ADSORPTION STUDIES FOR THE REMOVAL OF Ni (II), Pb(II) AND Cu(II) IONS FROM AQUEOUS SOLUTION USING ORANGE PEEL

BY

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BEING
A DISSERTATION SUMBITTED TO THE
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IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF
MASTERS DEGREE IN SCIENCE (M.Sc.) IN PHYSICAL CHEMISTRY

DECEMBER, 2015.

DECLARATION

I hereby declare that this is the product of my own research efforts under the supervision of Prof. M.B. Ibrahim, and has not been presented and will not be presented elsewhere for the award of M.Sc. Degree in Physical Chemistry. All reference sources have been duly acknowledged.

LIRWANU SALISU
(SPS/11/MCH/00026)

CERTIFCATION

This is to certify that this research work titled "*Adsorption Studies for the Removal of Ni(II), Pb(II) and Cu(II) Ions from Aqueous Solution Using Orange Peel"* and the subsequent preparation of this research work by Lirwanu Salisu (SPS/11/MCH/00026) was carried out under my supervision.

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APPROVAL PAGE

This dissertation has been examined and approved for the award of Master of Science (M.Science.) Degree in Physical Chemistry.

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All thanks and praises are due to Allah, the most Beneficent, the most Merciful, Master of time and circumstances, because without Him, all this effort would be impossible.

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Finally, my sincere gratitude goes to all those who have either contributed towards success of this work or have supported my efforts during the course of my studies at Bayero University, Kano.

DEDICATION

This effort is dedicated to my parents: Alhaji Salisu Dankane Dankama and Hajia Umma Badamasi Dankama.

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ABSTRACT

Adsorption of Ni (II), Pb(II) and Cu (II) ions from aqueous solution onto orange peel was investigated to evaluate the effects of contact time, initial metal ion concentration, adsorbent dose, pH and temperature. The optimal pHvalue for Ni (II), Pb(II) and Cu (II) ions adsorption was found to be 6.0. Percent metal ion removal increases with: increase in contact time from 75 to 86.25% for Ni (II), 77.5 to 83.75% for Pb(II) and 61.12 to 66.42% for Cu (II) adsorption; increase in initial metal ion concentration from 52.5 to 99.8% for Ni (II), 62.5 to 99.52% for Pb(II) and 11.43 to 98.61% for Cu (II) adsorption; increase in adsorbent dose from 83.75 to 97.5% for Ni (II), 81.25 to 96.2% for Pb(II) and 59.25 to 70.27% for Cu (II) ions adsorption. Adsorption data were modelled using the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models. Langmuir isotherm model described the adsorption process better than the other models, with best correlation coefficients(R^2 = 0.9981, 0.9993 and 0.9998 for Ni(II), Pb (II) and Cu (II) ions adsorption, respectively),and the values of separation factor, $R_L \approx 0$ (for all three adsorption processes) suggesting a chemisorptions process. The adsorption kinetics was found to follow pseudo-second order kinetic model with best correlation coefficients relative to the other kinetic models (R^2 = 0.9825, 0.9490 and 0.9993 for Ni(II), Pb(II) and Cu (II) ions adsorption respectively), and rate constant, k_2(gmg^{-1}min^{-1})= 7.19, -0.79 and -1.03 for Ni (II), Pb(II) and Cu(II) adsorption, respectively,which also implies a chemisorption process. Thermodynamic parameters (ΔG°, ΔS° and ΔH°) for sorption system were determined at three different temperatures (303, 313 and 323K). FT-IR characterization of the adsorbent before and after adsorption suggested the possible contribution of some functional groups (present in the adsorbent) in the biosorption of the metal ions.

CHAPTERONE

1.0 INTRODUCTION

Heavy metals pollution has become an environmental problem throughout the world because they can be accumulated in the food chain and caused serious problems, not only for ecosystems, but also for human health. With the onset of fast developing industries and energy stations, metal wastes are being discharged into the environment through many ways (Gode and Pehlivan, 2006).

Nickel is a toxic metal, which may be present in a wastewater. Nickel salts are commonly used in metal plating and its concentration in industrial wastewaters range from 3.4 to 900mg/L. The chronic toxicity of nickel to humans and the environment is well known and high nickel concentration causes lungs and bone cancers (Demirbas *et al.,* 2002).Lead (Pb) is the most common environmental pollutant found in soils. Unlike other metals, Pb has no biological role, and is potentially toxic to microorganisms (Sobolev and Begonia, 2008).Lead toxicity affects the central and peripheral nervous system, renal function and vascular system (Needleman, 2004). Copper is non-toxic, but its soluble forms are poisonous when ingested through misguided intent (Scheinberg, 1991). High level of copper in the body is associated with a disease known as Wilson's disease in humans (Crawford *et al.,* 1985).

To reclaim or recover the wastewater polluted by heavy metals, considerable research has been carried out in developing techniques for heavy metals removal from water and wastewater. Removal of heavy metals from water can be achieved by various methods (Das *et al.*, 2008). Conventional methods for water reclamation such as chemical precipitation, chemical oxidation or reduction, filteration, electrochemical treatment, ion-exchange, membrane processing and electrolytic methods have been traditionally employed. However, the shortcomings of most of these methods are of high operational and maintenance costs, generation of toxic sludge and the complicated procedure involved in the treatment (Tobin and Roux, 1998). Therefore, there is a need for some alternative methods which can overcome all these problems and treat wastewater in an appropriate way. As a result, adsorption technique is consideredbetter in water reclamation from heavy metals because of its convenience, environmental friendliness, ease of operation and simplicity of design (Faust and Aly, 1987).

In bio-adsorption, removal of metal ions helps in the effective usage of bio-wastes as metals stick on to the surface of biological materials, which have high metal binding capabilities and specific heavy metal selectivity. It may involve one process or a blend of processes like adsorption, electrostatic interaction, micro-precipitation, and Ion-exchange (Belochini and VegIio, 1997; Vijayaraghavan and Yun, 2008; Changlun and Xiangke, 2006). This study reveals about the importance of using an environmental pollution free approach for the removal of heavy metal ions from water/wastewater. It has been found that various low-cost adsorbents developed from different origins show little or poor sorption potential for the removal of aquatic pollutants as compared to commercial activated carbon. Therefore, the search to develop efficient sorbent is still going on. From last few decades, biosorption process has emerged as a cost effective and efficient alternative method for water and wastewater treatment, utilizing naturally occurring and agricultural waste materials as biosorbents, as these are cheaper, renewable, and abundantly available. At present, biosorption field has been enriched by a vast amount of studies published in different journals. Various biosorbents have been examined for the removal of diverse types of pollutants from water (Srinivasan and Viraraghavan, 2010; Davis *et al.*, 2003; Aksu, 2005; Romera *et al.,* 2006; Volesky, 2007; Vijayaraghavan and Yun, 2008; Mathialagan and Viraraghavan, 2008; Gadd, 2009).

Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups (such as –OH, -COOH and C=C) responsible for biosorption of heavy metals (Wase and Foster, 1997). The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents (Bulut and Tez, 2003).

In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, peel, soybean and cottonseed hulls, peanut shells, hazelnut shells, rice husk, sawdust, wool, and orange peel (Haser, 2003; Wan Ngah and Hanafiah, 2007). The use of orange peel as a biosorbent material presents strong potential due to its high content of cellulose, hemicellulose, pectin (galacturonic acid) and lignin. As a low-cost adsorbent, orange peel is an attractive option for biosorption of dissolved metals. Ajmal *et al.* (2000*)* employed orange peel for metal ions removal from simulated wastewater.Some authors reported the use of orange peel as a precursor material for the preparation of an adsorbent by common chemical modification such as alkaline, acid, ethanol and acetone treatment (Perez-Marin*et al.*, 2008).

The goal of this study was to investigate the extent of removal of heavy metal contaminants ($Ni^{2+,}$ Pb^{2+} and Cu^{2+}) from aqueous solution by orange peel. Maximum adsorption capacity of the adsorbent, adsorption intensity of the adsorbate on adsorbent surface and adsorption potentials of the adsorbent were estimated by Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models.

1.1 WATER RECLAMATION TECHNIQUES

Water reclamation from heavy metals is of special concern because the importance of water to human life cannot be overemphasized. Additionally, heavy metal ions are highly toxic even at low concentration within the water bodies. If the metal ions are ingested beyond the permissible level, they can cause serious health disorders (Dadhaniya *et al.,* 2009).

Methods for the removal of heavy metals from wastewater/effluent are classified in to three: physical, chemical and biological. Physical treatment method requires least energy and capital for operation but it is least effective in the detoxification of water polluted by heavy metals. Biological techniques tend to have greatest energy and large capital cost, as in many cases the biodegradation processes involve a particular microorganism that attacks a specific molecular site, so that complete and rapid biodegradation of many contaminants may require not only specific environmental conditions, but also changing conditions to satisfy the needs of the microbe (Hoeppel and Hinchee, 1994), however they are highly effective in reducing conventional pollutants. Chemical processes lie in between the other two both in energy and effectiveness. Various treatment processes for the detoxification of wastewater/effluents include: membrane filteration, ion-exchange, chemical oxidation, precipitation, flocculation, ozonation, coagulation and electrochemical treatment method. However, all these processes are costly and cannot be employed by small industries to treat wide range of wastewater (Mall *et al.,* 2005).

1.1.1 Coagulation

This involved the use of chemicals (coagulants) which may be organic or inorganic compounds such as aluminium sulphate, aluminium hydroxide, and chloride or high molecular weight cationic polymer compounds. The purpose of the addition of coagulant is to remove almost 90% of the suspended solids from the wastewater (Awaleh and Soubaneh, 2014). The coagulants cause the pollutants to agglomerate and subsequently settle out during sedimentation process.

1.1.2 Chemical Oxidation

Oxidation is defined as a process by which electrons are transferred from one substance to another.

This leads to a potential expressed in volts referred to a normalized hydrogen electrode. From this, oxidation potentials of different compounds are obtained. Chemical oxidation appears to be one of the solutions to be able to comply with the legislation with respect to discharge in a determined receptor medium (Awaleh and Soubaneh, 2014). It also considered as an economically viable previous stage to a secondary treatment of biological oxidation for the destruction of non-biodegradable compounds, which inhibit the process.

1.2.3 Ozonation

Ozone is a strong oxidant that presents the advantage over other oxidants because it introduces 'strange ions' in the medium. This action can be presented on humic acid by the following reaction scheme:

(aromatic,unsaturated and saturated aliphatics) + O_3 **(**1. Electrophilic attack 2. Dipolar cyclo addition)
↓
Oxidized humic acid
↓
total degradation CO_2 +H_2O, Cl^-,NH^+_4,NO^-_3
↓
1. eletrophilic attack → hydroxylation → Polyhydroxyaromatics quinoids
↓ low molecular weight aliphatic acids ←muconic acid derivatives←ring breakdown decyclization
2. dipolar cycloaddition → ozonide formation → decomposition

(Kerc *et al.,* 2003)

Ozone is effective in many applications like the elimination of colour, disinfection, elimination of smell and taste, elimination of magnesium and organic compounds. In standard conditions of temperature and pressure, it has a low solubility in water and is unstable. It has an average life of a few minutes. Therefore to have the necessary quantity of ozone in the reaction medium, a large quantity has to used (Awaleh and Soubaneh, 2014).

1.2.4 Membrane Technology

Membrane processes such as microfilteration, ultrafilteration, nanofilteration and reverse osmosis are increasingly being applied for treating oily or emulsion wastewater. Emulsions-membranes are the most useful with stable emulsions, particularly water-soluble oily wastes. Pre-treatment to remove large particles and free oil is needed, especially if thin-channel membrane equipment is used. The membrane unit is usually operated in a semi-batch recycle. The wastewater feed is added to the process tank at the same rate as clean permeate is withdrawn, thus keeping a constant level in the tank. The retentive retention containing the oil and grease is recycled to the process tank. When the oils, grease and other suspended matter reach a certain predetermined concentration in the tank, the feed is stopped and the retentive allowed to concentrate. Membranes have several advantages including being positive barrier to rejected components, thus, the quantity of the treated water is more uniform regardless of the influent variations, no extraneous chemicals are needed (Awaleh and Soubaneh, 2014).

1.2.5 Ion Exchange

This is a process in which ions of one substance concentrated at a surface as a result of electrostatic attraction to the charged sites at that surface. The equilibrium between a bulk phase and the surface layer may be established with regard to neutral or ionic particles. If the adsorption process of one or several ionic species is accompanied by the simultaneous desorption of an equivalent amount of ionic species, the process is referred to as an ion exchange (Dabrowski, 2001).

1.2.6 Chemical Precipitation

This involves the addition of chemicals to wastewater bodies in order to change the chemical compositions of the pollutants, so that the newly formed compounds settle out during sedimentation. Chemical precipitation is a conventional technology used to treat mining-influenced water, including acid mine drainage, neutral drainage, and pit lake water. Precipitation can be induced by the addition of an alkali, sulphide, coagulant or other reagent that will bond with dissolved metal ions (Dabrowski, 2001).

1.2.7 Flotation

This involves the use of small gas bubbles injected into the wastewater which causes pollutant particles in the wastewater to rise to the surface for subsequent removal. Froth floatation is a process for selectively separating hydrophobic materials from hydrophilic ones. It is applicable in many processing and industries and wastewater treatment processes. It has been described as the most important operation used for the recovery of sulphide ores (Dabrowski, 2001).

1.2.8 Adsorption Technique

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid. Granualar activated carbon is a particularly good adsorbent medium due to its high surface area to volume ratio. One gram of a typical commercial activated carbon has a surface area equivalent to 1,000 square meters (Awaleh and Soubaneh, 2014).

Adsorption process provides an attractive alternative for the treatment of contaminated water and effluents, especially if the adsorbent is inexpensive and does not require an additional pretreatment step before its application (Özcan *et al*., 2005). Adsorption is known to be a better technique due to its convenience, ease of operation and relatively low cost of application.

1.2 STATEMENT OF PROBLEM

The tremendous increase in the use of heavy metals over the past decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. The toxic heavy metal ions have high solubility in the aquatic environments and thus can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metal ions may accumulate in the human body. If the metal ions are ingested beyond the permissible limit, they can cause serious health disorders (Dadhaniya *et al.,* 2009).

To deal with such problems, adsorption method was employed because it is environmentally friendly, economically affordable and easier to operate compared to other conventional treatment techniques (Faust and Aly, 1987).

1.3SIGNIFICANCE OF THE STUDY

A number of treatment technologies like chemical precipitation, ion –exchange, electrochemical treatment, and membrane filteration have been employed to remove heavy metals from wastewater, but these technologies have their major problems which include large production of sludge which requires further treatment and long term environmental impact of sludge disposal and so on (Eccles, 1999).

The significance of this research was thatadsorption method was employed to avoid such side production of sludge which can further contaminate the environment. In addition, the study helped to clean leaving environment by utilizing the usually discarded peel of orange for water reclamation processes.

1.4JUSTIFICATION OF THE STUDY

Adsorption studies for the removal of heavy metals on to orange peel (both inner and oily skin) has been done before and reported in the literature. In order to differentiate my study from the previous ones, the outer oily skin of the peel was removed during the preparation of the adsorbent for the experiment. The aim here was that I want to test whether the inner skin of the peel can still adsorb a significant amount of the heavy metal ions from aqueous solution.

FT-IR spectrum of the raw orange peel (without oily part) evidenced the presence of some functional groups responsible for metal uptake. Similarly, from the results of the experiment, a significant amount of the metal ions was removed from the aqueous solution. This implies that the white inner skin of the orange peel is a potential resource for adsorbing some toxic heavy metal ions from aqueous solution.

1.5 BACKGROUND INFORMATION

1.5.1 Treatment Technologies for Metals and Hazardous Wastes

Chemical, biological, and physical wastewater treatment processes are currently the most commonly used methods of treating aqueous hazardous wastes. Chemical treatment transforms waste into less hazardous substance using such techniques such as pH neutralization, oxidation and reduction, and precipitation. Biological treatment uses microorganisms to degrade organic compounds in the waste stream. Physical treatment processes include gravity separation, phase change systems, such as air and stream stripping of volatiles from liquid wastes and various filtration operations, including adsorption (Grey *et al.,* 1994).

1.5.2Adsorption

In general, adsorption is the process of collecting soluble substances (adsorbates) that are in a solution, on to a suitable interface (with adsorbent).Similarly, adsorption is defined as a process in which a gas, liquid or solid (adsorbate) adheres to the surface of a solid or (less frequently) a liquid (adsorbent), but does not penetrate it. Example is in the adsorption of gases by activated carbon (charcoal).Adsorption is a different process from absorption, in which a substance diffuses into a liquid or solid to form a solution. In principle, adsorption can occur at any of the following interfaces:

i. Gas-solid interface (as in the adsorption of Volatile Organic Compounds on activated carbon).
ii. Liquid-solid interface (as in the adsorption of an organic pollutant on activated carbon).
iii. Gas-liquid interface (as in the flotation process)

1.5.2.1 Types of Adsorption

Depending on the nature of attractive forces existing between the adsorbate and adsorbent, adsorption can be classified into two types: physical adsorption and chemical adsorption.In physical adsorption or physisorption, the forces of attraction between the molecules of the adsorbate and the adsorbent are of weak van der Waals' type. Since the forces of attraction are weak, the process of physisorption can be easily reversed by heating or decreasing the pressure of the adsorbate (as in the case of gases). On the other hand, in chemical adsorption or chemisorption, the forces of attraction between the adsorbate and the adsorbent are very strong; the molecules of adsorbate form chemical bonds with the molecules of the adsorbent (Dabrowski, 2001).

1.5.3 Adsorption Isotherms

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of materials adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an *adsorption isotherm*. Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational conditions and to design and optimize an operating procedure (Xu *et al.*, 2008; Pacyna *et al*., 2001; Mas *et al.*, 2010).

Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between the adsorbent and the adsorbate are described by the adsorption isotherms. The Langmuir and, Freundlich isotherm models are the most common isotherm models used to describe adsorption equilibrium for water and wastewater treatment applications. Other isotherm models are BET (Bruner, Emmett and Teller) isotherm, Temkin isotherm and Dubinin-Radushkevich (D-R) isotherm.However, fitting experimental data to only one isotherm model is not necessary to imply that a ‘pure' adsorption phenomenon has taken place. Therefore, different models should be employed (Abbasi and Alikarami, 2012).

1.5.3.1 Langmuir Adsorption Isotherm

Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent sorption energies and no interaction between adsorbed species. In other words, Langmuir isotherm assumes that a monolayer of adsorbate is formed on a uniform adsorbent surface, using the partially protonated groups of the adsorbent. The Langmuir isotherm has been successfully applied to many real sorption processes, and is expressed as follows:

$$q_e = \frac{Q_{\max} b C_e}{1 + bC_e} \quad \ldots\ldots(1)$$

Where q_e is the amount of substance adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), b is a constant related to the energy or net enthalpy of adsorption (L/mg), and Q_{max} represents the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/g). It also represents a practical limiting adsorption capacity when the surface is fully covered with adsorbate species and allows the comparison of adsorption performance, particularly in cases where the adsorbent did not reach its full saturation in experiments (Bayat, 2002). The Langmuir equation can be described by the linearized form as:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}\,b} + \frac{C_e}{Q_{max}} \quad \text{..} \quad (2)$$

By plotting (C_e/q_e) versus Ce, Q_{max} and b can be known if a straight line is obtained. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L which is defined by:

$$R_L = \frac{1}{1 + b\,C_{\square}} \quad \text{..} \quad (3)$$

Where b is the Langmuir energy constant related to heat of adsorption (Aksu and Isoglu, 2005) and C_o is the initial adsorabte concentration (mg/L). R_L value indicates the type of isotherm. The condition, $0<R_L< 1$ indicates favourable adsorption (physisorption), $R_L=0$ indicates irreversible adsorption (chemisorption), $R_L>1$ indicates unfavourable (chemisorption) $R_L=1$indicates linear adsorption (both physisorption and chemisorption)and when R_L□0 then this means that the adsorption process cannot be explained using Langmuir isotherm (McKay *et al.*, 1982).

1.5.3.2 Freundlich Adsorption Isotherm

In 1906, H.M.F. Freundlich proposed an empirical equation in order to study the relationship between concentration of metal ion in the adsorbent and at equilibrium solution. It is expressed by the following equation:

$$q_e = k_F (C_e)^{1/n} \quad \text{..} \quad (4)$$

Taking logarithm on both sides gives

$$log q_e = log k_F + \frac{1}{n} log C_e \quad \text{..} \quad (5)$$

Where k_F (Lg^{-1}) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. C_e is the equilibrium concentration of the metal ion in the solution (mgL^{-1}). The value of k_F and n determines the nature of the curve and the extent of the adsorption If n> 1, the adsorption is favoured (physisorption), if n<1 adsorption is not favoured (chemisorption) and for n=1 adsorption is linear (a combination of both chemical and physical adsorption processes). Values of k_F and n were calculated from the intercept and slope of the linear plots of log q_e versus log C_e, respectively (Bayat, 2002).

1.5.3.3 Dubinin-Radushkevich (D-R) Isotherm

This isotherm was proposed by Dubinin-Radushkevich in 1947. It assumes that the porous nature of the adsorbent determines the rate of adsorption. The linearized equation of D-R isotherm can be stated as:

$$ln q_\varepsilon = ln q_{max} - \beta\varepsilon^2 \quad \text{………………………………………..…………………} (6)$$

Where, q_e = equilibrium adsorption capacity(mg/g)

q_{max} = maximum adoption capacity (mg/g)

β = activity coefficient of mean free energy (mol^2/J^2)

ε = polanly potential(J/mol)

Where, $\varepsilon = RT ln(1 + \frac{1}{C_e})$ ……………………………………………………………...…….. (7)

A linearized plot of $ln q_e$ against ε^2 enables to determine the value of β and q_{max} from the slope and intercept respectively. From the value of β, biosorption mean free energy, E (kJ/mol) is determined as follows:

$$E = \frac{1}{(-2\beta)^{\frac{1}{2}}} \quad \text{……………………………..………………………………………..….. } (8)$$

If the value of E lies between 8 to 16 kJ/mol, the process is said to follow chemical ion exchange, while if the value of E < 8 kJ/mol, then the process follows physical adsorption.

1.5.3.4 Temkin Isotherm Model

Temkin model assumes that there is a uniform distribution of surface binding energy. Always heat of adsorption falls linearly and there is an interaction between the adsorbate and adsorbing species.

It is expressed as:

$$q_e = BlnA + BlnC_e \text{……………………………………………………………………….………} (9)$$

Where $B = \frac{RT}{b}$ ……………………………………………………………………..……….. (10)

A = Temkin isotherm constant

B = constant related to heat of sorption

b = heat of sorption (J/mol)

R = molar gas constant (8.314J/mol/K)

T = absolute temperature

The isotherm constants, Aand b are obtained from the plot of q_e versus lnC_e. While the value of “b” is found by substituting the value of B in equation (10). The heat of sorption,b ($Jmol^{-1}$) indicating a physical adsorption is usually in the range of 20 to 40 kJ/mol (Dabrowski, 2001).

1.5.4 Adsorption Thermodynamics

1.5.4.1 Van’t Hoff Equation

The Van’t Hoff Isochore or Van’t Hoff equation in chemical thermodynamics relates the change in equilibrium constant, K, of a chemical equilibrium to the change in temperature, T, given the standard enthalpy change, ΔH°, for the process. It was proposed by Dutch Chemist Jacobus Henricus Van’t Hoff in the year 1884.The Van’t Hoff equation has been widely utilized to explore the changes in state functions in a thermodynamic system. The Van’t Hoff plot, which is derived from this equation, is especially effective in estimating the change in enthalpy, or total energy, and entropy, or amount of disorder, of a chemical reaction. Under standard conditions, the Van’t Hoff equation is given as;

$$\frac{dlnk}{dT} = \frac{-\Delta H^{\circ}}{RT^{2}} \tag{11}$$

$$\frac{dlnk}{d\left({}^{1}\!/_{T}\right)} = \frac{-\Delta H^{\circ}}{R} \tag{12}$$

The definite integral between temperatures, T_1 and T_2 is

$$ln\left(\frac{K_1}{K_2}\right) = \frac{-\Delta H^{\circ}}{R\left(\frac{1}{T_2} - \frac{1}{T_2}\right)} \tag{13}$$

In this equation, K_1 and K_2 are the equilibrium constants at absolute temperatures, T_1 and T_2 respectively, and ΔH° is assumed constant.

1.5.4.2 Development of Van’t Hoff Equation from Thermodynamics

From Gibb’s free energy and Gibb’s free energy isotherm equation respectively;

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{14}$$

$$\Delta G^{\circ} = -RTlnK \tag{15}$$

$$lnK = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{16}$$

1.5.4.3 Van’t Hoff Plot

For a reversible reaction,, the equilibrium constant can be measured at a variety of temperatures. This data can be plotted on a graph with lnK on the y-axis and ${}^{1}\!/_{T}$ on the x-axis. The data should have a linear relationship, the equation for which can be found by fitting the data using the linear form of the Van’t Hoff equation.

$$lnK = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{17}$$

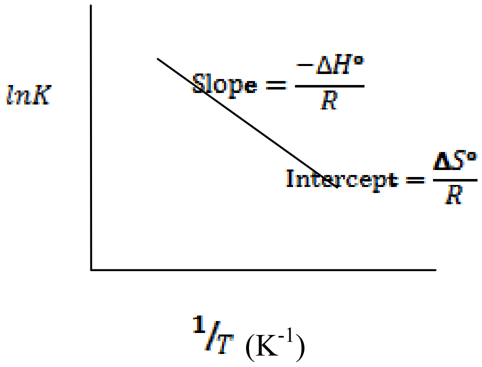
This graph is called the Van’t Hoff plot and is widely used to estimate the enthalpy and entropy of a chemical reaction. From this plot, $\frac{-\Delta H^\circ}{R}$ and $\frac{\Delta S^\circ}{R}$ are the slope and the intercept of the linear fit. By measuring the equilibrium constant, K, at different temperatures, the Van’t Hoff plot can be used to assess a reaction when temperature changes (Kim and Tae Woo, 2012; Ichikawa *et al.,* 2010). Knowing the slope and intercept from the Van’t Hoff plot, the enthalpy and entropy of a reaction can easily be obtained using:

ΔH = - R x Slope; and

ΔS = R x intercept

The Van’t Hoff plot can be used to determine the enthalpy of a chemical reaction. Change in enthalpy can be positive or negative, leading to two major forms of the Van’t Hoff plot as:

- **Endothermic Reaction Van’t Hoff Plot**



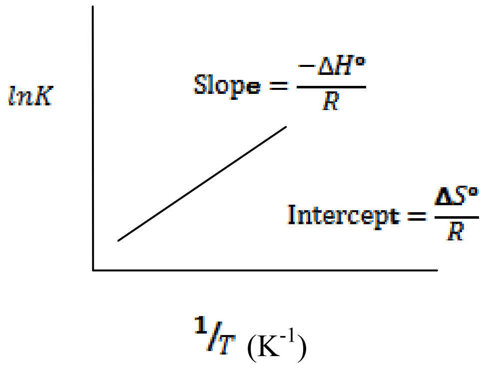
For an endothermic reaction, heat is absorbed, making the net enthalpy change positive. Thus, according to the definition of the slope:

$\text{Slope} = \frac{-\Delta H^\circ}{R}$; ΔH > 0 and R is the gas constant

Thus, $\text{Slope} = \frac{-\Delta H^\circ}{R} < 0$

Therefore, for an endothermic reaction, the Van’t Hoff plot should always have a negative slope

- **Exothermic Reaction Van’t Hoff Plot**



For an exothermic reaction, heat is released, making the net enthalpy change negative. Thus, according to the definition of the slope:

Slope $= \frac{-\Delta H^{\circ}}{R}$; ΔH < 0 and R is the gas constant

Slope $= \frac{-\Delta H^{\circ}}{R} > 0$

Therefore, for an exothermic reaction, the Van’t Hoff plot should always have a positive slope.

1.5.4.4 Deduction of Thermodynamic Parameters from Van’t Hoff Plot

Thermodynamics analysis provides valuable information on the mechanism ofadsorption.

The thermodynamic parameters, Gibb’s free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) of the adsorption processes were calculated using the following equations:

$$\Delta G^{\circ} = -RT\ln K \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

From Van’t Hoff equation;

$$lnK = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

Where K is a constant representing the ratio $\frac{q_e}{C_e}$

Note that q_e is measured in mg/g and C_e is measured in mg/L. mg/g(w/w) and mg/L(w/v) can both be expressed in parts per million(ppm) unit. This implies that K is a dimensionless constant. Therefore;

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

Where, Ceis the concentration of the metal ion (mg/L), q_e is the amount of metal ion at equilibrium in unit mass of adsorbent (mg/g), R is the gas constant (8.314J/mol/k) and T is the temperature (K). The values of ΔS° and ΔH° were obtained from the intercept and slope of the linear plot of $\ln\left(\frac{q_e}{C_e}\right)$ versus$\frac{1}{T}$.

1.5.5 AdsorptionKinetics

The controlling mechanism or rate determining step of metal uptake on the adsorbent was studied by pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models. From the literature, biosorption of divalent metal ions by various adsorbents mostly followed pseudo-second order reaction (Ho *et* a*l.,* 2001; Krishnan and Anirudhan, 2003).

1.5.5.1 Pseudo-First Order Kinetic Model

This model assumes that the rate of adsorption is directly proportional to the number of adsorption sites on the adsorbent. It is expressed as;

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

Where q_e and q_t are the amount (mg/g) of metal ions adsorbed at equilibrium and at time, t, respectively and k_1 is the equilibrium constant.Thus, a plot of log (q_e - q_t) against t gives the value of k_1 from the slope.

1.5.5.2 Pseudo-Second Order Kinetic Model

This model assumes that the rate of adsorption is based on the square of the number of vacant sites on the adsorbent. It is expressed as;

$$\frac{t}{q_t} = -\frac{1}{k_2 q_e^2} + \frac{t}{q_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

A plot of t/q_t against t predicts the values of k_2 and q_e from the intercept and slope respectively.

1.5.5.3 Intra-Particle Diffusion Model

This model describes about the diffusion of the adsorbate particles from the outer surface into the pores of the composite (Weber and Morris., 1963). It is expressed as;

$$q_t = K_d t^{0.5} + I \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (23)$$

Where, $k_d$is the intra-particle diffusion rate constant (mg/gmin$^{1/2}$). “I” characterizes the extent of the diffusion. A plot of q_t against $t^{½}$ gives the values of $k_d$and I from the slope and intercept respectively.

1.5.6 Toxicity and Sources of Heavy Metals in the Environment

Heavy metals are natural constituents on earth commonly known with properties such as having persistence, high toxicity and also serving as non-biodegradable pollutants when they accumulate in the ecosystem. The term heavy metals have been given a wide range of meaning by different authors. Many different definitions have been proposed based on density, atomic number or atomic weight and chemical properties or toxicicity (Duffus, 2002). According to Parker (1989), Lozet and Mathieu (1991) and Morris (1992), heavy metal is a metal with specific gravity greater than 5. Nriagu and Pacyna (1988); Hawkes (1997) describe heavy metal as a general collective term which applies to the group of metals and metalloids with atomic density greater than 4g/cm^3. Rauf *et al.*(2002) defined heavy metal as a large group of chemical elements with atomic mass greater than 50 carbon units. According to Duffus (2002), heavy metal is a meatl ion which is hard or non-polarisable, preferentially form complexes with similar non-polarisable ligand and the bonding in these complexes is mainly ionic, or a soft metal ion preferentially binds to polarisable, soft ligand to give rather more covalent bonding.Heavy metals can be classified into three different types, which include toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co. Sn etc.) precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and Radionuclides (such as U, Th, Ra, Am) (Wang and Chen, 2009).

Source of heavy metals that penetrate into the water system can be from both natural and anthropogenic sources. The main source of heavy metal contamination involves urban industrial aerosols, solid wastes from animals, mining activities, also industrial and agricultural chemicals. Sometimes most heavy metals contaminate the water system through various industrial activities or even from acid rain, which breaks down the soils and rocks, releasing heavy metals into water resources (Alluri *et al*., 2007). Table 1.1 (page 21) summarizes the variety of sources of heavy metals, diseases/disorders they caused as well as their maximum permissible limits in drinking water.

The presence of heavy metals in the environment leads to a growing number of environmental problems such as the deterioration of several ecosystems due to its persistent accumulation. For instance, nickel is one of the carcinogenic elements which cause serious lung and kidney problem aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis if its permissible level is exceeded (Borba *et al*., 2006). Lead (Pb) might also cause damage to the kidney, liver and reproductive system. The toxic symptoms of nickel are anaemia, insomnia, muscles weakness, headache, hallucination and renal damages (Naseem and Tahir, 2001). The emission of heavy metals into the environment from mining operations will pollute the surface and also underground water sources. This may lead to soil pollution and the increasing rate of pollution when mined ores are dumped on the ground surface for manual dressing (Batterbee *et* *al*., 1988; Nriagu, 1989 and Garbarino *et al*., 1995). When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissues (Trueby, 2003). Animals that gaze on such contaminated plants and drink from polluted waters, as well as marine lives that breed in heavy-metal- polluted waters also accumulated such metals in their tissues and milk, if lactating (Horsfall and Spiff, 1999). All these require established wastewater regulations to minimize the human and environmental exposure to hazardous heavy metals.

Table 1.1: Sources, Health implication and Maximum Contaminant Level (MCL) of Some Heavy Metals in Drinking Water (Alluri *et al*., 2007; Babel and Kurniawan, 2003).

Metal	**Source**	**Associated Diseases/Disorders**	**Maximum Contaminant Level (MCL) in Drinking Water (mg/L)**	
			SON (2007)	WHO (1993)
Lead	Paint, pesticides, smoking, mining, automobile emission etc.	Anaemia, vomiting, coma, constipation etc.	0.01	0.0015
Copper	Mineral supplements, industrial emissions, oysters, insecticides etc.	Kidney diseases, tuberculosis, arthritis etc.	1	0.05
Nickel	Industrial aerosols, fertilizers, metal plating etc.	Lung and bone cancers, kidney disorder, pulmonary fibrous etc.	0.02	0.006
Zinc	Refineries, Metal plating, plumbing.	Depression, lethargy etc.	3	0.8
Cadmium	Welding, electroplating, Cd-Ni batteries.	Kidney diseases, mental retardation etc.	0.003	0.003
Chromium (VI)	Metal plating, mining,petroleum refining.	Asthma and lung cancer.	0.05	0.05
Arsenic	Mining, Smelting process, volcanoes, glass manufacture	Hemorrhage, Severe diarrhea, headaches etc.	0.01	0.01

1.6 RESEARCH QUESTIONS

At the end of this research, the following questions should be answered viz:

i. Does orange peel show a good adsorptive ability for the removal of toxic metal ions from aqueous solution?

ii. Does variation of some experimental conditions offer a significant effect for the removal of toxic metal ions from aqueous solution?

iii. Do values of all experimental data obtained from this research show a significant agreement with those obtained from previous similar studies?

1.7 RESEARCH HYPOTHESIS

The research is aimed to determine if orange peel is a possible resource for heavy metals removal and if metal uptake is dependent on change in experimental conditions. Banana peel and other natural waste materials have been successful for biosorption of heavy metal ions, in part due to the presence of some component functional groups such as carboxylic and hydroxyl groups (Wase and Foster, 1997). Due to the fact that these functional groups are present in orange peel, the hypothesis here was that orange peel would be successful in removing toxic metal ions from aqueous solution if employed.

1.8 SCOPE AND LIMITATION OF THE STUDY

Fresh orange peel without any chemical modification was used as an adsorbent for the removal of Ni(II), Pb(II) and Cu(II) ions from their aqueous solutions prepared from the nitrate salts of the metals. All experiments were carried out in batch and in triplicate.

1.9 AIM AND OBJECTIVES OF THE STUDY

The aim of this work was to determine whether prepared orange peel could be used to remove heavy metal ions from aqueous solutions through the following objectives:

i. To determine the effect of contact time between adsorbate and adsorbent on heavy metal ions removal.

ii. To determine if metal removal is dependent on the strength of the adsorbent dosage.

iii. To determine if variation exists in the efficiency of heavy metal uptake depending on the specific metal and its concentration.

iv. To determine the effect of pH on heavy metal ions removal.

v. To determine the effect of temperature on heavy metal uptake by adsorbent.To determine which of the isotherm models describe the adsorption of the metals ions onto orange peel better than the others

vi. To determine if the available functional groups present in the biosorbent (orange peel) participate in the biosorption process.

CHAPTER TWO

2.0 LITERATURE REVIEW

The idea of using various agricultural products and by-products for heavy metal removal from aqueous solution has been investigated by so many of authors. Friedman and Waiss (1972), Randall *et al.*, (1974) have investigated the efficiency of number of different organic waste materials as adsorbents for heavy metals. The obvious advantages of this method compared to others are lower cost involved when organic waste materials are used. Activated carbon adsorption appears to be a particularly competitive and most effective process for heavy metals removal at trace quantities (Huang and Blankenship, 1984).

For that reason, the uses of low-cost materials as possible biomass for metal removal from wastewater have been highlighted (Panday *et al.,* 1985). These materials range from industrial products, industrial wastes and some natural materials including agricultural products and by-products as mentioned earlier.

The available literature as summarized in Table 2.1 and 2.2 (page 25 and 26) showed that some of these non-conventional adsorbents possess good adsorption capacity for heavy metal removal from industrial effluents.

Table 2.1: Summarized Review of Adsorption Capacities of some Biosorbents for the Removal of Heavy Metal Ions.

Type of adsorbent	**Maximum adsorption capacity (mg/g) and maximum % Adsorption***					**Source/Reference**
	Cd^{2+}	**Cr^{3+}**	**Cr^{6+}**	**Zn^{2+}**	**Hg^{2+}**	
Orange peel (White inner skin)	-	-	125	-	-	Masri *et al.*, 1974
Orange peel (outer skin)	-	-	275	-	-	Masri *et al.*, 1974
Nut shell	1.3	-	1.47	-	–	Orhan and Buyukgungor, 1993
Sawdust	-	-	10.1 97.85*	-	-	Bryant *et al.*, 1992; Ibrahim and Jimoh, 2011
Black oak bark	25.9	-	-	-	100	Teles and Gonzalez, 1994
Peanut skins	74	-	-	-	-	Randall *et al.*, 1978
Rice husk ash	20.24	-	-	-	66.66	Kumar and Bandyopadhyay, 2006
Moss	46.5	-	-	-	-	Low and Lee, 1991
Lignin	-	-	-	95	-	Srivastava *et al.*, 1994
Red wood bark	27.6	-	-	-	250	Masri *et al.*, 1974
Powdered *Zea mays* cob	77.1*	-	-	-		Ibrahim, 2012
Pinas pinaster bark	8	19.45	-	-	-	Teles and Gonzalez, 1994
Senna leaves	-	-	250	-	-	Masri *et al.*, 1974
Amberlite IRA 400(CI) Resin			99.92*			Ibrahim and Jimoh, 2008
Granular *Zea mays* cob	69.9*	-	48.5*	-	-	Ibrahim, 2012; Ibrahim and Jimoh, 2011
Modified peat	-	76	-	-	-	Kertman *et al.*, 1993
Modified wool	87	-	17	-	632	Masri *et al.*, 1974
Exhausted coffee	1.48	-	1.42	-	-	Orhan and Buyukgungor, 1993
Copper-coated moss	-	18.9	7.1	-	-	Low and Lee, 1991

Table 2.2: Summarized Review of Adsorption Capacities of Some Biosorbents for the Removal of Ni (II), Pb(II), Fe(II) and Cu (II) Ions.

Type of adsorbent	**Maximum adsorption capacity (mg/g)/ maximum % Adsorption***				**Source/Reference**
	Ni (II)	**Pb (II)**	**Cu(II)**	**Fe(II)**	
Sawdust (Dalbergia Sissoo)	10.47	0.6216	-		Rehman *et al*., 2006
Sawdust (Oak tree)	3.37	-	-	95*	Argun *et al*., 2007; Ibrahim and Jimoh, 2011
Walnut sawdust	6.43	-	-		Bulut and Tez, 2003
Groundnut shells	7.49	-	-		Shukla and Pai, 2005
Redwood bark	-	6.8182	-		Masri *et al*., 1974
Pinus pinaster bark	-	3.33	-		Teles and Gonzalez, 1994
Jute fibres	5.26	-	-		Shukla and Pai, 2005
Corn cobs	13.5	8.29	7.62		Zacaria *et al*., 2002
Granular *Zea mays* cob	72.8*	-	-	100*	Ibrahim, 2012; Ibrahim and Jimoh, 2011
Granular coal	97.5*	-	-	98.57*	Ibrahim, 2012; Ibrahim and Jimoh, 2011

2.1 CONVENTIONAL METHODS FOR HEAVY METALS REMOVAL

Numerous treatments on the heavy metals removal from contaminated water have already been applied years ago, which can be divided into biological, chemical and physical processes. However, in most treatments, physical and chemical processes are more pronounced. The conventional methods for heavy metal removal include chemical precipitation, membrane filtration, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, evaporation, oxidation, and activated carbon adsorption (Yu *et al.*, 2000). Chemical precipitation is the most widely used for heavy metal removal from inorganic effluents based on pH adjustment in a basic solution. Coagulation-flocculation is also employed to treat wastewater with heavy metals by adding a coagulant during the coagulation process (Aziz *et al.*, 2008).

2.1.1. Shortcomings of Conventional Methods

There are so many problems which emerge during the conventional treatment of effluents.These include high operational and maintenance costs, generation of toxic sludge, low selectivity, and complicated procedure involved in the treatment (Wu *et al*, 2004). The shortcomings of conventional treatment of effluents are listed in Table 2.3 (page 28).

Table 2.3: Conventional Methods for Heavy Metals Removal and their Disadvantages (Eccles, 1999)

Conventional method	**Disadvantages**
Chemical precipitation	• Large production of sludge that require further treatment • Slow metal precipitation • Poor setting • Aggregation of metal precipitates and • Long term environmental impacts of sludge disposal
Coagulation –Flocculation	• This treatment method might destabilize any colloidal particles and further results in sedimentation
Ion Exchange	• High initial capital for operation • High maintenance cost
Membrane filtration	• Low flow rate • High initial capital for operation • High maintenance cost
Electrochemical treatment	• High initial capital cost

2.2 ADSORPTION METHOD

Adsorption process has gained interest as a more promising method for the long term as it is considered better in water treatment because of its convenience, ease of operation and simplicity of design (Faust and Aly, 1987). The term “adsorption” is referred to as a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions (Babel and Kurniawan, 2003) The advantages of adsorption process in removing or minimizing the heavy metals even at low concentration enhance its application as one practical treatment.

The effectiveness of the adsorption process is mainly influenced by the nature of solution in which the contaminants are dispersed, the molecular size, and the polarity of the contaminant as well as the type of adsorbent used. Adsorption also exists due to the attractive interactions between a surface and the species being adsorbed at certain molecular level (Dabrowski, 2001)

2.2.1 Motivation for the Use of Adsorption Process

Many researchers considered adsorption process as a better and effective technique for wastewater treatment due to the fact that, many industrial wastewaters contain substances that:

i. Are difficult to remove via conventionally secondary treatment.
ii. Are toxic or hazardous.
iii. Have the potential for creating noxious vapours or odours, or for imparting colour to the wastewater.
iv. Are present in very high concentrations that make their removal via other methods difficult.
v. Are non-biodegradable pollutants.

2.2.2 Adsorption

In any adsorption process, the material being adsorbed (e.g., a pollutant) is simply but effectively removed from one phase (e.g., a wastewater) and transferred to another phase (e.g., activated carbon). This means that adsorption is a *physical separation process* in which the adsorbed material is not chemically altered. Since the chemical characteristics of the adsorbed material are not changed, the use of adsorption in wastewater treatment is associated with the removal of hazardous materials from the wastewater and its subsequent transfer to the activated carbon (for example). This implies that the activated carbon now contains the hazardous materials. Therefore, appropriate actions must then be taken to treat the spent activated carbon at the end of a cycle. The carbon can be:

i. Regenerated (i.e., the hazardous material may be removed via stripping).
ii. Disposed of (together with the pollutants it contains) in a landfill.
iii. Destroyed (together with the pollutants it contains) in an incinerator (Ozcan *et al.*, 2005).

2.3 COMMON ADSORBENTS

The following are some of the common adsorbents employed in wastewater treatment:

i. Activated carbon: a char-like material with high surface area.
ii. Silica gel: hard, granular, porous material made by the precipitation from sodium silicate solutions treated with an acid.
iii. Activated alumina: aluminum oxide activated at high temperature and used primarily for moisture adsorption.
iv. Aluminosilicates (molecular sieves): porous synthetic zeolites used primarily in separation processes.

2.3.1 Activated Carbon as an Adsorbent

Activated carbon is by far the most common adsorbent used in wastewater treatment. Since, during adsorption, the pollutant is removed by accumulation at the interface between activated carbon (adsorbent) and the wastewater (liquid phase), the adsorption capacity of activated carbon is always associated with very high surface area per unit volume.

The high surface area characteristic of activated carbon is obtained with a two-step process used in carbon manufacturing:

i. Pyrolysis of raw material (typically a high carbon source such as coal, wood and nut shells) to drive off (distil) the lighter fraction, producing a charred, highly carbonaceous solid residue;

ii. The second step is the activation of the charred residue via oxidation (typically with air or steam) to form a network of pores and passages with high surface area.

The pores in activated carbon typically range from 10 to 10,000Åin diameter. Pores having a diameter larger than 1000Å are called macropores, while those having a diameter smaller than 1000Å are called microspores. Micropores are primary responsible for the adsorption characteristics of activated carbon (Pope, 2003).

Typically, surface areas in activated carbons range from 500 to 1500m^2/g of carbon. Activated carbon is produced in particle sizes up to a few millimetres, and the total surface area available for adsorption is not significantly affected by the particle size since micropore structure responsible for adsorption does not change appreciably with particle size. This implies that the total adsorption capacities of small and large particles are not different although the time taken to achieve equilibrium can differ significantly because of diffusion effects (Dabrowski, 2001).

Carbon having large particle sizes of 1mm or more is called “granular”. This material can be packed in columns through which a liquid can be passed, and can be regenerated after use.

Carbon having smaller particle sizes of the order of tens of µm is called “powdered”.This material can only be used by direct addition to a liquid and must be removed after use (e.g., by filtration) and disposed of. In general, the larger the particle size, the more expensive is the carbon.

Two sizes of activated carbon are typically used in wastewater treatment:

i. Granular Activated Carbon (GAC) — with a particle size larger than 0.1mm (100µm) and it is commonly used in adsorption columns

ii. Powdered Activated Carbon (PAC) - With a particle size smaller than 74µm and it is commonly used by direct addition.

The apparent densities of GAC and PAC are 0.22 to 0.5 kg/L and 0.34 to 074kg/L respectively, while the real density is between 2 to 2.l kg/L.Activated carbon is regarded as a widely used adsorbent for heavy metals removal due to its large specific surface area and affinity to metals.Despite this, its highly expensive cost of production and operations, as well as its needs for certain complexing agents that will improve its removal performance lead to a development of alternative adsorbentswith similar characteristics, high regeneration capability, easy availability and cost effectiveness to replace it(Özcan *et al.*, 2005). To date, hundreds of studies on the use of low-cost adsorbents have been published. Agricultural wastes and natural substances have been studied as potential low-cost adsorbents for the treatment of wastewater plagued with heavy metals.

2.4 LOW-COST ADSORBENTS

In recent years, effort on searching for materials which are available in large quantities such as natural materials, agricultural wastes or industrial by-products that can be utilized as low-cost adsorbents has been intensified by many researchers. Low-cost adsorbents are defined as materials that are abundant in nature, or that are by-products or waste materials from another industry (Bailey *et al*., 1999). An adsorbent can be termed as low-cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Nasim *et al*., 2004). Previous adsorption studies have been focused on plant wastes such as the maize leaf (Babarinde *et al*., 2006), orange peel (Ekpete *et al.,* 2010), rice husk ash and coconut husk (Olayinka *et al.*, 2009), and tea waste leaves (Ahluwalia and Goyal, 2005) which can be used either in their natural form or after some physical and chemical modifications. The conversion of these materials into adsorbents can help to reduce the cost of waste disposal and provide an alternative treatment to replace the commercial activated carbon (Kurniawan, 2006a; Kurniawan, 2006b).

Ekpete *et al.,*2010 employed orange peel for the removal of Cr(VI) and Zn(II) ions from aqueous solution. The optimum removal occurred at a pH of 3 and at 30^0C temperature. Langumir model yielded the maximum adsorption capacity of 8.068 and $1.078 mgg^{-1}$ for Cr(VI) and Zn (II) ions respectively.

Perez-Marin*et al.,* 2008 employed orange peel for the removed of cadmium, zinc and lend. The maximum removal was found to be 0.25mmol/g.

Annadural *et al*., 2003 employed orange peel for the removal of Cu^{2+}, Co^{2+}, Ni^{2+} Zn^{2+} and Pb^{2+} from water, at 30^0C, optimum pH of 7 and concentration range of $5\text{-}25 mgL^{-1}$. The maximum adosption capacity was found to be $7.75 mgg^{-1}$ for the removal of Pb^{2+}.

Gönen and Serin (2012) utilize orange peel for the removal of Ni(II) ions from aqueous solution at optimum pH of 5. The maximum removal capacity was found to be $62.3 mgg^{-1}$ at 25^0C.

CHAPTER THREE

EXPERIMENTAL

3.0 MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Chemicals and Reagents

All the chemicals and reagents used were of analytical grade purity and used without further purification. These include the metal salts of Ni(II), Pb(II) and Cu(II) ions (i.e. $Ni(NO_3)_2.6H_2O$, $Pb(NO_3)_2$ and $Cu(NO_3)_2.3H_2O$), concentrated HNO_3, concentrated HCl and NaOH crystals.

3.1.2 Equipments and Apparatus

The following equipments/apparatus were used during this study: digital pH meter (Jenway 3320), flame atomic absorption spectrophotometer (Perkin Elmer, Analyst 100), FT-IR –spectrophotometer (Cary 630), orbital shaker (Innova 4000), analytical weighing balance (Mettler Toledo PB602-S), analytical sieve, volumetric flasks (l000cm^3, 500cm^3, 250cm^3 and 100cm^3), beakers (500cm^3, 250cm^3, 100cm^3 and 50cm^3), measuring cylinders (100cm^3, 50cm^3 and 10cm^3), 75mm funnels, filter papers (Advantec, 5A), masking tape, syringe (10 cm^3), conical flask etc.

3.1.3 Preparation of the Adsorbent

Orange peel was obtained from a local market. The collected biomass was extensively washed with tap water to remove any particulate (external dirt and sand), and then washed with distilled water. The biosorbent was cut into small pieces, oven-dried at 105°C, crushed and sieved through an analytical sieving material to obtain a powdered orange peel which was used in the adsorption experiments (Gönen and Serin, 2012)

3.1.4 Preparation of Standard Solutions and Reagents

Standard solution (1000mg/L) of each metal ion was prepared by dissolving required amount of nitrate salt of the metal ion [$Ni(NO_3)_2.6H_2O$, $Pb(NO_3)_2$ and $Cu(NO_3)_2.3H_2O$] into 0.1M nitric acid. The experimental solutions of desired concentrations were prepared by successive dilutions of the standard stock solutions using 0.1M nitric acid solution. Also, 0.5M NaOH and 0.5M HCI solutions used for pH adjustments were prepared (Zahra *et al.,* 2013).

3.1.4.1 Preparation of 0.1M Nitric Acid Solution

This was prepared by shaking 6.7cm^3 of 15M HNO_3 with about 500cm^3 of distilled water and made it to the mark with same distilled water in l000cm^3 volumetric flask.

3.1.4.2 Preparation of 1000mgL $^{-1}$ Nickel (II) Stock Solution

This was prepared by dissolving 4.95g of $Ni(NO_3)_2.6H_2O$ in some 0.1M HNO_3 and made it to the mark using the same solution of 0.1M HNO_3 in 1000cm^3 volumetric flask.,

3.1.4.3 Preparation of 1000mgL $^{-1}$ Lead (II) Stock Solution

This was prepared by dissolving 1.599g of $Pb(NO_3)_2$ in some 0.1M HNO_3 made it to the mark using the same solution of 0.1M HNO_3 in 1000cm^3 volumetric flask,

3.1.4.4 Preparation of 1000mgL $^{-1}$ Copper (II) Stock Solution

This was prepared by dissolving 3.8g of $Cu(NO_3)_2.3H_2O$ in some 0.1M HNO_3 and made it to the mark using the same solution of 0.1M HNO_3 in 1000cm^3 volumetric flask.

3.1.4.5 Preparation of 0.5M HC1 Solution

This was prepared by shaking 20.8cm^3 of 12M HCl with some distilled water and made it to the mark with the same distilled water in a 500cm^3 volumetric flask.

3.1.4.6 Preparation of 0.5M NaOH Solution

This was prepared by dissolving 10g of NaOH in some quantity of distilled water and finally made it to the mark with the same distilled water in a 500cm^3 volumetric flask.

3.2 BATCH ADSORPTION AND OPTIMIZATION STUDIES

In order to determine the effects of physicochemical parameters such as pH, adsorbent dosage, contact time, initial metal ion concentration of solution and temperature, the adsorption experiments were performed by batch equilibrium method. The experiments were carried out in 250cm^3 conical flasks by mixing a pre-weighed amount of adsorbent with 100cm^3 of each metal ion solutions of desired concentrations and pH at room temperature using an orbital shaker operating at 200rpm. Initial pH of solutions was adjusted using 0.5M HCl and 0.5M NaOH solutions. The samples were removed from the shaker at pre-determined time intervals and metal ion solutions were separated from the adsorbent by filtration and the filtrates were analysed by using Atomic Absorption Spectrometry (AAS) to determine the equilibrium metal ion concentrations (Zahra *et al.,* 2013). All results presented in this report are average of triplicate readings.The percentage removal of metal ions and the amount of metal ions adsorbed on orange peel at equilibrium (q_e) were calculated using the following equations:

$$\% \text{ Removal} = \frac{(C_i - C_e)100}{C_i} \quad \text{……………..…………………………………………………….. (24)}$$

$$\textit{Adsorption capacity at equilibrium}, q_e \ (mgg^{-1}) = \frac{(C_i - C_e) \times V}{m} \quad \text{……………..………..… (25)}$$

Where C_i = initial adsorbate concentration (mg/L), C_e = equilibrium metal ion concentration in the solution (mg/L), V = volume of the solution (cm^3), m = mass of adsorbent (g)

3.2.1 Effect of Contact Time

Influence of contact time on adsorption of Ni (II), Pb(II) and Cu(II) ions onto orange peel was investigated by mixing 1g of orange peel with 100cm^3 of 20mgL^{-1} initial concentration for each metal in a 250cm^3 conical flask at a constant temperature (25°C). The mixture was agitated for 5min of contact time and then filtered. This procedure was repeated with same fresh mixtures but with different agitation periods of 10, 15, 30, 45, 60, 120 and 180 min. The filtrates were taken for AAS analysis in clean sample bottles.

3.2.2 Effect of Adsorbent Dose

Different doses (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5g) of the peel were weighed and transferred into separate conical flasks and 100cm^3 of 20mg/L initial concentration of each of the metal ions solutions were added to each flask and the mixtures agitated for 30minutes. The contents of the flasks were filtered and the filtrates taken, for AAS analysis.

3.2.3 Effect of Initial Concentration

To study this effect, 100cm^3 of each of the metal ions solutions of desired concentrations (10, 15, 30, 45, 60, 75, 90, and 105mg/L) were mixed with 1.0g of the adsorbent and agitated for 30 minutes. The mixtures were filtered and the filtrates analyzed by AAS.

3.2.4 Effect of Adsorbate pH

To study this effect, 100cm^3 of 20mg/L of each of the metal ions solutions at pH 2, 4, 6, 8 and 10 were mixed with 1g of the adsorbent. The pH adjustments were made using 0.5M NaOH and 0.5M HCl solutions. The mixtures were agitated for 30 minutes. The mixtures were then filtered and the filtrates analyzed by AAS.

3.2.5 Effect of Temperature

To investigate this effect, experiments were conducted by mixing 100cm^3 of 20mg/L initial metal ions concentrations with 1g of adsorbent at a temperature of 303, 313 and 323K. The mixtures were agitated for 30 minutes after which they were filtered and the filtrates analyzed by AAS.

3.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR) ANALYSIS

In order to determine which functional groups were responsible for metal uptake, FT-IR spectra of the orange peel before and after adsorption of each metal ion was recorded in the range of 650-4000cm^{-1}. Comparison of these spectra enables us to conclude that adsorption has taken place. The FT-IR spectroscopic analysis of the adsorbent before and after adsorption was carried out as follows:

Infrared energy was emitted from a glowing blackbody source. This beam passed through an aperture which controlled the amount of energy presented to the sample (and, ultimately, to the detector). The beam entered the interferometer where the "spectral encoding" took place and the resulting interferogram then exits the interferometer. The beam entered the sample compartment where it is transmitted and the resulting specific frequencies of energy, which are uniquely characteristic of the sample (orange peel), were absorbed. The beam finally passed to the detector where final measurement took place. Here, the signals were measured by detectors which were specially designed to measure the special interferogram. The measured signal was digitized and sent to the computer where the Fourier transformation took place. The final infrared spectrum was presented to the user for interpretation and any further manipulation.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

The outcome of all studies in this work which include the effects of some physicochemical parameters (such as contact time, initial concentration and pH) on the adsorption process, adsorption isotherms, adsorption thermodynamics and kinetics, as well as FT-IR spectroscopic analysis were presented as follows:

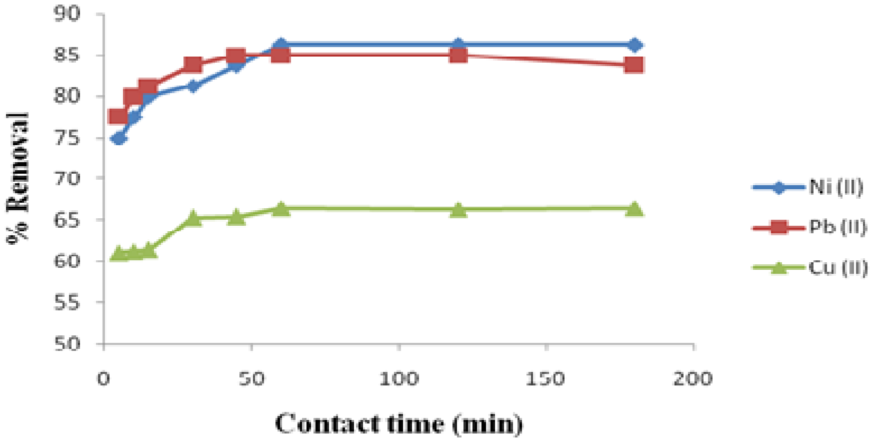


Figure 4.1: Effect of Contact Time on Adsorption of Ni (II), Pb (II) and Cu (II) Ions onto Orange Peel

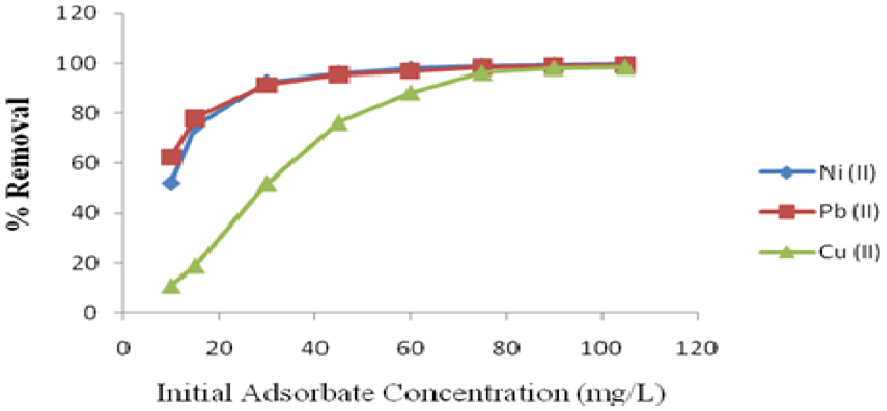


Figure 4.2: Effect of Initial Adsorbate Concentration on Adsorption of Ni (II), Pb (II) and Cu(II) Ions onto Orange Peel

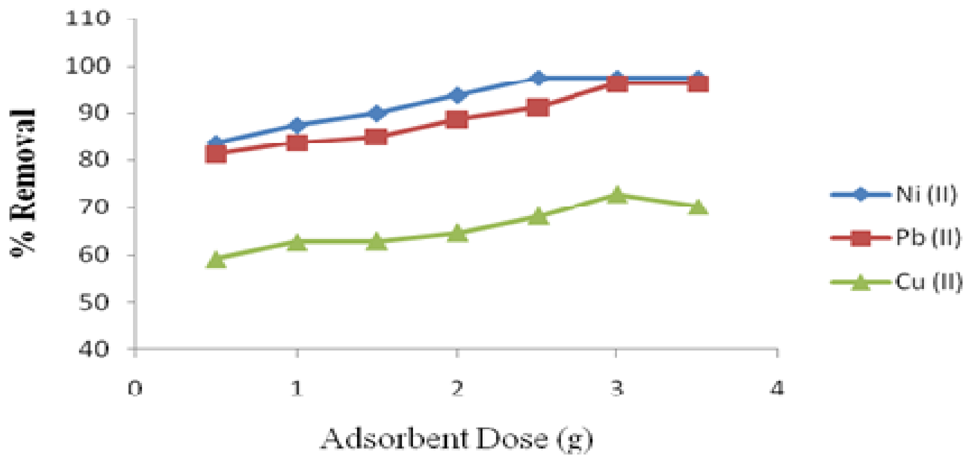


Figure 4.3: Effect of Adsorbent Dose on Adsorption of Ni (II), Pb (II) and Cu (II) Ions onto Orange Pee

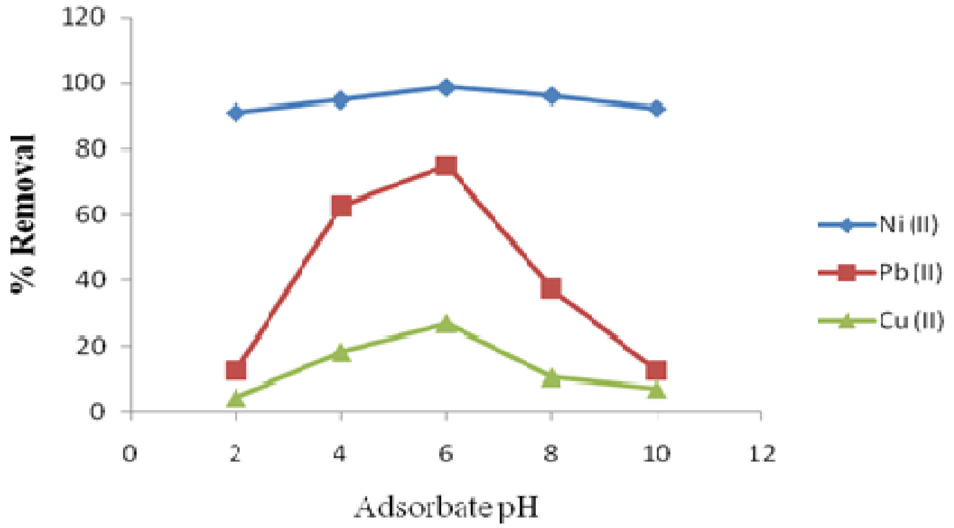


Figure 4.4: Effect of Adsorbate pH on Adsorption of Ni (II), Pb (II) and Cu (II) Ions onto Orange Peel

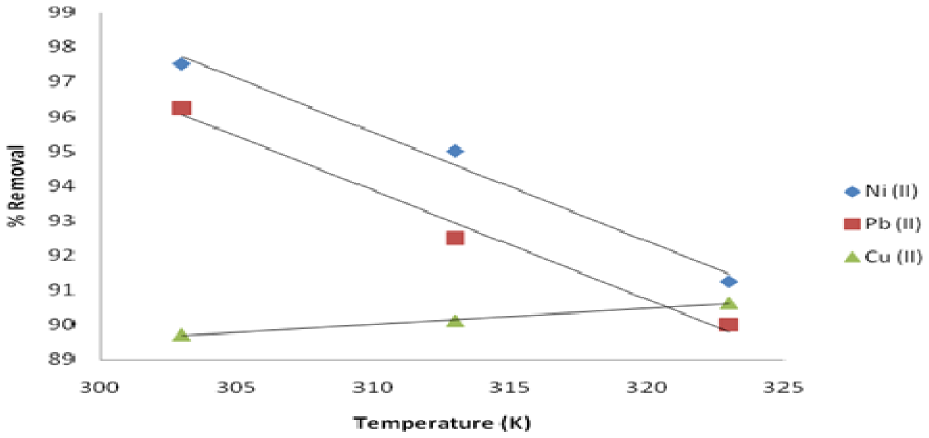


Figure 4.5: Effect of Temperature on Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel

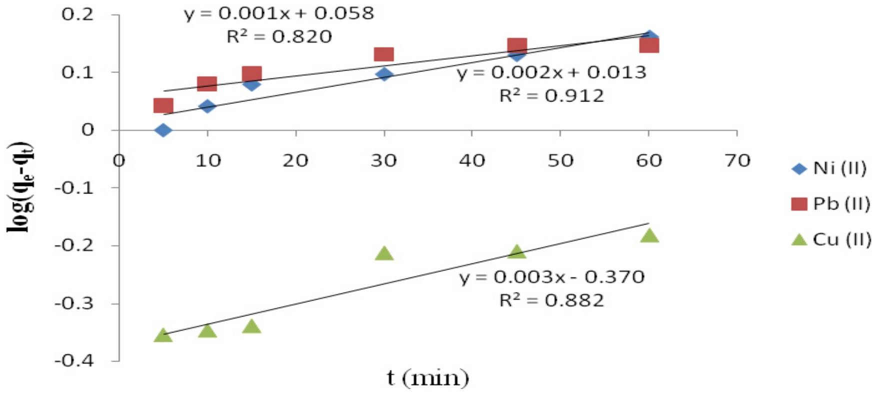


Figure 4.6: Pseudo First Order Kinetic Plots for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel

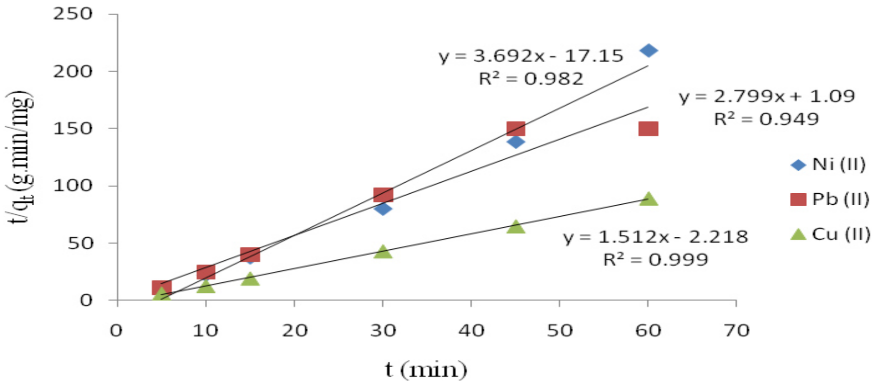


Figure: 4.7: Pseudo Second Order Kinetic Plots for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel

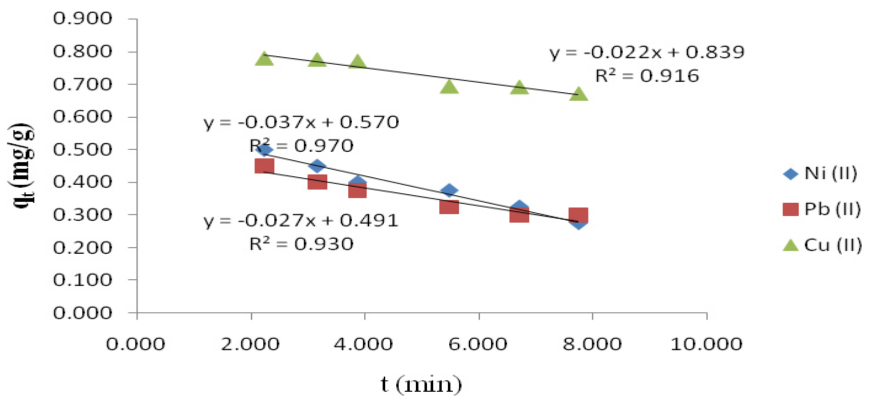


Figure: 4.8: Intraparticle Diffusion Model Plots for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel

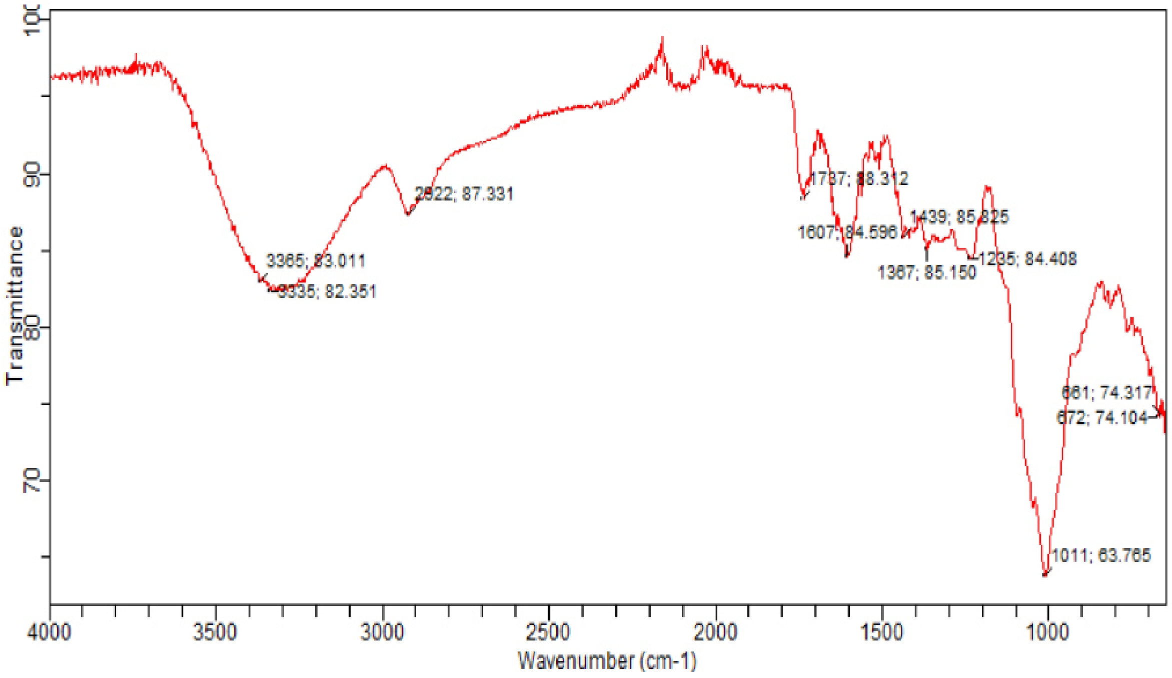


Figure 4.9: FT-IR Spectrum of Original Orange Peel before Adsorption

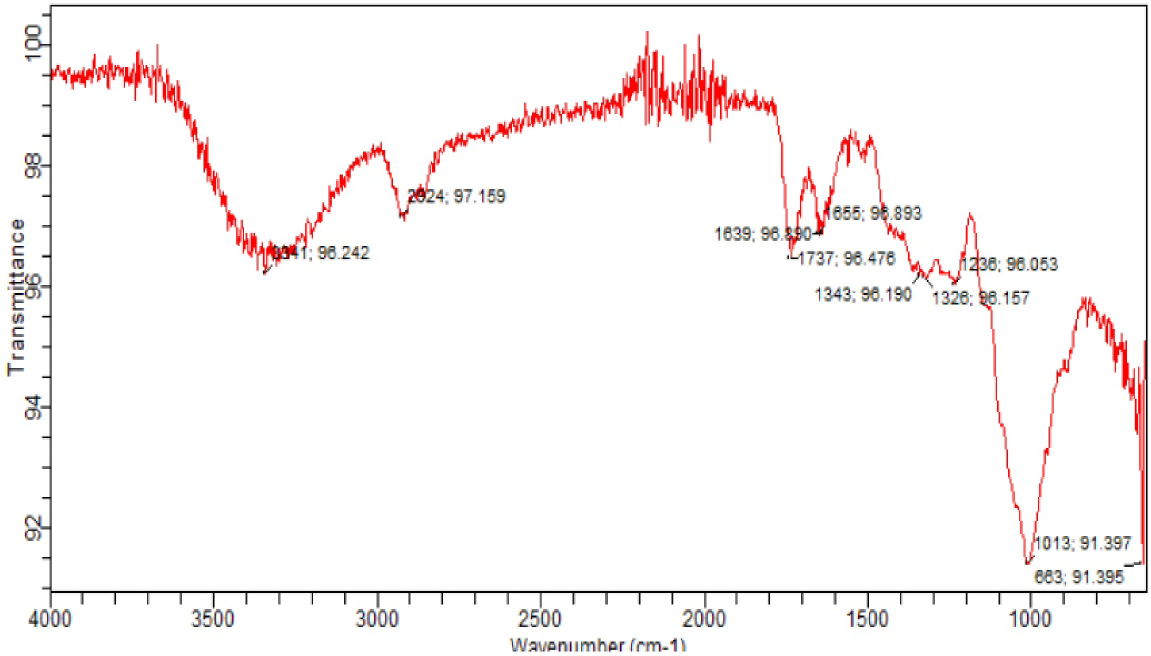


Figure 4.10: FT-IR Spectrum of Orange Peel after Adsorption of Ni(II)

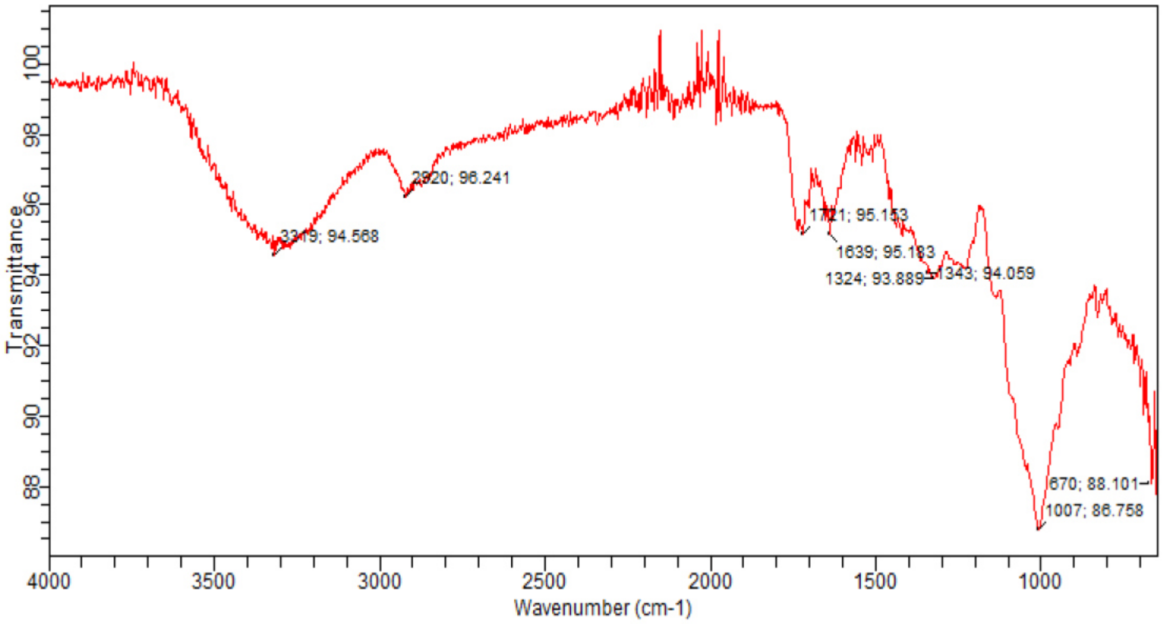


Figure 4.11: FT-IR Spectrum of Orange Peel after Adsorption of Pb(II)

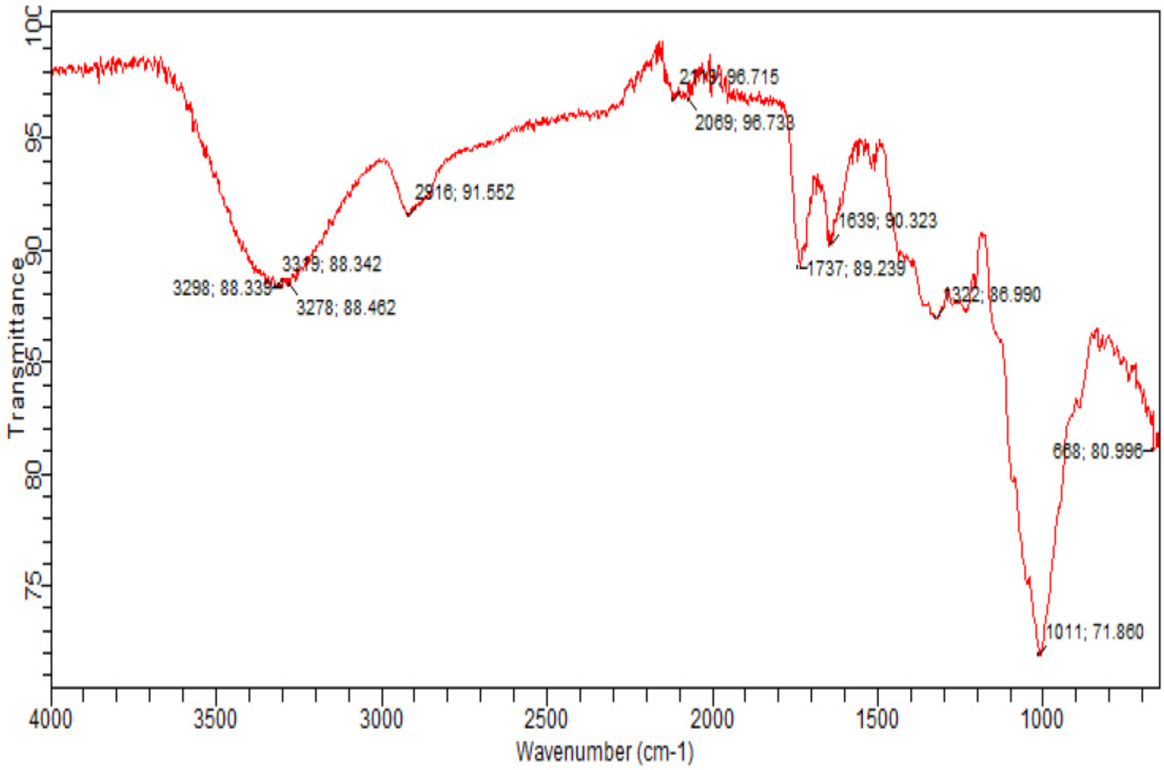


Figure 4.12: FT-IR Spectrum of Orange Peel after Adsorption of Cu(II)

Table 4.1: Isotherm Parameters for Ni(II), Pb(II) and Cu(II) Adsorption onto Orange Peel.

Isotherm Model	**Parameter**	**Values**		
		Ni (II)	**Pb (II)**	**Cu (II)**
Langmuir	Q_{max} (mg/g)	1.29	1.33	0.81
	b (Lmg^{-1})	-1.38	-1.49	-0.38
	R_L	-0.04	-0.03	-0.15
	R^2	0.9981	0.9993	0.9998
Freundlich	$K_F(Lg^{-1})$	2.19	5.98	3.98
	n	-4.31	-1.95	-1.74
	R^2	0.987	0.9953	0.9991
Dubinin-Radushkevich	q_{max} (mg/g)	0.96	0.99	2.65
	E (kJ/mol)	1.20	1.22	0.41
	R^2	0.9757	0.9311	0.9983
	A	-2.54	-3.05	-1.02
Temkin	b (kJ/mol)	-5.51	-6.24	-3.13
	R^2	0.9978	0.9969	0.9996

Table 4.2: Thermodynamics Parameters for Ni(II), Pb(II) and Cu(II) Ions Adsorption at Different Temperatures.

Metal Ion	**ΔH° (kJ/mol)**	**ΔS° (kJ/molK)**	**ΔG°**		
			303K	**313K**	**323K**
Ni(II)	-54.83	-0.17	-3.32	-1.62	0.08
Pb(II)	-43.57	-0.14	-1.15	0.25	1.65
Cu(II)	4.39	0.01	1.36	1.26	1.16

Table 4.3: Adsorption kinetics Parameters for Ni(II), Pb(II) and Cu(II) Ions Adsorption onto Orange Peel**.**

Metal Ion	**Pseudo-first Order Model**		**Pseudo-second Order Model**		**Intraparticle Diffusion Model**	
	k_1(min^{-1})	**R^2**	**k_2(g/mgmin)**	**R^2**	**k_d(mg/gm$^{1/2}$)**	**R^2**
Ni (II)	-0.005	0.9120	7.19	0.9825	-0.04	0.9162
Pb (II)	-0.002	0.8204	-0.8	0.9490	-0.03	0.9301
Cu (II)	-0.007	0.8820	-1.03	0.9993	-0.02	0.9708

4.2DISCUSSION

4.2.1Effect of Contact Time

Figure 4.1 indicates that the uptake of Ni(II), Pb(II) and Cu(II) ions onto orange peel increased as the contact time increases. The rapid removal of the metal ions was noticed from 75 to 86.25% for Ni(II), 77.5 to 85% for Pb(II) and 61.12 to 66.42% for Cu(II) with contact time variation from 5 to 180 minutes for all the three metal ions. This is because at the initial or early stages, more number of potentially active/vacant sites is available for adsorption.

As the contact time increases maximum number of metal ions got adsorbed to the available adsorption sites. As a result, it is difficult for the metal ion to search for the very fewer remaining sites. Therefore, rate of adsorption decreases in the later stages. This observation is similar to that reported by El-Said *et al*., (2010) for the removal of Cd(II) and Hg(II) onto Rice Husk Ash.

Hence, 45 minutes was considered to be optimum contact time for Pb(II) ions removal by orange peel and 60 minutes for Ni(II) and Cu(II) ions removal by the adsorbent. This is because at these times (45 and 60 minutes) no change was observed for Pb(II) ions, Cu(II) ions and Ni(II) ions removal by orange peel, which shows that the systems have reached equilibrium points. The adsorption of metal ion by adsorbent also depends on the interactions of functional groups between the solution and adsorbent surface. Adsorption can be assumed to be complete when equilibrium is achieved between the solute of the solution and the absorbent. However, specific time is needed to maintain the equilibrium interactions to ensure that the adsorption process is complete (El-Said *et al*., 2010).

4.2.2Effect of Initial Concentration

Initial concentration of metal ions can alter the metal removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of the surface functional groups to bind metal ions.

For all the metal ions, it is clear from Figure 4.2 that the extent of adsorption was rapid in the initial stages and became slow in later stages till saturation was attained. This is obvious from the fact that a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites were difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases (El-*Nemr et al.,* 2008).

It is generally assumed that as adsorbate concentration increases, the amount of metal ions removed should increase according to Ibrahim and Jimoh (2011). From Fig.4.2, the trend justified the assumed phenomenon. In addition, increase in concentration of the adsorbate brings about increase in competition between the adsorbate molecules for available binding sites. This in turn increases the amount of metal ions removed (Ibrahim and Jimoh, 2011).

4.2.3 Effect of Adsorbent Dose

Adsorbent dose is another parameter used to determine the capacity of adsorbent at a given concentration of the adsorbate.Figure 4.3 shows that the adsorption of metal ions increased from 83.75 to 97.50% for Ni(II), 81.25 to 96.25% for Pb(II) and 59.25 to 72.87% for Cu(II) as orange peel dose increased from 0.5 to 3.5g/100cm^3 in the test solution, while keeping other parameters constant. Increase inadsorption with adsorbent dose can be attributed to increased adsorbent surface area and in turn,availability of more adsorption sites (Bhattacharya *et al*., 2008; Wang and Lin, 2008).

The maximum removal of Cu(II) and Pb (II) ions was found to be 72.87 and 96.25% at 3g of adsorbent respectively, while that of Ni(II) ions was found to be 97.50% at 2.5g of adsorbent. Further addition of the adsorbent beyond 2.5g for Ni(II) and 3g for Cu (II) and Pb(II) did not show any significant removal of metal ions. Thus, the maximum adsorption had taken place at the optimum adsorbent dose of 2.5g for Ni (II) ions and 3g for Cu(II) and Pb(II) ions. Hence, the metal ions concentration in the solution remains constant. This was due to the overlapping or aggregation of adsorbent surface area available to metal ions and an increase in diffusion path length; a trend similar reported by Bansal *et al.* (2009) and Opeolu *et al.* (2009).

4.2.4 Effect of pH

The removal of metal ions from aqueous solution by adsorption depends on the pH of the solution since it affected adsorbent surface charge and degree of ionization of the species of adsorbate. Fig.4.4 shows that the adsorption of metal ions was strongly influenced by pH.

Under highly acidic conditions (i.e. pH = 2) removal of Ni(II), Pb(II) and Cu(II) ions was found to be low. This may be due to the competition between hydrogen ions (H^+) and metal ions for the same adsorption sites (Puranik arid Paknikar, 1999).

The maximum removal efficiency was found to be 98.75, 75.00 and 26.92% for Ni(II), Pb(II) and Cu(II) ions at the optimum pH of 6, respectively. At higher pH >6, the adsorption removal of the metal ions decreases. This may be due to the formation of insoluble precipitates (metallic hydroxides) by the metallic ions in the solution. For example, in the case of Pb^{2+} (at lower pH below 6), Pb^{2+} is the major lead-containing species, at higher pH values, the polymeric hydroxo-complexes, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$ and $Pb(OH)_4^{2+}$ predominate (El-Said *et al.*, 2010). Reactions of Ni^{2+}, Pb^{2+} and Cu^{2+} with aqueous hydrochloric acid (HCl) and aqueous sodium hydroxide (NaOH) were presented by the following chemical reactions;

<u>Reactions Ni^{2+}</u>

With aqueous HCl

$Ni^{2+}{}_{(aq)} + HCl_{(aq)} \rightarrow NiCl_{2(s)} + H_{2(g)}$

$NiCl_2\,(s) + 6H_2O\,(l) \longrightarrow [Ni(H_2O)_6]^{2+}(aq)$

Moisture Green stable solution

With aqueous NaOH:

$Ni^{2+}{}_{(aq)} + 2NaOH_{(aq)} \rightarrow Ni(OH)_{2(s)} + 2Na^{2+}$

Insoluble precipitate

<u>Reactions of Pb^{2+}</u>

With aqueous HCl

$Pb^{2+}{}_{(aq)} + 2HCl_{(aq)} \rightarrow PbCl_{2(s)} + H_{2(g)}$

Insoluble white precipitate

With Aqueous NaOH

$Pb^{2+}{}_{(aq)} + 2NaOH_{(aq)} \rightarrow Pb(OH)_{2(s)} + 2Na^{2+}{}_{(aq)}$

Insoluble white precipitate

$Pb^{2+}{}_{(aq)} + 4NaOH_{(aq)} \rightarrow Pb(OH)_4{}^{2-}{}_{(s)} + 4Na^{+}{}_{(aq)}$

$4Pb^{2+}{}_{(aq)} + 4NaOH_{(aq)} \rightarrow Pb_4(OH)_4{}^{4+}{}_{(s)} + 4Na^{+}{}_{(aq)}$

$6Pb^{2+}{}_{(aq)} + 8NaOH_{(aq)} \rightarrow Pb_6(OH)_8{}^{4+}{}_{(s)} + 8Na^{+}{}_{(aq)}$

<u>Reactions of Cu^{2+}</u>

With aqueous HCl

$Cu^{2+}{}_{(aq)} + 2HCl_{(aq)} \rightarrow CuCl_2 + H_{2(g)}$

Yellow-brown precipitate

With aqueous NaOH

$Cu^{2+}{}_{(aq)} + 2NaOH_{(aq)} \rightarrow Cu(OH)_{2(s)} + 2Na^{2+}$

Insoluble light-blue precipitate

4.2.5 Effect of Temperature

From Figure 4.5, it was observed that by increasing the temperature percentage removal of Ni(II) and Pb(II) ions decreases from 97.5 to 91.25% and 96.25 to 90% respectively, while that of Cu(II) ions increases from 89.71 to 90.64%. For Ni(II) and Pb(II) ions, the decrease in percentage removal of metal ions with increase in temperature showed that the adsorption ofNi(II) and Pb(II) ions onto orange peel was exothermic in nature, while for Cu(II) ions, the increase in percentage removal with increase in temperature showed that the adsorption process was endothermic in nature (Guerra *et al*., 2008).

Where endothermic adsorption occurs, this may be attributed to the amount of hydration of the metal ions in the solution. However, for endothermic adsorption where negative ΔH° wasnoticed, it suggests that the adsorption energy supersedes that of dehydration and hence an overallexothermic process was noticed (Chen and Wang, 2006).

4.2.6 Adsorption Isotherm Models

The four isotherm models parameters along with their correlation coefficients are listed Table 4.1. The fitting of the data obtained from adsorption of Ni(II), Pb(II) and Cu(II) ions onto orange peel to these isotherm models showed that the linearity of the Langmuir model was highest of all the three other models (R^2 = 0.9981 for Ni(II), R^2 = 0.9993 for Pb(II) and R^2 = 0.9998 for Cu(II)). This shows that the adsorption of Ni(ll), Pb(II) and Cu(II) ions onto orange peel is more of monolayer rather than adsorption on a surface having heterogeneous energy distribution. The values of separation factor, R_L, for Ni (II), Pb(II) and Cu (II) adsorption were found to be -0.04, -0.03 and -0.15 respectively, which for all practical reasons can be approximated to be 0, and fall within the range "$0 < R_L < 1$" for favourable adsorption(McKay *et al*., 1992). This suggests that the adsorption followed chemisorption, and that the Langmuir model can best be used to explain the adsorption of these metal ions onto orange peel.

The linearity (from R^2 values) of the Temkin model is the second best afterthat of Langmuir. The values of heat of sorption, b ($kJmol^{-1}$) for Ni (II), Pb(II) and Cu(II) adsorption were found to be -5.51, -6.24 and -3.13 respectively. These values are all far less than the typical heat of adsorption range of 20 - 40 $kJmol^{-1}$ indicating a physisorption process. This suggested that the adsorption followed chemisorptions and Temkin model can be used to explain the adsorption of these metal ions onto orange peel (Dabrowski, 2001).

In the case of Freundlich model, the linearity (from R^2 values) is good enough to show that the model can be used to describe the adsorption processes of Ni (II), Pb(II) and Cu (II) ions on to orange peel. The values of Freundlich constant(n) related to adsorption intensity for Ni (II), Pb(II) and Cu (II) ions adsorption were found to be -4.31, -1.95, and -1.74 respectively, which are all less than 1, this indicates that the adsorption followed chemisorption (Bayat, 2002).

For Dubinin-Radushkevich (D-R) model, the values of biosorption mean free energy, E ($kJmol^{-1}$) for Ni (II), Pb(II) and Cu (II) adsorption were found to be 1.20, 1.22 and 0.41 respectively. These values are all far less than 8$kJmol^{-1}$ which indicated favourable physisorption of these metal ions onto orange peel. Hence D-R model can be used to describe the adsorption of Ni (II), Pb(II) and Cu (II) ions onto orange peel (Bayat, 2002).

4.2.7Thermodynamic Description for Ni (II), Pb(II) and Cu (II) Adsorption

The calculated values of thermodynamic parameters,ΔG° , ΔH° and ΔS° obtained from Van't Hoff plot (Appendix IV) were presented in Table 4.2. The ΔG° values were calculated at three different temperatures (303K, 313K and 323K) for each metal ion. The negative values of ΔG° at 303 and 313K for Ni(II) adsorption and at 303K for Pb(II) adsorption suggested that the adsorption was spontaneous in nature. While the positive value of ΔG° at 303 and 323K for Pb(II) adsorption and at three different temperatures for Cu(II) adsorption showed that the adsorption is not feasible and follows chemisorption (Goncalves *et al*., 2008; Guerra *et al*., 2008).

For Ni(II) and Pb(II) adsorption, the negative values of ΔH° indicate the exothermic nature of these metal ions onto orange peel. In the case of Cu(II) adsorption, ΔH° is positive, implying that the adsorption process was endothermic in nature. In the case of entropy change of the system, ΔS°, the negative values of ΔS° for Ni(II) and Pb(II) adsorption confirmed the decreased randomness at the adsorbent-adsorbate interface during biosorption (Aksu and Isoglu, 2005). The positive values of ΔS° during Cu(II) adsorption indicated that there is increased randomness at the adsorbent-adsorbate interface during the adsorption of Cu(II) ions onto orange (Guerra *et al*., 2008).

4.2.8Kinetic Studies

From the kinetic plots for Ni(II), Pb(II) and Cu(II) ions adsorptions (Fig. 4.6 to 4.8) for pseudo first order, pseudo second order and intra-particle diffusion model respectively, it can be observed that the fitting of the kinetic data in Fig. 4.7 and Fig. 4.8 is far better than that in Fig. 4.6. This indicates that the adsorption Ni(II), Pb(II) and Cu(II) ions followed pseudo second order kinetic model with intra-particle diffusion as the rate determining step. This implies that the adsorption is by chemisorptions. It can further be justified by comparing the correlation coefficient (R^2) values obtained from the kinetic study of all the three models. Table 4.3 showed that R^2 values of pseudo second order model are far less than 1 compared to R^2 values for pseudo second order model and intra-particle diffusion model. Additionally, the higher value of the rate constant (k) in the case of pseudo second order model for Ni(II) adsorption further proved that the adsorption process followed pseudo second order model (Ho and McKay, 1999; Aharoni *et al*., 1970).

4.2.9Fourier Transform Infrared (FT-IR) Spectroscopy

Orange peel consists mainly of cellulose, hemicelluloses, pectin, lignin, limonene and many other low molecular weight compounds. Perez-Marin *et al.* (2008) studied orange peel for the removal of cadmium from aqueous solution by adsorption. In his work, FT-IR spectrum of the orange waste evidenced the presence of carboxyl and hydroxyl groups, which are important functional groups for metal uptake by biological materials.

The FT-IR spectrum of raw orange peel (before adsorption) was shown in Fig. 4.9. The broad strong bands at 3365 and 3335cm^{-1} are attributed to asymmetrical and symmetrical stretching vibrations of —OH groups of cellulose, hemicellulose, pectin and lignin components in the orange peel respectively. The band at 2922cm^{-1} is attributed to C — H stretching vibration of methyl, methylene and methoxy groups. The peak observed at 1737cm^{-1} is the stretching vibration due to non-ionic carboxyl groups (-COOH and —$COOCH_3$), and may be due to carboxylic acids or their esters. The band at 1607cm^{-1} may be due to C = C stretching that can be attributed to aromatic C — C bond. The peaks between 1439 to 1235cm^{-1} may be as a result of symmetrical stretching of ionic carboxylic group (-COO) of pectin component of the orangepeel. The intense band at 1011cm^{-1} is attributed to C-O-R group. Comparing the spectrum of original peel before adsorption with those after adsorption of Ni(II), Pb(II) and Cu(II) ions, differences in the positions of the absorbance peaks appeared.

The asymmetrical and symmetrical stretching vibration at 3365 and 3335cm^{-1} were significantly distorted after adsorption, suggesting that chemical interactions occur between the metal ions and the hydroxyl groups on the biosorbent surface.

After Ni(II), Pb(II) and Cu(II) adsorption, slight shifting was observed on the symmetrical —OH band (3335 to 3341cm^{-1}; 3335 to 3319cm^{-1}; and 3335 to 3278cm^{-1}respectively). After Cu(II) adsorption, another absorption band appeared at 3319cm^{-1}, which is a clear indication that —OH group was involved in adsorption of these metal ions.

The peak at 1607cm^{-1} (C=C stretching), shifted to 1639cm^{-1} after adsorption of each of Ni(II), Pb(II) and Cu(II) ions. This is an indication that C=C functional group was involved in the adsorption of these metal ions.

The peak at 1737cm^{-1} (stretching due to non-ionic carboxyl group) remain the same even after adsorption of Ni(II) and Cu(II) ions, while after adsorption of Pb(II) ions, this peak shifted to 1721cm^{-1}. These, along with other changes observed before and after adsorption confirmed that most of the functional groups present in this biosorbent (orange peel) are responsible for metal uptake.

The following is an example of the mechanism which shows the involvement of some component functional groups of the adsorbent in the adsorption process:

For pseudo-second order reaction;

$$Rate = \frac{[OH^-]}{dt} = k_2[OH^-]^2$$

$$2OH^- + Pb^{2+} \leftrightharpoons Pb(OH)_2$$

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.0 SUMMARY

Chapter one discussed about the introductory/basic aspects concerning adsorption process, in which adsorption was defined as the adhesion of chemical species (adsorbates) onto the surface of particles (adsorbents). It talked about the main purpose of carrying out the study, which was to test the ability of low-cost adsorbent to adsorb Ni(II), Pb(II) and Cu(II) ions from aqueous solution. It also touches an introductory aspect of heavy metals and their impacts to human health in the environment, in which heavy metals were defined as those metals with atomic density greater than $4g/cm^3$ or 5times or more greater than water and are toxic even at low concentration. The aim and objectives as well as areas covered by the research were also discussed in this chapter.

Chapter two of this study discussed about the previous works and findings by different authors (which enable us to make so many comparisons). It also talked about the methods for effluent/waste water treatment i.e., both conventional and adsorption methods. Some of the conventional methods discussed were chemical precipitation, coagulation flocculation, ion-exchange, electrochemical treatment and membrane filtration method. This chapter also highlights some of the shortcomings of conventional methods over adsorption method, in which sludge disposal problems, high initial capital for operation, high maintenance cost among others were found to be the major problems concerning the conventional method for effluent or wastewater treatment. Both common and low-cost adsorbents were also discussed in this chapter; in which activated carbon was considered to be the most commonly used adsorbent.

Chapter three discussed about the framework of this research. It starts with list of equipments/apparatus used during the course of carrying out the experiments for this study. This was followed by preparation of the orange peel for adsorption experiments, i.e., converting it into powdered form after thorough washing and drying.

Preparation of standard (stock) solutions of the three metal ions was carried out by dissolving required (measured) amount of nitrate salt of the metal into 0.1M nitric acid. The experimental solutions of desired concentrations were then prepared by successive dilutions of the standard stock solutions. Effects of factors affecting adsorption i.e. contact time, initial concentration, adsorbent dose, pH and temperature were also discussed by carrying-out batch adsorption experiments. These were carried out by varying one parameter (e.g. contact time) and keeping other parameters (e.g., pH, temperature, concentration, adsorbent dose) constant.

Equilibrium isotherm study was also carried out in this chapter, in which four isotherm models were employed i.e., Langmuir, Freundlich, D-R and Temkin isotherm model. For each model, there is an equation used to evaluate some parameters or constants used to describe the adsorption process. For Freundlich model, K_F and n (Freundlich constant related to adsorption capacity and adsorption intensity, respectively) determines the extent and nature of the adsorption. If $n>1$, thus, adsorption is favoured. For Langmuir, b and R_L are called Langrnuir energy constant and separation factor respectively. If $0< R_L<1$, adsorption is favoured. For Temkin model, A and b_T are called Temkin isotherm constant and constant related to heat of sorption, respectively. Values of b_T between 20-40 $kJmol^{-1}$ indicate favourable adsorption. For D-R isotherm, $\beta(mol^2/kJ^2)$, ε (kJ/mol) and E (kJ/mol) are called activity coefficient of mean free energy, Polanyi potential and biosorption mean free energy. If $E<8$ kJ/mol, then physical adsorption is favoured. Thermodynamics study was carried out at three different temperatures to determine parameters ($\Delta G°$, $\Delta S°$ and $\Delta H°$) which provide valuable information on the adsorption mechanism. Kinetics study was carried-out to determine the controlling mechanism and rate determining step of the metal uptake on the adsorbent. This was studied using pseudo-first and second order kinetic models as well as intraparticle diffusion model. For each kinetic model, R^2 (correlation coefficient) value determines the applicability of the model. R^2 values approaching to 1 indicates that the model is applicable.

Chapter four discussed about the results of the experiments performed. For those factors affecting adsorption process, increase in contact time, initial concentration and adsorbent dose leads to increase in percentage removal of all the metal ions. While in the case of pH, there is both increase and decrease in percentage removal for all the metal ions. Increase in temperature causes decrease in percentage removal in the case of Ni(II) and Pb(II) ions and increase in percentage removal in the case of Cu(II) ions. For isotherm models, for each of Ni(II), Pb(II) and Cu(ll) adsorption, D-R isotherm model is the best model for describing the adsorption process with E(kJ/mol)= 1.20, 1.22, and 0.41 for Ni(II), Pb(II) and Cu(II) ions adsorption respectively. For thermodynamic parameters, the values of $\Delta H°$ for Ni(II) and Pb(II) adsorption were found to be negative, while that of Cu(II) adsorption was found to be positive, this implies exothermic and endothermic adsorption process respectively. For Ni(II) adsorption, $\Delta S°$ is negative and that of Cu(II) adsorption is positive. This indicates decreased and increased randomness at surface-solution interfaces in both cases respectively. The negative $\Delta G°$ values for Ni(II) adsorption at 303 and 313K and at 303K for Pb (II) adsorption confirmed a spontaneous adsorption process, while a positive $\Delta G°$ values in the case of Cu(II) adsorption at three different temperatures and at 313 and 323K for Pb (II) adsorption suggested that a chemical sorption process occurred under the experimental conditions. For kinetic study, R^2 values approaching to 1 showed that adsorption of Ni(II), Pb(II) and Cu(II) ions onto orange peel followed pseudo-second order model, compared to R^2 values far less than 1 in the case of pseudo-first order kinetic model.

5.1 CONCLUSION

Some factors affecting the adsorption process such as contact time and initial concentration and adsorbent dose were found to have influence on the removal of the metal ions because a significant removal of metal ions was observed by varying the factors. The adsorption data is best described by Langmuir isotherm, with best correlation coefficient, R^2=0.9981, 0.9993 and 0.9998 and maximum adsorption capacity, Q_{max}=1.29, 1.33 and 0.81mg/g for Ni(II), Pb(II) and Cu(II) adsorption, respectively. The adsorption processes followed pseudo-second order kinetics with good correlation coefficient, R^2=0.9825, 0.9490 and 0.9993 and pseudo-second order rate constant, k_2=7.19, -0.8 and -1.03g/mgmin for Ni(II), Pb(II) and Cu(II) adsorption, respectively. Adsorption of Ni(II) and Pb(II) ions onto orange peel was exothermic in nature, while that of Cu(II) was endothermic in nature. Although the adsorption capacity of the orange peel is not as high as that of commercial activated carbon, low-cost of the material together with its adsorptive ability could offer a promising procedure for the removal of metal ions from industrial effluents.

5.2 RECOMMENDATIONS

There are many areas in which the work of this study can be further investigated viz:

i. Chemical activation of the low-cost orange peel should be carried out to find out whether there is variation in metal uptake between the activated orange peel and the natural orange peel without chemical treatment.

ii. Work should be undertaken into the adsorption characteristics of orange peel with regard to actual effluent from industry.

iii. Research also needs to be undertaken to determine regeneration mechanisms for orange peel that has been used to adsorb metal ions. A method must be developed if orange peel used for the adsorption is to be re-used.

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APPENDICES

Appendix I

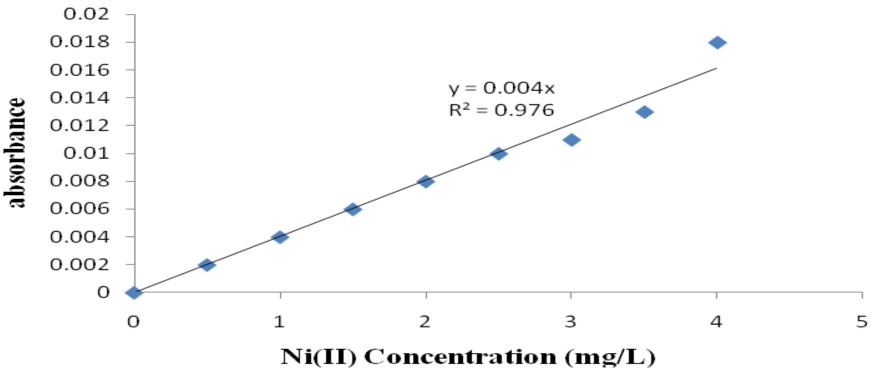

Fig. I.a: Standard Calibration Curve for Ni (II)

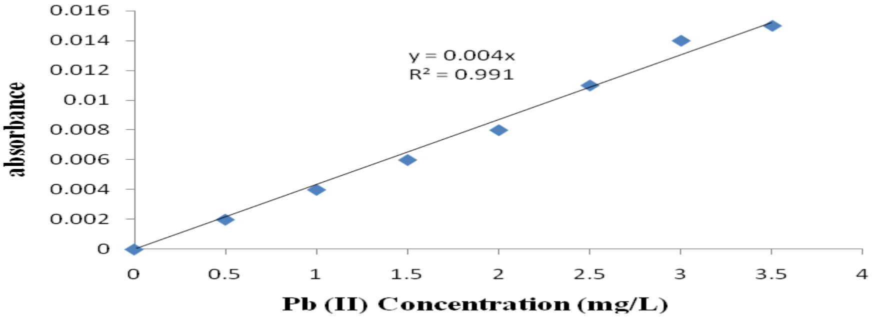

Fig. I.b: Standard Calibration Curve for Pb(II)

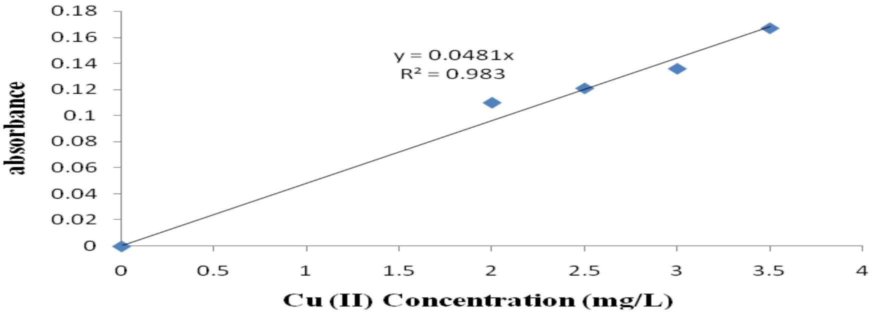

Fig. I.c: Standard Calibration Curve for Cu(II)

Appendix II

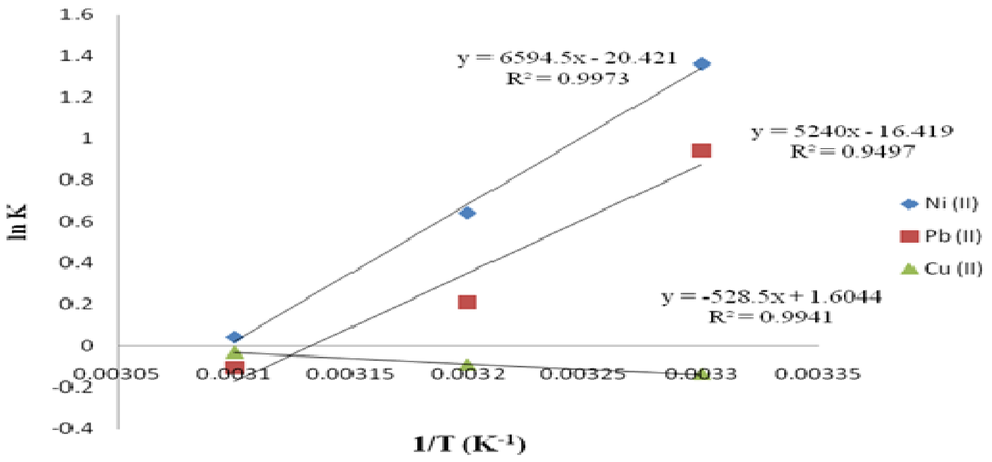

Fig. II.a: Van't Hoff's Plots for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel

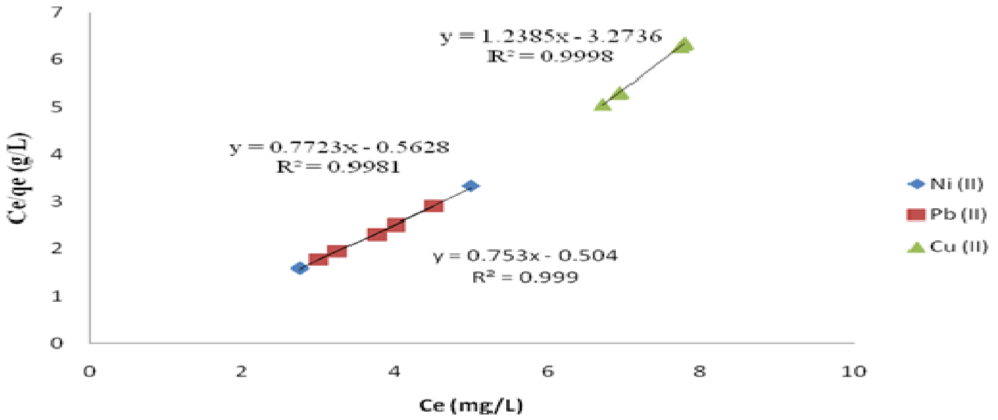

Fig. II.b: Langmuir Isotherms for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel.

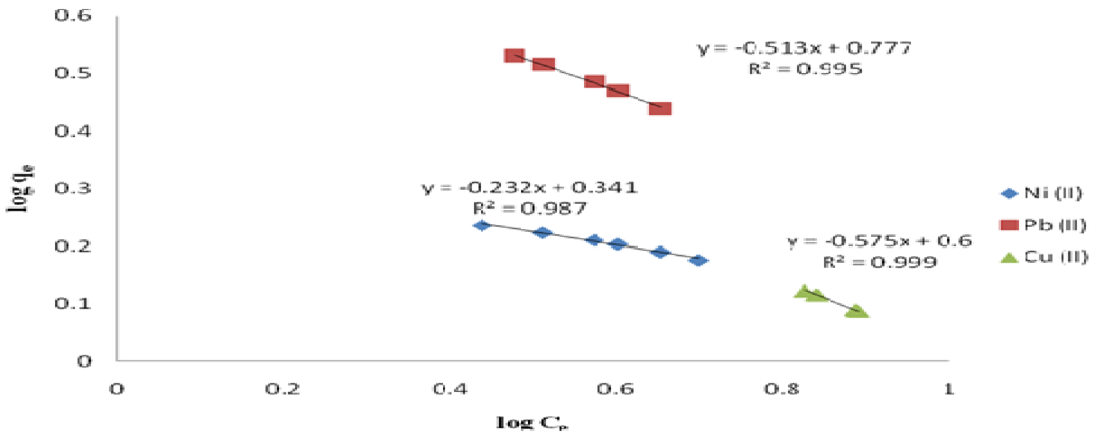

Fig. II.c: Freundlich Isotherms for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel.

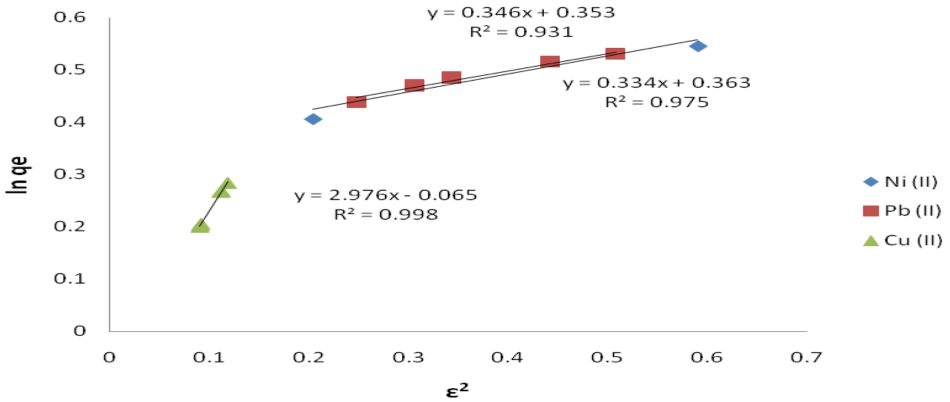

Fig. II.d: D-R Isotherms for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel.

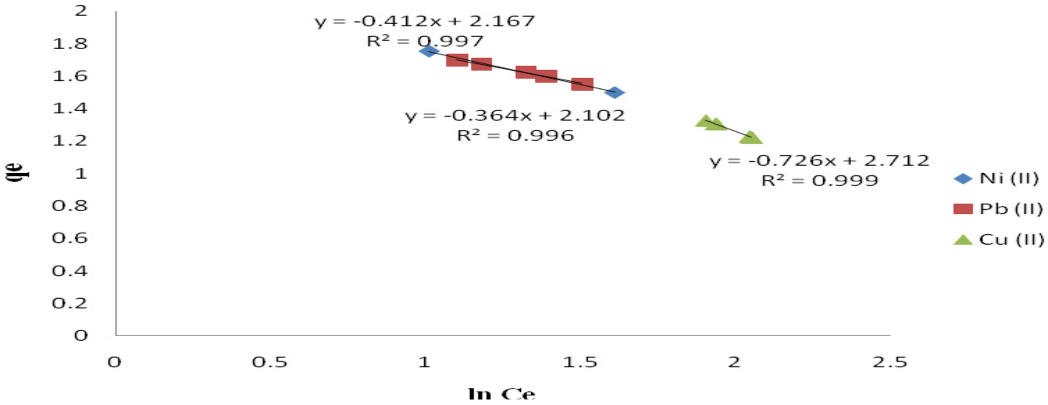

Fig. II.e: Temkin Isotherms for Ni (II), Pb (II) and Cu (II) Adsorption onto Orange Peel.

APPENDIX III

Table III.a: Effect of Contact Time on Ni(II), Pb(II) and Cu(II) ions Adsorption

Contact Time (Minute)	% Removal		
	Ni (II)	**Pb (II)**	**Cu (II)**
5	75.00	77.50	61.12
10	77.50	80.00	61.23
15	80.00	81.25	61.43
30	81.25	83.75	65.28
45	83.75	85.00	65.38
60	86.25	85.00	66.42
120	86.25	85.00	66.32
180	86.25	83.75	66.42

Table III.b: Effect of Initial Concentration on Ni(II), Pb(II) and Cu(II) ions Adsorption

Initial Concentration (mg/L)	% Removal		
	Ni (II)	**Pb (II)**	**Cu (II)**
10	52.5	62.5	11.43
15	75.0	78.33	19.20
30	92.5	91.67	52.25
45	96.1	95.56	76.48
60	97.9	97.10	88.57
75	99.0	98.67	96.40
90	99.4	99.20	98.24
105	99.8	99.52	98.61

Table III.c: Effect of Adsorbent Dose on Ni(II), Pb(II) and Cu(II) ions Adsorption

Adsorbent Dose (g)	% Removal		
	Ni (II)	**Pb (II)**	**Cu (II)**
0.5	83.75	81.25	59.25
1.0	87.50	83.75	62.79
1.5	90.00	85.00	62.89
2.0	93.75	88.75	64.66
2.5	97.50	91.25	68.19
3.0	97.50	96.25	72.87
3.5	97.50	96.25	70.27

APPENDIX IV

Table IV.a: Effect of pH on Ni(II), Pb(II) and Cu(II) ions Adsorption

pH	**% Removal**		
	Ni (II)	**Pb (II)**	**Cu (II)**
2.0	91.25	12.50	4.57
4.0	95.00	62.50	18.30
6.0	98.75	75.00	26.92
8.0	96.25	37.50	10.71
10.0	92.50	12.50	7.38

Table IV.b: Effect of Temperature on Ni(II), Pb(II) and Cu(II) ions Adsorption

Temperature (K)	**% Removal**		
	Ni (II)	**Pb (II)**	**Cu (II)**
303	97.50	96.25	89.71
313	95.00	92.50	90.12
323	91.25	90.00	90.64

Table IV.c: Data for plotting Langmuir, Temkin and D-R Isotherm for Ni(II) Adsorption at Different Contact Times.

S/N	**Time (min)**	**C_e (mg/L)**	**q_e (mg/g)**	**log C_e**	**ln C_e**	**log q_e**	**ln q_e**	**ε^2 (kJ^2/mol^2)**	**$\frac{C_e}{q_e}$ (g/L)**
1	5	5	1.50	0.6990	1.6094	0.1761	0.4055	0.2043	3.333
2	10	4.5	1.55	0.6532	1.5041	0.1903	0.4383	0.2472	2.9032
3	15	4	1.60	0.6021	1.3863	0.2041	0.4700	0.3060	2.5000
4	30	3.75	1.625	0.5740	1.3218	0.2109	0.4855	0.3430	2.3077
5	45	3.25	1.675	0.5119	1.1787	0.2240	0.5158	0.4418	1.9403
6	60	2.75	1.752	0.4393	1.0116	0.2368	0.5452	0.5905	1.5942

Table IV.d: Data for plotting Langmuir, Temkin and D-R Isotherm for Pb(II) Adsorption at Different Contact Times.

S/N	**Time (min)**	**C_e (mg/L)**	**q_e (mg/g)**	**log C_e**	**ln C_e**	**log q_e**	**ln q_e**	**ε^2 (kJ^2/mol^2)**	**$\frac{C_e}{q_e}$ (g/L)**
1	5	4.5	1.55	0.6532	1.5041	0.1903	0.4383	0.2472	2.9032
2	10	4.0	1.60	0.6021	1.3863	0.2041	0.4700	0.3060	2.5000
3	15	3.75	1.625	0.5740	1.3218	0.2109	0.4855	0.3430	2.3077
4	30	3.25	1.675	0.5119	1.1787	0.2240	0.5158	0.4418	1.9403
5	45	3.00	1.70	0.4771	1.099	0.2304	0.5306	0.5080	1.7647
6	60	3.00	1.70	0.4771	1.099	0.2304	0.5306	0.5080	1.7647

APPENDIX V

Table V.a: Data for plotting Langmuir, Temkin and D-R Isotherm for Cu(II) Adsorption at Different Contact Times.

S/N	Time (min)	C_e (mg/L)	q_e (mg/g)	log C_e	ln C_e	log q_e	ln q_e	ε^2 (kJ^2/mol^2)	$\frac{C_e}{q_e}$ (g/L)
1	5	7.7755	1.222	0.891	2.051	0.0871	0.2005	0.0899	6.3630
2	10	7.7547	1.225	0.889	2.048	0.0881	0.2030	0.0903	6.3304
3	15	7.7131	1.229	0.887	2.043	0.0896	0.2062	0.0912	6.2760
4	30	6.9439	1.306	0.842	1.938	0.1160	0.2670	0.1111	5.3170
5	45	6.9231	1.308	0.840	1.935	0.1170	0.2685	0.1120	5.2929
6	60	6.7152	1.328	0.827	1.904	0.1232	0.2840	0.1183	5.0570

Table V.b: Data for plotting Pseudo First Order, Pseudo Second Order and Intraparticle Diffusion kinetics graphs for Ni(II) Adsorption at Different Contact Times.

S/N	Time (min)	$t^{½}$ ($min^{1/2}$)	q_e (mg/g)	q_t (mg/g)	(q_e - q_t)(mg/g)	log (q_e - q_t)	$\frac{t}{q_t}$ (gmin/mg)
1	5	2.2361	1.500	0.500	1.00	0	10.00
2	10	3.1623	1.550	0.450	1.10	0.0414	22.22
3	15	3.8730	1.600	0.400	1.20	0.0792	37.50
4	30	5.4772	1.625	0.375	1.25	0.0969	80.00
5	45	6.7082	1.675	0.325	1.35	0.1303	138.46
6	60	7.7460	1.725	0.275	1.45	0.1614	218.18

Table V.c: Data for plotting Pseudo First Order, Pseudo Second Order and Intraparticle Diffusion kinetics graphs for Pb(II) Adsorption at Different Contact Times.

S/N	Time (min)	$t^{½}$ ($min^{1/2}$)	q_e (mg/g)	q_t (mg/g)	(q_e - q_t)(mg/g)	log (q_e - q_t)	$\frac{t}{q_t}$ (gmin/mg)
1	5	2.2361	1.550	0.450	1.10	0.0414	11.11
2	10	3.1623	1.600	0.400	1.20	0.0792	25.00
3	15	3.8730	1.625	0.375	1.25	0.0969	40.00
4	30	5.4772	1.675	0.325	1.35	0.1303	92.31
5	45	6.7082	1.700	0.300	1.40	0.1461	150.00
6	60	7.7460	1.700	0.300	1.40	0.1461	150.00

APPENDIX VI

Table VI.a: Data for plotting Pseudo First Order, Pseudo Second Order and Intraparticle Diffusion kinetics graphs for Cu(II) Adsorption at Different Contact Times.

S/N	Time (min)	$t^{½}$ ($min^{1/2}$)	q_e (mg/g)	q_t (mg/g)	(q_e - q_t)(mg/g)	log(q_e - q_t)	$\frac{t}{q_t}$ (gmin/mg)
1	5	2.2361	1.222	0.7800	0.442	-0.355	6.4103
2	10	3.1623	1.225	0.7755	0.450	-0.347	12.8950
3	15	3.8730	1.229	0.7713	0.458	-0.340	19.4477
4	30	5.4772	1.306	0.6944	0.612	-0.213	43.2028
5	45	6.7082	1.308	0.6923	0.616	-0.210	65.0007
6	60	7.7460	1.328	0.6715	0.657	-0.182	89.3522

Table VI.b: Data for plotting Van't Hoff's Plot for Ni(II) Adsorption at Different Temperatures

T(K)	$\frac{1}{T}$(K^{-1})	C_e (mg/L)	q_e (mg/g)	$\frac{q_e}{C_e}(Lg^{-1})$	$ln\left(\frac{q_e}{C_e}\right)$
303	0.0033	0.50	1.950	3.900	1.3610
313	0.0032	1.00	1.900	1.900	0.6420
323	0.0031	1.75	1.825	1.043	0.0421

Table VI.c: Data for plotting Van't Hoff's Plot for Pb (II) Adsorption at Different Temperatures

T(K)	$\frac{1}{T}$(K^{-1})	C_e (mg/L)	q_e (mg/g)	$\frac{q_e}{C_e}(Lg^{-1})$	$ln\left(\frac{q_e}{C_e}\right)$
303	0.0033	0.75	1.950	2.5667	0.9426
313	0.0032	1.50	1.850	1.2333	0.2097
323	0.0031	2.00	1.800	0.9000	-0.1054

Table VI.d: Data for plotting Van't Hoff's Plot for Cu(II) Adsorption at Different Temperatures

T(K)	$\frac{1}{T}$(K^{-1})	C_e (mg/L)	q_e (mg/g)	$\frac{q_e}{C_e}(Lg^{-1})$	$ln\left(\frac{q_e}{C_e}\right)$
303	0.0033	2.0582	1.7942	0.8717	-0.1373
313	0.0032	1.9751	1.8025	0.9123	-0.0915
323	0.0031	1.8711	1.8129	0.9689	-0.0316