ADSORPTION OF ZINC ION IN AQUEOUS SOLUTION USING DANGARA CLAY

BY

OGUNYEMI STANLEY ALEAKWE

PSC1808556

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF BENIN,
BENIN CITY,

JANUARY, 2023

ADSORPTION OF ZINC ION IN AQUEOUS SOLUTION USING DANGARA CLAY

BY

OGUNYEMI STANLEY ALEAKWE

PSC1808556

A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BENIN, BENIN CITY, IN PARTIAL FULFILLMENT TO THE REQUIREMENT FOR THE AWARD OF BACHELOR OF SCIENCE DEGREE (B.SC).

JANUARY, 2023

DEDICATION

This project is dedicated to God almighty for his unfailing support and guidance, provision and protection that sustained me throughout the period of this research, to my family and friends for their support morally, financially and emotionally.

CERTIFICATION

We the under signed hereby certify that this project work was carried out by OGUNYEMI STANLEY ALEAKWE with the matriculation number PSC1808556 in the Department of Chemistry for the award of BACHELOR OF SCIENCE Degree in Chemistry.

……………………………… ………………

OGUNYEMI. A. STANLEY DATE

(Student)

………………………………. ……………...

DR. E.E.I. IRABOR DATE

Project Supervisor

………………………………. …..…………

PROF. U. J. IYASELE DATE

Head of Department

ABSTRACT

The adsorption properties of the Dangara middle layer clay were examined to determine the adsorption of the heavy metal, zinc. The effect of variation in parameters such as, adsorbent dosage, initial concentration, contact time, pH and temperature were observed. The result obtained showed that the optimum equilibrium adsorption was 99.578% at pH 8, 99.576% at 1.0g adsorbent dosage, 99.578% at contact time of 60minutes, 99.61% at 10ppm initial concentration, and 99.61% at temperature of 40ºC. The experimental data were analyzed by both the Langmuir and Freundlich isotherm model. The result obtained shows that the Dangara middle layer clay is an effective adsorbent for the adsorption of the heavy metal Zinc from an aqueous solution.

ACKNOWLEDGEMENT

I thank God almighty for his love, grace, faithfulness and protection throughout my stay in the department of Chemistry.

My sincere gratitude goes to my project supervisor, Dr. E.E.I IRABOR, whose constant guidance, correction, encouragement and words of wisdom effected greatly the successful completion of this project even with his tight schedule. I also hold in high esteem, the Head of Department of Chemistry, Prof. U. J. Iyasele, my course adviser, Dr. (Mr.) A.E. Aiwonegbe, and the other lecturers and laboratory technicians in the Department of Chemistry for their relentless effort.

My sincere gratitude goes to my parents, Mr. and Mrs. Ogunyemi, whose support from finances to words of wisdom and encouragement, to consistent prayers saw me throughout this period. This research and entire journey would not have been worth the while without my friends, Emmanuel, Ohbed Confidence, Odinaka, Mr.Okhips, Atesiwa and Deborah. I am indeed very grateful.

TABLE OF CONTENTS

CHAPTER ONE

1.1 INTRODUCTION

Clay is a term used to describe a group of fine-grained, silicate minerals known as aluminum phyllosilicates, containing variable amounts of chemically active minerals associated water. Clay is plastic when wet, which means it can be easily shaped. When dry, it becomes firm, and when subject to high temperature, known as firing, permanent physical and chemical changes occur. It is a soft, loose, earthy material containing particles with a grain size of less than 4 micrometres (μm). It contains clay minerals (hydrous aluminium phyllosilicates, e.g. kaolin *(Bergaya, Faïza; Theng, B. K. G.; Lagaly, Gerhard., 2006).*

Heavy metal absorbents are use for the removal of heavy metals in aqueous solutions. Chitosan is an efficient adsorbent for the removal of heavy metals *(Ren et al., 2008).*

The biopolymer chitosan is attracting considerable interest as a matrix for adsorbent material development, since this biopolymer has a high density of hydroxyl groups (–OH) and primary amines (–NH2) that act as active adsorption sites, making it an efficient adsorbent (online). Adsorption of heavy metals by clay and clay composites involves a number of complex adsorption processes, including ion exchange, surface complexation, and direct heavy metal bonding. cations to clay surfaces (*Catalano and Brown 2005; CatalanoSari et al., 2007; Deng et al., 2006).*

The chemical nature and pore structure of clay materials generally influence their adsorption capability. In order to increase its adsorption capacity, modification of the pore structure of clay materials has been conducted chemically as well as physically. Inorganic acids, bases, salts, and surfactants have been used for modification of clay minerals. A combination of chemical and physical treatment process has also been employed to modify the surface and structure of clay minerals. The modification of clay minerals using acid can alter the crystalline structure of the clay minerals. The clay minerals modified with quaternary ammonium surfactant have a high affinity towards most of hydrophobic organic compounds. *(Res. J., 2012)*

Clay minerals are phyllosilicate minerals with layered structural units consisting of one or two tetrahedral silica sheets wrapped around an octahedral aluminum sheet. *(Velde.,1995)*. They have particles that are less than 2 µm.in size. Si2O6 (tetrahedral sheets) has a (OH)4 unit and is made up of per silicon atom which is surrounded by four hydroxyl groups tetrahedron configuration by comparison, an octahedral arrangement consists of Fe, Mg or Al atoms surrounded by six hydroxyl or oxygen atoms, such as in the composition of Al2(OH)6 *(Hendricks 1942; Gale et al., 1990)*.Between the silicate layers, clays have three distinct inner surfaces, sides, and outer surfaces.

The outer and interlayer surfaces are vulnerable to damage. During the ion exchange and adsorption processes, the ion exchange and a small amount of net negative energy is generated by most clay minerals. Isomorphic substitution results in a surface charge. In addition, Clay mineral particle edges can generate charges as a consequence of a split primary, according to the pH of the suspension Si–O and Al–O bonds, for example *(Leroueil et al., 1979).* Clays have a wide range of physical characteristics, including Particle fineness, toughness, strong plasticity and associativity Shrinkage that is acceptable, refractoriness that is strong, and the ability to decorate surfaces *(Odoma et al., 2013).*

As a consequence, clays have small particle sizes and large specific surface areas because of their porous structures, which encourage physical movement of dissolved species, as well as chemical reactions. There are Crystallinity, electrostatic repulsion, and other factors all contribute to interactions. The presence of a porous surface area suggests a strong bonding force on the surface. The clays' surface *(Reichle., 1986).* Clays differ from one another in their internal layer structures. There are two kinds of clay materials: amorphous and crystalline. *(Chen et al., 2000).* The crystal structures of crystalline clays can be divided into classes, such as 1:1 form.1:1 type tube (halloysite), 2:1 type sheet (kaolinite)The standard mixed layer (montmorillonite, smectite, vermiculite)layer-chain type 2:1 (Chlorite group) and type (Chlorite group)(Sepiolite, attapulgite) Kaolinite, chemically expressed as $Al_2Si_2O_5(OH)_4$, has the theoretical components of Al_2O_3(39.53%), SiO_2(46.53%), and H_2O(13.94%), in the case of the oxides. The chemical formula demonstrates that no substitution appears involving Si^{4+}substituted by Al^{3+}in the layer of tetrahedronand Al^{3+}substituted by other ions (Na^+, K^+,Zn^{2+},Mg^{2+},).Clay forms from volcanic ash. It gets its name from Fort Benton in Wyoming, where it occurs in large amounts. People can also find this clay in other places where volcanic ash has settled into the ground.

1.1.1 Background of the Research.

Clay comes from the ground, usually in areas where streams or rivers once flowed. It is made from minerals, plant life, and animals—all the ingredients of soil. Over time, water pressure breaks up the remains of flora, fauna, and minerals, pulverising them into fine particles. *(Fortnum.,2022)*

Clay is consumed orally by children, women with pregnancy and others with geophagia. It is possible that Many clay eater are led in the footsteps of their peers, family, or cultural practices. Clays or other ingredients, such as bitter kola, are consumed by pregnant women to aid or avoid vomiting, to treat swollen knees, to adsorb poisons consumed by the mothers, and to give birth to children with smooth skin *(Ejike et al., 2017)*

Bentonite clay is popular in the Nigerian, West African market but is commonly-known with the local names such as NZU or NDOM in Efik. (*online*)

Apart from mineral elements in air and water, clay can be a goo channel for getting chemical and biological agents. Radioactive compounds, organic chemicals, and trace elements are examples of such agents.

Clay is rich in essential minerals such as Ca, Fe, K and Zn but also include potentially harmful heavy metals such as Arsenic (As), Cadmium (Cd) and Lead (Pb) at very low concentrations.

Some other metals are xenobiotics i.e. they have no useful role in human physiology (and most other living organisms) an it is likely to cause disorders even a the minimum level of exposure. Among Some other metals are xenobiotics i.e. they have no useful role in human physiology (and most other living organisms) and may cause disorders even at trace levels of exposure. Among all heavy metal pollutants, lead is the most common and one of the most toxic, reaching water sources from various industrial activities such a oil refinery mining, meta coating and finishing, an manufacturing of battery. The maximum contaminant level of lead in drinking water allowed by the Environmental Protection Agency (EPA) and the World Health Organization (WHO) is15 and 50 µg/L, respectively. When lead concentrations become elevated, serious health problems can occur. Lead poisoning can cause kidney damage, anemia, and toxicity symptoms including impaired kidney function, hypertension, and headache.

1.1.2 Statement Of Problem

Due to th too much release of heavy metals into the environment by industrialization and urbanization has been critical problem Currently, with the high increasin population, heavy metals become contaminants of great concern. There is a strong need to reconsider the consumption of water to ensure that it is free of pollution. Organic pollutants which are susceptible to biological degradation while heavy metals do not degrade into harmless product, The presence of heavy metal ions, is a major concern due to their toxicity to many life forms.

1.1.3 Justification/ Relevance Of Study

This stud shows a detailed outline analysis of clays and clay minerals as successful, effective, result oriented, and low-cost adsorbent. It also summarized their effect, adsorptive potential, compositions, and outcomes. The main purpose is to give more light about the natural or modified forms of clay minerals and their great adsorption capacities fo numerous toxic heavy metals from aqueous solution. It also successfully emphasizes the clay and its modified forms as a good adsorbent.

1.1.4 Scope of Work

This project work covers

1. Purchase of the clay sample
2. Pulverization and sieving of sample
3. The study of the amount of Iron in concentrations adsorbed by the clay when it is modified and when it is in its unmodified state.
4. The study of the clay samples under different conditions of time, concentrations , weight, pH and temperature.

1.1.5 Aim and Objectives

The aim of this study is to investigate if Clay can adsorb Iron ions from its aqueous solutions and how much of these metal ions can be adsorbed by the clay in its raw state and when modified. To meet the above aim, the following objectives were set;

1. Obtaining the clay from benin geopolitical zone

2. Charactrerization of the clay

3. To determine the optimum pH for the maximum adsorption to take place

4. To determine the amount of selected metal ions present in Clay samples.

1.2 Literature And Review

1.2.1 Clay: Clay is a finely-grained natural rock or soil material that, along with other materials such as stone and wood, has been used as for construction for thousands of years. It is composed of one or more clay minerals (such as kaolinites or smectites), sometimes with small quantities of quartz, metal oxides and organic matter. Clay is formed very slowly as a result of the weathering and erosion of rocks containing the mineral group known as feldspar.

Due to the particle size (typically, a grain size of less than 4 micrometres (μm)), and water content, clays have a high plasticity until they are dried or fired, at which point they become hard and brittle.

Clay is the oldest ceramic substance that has been discovered. Clay's properties were discovered by prehistoric humans, who used it to make pottery. Clay tablets were the first known writing medium, and some of the earliest pottery shards have been dated to about 14,000 BC.

Clay has good robustness, stability and durability. It is fire-resistant and capable of withstanding seismic activity, giving it a potential lifespan of 100 years or more.

1.2.2 Clay Minerals

Clay minerals such as kaolinite, smectite, chlorite, micas are main components of raw materials of clay and formed in presence of water. A large number of clays used to form the different structure which completely depends on their mining source. They are known as hydrous phyllosilicate having silica, alumina and water with variable amount of inorganic ions like Mg^{2+}, Na^{+}, Ca^{2+} which are found either in interlayer space or on the planetary surface. Clay minerals are described by presence of two-dimensional sheets, tetrahedral (SiO_4) and octahedral (Al_2O_3). There are different clay minerals which are categorized based on presence of tetrahedral and octahedral layer in their structure like kaolinite (1:1 of tetrahedral and octahedral layers), smectite group of clay minerals (2:1 of tetrahedral and octahedral layers) and chlorite (2:1:1 of tetrahedral, octahedral and octahedral layers). The particle size of clay minerals is <2microns which can be present in form of plastic in presence of water and solidified when dried. The small size and their distinctive crystal structure make clay minerals very special with their unique properties including high cation exchange capacity, swelling behavior, specific surface area, adsorption capacity, etc. which are described in this chapter. Due to all these unique properties, clay minerals are gaining interest in different fields. Most of the chemical and physical properties of the soil including swelling - shrinking capacity, cation exchange capacity etc. are due to presence of the clay minerals in soil. Clay minerals are look like micas due to their chemical composition

1.2.3 Varieties Of Clay Minerals

There are three main groups of clay minerals:

Kaolinite: This also includes dickite and nacrite; formed by the decomposition of orthoclase feldspar (e.g. in granite); kaolin is the principal constituent in china clay.

Kaolinite is the purest of clays, meaning that it varies little in composition. It also does not absorb water and does not expand when it comes in contact with water. Thus, kaolinite is the preferred type of clay for the ceramic industry.

Illite: This includes glauconite (a green clay sand) and are the commonest clay minerals; formed by the decomposition of some micas and feldspars; predominant in marine clays and shales.

Illite is similar to muscovite and is the most common clay mineral, often composing more than 50 percent of the clay- mineral suite in the deep sea.

They have characteristic of weathering in temperate climates or in high altitudes in the tropics, and typically reach the ocean via rivers and wind transport.

The Illite clays have a structure similar to that of muscovite, but is typically deficient in alkalies, with less Al substitution for Si. Thus, the general formula for the illites is:

$K_yAl_4(Si_{8-y},Al_y)O_{20}(OH)_4$, usually with $1 < y < 1.5$, but always with $y < 2$.

Because of possible charge imbalance, Ca and Mg can also sometimes substitute for K.

Illite type clays are formed from weathering of K and Al- rich rocks under high pH conditions. Thus, they form by alteration of minerals like muscovite and feldspar. Illite clays are the main constituent

The K, Ca, or Mg interlayer cations prevent the entrance of H_2O into the structure. Thus, the illite clays are non-expanding clays.

Smectites or montmorillonites: This includes bentonite and vermiculite; formed by the alteration of mafic igneous rocks rich in Ca and Mg; weak linkage by cations (e.g. Na^+, Ca^{++}) results in high swelling/shrinking potential.

The most common smectite is Montmorillinite, with a general chemical formula : $(½Ca,Na)(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4.nH_2O$

Montmorillinite is the main constituent of bentonite, derived by weathering of volcanic ash. Montmorillinite can expand by several times its original volume when it comes in contact with water. This makes it useful as a drilling mud (to keep drill holes open), and to plug leaks in soil, rocks, and dams.

Montmorillinite, however, is a dangerous type of clay to encounter if it is found in tunnels or road cuts. Because of its expandable nature, it can lead to serious slope or wall failures.

1.2.4 Formation Of Clay Minerals

Clays and clay minerals occur under a fairly limited range of geologic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. Most clay minerals form where rocks are in contact with water, air, or steam. Examples of these situations include weathering boulders on a hillside, sediments on sea or lake bottoms, deeply buried sediments containing pore water, and rocks in contact with water heated by magma (molten rock). All of these environments may cause the formation of clay minerals from preexisting minerals. Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits that are of economic interest (for example, bentonites‹primarily montmorillonite‹used for drilling muds and clays used in ceramics).*(Blatt, H., Middleton, G., and Murray, R., 1980)*

1.2.5 Classification Of Clay Mineral

Clays ar divided into classes or groups such as smectites (montmorillonite, saponite), mica (illite), kaolinite, vermiculite, serpentine, pyrophyllite (talc), and sepiolite etc. It was Grim, in 1962, who first proposed the classification of clay minerals, which lead to the basis for outlining the nomenclature and the differences between various clay minerals. According to Grim, important groups of clay minerals are kaolinite, montmorillonite, and illite.

China clay, a primary, ancient, and purest clay, used first by the Chinese. Its main component is kaolinite, however, in addition it is a mixture of different minerals which frequently contains quartz, mica, feldspar, illite, and montmorillonite.

- **Classification Of Clay Mineral According To Grim (Grim 1962)**

1.Amorphous: (Allophane group)

2.crystiline :

(a) Two layer types (sheet structures having units of one layer of silica tetrahedrons and one layer of alumina octahedrons)Examples: Kaolinite group and Halloysite group.

b) Three-layer types (sheet structures having two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer) Examples: Smectite group, sodium montmorillonite, Calcium montmorillonite, Beidellite, Vermiculite, Illite

(c) Regular mixed-layer types (ordered stacking of alternate layers of different types) Example: Chlorite group.

(d) Chain-structure types (hornblende-like chains of silica tetrahedron linked together by octahedral group of oxygen and hydroxyl containing Al and Mg atoms Examples: Sepiolite, Palygorskite (attapulgite).

1.2.6 Structure Of Clay Minerals

The atomic structure of the clay mineral are of two basic units, an octahedral sheet and a tetrahedral sheet. The octahedral sheet consist of closely packed oxygen's and hydroxyls in which aluminum, iron, and magnesium atoms are arranged in octahedral coordination. When aluminum with a positive valence of three is the caution present in the octahedral sheet, only two-thirds of the possible positions are filled in order to balance the charges. When only two-thirds of the positions are filled, the mineral is termed dioctahedral. When magnesium with a positive charge of two is present, all three positions are filled to balance the structure and the mineral is termed trioctahedral.

The structures of some most important clay minerals as followed

1. Kaolinite structure: The basic kaolin mineral structur consisting the minerals kaolinite, dickite, nacrite, and halloysite is a layer of a single tetrahedral sheet and a single octahedral sheet. These two sheets ar joined to form a unit in which the tips of the silica tetrahedrons are joined with the octahedral sheet. All of the apical oxygens of the silica tetrahedrons point in the same direction so that these oxygens and/or hydroxyls, which may be present to balance the charges, are shared by the silicons in.

2. Smectite Structure:

The major smectite minerals are sodium montmorillonite, calcium montmorillonite, saponite (magnesium montmorillonite), nontronite (iron montmorillonite), hectorite (lithium montmorillonite), and beidellite (aluminum montmorillonite). Smectite minerals are composed of two silica tetrahedral sheets with a central octahedral sheet and are designated as a 2:1 layer mineral. Water molecules and cations occupy the space between the 2:1 layers.

3. Illite Structure:

Illite is a clay mineral mica, which was named by *Grim et al. (1937).* The structure is a 2:1 layer in which the interlayer cation is potassium. The size, charge, and coordination number of potassium is such that it fits snugly in the hexagonal ring of oxygens of the adjacent silica tetrahedral sheets. This gives the structure a strong interlocking ionic bond which holds the individual layers together and prevents water molecules from occupying the interlayer position *(Bailey, S.W.,1988)*

1.2.7 Uses Of Clay

Generally, clays are used for making pottery, both utilitarian and decorative, and construction products, such as bricks, walls, and floor tiles. Different types of clay, when used with different minerals and firing conditions, are used to produce earthenware, stoneware, and porcelain.

The use of clay in pottery making antedates recorded human history, and pottery remains provide a record of past civilizations. As building materials, bricks (baked and as adobe) have been used in construction since earliest time. Impure clays may be used to make bricks, tile, and the cruder types of pottery, while kaolin, or china clay, is required for the finer grades of ceramic materials. Another major use of kaolin is as paper coating and filler; it gives the paper a gloss and increases the opacity. Refractory materials, including fire brick, chemical ware, and melting pots for glass, also make use of kaolin together with other materials that increase resistance to heat. Certain clays known as fuller's earth have long been used in wool scouring. In rubber compounding, the addition of clay increases resistance to wear and helps eliminate molding troubles.

Clay materials have a wide variety of uses in engineering. Earth dams are made impermeable to water by adding suitable clay materials to porous soil; water loss in canals may be reduced by adding clay. The essential raw materials of portland cement are limestone and clays, commonly impure. After acid treatment, clays have been used as water softeners; the clay removes calcium and magnesium from the solution and substitutes sodium. A major use of clay is as drilling mud—i.e., heavy suspension consisting of chemical additives and weighting materials, along with clays, employed in rotary drilling.

1.3 Heavy Metal

Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons *(Jaishankar et al., 2013; Nagajyoti et al., 2010).* The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel and zinc, all of which cause risks for human health and the environment *(Lambert et al., 2000).* Heavy metals enter the surroundings by natural means and through human activities. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops and many others *(Morais et al; 2012).*

Heavy metals are widespread pollutants of great concern as they are non-degradable and thus persistent. These metals are used in various industries from which effluents are consequently discharged into the environment. Introduction of metals in various forms into the environment can produce numerous modifications of microbial communities and affect their activities *(Doelmanet et al; 1994, Hirok, 1994; Staezecka and Bednatz, 1993).* Common sources of heavy metal pollution include discharge from industries such as electroplating, plastics manufacturing, fertiliser producing plants and wastes left after mining and metallurgical processes *(Zouboulis et al; 2004).*

1.3.1 Effects of heavy metal on plants and animals

The excess of heavy metals in the soil inhibits the development of microorganisms and disrupts processes related to the transformation of organic matter. It also causes the accumulation of toxic elements in plant tissues, leading to disturbances in plant reproduction and thus lowering their nutritional value Excessive accumulation of the mentioned elements in the soil, however, is harmful to plants in particular.

In soil, heavy metals can occur in different forms—dissolved in soil solution, exchangeable in organic and inorganic components, being structural components of soil grids, and as insoluble sediments with other soil components. The first two forms are the most available to plants. The concentration of elements in the soil depends on the pH of the soil—the higher (to slightly alkaline) the higher the immobilization of elements. The mobility of heavy metals in the soil varies. In acidic soils, Cd, Ni, and Zn are particularly mobile, Cr is moderately mobile and Cu and Pb are immobile. In neutral and alkaline soils, Cr is highly mobile, Cd and Zn are moderately mobile, and Ni is immobile. Other factors, such as cation exchange capacity, redox potential, organic matter content, type and amount of clay minerals, and oxide content of antagonistic elements Fe, Al, and Mn, also determine the increase of heavy metals in the soil and thus their availability to plants.

Another toxic element is lead. Its natural content in soil is strongly related to the composition of the rock substrate. It is characterized by the lowest mobility among heavy metals. The highest Pb content in soil is found in highly industrialized areas. Lead can enter the body from two sources—the food chain and through inhalation of soil dust. It is a very dangerous metal with negative effects on humans, animals, and plants. Excess lead leads to reduced yields and dark green or red spots on leaves. Lead content in soil exceeding 500 mg kg−1 is a toxic value. A characteristic feature of this heavy metal is its accumulation in the human body, as it does not disintegrate in this environment. Getting into the human body a dose of about 20–50 g leads to death.

1.3.2 Sources of heavy metal in the soil

Heavy metals can be entered into the soil in different ways. Sources of heavy metals pollution include natural processes and anthropogenic activities.

- **Natural Sources**

Heavy metals occur naturally in many soils, on different concentrations. The metals in natural, unpolluted soils originate percussively from the lithosphere, accordingly from the mineral part of the soil that forms the rocks and minerals that makeup the Earth's crust. Naturally present elements reach to the soil from the parent substrate due to epigenetic processes of weathering of parent materials at levels that are regarded as trace and rarely toxic *(Alloway, 2013;Yanagi, 2011).*

- **Anthropogenic Sources**

Sources of heavy metals include mining, industrial production (foundries, smelters, oil refineries, petrochemical plants, pesticide production, chemical industry), untreated sewage sludge and diffuse sources such as metal piping, traffic and combustion by-products from coal-burning power stations. According to UNEP/GPA (2006a), an increasingly serious global problem is the management of electronic waste (e-waste), particularly the disposal of used computers and mobile phones, which contain over 1 000 different materials, many of which are toxic to humans.

1.3.3 Removal of Heavy Metals From Wastewater

Various treatment technologies employed for the removal of heavy metals include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis and adsorption *(Fu & Wang., 2011).* Among these methods, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions and costly disposal. The adsorption method is a relatively new process and is emerging as a potentially preferred alternative for the removal of heavy metals because it provides flexibility in design, high-quality treated effluent and is reversible and the adsorbent can be regenerated *(Fu & Wang.,2011).*

1.3.4 Zinc

Zinc is a chemical element with the symbol Zn and atomic number 30. Zinc is a slightly brittle metal at room temperature and has a shiny-greyish appearance when oxidation is removed. It is the first element in group 12 of the periodic table. It is a silvery-white color metal with a blue tinge. It tarnishes in air. Most zinc is used to galvanise other metals, such as iron, to prevent rusting.

In some respects, zinc is chemically similar to magnesium: both elements exhibit only one normal oxidation state (+2), and the Zn2+ and Mg2+ ions are of similar size. Zinc is the 24th most abundant element in Earth's crust and has five stable isotopes. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral. The largest workable lodes are in Australia, Asia, and the United States. Zinc is refined by froth flotation of the ore, roasting, and final extraction using electricity (electrowinning). Zinc has a melting point of about 692.68 K (419.53 °C, 787.15 °F) and boiling point of 1180 K (907 °C, 1665 °F) with density of 7.14 g/cm3 near room temperature and 6.57 g/cm3 when liquid.

Zinc is Recognized as a unique metal by: *Rasaratna Samuccaya (1300).*

1.3.5 Sources Of Zinc

- **Industrial Source**

Although zinc occurs naturally zinc is mostl found i the environmen due to human activitie like Mining, smelting metals (like zinc, lead and cadmium) and steel production, as well as burning coal and certain wastes can release zinc into the environment. In some cases, Industries also can release dust containin a grea amount of zinc into the air we breathe. Eventually, the zinc dust will settle out onto the soil and surface waters. Rain and snow also can remove zinc dust from the air. Most of the zinc in lakes, rivers and streams does not dissolve, but settles to the bottom. Some fish in these waters may contain high levels of zinc. High levels of zinc in the soil, water and air are often found along with high levels of other metals like lead and cadmium.

- **Natural Sources**

Zinc occurs naturally in air, water and soil, and in some foods like oysters, but it's also plentiful in red meat and poultry. Other good sources are beans, nuts, crab, lobster, whole grains, breakfast cereals, and dairy products.

1.3.6 Health Effects Of Zinc

Zinc can effectively reduce inflammation, boost immune function, reduce your risk of age-related diseases, speed wound healing and improve acne symptoms and it can also promote blood sugar management. Zinc supplements are tolerated generally But taking too much zinc can cause side effects like diarrhea, stomach pain, and vomiting, loss of appetite and headaches in some persons.

1.3.7 Uses Of Zinc

Most zinc is used to galvanise other metals, such as iron, to prevent rusting. Galvanised steel is used for car bodies, street lamp posts, safety barriers and suspension bridges. Large quantities of zinc are used to produce die-castings, which are important in the automobile, electrical and hardware industries. *(Online)*

1.4.0 Adsorption

Adsorption can be defined as a process in which material (adsorbate) travels from a gas or liquid phase and forms a superficial monomolecular layer on a solid or liquid condensed phase (substrate). Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface. This can occur because of physical forces or by chemical bonds. Usually it is reversible (the reverse process is called desorption); then it is responsible not only for a subtraction of substances but also for release. In most of the cases, this process is described at the equilibrium by means of some equations that quantify the amount of substance attached on the surface given the concentration in the fluid. These equations are called isotherms (the most famous are the Langmuir and the Freundlich equations) because of the dependence of their parameters on the temperature, which is one of the most important environmental factors affecting adsorption. Adsorption has a fundamental role in ecology: it regulates the exchanges between geosphere and hydrosphere and atmosphere, accounts for the transport of substances in the ecosystems, and triggers other important processes like ionic exchange and enzymatic processes *(Y. Artioli., in Encyclopedia of Ecology, 2008).*

1.4.1 Examples Of Adsorption

1. Gas like N_2, H_2 etc. get adsorbed on the surface of activated charcoal

2. Condensing water molecules sticks to a drinking glass

3. Painting is a form of chemical adsorption

1.4.2 Adsorbent

Adsorbent is the solid or liquid on whose surface, molecules of solids, liquid or gases are adsorbed. Solid, particularly in timely divided state, have large surface area and therefore act as good adsorbents e.g. activated charcoal, silica gel, alumina, clay, colloids etc.

1.4.3 Adsorbate

This is the gas or liquid that is accumulated over the surface of a liquid/solid i.e. substance that is deposited on the surface of another substance. E.g. the gases N_2, H_2, water molecules, paint are absorbates.

1.4.4 Types Of Adsorption

Depending upon the nature of the forces involved, two main types of adsorption process may be distinguished. these processes are:

1) Physical adsorption or the Physisorption

2) Chemical adsorption or Chemisorption

- **Physisorption**

Physisorption or physical adsorption is adsorption by van der Waals force it is a weak intermolecular attraction that takes place below the critical temperature of the adsorbate and can result in the development of a monolayer or multilayer. In keeping with idea that physical adsorption may lead to the formation of multilayer, these lead to more dependence on the nature of the adsorbate than that of solid adsorbent *(Hegazi., 2013)*.

- **Chemisorption**

In chemical adsorption, If the adsorbate molecules are bound to the surface of adsorbent by chemical bonds, the adsorption is known as chemical adsorption or chemisorptioIt is an irreversible adsorption.

1.4.5 Factor Affecting Rate Of Adsorption

1. Nature of absorbent

The adsorption of the gas depends on the nature of the adsorbent. A gas can be adsorbed on different absorbent surfaces in different amounts. For example, Hydrogen is weakly adsorbed on the alumina surface whereas it is strongly adsorbed on the nickel surface under certain conditions.

2. Surface Area

When we increase the surface area of the adsorbent there is an increase in the adsorption of gases. This is because when we increase the surface area there is more number of adsorbing sites. So finely divided solids and some porous substances are good adsorbents.

3. Nature of the Gas

In general, if a gas is more liquefiable it will be more easily absorbed. For example, gases like NH_3, HCl, Cl_2, CO_2, which can be liquefied easily are more readily adsorbed on the solids surface rather than permanent gases like O_2, H_2, etc.

4. Exothermic Nature

The heat of adsorption can be defined as the energy liberated when 1g mole of a gas is adsorbed on a solid surface. When the temperature is increased the kinetic energy of the gas molecules also increases which results in more number of collisions between the molecules and the surface.

5. Pressure

On the solid surface, there is a fixed number of adsorption sites where gas molecules can be adsorbed. Initially when the pressure has increased the rate of adsorption increases due to an increase in the gas molecules striking on the surface. Thus, an increase in the pressure increases the rate of adsorption linearly. But after sometime, it will reach a point when the pressure has no effect on the rate of adsorption as the number of adsorption sites is fixed and no more adsorption can happen in those sites. Hence, at that point, the extent of adsorption will be independent of the pressure.

1.4.6 Application Of Adsorption

1) Preparation of gas masks using activated charcoal.

2) Froth floatation method used for concentration of sulphide ores.

3) Use of silica gel to remove moisture.

4) Ion exchange method used to soften water.

5) Adsorption chromatography.

6) Use of charcoal powder to remove coloured impurities from sugar.

7) Use of charcoal for making high vacuum.

8) Action of soaps and detergents.

9) Formation of emulsions in cosmetics etc.

10) Heterogeneous catalysis.

1.4.7 Adsorption Isotherm

The adsorption isotherm is a graph that shows the surfactant concentration against the amount of surfactants adsorbed onto unit mass solid, when the solid (skin, hair, powder) is applied with a surfactant solution at a fixed temperature and reaches the equilibrium concentration.

1.4.8 Freundlich Theory

Freundlich adsorption gives the variation in the quantity of gas adsorbed by a unit mass of solid adsorbent with the change in pressure of the system for a given temperature. The expression for the Freundlich isotherm can be represented by the following equation:

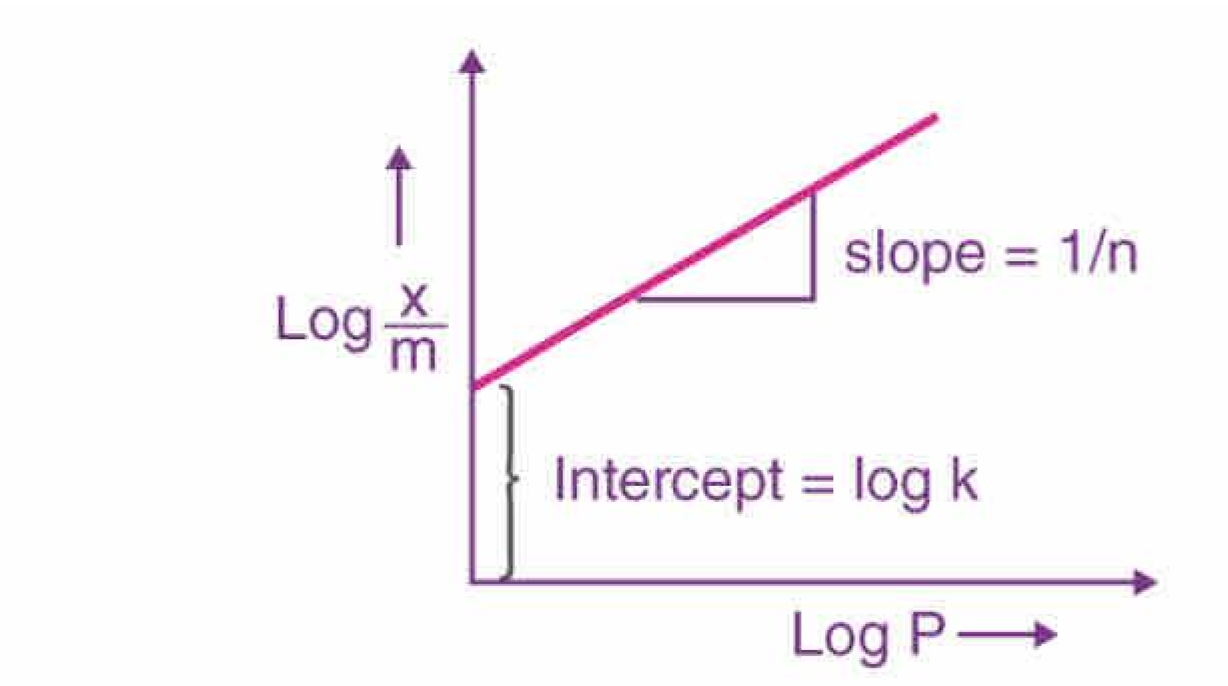
$$\frac{x}{m} = kP^{\frac{1}{n}}$$

where n>1

Where x is the mass of the gas adsorbed, m is the mass of the adsorbent, P is the pressure and n is a constant which depends upon the nature of the adsorbent and the gas at a given temperature. Taking the logarithm on both the sides of the equation, we get;

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log P$$

The plot of this equation is a straight line as represented by the following curve:



The Freundlic theory states that, at a constant temperature, the amount of adsorbate bound per unit weight of adsorbent, Q e (adsorption efficiency of the adsorbent) is a logarithmic function of the residual concentration in the fluid phase at equilibrium, C e.

1.4.9 Langmuir Theory

The Langmuir adsorption isotherm is used to describe the equilibrium between adsorbate and adsorbent system, where the adsorbate adsorption is limited to one molecular layer at or before a relative pressure of unity is reached *(H.J. Tobschall., 2006)*

The Langmuir adsorption isotherm was derived by the US chemist Irving Langmuir (1881–1957), using the kinetic theory of gases and making the assumptions that:

(1) the adsorption consists entirely of a monolayer at the surface.

(2) there is no interaction between molecules on different sites and each site can hold only one adsorbed molecule.

(3) the heat of adsorption does not depend on the number of sites and is equal for all sites.

The Langmuir adsorption isotherm is of limited application since for real surfaces the energy is not the same for all sites and interactions between adsorbed molecules cannot be ignored.

Equation:

$\theta = bp/(1+bp)$.

CHAPTER TWO

2.0 MATERIALS AND METHOD

2.1 MATERIALS

Zinc sulphate

Hydrochloric acid

Sodium hydroxide pellet

eionized water

2.1.1 EQUIPMENT AND GLASSWARE

Beakers

Sample container

pH meter

Orbital shaker

Filter paper

Syringe

Atomic Absorption Spectrophotometer

Analytical weighing balance

Funnel

Milling machine

Volumetric flask

Measuring cylinder

2.2 METHOD

2.2.1 ADSORBENT PREPARATION

A Raw Dangara middle-layer clay was used as the adsorbent. The clay was then crushed in a milling machine to a small granules (mesh size) and was stored in a polythene bag. Withou any further modification or treatment.

2.2.2 ADSORBATE PREPARATION

All chemicals used were of analytical grade. Stock standard solution of Zn^{2+} has been prepared by dissolving the appropriate amount of its nitrate salt in deionised water, acidified with small amount o hydrochloric acid. This stock solution was then diluted to specified concentrations Clay surface area of 15.72 m2/g, mean particle size o 212 µm) was obtained from Dangara, Abuja, Nigeria. All plastic sample bottles and glassware were cleaned, then rinsed with deionised water and dried at 60˚C in a tem- perature controlled oven. All measurements were conducted at the room temperature (28°C). The con- centration of Zn^{2+} was measured using a double beam flame atomic absorption spectrophotometer.

Preparation of acid and base solution

0.1M NaOH

4.0g of sodium hydroxide pellets was accurately weighed and dissolved in 100ml distilled water. This solution was transferred into a 1000cm3 volumetric flask and more distilled water was added to meet the 1000mg/l mark.

0.1M HCL

8.50 ml of hydrochloric acid (HCL) was diluted with distilled water to make up the volume to 1000 ml.

2.3 ADSORPTION RATE STUDY

2.3.1 EFFECT OF pH

The effect of pH was studied by measuring 100ml of the 50ppm solution into 6 different beakers and their pH was varied to obtain values of 4, 5, 6, 7, 8, and 9 using 0.1M NaOH and 0.1M HCl. 1g of clay was added to each solution and then placed in the orbital shaker for 60 minutes. The mixtures were filtered and the filtrates were analyzed using the atomic adsorption spectrophotometer and the values were recorded.

EFFECT OF ADSORBENT DOSAGE

Adsorbent at varying level of 1g, 5g, 10g, 15g and 20g were taken separately into 5 sample bottles, 100ml of 50mg/l Zn2+ solution with pH constant at PH9 was added to each bottle, then shaken with a mechanical shaker for 60mins.The mixtures were filtered and each of the filtrates analyzed using pg AA500F AAS.To determine the unadsorbed Zn2+ concentration in the supernatant solution.

2.3.3 EFFECT OF CONTACT TIME

I order to get the equilibrium adsorption time, 100ml solution of the initial 50 ppm solution was measured in 5 different beakers and 1g of the clay sample was weighed and added int each beakers. It was allowed in the orbital shaker for different time intervals (5, 10, 20, 30, and 60 minutes). The mixture was then filtered and the resulting filtrates of the metal solution were analyzed using the atomic adsorption spectrophotometer and values were recorded.

2.3.4 EFFECT OF CONCENTRATION

Various concentrations (10ppm, 20ppm, 30ppm, 40ppm, and 50ppm) of the aqueous solution were prepared from the stock solution by measuring 10, 20, 30, 40, and 50ml respectively and then filled with distilled water to meet the 1000ml mark.

100ml of each concentration was measured into a beaker and 1g of clay was added into each solution, stirred, and then transferred to the orbital shaker for 5 minutes. Afterward, the mixtures were filtered and the filtrate was analyzed using Atomic Adsorption Spectrophotometer and the values were recorded.

2.3.5 EFFECT OF TEMPERATURE

In order to study the effect of temperature, 100ml of 10ppm of the aqueous solution was measured into five different beakers and 1g of clay was added into each and was heated to 40°c, 50°c, 60°c, 70°c, and 80°c respectively, and allowed to settle before filtering. The mixtures were filtered and the filtrate was analyzed using the atomic adsorption spectrophotometer.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

The tables below were produced from the result of the Atomic Adsorption Spectrophotometer analysis carried out on the various filtrates obtained from the experiment using Dangara clay in the heavy metal solution.

TABLE 1.0: EFFECT OF pH ON ADSORPTION OF ZINC

pH	INITIAL CONCENTRATION (ppm) (Co)	EQUILIBRIUM CONCENTRATION (mg/l) (Ce)	AMOUNT ADSORBED (mg/l) (Co-Ce)	ADSORPTION PERCENTAGE (%)
4.00	50.00	10.021	39.979	79.958
5.00	50.00	8.899	41.101	82.202
6.00	50.00	8.841	41.159	82.318
7.00	50.00	3.679	46.321	92.642
8.00	50.00	0.414	49.586	99.172
9.00	50.00	0.297	49.703	99.406

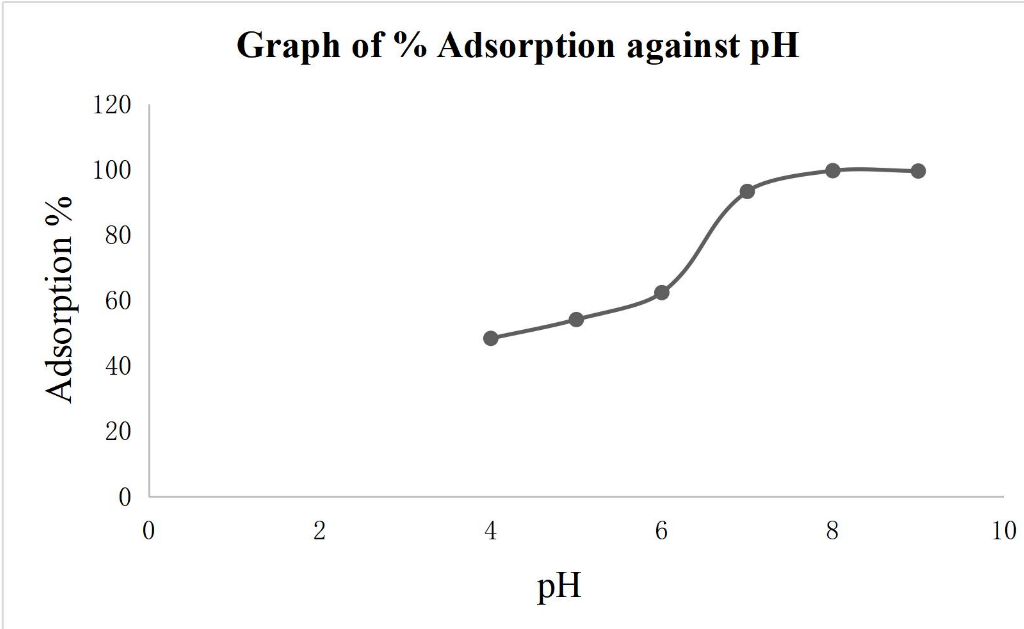


FIG 1: GRAPH OF % ADSORPTION AGAINST pH

As illustrated in the graph of adsorption % against pH value, the pH significantly influences the removal efficiency of zinc ion (Zn^{2+}) ions in the aqueous solution. The result shows that the removal of copper was increased from a minimum of 48.32% to a maximum of 99.578%. Maximum removal efficiency of copper from the aqueous solution increases with increasing pH from 3-8 with an exception to pH9. The maximum removal was obtained at pH8 with 1g of clay and 50ppm concentration. This result is a proof that pH value is a key adsorption parameter that strongly affects heavy metal removal because at lower pH the adsorption of copper is low due to the saturation of H^+ at the adsorption sites but with an increase with pH the sorption sites becomes available, (Bouamama Abbar *et al*., 2017).

TABLE 2.0: EFFECT OF ADSORBENT DOSAGE ON THE ADSORPTION OF ZINC

ADSORBENT DOSAGE (gram)	INITIAL CONCENTRATION (ppm) (Co)	EQUILIBRIUM CONCENTRATION (mg/l) (Ce)	AMOUNT ADSORBED (mg/l) (Co-Ce)	ADSORPTION PERCENTAGE (%)
1g	50.00	0.301	49.699	99.398
5g	50.00	0.290	49.710	99.42
10g	50.00	0.214	49.786	99.572
15g	50.00	0.111	49.889	92.822
20g	50.00	0.121	49.879	99.758

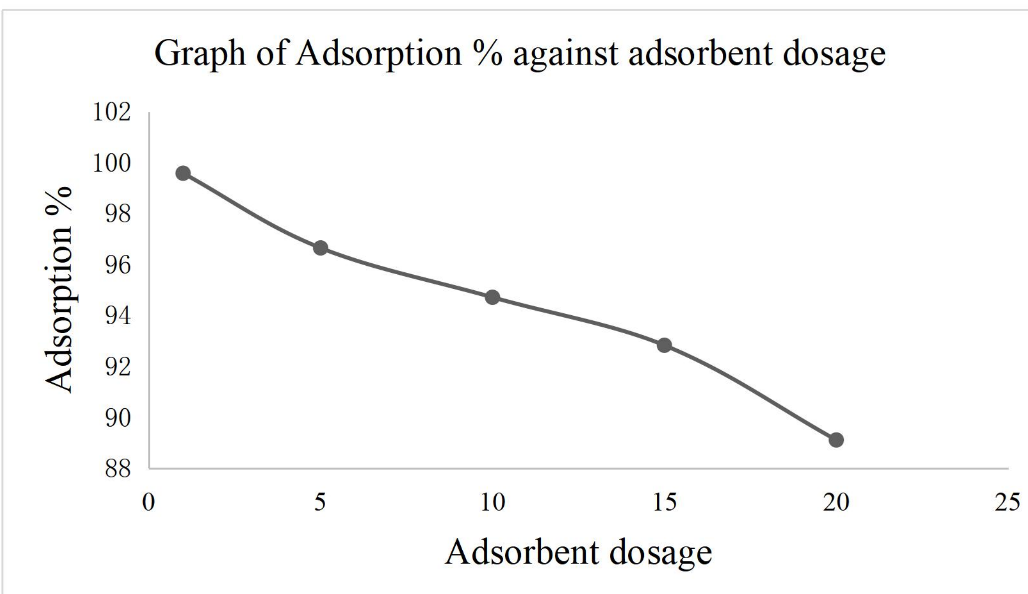


FIG 2: GRAPH OF ADSORPTION % AGAINST ADSORBENT DOSAGE

The graph illustrated in figure 2 shows the adsorption % against adsorbent dosage. It was observed from the graph that the removal efficiency of the Zinc reduces with an increase in adsorbent dosage. Using pH8 and 50ppm concentration of the aqueous copper solution, the maximum percentage removal of zinc was obtained at 99.576% at dosage of 1g. The decrease in adsorption capacity as the adsorbent dosage increases maybe because increased adsorbent dosage would provide increased amount of adsorption sites which leaves the sites unsaturated during the adsorption reaction (Li *et al*., 2013). The decrease in adsorbent removal could also be as a result of the decrease in total adsorption surface area and an increase in diffusion path length as a result of the overlapping of adsorption sites (Ahluwalia and Goyal, 2007).

TABLE 3.0: EFFECT OF CONTACT TIME ON ADSORPTION

TIME (minutes)	INITIAL CONCENTRATION (ppm) (Co)	EQUILIBRUIM CONCENTRATION (mg/l) (Ce)	AMOUNT ADSORBED (mg/l) (Co-Ce)	ADSORPTION %
5	50.00	0.593	49.474	98.948
10	50.00	0.387	49.448	98.896
20	50.00	0.206	49.524	99.048
30	50.00	0.168	49.709	99.418
60	50.00	0.124	49.789	99.578

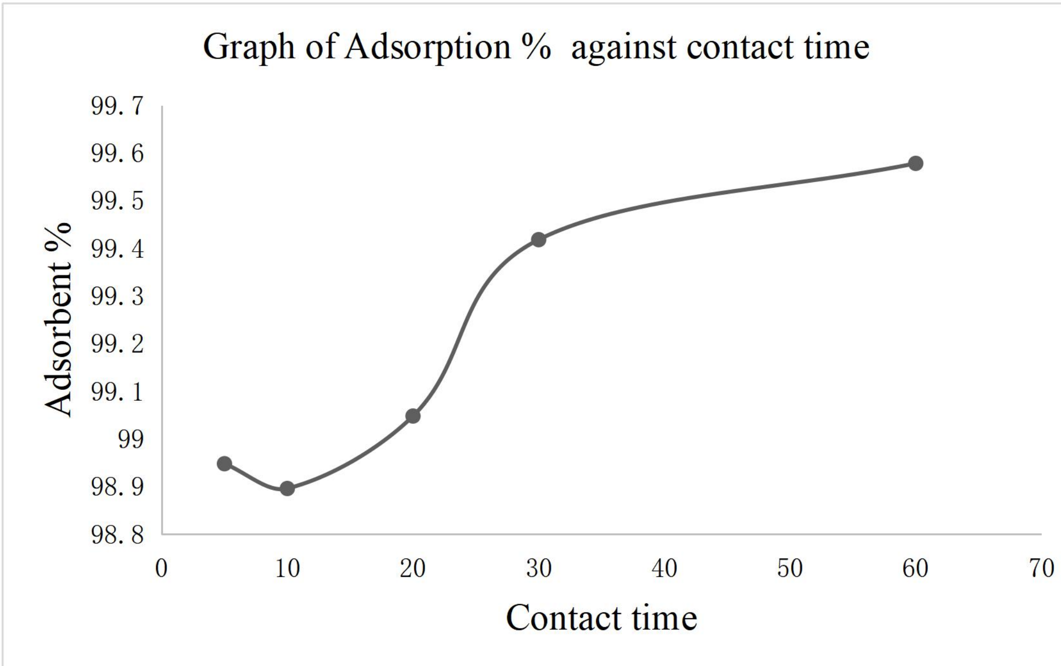


FIG 3: GRAPH OF ADSORPTION % AGAINST CONTACT TIME

From the graph of % adsorption against time, it was observed that the removal was increased with increased contact time. The result obtained indicated that Cadmium removal increased from 98.896% to 99.578% with contact time from 10 to 50 minutes. This adsorption process was carried out with 50ppm and pH8 aqueous solution using 1g of adsorbent dosage (clay). The graph of % adsorption against time shows that as the time of adsorption is changed, efficiency first decreased and further increases and as time progresses the surface coverage of the adsorbent is high and further no adsorption takes place. (Padmarathy *et al.,* 2016).

TABLE 4.0: EFFECTS OF INITIAL CONCENTRATION ON ADSORPTION OF ZINC ION

INITIAL CONCENTRATION (PPM) (Co)	EQUILIBRIUM CONCENTRATION (mg/l) (Ce)	AMOUNT ADSORBED (mg/l) (Co-Ce)	ADSORPTION %
10	0.000	9.961	99.61
20	0.025	19.918	99.59
30	0.058	29.846	99.49
40	0.101	39.816	99.54
50	0.121	49.787	99.574

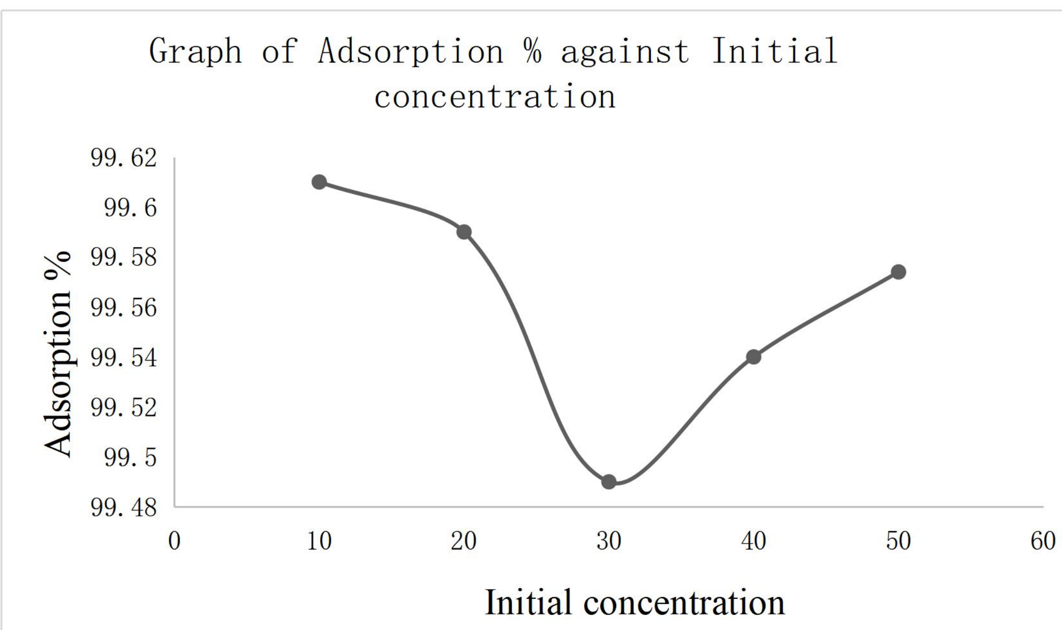


FIG 4: GRAPH OF ADSORPTION % AGAINST INITIAL CONCENTRATION

The graph of adsorption % against initial concentration illustrated above shows that there's a reduction in the removal of Zinc with an increase in concentration. The concentration varied but the pH value (pH8) and adsorbent dosage (1g) remained constant with 50ppm as its concentration. The maximum adsorption % was given at 99.61 and minimum adsorption % at 99.49. Higher concentration of the Zinc aqueous adsorbs lower % of copper because of the competitive dispersion of metal ion has increased at the sites available at the adsorbent surface (Wasewar, 2010). At lower concentrations, the amount of copper ion present in the adsorption medium are adsorbed by specific sites and the ratio between the adsorption sites and initial concentration is high. When the initial concentration increases, the ratio reduces and the specific sites are saturated. This result shows that the initial concentration of the Cu^{+} influences the removal of Zinc from its aqueous solution (Aravindhan *et al*., 2007).

TABLE 5.0: EFFECTS OF TEMPERATURE ON ADSORPTION OF COPPER ION

TEMPERATURE ()	**INITIAL CONCENTRATION (ppm) (Co)**	**EQUILIBRIUM CONCENTRATION (mg/l) (Ce)**	**AMOUNT ADSORBED (mg/l) (Co-Ce)**	**ADSORPTION %**
40°C	10.00	0.023	9.961	99.61
50°C	10.00	0.024	9.960	99.60
60°C	10.00	0.031	9.956	99.56
70°C	10.00	0.068	9.951	99.51
80°C	10.00	0.095	9.947	99.47

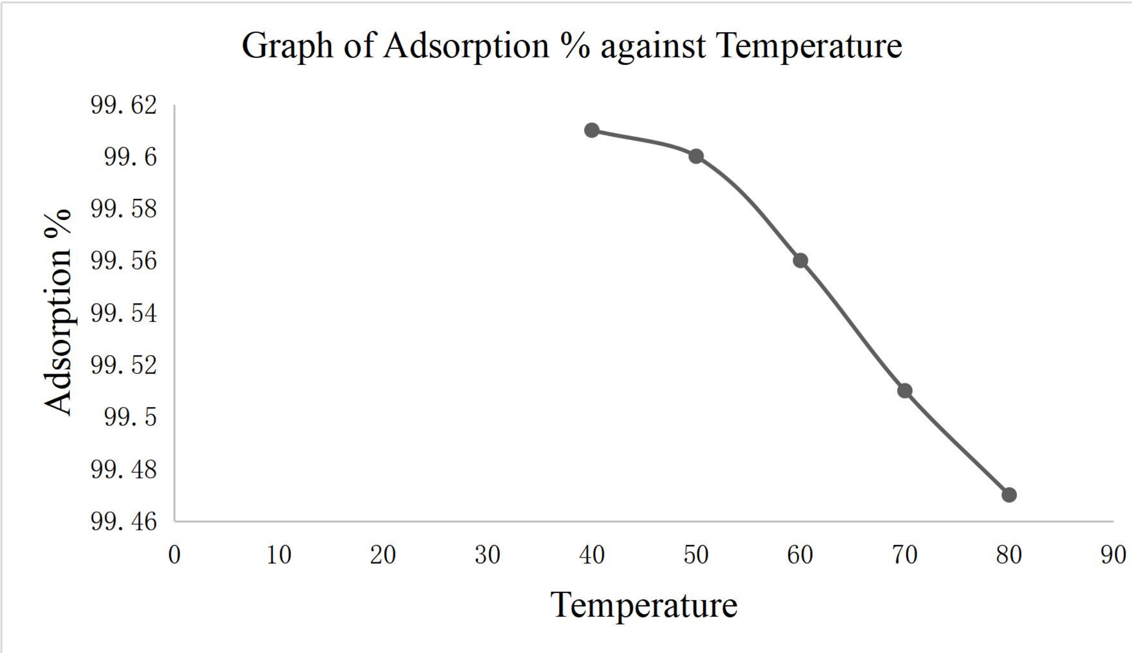


FIG 5: GRAPH OF ADSORPTION % AGAINST TEMPERATURE

As illustrated in the graph above, there's a decrease in adsorbent % removal as the temperature increases. This process carried out with 10ppm aqueous solution and pH value of 8 with 1g of clay under 60 minutes obtained maximum removal at 40 with an adsorption % of 99.61 which decreased to 99.47% with an increase in temperature. This confirms that the process of removal is exothermic as the as the adsorbent removal decreases with increasing temperature (Sharma, 2008).

TABLE 6: LANGMUIR ADSORPTION ISOTHERM RELATIONSHIP

Equilibrium concentration (C_e)	**Maximum Adsorption Capacity (q_e)**	**C_e/q_e**
0.039	0.996	0.039
0.082	1.992	0.041
0.154	2.985	0.052
0.134	3.987	0.034
0.213	4.979	0.043

$q_e =$

Where V is the volume of the Zn^{2+}solution in ml

m is the mass of the clay in gram (adsorbent dosage).

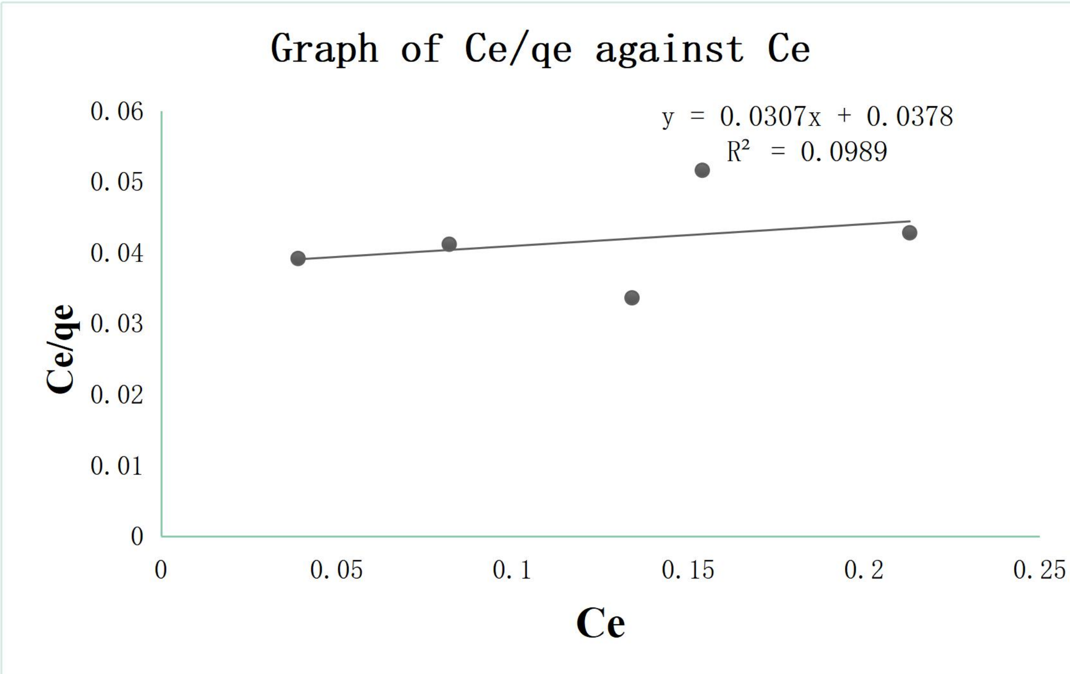


FIG 6: GRAPH OF C_e/q_e AGAINST C_e

The graph illustrated above shows that the experimental data fitted well for the Langmuir adsorption isotherm model. The straight line formed is proof that this adsorption process obeyed the Langmuir adsorption equilibrium.

TABLE 7: FREUNDLICH ADSORPTION ISOTHERM RELATIONSHIP

Log C_e	**Log q_e**	**LogC_e/q_e**
-1.409	-0.002	704.5
-1.086	0.299	-3.63211
-0.813	0.475	-1.71158
-0.873	0.601	-1.45258
-0.672	0.697	-0.96413

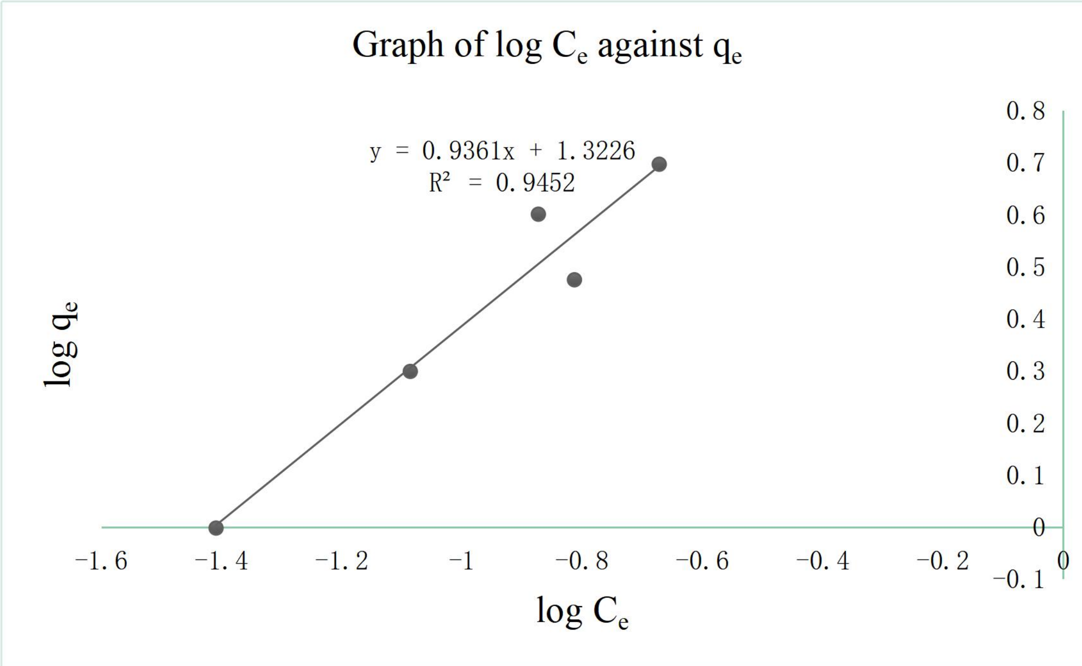


FIG 7: GRAPH OF LOG C_e AGAINST LOG q_e

The graph above shows that the experimental data obtained from the adsorption process obeyed the Freundlich adsorption isotherm and fitted well to the entire isotherm.

CONCLUSION

The purpose of this study was to determine the suitability of Dangara middle layer clay as an adsorbent for the removal of Zinc ions from its aqueous solution. Parameters like pH, adsorbent dosage, contact time, initial concentration, and temperature had an influence in the removal efficiency of zinc ons. The optimum pH was 8, the optimum time 60mins, the initial metal concentration (50ppm) used had less removal percentage compared to the value of a lower concentration (10ppm). The preferred temperature for maximum adsorption was observed at 40

The adsorption data were fitted to Langmuir isotherm and Freundlich isotherm. Freundlich model was found to be the best model for Cadmium with the R^2 value of 0.9452. Therefore, raw Dangara middle layer clay can be used as an effective adsorbent for the removal of copper ion (Zn^{2+}) from an aqueous solution.

RECOMMENDATION

The results from this research shows that clay is an excellent adsorbent and can be adapted for use in the treatment of waste or industrial water (i.e., effluents that contains heavy metals) before being discharged into water bodies. However, consumption of this clay i.e., edible clay can be harmful as these trace metals like copper which are important for survival can be adsorbed and excreted out by the human body. Excessive consumption of edible clay can lead to several underlying health issues. Clay is inexpensive to obtain, it has a large surface site and it is readily available for use. Clay can therefore it can be used exclusively or combined with other effective adsorbent for the efficient removal of heavy metals in an aqueous solution.

REFERENCE

Allard, A.-S. ., Renberg, L. and Neilson, A.H. (1996). Absence of 14co2 evolution from 14C-labelled EDTA and DTPA and the sediment/water partition ratio. *Chemosphere*, 33(4), pp.577–583.

Bolton, H., Li, S.W., Workman, D.J. and Girvin, D.C. (1993). Biodegradation of Synthetic Chelates in Subsurface Sediments from the Southeast Coastal Plain. *Journal of Environmental Quality*, 22(1), pp.125–132.

Bonglaisin, J.N., Mbofung, C.M.F. and Lantum, D.N. (2011). Intake of Lead, Cadmium and Mercury in Kaolin-eating: A Quality Assessment. *Journal of Medical Sciences*, 11(7), pp.267–273.

Buccigrossi, V., Russo, C., Guarino, A., de Freitas, M.B. and Guarino, A. (2017). Mechanisms of antidiarrhoeal effects by diosmectite in human intestinal cells. *Gut Pathogens*, [online] 9(1). Available at: https://gutpathogens.biomedcentral.com/articles/10.1186/s13099-017-0172-2 [Accessed 14 Nov. 2019].

Bucheli-Witschel, M. and Egli, T. (2001). Environmental fate and microbial degradation of aminopolycarboxylic acids. *FEMS Microbiology Reviews*, 25(1), pp.69–106.

Catalano, J.G. and Brown, G.E. (2005). Uranyl adsorption onto montmorillonite: Evaluation of binding sites and carbonate complexation. *Geochimica etCosmochimica Acta*, 69(12), pp.2995–3005.

Li, Z.A., Zhaung, P., Mcbride, B., Zou, B., and Wang, G., (2013). Health risk assessment for consumption of fish originating from ponds near Dabaoshan mine, south China. *Environmental Science and Research Journal.***20**: 58445854

Malkoc, E. and Nuhoglu, Y. (2010). *Nickel (II) Adsorption Mechanism from aqueous solution by a new Adsorbent- Waste Acorn of Quercus ithaburensis. AIChE Environmental Progress &Sustainable Energy, (vol 29. No. 3)*

Maron, S. H. and Lando, J. B. (1974) *Fundamentals of physical chemistry*: Macmillan publishing Co., London

Moor , W. J. (1972). *Physical Chemistry* . Prentice Hall, 4th Ed

Narjala Rama Jyothi (2020). *Heavy Metal Sources and Their Effects on Human Health*. DOI: 10.5772/intechopen.95370

Nasre-Dine Ahfira, Laurent Bizeta, and Davy Duriattic (2017). *Experimental investigation on removal of heavy metals by flaxfibres*

Odika P.O. and Onyia N.I. (2017). *A Review of the Health Implications of Heavy Metals in Food Chain in Nigeria.* https://doi.org/10.1155/2020/6594109

Padmavathy, K.S., Madhu, G., and Haseena, P.V., (2016). Procedia Technology **24:**

Padmavathy, V., Vasudevan, P. and Dhingra, S. C. (2003).*Biosorption of nickel (II) ions on Baker's yeast, Process Biochemistry, 38, 1389 – 1395*

Panchenkov, G. M. and Lebedev, V. P. (1976). Chemical Kinetics and Catalysis, Mir Publishers

Pavlov, K. F., Romankov, P. G., and Noskov, A. A. (1979)*Examples and Problems to the Course of Unit Operations of Chemical Engineering.* Mir Publishers, Moscow

Potorzhinskii, I., and E. Serpionova (1970) *Adsorption of vapours of organic solvents from a stream of moist air by activated carbon, Tr. Mosk. Khim. Tekhnol*. Inst 65 (1970): 79-82

Rajaaei, G., Mansouri, H.J and Hamidian, A.H., (2012). *Metals concentration in water the water of Chan nimehreservoirs, Iran. Bulletin of Environmental Contamination and Toxicology.* **3**: 495-500

Roginsky, S. Z. (1948) *Adsorption and Catalysis on Heterogeneous Surfaces, Moscow, USSR Acad.of Sc*

Romero-Gonzlez, J., Peralta-Videa, J.R., Rodriguez, E., Delgado, M., and Gardea J.L. (2006) *Potential of Agave lechuguilla biomass for Cr (III) removal from aqueous solutions: Thermodynamic Studies, Bioresource Technology, 97, 178 – 182*

APPENDIX

EFFECT OF pH

S/N	pH	UNIT	A	B	EQUILIBRIUM
1	4	mg/L (Zn^{2+})	25.62	26.06	25.840
2	5	mg/L (Zn^{2+})	23.63	22.292	22.961
3	6	mg/L (Zn^{2+})	18.91	18.77	18.840
4	7	mg/L (Zn^{2+})	3.900	2.86	3.380
5	8	mg/L (Zn^{2+})	0.202	0.22	0.211
6	9	mg/L (Zn^{2+})	0.25	0.278	0.264

For pH4:
Mean = 25.62+26.06
= = 25.840

EFFECT OF ADSORBENT DOSAGE

S/N	DOSAGE	UNIT	A	B	EQUILIBRIUM
1	1g	mg/L (Zn^{2+})	0.213	0.211	0.212
2	5g	mg/L (Zn^{2+})	1.68	1.676	1.678
3	10g	mg/L (Zn^{2+})	2.704	2.59	2.647
4	15g	mg/L (Zn^{2+})	4.04	3.138	3.589
5	20g	mg/L (Zn^{2+})	5.60	5.296	5.448

For 1g:

Mean = 0.213+0.211
= = 0.212

EFFECT OF CONTACT TIME

S/N	TIME (mins)	UNIT	A	B	EQUILIBRIUM
1	5	mg/L (Zn^{2+})	0.49	0.562	0.526
2	10	mg/L (Zn^{2+})	0.60	0.504	0.552
3	20	mg/L (Zn^{2+})	0.51	0.448	0.479
4	30	mg/L (Zn^{2+})	0.332	0.25	0.291
5	60	mg/L (Zn^{2+})	0.21	0.212	0.211

For 5 minutes:

Mean = 0.49+0.562
= = 0.526

EFFECT FOR INITIAL CONCENTRATION

S/N	CONCENTRATION (ppm)	UNIT	A	B	EQUILIBRIUM
1	10	mg/L (Zn^{2+})	0.038	0.04	0.039
2	20	mg/L (Zn^{2+})	0.080	0.084	0.082
3	30	mg/L (Zn^{2+})	0.152	0.156	0.154
4	40	mg/L (Zn^{2+})	0.177	0.191	0.134
5	50	mg/L (Zn^{2+})	0.21	0.216	0.213

For 10ppm

Mean = 0.038+0.04
= = 0.039

EFFECT FOR TEMPERATURE

S/N	TEMPERATURE (	UNIT	A	B	EQUILIBRIUM
1	40	mg/L (Zn^{2+})	0.04	0.038	0.039
2	50	mg/L (Zn^{2+})	0.049	0.031	0.040
3	60	mg/L (Zn^{2+})	0.050	0.038	0.044
4	70	mg/L (Zn^{2+})	0.048	0.05	0.049
5	80	mg/L (Zn^{2+})	0.048	0.058	0.053

For 40

Mean = 0.04+0.038
= = 0.039

The maximum adsorption capacity was calculated from Langmuir and Freundlich isotherm graphs. The amount of Zinc ion adsorbed per unit mass of clay was calculated by using the mass balance equation given as;

$q_{e}=$

Where;
q_e is the maximum adsorption capacity
Co is the initial concentration.
Ce is the equilibrium concentration of Zn^{2+}solution in mg/L
V is the volume of the Zn^{2+}solution in ml

m is the mass of the clay in gram (adsorbent dosage).
The mass in gram is converted t mg/l by multiplying by 1000

For 10ppm
$q_{e=}$

= 0.996

For 20ppm
=1.992

For 30ppm
=2.985

For 40ppm

=3.987

For 50ppm
=4.979