments were made to determine the selectivity of heavy metal uptake. The metal uptake of the biosorbent and the matrix system was quantitatively evaluated using the heavy metals lead, cadmium, nickel, and zinc. The experimental results are in a good correspondence with the Langmuir-isotherm-model as the experiments in an adsorption column were made with synthetic and real wastewater, caused by the accumulator industry, contaminated with lead and zinc. The results show that the biosorbent is suitable for using it in an adsorption column. (Wilke, Bunke and Buchholz, 2004).

2.1.1 Theory of Adsorption

Adsorption is a unit operation, which is mostly widely used as a physical and chemical treatment process for the removal of soluble organic, toxic organic or pollutant that are difficult to degrade biologically. Adsorption operation exploits the ability of certain solids preferentially to concentrate specific substance from solution onto their surface, adsorbent have what is called active centers where the binding forces between the individual actions of the solid structure are not completely saturated. At this active center, an adsorption of foreign molecule takes place. The adsorption process generally is of an exothermic nature, with increasing temperatures and decreasing adsorbent concentration the adsorption capacity decrease in this manner, the component of wither gaseous or liquid solutions can be separated from each other. Physical adsorption results from molecule condensation in the capillarity of the solid while Chemical adsorption results from the formation of a non-molecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules. The nature of the adsorbent materials plays an important role in the efficiency of adsorption process in wastewater treatment (Treyba, 1980).

2.1.2 Biosorption Principle

Biosorption is a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. Biomass exhibits this property, acting just as a chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria which was found responsible for this phenomenon. Opposite to biosorption is metabolically driven active bioaccumulation by living cells. That is an altogether different phenomenon requiring a different approach for its exploration. Pioneering research on biosorption of heavy metals has led to identification of a number of microbial biomass types which are extremely effective in concentrating metals. Some of the biomass types come as a waste by-product of large-scale industrial fermentations (the mold Rhizopus or the bacterium Bacillus subtilis). Other metal-binding biomass types, certain abundant seaweeds (particularly brown algae e.g. Sargassum, Ecklonia), can be readily collected from the oceans. These biomass types, serving as a basis for

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metal biosorption processes, can accumulate in excess of 25% of their dry weight in deposited heavy metals: Pb, Cd, U, Cu, Zn, even Cr and others. Research on biosorption is revealing that it is sometimes a complex phenomenon where the metallic species could be deposited in the solid biosorbent through different sorption processes of ion exchange, complexation, chelation, microprecipitation, etc. (Mc Corwather 2006).

A whole new family of suitably "formulated" biosorbents can be used in the process of metal removal and detoxification of industrial metal-bearing effluents. The sorption packed-column configuration is the most effective mode of application for the purpose. Recovery of the deposited metals from saturated biosorbent can be accomplished because they can often be easily released from the biosorbent in a concentrated wash solution which also regenerates the biosorbent for subsequent multiple reuse. This and extremely low cost of biosorbents makes the process highly economical and competitive particularly for environmental applications in detoxifying effluents of e.g.

- Metal-plating and metal-finishing operations.

- Mining and ore processing operations.

- Metal processing, battery and accumulator manufacturing operations.

- Thermal power generation (coal-fired plants in particular).

- Nuclear power generation, (etc.)

Different types of science background, from engineering to biochemistry, can make a significant contribution in elucidating the biosorption phenomenon. Interdisciplinary efforts are mandatory and represent quite a challenge. Preparing biosorption for application as a process requires mainly chemical engineering background. Good understanding of the sorption operation is mandatory. While ongoing research is essential for improving and optimizing metal biosorption effectiveness, wastewater purification applications of the biosorption process are readied for pilot testing of this alternative new technology. Optimization of specific biosorption process applications has to be done in conjunction with industrial users/clients and requires specific

process engineering expertise and a serious development capital commitment (Mohanty *et al.*, 2005).

2.1.3 Adsorption isotherm

To examine the relationship between sorbed (qe) and aqueous concentration Ce at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most widely used. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. To get the equilibrium data, initial concentration are to be varied while the adsorbent mass in each sample is to be kept constant. For hours of equilibrium periods for sorption experiments which are used to ensure equilibrium conditions.

The Langmuir model takes the form

$$q_e = k_L C_e / 1 + a_L c_e$$

where qe (mg/g) is the amount of metal ions adsorbed onto the unit mass of the adsorbent to form a complete monolayer on the surface. K_L is the Langmuir equilibrium constant which is related to the affinity of binding sites; Ce the solution phase metal ion concentration, and αL is the Langmuir constant (Aksu, 2001). The constants KL and αL are the characteristics of the Langmuir equation and can be determined from a linerized form of the Langmuir equation, represented

$$Ce / qe = 1/K_L + a_L / K_L * C_e$$

Therefore, a plot of Ce / qe) versus Ce, gives a straight line of slope αL / KL and intercept 1/KL. The constant KL is the Langmuir equilibrium constant and the ratio αL / KL gives the theoretical monolayer saturation capacity.

Therefore, only monolayer adsorption occurred on its surface, in spite of any surface modification. The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor (RL), defined by:

$$R_L = 1 / 1 + K_L C_O$$

Where KL is the Langmuir constant and Co is the initial concentration of metal ion. The value of RL indicated the type of Langmuir isotherm to be irreversible (RL= 0), favourable (0<RL<1 that is when curves are convex upward), linear (RL=1 that is rising diagonal), or unfavourable (RL>1 that is when curves are concave upward) for uptake of solute (Kadirvelu *et al.* 2001).

Figure 1.0

An equilibrium curve
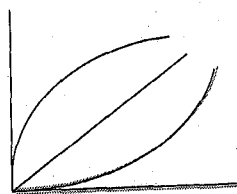
Comparison of Langmuir and Freundlich isotherm constants obtained from studies using adsorbents shows that the values obtained are comparable Using Langmuir isotherm, the equilibrium data yielded the ultimate adsorption capacity (Schmuhl *et al.* 2001).

2.1.4 Biopolymer

Biopolymers are polymers produced by living organisms. Cellulose, starch and chitin, proteins and peptides, and DNA and RNA are all examples of biopolymers, in which the monomeric units, respectively, are sugars, amino acids, and nucleotides (Mohanty *et al.,* 2005). Cellulose is both the most common biopolymer and the most common organic compound on Earth. About 33 percent of all plant matter is cellulose. Some biopolymers are biodegradable. That is, they are broken down into CO_2 and water by microorganisms. In addition, some of these biodegradable biopolymers are compostable. That is, they can be put into an industrial composting process and will break down by 90% within 6 months.

A major but defining difference between polymers and biopolymers can be found in their structures. Polymers, including biopolymers, are made of repetitive units called monomers. Biopolymers often have a well defined structure, though this is not a defining characteristic (example: ligno-cellulose): The exact chemical composition and the sequence in which these units are arranged is called the primary structure, in the case of proteins. Structural biology is the study of the structural properties of the biopolymers. In contrast most synthetic polymers have much simpler and more random (or stochastic) structures. This fact leads to a molecular mass

distribution that is missing in biopolymers. In most in vivo systems all biopolymers of a type (say one specific protein) are all alike: they all contain the similar sequences and numbers of monomers and thus all have the same mass. This phenomenon is called monodispersity in contrast to the polydispersity encountered in synthetic polymers. As a result biopolymers have a polydispersity index of 1 (Stupp and Braun 1997).

2.1.4.1 Applications of biopolymer:

The applications of biodegradable polymers have been focused on three major areas: medical, agricultural, and consumer goods packaging. Some of these have resulted in commercial products. Because of their specialized nature and greater unit value, medical device applications have developed faster than the other two. This provides an overview of special applications in the following areas: electronics, photonics, aerospace, medicine and pharmacy, food and agriculture, packaging, construction engineering, biotechnological production of monomers for chemical polymer synthesis, conversion of raw materials, corrosion, composing, environmental impacts, and health issues, legal, ecological and economic aspects (Kasapis, Norton and Ubbink 2009).

Natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentration to parts per billion concentrations. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly (Deans and Dixon, 1992).

2.1.5 Neem Tree

Neem or neem tree, a family mahogany botanical named "Azadirachta indica" or popularly known as "Margosa, Cachia, Ike tree, Dongoyaro" has the potential to boost the economic development of this country. The Neem tree is noted for its drought resistance. Normally it thrives in areas with sub-arid to sub-humid conditions, with an annual rainfall between 400 and 1200 mm. It can grow in regions with an annual rainfall below 400 mm, but in such cases it depends largely on ground water levels. Neem can grow in many different types of

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soil, but it thrives best on well drained deep and sandy soils. It is a typical tropical to subtropical tree and exists at annual mean temperatures between 21-32°C. It can tolerate high to very high temperatures and does not tolerate temperature below 4°C.

Neem is a life giving tree, especially for the dry coastal, southern districts. It is one of the very few shade-giving trees that thrive in the drought prone areas. The trees are not at all delicate about the water quality and thrive on the merest trickle of water, whatever the quality. In the north it is very common to see neem trees used for shade lining the streets or in most people's back yards. In very dry areas, the trees are planted in large tracts of land, in whose shade fireworks factories function, it is an out standing example of plants with many commercially exploitable properties, has many uses which cut across medicinal pharmaceuticals and industrial (Adeyinka, Liang, and Tina, 2007).

The exchange/sorption properties of neem leave are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactone, which have a high affinity for metal ions (Tan et al. 1993).

2.2 Introduction to Lead

Lead, symbol Pb (Latin plumbum, a lead weight), dense, bluish-gray metallic element was one of the first known metals. The atomic number of lead is 82; the element is in group 14 (or IVa) of the periodic table with relative atomic mass 207.19.

2.2.1 Properties of lead

Metallic lead is a soft, malleable, ductile metal. When gently heated it can be force through annular holes or dies. It has low tensile strength and is a poor conductor of electricity. A freshly cut surface has a bright silvery luster, which quickly turns to the dull, bluish-gray color characteristic of the metal. Lead melts at 327.46°C (621.43°F), boils at 1749°C (3180°F), and has a specific gravity of 11.35; the atomic weight of lead is 207.2.

Lead is soluble in nitric acid but is little affected by sulfuric or hydrochloric acids at room temperature. In the presence of air, it slowly reacts with water to form lead hydroxide, which is

slightly soluble. Lead is toxic when taken internally; although ordinary water usually contains salts that form a coating on pipes, inhibiting the formation of soluble lead hydroxide, pipes used for carrying drinking water should not contain lead.

Lead occurs naturally in eight isotopic forms, of which four are stable and four radioactive. The stable isotopes, lead-206, lead-207, and lead-208, are, respectively, the end products of the uranium, actinium, and thorium series of radioactive decay; lead-204, also stable, has no natural radioactive precursors.

2.2.2 Uses of Lead

Lead is used in enormous quantities in storage batteries and in sheathing electric cables. Large quantities are used in industry for lining pipes, tanks, and X-ray apparatus. Because of its high density and nuclear properties, lead is used extensively as protective shielding for radioactive material. Among numerous alloys containing a high percentage of lead are solder, type metal, and various bearing metals. A considerable amount of lead is consumed in the form of its compounds, particularly in paints and pigments.

2.2.3 Production of lead

Principal sources of lead are found in Australia, the United States, Canada, Mexico, Peru, Serbia, and Russia. The United States consumes about half of the world production of lead, and it formerly produced about one-third of the world supply. Since World War II ended in 1945, the richest veins of galena have been exhausted, and U.S. output has been greatly reduced.

2.2.4 Compounds of Lead

Basic lead carbonate, $(PbCO_3)_2 \cdot Pb(OH)_2$, called white lead.

Lead monoxide, or litharge (PbO), a yellow, crystalline powder formed by heating lead in air.

Lead chromate, or chrome yellow ($PbCrO_4$) prepared by the reaction of lead acetate and potassium bichromate.

Lead acetate ($Pb(C_2H_3 O_2)_2 \cdot 3H_2O$), a white, crystalline substance called sugar of lead because of its sweet taste, is prepared commercially by dissolving litharge in acetic acid.

Lead tetraethyl ($Pb(C_2H_5)_4$) is the chief constituent of the antiknock compound added to gasoline to prevent premature detonation in internal-combustion engines; it is considered a significant contributor to air pollution.

2.2.5 Lead Poisoning

Lead taken internally in any of its forms is highly toxic; the effects are usually felt after it has been accumulated in the body over a period of time. The symptoms of lead poisoning are anemia, weakness, constipation, colic, palsy, and often a paralysis of the wrists and ankles. Flaking lead-based paints and toys made from lead compounds are considered serious hazards for children. Children are especially at hazard from lead, even at levels once thought safe. Lead can reduce intelligence, delay motor development, impair memory, and cause hearing problems and troubles in balance. In adults, one lead hazard at levels once thought safe is that of increased blood pressure. Present-day treatment of lead poisoning includes the administration of calcium disodium ethylenediaminetetraacidic acid, or EDTA, a chelating agent; lead is removed from the body by displacing the calcium in EDTA and forming a stable complex that is excreted in the urine (Redmond, 2008).

2.3 Water

Water is a chemical substance with the chemical formula H_2O. Its molecule contains one oxygen and two hydrogen atoms connected by covalent bonds. Water is a liquid at ambient conditions, but it often co-exists on Earth with its solid state, ice, and gaseous state, water vapor or steam. Water in three states: liquid, solid (ice), and (invisible) water vapor in the air. Water covers 70.9% of the Earth's surface and is vital for all known forms of life On Earth surface. A very small amount of the Earth's water is contained within biological bodies and manufactured products (Donald, 2008). Clean drinking water is essential to human and other life forms. Access to safe drinking water has improved steadily and substantially over the last decades in almost every part of the world. There is a clear correlation between access to safe water and GDP per

capita. However, some observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability (Kulshreshtha, 1998). A recent report (November 2009) suggests that by 2030, in some developing regions of the world, water demand will exceed supply by 50 % (Ponpo, 2000).

Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Approximately 70 % of freshwater is consumed by agriculture (Berati, 2007).

2.3.1 Chemical and Physical Properties

Water is the chemical substance with chemical formula H_2O: one molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom.

The major chemical and physical properties of water are:

Water is a tasteless, odorless liquid at standard temperature and pressure. The color of water and ice is, intrinsically, a very slight blue hue, although water appears colorless in small quantities. Ice also appears colorless, and water vapor is essentially invisible as a gas. This dipolar nature contributes to water molecules' tendency to form hydrogen bonds which cause water's many special properties. Water is a good solvent and is often referred to as the universal solvent. Substances that dissolve in water, e.g., salts, sugars, acids, alkalis, and some gases – especially oxygen, carbon dioxide (carbonation) are known as hydrophilic (water-loving) substances, while those that do not mix well with water (e.g., fats and oils), are known as hydrophobic (water-fearing) substances (Heyden, 2006).

2.3.2 Effects on Life

From a biological standpoint, water has many distinct properties that are critical for the proliferation of life that set it apart from other substances. It carries out this role by allowing organic compounds to react in ways that ultimately allow replication. All known forms of life depend on water. Water is vital both as a solvent in which many of the body's solutes dissolve and as an essential part of many metabolic processes within the body. Metabolism is the sum

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total of anabolism and catabolism. In anabolism, water is removed from molecules (through energy requiring enzymatic chemical reactions) in order to grow larger molecules (e.g. starches, triglycerides and proteins for storage of fuels and information). In catabolism, water is used to break bonds in order to generate smaller molecules (e.g. glucose, fatty acids and amino acids to be used for fuels for energy use or other purposes). Without water, these particular metabolic processes could not exist.

2.3.2.1 Aquatic life forms

Hydrobiology and Aquatic

Earth's surface waters are filled with life. The earliest life forms appeared in water; nearly all fish live exclusively in water, and there are many types of marine mammals, such as dolphins and whales. Some kinds of animals, such as amphibians, spend portions of their lives in water and portions on land. Plants such as kelp and algae grow in the water and are the basis for some underwater ecosystems. Plankton is generally the foundation of the ocean food chain. Aquatic vertebrates must obtain oxygen to survive, and they do so in various ways. However as invertebrate life evolved in an aquatic habitat most have little or new specialization for respiration in water.

2.3.2.2 Health and pollution

Water fit for human consumption is called drinking water or potable water. Water that is not potable may be made potable by filtration or distillation, or by a range of methods. Water that is not fit for drinking but is not harmful for humans when used for swimming or bathing is called by various names other than potable or drinking water, and is sometimes called safe water, or "safe for bathing". Chlorine is a skin and mucous membrane irritant that is used to make water safe for bathing or drinking. Poor water quality and bad sanitation are deadly; some five million deaths a year are caused by polluted drinking water. The World Health Organization estimates that safe water could prevent 1.4 million child deaths from diarrhea each year.

2.3.2.3 Agriculture

The most important use of water in agriculture is for irrigation, which is a key component to produce enough food. Irrigation takes up to 90% of water withdrawn in some developing countries and significant proportions in more economically developed countries. Water as a scientific standard, the gram was defined in France to be equal to "the absolute weight of a volume of pure water equal to a cube of one hundredth of a meter, and to the temperature of the melting ice (Anderson 1991).

2.3.2.4 for drinking

The human body is anywhere from 55% to 78% water depending on body size. To function properly, the body requires between one and seven liters of water per day to avoid dehydration; the precise amount depends on the level of activity, temperature, humidity, and other factors. Most of this is ingested through foods or beverages other than drinking straight water. It is not clear how much water intake is needed by healthy people. The popular claim that "a person should consume eight glasses of water per day" seems to have no real basis in science. Similar misconceptions concerning the effect of water on weight loss and constipation have also been dispelled (Marq de Villiers, 2003)

Humans require water that does not contain too many impurities. Common impurities include metal salts and oxides (including copper, iron, calcium and lead) (Roddick, et al 2004) and/or harmful bacteria, such as Vibrio. Some solutes are acceptable and even desirable for taste enhancement and to provide needed electrolytes.

2.3.2.5 Washing

The propensity of water to form solutions and emulsions is useful in various washing processes. Many industrial processes rely on reactions using chemicals dissolved in water, suspension of solids in water slurries or using water to dissolve and extract substances. Washing is also an important component of several aspects of personal body hygiene.

2.3.2.6 Recreation

Humans use water for many recreational purposes, as well as for exercising and for sports. Some of these include swimming, waterskiing, boating, surfing and diving. In addition, some sports, like ice hockey and ice skating, are played on ice. Lakesides, beaches and water parks are popular places for people to go to relax and enjoy recreation.

2.3.3 Chemical uses

Water is widely used in chemical reactions as a solvent or reactant and less commonly as a solute or catalyst. In inorganic reactions, water is a common solvent, dissolving many ionic compounds. In organic reactions, it is not usually used as a reaction solvent, because it does not dissolve the reactants well and is amphoteric (acidic and basic) and nucleophilic. Nevertheless, these properties are sometimes desirable.

2.3.4 Water industry

The water industry provides drinking water and wastewater services (including sewage treatment) to households and industry. Water supply facilities include water wells cisterns for rainwater harvesting, water supply network, water purification facilities, water tanks, water towers, water pipes including old aqueducts. Atmospheric water generators are in development. Drinking water is often collected at springs, extracted from artificial borings (wells) in the ground, or pumped from lakes and rivers. Building more wells in adequate places is thus a possible way to produce more water, assuming the aquifers can supply an adequate flow. Other water sources include rainwater collection. Water may require purification for human consumption. This may involve removal of undissolved substances, dissolved substances and harmful microbes. Popular methods are filtering with sand which only removes undissolved material, while chlorination and boiling kill harmful microbes. Distillation does all three functions. More advanced techniques exist, such as reverse osmosis and adsorption. Desalination of abundant seawater is a more expensive solution used in coastal arid climates. The distribution of drinking water is done through municipal water systems, tanker delivery or as bottled water. Governments in many countries have programs to distribute water to the needy at no charge.

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Others argue that the market mechanism and free enterprise are best to manage this rare resource and to finance the boring of wells or the construction of dams and reservoirs. Reducing usage by using drinking (potable) water only for human consumption is another option. In some cities, sea water is extensively used for flushing toilets citywide in order to conserve fresh water resources.

Polluting water may be the biggest single misuse of water; to the extent that a pollutant limits other uses of the water, it becomes a waste of the resource, regardless of benefits to the polluter. Like other types of pollution, this does not enter standard accounting of market costs, being conceived as externalities for which the market cannot account. Thus other people pay the price of water pollution, while the private firms' profits are not redistributed to the local population victim of this pollution. Pharmaceuticals consumed by humans often end up in the waterways and can have detrimental effects on aquatic life if they bioaccumulate and if they are not biodegradable. Wastewater facilities are storm sewers and wastewater treatment plants. Another way to remove pollution from surface runoff water is bioswale (DeMan, 1999).

2.3.5 Water is described in many terms and contexts:

2.3.5.1 According to state

Solid – ice , liquid – water, gaseous – water vapor

2.3.5.2 According to occurrence

Groundwater, Melt water, meteoric water, connate water, Fresh water, Surface water, Mineral water – contains many minerals, brackish water, Dead water – strange phenomenon which can occur when a layer of fresh or brackish water rests on top of denser salt water, without the two layers mixing, Seawater, brine.

2.3.5.3 According to uses

Tap water, Bottled water, Drinking water or potable water – useful for everyday drinking, without fouling, it contains balanced minerals that are not harmful to health, Purified water, laboratory-grade, analytical-grade or reagent-grade water – water which has been highly purified

for specific uses in science or engineering. Often broadly classified as Type I, Type II, or Type III, this category of water includes, but is not limited to, the following:

Distilled water, Double distilled water, Deionized water and Reverse osmosis plant Water.

2.3.5.4 According to other features

- Soft water – contains fewer minerals.

- Hard water – from underground, contains more minerals, distilled water, double distilled water, deionized water – contains no minerals.

- Water of crystallization — water incorporated into crystalline structures.

- Hydrates — water bound into other chemical substances.

- Heavy water – made from heavy atoms of hydrogen – deuterium. It is in nature in normal water in very low concentration. It was used in construction of first nuclear reactors.

- Titrated water.

2.3.5.5 According to microbiology

Drinking water, Wastewater, storm water or surface water. (DeMan, 1999).

TABLE 2.1 UNEP set standards for heavy metal content of Health for developing countries

Element	Tolerance contents of elements in cultivated soils with regards to the health of vegetation, livestock and man*
Mn	-
Co	1-10
Pb	0.1-2
Zn	10-50
Fe	-
Cu	5-20
Ni	10-50
Cr	10-50

* UNEP & BMFT (1983)

TABLE 2.2 the minimum requirements set out by the Nigerian Standards for Drinking Water Quality (Chemical Parameters - Inorganic Constituents)

Parameter	Maximum Permitted Level (mg/L)	Health Impact
Mang. (Mn^{+2})	0.20	Neurological disorder
lead (Pb)	0.01	Cancer, interference with Vitamin D metabolism, affect mental development in infants, toxic to the central and peripheral nervous systems
Zinc (Zn)	3	None
Iron (Fe^{+2})	0.3	None
Cupper (Cu^{+2})	1	Gastrointestinal disorder
Nickel (Ni)	0.02	Possible carcinogenic
Chromium (Cr^{6+})	0.05	Cancer

Source: (SON, 2007)

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Chapter Three

3.0 Research Methodology

3.1 Chemical, Reagents, Materials and Equipments used

3.1.1 Chemical and Reagents

Table 3.1; Lists Chemical/Reagent used for the Experiment

MATERIALS	SOURCE	REMARK
Neem leaves (adsorbent)	In my house back yards	tropical to subtropical tree
Distilled water	Chemistry laboratory, FUT Minna	Liquid
Lead (11) nitrate $(Pb(NO_3)_2)$	Chemistry laboratory, FUT Minna	Analytical reagent grade (salt)
Nitric acid (HNO_3)	Near Mobil market, Minna	Analytical reagent grade (salt)
Citric acid $(C_3H_4OH(COOH)_3)$	Near Mobil market, Minna	Analytical reagent grade (salt)
Sulfuric acid sodium hydroxide	Chem. Lab. FUT Minna	Analytical reagent

3.1.2 Materials and Equipments

Table 3.2: List of Materials/Equipment Used for the Experiment

S/N	APPARATUS/ EQUIPMENT	CAPACITY/ SOURCE	REMARK
1.	Shaker	Soil Science Lab. FUT Minna	Electrical
2.	Atomic Abs. Spec .(AAS)	,,	Digital display
3.	Sieves	,,	Mesh
4.	Grinding mill	Chemistry Lab., FUT Minna	mortar and pestle
5.	Oven	,,	Electrical
6.	Water Deionizer	,,	,,
7.	Ph Meter	,,	Digital display
8.	Weighing Balance	,,	,,
9	Beakers	,,	Glass ware
10.	Measuring Cylinder	,,	,,
11.	Volumetric flask	,,	,,
12.	Funnel	,,	,,
13.	Whatman filter paper	Near Mobil market, Minna	Plastic
14.	Sample can	,,	Analytical (paper)
			Rubber

3.2 Preparation of Neem leaves

3.2.1 Chemical Activation of adsorbent:

The Neem leaves were dried for a period of three days in the oven at 100 $^{\circ}$C. The Neem leaves were cleaned with distilled deionised water and dried at room temperature. The leaves were grounded with the grinding mill. The ground Neem leaves was sieved and was of particle size 0.5mm. This was to allow for shorter diffusion path, thus allowing the adsorbate (Neem leaves) to penetrate deeper into the effluent more quickly, resulting in a higher rate of adsorption.

3.2.2 Chemical modification of adsorbent

The air dried activated neem leave was weighed and divided into 2 parts. 20 g of the first part labeled "A" was left untreated and called "unmodified neem leave" (UNL) and 20 g of the second part labeled "B" was acid treated by soaking in excess 0.5 M HNO_3 solution for some minutes. It was then filtered through a whatman filter paper and rinsed with distilled deionized water. The rinsed adsorbent was later air dried for 12 h and then dissolved it in excess 0.5 M Citric acid solution. The suspension were stirred for some min and left to stand for hours at 28 °C and called 0.5 M modified neem leave (MNL), after which the mixture was filtered off using whatman filter paper. The treatment of the adsorbent with 0.5M HNO_3 solution and Citric acid aids the removal of any debris or soluble biomolecules that might interact with metal ions during sorption. The residue in the filter paper was then rinsed with distilled deionized water. The washed residue was air dried. The two working adsorbents were stored in air tight plastic containers.

3.3 Preparation of Synthetic Wastewater

The entire chemical used was analytical reagent grade. In order to avoid interference with other element in the wastewater, the experiment was conducted with aqueous solution of lead (II) nitrate. 1000 mg/l stock Pb (II) solutions (1000mg/l) was prepared by dissolving 1.6 g solution of lead (II) nitrate ($Pb(NO_3)_2$) in 1000ml volumetric flask of distilled deionized water. From the stock solutions, working solution of initial concentration (5 &10 mg/l) and other solutions of lead were prepared by serial dilution (diluting the stock solution with distilled deionised water) by filling differently in to a conical flask with 100ml capacity with 10, 20, 30, 40 & 50mg/l of the synthetic wastewater. For quality control purpose, any possible contamination was avoided.

3.4 Adsorption Experiment

The experiments were carried out in the batch mode for the measurement of adsorption capabilities (investigating the mode and magnitude). The initial constant concentration used was 10.00mg/l of Lead and the contacting time was varied from 30 to 150 minutes, so as to obtain the optimum contact time for the process. The bottles with 10, 20, 30, 40 & 50mg/l of the synthetic wastewater were taken differently, and 1g of Neem leaves (grounded) of both the modified and unmodified samples were added, bottles were shaken thoroughly for a predetermined period at room temperature in a reciprocating electric shaker (equilibration) for 90 minutes at 300 rpm. The separation of the adsorbents and solutions was immediately carried out by filtration with Whatman filter paper and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an Atomic Absorption Spectrophotometer (AAS) for residual lead (11) concentration in the solution. The effects of different initial Pb (11) concentrations, contact time, chemically modified and unmodified adsorbents on the adsorption capacity were also studied.

Chapter four

4.0 RESULTS AND DISCUSSIONS

4.1 Table of Results

Table 4.1

Data for the evaluation of optimum contact time of lead adsorption for an unmodified adsorbent

S/N	TIME MIN.	INITIAL CONC. (C_O) ppm (mg/l)	EQUILIBRIUM CONC. (C) ppm (mg/l)	FRACTION ADSORBED	% ADSORBED
1	30	10	0.50	0.950	95.00
2	60	10	0.40	0.960	96.00
3	90	10	0.30	0.970	97.00
4	120	10	0.40	0.960	96.00
5	150	10	0.60	0.940	94.00

Table 4.2

Data for the evaluation of optimum contact time of lead adsorption for a modified adsorbent

S/N	TIME MIN.	INITIAL CONC. (C_O) ppm (mg/l)	EQUILIBRIUM CONC. (C) ppm (mg/l)	FRACTION ADSORBED	% ADSORBED
1	30	5	0.15	0.970	97.00
2	60	5	0.10	0.980	98.00
3	90	5	0.06	0.988	98.80
4	120	5	0.08	0.984	98.40
5	150	5	0.18	0.964	96.40

Table 4.3

Data for effect of initial Pb (II) concentration on fraction adsorbed for unmodified adsorbent

S/N	TIME MIN.	INITIAL CONC. (C_O) ppm (mg/l)	EQUILIBRIUM CONC. (C) ppm (mg/l)	FRACTION ADSORBED	% ADSORBED
1	90	10	00.30	0.970	97.00
2	90	20	00.60	0.970	97.00
3	90	30	05.00	0.833	83.80
4	90	40	12.00	0.700	70.40
5	90	50	24.00	0.520	52.40

Table 4.4

Data for effect of initial Pb (II) concentration on fraction adsorbed for a modified adsorbent

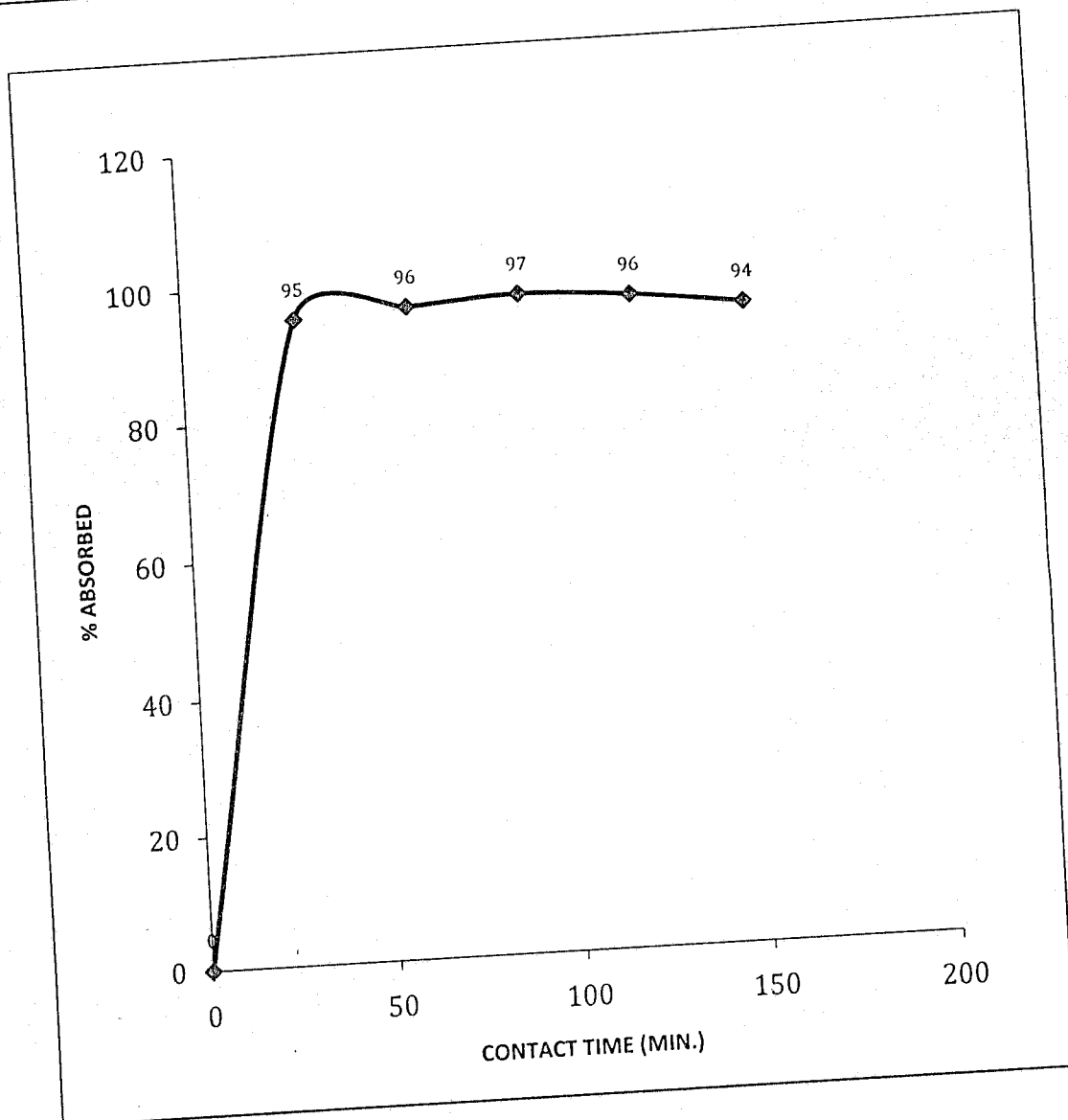| S/N	TIME MIN.	INITIAL CONC. (C_O) ppm (mg/l)	EQUILIBRIUM CONC. (C) ppm (mg/l)	FRACTION ADSORBED	% ADSORBED
1	90	10	00.20	0.980	98.00
2	90	20	00.50	0.975	97.50
3	90	30	04.00	0.867	86.70
4	90	40	11.00	0.725	72.50
5	90	50	20.00	0.600	60.00

Figure 4.1

THE GRAPH OF % ABSORBED AGAINST CONTACT TIME (unmodified)
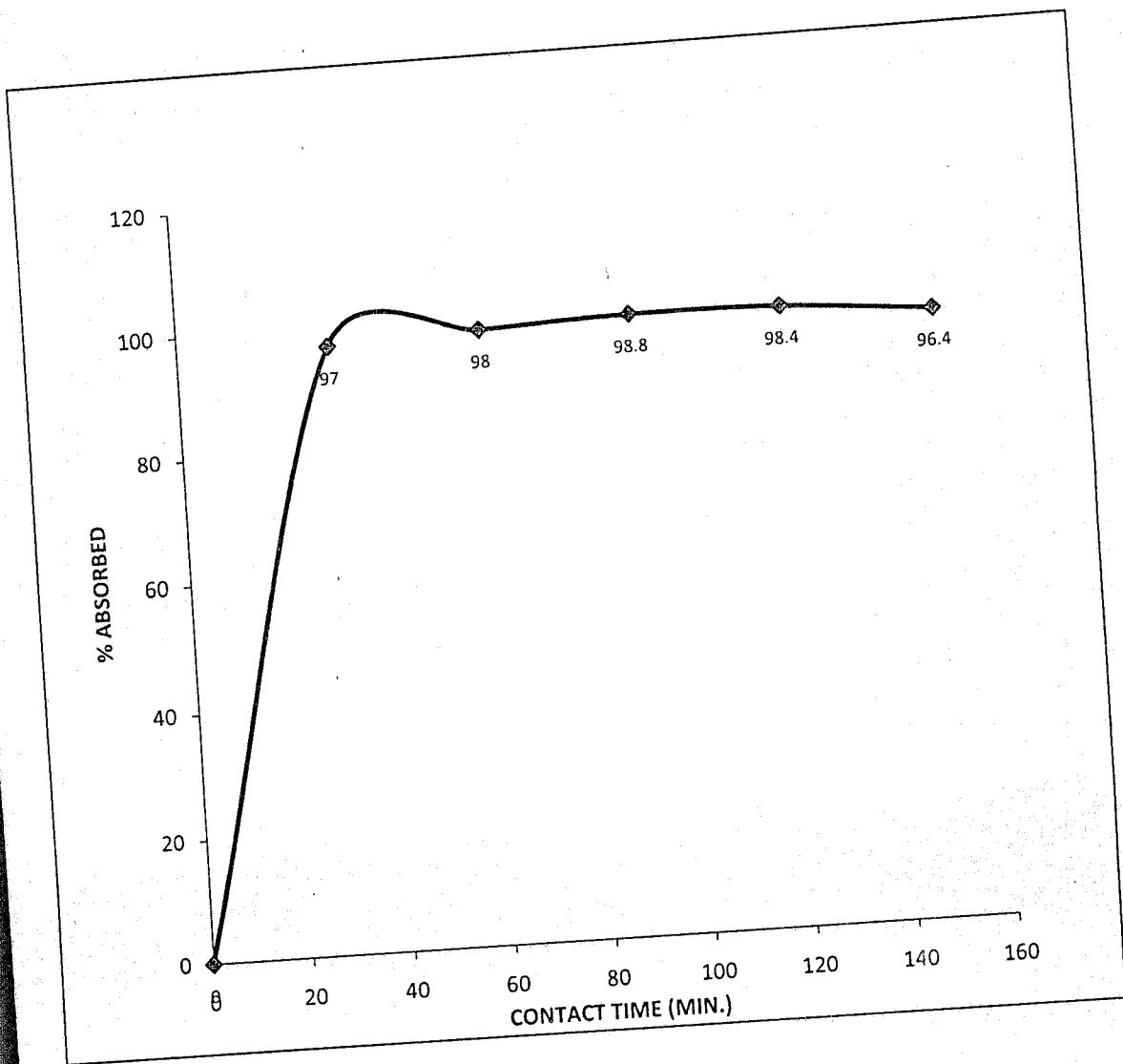
25

Figure 4.2

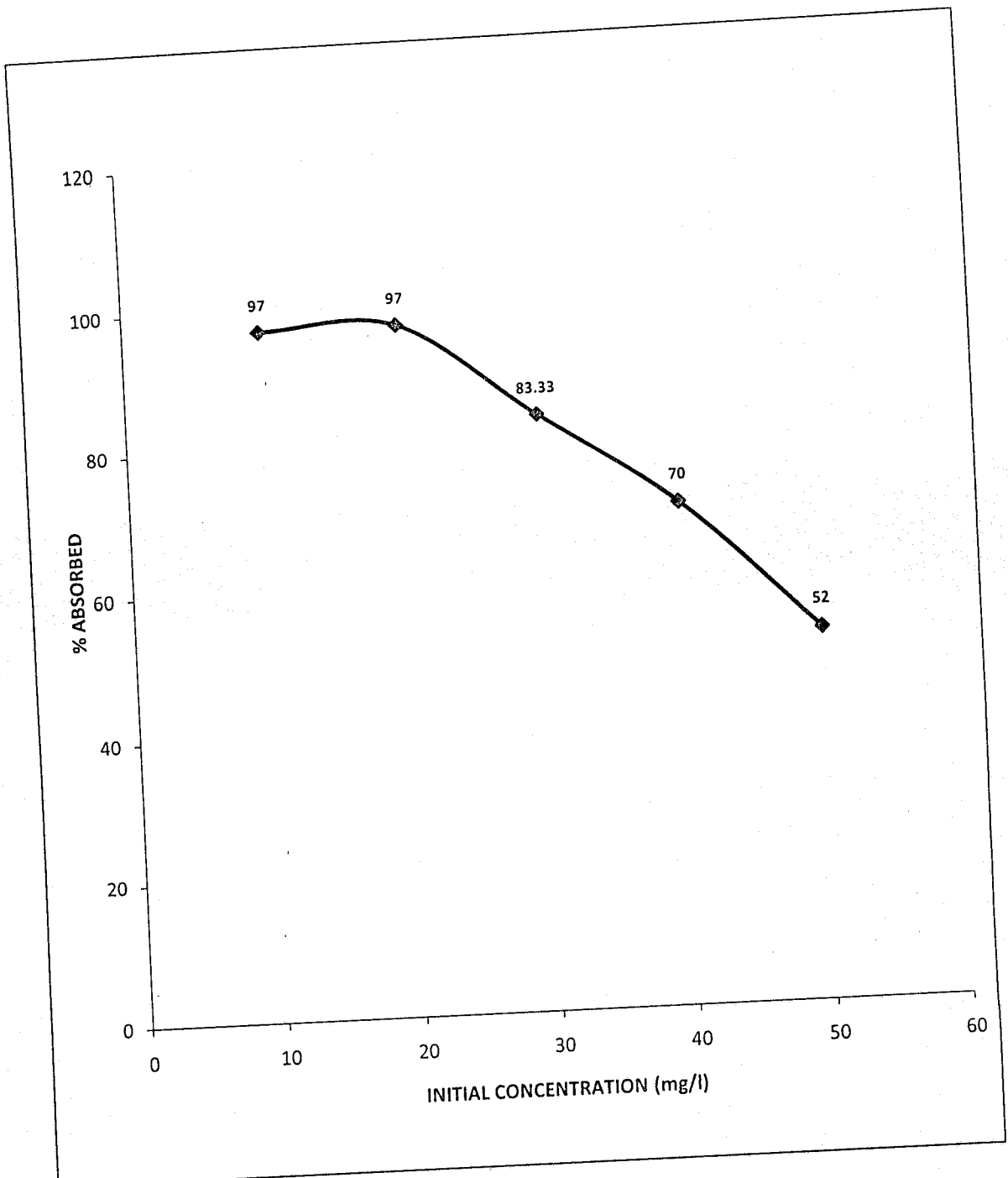THE GRAPH OF % ABSORBED AGAINST CONTACT TIME (modified)

Figure 4.3

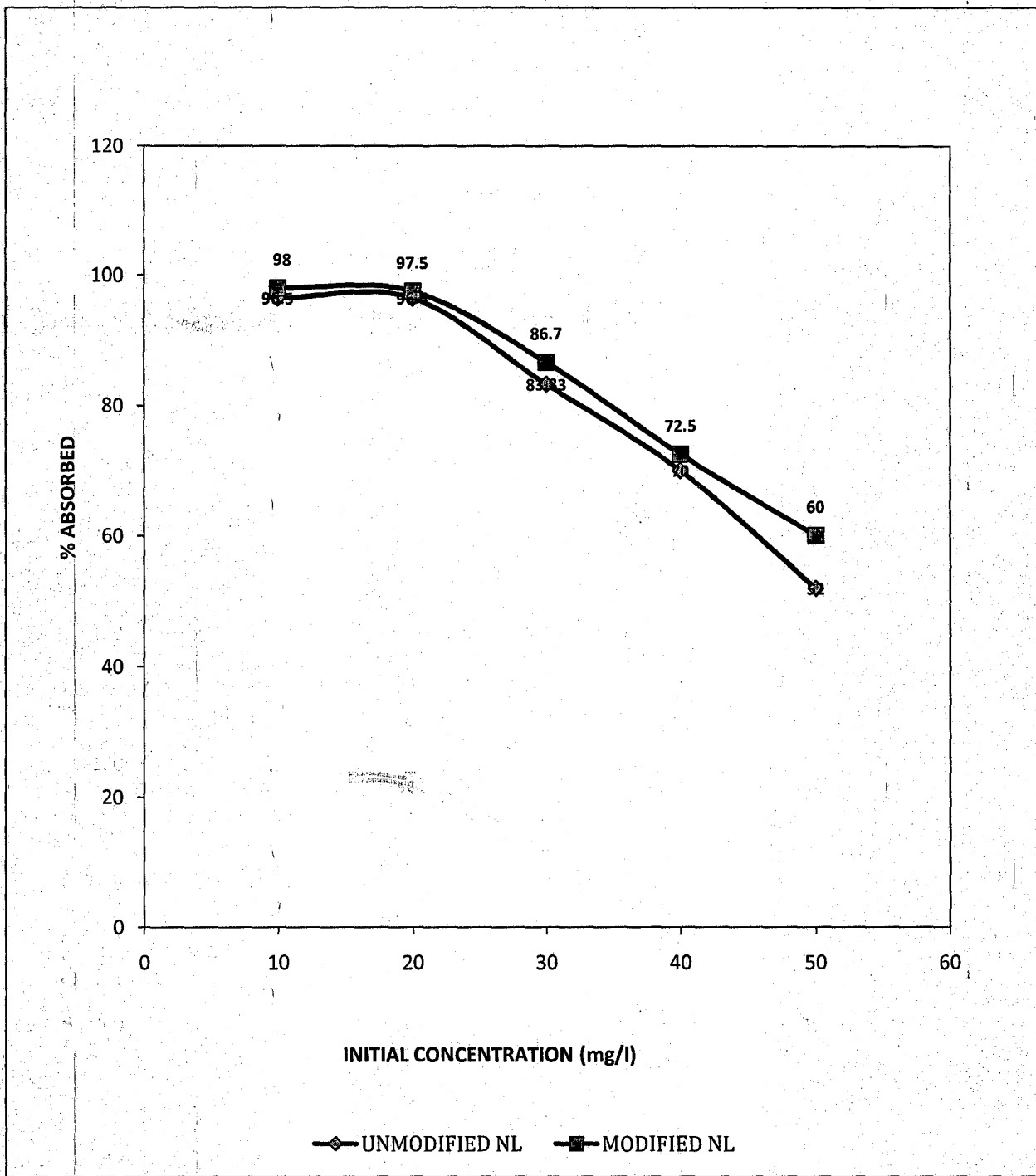A GRAPH OF % ABSORBED AGAINST INITIAL CONCENTRATION

Figure 4.4

A GRAPH OF % ABSORBED AGAINST INITIAL CONC. FOR A MODIFIED & UNMODIFIED ADSORBENT

4.2 Discussion of Results

4.1.1 Data analysis

The results were expressed as:

The amount of Pb^{2+} and fraction adsorbed (c_o-c / c_o) in mg/L from each metal solution by the various adsorbents at optimum contact time of 90 minutes was computed by using the following equation:

> Fraction adsorbed = (c_o-c / c_o)

> The removal efficiency, E (% absorbed) of the adsorbent on Pb,

$$E (\%) = [(Co - C) / Co] \times 100$$

Where

Co and C are the initial and equilibrium concentration of lead ion solutions (mg/l), respectively.

4.2 Factors influencing the adsorption of Lead ions

The influence of several operational parameters such as, contact time, concentration, modification and was investigated.

4.2.1 Effect of contact time:

Results (table 1.0 and 2.0) and the calibrated curve that was plotted, of constant adsorbate concentrations (10 and 5 mg/l) at various times; ranging from 30, 60, 90, 120 and 150min (figure 1.0 and 2.0) indicates that removal efficiency (% absorbed) increased with an increase in contact time before equilibrium is reached. Other parameters such as dose of the adsorbent and agitation speed was kept optimum (constant), It can be seen that Pb removal efficiency increased from 95 % to 97 % when contact time was increased from 30 to 90 min and started decreasing from 96 % to 94 % when the contact time was increased from 120 to 150 min. Optimum contact time for the adsorbents was found to be 90 min because it was the point at which the percentage absorbed was most desirable at constant concentrations. Hence the Neem leaves require a shorter contact time, this result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system (Iqbal, Edyvean, 2004 and Loofa, 2005).

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4.2.2 Effect of initial adsorbate concentration:

For a strictly adsorptive reaction, in the optimized period of contact, the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial lead ion concentration (Bailey and Brian, 1999), (table 2.0 & figure 2.0). The adsorption capacity of treated biosorbent was systematically studied by varying the initial concentration of lead ions between 10 and 50 mg/l with a constant sorbent dose of 1 g. The percent removal of lead ion is a function of initial concentration, as the results shows that Pb^{+2} removal efficiency is found to be 97 % up to initial concentration of 20 mg/l but when the concentration increased from 30 to 50 mg/l, there was a decreased in Pb^{+2} removal efficiency from 83.30 % to 52.00 %.

4.2.3 Effect of Chemical modified and Unmodified of adsorbent:

The characteristics of the two adsorbents unmodified Neem leaves (UNL) and 0.5 M modified Neem leaves (0.5 MNL). The results shows a trend in which the specific surface area of the adsorbents increased with chemical modification and the variations in percentage removal of lead ion by the two adsorbents (UNL and 0.5 MNL) are indicated in table 3.0 & 4.0 and figure 3.0. There was slight increase in the percentage of each adsorbents and the sequence of increase in percentage of each Pb^{+2} adsorbent is: UNL < 0.5 MNL. This may be attributed to the increase in the number of functional groups on the modified adsorbent (0.5MNL), as the incorporations of HNO_3 and citric acid into the neem leave for chemical modification tends to increases the adsorption capacity by increasing the no of binding sites (Abia *et al.*, 2003). This acidic treatment for modification helps in the removal of lignin before their application and to increase efficiency. From the results for example, it was observed that at optimum time (90 min.) and initial conc. (10 mg/l), the percentage removal for an unmodified neem leave (UNL) 97 % < the % removal for a 0.5 M modified neem leave (MNL) 98%.

4.2.4 Effect of adsorbent particle size:

Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of lead ions. The uptake of lead ions at different adsorbent particle sizes increased with decrease in sorbent particle diameter. The presence of large number

of smaller particles provides the sorption system with more active and larger surface area available for lead ion removal and it also reduces the external mass transfer resistance. Also, the time required for 50% of the total adsorption is less with the particles of smaller size (Qadeer and AKhtar, 2005). But for the purpose of this work, a particle size of 0.5mm was used throughout.

Chapter Five

5.0 CONCLUSION AND RECOMENDATIONS

5.1 Conclusion

The removal of lead ions (Pb^{2+}) in synthetic wastewater by using biosorption technology was studied. Based on the results, the following conclusions can be drawn.

The ground Neem leaves was efficient as a biomaterial in removal of lead ions from the synthetic wastewater. The optimum contact time for the adsorbents was found to be 90 min and the adsorption equilibrium data follows Langmuir isotherm. The percentage removal of lead ion is a function of initial concentration and modification, results shows that at lower concentrations neem leave can be effectively used in the heavy metal removal (lead ion) in industrial wastewater as the equilibrium concentrations were found to be reasonable and within the tolerance levels when matched against the set standards, hence pose no danger to Soil, man and livestock. Therefore, biosorption is very important because it is the dissolved and difficult to decompose organic substance that is selectively removed by the adsorbent.

5.2 Recommendations

The procedure need to be optimized and validated for different type of metallic waste water.

This adsorbent can be a good candidate for adsorption of not only lead ions but also other heavy metal ions (like Nickel) in wastewater stream.

Based on the recent lead poisoning outbreak in Zamfara state of Nigeria and because the intake of food that is contaminated by heavy metals are harmful to human health, therefore several laws should be put in place to restrict the indiscriminate discharge of wastewater by industries.

There is need for characterization of the formulations in future studies to check any form of interference.

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