THE REMOVAL OF ZINC ION FROM AQEOUS SOLUTION USING CELLULOSE

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CERTIFICATION

This is to certify that this project was carried out by **EZIMAH JOY CHIDINMA**, with the matriculation number: **PSC1707315**, student of the Department of Chemistry, Faculty of Physical Science, University of Benin, Benin City, Edo State.

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DEDICATION

I dedicate this research project to the almighty God for His wisdom, guidance, and His help all through the period of this research work and I also dedicate this to my parents MR and MRS EZIMAH for their support financially, morally and spiritually in making sure I achieve this great success.

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Not left out are my Team mates; I acknowledge them for their co-operation and understanding towards achieving a common goal.

TABLE OF CONTENTS

ABSTRACT

This study utilized cellulose for the adsorption of Zn(II) from aqueous solution via batch adsorption process. The effect of the adsorption parameters: Adsorbent Dosage, Initial Concentrations, and Contact time were investigated. examined under various conditions using heavy metal ion (Zn^{2+}) as the adsorbate. The amounts of Zn(II) adsorbed were estimated by using flame atomic absorption spectrophotometer. It was found to obey the langmuir isotherm as it gave the best fit to the isotherm data. The result of kinetic studies revealed that the adsorption process obeyed pseudo-second order. After the completion of the adsorption process of Zn(II), the result obtained shows that cellulose can be used as an effective adsorbent for the removal of Zinc ion (Zn^{2+}) from aqueous solution

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 BACKGROUND OF STUDY

The increase in use of potentially toxic elements over the past few decades has unavoidably resulted in the flux of metallic substances in the aquatic and terrestrial environment (Jimoh et al., 2012). These metals once released through anthropogenic activities cannot be destroyed or degraded and thus persist indefinitely in the environment, accumulate in living tissues throughout the food chain and pose a serious menace to human and public health (Renuga et al., 2010).

Numerous concerted efforts have been made in the removal of heavy metals, which includes the use of conventional methods such as ion exchange, membrane processing, electrolytic methods, chemical oxidation or chemical reduction, filtration, chemical precipitation and electrochemical treatment (Selvaraj et al., 2003). However, most of these methods are not economically feasible for small and medium size industries. They also suffered from high operational and maintenance costs, generation of toxic sludge and elaborated procedure involved in the wastewater treatment. Commercial activated carbon is unequivocally accepted as universal adsorbent for wastewater treatment, but due to its cost, developing country like Nigeria cannot avoid this treatment technique as consequence of low income per capital (Bhatnagar and Sillanp, 2010).

In addition, adsorption technique was considered better in wastewater treatment because of simplicity of design, convenience and ease of operation (Wasewar et al., 2009). In the past two decades, biosorption process has emerged as a cost effective and efficient alternative method for wastewater treatment utilizing naturally occurring agricultural waste materials as biosorbents.

Heavy metal pollution is considered as a major problem of increasing magnitude as nearly all heavy metals are highly toxic, non-biodegradable, non-thermo-degradable and readily accumulate to toxic levels (Tuzen *et al.*, 1998). Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. The release of these metallic species into the environment possesses major threat to the ecosystem affecting plants, animals as well as humans. The increase in usage of heavy metals in industrial activities has occasioned their existence in wastewater (Iqbal et al., 2005). For example, zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing.

Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, smelting, alloy industries and storage batteries industries, etc. (Kadirvelu, K et al., 2001). Therefore, the need for removal and treatment of heavy metals arises. In most developed and developing countries, strict environmental regulations, with regard to contaminants discharged from industrial operations, are introduced. This means that industries need to develop on-site or in-plant facilities to their own effluents

and minimize the contaminant concentrations to acceptable limits prior to their discharge. Various techniques have been employed for the treatment of metal bearing industrial effluents, which usually come under two broad divisions: abiotic and biotic methods.

Commonly, a density of at least 5g/cm^3 is used to define a heavy metal and to differentiate it from other, “light” metals. With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids, such as arsenic, that are able to induce toxicity at low level of exposure [Duffus, 2002]. In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications [Bradly, 2002]. Even at trace level, exposure to heavy metals can cause risk for human beings (Jamil et al., 2010; Khan et al., 2008; Singh et al., 2010; Peng et al., 2004). Because of heavy metals tend to accumulate in living organisms and most of they are carcinogenic. They can cause various symptoms including organ damage, high blood pressure, reduced growth and development, speech disorders, sleep disabilities, fatigue, poor concentration, aggressive behavior, irritability, depression, mood swings, increased allergic reactions, vascular occlusion, autoimmune diseases, oxidative stress and memory loss (Lee et al., 2012; Qu et al., 2013). Also they can disrupt the human cellular enzymes (Ageena, 2010). Due to the toxicity of heavy metals, the importance of

using new methods/studies for the production of adsorbents that can be used for this purpose have increased vastly.

1.1.2 Zinc and its Importance

Zinc is a bluish-white metal. It is found in group IIB of the periodic table. It is brittle and crystalline at ordinary temperature. But it become ductile and malleable when heated at temperature ranges from 1100 to 1150C. It is tremendously reactive metal that will combine with oxygen and other non-metals and will react with dilute acids to release hydrogen. Zinc metal and zinc alloys are very resistant to corrosion. Due to its extensive usage in electroplating, metal plating, chemical manufacturing industries, etc. The demand of zinc has been increasing globally. Zinc is used in galvanization of steel to the manufacture of the negative plates in electrical batteries, preparation of alloys. Zinc is used in plastics, cosmetics, wallpaper, printing inks, photocopier paper etc as a pigment. In the production of rubber, it plays an important role as a catalyst during manufacture. Zinc oxide used in ointments for burns and skin protection. Zinc pyrithione used in anti-dandruff shampoos. Zinc chloride used in the manufacture of artificial silk. It is also used in printing and dyeing textiles. Zinc is also a metallic element found in the body as divalent cations, which does not undergo metabolism. Zinc interacts electro-statically with anions (i.e. carbonate, hydroxides, and oxalate) and negatively charged moieties on macromolecules such as proteins. Zinc as well form chelation

complexes with amino acids and multidentate organic acids such as ethylenediaminetetraacetic acid. Zinc compounds are also used in the drug industry as ingredients in some common products, like vitamin supplements, sun blocks, diaper rash ointments, deodorants, athlete's foot preparations and poison preparations, and antidandruff shampoos (ATSDR, 2005). Zinc occurs naturally in many foods. Even zinc is important for human health if a pregnant woman doesn't get enough amount of zinc, her babies may have birth defects.

1.1.3 Emissions of Zinc

Zinc is widely used in many industries such as paint, batteries, fertilizers and pesticides, galvanization, pigment, polymer stabilizers, fossil fuel and combustion, electroplating, paper and pulp, pharmaceutical, textile mills, mining industries, etc. These industries are the main source of zinc pollution. The waste generated from these industries directly discharge to the environment and the water is polluted with zinc due to the excessive amount of zinc (Harte *et al.,* 1991). Zinc is also available in some medicated shampoos contain zinc pyrithione to control dandruff. Residues of zinc from zinc-plated cold water tanks leach into tap water and are flushed away when water is used.

1.1.4 Environmental Effects of Zinc

The excessive intake of zinc into the body through food, water or other dietary supplements can also affect human health. The recommended dietary allowances of zinc for man are 11mg/day and for women is 8mg/day (ATSRD,

2005). Beyond this limit it may cause many health problems like stomach cramps, nausea and vomiting. High level ingestion of zinc for several months can cause anaemia, damage the pancreas and decrease the levels of cholesterol. Ingesting low level of zinc compounds like zinc acetate and zinc chloride may cause skin irritation. Insufficient amount of zinc in diet can cause loss of appetite, decreased sense of taste and smell, decreased immune function, slow wound healing and skin sores.

Cellulose is abundant in nature and can be extracted from various agricultural wastes such as corncob, pineapple peel, rice husk (Dai et al., 2018, Li et al., 2007, Muhammad et al., 2019). Cellulose fiber extracted from rice husk fits in as an adsorbent for adsorption process due to its ion exchange properties.

1.1.5 STATEMENT OF PROBLEM

Zinc occurs naturally in air, water and soil but zinc concentrations are rising unnaturally, due to addition of zinc through human activities (industrial activities, such as mining, coalification and waste combustion) and when absorbed by people can cause experience such as a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. High concentrations of zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. A form of zinc in zinc chloride can cause respiratory disorders.

Zinc can be a danger to unborn and newborn children when absorbed through a carrier mother's blood or milk.

1.1.6 RELEVANCE OF STUDY

As a result of urbanization and industrial revolution, the environment has been badly affected by pollution resulting from human activities. The findings from this research would be useful in addressing some of the environmental pollution. This study reviews the need to find an economical adsorbent for the removal of heavy metals in aqueous solution and also the metal-binding capacities of cellulose for Zn^{2+}.

1.1.7 SCOPE OF WORK

This work is limited to the use of cellulose to remove Zn2 ion from aqueous solution hoping that the result gotten could be scaled up to be applied to industries. This can help reduce unemployment if the youths can gather these wastes, sort them into various types and sell them to companies for the treatment of industrial effluents instead of other expensive chemical methods.

1.1.8 AIMS AND OBJECTIVES OF WORK

The aim of this study is to determine the adsorption capacity of cellulose, as a low cost and efficient adsorbent for the removal of Zn(II) from aqueous solutions.

To achieve this aim, the following objectives were set;

1. To obtain the cellulose and identify it using XRD, SEM, and FTIR

2. To use cellulose as an adsorbent to uptake Zn^{2+} and the following parameters were optimized; Adsorbent dosage, Initial concentrations and contact time.

1.2. LITERATURE REVIEW

Heavy Metals have been of major environmental concern from time immemorial. Man began to face challenges in health as rate of Heavy metal bearing effluent increased which are discharged into the environment and water body due to rapid urbanization (Babel and Kurniawan, 2003). Heavy metals are usually defined as metals having density more than 5g/cm3 (Nies, 1999). They are classified as essential and non-essential metals. The metals which are need for normal cellular growth are essential metals e.g. zinc, nickel, copper, etc. Such metals are required in low concentrations, but at higher concentrations all heavy metals have detrimental effects to organisms (Grosse and Anton, 2004). If the metals have no known biological function, they are called as non-essential metals e.g, lead, cadmium, mercury, (Rehman, 2006). Such metals are toxic at any concentration. The essential heavy metals exert biochemical and physiological functions in plants and animals. They are important constituents of several key enzymes and play important roles in various oxidation-reduction reactions (WHO, 1996). There are 90 naturally occurring elements in periodic table, 21 are non-metals, 16 are light metals and the remaining 53 (with As included) are heavy metals. In periodic table, transition elements are mostly heavy metals. They have incompletely filled ‘d’orbitals which allow heavy-metal cations to form complex compounds that may or may not be redox-active.

In this way, heavy metals play an important role as 'trace elements' (cobalt, copper, nickel, and zinc) in sophisticated biochemical reactions and are important cofactors for metallo-proteins and enzymes (Janseen, *et al.,* 2010). The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg (Hammed *et al*., 2017). The toxicity of heavy metal ions starts when their concentration becomes higher. The list of essential and non-essential heavy metals is given *(***Table 1.1**) below;

Category of heavy metals	**Example of heavy**
Essential	Copper (Cu) Nickel (Ni) Iron (Fe) Zinc (Zn) Magnesium (Mg)
Non-essential	Lead(Pb) Mercury (Hg) Cadmium (Cd) Tin (Sn) Arsenic (As)

Table 1.1.*Essential and non-essential heavy metals*(Saba and Shamin,2017)

1.2.1. SOURCES OF HEAVY METALS

Heavy metals are released into the atmosphere from a wide range of natural and anthropogenic (man-made) sources. Soil serves as a major reservoir for contaminants as it can bind to various chemicals. Naturally, heavy metals are contained in minerals found in rocks and salts. When rocks undergo weathering, cations of heavy metals find their way into surface and ground water level causing water pollution.

Historically, agriculture was the first major human influence on the soil (Scragg, 2006). Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production (Zhang and Zhang, 2007). Nevertheless, the long-term excessive application has resulted in the heavy metal contamination of soils. The vast majority of pesticides are organic compounds, and a few are organic - inorganic compound or pure mineral, and some pesticides contain Hg, As, Cu, Zn and other heavy metals (Scragg, 2006). Heavy metals are the most reported pollutants in fertilizers. Heavy metal content is relatively low in nitrogen and potash fertilizers, while phosphoric fertilizers usually contain considerable toxic heavy metals. Heavy metals in the compound fertilizers are mainly from master materials and manufacturing processes.

ANTHROPOGENIC PROCESSES

Industries, agriculture, wastewater, mining and metallurgical processes, and runoffs also lead to the release of pollutants to different environmental compartments. Anthropogenic processes of heavy metals have been noted to go beyond the natural fluxes for some metals. Metals naturally emitted in wind-blown dusts are mostly from industrial areas. Some important anthropogenic sources which significantly contribute to the heavy metal contamination in the environment include automobile exhaust which releases lead; smelting which releases arsenic, copper and zinc; insecticides which release arsenic and burning of fossil fuels which release nickel, vanadium, mercury, selenium and tin. Human activities have been found to contribute more to environmental pollution due to the everyday manufacturing of goods to meet the demands of the large population (He and Yang, 2005).

NATURAL PROCESSES

Many studies have documented different natural sources of heavy metals. Under different and certain environmental conditions, natural emissions of heavy metals occur. Such emissions include volcanic eruptions, sea-salt sprays, forest fires, rock weathering, biogenic sources and wind-borne soil particles. Natural weathering processes can lead to the release of metals from their endemic spheres to different environment compartments. Heavy metals can be found in the form of hydroxides, oxides, sulphides, sulphates, phosphates, silicates and organic compounds. The most common heavy metals are lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), zinc (Zn) and

copper (Cu). Although the aforementioned heavy metals can be found in traces, they still cause serious health problems to human and other mammals (Herawati *et al.,* 2000)

1.2.2. ENVIRONMENTAL IMPACTS OF HEAVY METALS

The presence of heavy metals in the environment leads to a number of adverse impacts. Such impacts affect all spheres of the environment, that is, hydrosphere, lithosphere, biosphere and atmosphere. Until the impacts are dealt with, health and mortality problems break out, as well as the disturbance of food chains.

1.2.3. EFFECT OF HEAVY METALS CONTAMINATION

Heavy metals contamination is becoming a serious issue of concern around the world as it has gained momentum due to the increase in the use and processing of heavy metals during various activities to meet the needs of the rapidly growing population. Soil, water and air are the major environmental compartments which are affected by heavy metals pollution.

1.2.3.1. EFFECTS ON WATER

Although there are many sources of water contamination, industrialization and urbanization are two of the culprits for the increased level of heavy metal water contamination. Heavy metals are transported by runoff from industries, municipalities and urban areas. Most of these metals end up accumulating in the soil and sediments of water bodies (Musilova *et al.,* 2016). Heavy metals can be found in traces in water sources and still be very toxic and impose serious health problems to humans and other ecosystems. This is because the toxicity level of

a metal depends on factors such as the organisms which are exposed to it, its nature, its biological role and the period at which the organisms are exposed to the metal. Food chains and food webs symbolizes the relationships amongst organisms. Therefore, the contamination of water by heavy metals actually affects all organisms. Humans, an example of organisms feeding at the highest level, are more prone to serious health problems because the concentrations of heavy metals increase in the food chain (Lee *et al*, 2002)

1.2.3.2. EFFECT ON SOIL

Emissions from activities and sources such as industrial activities, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues and spillage of petrochemicals lead to soil contamination by heavy metals. Soils have been noted to be the major sinks for heavy metals released into the environment by aforementioned anthropogenic activities. Most heavy metals do not undergo microbial or chemical degradation because they are non-degradable, and consequently their total concentrations last for a long time after being released to the environment (Lepp, 2012). The presence of heavy metals in soils is a serious issue due to its residence in food chains, thus destroying the entire ecosystem. As much as organic pollutants can be biodegradable, their biodegradation rate, however, is decreased by the presence of heavy metals in the environment, and this in turn doubles the environmental pollution, that is, organic pollutants and heavy metals thus

present. There are various ways through which heavy metals present risks to humans, animals, plants and ecosystems as a whole. Such ways include direct ingestion, absorption by plants, food chains, consumption of contaminated water and alteration of soil pH, porosity, color and its natural chemistry which in turn impact on the soil quality (Musilova *et al.,* 2016)

1.2.3.3. EFFECTS ON AIR

Industrialization and urbanization, due to rapid world population growth, have recently made air pollution as a major environmental problem around the world. The air pollution was reported to have been accelerated by dust and particulate matters (PMs) particularly fine particles such as PM2.5 and PM10 which are released through natural and anthropogenic processes. Natural processes which release particulate matters into air include dust storms, soil erosion, volcanic eruptions and rock weathering, while anthropogenic activities are more industrial and transportation related (Soleimani and Amini 2018).

SOURCES OF HEAVY METALS AND THEIR CYCLING IN THE SOIL-WATER-AIR ORGANISM ECOSYSTEM

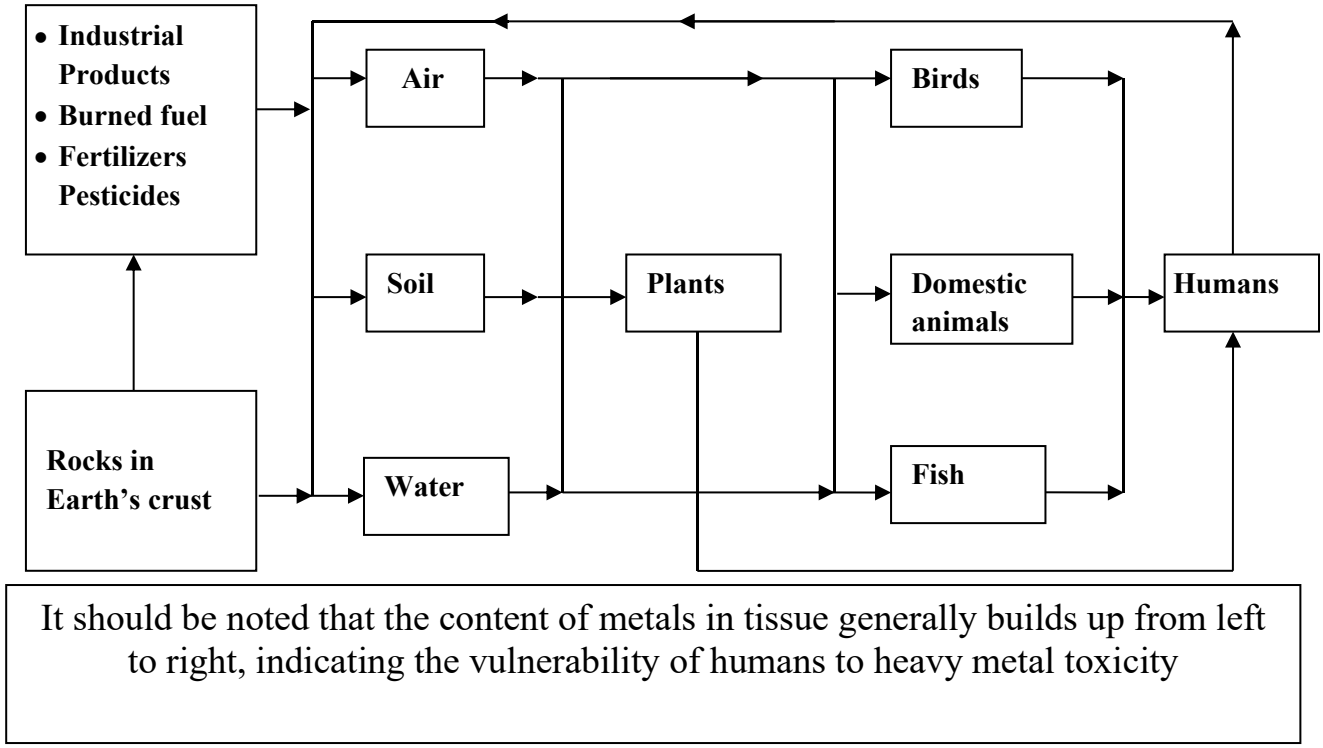


Figure 1.1. *Sources of heavy metals and their cycle in the environment* (Vhahangwelw M. and Khathutshelo L. 2018)

1.2.4. MECHANISM OF HEAVY METAL POISONING

When enzymes and proteins in cell membranes in the body are attacked by heavy metals, transported via the blood stream, they interfere with the working of the body system, the combined result of this attack leads to a variety of health

problems ranging from cancer to heart diseases. The points of attack are the enzyme atoms and also the free amino (-NH_3) and carbonyl (-COOH) groups if found in proteins.

Hexavalent chromium, for example, is highly toxic as are mercury vapour and many compounds. These fine elements have a strong affinity for sulphur; in the human body they usually bind, via thiol groups (-SH) to enzymes responsible for controlling the speed of metabolic reactions.

1.2.5. HEALTH EFFECT OF HEAVY METALS

Zinc occurs naturally in air, water and soil but zinc concentrations are rising unnaturally, due to addition of zinc through human activities (industrial activities, such as mining, coal and waste combustion) and when absorbed by people can cause experience such as a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. High concentrations of zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia.

1.3. THE THEORY OF ADSORPTION

The adsorption theory deals with the intermolecular interaction between the adhesive and surface of the substrate. Specifically, the forces of attraction between the atoms of the molecules in the adsorbent and the atoms of the molecules on the surface of the substrate form intermolecular bonds. This intermolecular bond formation results in adsorption. Molecules of gases or

liquids or the solutes in solutions adhere to the surface of the solids. In adsorption process, two substances are involved. One is the solid or the liquid on which adsorption occurs and it is called adsorbent. The second is the adsorbate, which is the gas or liquid or the solute from a solution which gets adsorbed on the surface.

Adsorbent: The substance on whose surface the adsorption occurs is known as adsorbent.

Adsorbate: The substance whose molecules get adsorbed on the surface of the adsorbent (i.e. solid or liquid) is known as adsorbate.

Adsorption is different from absorption. In absorption, the molecules of a substance are uniformly distributed in the bulk of the other, whereas in adsorption molecules of one substance are present in higher concentration on the surface of the other substance.

1.3.1. MECHANISM OF ADSORPTION

Adsorption process takes place in three basic steps namely, macro transport, micro transport and sorption.

a. **Macro Transport**: This involves the movement of the solute molecules from the bulk of the fluid to the external surface or pore of the adsorbent
b. **Micro Transport:** This involves the diffusion of the solute molecules from the pore mouth though the micro pore system of the adsorbent to the interior or immediate vicinity of the internal adsorbent surface (i.e. the adsorption site)

c. **Sorption:** The third mechanism of adsorption involves sorption of the solute molecules onto the internal surface of the adsorbent

1.3.2. TYPES OF ADSORPTION

Depending on the type of attractions between adsorbate and adsorbent, the adsorption can be divided into two types. Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vander Waal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption.

Physical Adsorption or Physisorption:

When the force of attraction existing between adsorbate and adsorbent are weak Vander Waal forces of attraction, the process is called Physical Adsorption or Physisorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. ΔH adsorption is 20-40KJ/mol. takes place at low temperature below boiling point of adsorbate. As the temperature increases in, process of Physisorption decreases.

Characteristics of Physisorption:

Energetics and kinetics: Physisorption is an exothermic process. However it is characterized by low enthalpy values (20– 40 kJ mol^{-1}), due to 45 weak van derWaals forces of attraction. The activation energy for physisorption is also very low and hence it is practically a reversible process.

Effect of temperature: Since physical adsorption is an exothermic process, it occurs more readily at lower temperatures and decreases with increase in temperature (Le-Chatelier's Principle).

Effect of pressure: In case of physisorption of gases over solids, the extent of adsorption increases with increase in pressure as the volume of the gases decrease during adsorption (Le-Chatelier's Principle).

Specificity: Since the van der Waals' forces are universal, a given surface of an adsorbent does not show any preference for an adsorbate in physisorption i.e. it is not specific with respect to adsorbent.

Nature of adsorbate: However, the extent of adsorption depends on the nature of gas (adsorbate). In general, easily liquefiable gases with higher critical temperatures) are readily adsorbed as the van der Waals' forces are stronger, especially, near the critical temperatures.

Surface area of adsorbent: The extent of adsorption increases with the increase of surface area of the adsorbent. Hence finely powdered metals and porous substances having large surface areas perform well as adsorbents.

Chemical Adsorption or Chemisorption:

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption. It can

take place at 46 all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

Characteristics of Chemisorption

Energetics and kinetics: Chemisorption is also an exothermic process and the enthalpy values are higher (80-240 kJ mol-1) as it involves formation of chemical bonds. However, the activation energy for chemisorption is high and occurs slowly. Hence it is also called activated adsorption. It is practically irreversible.

Effect of temperature: Even though chemical adsorption is an exothermic process, it does not occur slowly at lower temperature due to high kinetic energy barrier. Hence, like most chemical changes, the extent of chemisorption increases with increase in temperature up to certain limit and then after that it starts decreasing. It is also observed that, in some cases, physisorption of a gas adsorbed at low temperature may change into chemisorptionat a high temperatures**.**

Effect of pressure: The chemisorption is not appreciably affected by small changes in pressure. However, very high pressures are favourable for chemisorption.

High specificity: Chemisorption is highly specific and occurs only if there is some possibility of chemical bonding between adsorbent and adsorbate.

Surface area: Like physisorption, chemisorption also increases with increase of surface area of the adsorbent.

1.3.3 FACTORS AFFECTING ADSORPTION

The most important factors affecting adsorption are;

- **Surface area of adsorbent:** Larger sizes imply a greater adsorption capacity.
- **Particle size of adsorbent**: Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained).
- **Contact time or residence time:** The Longer the time the more complete the adsorption will be. However, the equipment will be larger.
- **Temperature:** Temperature changes affect mainly two parameters; Kinetic energy and solubility. Increase in temperature generally increases the kinetic energy of the adsorbing species, the increased kinetic energy results in faster rate of diffusion of the adsorbate from the surface thus resulting in an increase in the rate of adsorption. Increase in temperature also leads to increase in solubility of the adsorbate, hence a faster rate of adsorption.
- **Solubility of solute (adsorbate) in liquid (wastewater)**: Substances slightly soluble in water will be more easily removed from water (i.e. adsorbed) that substances with high solubility. Also, non-polar substances will be more easily removed than polar substances since the latter have a greater affinity for water.

- **Affinity of the solute for the adsorbent**: The surface of adsorbent is only slightly polar. Hence non-polar substances will be more easily picked up by the adsorbent than polar ones
- **Concentration for solute:** A high concentration gradient increases the rate of adsorption, though a high concentration of solute can eventually have a negative effect of adsorption capacity
- **pH:** This is the most important parameter which affect adsorption process. As pH of a solute system increases, the rate of adsorption increases up to an optimum, above which the rate starts decreasing.

1.3.4. ADSORBENTS

An adsorbent is a material which will allow a liquid, gas or dissolved solid to adhere to its surface. An absorbent is a material which will take in the liquid or gas uniformly. Materials classified as adsorbents must have high internal surface area for efficiency. However, only some solid materials have the selective adsorption capacity to adsorb molecules onto their surfaces. Adsorptive properties are directly related to the porosity of the adsorbent. In energy systems, some thermo-physical properties are required for a good choice of adsorbent;

- Good compatibility with adsorbate
- High surface area
- High adsorption capacity

- Quick response of adsorption capacity to temperature change
- High thermal conductivity
- High mass diffusivity
- Thermal stability

Adsorbents can be classified according to their pore sizes, nature of surfaces and nature of structures.

1.3.5. APPLICATION OF ADSORPTION

Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications. Some of the important applications include;

1. In heterogeneous catalysis:

Surface active materials are widely used as catalyst mostly due to adsorption processes. If the surface active materials (adsorbents) have different phase with that of substrates, then the catalysis is called heterogeneous catalysis. A system where both the catalyst and substrate are in same phase is called homogeneous catalysis. In removal of coloring material: Many colored materials or impurities are removed through adsorption by suitable surface active materials like charcoal. Activated charcoal has been extensively used for this purpose. In ion exchange resins: Several polymeric materials are used for the separation of ionic substances in chromatography through ion-exchange.

2. In adsorption indicators

Several dyes like eosin and fluoresein are used as indicators in the titrations of Cl-, Br – etc. against Ag^+(Fajan's method).

3. In gas masks

Activated charcoal is used to remove toxic gases in gas masks.

4. In dyeing of cloth

Many substances work as mordants for dyeing of cloths. Several metal cyanogen complexes, alums work as efficient mordants in dyeing cloths.

5. In dehumidizers

Many substances when they adsorb water change their colour. Silica and alumina gels are used as adsorbents for removing moisture. Silica is colourless but after adsorbing water becomes blue.Silica is colourless but after adsorbing water becomes blue.

1.5.1. LANGMUIR ISOTHERM MODEL

Langmuir, in 1918 observed sorption phenomena and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. He proposed the sorption isotherm based on the assumptions that;

1. Adsorbates are chemically adsorbed at a fixed number of well-defined sites,
2. Each site can only hold one adsorbate specie;
3. All sites are energetically equivalent and

4. That there are no interactions between the adsorbate species.

The Langmuir isotherm equation is written as:

$Q = \frac{Q_{max} bc}{1+bc}$

Where Q_{max} is the maximum adsorption capacity of the material assuming a monolayer of adsorbate up taken by the adsorbent, C is the supernatant concentration after the equilibrium of the system and b the Langmuir affinity constant.

The linear form of Langmuir's isotherm model is given by the following equation,

$$C_e/Q_e = 1/Q_o b + \left(1/Q_o\right) C_e$$

where C_e is the equilibrium concentration of the adsorbate, Q_e is the amount of adsorbate adsorbed per unit mass of adsorbate (mg/g), and Q_o and b are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. A graph of C_e/Q_e plotted against C_e is a straight line with slope $1/Q_o$

1.5.2. FREUNDLICH ISOTHERM MODEL

The Freundlich isotherm is based on the assumption of non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented below (Freundlinch 1906).

Q = KC a/n

Where k and n are constants, which correlate to the maximum adsorption capacity and sorption intensity respectively. Q is the amount of heavy metal adsorbed per gram of adsorbent.

The linearlized Freundlich is given as

Log Q = log k + 1/n Log C

A plot of log Q against log C gives a straight line graph whose slope is n and intercept is k

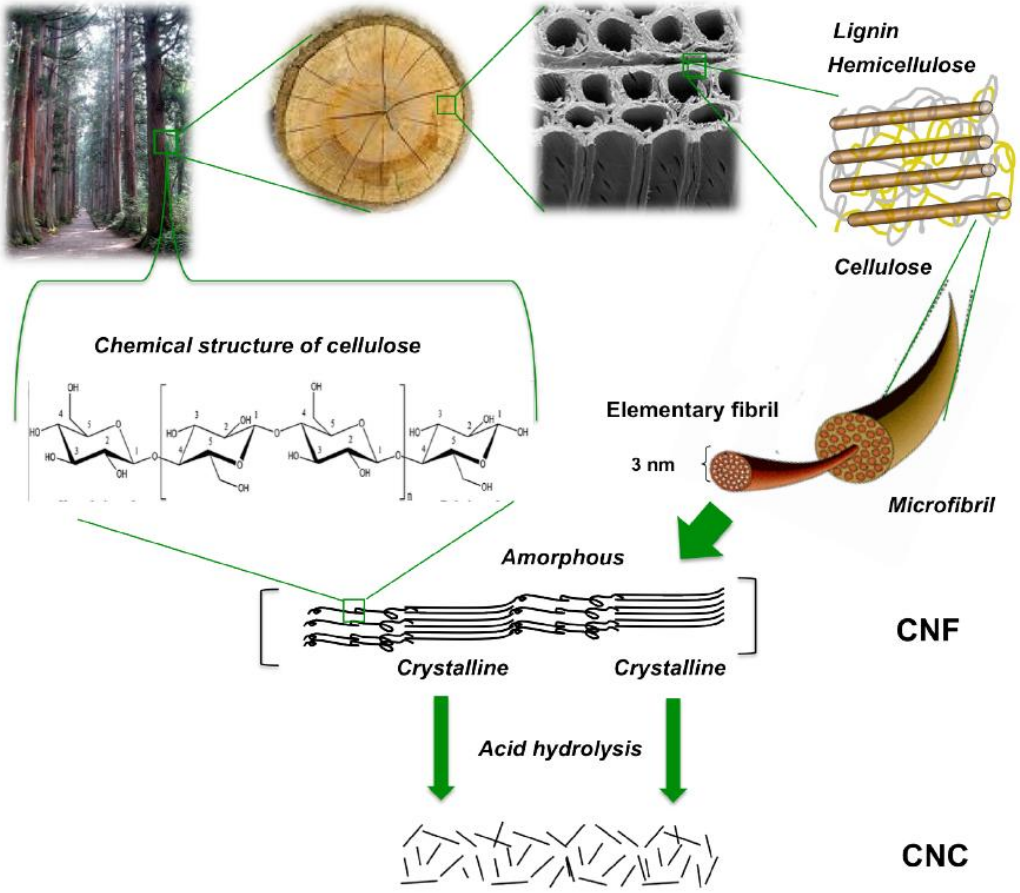
1.6.0 CELLULOSE AND ITS HIERARCHICAL STRUCTURES

Cellulose is a polysaccharide consisting of a linear chain of several hundreds to over ten thousand β-(1→4)-linked D-glucose units with the formula $(C_6H_{10}O_5)_n$ (Updegraff, 1969). Being a carbohydrate polymer the molecular structure of cellulose possesses a large number of hydroxyl groups (three per anhydroglucose unit), which forms vast intra- and intermolecular hydrogen bonds. To constitute the preferred chair conformation or preferred bond angles, every second anhydroglucose unit is rotated 180° in the plane. Its chemical reactivity is largely due to the reactivity of the hydroxyl groups (O'Connell et al., 2008). Cellulose is odorless, nontoxic, hydrophilic and biodegradable. Cellulose is widely available in nature and closely relevant to people´s daily life in the form of paper, textiles etc (smook, 2003).

In nature, cellulose does not appear as an isolated individual molecule, but it is built up of self-assembled individual cellulose chain forming fibers. Cellulose

has a hierarchical structure from the nano-scale building up to the micro scale by nature.

Typically, approximately 36 glucan chain assemblies are bound together through van der Waals forces and both intra- and intermolecular hydrogen bonds into larger units known as elementary fibrils (protofibrils) with the diameter approximately 3.5 nm, which pack into larger units called microfibrils, and these are in turn assembled into the familiar cellulose fibers (Habibi, 2014). However, celluloses from different sources may exhibit different ways of packing as monitored by the biosynthesis conditions yielding different morphologies (Williamson et al., 2002).



1.6.1 CELLULOSE-BASED MATERIALS

Many cellulose-containing materials are used for the adsorption of heavy metals (Zwain et al., 2014) (Wan et al., 2008). These are often waste materials. Bagasse is one such material containing 50% cellulose (Ahluwalia et al., 2007). It can be used in native and immobilized forms to adsorb Cu (III) and Cu (VI) ions from tannery wastewater (Ullah et al., 2013). Khoramzadeh et al in 2013 used it to biosorb mercury from aqueous solutions. It can also be chemically modified using succinic anhydride and EDTA dianhydride to introduce chelating agents, such as amines and carboxylic acid. Bagasse can be

mercerized prior to modification for improved resistance (Karnitz et al., 2007.) Due to its composition, other adsorbent materials, e.g., activated carbon, can also be derived from it (Mohan et al., 2002). Zhou et al in 2014 used a cellulose-based material for the adsorption of Pb(II). Gaballah et al in 2003 used wood bark for the removal of arsenic, copper, cadmium, chromium, lead, iron, mercury, zinc, and nickel from wastewater. Agricultural materials produce large amounts of waste after processing. The waste is often high in cellulose content. Therefore, research and development is trending towards the use of agricultural waste materials as adsorbents of heavy metals in effluents from multiple sources (Teixeira et al., 2004). For example, rice husk, waste from rice processing mills, has high cellulosic content (Hegazi, 2013). It can be used in powder form without any chemical or physical treatment to adsorp Cd(II), Pb(II), Al(III), Cu(II), and Zn(II) ions from laboratory effluents (Teixeira et al., 2004). Vieira et al in 2014 used rice husk for the adsorption of lead and copper ions. In this study, rice husk was also used for the adsorption of lead and copper ion from aqueous solution.

1.6.2 RICE HUSK AS A CELLULOSE

Rice husk is a by-product produced from rice mills. Each kilogram of rice produces an average of 280 grams of the husk or as much as 20% to 30% of the weight of dry rice milled, so that the accumulation of rice husk waste on average each year is more than 10 million tons (Danarto et al., 2010). Rice husk

is a hard layer which includes kariopsis which consists of two leaf shapes, namely petal husks and crown husks, where in the rice milling process, the husks will be separated from rice grains and become waste material or grinding waste. From rice mills it will produce about 25% of husk, 10% of bran, and 65% of rice (Haryadi, 2006). Rice husk is a lignocellulosic material derived from agricultural waste, which has an abundant presence. Rice husk is one of the biomass that has the greatest chemical composition of organic carbon, which is 45% - 50%. The high composition of organic carbon indicates that there is a lot of cellulose in the rice husk (Prabawati and Wijaya, 2008). The main component of rice husk is silica (15-17%) (Leiva et al., 2007; Stefani et al., 2005), other components are cellulose (35%), hemicellulose (25%), and lignin (20%) (Shukla et al, 2013). Due to its high cellulose content, rice husks can be used as a source of cellulose and can be used as a material that has benefits.

Cellulose is a material commonly used in several biological-based applications such as cosmetics and medicines, because it is environmentally friendly, easily recycled, and is one of the renewable materials. Cellulose has a chemical structure consisting of β-1.4 glyosidic. Extracted cellulose is stable, biodegradable, thermal stability (Long et al., 2018), and good crystallinity (Yang et al., 2018). Cellulose also has complex crystalline and amorphous morphological forms. In addition, cellulose has interesting properties, such as biocompatible, renewable and can be degraded.

Cellulose from rice husk have been used in many applications including to make cellulose nanoparticles with high fluorescence (Kalitaa et al, 2015), cellulose nanocrystals as reinforce in gelatin hydrogels for drug delivery (Ooia, et al, 2016), cellulose acetate (Das et al, 2014) and using of rice husk cellulose for biomedicine (Shukla et al, 2013).

CHAPTER TWO

MATERIALS AND METHOD

2.1. Materials

Cellulose was commercially obtained from Pyrex stores in Benin city.

Apparatus/ Machines

- Mechanical shaker
- Oven
- A Varian GTA model 100 Atomic Absorption Spectrometer (AAS) operating with an air–acetylene flame, to determine the effect of metal initial concentration of the solutions
- Volumetric Flask
- ATY224 SHIMADZU Weigh balance
- Graduated Measuring Cylinder

All the equipment listed above are of analytical standards.

2.1.1 Reagents

All chemicals used for this work were of analytical grade, purchased from pyrex stores

- Zinc sulphate Heptahydride ($ZnSO_4$ .7 H_2O) of 99% purity
- Distilled water

METHOD

2.1.2 CHARACTERIZATION OF CELLULOSE

The cellulose was characterized using the functional group (FTIR) and morphological (X-Ray Diffractometer) method and the procedures are given as follows

FTIR PROCEDURE

100mg of KBr (potassium bromide) salt, and 5mg of the sample were weighed. Finally, sample was placed in an evacuable KBr dye and a 13mm clear disk is pressed in a hydraulic press to form KBr pellet. Thereafter, the pelletized sample (which was formed inside an evauable chamber) was put in a cell holder (universe demountable cell) and was inserted into the machine (FTIR) and Scanned at a range of 350-400nm. Immediately, after a few seconds the spectrum was displayed on the computer screen, and also the inspected compounds page.

SETTING OF THE XRD – EQUIPMENT:

This is usually run **(SCAN RANGE)** between 0^o to 120^o thetta Bragg angle depending on the type of the minerals in question. The running rate **(SCAN SPEED)** is between 2 to 10^0 per minute. The voltage recommended level is 40V and the current recommended level is set at 30A. The auto- silts (divergence, scatter and receiving) used for the various apertures control are of sizes 1.0,1.0 and 0.3^0.

BULK ANALYSIS

The powdered sample prepared is regarded as **BULK** Sample. The sample was smeared evenly on the sample holder made of aluminum material, with the aid of smooth slide or any material with smooth surface edge.

The setting was between angle of 2^o to 6^o theta as the bulk sample scanning range. The running rate (scanning speed) was set at 6 per minutes.

The holder was carefully placed on the loading point of the movable **GONIOMETER** arm that contained a clamp capable of gripping the sample firmly. The window indicating readiness after properly closed. By commanding the soft wares, the analysis commenced automatically.

The pronounced **PEAKS OR DIFFRACTOGRAMMS** displayed, express the minerals composition at the various angle of the degree theta.

ORIENT ANALYSIS

The purpose of this ananlysis, is to separate the 'Gangue' and 'Tenor' inherent in the sample. Having obtained powdered sample, about 5-10g was put into a clean

test tube with the aid of spatula. Distill water was added to dissolve the sample and subsequently placed inside centrifuge machine. This was allowed to run at 5rpm for 5 minutes after which it was removed and the floating materials was decanted.

Another distill water was added, mixed thoroughly and again placed inside the centrifuge machine and run the second time. This process went on for at least three to five times depending on the rate at which individual sample goes into a clear suspension. After decanting severally, about 3-5 drops of **0.6% sodium hexameta phosphate solution** was added. At this point a clear suspension of clay is formed above, while the other unwanted samples settled at the bottom of the test tube.

Dropper was used to take some quantity of the suspended clay and applied it on a clean labeled glass slides. This was allowed to dry for at least **24hrs**, before ready for **XRD** analysis.

Being an **ORIENT** sample, the sample was run at scan range of 2^{o} to 45^{o} theta Bragg angle, while the scan speed was set at 6 degrees per minutes.

GENERATION OF RAW DATA:

After about 10 to fifteen minutes, the analysis has finished and the **RAW** datas generated is collated automatically, followed the manual **BASIC PROCESS** to generate the **PKK** (Peaks constant) of the raw datas.

The background correction of the **PKK** is set at **YES** value which automatically terminates error(s) that might have occurred during manual rearrangement of data.

The PKK generated is further treated by **SEARCH-MARCH MENU** which is necessary, to relate the obtained diffractogramms with the elucidated known minerals in the **LIBRARY.**

The MACHINE's LIBRARY usually used is the comprehensive **USR (UNIVERSAL**). By accepting or rejecting entry of the marched peaks, the obtained peaks or diffractogramms is successfully related and identified as **ACCEPTED PEAKS,** which bears the minerals names, chemical symbols, and the chemical names. of the already known ones that correlate with the newly **RUN data, basic process**, and **search –march raw data**.

2.2 SAMPLE COLLECTION AND TREATMENT

The cellulose used as the adsorbent was obtained from pyrex stores.

ADSORBATE PREPARATION

- **Standard Zinc Stock Solution**

  Zinc sulphate heptahydrate stock solution of 1000ppm was prepared by diluting 4.398g of $ZnSO_4 \cdot 7H_2O$ (weighed analytically) into a 1L volumetric flask of distilled water. Zinc (II) ion standard solutions (10 – 50 ppm) were prepared by diluting the stock solution with desired concentration using distilled water. The absorbance of the standard solution were measured to make a calibration curve for measuring the Zn concentration after adsorption process.

Calculation:

Concentration of stock of Zn in 1000ppm

= Molecular Mass of $ZnSO_4 \cdot 7H_2O$ solute in grams/ Atomic Mass of Zn × 100

× Percentage purity of the $ZnSO_4 \cdot 7H_2O$

2.2.1. ADSORPTION EXPERIMENT

- Adsorption measurements adopts the batch technique at room temperature. All the adsorption experiments were carried out in normal PH conditions.
- The Cellulose is added to the adsorbate.
- The solutions are shaken vigorously for a given time period to reach equilibrium. The mixtures were taken to the shaker at 1000rpm and the supernatant obtained was decanted and used for the next step. The concentration of the Zn in the supernatant was calculated by using a Varian GTA model 100 Atomic Absorption Spectrometer (AAS) operating with an air–acetylene flame, to determine the effect of contact time and adsorbent dosage at a constant initial concentration of the solutions, yielding the final concentrations of Zn for each samples, after adsorption.
- The adsorption parameters that affected the adsorption process were studied.
- Effect of contact time was investigated by varying (5, 10, 20, 30, 40, 50, 60, 90, 120, 180 min), with varying adsorbent dosages /weights (0.2, 0.4, 0.6, 0.8, 1.0 g).
- The amount of Zn (II) ion adsorbed unto cellulose was calculated using the following equation.

$$q_t = \frac{(C_o - C_t)\, V}{m} \text{ (L)}$$

- Where q_t, C_o , C_t , V and m are amount of Zn(II) ion adsorbed per gram of the adsorbent at any time t (mg/L), initial Concentration of the Zn concentration (mg/L), concentration of the Zn (II)ion at time t (mg/L), volume of the Zn (L), and amount of adsorbent used (g).
- Langmuir and Freundlich isotherm models will be fitted to the adsorption data and their constants will be evaluated. Satisfactory conformity between experimental data and the model-predicted values will be expressed by the correlation coefficient (R^2).

ATOMIC ADSORPTION SPECTROMETRY

Atomic Absorption Spectroscopy (AAS) is a for determining the concentration of particular mental element in a sample (Berhard.1999). the technique can be used to analyze the concentration of over 70 different metals in a solution.

CHAPTER THREE

2.0 RESULTS AND DISCUSSION

2.1 Characterization of cellulose

2.1.1 Functional group (FTIR analysis)

Figure 3.1 shows the FTIR spectra of furfural Schiff base obtained at a wavelength of 4000 – 650 cm^{-1}. The functional groups in the cellulose and their characteristics is given in FIG 3.1.

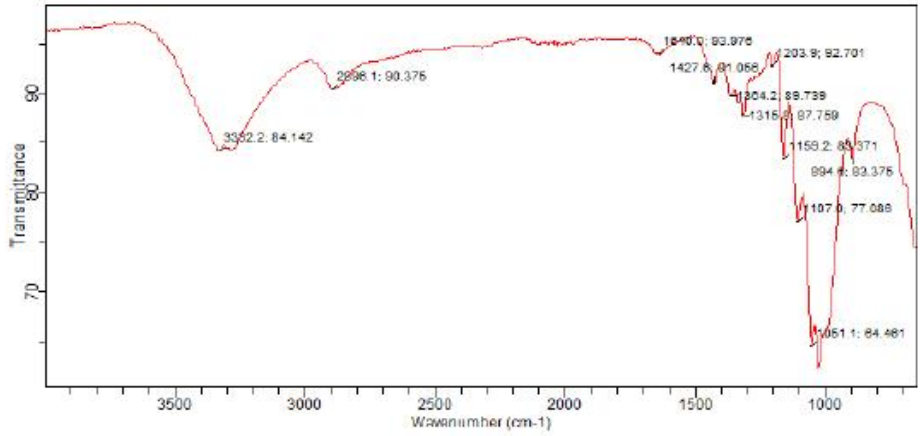


FIG 3.1: FTIR CELLULOSE

Fig3.1 Show the FTIR Spectrum of Cellulose, the strong and broad band around 3882.2cm^{21} 15 attributed to the brychoxy / (0-H) Stretching vibration of the cellic love molecules, . Typically C-H Stretching mode of anth-symmetric - Vibration of CH3 and CH_2 a 2896.cm^2 and a weak non infense symmetric stretching Vibration of CHz and CH_2 Jat 2816-3cm^{21} respectively are Observed & band medium band that appear at about 1427.6cm-1 may be ascribed to C-H bending Vibration of CH_2 CH_2 of the cellulose material Jand The ad medium band at 1315.9cm is due to E-H bend mng vibration of CH_4 group of the material.the medium sharp bend seen at 1159-2 Cm^2 mary be due to the Stretching Vibration of C-O of the deplche Carbony group of the cellulose and fully a strong sharp and to highly intense band seen at 10151·lent may be due to C-0 Stretch of the Carbony Carbon and Oxygen of the cellulose material. The

Characteristic groups and bonding Observed in this spectrum are primary that give this material properties of Cellulose a unique adsorptive properties.

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P1_20210726_110353_G01_S01_M01-Evaluation report (P1_20210726_110353_G01_S01_M01)

General information

Analysis date	2021-07-26 14:42:43	Measurement start time	2021-07-26 11:03:53
Analyst	Administrator	Operator	Administrator
Sample name	P1	Comment	
Measured data name	C:\WallPaper\26-07-2021\THE TWO\P1_20210726_110353_G...	Memo	

Qualitative Analysis Results

Phase name	Formula	Figure of merit	Phase reg. detail	Space Group	DB Card Number
Chaoite	C	1.438	S/M(PDF-4 Minerals 2020 R...	147 : P-3	00-022-1069
Delhayelite	(K , Na)10 Ca5 Al6 Si32 O8...	3.249	S/M(PDF-4 Minerals 2020 R...	59 : Pmmn:2	00-012-0286
Garnet	3 (Ca , Fe , Mg) O · (Al , Fe...	3.217	S/M(PDF-4 Minerals 2020 R...	230 : Ia-3d	00-002-0981
Milarite	K2 Ca4 Al2 Be4 Si24 O60 · H...	2.261	S/M(PDF-4 Minerals 2020 R...	192 : P6/mcc	00-012-0450
Chlorapatite	Ca5 (P O4)3 Cl	3.393	S/M(PDF-4 Minerals 2020 R...	14 : P121/a1	00-024-0214
Cristobalite	Si O2	2.342	S/M(PDF-4 Minerals 2020 R...		00-003-0276
Refikite	C20 H32 O2	0.352	S/M(PDF-4 Minerals 2020 R...	18 : P21212	00-028-2009

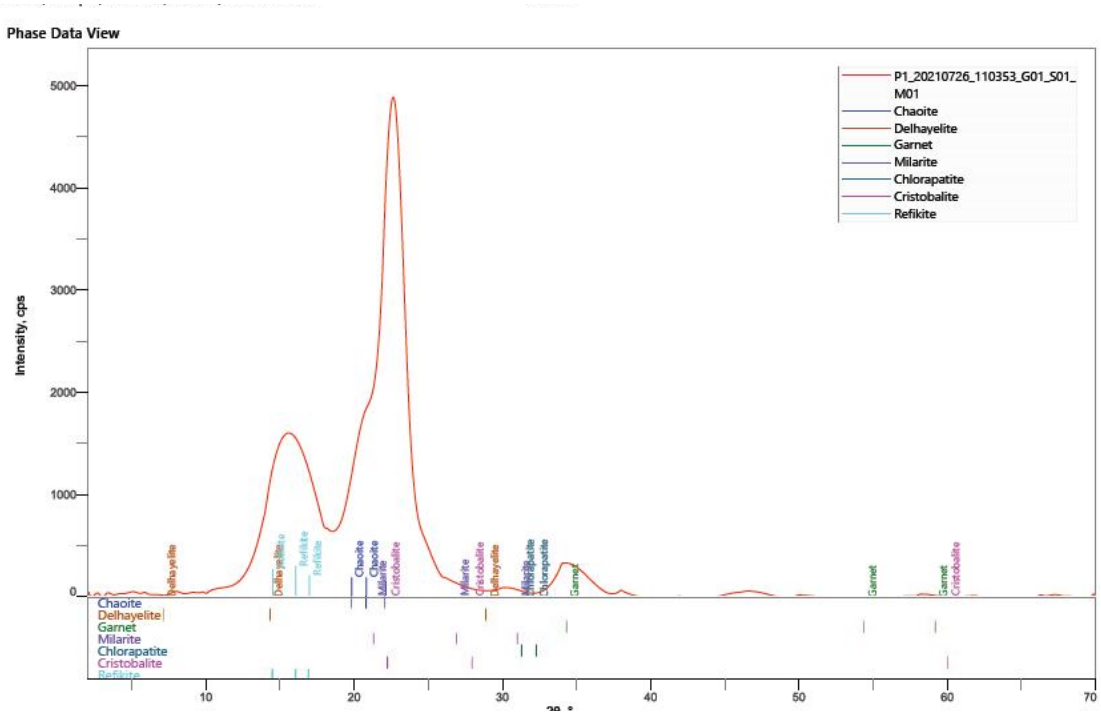
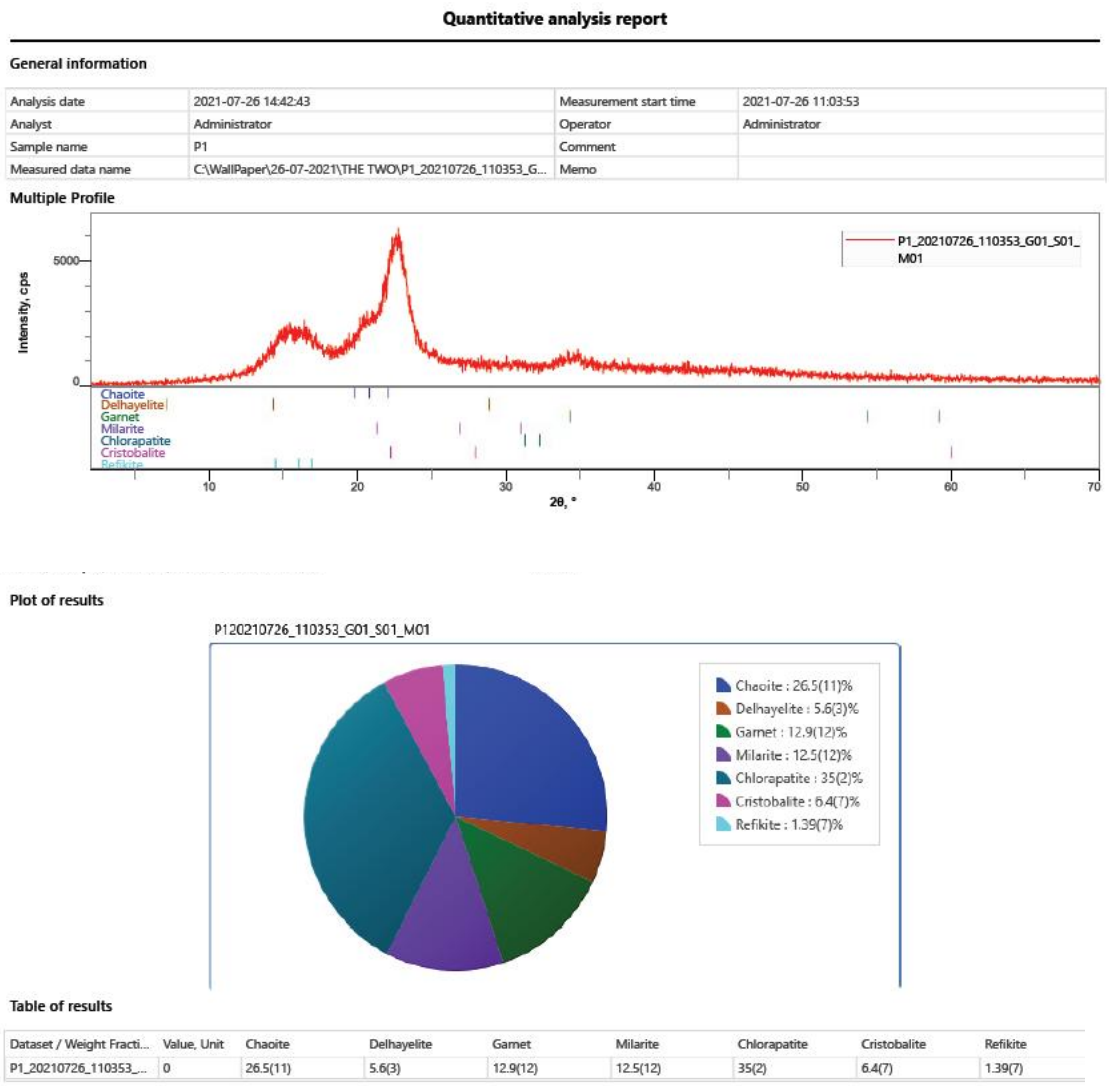


FIG 3.2: SEM CELLULOSE



Quantitative analysis report

General information

Analysis date	2021-07-26 14:42:43	Measurement start time	2021-07-26 11:03:53
Analyst	Administrator	Operator	Administrator
Sample name	P1	Comment	
Measured data name	C:\WallPaper\26-07-2021\THE TWO\P1_20210726_110353_G...	Memo	

Multiple Profile

Plot of results

Table of results

Dataset / Weight Fracti...	Value, Unit	Chaoite	Delhayelite	Garnet	Milarite	Chlorapatite	Cristobalite	Refikite
P1_20210726_110353_...	0	26.5(11)	5.6(3)	12.9(12)	12.5(12)	35(2)	6.4(7)	1.39(7)

FIG3.3: XRD CELLULOSE

Figure 3.3 gives the XRD spectra of cellulose obtained by the XRD machine.

The XRD profile of hydrolyzed CelluloseThe XRD profile of hydrolyzed Cellulose ore depicted in for 2 Ushow - Volitterent patterns pasks patterns. the peak of the hydrolyzed cellulose e placed at 2ttet (26) angle #15:01 Clors latice refle. Ctr) 22.64 Cleaz lactica ref The lection), £24 29.06 Cl-122 Lartice reflection), and 34 08 (1310 lactice reflections. the peaks in the XRD profile of

hychelyzed Cellulose are share Indicating that the volume fraction of the Crystalline phase conting Contained within the hydrolysed Cellulose is high. However,, The muchassica We Can the mechanical and thermallproperties Say that Et Cellulose we can be dependent On the Crystalline Characteristics especially, the reinforcingCapability and mechanical strengted of Cellulose are deciding factors. for the use in environmental remediation technologie. The Crystalline peak was observed at 22.64^{o} with an nitensity of 15 100%, confirms the presence of Crystalline Cellulose. The Crystallite She is also supportive of the description of Crystallinity of the Celloluse. The report in agreement with the report of other researchers, it correspond with the report of Trilokesh et al 2019 and Sosiati et af 2014Capability and mechanical strengted of Cellulose are deciding factors. for the use in environmental remediation technologie. The Crystalline peak was observed at 22.64^{o} with an nitensity of 15 100%, confirms the presence of Crystalline Cellulose. The Crystallite She is also supportive of the description of Crystallinity of the Celloluse. The report in agreement with the report of other researchers, it correspond with the report of Trilokesh et al 201use ore depicted in for 2 Ushow - Volitterent patterns pasks patterns. the peak of the hydrolyzed cellulose e placed at 2ttet (26) angle #15:01 Clors latice refle. Ctr) 22.64 Cleaz lactica ref The lection), £24 29.06 Cl-122 Lartice reflection), and 34 08 (1310

lactice reflections. the peaks in the XRD profile of hychelyzed Cellulose are share Indicating that the volume fraction of the Crystalline phase conting Contained within the hydrolysed Cellulose is high. However,, The muchassica We Can the mechanical and thermall properties Say that Et Cellulose we can be dependent On the Crystalline Characteristics especially, the

ABSORBENT DOSAGE(GRAM)	EQUILIBRIUM CONCENTRATION(MG/L)	AMOUNT ADSORBED(MG/L)	ADSORPTION %
0.20	35.85	14.15	28.30
0.40	32.48	17.52	35.04
0.60	23.00	27.00	54.00
0.80	21.50	28.50	57.00
1.00	19.00	31.00	62.00

reinfoCapability and mechanical strengted of Cellulose are deciding factors. for the use in environmental remediation technologie. The Crystalline peak was observed at 22.64^{o} with an nitensity of 15 100%, confirms the presence of Crystalline Cellulose. The Crystallite She is also supportive of the description of Crystallinity of the Celloluse. The report in agreement with the report of other researchers, it correspond with the report of Trilokesh et al 2019 and Sosiati et af 2014

Table 3.1**: EFFECT OF ADSORBENT DOSAGE ON ADSORPTION OF Zinc**

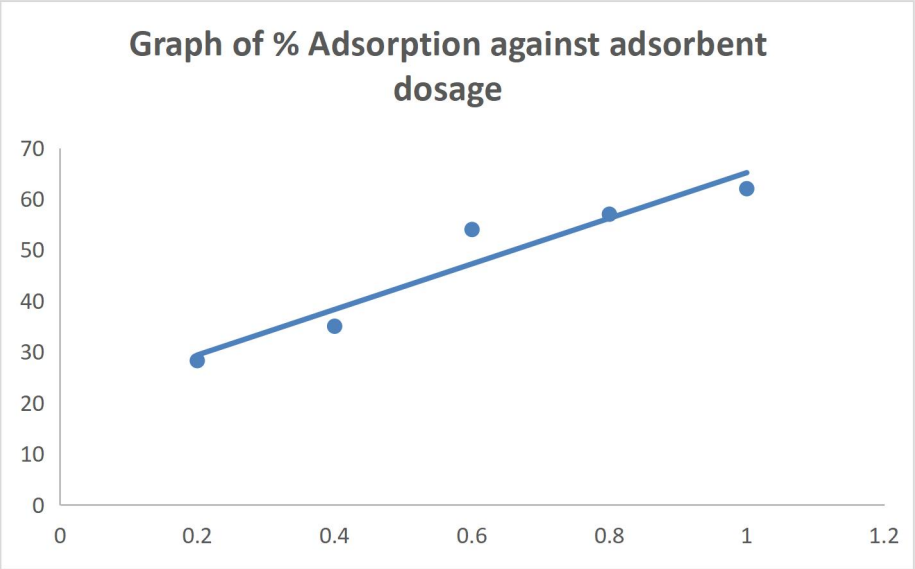


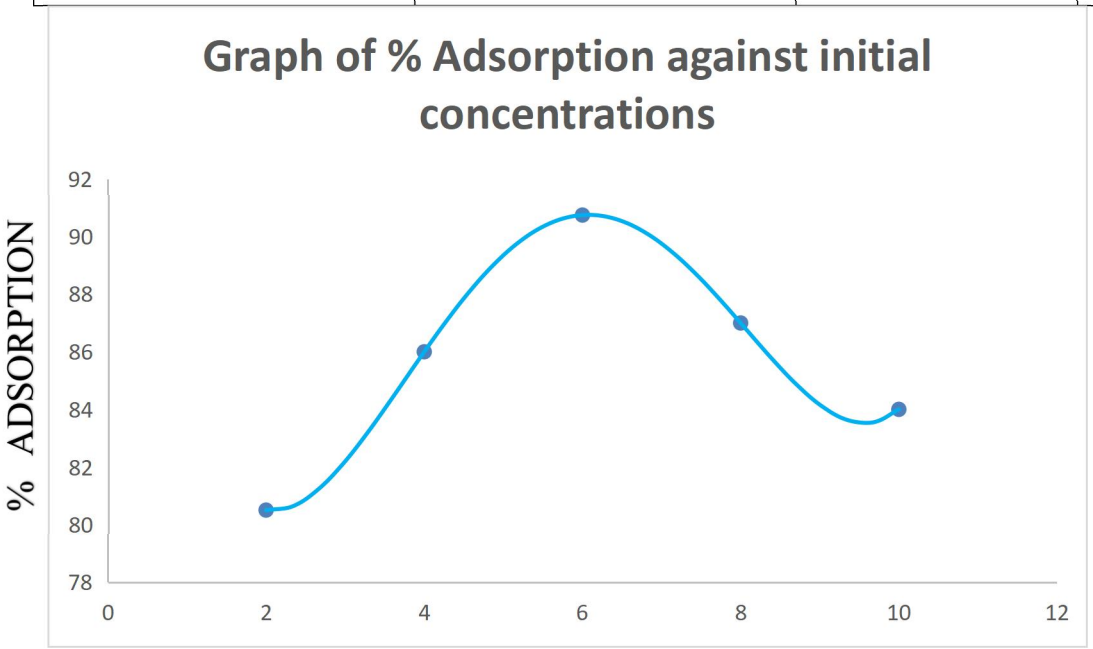
Figure 3.4: Graph Showing Effect of Adsorbent Dosage On Adsorption Of Zn^{2+}

From fig 3.1 above, it is evident that the fraction of the metal removed from the aqueous phase increased with an increase in the adsorbent dosage. such behavior is obvious since the metal uptake capacity of the adsorbent increased as its dosage was increased. this was so because the number of active sites available for metal uptake were more as the amount of the adsorbent increased. This increase in equilibrium adsorption capacity per unit mass of adsorbent may be due to higher adsorbent dose providing more active adsorption site which result in the adsorption site remaining saturated during the adsorption reaction (Li et al., 2013). Maximum adsorption was 62.00% at 1.0g

Table 3.2: EFFECT OF METAL ION CONCENTRATION ON ADSORPTION OF Zn^{2+}

The data drawn with the 30ml of aqueous solution ,1g adsorbent dosage, and 50mins contact time are shown below:

INITIAL CONCENTRATION(mg/l)	EQUILIBRIUM CONCENTRATION(mg/l)	AMOUNT ADSORBED(mg/l)	ADSORPTION %
10.00	2.08	7.92	79.50
20.00	5.98	14.02	70.10
30.00	9.08	20.92	67.30
40.00	14.20	25.80	64.50
50.00	19.00	31.00	62.00



INITIAL CONCENTRATIONS

Figure 3.5: Showing Effect of Metal Ion Concentration On Adsorption of Zn^{+}

From fig 3.5 above, the percentage removal of Zinc from aqueous solution is observed to decrease from 79.50% to 62.00% by varying iron concentrations in the aqueous solution from 10mg/l to 50 mg/l. Maximum adsorption percentage was observed at 10ppm (79.50% being adsorbed). Even though the removal efficiency decreases with increase in initial concentration, the change is only less. It shows that initial concentration has little effect on adsorption (Padmavathy et al., 2016).

Table 3.3: **EFFECT OF TIME ON ADSORPTION OF Zn^{2+}**

The uptake of Zn^{2+} by cellulose was examined at different time intervals and the results are shown below:

TIME	EQUILIBRIUM CONCENTRATION	AMOUNT ADSORBED	ADSORPTION %
5.00	22.38	27.62	69.00
10.00	21.44	28.56	69.70
20.00	20.74	29.26	71.90
40.00	19.69	30.31	73.20

50.00	18.88	31.12	75.60
60.00	17.76	32.24	79.30
70.00	16.29	33.71	82.00
90.00	15.74	34.26	87.00
120.00	13.94	36.06	89.50
150.00	13.32	36.32	89.90
180.00	12.83	37.17	90.30
190.00	12.49	37.51	90.70

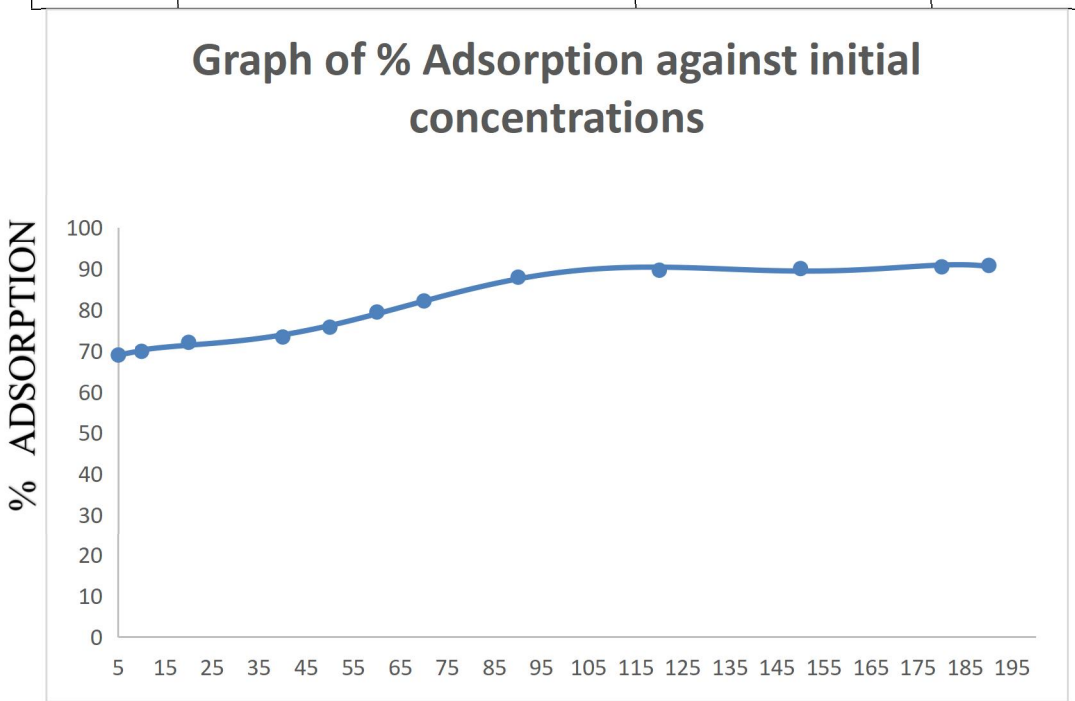


Figure 3.5: Showing Effect of Time On Adsorption of Zn^{2+}

it can be seen from fig 3.5 above that there was an increase in the percentage of nickel adsorbed within the first 190mins. Maximum adsorption time was at 190 mins (74.00% being adsorbed). As time progresses, surface coverage is high and further, little or no adsorption takes place (Padmavathy et al., 2016).

3.1 ADSORPTION ISOTHERMS

The isotherm constants for isotherm models at specific initial concentration values were determined from the respective plots as shown in fig3.6 and fig3.7 and along with the correlation regression coefficients (R^2). R^2 of Zn^{2+} for Frendlish isotherm was higher than that of the Langmuir isotherm, therefore the experimental data was better fitted to the Frendlish isotherm.

Table 3.5**: LANGMUIR ADSORPTION ISOTHERM**

DOSAGE	EQUILIBRIUM CONCENTRATIOS (mg/l)	AMOUNT ADSORBED (qe)	Ce/qe
1.00	1.86	0.081	22.96
1.00	3.60	0.164	21.95
1.00	3.94	0.261	15.09
1.00	4.68	0.353	13.26
1.00	7.40	0.462	16.02

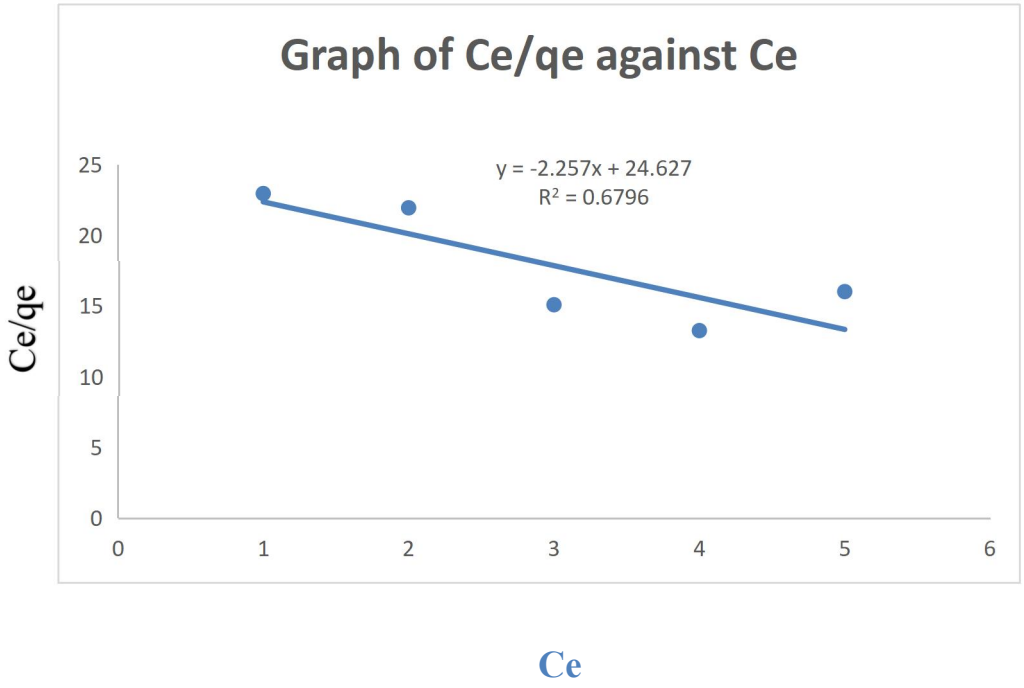


FIG 3.5: LANGMUIR ADSORPTION ISOTHERM

The freudlich model was well fitted with R^2 values of 0.9341

X/M($\frac{amount\ of\ Zn(II)\ adsorbed}{mass\ of\ cellulose\ used}$ **)**	**Log X/M**	**Ce(equilibrium conc)**	**LOG Ce**
0.081	-1.092	**1.86**	0.270

0.164	-0.785	**3.60**	0.556
0.261	-0.583	**3.94**	0.595
0.353	-0.452	**4.68**	0.670
0.462	-0.335	**7.40**	0.869

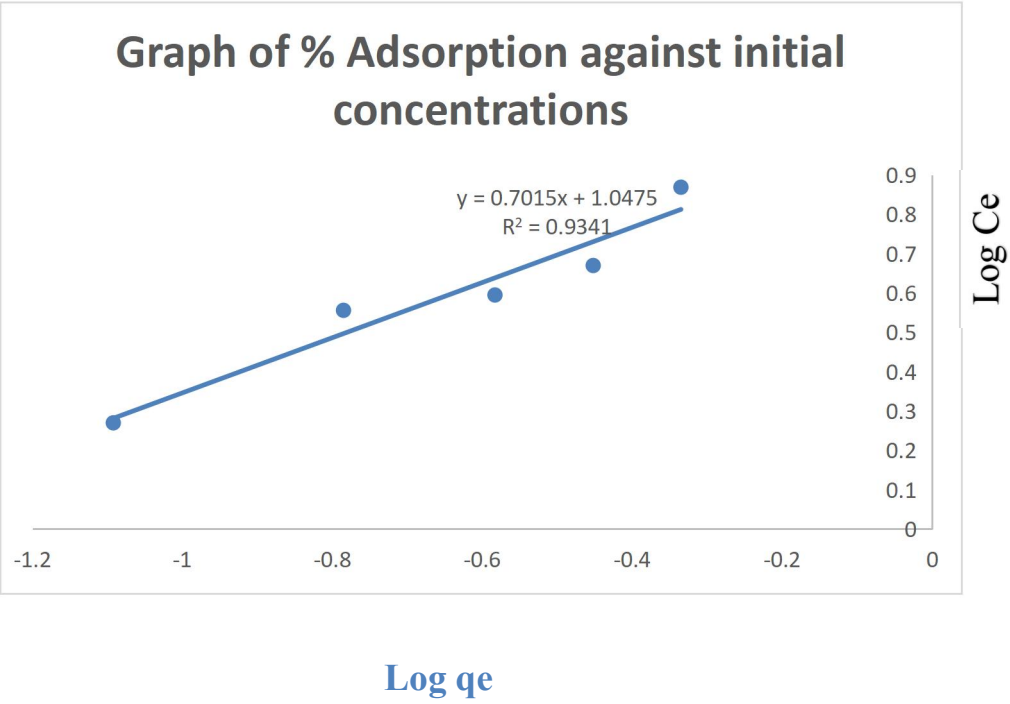


Figure 3.6: FREUDLICH ADSORPTION ISOTHERM

The graph above indicates that the experimental data fitted well to the entire freudlich adsorption model. The intercept is an indication of adsorption capacity and the slop is adsorption intensity. A relatively slight slope n<<1 indicates that adsorption intensity is favorable over the entire range of concentration studied, while a steep slope n<1 means that adsorption is good at

high concentration but much less concentration (Eren, 2008). A high value of the intercept K, is indicative of a high adsorption capacity.

DISCUSSION

Studies were carried out for the removal of Zinc metal from an aqueous solution by the adsorbent material cellulose. Parameters studied included time of contact for adsorption, adsorbent dosage, initial metal ion concentration of the solution. On the analysis of the data, the following conclusions were drawn:

- The optimum time of contact was found to be 190minutes
- The decrease in the initial concentration of the Zinc ion resulted in higher removal of Zn.
- An increase in the adsorbent dosage had resulted in an increase in the % removal of zinc
- The adsorption isotherms had followed freundlich equation with an R^2 value of 0.9341.

CONCLUSION

From this research, cellulose was seen to be a good adsorbent and can be recommended for use in the treatment of industrial water (containing heavy metals) before being discharged into water bodies. Cellulose is in expensive and readily available for use; therefore, it can be used wholly or combined with other effective adsorbent for the removal of heavy metal in aqueous solution.

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APPENDIXES

qe = Amount of metal ion per adsorbent

Ce = Equilibrium concentration of metal (mg/l)

Co= Initial metal ion concentration X= Amount of metal ion adsorbed

CALCULATIONS OF VALUES

Calculation of values from the langmuir and Freundlich Isotherm Values for Cu and Pb on the Langmuir isotherm.

Ce/qe=1/Qmb+ Ce/Qm

Since a graph of Ce/qe was plotted against Ce

Then I/Qm = slope = 0.5944

1/Qm=0.5944

Qm= 1.6824

1/Qmb = intercept = 9.3076

b=1/(intercept x Qm)

b= 1/(9.3076 x 1.6824)

b= 0.0638