

REMOVAL OF CHROMIUM FROM SIMULATED AQUEOUS SOLUTION USING INTERCALATED AHOKO KAOLIN

This study investigates the removal of chromium from simulated aqueous solution of potassium chromate using intercalated Nigeria Ahoko kaolin. One of the most important problems of contamination at present is the existence of heavy metals owed to their toxicity and cumulative properties. Adsorption process was used for the removal of chromium in this study. The adsorbent was initially refined to remove the quartz content. The adsorbent was intercalated with potassium dihydrogen phosphate for effective Chromium removal. Both batch and column studies were investigated. The conditions for the experiment were effect of pH of the adsorbate, concentration of the adsorbate, time and adsorbent dose for the batch adsorption studies and effect of flow rate for the column adsorption studies. The coefficient of determination for the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms were low, this might be as a result of the process condition e.g temperature that was not considered. However, Langmuir adsorption still gave the best fit. For the column study, the breakthrough occurred faster and the breakpoint time decreased at a higher flowrate. The result showed that Nigerian Ahoko Kaolin intercalated with potassium dihydrogen phosphate is effective adsorbent in chromium removal from aqueous solution. Generally, Nigeria Ahoko kaolin can be utilized as potential adsorbent.

CHAPTER ONE

1.0

INTRODUCTION

1.1 Background of the Study

One of the major problem of contamination at present is the existence of heavy metals owing to their toxicity and cumulative properties (Monika, Garg and Kadirvelu, 2009). Pollution of water with toxic substances is of major concern for human health as well as for the environmental quality. A large quantity of wastes containing chromium has been directly discharged into the environment in recent years (Bhattacharya and Gupta, 2008). Trivalent chromium (Cr) compounds are considered to be less toxic than the hexavalent compounds and are neither irritating nor corrosive under normal conditions as well. All forms of Cr are however, toxic when they exist at high levels. Through a large number of activities like tannery industry, metal finishing industry, inorganic chemicals production, steel industries, electroplating etc., chromium can be released into the environment. At high acidic medium (pH=1.0), Cr (VI) ions mostly exist as $\text{H}_2\text{Cr}_2\text{O}_4$. There is equilibrium between $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- species at a pH of 2-6. Cr can enter the air, water and soil mostly in form of Cr (III) and Cr (VI). Health effects may occur immediately or shortly after exposure to high levels of Cr particles, it also causes skin irritation and allergic reactions, kidney damage, liver damage after eating food or drinking water contaminated with hexavalent Cr (Abbas, Farooq, Ilyas, 2010).

A good number of technologies are available for removal of Cr from aqueous solution, namely reverse osmosis, chemical precipitation, ion exchange and solvent extraction among others. These methods are either uneconomical or inefficient, but adsorption has become a preferred method for removal of metals from aqueous solution due to its simplicity, easiness in handling, availability of various adsorbents and more efficiently in the removal of heavy metals at lower concentration

(Abbas *et al.*, 2010). Kaolin clay [a layered silicate mineral, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$], is one of the adsorbents which is rarely used due to its low cation exchange capacity and its small surface, which is not more than $20 \text{ m}^2/\text{g}$ (Suraj, Iyer and Lalithambika, 1998). Kaolin exhibits low absorption and adsorption properties which are directly related to the low surface charge on the particle and must be modified to improve its adsorption property. Intercalation is a surface modification method in which there is insertion of a material between the layers of another material. In this case, a chemical will be inserted into the clay substrate.

Chemicals modification methods have been used to improve the adsorption capability of kaolin. Chemicals such as sulphate, phosphate, humic acid, hydrazine, formamide and dimethylsulphoxide can effectively improve the cation adsorption capacity of kaolin. Studies have described the adsorption of Cr (VI) from aqueous solution. Talokar (2011) studied the removal of Cr from waste water by adsorption using low cost agricultural biomass as adsorbent. Also, Guerra, Helen, Paulo, Rubia and Claudio (2010) have also studied adsorption of Cr (VI) ions on Brazilian smectite, but no work has been carried out on the intercalation of Ahoko kaolin for adsorption studies.

1.2 Statement of the Problem

Pollution of water with toxic substances poses major challenge to human health as well as for the environmental quality. Also different methods for the removal of Cr have been reported but these methods are either expensive or inefficient, hence, a low cost adsorbent material which can perform the same function should be investigated.

1.3 Aim and Objectives

The aim of this project is to remove Chromium from simulated aqueous solution using intercalated Ahoko Kaolin. The followings are the objectives of this project:

1. To analyze the characteristics of intercalated and non-intercalated Ahoko kaolin.
2. To determine the adsorption capacity of the intercalated Ahoko kaolin.
3. To investigate and evaluate the influence of adsorption parameters on the adsorption proficiency of the intercalated and non-intercalated Ahoko Kaolin.
4. To investigate and evaluate the adsorption performance of the intercalated Ahoko kaolin using batch and continuous adsorption processes.

1.4 Scope of the Study

The scope of this research work is set to remove chromium from simulated aqueous solution through Ahoko kaolin intercalation. Kaolin exhibits low absorption and adsorption properties, reason why it needs to be modified. This can effectively be improved by chemicals such as sulphate, phosphate, humic acid, dimethylsulphoxide and formamide. This research work is limited to modification of Ahoko kaolin through a process called “Intercalation” (a term which indicates the insertion of a material between the layers of a clay substrate) by phosphate.

Also, few studies have been reported on the modification of kaolin but to our knowledge, no work has been carried out in the use of Ahoko kaolin. The work will be experimental; Scanning Electron Microscope (SEM) will be used for micro structural characteristics of the clay compounds, Fourier

Transform Infra-Red (FTIR) for determination of the functional groups present in the clay compound, X-ray Diffraction (XRD) for structural characteristics of the samples and Atomic Absorption Spectrophotometer (AAS) for metal analysis.

CHAPTER TWO

2.0

LITERATURE REVIEW

2.1 Introduction

Pollution is defined as the introduction of contaminants into the environment causing instability, disorder, harm or discomfort to the ecosystem (TnauAgritech, 2013). Pollution can be in the form of chemical substances, or energy such as noise, heat, or light energy. The elements of pollution which is the pollutant can be foreign substances or energies, or naturally occurring. The cause of pollution can either be natural or man-made. Natural pollution occurring naturally does not cause excessive harm to human lives due to its regeneration ability while the man-made pollution is as a result of human activities and are very difficult to remove from the environment (Lin and Juang, 2002). Pollution occurs when the ecosystem finds it difficult to remove substances that are introduced into the environment; it can be by air, noise, water, radioactive and thermal.

Pollution control is the process in which pollutants that are released into the environment are reduced or eliminated. Water pollution can be defined as any chemical, physical or biological change in the quantity of water which has a harmful effect on any living thing (Monika, Grag and Kadirvelu, 2009). Water pollution can be controlled by physical, chemical and biological methods. In physical method, the pollutants are allowed to settle out or are passed through a filter where they are trapped. Also, chemical reactions can be used to remove pollutants from water, for

example, addition of alum and lime (calcium hydroxide) to water forms a thick sticky precipitate and in settling out, it traps and carries with it solid particles, dead bacteria and other components of water pollutant. Biological agents are also used for removal of pollutants from water. Chemicals in polluted water are attacked by aerobic bacteria (those that need oxygen to survive) and anaerobic bacteria (those that do not require oxygen) converting them to a harmless form. Chemical pollution is caused by substances of chemical nature including hydrocarbon pesticides, metals such as mercury, lead, cadmium, chromium. Chromium (Cr) finds its way into the environment through both natural processes and human activities (Sharma and Foster, 1995).

Too much Cr (III) causes severe skin rash or other more serious symptoms. Cr (VI) which is the most dangerous form of chromium causes health problems including; allergic reactions, skin rash, nose irritations and nose bleed, weakened immune system, genetic material alteration, kidney and liver damage and may even cause death (Abbas *et al.*, 2010). It is therefore very important that more researches should be conducted in removing these contaminants from the ecosystem.

2.2 Adsorption

Adsorption process is said to be one of the best water treatment technologies around the world. Adsorption is the binding of molecules or particles to a surface; materials are transferred from a fluid phase to a solid phase. This binding to the surface is usually weak and reversible (Ruthven, 1984). The fluid that dissolves or suspends the material of interest is bound but compounds having taste or odour or colour tend to bind strongly. It can also be defined as a process where atoms, ions, molecules or bio-molecules of gas, liquid or dissolved solids adhere to the surface of another substance; collection of a gas or liquid molecules on the surface of another substance or a process where gas or liquid solute accumulates on the surface of a liquid or solid. Adsorption

process is a surface phenomenon, an exothermic process and it is always favoured by low temperature (Adebowale, Unuabonah and Olu-Owolabi, 2006).

Adsorption is normally described through adsorption isotherms defined as the amount of adsorbate on the adsorbent as a function of pressure (for gas) or concentration (for liquid) at a constant temperature. Adsorption isotherm is an equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature (Adebowale *et al.*, 2005). To allow comparison of different materials, the quantity adsorbed is almost at all times normalized by the mass of the adsorbent. The adsorbed amount is always a fraction of a monolayer; the adsorbent must have a large specific surface area to adsorb a substantial amount of material. For typical adsorbents, the specific surface area ranges from 0.1 to 1.0 km²/kg, that is, the area of a football field in a kg of adsorbent. Usually to adsorb a substantial amount of material, the adsorbent must have a large specific surface area. Examples of adsorption are: Water vapours adsorbed by silica gel, NH₃ adsorbed by charcoal, adsorption of gasoline vapour in automobile fuel tanks by carbon canister, deodorization of drinking water by carbon filter (Guerra *et al.*, 2010).

Adsorption involves accumulation of the molecular species at the surface while absorption is the assimilation of molecular species throughout the bulk of the solid or liquid (Aras, Arikian and Soboler, 2010). Adsorption is a surface phenomenon and an exothermic process while absorption is a bulk phenomenon and an endothermic process. Also, adsorption is favoured by low temperature and increases steadily to equilibrium while absorption is not affected by temperature and it occurs at a uniform rate.

Adsorption is used widely in industrial applications such as activated charcoal, synthetic resins and purification of water. It operates in most natural physical, biological, and chemical systems (Reddad, 2002).

Not wholly surrounded by other atoms, atoms on the clean surface experience a bond deficiency; this is the reason why it is energetically favourable for them to bond with whatever happens to be available (Tiwari, Singh and Saksena, 1995). The exact nature of the bonding is dependent on the details of the species involved. Examples of adsorbent are activated carbon, silica gel, activated alumina and zeolites (Orumwense, 1995).

The classification of adsorption is dependent on the following:

2.2.1 Physisorption or Physical Adsorption

The forces of attraction existing between the adsorbent and the adsorbate are Van der Waal forces. This type of adsorption is also known as Van der Waal's adsorption. This can easily be reversed through heating or by decreasing the pressure (Value and Amrita, 2013).

2.2.2 Chemisorption or Chemical Adsorption

The forces of attraction that exist between the adsorbate particles and the adsorbent have almost the same strength as chemical bonds. This is also known as Langmuir adsorption (Value and Amrita, 2013). This type of adsorption cannot be easily reversed.

2.3 Factors Affecting Adsorption

2.3.1 Nature of Adsorbate and Adsorbent

Gases that are easily liquefiable such as: NH_3 , Cl_2 , CO_2 and SO_2 , among others are easily adsorbed (the Van der Waals' forces are stronger most especially near the critical temperature) compared to elemental gases, for example, H_2 , O_2 and N_2 among others (while chemisorption is specific in

nature) (Hutson and Yang, 1987). So also, porous and finely powdered solid for example fullers earth and charcoal are adsorbed more compared to the hard non-porous materials.

2.3.2 The Surface Area of the Solid Adsorbent

The larger the solid surface of the adsorbent, the greater the extent of adsorption. So also, the surface area of a powdered solid adsorbent depends upon its particle size; the smaller the particle size, the greater its surface area (Hutson and Yang, 1987).

2.3.3 Activation of the Solid Adsorbent

Activation of the adsorbent is a process of increasing the adsorbing power of an adsorbent. This can be achieved in several ways; the specific area of the adsorbent can be increased by making the surface of the solid rough or by finely dividing the adsorbent or by carrying out a specific treatment of the adsorbent (Hutson and Yang, 1987). For example, by heating to a temperature between 650K and 1330K in vacuum or in superheated steam, wood charcoal can be activated.

2.3.4. Experimental conditions

2.3.4.1. Effect of Pressure

The extent of adsorption is increased with increase in the pressure of the adsorbate gas. The extent of adsorption increases rapidly with pressure at low temperature. Also, the extent of adsorption is directly proportional to the pressure at small range of pressure while the adsorption tends to achieve a limiting value at high pressure (Yavuz and Guzel, 2003).

2.3.4.2 Effect of Temperature

According to Le-Chatelier's principle, adsorption is accompanied by evolution of heat, the magnitude of adsorption decreases with increase in temperature (Yavuz and Guzel, 2003).

2.4 Adsorption Isotherm

This is a mathematical equation describing the relationship between the pressure of the adsorbate and the extent of adsorption at a constant temperature.

2.4.1 Langmuir Adsorption Isotherm.

Irving Langmuir in 1916 published a new model isotherm for gases adsorbed to solids (Itodo, 2009). One of the assumptions the isotherm was based is that there is a dynamic equilibrium existing between the adsorbed gaseous molecules and the free gaseous molecules. Langmuir's adsorption isotherm is based on kinetic theory of gases.

- Adsorption takes place on the surface of the solid only till the whole of the surface is completely covered with a uni-molecular layer of the adsorbed gas (Suraj *et al.*, 1998).
- Adsorption is made up of two opposing processes; Condensation of the gas molecules on the solid surface and evaporation (desorption) of the gas molecules from the surface back into the gaseous phase.
- Condensation rate depends on the uncovered surface of the adsorbent which is available for condensation (Jarraya, 2010). The rate of condensation is usually high at the beginning when the whole of the surface is uncovered, and progressively decreases when the surface is covered more and more. Conversely, the rate of evaporation depends on the covered surface thereby increases as more and more of the surface is covered. Ultimately, equilibrium is attained when the rate of condensation equals the rate of evaporation (adsorption equilibrium).

- Rate of condensation also depends on the pressure of the gas because according to the kinetic theory of gases, the number of molecules striking per unit area is proportional to the pressure (Dada, Olalekan, Olatunya and Dada, 2012).

Langmuir theory of uni-molecular adsorption is valid at low pressures and high temperatures only. Additional layers are formed when the pressure is increased or temperature lowered. This has in turn led to the modern concept of multilayer adsorption.

The model assumes that the adsorbent has S sites per unit mass; S_0 are unoccupied and S_1 are occupied by adsorbate molecules. This assumption of having S number of sites implies that there is a limit to the amount that can be adsorbed (Itodo, 2009).

$$S = S_0 + S_1 \quad (2.1)$$

An assumption that the rate of adsorption or condensation of a gas on to the sites is proportional to the product of the number of unoccupied sites and the pressure of the gas is made.

$$r_{\text{condensation}} = k_2 P S_0 \quad (2.2)$$

It is assumed that the rate of desorption or evaporation is proportional to the number of occupied sites (Cama, Metz and Ganor, 2002)

$$r_{\text{evaporation}} = k_1 S_1 \quad (2.3)$$

The rate of adsorption is equal to the rate of desorption at equilibrium.

$$r_{\text{condensation}} = r_{\text{evaporation}} \quad (2.4)$$

$$k_2 P S_0 = k_1 S_1$$

$$k_2 P (S - S_1) = k_1 S_1 \quad (2.5)$$

The amount adsorbed can be expressed as a fraction of the sites that are occupied (Hutson and Yang, 1987)

$$\theta = S_1/S \quad (2.6)$$

$$k_2P(1 - \Theta) = k_1\Theta$$

$$\Theta = \frac{k_2P}{k_1 - k_2P} = \frac{KP}{1 - KP}$$

Where

$$K = \frac{k_2}{k_1} \quad (2.7)$$

K which is the equilibrium constant is the ratio of the adsorption rate constant and the desorption rate constant. The adsorption is linear in pressure in the limit of low pressures and the isotherm has a slope equal to the equilibrium constant.

2.4.2 Freundlich Adsorption Isotherm

Freundlich in 1909 expressed an empirical equation for the representation of an isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure (Jarraya, 2010). This is known as Freundlich Adsorption isotherm or Freundlich Adsorption equation. Here, a monomolecular layer is formed on the surface of the adsorbent by the adsorbate. The extent of adsorption varies linearly with pressure, $x/m \propto p$ while it becomes independent of pressure, $x/m \propto p_0$ and x/m depends upon pressure raised to powers $x/m \propto p^{1/n}$ at moderate pressure. A graph of $\log x/m$ against $\log p$ gives a straight line of slope $1/n$ and intercepts $\log k$ as shown in Figure 2.1.

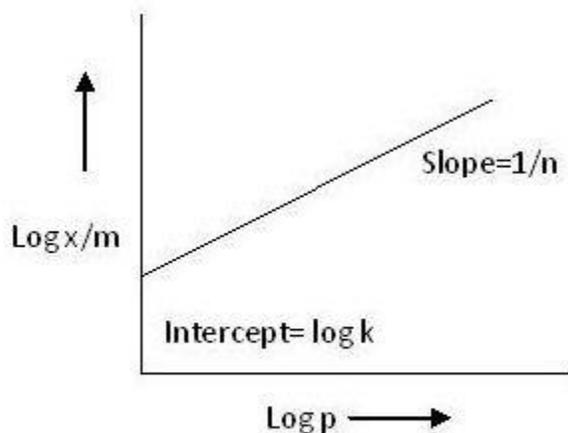


Figure 2.1: Plot of log x/m against log p (Bailey, 1988).

$$x/m = kP^{\frac{1}{n}} \quad (2.8)$$

x = amount of adsorbate.

m = weight of the adsorbate.

x/m = Adsorption per gram of adsorbent.

P = pressure.

K and n are constants and their values depend on adsorbate at a particular temperature, usually n is greater than one which implies that the amount of the gas adsorbed does not increase as rapidly as the pressure.

Freundlich failed to predict the adsorption value at higher pressure even though he successfully established the relationship between adsorption and pressure at lower values (Tan, Ahmad and Hameed, 2009).

2.5 Clay Mineral Structure

There are different minerals that can be found in clay structure. The different minerals are discussed below.

2.5.1 Kaolin Minerals

The basic kaolin minerals structure comprises the minerals Kaolinite, Dickite, Nacrite and Halloysite which is a layer of a single tetrahedral sheet and a single octahedral sheet (Grim, 1962).

The two sheets combine to form a unit in which the tips of the silica tetrahedrons are joined with

the octahedral sheet. All the apical oxygen of the silica tetrahedrons point in the same direction in other that these oxygen and/or hydroxyls which may be present to balance the charges are shared by the silicon in the tetrahedral sheet and the aluminum in the octahedral sheet. Kaolinite has the structural formula $Al_4Si_4O_{10}(OH)_8$ and theoretical chemical composition SiO_2 , 46.54%; Al_2O_3 , 39.50%; and H_2O , 13.96% (Jepson and Rowse, 1975). Aluminum atom fills only two-thirds of the octahedral positions. The aluminium atoms are surrounded by four oxygens and eight hydroxyls.

The kaolinite structure has balanced charges. The minerals of the kaolin group; Kaolinite, Dickite, Nacrite and Halloysite are made up of 1:1 layers of combined octahedral and tetrahedral sheets which are continuous in the a- and b-axis directions and are also stacked one above the other in the c-axis direction. What makes the difference in the kaolin minerals is the manner by which the layers of the unit are stacked above each other (Weaver, 1976).

Dickite consists of two unit layers, Nacrite, six unit layers and Halloysite occurs in two forms: hydrated in which there is a layer of water molecules between the layers and dehydrated (Murray, 1994). The hydrated form has 10 \AA as its basal spacing while the dehydrated form 7.2 \AA . Kaolinite has a shape which is in pseudo-hexagonal plates and stacks.

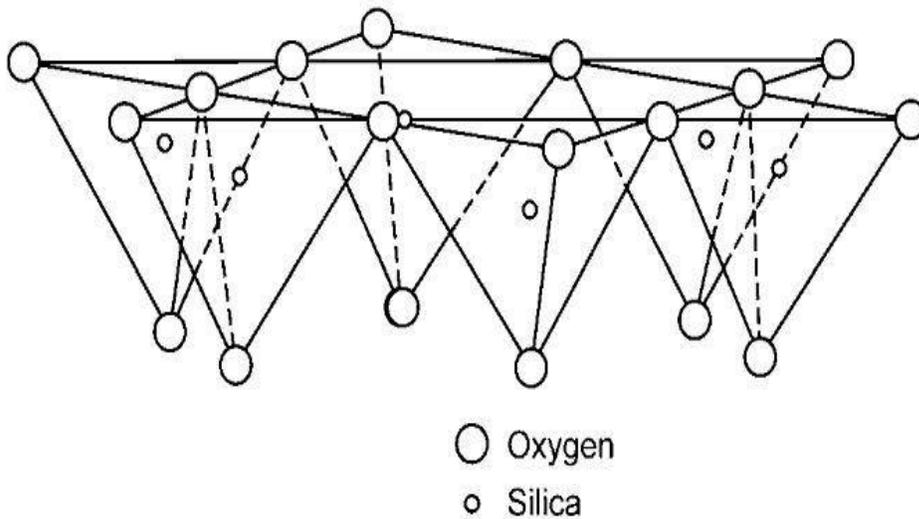


Fig 2.2: Diagrammatic sketch of the tetrahedral structure (Murray, 2007)

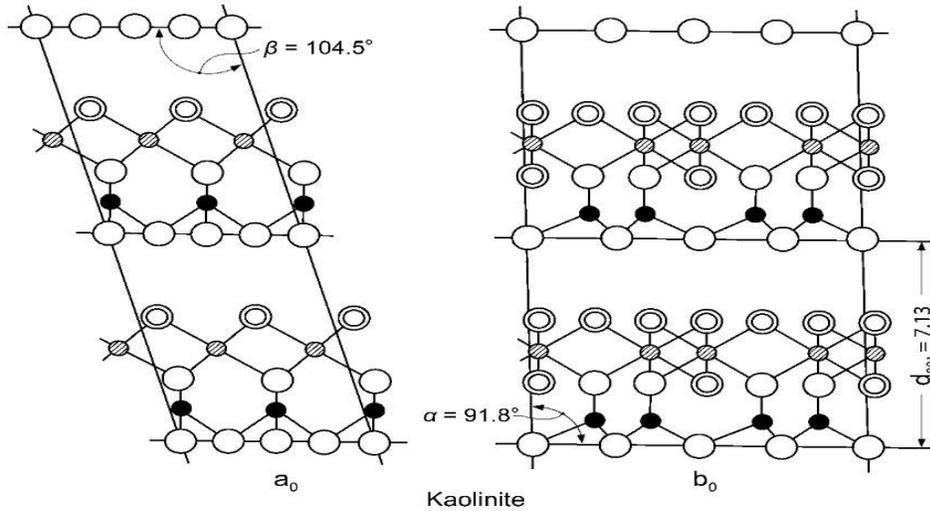


Fig 2.3: Diagrammatic sketch of Kaolinite structure (Murray, 2007)

2.5.2 Smectite Minerals

Smectite minerals consist of sodium montmorillonite, calcium montmorillonite, saponite (magnesium montmorillonite), nontronite (iron montmorillonite), hectorite (lithium montmorillonite) and beidellite (aluminum montmorillonite) (Güven, 1988). Smectite minerals are made up of two silica tetrahedral sheets with a central octahedral sheet and are designated as 2:1 layer mineral. Water molecules and cations occupy the space between the 2:1 layers. The theoretical formula is $(\text{OH}_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot \text{NH}_2\text{O})$ (interlayer) and the theoretical composition without the interlayer material is SiO_2 , 66.7%; Al_2O_3 , 28.3% and H_2O , 5%. In smectites however, there is substitution of aluminum for silicon up to 15% in the tetrahedral sheet (Grim, 1968) and magnesium and iron for aluminum in the octahedral sheet.

The smectite mineral is calcium montmorillonite (basal spacing of 14.2 Å) if the layer charges deficiency is balanced by the interlayer cation calcium and water. This is the most common of the smectite. It is called sodium montmorillonite if the charge deficiency is balanced by sodium ions and water with a basal spacing of 12.2 Å, beidellite if the octahedral positions are filled by aluminum, saponite if filled by magnesium and nontronite if filled by iron. The X-ray diffraction data are sometimes difficult to analyze because the smectite mineral particles are small (Komadel and Nigrin, 1992).

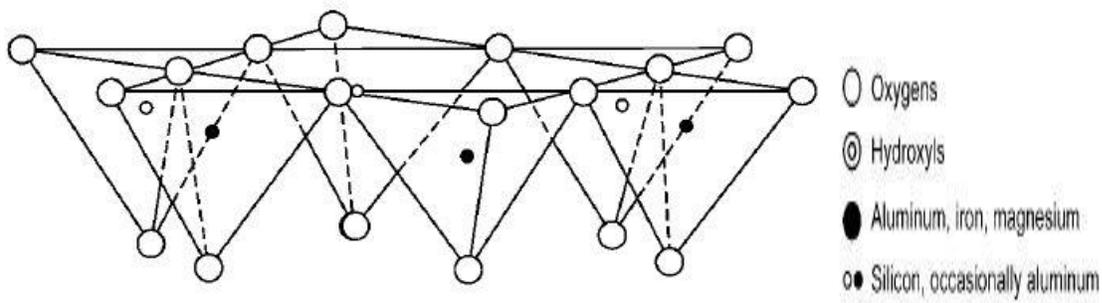


Figure 2.4: Diagrammatic sketch of the structure of smectites (Murray, 2007).

2.5.3 Illite Mineral

Illite is a clay mineral mica named by Grim, Bray and Brandley, (1937). The interlayer cation is potassium with the structure of 2:1. The coordination number, size and charge

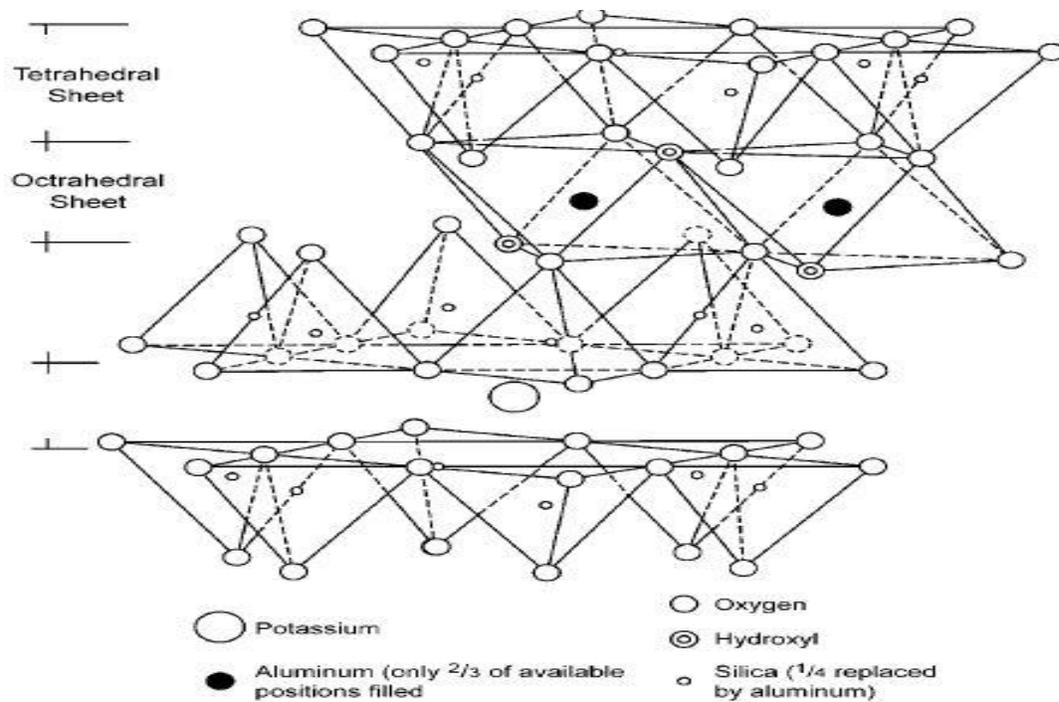


Fig 2.5: Diagrammatic sketch of the structure of illite (Moore and Reynolds, 1997).

of potassium are such that it fits too close in the hexagonal ring of oxygen of the adjacent silica tetrahedral sheets. A strong interlocking ionic bond is given to the structure holding the individual layers together and preventing water molecules from occupying the interlayer positions like it does in the smectites. Illite is commonly associated with most kaolins and smectites (Murray, 2007).

2.5.4 Chlorite Mineral

This is usually present in shales and also in other clays which are associated with coal seams. Random stacking of the layers and some hydration is the difference between clay mineral chlorites and well-crystallized chlorites (Ross and Shannon, 1926). Chlorite is a 2:1 layer mineral which has an interlayer brucite sheet $Mg(OH)_2$. A quite range of cation substitutions exist in chlorites, most commonly, Mg^{2+} , Fe^{2+} , Al^{3+} and Fe^{3+} . The general composition of chlorite is $(OH)_4(SiAl)_8(MgFe)_6O_{20}$. Chlorite has a basal spacing

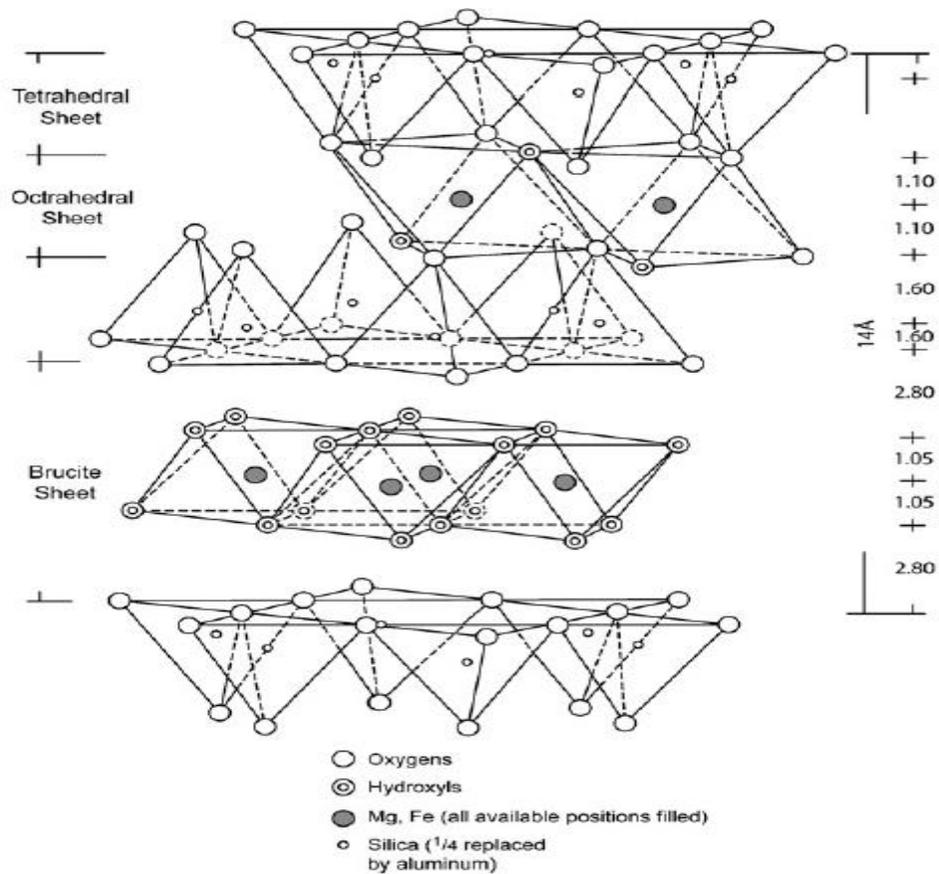


Figure 2.6: Diagrammatic sketch of the structure of chlorite (Bailey, 1988).

d (001) of about 14 Å. Chlorite is generally intimately intermixed with other clay minerals (Bailey, 1988).

2.5.5. Palygorskite (Attapulgite): Sepiolite

Palygorskite and Sepiolite are 2:1 layer silicates with the tetrahedral sheets linked infinitely in two dimensions (Balci, 1999). They are however structurally different from other clay minerals in that the octahedral sheets are continuous in only one dimension and the tetrahedral sheets divided into ribbons by the periodic inversion of rows of tetrahedrons. Sepiolite has the channel between its ribbon strips larger than in palygorskite (Jones and Galan, 1988). Both of these clay minerals are magnesium

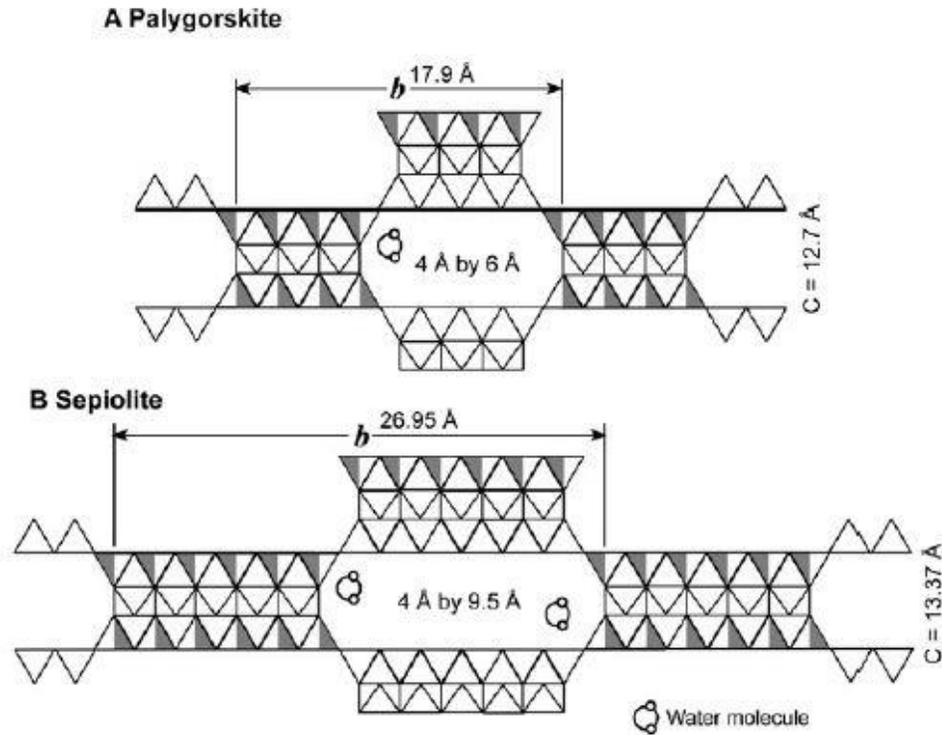


Fig 2.7: Diagrammatic sketch of the structure of (a) palygorskite and (b) sepiolite (Murray, 2007)

silicates but palygorskite has higher alumina content. Palygorskite has a general formula $(\text{OH}_2)_4(\text{OH})_4\text{Mg}_5\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$ and Sepiolite $(\text{OH}_2)_4(\text{OH})_4\text{Mg}_8\text{Si}_{12}\text{O}_{30}\cdot 8\text{H}_2\text{O}$. The two clay materials have two kinds of water, the first coordinated to the octahedral cations and the other loosely bonded in the channels known as zeolitic water. The sepiolite elongates are usually longer than the palygorskite elongates (Murray, 2007).

2.6 Clay and Clay Minerals

The first American geologist to specialize in clay study was Professor Heinrich Ries of Cornell University who studied the clay resources of many of the eastern states by describing their ceramic properties (Ries, 1908). There was no adequate analytical technique for identifying the ultrafine

particles which makes up the clay minerals. X-ray diffraction was used to identify the clay minerals in the middle and late 1920s.

A clay material is defined as any fine-grained, natural, earthy, argillaceous material (Grim, 1962). The word “clay” has ambivalent definitions (Grim, 1968). It is used in defining any soil particle which is smaller than $2\mu\text{m}$ while on the other hand it includes a large group of microcrystalline secondary minerals which is based on hydrous aluminum or magnesium silicates that have sheet like structures. It materials have been a part of human existence since antiquity. Clay is a rock term and is also used as a particle size term. It is an abundant raw material that has an amazing variety of uses and properties which are largely dependent on their mineral structure and composition (Murray, 1994).

Clays and clay minerals are very important industrial minerals. Grim in 1968 summarized what is known as clay mineral concept which stated that clays are essentially made up of small group of minerals commonly known as the clay minerals. These clay minerals are hydrous aluminium silicates and iron and magnesium substitute for the aluminium in some of these minerals. Clays have over one hundred documented industrial applications (Brown, 1994). In order to evaluate the physical properties, the identity of all the clay minerals present in a clay material must be determined. The clay mineral groups consist of kaolin, smectite, palygorskite-sepiolite, illite, chlorite and mixed layered clays. These clays have different properties which are related to their structure and composition (Murray, 2007).

The relative abundance and identity of the clay minerals present in a clay mineral is referred to as the clay mineral composition (Ross and Shannon, 1926). Non clay minerals that are usually associated with the clay minerals include quartz, feldspar, mica, calcite, dolomite, opal C-T, and

some minor amounts of heavy and trace minerals such as ilmenite, rutile, brookite, anatase, sphene, kyanite, goethite, hematite, augite, florencite, and barite.

2.7 Classification of Clay Minerals

Clay minerals are majorly classified into two. These are:

- Amorphous (Allophane group)
- Crystalline

Crystalline is further divided into

- A. Two-layer type – Sheet structure composing of units of one layer of silica tetrahedrons and one layer of alumina octahedrons.
 - Equidimensional-Kaolinite group (Kaolinite, Dickite and Nacrite)
 - Elongate-Halloysite (Grim, 1968)
- B. Three-layer types - Sheet structures composing of two layers of Silica tetrahedrons and one central dioctahedral or trioctahedral layer.
 - Expanding lattice
 - Equidimensional-Smectitegroup (Sodium montmorillonite, calcium-montmorillonite and beidellite)
 - Elongate-Smectite (Nontronite, saponite, hectorite)
 - Non-expanding lattice- Illite group
- C. Regular mixed layer types (ordered stacking of alternate layers of different types)-chlorite group.
- D. Chain-Structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyl containing Al and Mg atoms-Sepiolite, Palygorskite (attapulgitite) (Grim,1968).

2.8 Properties of Clay Minerals

Some of the properties by which clay minerals are characterized are as follows:

- A layer structure with one dimension in the nanometer range; the thickness of the 1:1 layer is about 0.7nm and that of 2:1 layer is about 1nm.
- The anisotropy of the layers or particles.
- The existence of several types of surfaces: external basal (planar) and edge surfaces as well as internal (interlayer) surfaces.
- The ease with which the external and the internal surface can be modified (by adsorption, ion exchange, or grafting).
- Plasticity.
- Hardening on drying or firing; this is applicable to most (but not all) clay minerals (Bailey, 1980).

2.9 Uses of Kaolin

Kaolin is a very important industrial clay mineral. It is less reactivity when incorporated into most industrial formulations accounts for many of its important applications. Properties like low surface charge, relative, soft and non-abrasiveness; relatively low cost, low surface area, white colour, low ion exchange etc. are important determinants in the industrial applications. Some of the industries where kaolin is applicable are as follows:

2.9.1 Paper

Kaolin is used in filling and coating of paper. It is mixed with the cellulose fibers in wood pulp as filler and mixed with water, adhesives and various additives as a coating. This coating makes the paper smoother, brighter, glossier, more opaque and improves the printability (Bundy, 1993). The hydrophilic nature of kaolin makes it easily dispersible in aqueous systems. The brightness of the paper is a function of the brightness of the grade of kaolin used. Decrease in particle size results in increase in gloss. Kaolin is not a perfect filler but meets several criteria. Kaolin is applicable in white papers as found in printing grades, newsprint, and uncoated book paper. Paper is filled to extend fibers for reduction of cost and to improve several properties like opacity, brightness, smoothness, and printability. Opacity and brightness are the two most important properties contributed by kaolin.

2.9.2 Paint

About 600,000 tons annually are used worldwide as an extender pigment in paint. It is largely used as a pigment extender in water-based interior latex paints. It is also used extensively in interior water-based paints. Kaolins contribute to suspension, viscosity and leveling of paints (Bundy, 1993). Calcined kaolin improves the scrub ability of paint. Use of delaminated kaolins in paints promotes the wash ability (ease with which a stain can be removed through washing) and enamel holdout (ability of a substance to prevent entry of enamel into its interior structure).

2.9.3 Ceramics

Ceramics is the manufacture of products from earthen materials when high temperature is applied (Grim, 1962). Kaolin is utilized in a wide range of products in ceramics, which include dinnerware, tile, sanitary ware, pottery, refractories and electrical porcelain. Kaolinitic clays like kaolins and ball clays are used as major ingredients in many ceramic products. The ceramic properties of clay materials depends on the clay mineral composition and properties like particle size distribution,

presence of organic material and the non-clay mineral composition (Bundy, 1993). The most important factor which determines the ceramic properties is the clay mineral composition. Important physical and chemical properties which kaolin and ball clay impart into ceramics are, plasticity, green strength, fired strength, dry strength, refractoriness, low to zero absorption of water, controlled shrinkage and ease of casting in sanitary ware. The non-clay mineral components such as quartz, feldspar and other mineral additives play very important role in the determination of the firing characteristics.

2.9.4 Rubber

The stiffening and reinforcing properties of kaolin makes it to be used in rubber, so also is its low cost in comparison with other pigment. Kaolin is used in non-black rubber goods where wear resistance is important (Grim, 1968). Examples are shoe heels, soles, tires, conveyor belt covers and bicycle tires. Delaminated kaolin with a high aspect ratio is used as filler in the white sidewall tire since it acts as a barrier to air leakage. Special modified kaolins are also used to get better dispersion in the rubber and also for improved reinforcement.

2.9.5 Plastics

Kaolin can be used as filler in plastics because it encourages smooth surface production, reduces cracking and reduction of size during curing, improves thermal stability, improves the impact strength, aids resistance to weathering and chemical action and controls the flow properties as well (Murray, 2007). The most important use of kaolin is in polyvinyl chloride (PVC) coatings on wire and cable. The finer the particle sizes of the kaolin, the better the reinforcement of the physical properties in all polymers. Chemical bond between the kaolin filler and polymer is produced from coupling agents which provides further improvement in strength. The impact strength of plastics can substantially increase by fine particle kaolins.

2.9.6 Ink

Kaolin is the major inorganic pigment used in ink. The importance of kaolin in ink is to improve ink holdout (similar to those of paper coating and paint) and to extend both coloured and white pigments (Murray, 2007). Gravure printing represents the biggest ink market for kaolin because large amount of kaolin (5-15%) is required. Kaolin helps in the extension of the colorant, sharpens dot formation and improves the hold out. Kaolin is used in inks with low viscosity for flexographic printing. Surface modification of kaolin to make it hydrophobic increases its usefulness in oil-based inks.

Kaolin also finds its application in catalyst, fibre glass, Portland cement, alum, adhesive, fertilizer and food additives.

2.10 Adsorbent

Adsorbent is defined as a porous substance that has a high surface area and the ability to absorb or adsorb other substances using intermolecular forces onto its surface (Tarley and Arruda, 2004). There are different types of adsorbents that can remove chromium ions from aqueous solution. They include activated carbon, silica gel and activated alumina among others.

2.10.1 Activated Carbon

Activated carbon also known as activated charcoal is a form of carbon which has been processed with oxygen thereby creating millions of tiny pores between the carbon atoms (Chern and Chien, 2002). This causes the surface area to be increased from 500 to 1500 m²/g. The material is made suitable for adsorption due to the increased surface area. The impure molecules are held within the carbon's internal pore structure by electrostatic attraction or chemisorption. A pound of activated carbon has the surface area equivalent to six football fields. The surface of the activated carbon is

non-polar which makes it to have an attraction for non-polar adsorbate like organics (Nunes, Franca and Oliveira, 2009).

Usually, activated carbon is made from charcoal but can also be produced from wood, peat or coconut shell. Pore size distribution is very important for the practical application. The carbon material usually has a pore structure larger in size than the material it is trying to adsorb (Sivakumar and Palanisamy, 2009). It is applicable in air and water purification and in recovery or removal of precious metals. Monser and Nafaa, (2002) worked on removal of copper, zinc, chromium and cyanide from waste water using modified activated carbon while (Mohan and Kunwar, 2002) studied the single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse.

2.10.2 Silica Gel

Silica gel functions on physisorption basis where adsorption occurs as a result of Van der Waals interactions and capillary condensation at high humidity. The force of adsorption is less than for zeolites which results in an adsorption capacity that is lower at low concentrations of adsorbents. The high adsorption capacity and or good regeneration behaviour of silica gel can be exploited fully when only moderately low dew points need to be achieved (Li, Yang, Deyi and Licheng, 2011). Suitability of silica gels for adsorption of liquids or gases and vapours varies based on the distribution of pore size. Narrow and wide pore silica gels exhibit different degrees of stability against liquid water. In case of a narrow pore silica gel, liquid water can lead to the destruction of the silica gel pore while wide pore silica gel is not affected by the presence of liquids.

Silica gel is a partially dehydrated form of polymeric colloidal silicic acid. It possesses an amorphous micro-porous structure which has a distribution of pore opening sizes of roughly 3-60 angstroms (Puanngam and Fuangfa, 2008). These interconnected pores form a vast surface area which attracts and hold water by adsorption and capillary condensation which allows silica gel to adsorb up to 40% of its weight in water. Also, silica gel is extremely efficient at temperatures below 77 °F (25 °C) but loses some of its adsorbing capacity as the temperature begins to rise. Wasay, Haran and Tokunaga, (1996) worked on adsorption of fluoride, phosphate and arsenate ions on lanthanum-impregnated silica-gel. Puanngam and Fuangfa, (2008) also worked on preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg (II) ions.

2.10.3 Activated Alumina

Activated alumina is a filter media which is made by treatment of aluminium ore so that it becomes porous and highly adsorptive. It removes variety of contaminants, excessive fluoride, arsenic and selenium inclusive (Hameed, 2009). Some of the advantages include ease of handling, non-corrosive nature, capacity for repeated regeneration, inert towards water, stability to fairly high temperature, low resistance to gas flow, and great mechanical strength. Activated alumina is used in liquid and gaseous desiccation in petrochemical industry. It is widely applicable as a dryer in textile industry, oxygen making industry and automatic instrument with non heat regeneration (Bhattacharya and Gupta, 2008). The medium requires periodic cleaning with an appropriate regenerant such as alum or acid for it to remain effective. Hano, Hirokazu, Makoto, Kohei and Shunji (1997) worked on the removal of phosphorus from waste water by activated alumina adsorbent. Bhattacharya and Gupta (2008) also worked on adsorption of Zn (II) from aqueous solution by using different adsorbents like activated alumina.

2.11 Review of Low Cost Adsorbent for Chromium Ions

An adsorbent is referred to as “low-cost” if it requires minimal processing, abundant in nature and/or a by-product or a waste from an industry (Li *et al.*, 2011). Materials from industrial or agricultural operation or natural material is one of the resources for low cost adsorbent. These materials have little economic value and are inexpensive since they are locally and easily available in large quantities. Examples of some low cost adsorbent are:

2.11.1 Chitosan

Chitosan has been recognized recently as a biopolymer having a significant potential for use as biosorbent for metal ions removal. Chitosan and its derivatives are examples of value-added materials and are produced from chitin which a natural carbohydrate polymer is found in the skeleton of crustaceans such as crab and shrimp (Ahenach, Cool and Vansant, 1998). Chitosan can effectively adsorb metals through establishment of their different interactions with its amino and hydroxyl groups.

Chitosan is a polymer which is obtained from deacetylation of chitin. Selectively and chemically modifying the structure of this biopolymer through cross linking with glutaraldehyde or epichlorohydrin can increase the adsorption performance. Also, by controlling the number of adsorption process and fine-tuning the operational parameters, the best recovery conditions can be achieved.

2.11.2 Zeolite

Zeolite is a Greek word meaning “boiling stone” and was discovered as a natural mineral in 1756 by a Swedish mineralogist, Cronstedt A. F. (Tschernich, 1992). This discovery showed that the zeolite’s crystalline structure adsorbs molecules readily, slowly or not at all with the ability to

selectively adsorb by size and polarity which makes them efficient agents for drying and purification of liquids and gases. Zeolites are highly crystalline belonging to an important class of hydrated aluminosilicate minerals of group I and group II elements.

They are based on fundamental building blocks of tetrahedral SiO_4 and AlO_4 giving rise to a three dimensional network. The mechanism of adsorption in zeolite is dependent on factors such as the pore size of the zeolite, the physical and chemical composition of the adsorbate and the ion exchange. The mechanisms include equilibrium selective adsorption, rate selective adsorption, shape selective adsorption, ion exchange and reactive adsorption. (Jianwei, Yanhui, Zhiliang and Yunqing, 2011). The specific properties of zeolites influence the adsorption properties whichever mechanism controlled the process. (Brown and Groszek, 2000). An important characteristic of all zeolites is their adsorption ability as it directly influences the use of the material as a catalyst and separator. Li *et al.* (2011) worked on surfactant modified zeolite as an adsorbent for removal of humic acid from water. Zhan, Lin and Zhu (2011) also worked on removal of nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent.

2.11.3 Kaolin

Kaolin can be a rock and a mineral term. If it contains predominantly kaolinite and /or one of the other kaolin minerals, it is considered as a rock term. It is considered as a mineral term being the group name for the minerals kaolinite, Dickite, Nacrite and Halloysite (Aras, Arikian and Soboler, 2007). The most common kaolin mineral is the kaolinite. To enhance certain physical properties (such as brightness, whiteness, opacity, particle size, shape and distribution and viscosity), to reduce or remove impurities and to be applicable for most industrial use, kaolin must be beneficiated by either dry or wet processing (Bailey, 1993). Impurities that are commonly found

in kaolin include; quartz, mica, illite, smectite, feldspar, goethite, hematite, anatase, ilmenite, rutile, trace quantities of tourmaline, zircon, kyanite and few other heavy minerals. Blue-white whiteness is preferred to cream-white, however, most kaolin is cream white and this is referred to as the yellowness factor or b-value. Some kaolin have good rheology because the structure has little or no charge deficiencies, they have a relatively low surface area ($8-15\text{m}^2/\text{g}$), exhibit good crystalline morphology and are fine, but they have a relatively broad particle size distribution (Hutson and Yang, 1987)

Kaolin is also soft which makes it non-abrasive. This property makes kaolin very important in many industrial applications because kaolin is softer than almost all the materials with which it comes into contact which makes the wear and tear of equipment and machinery to be low. Pure kaolins are relatively refractory and melt or fuse at a temperature of about $1850\text{ }^\circ\text{C}$ (Bailey, 1993). Other important physical and chemical properties are that kaolin is non reactive over a pH range of 4-9, has low heat and electricity conductivity, hydrophilic, dispersing readily in water and can be treated thermally or calcined to produce products that are excellent fillers and extender (Murray,1994).

2.12 Chromium Ions

Cr, a natural occurring element exist in six valence states 0, II, III, IV, V and VI represent the number of bonds an atom is capable of making. Cr can exist in air, water, soil and food. Common exposure pathways include ingestion, inhalation or dermal contact. The most common Cr species found environmentally are the trivalent (Cr-III) and hexavalent (Cr-VI) (Sharma and Foster, 1995). The trivalent is the most stable form occurring naturally in animals, plants, rocks and soils with its

compounds usually insoluble in water while hexavalent Cr is the second most stable form, rarely occurs in natural, most toxic and many of its compounds are soluble. Most Cr-VI in the environment is created by human activities (Monika *et al.*, 2009). Some of the industries with the largest contribution to chromium levels are leather tanning operations, metal processing, stainless steel welding, chromate production and chrome pigment production.

Some toxic effects of Cr compounds to humans or laboratory animals include developmental issues, damage to skin, respiratory, reproductive, digestive systems and cancer.

2.13 Modification of Clay

Surface modification of kaolin can be carried out by coupling agent, calcination, acid modification, alkali activation, mechano-chemical activation and intercalation.

2.13.1 Acid Modification

Acid modification is one of the most common chemical modifications of clay. It is done by treating clay with a mineral acid solution, usually HCl or H₂SO₄. The aim of this is to obtain a partly dissolved material of increased specific surface area, porosity and surface acidity (Komadel, 1994). The greatest and the most common anthropogenic source of acidity is mining waste containing sulphides. Acid-activated clays are mainly for acid –treated bentonites. Acid-activated bentonites have been a traditional product for many decades (Christidis, Scott and Dunham, 1997). Usually, a Ca²⁺ bentonite was treated with inorganic acids in replacing divalent calcium ions with a monovalent hydrogen ions, to leach out ferric, ferrous, aluminium and magnesium ions thereby altering the layers of smectite and increasing the specific surface area and porosity (Weiss, Choy, Meyer and Becker, 1981).

2.13.2 Thermally Modified Clay

Modification of the clay minerals structure and composition can also be by heating. The exact temperatures at which changes take place vary from one mineral group of clay to another, so also for different specimen within a particular group (Riley, 1951). The temperatures are also a function of the size of the particle and the heating state. The temperature ranges in which significance changes occur in the structure of clay minerals can be grouped into four.

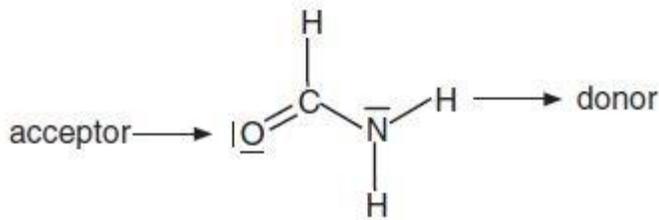
1. Temperatures low enough to cause partial freezing of clay suspensions or pastes (-5 °C): some of the water is converted into ice in this temperature range. However, at a temperature as low as -60 °C, a significant amount of water remains in a liquid or semi-liquid state which forms a film that separates the mineral surface from the ice (Mason, 1994).
2. Temperatures above dehydration but below dehydroxylation: clays lose adsorbed and hydration water when the temperature is raised from ambient to that of the onset of dehydroxylation (Mason, 1994). This cause the interlayer spaces to collapse while pore space is changed and the acidity of the clay mineral surfaces and interlayers is altered substantially.
3. Temperatures above dehydroxylation but below those leading to complete structure destruction.
4. Temperatures at which new phases crystallize: Clay minerals lose their original identity when new phases crystallize.

Clay minerals can be heated in forms like

- i. Without any admixtures or pre-treatment.
- ii. Mixed with different kinds of reagents before heating.
- iii. After treatment such as acid-activation.
- iv. After preheating and pre-treatment.

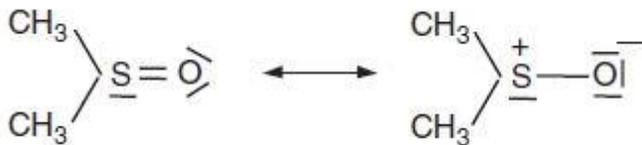
2.13.3 Intercalation

Intercalation is the penetration of organic molecules (or ion) into the interlayer space of clay minerals. Different types of organic compounds react with clay minerals in some particular ways (Lipsicas, Raythatha, Giese and Constanzo, 1986). Kaolin species like Kaolinite, nacrite and dickite adsorb different types of neutral organic compounds between the layers. Kaolinites and 2:1 clay mineral are identified by clay mineral organic reactions. Covalent bonds formed between reactive surface groups and organic species is an important step to hydrophobise the surface of clay mineral particles (Murray, 1994). The hydroxyl groups on the interlayer surface of kaolinite are accessible to the grafting agents when the interlayer space is expanded by intercalation.



Scheme 1 (Murray, 2007)

Other suitable molecules can displace intercalated guest molecules. Intercalation expands the pore and surface area thereby enhancing the adsorption process.



Scheme 2 (Murray, 2007)

Kaolin can intercalate various organic molecules

Organic guest compounds that are directly intercalated are

- Compounds that form hydrogen bonds like hydrazine, urea and formamide. The guest molecules must contain two separated groups in order to break the hydrogen bonds between the layers as seen in scheme 1. The carbonyl group accepts while the amide group donates hydrogen bonds (Lipsicas *et al.*, 1986).
- Compounds with high-dipole moments. Examples are: Dimethylsulphoxide (DMSO) and pyridine-N-oxide as seen in scheme 2.
Potassium, Rubidium, Caesium and ammonium salts of short-chain fatty acids (acetates, propionates, butyrates and isovalerates).
- Compounds that have bulky substituents are not intercalated but many of them are intercalated by either displacement or entraining reactions. Most intercalated guest compounds can easily be desorbed by washing with water or by heating (Murray, 2007).

2.14. Mechanism of Intercalation

Intercalation compounds can be prepared by reaction of the kaolinite with the guest molecules in form of liquids, melts or concentrated solutions at about 60-80°C. Intercalation process is slow requiring several days. The reaction rate depends on the type of guest compounds, temperature, concentration, type of kaolinite and the particle size (Riley, 1951). The degree of reaction defined in this way is different from the effective degree of reaction. The degree of reaction as a function of time mostly increases in the form of an S-shaped curve. Quantitative reaction is not reached by many kaolinite.

Weiss and co-workers concluded from neutron scattering data that the reaction is started by the migration of protons or re-orientation of OH groups under the influence of the dipole moment of the guest molecules adsorbed at the external basal plane surfaces (Weiss *et al.*, 1981). As a result

of this, an elastic deformation of the kaolinite layer near the basal plane that opens the interlayer space is formed. Electron resonance spectroscopy showed that the kaolinite layer is deformed by the intercalated guest compounds (Lipsicas *et al.*, 1986). The first guest molecule only penetrates between the silicate layers when one or both layers begin to curl, a zone of deformation is created which depends on the elastic properties of the silicate layer. The layer rolls up and promotes the penetration of guest molecules after the nucleation step.

2.15 Characterization Techniques

To carry out this research, the following analytical equipments were used and their modes of operation are discussed thus.

2.15.1 Fourier Transform Infrared Spectrometer (FTIR)

Infrared light was discovered in the 19th century, infrared absorption spectroscopy is the method used for determination of the structures of molecules with the molecules' characteristic absorption of infrared radiation. Infrared region is usually in the region of 12800-10cm⁻¹, this can be divided into near infrared region (12800-4000cm⁻¹), mid-infrared region (4000-200cm⁻¹) and far infrared region (50-1000cm⁻¹) (Bharska and Gopalakrishnarao, 2010). FTIR spectrometer is made up of a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer.

Radiation is generated by the source which passes the sample through the interferometer and reaches the detector; the signal is then amplified and converted to digital signal by the amplifier and analogue-to-digital converter respectively. The signal is eventually transferred to a computer in which Fourier transform is carried out. Samples molecules absorb radiation of specific wavelengths selectively when exposed to infrared radiation; this causes the dipole moment of sample molecules to change. (Brown and Groszek, 2000). The vibrational energy gap determines

the frequency of the absorption peak. The number of absorption peaks is related to the number of vibrational freedom of the molecule while the intensity of absorption peaks is related to the number of vibrational freedom of the molecule. The intensity of the absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels. Therefore, analysing the infrared spectrum, abundant structure information of a molecule can be obtained

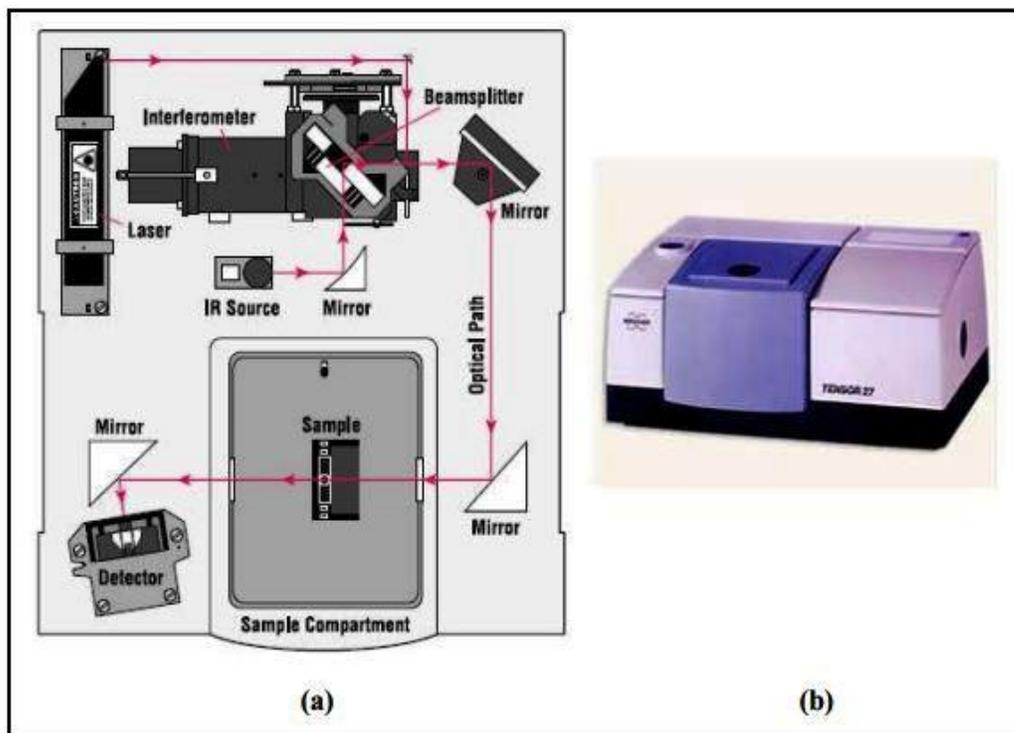


Figure 2.8: FTIR (a) showing the schematic diagram, (b) FTIR Instrument

(Brown and Groszek, 2000)

2.15.2. Scanning Electron Microscope (SEM)

SEM uses a focused beam of high-energy electrons for generation of a variety of signals at the surface of solid specimens. The signals derived from electron sample interactions reveal

information about the sample which includes the external morphology (texture), chemical composition, crystalline structure, and orientation of materials making up the sample (Rue and Ott, 1974). The SEM can also perform analyses of selected point locations on the sample; this method is useful in quantitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). SEM essential components are electron source (“Gun”), electron lenses, sample stage, detectors for all signals of interest, display/data output devices, infrastructure requirements (power supply, vacuum system, cooling system, vibration-free floor, room free of ambient magnetic and electric fields. Accelerated electrons in an SEM carry meaningful amounts of kinetic energy which usually disappears as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample (Jepson and Rowse, 1975).

These signals include secondary electrons (which produces SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD which are used for determination of crystal structures and orientations of minerals), photons (characteristic x-rays which are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL) and heat (Rue and Ott, 1974).

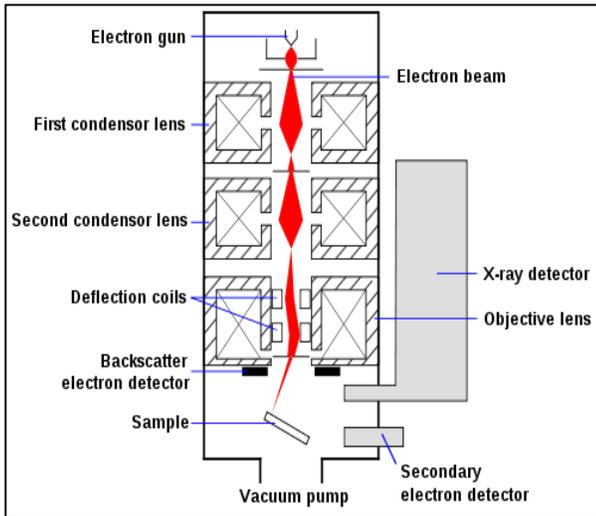


Figure 2.9: SEM (a) showing the schematic diagram, (b) SEM Instrument (Rue and Ott, 1974)

As the excited electrons return to lower energy states, X-rays that are of a fixed wavelength are generated. Thus, characteristic X-rays are produced for each element in a mineral that is “excited” by the electron beam.

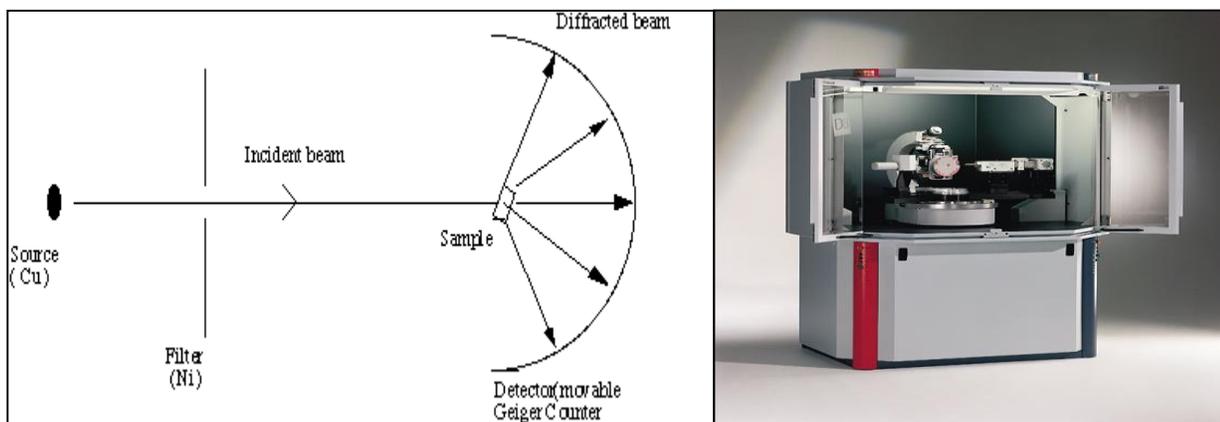
2.15.3 X-Ray Diffraction (XRD)

The exact nature of x-rays was not known when it was discovered in 1895 by Wilhelm Conrad Rontgen (the first Nobel laureate in Physics) (Moore and Reynolds, 1997). At that time, it was believed that crystals were made up of many repeating blocks and that each repeating block contained a constant number of the same type of atoms and the researchers of that time were able to show that simple crystals should have repeating units of the size needed for their proof of the wave-like nature of x-rays from simple calculations using density, atomic numbers and Avogadro’s number (Moore and Reynolds, 1997). As a means of analysing crystals structure, Bragg and his father, collimated x-rays in order to diffract off different crystal planes. The x-rays were collected in an ionization chamber and the ionization was measured as a function of the

incident angle of the X-rays. This method made the determination of the crystalline spacing for a number of substances possible.

X-ray diffraction (XRD) is an analytical technique which looks at X-ray scattering from crystalline materials. A unique fingerprint of X-ray intensity versus scattering angle that is characteristic of its crystalline atomic structure is produced by each material. By comparing the XRD pattern of an unknown material to a library of known patterns, qualitative analysis is possible (Middlebury, 2001). XRD is used to confirm the structural characteristics of synthesized samples since it gives a special fingerprint of specimen under investigation. The principle of XRD is based on phenomena of scattering whereby crystals perform the function of diffraction grating towards an incident X-ray. The X-rays are scattered by the atoms in the crystal in every direction and in a way which is unique to specific material (Bailey, 1980).

When fast moving particles are decelerated suddenly, X-rays are normally produced. Usually, this takes place in an X-ray tube where emission of the electrons from the cathode takes place and are accelerated through the vacuum where they strike a metal target anode. Metallic elements which are used as anode in X-ray generation include Copper, Cobalt, Chromium and Molybdenum.



(a)

(b)

Figure 2.10: XRD (a) showing the schematic diagram, (b) SEM Instrument (Moore and Reynolds, 1997)

2.15.4 Atomic Absorption Spectrometer (AAS)

Each element has a different set of energy levels which give rise to very narrow absorption lines; this makes the selectivity in AAS very important. The monochromator is also very important in obtaining a linear calibration curve (Beer's Law), the absorbing species bandwidth must be broader than that of the light source; which is difficult to achieve with ordinary monochromators (El-Shafey, 2007). The monochromator selects the specific wavelength of light absorbed by the sample excluding other wavelengths. Specific wavelength of light selection allows the determination of the specific element of interest when it is in the presence of other elements. The monochromator directs the light directed onto a detector usually a photomultiplier tube which converts the light signal into an electrical signal proportional to the light intensity.

Characteristic wavelengths of light are absorbed by atoms of different elements. To analyze a sample checking if it contains a particular element means light is being used from that element. The sample is converted to ground state free atoms in the vapour state and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporized sample i.e. the sample is atomized. The greater the number of atoms in the vapour, the more radiation is absorbed (Intech, 2013). A calibration curve is constructed through running of several samples of known concentration of the element under the same conditions as unknown. The amount absorbed by the standard is compared with the calibration curve which enables the calculation of the elemental concentration in the unknown sample.

From the monochromator, radiation on the detector produce direct current signal through amplifier then the absorbency can be read from the readout

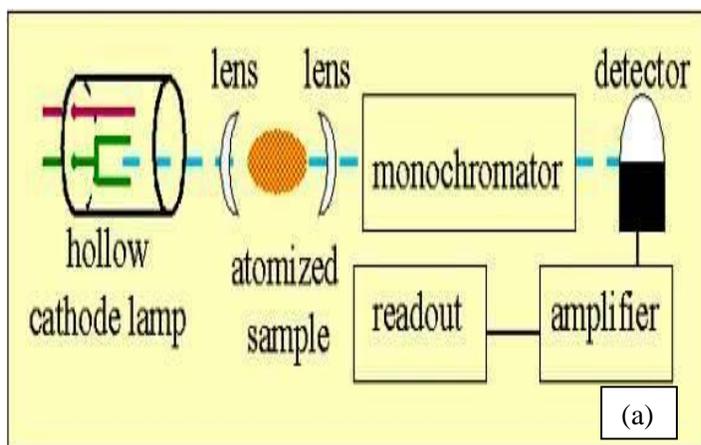


Figure 2.11: AAS (a) showing the schematic diagram (Intech, 2013).

2.16 Summary of Literature Review

Vital conclusions can be drawn from the review of literatures of some authors who have worked on similar projects. First, it was discovered that chemical pollution are caused by substances of chemical nature including metals such as chromium (Abbas *et al.*, 2010). The most common chromium species found environmentally are the trivalent (Cr-III) and hexavalent (Cr-VI). Cr-III is the most stable form while Cr-VI is the second most stable form. Cr finds its way into the environment through both natural processes and human activities. Some toxic effects of chromium

compounds to humans include damage to skin, respiratory, reproductive, digestive systems and cancer.

Chromium causes chemical pollution in the environment and the best technology that can be used for its removal is adsorption. Adsorption was found to be a preferred method of removal over other technologies like reverse osmosis, chemical precipitation, ion exchange, among others. This is because of its simplicity, easiness in handling, and availability of various adsorbents (Chern and Chien, 2002). Secondly, kaolin was found to be a low cost adsorbent with a low absorption and adsorption properties which are directly related to the low surface charge on the particle and must therefore be modified to improve its adsorption property (Aras *et al.*, 2007). Thirdly, it was established that surface modification of kaolin can be carried out by intercalation (a process of inserting organic molecules or ions into the interlayer space of clay minerals) (Lipsicas *et al.*, 1986). This review will be useful in the study of subsequent works.

CHAPTER THREE

3.0 RESEARCH METHODOLOGY

3.1 Materials and Chemicals Used

Table 3.1 Lists of Materials and Chemical Used

S/No	Material/Chemical	Source
1	Potassium Chromate (K_2CrO_4)	Commercial
2	Distilled water	Chemistry Department, FUT, Minna
3	HCl and NaOH	Chemical Engineering Department, FUT, Minna
4	Kaolin	Ahoko, Kogi State
5	Potassium Dihydrogen Phosphate	Chemical Engineering Department, FUT, Minna
6	Sample bottles	Commercial
7	Glass wool	Commercial
8	Filter paper	-

3.2 Equipment

Table 3.2 List of Equipment Used

S/No	Equipment	Manufacturer
1	Beakers	Pyrex, England
2	Water bath Shaker	Lsb-030s, DaihanLabtech, Korea
3	Weighing balance	Cyberlab, USA
4	Conical flasks	Microteknik, India
5	Beakers	Pyrex, England
6	Drip bag	Dana house, Minna
7	Flow set	Dana house, Minna
8	Measuring cylinder	Pyrex, England
9	Oven	N505f, GenlabWidnes, England
10	Crucible	Carbolite, England
11	Atomic Absorption Spectrophotometer	AA600 Shimadzu, Japan
12	Fourier Transform Infrared Spectrophotometer	8400S Shimadzu, Japan

3.3 Source and Analysis of Sample

Ahoko clay deposit is located between Abuja, Federal Capital Territory and Lokoja (Kogi state). The mine area covers to over 39 hectares of land. The raw samples were initially analyzed by XRD, SEM and FTIR. This was done to know the constituent minerals and the impurities that are present.

3.4 Refining of Sample

The sample used was that refined by (Kovo, 2011).

3.5 Modification of the Adsorbent

100 g of the clay samples were equilibrated with 2 L of 200 mg/L of potassium dihydrogen phosphate (KH_2PO_4) in a water bath shaker for a period of 24 h. The samples were then washed three times with a portion of 1L doubly distilled water for complete removal of excess H_2PO_4^- ions. The clay sample was later dried in an oven at a temperature of 70 °C

3.6 Preparation of Adsorbate

A stock solution containing 1000 mg^{-1} of Cr was prepared from Potassium chromate salt (K_2CrO_4). 40, 50, 60, 70 and 80 mg/L were obtained by fresh dilutions. The pH of the working solutions was adjusted to the required values by adding 0.1M HCl or NaOH.

3.7 Experimental Method

Both batch and continuous adsorption studies were carried out.

3.7.1 Batch Studies

Batch adsorption experiments were carried out at ambient temperature. Batch experiments were run in 250 mL beakers using water bath shaker at 150 rpm. Only a parameter was changed at a particular time while all others were kept constant. The conditions for the experiment are as follows;

3.7.1.1 Effect of pH of the Adsorbate

0.4 g of both phosphate intercalated and non- intercalated samples in 100 mL of 40 ppm aqueous solution of chromium, agitated for a period of 120 min with variation of pH from 2.0 to 6.0.

3.7.1.2. Effect of Time

0.4 g of both phosphate intercalated and non- intercalated samples in 100 mL of 40 ppm aqueous solution of chromium, agitated for interaction time of 30, 45, 60, 90 and 120 min at a pH of 6.0 ± 0.2 .

3.7.1.3 Effect of Adsorbent Dose

100 mL of 40 ppm aqueous solution of chromium varied with doses of intercalated and non- intercalated clay samples of 0.2, 0.3, 0.4, 0.5, and 0.6 g. Samples were agitated for a period of 120 min at a pH of 6 ± 0.2 .

3.7.1.4. Effect of Concentration of the Adsorbate

0.4 g of both phosphate intercalated and non- intercalated samples with variation of adsorbate concentration at 40, 50, 60, 70 and 80 mg/L, agitated for 120 min at a pH of 6.0 ± 0.2 .

The required pH of each solution was adjusted with 1M HCL or 1M NaOH before the adsorbent was mixed. The stirring was kept constant throughout the experiment. After the completion of each experiment, the flask was withdrawn from the shaker at the predetermined time interval and the supernatant was separated by filtration using filter paper. The final concentration was then analyzed by AAS.

The percentage removal of chromium from the aqueous solution can be calculated

$$\frac{C_{initial}-C_{final}}{C_{initial}} \times 100 \quad (3.1)$$

Here, $C_{initial}$ is the initial metal ion concentration and C_{final} is the final metal ion concentration.

The uptake of metal at equilibrium time was calculated from

$$q_e = \frac{(C_0 - C_e)v}{1000w} \quad (3.2)$$

Where q_e is the amount of adsorbed chromium in mg/g. C_0 and C_e are the initial and equilibrium metal ion concentration in mg/L, v is the volume of the aqueous solution in ml and w is the weight of the adsorbent in g.

3.7.2. Column Studies

Column studies were carried out in a glass column of a known diameter and height. Glass wool was used in packing the adsorbent at both end of the glass. A known concentration of aqueous Chromium was passed in through a drip bag (storage bag) connected to a flow set (valve) used in the adjustment to the desired flow rate. Samples were then collected at predetermined time interval for analysis of the sample by AAS.

3.7.2.1 Effect of flow rate

At constant bed height of 3cm and inlet concentration of the adsorbate at 20 mg/L, the flow rate was varied between 6 mL/min and 10 mL/min.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

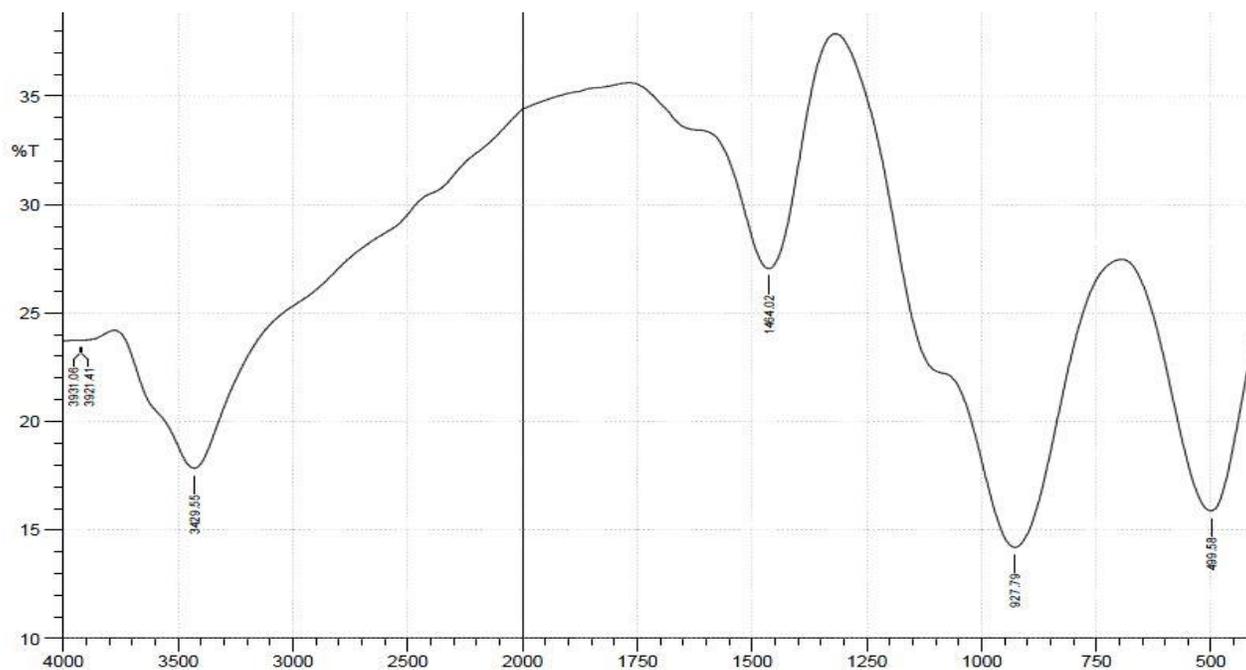
This chapter shows the initial characterization and analysis of the intercalation of the starting material. The determination of the concentration of chromium metal using the non- intercalated and intercalated kaolin as adsorbent by varying the pH, adsorbate concentration, time and adsorbent dose was also presented in the chapter.

4.1 Characterization of the sample

Both non-intercalated and intercalated kaolin were characterized and analyzed. The results are presented in figures 4.1 - 4.8.

4.1.1 FTIR Analysis

The starting and the intercalated samples were analyzed with the aid of FTIR. The result is presented in figure 4.1 and 4.2 below.



1/cm

Fig 4.1: FTIR Spectrum for non-intercalated Kaolin

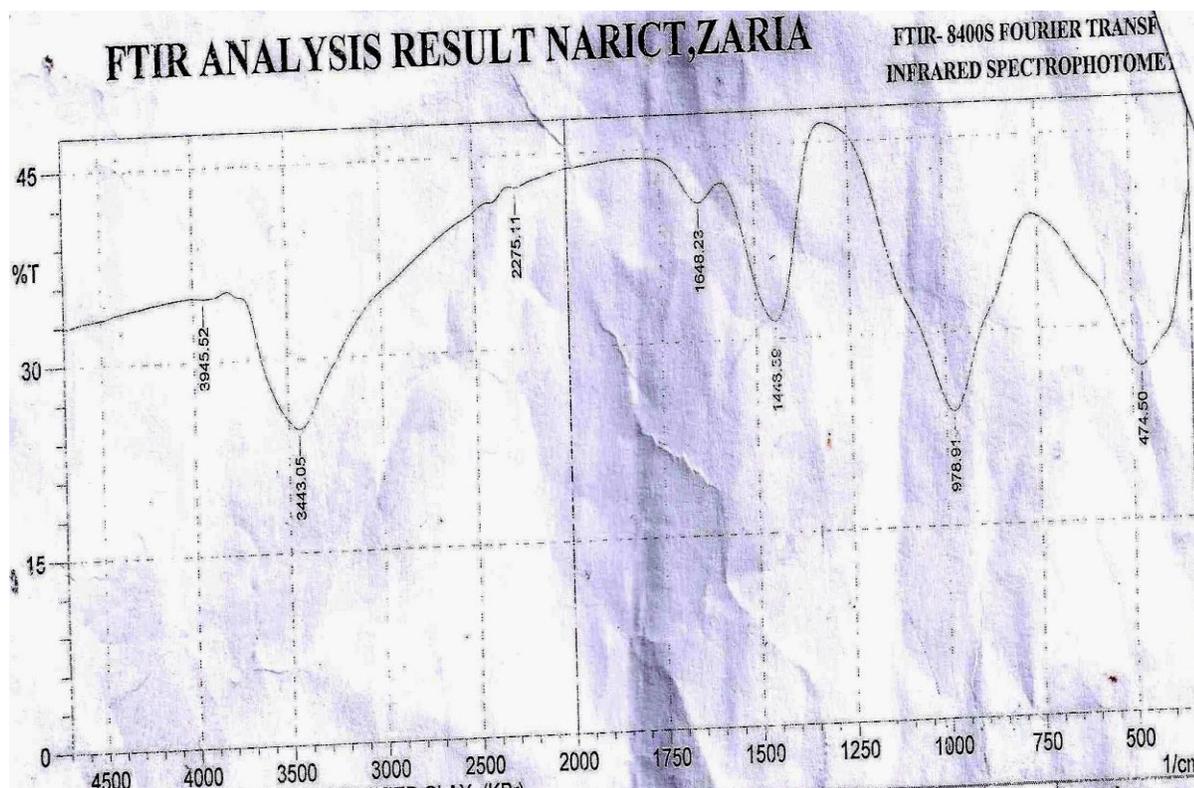


Fig 4.2: FTIR Spectrum for intercalated Kaolin

FTIR was used to determine the functional groups in the sample. The FTIR spectrum of the non-intercalated kaolin ($400\text{-}4000\text{cm}^{-1}$) shown in figure 4.1 displayed the major band 3429.55 cm^{-1} O-H stretches. Also, from Fig 4.2, the FTIR spectrum ($400\text{-}4500\text{cm}^{-1}$) displayed the major bands 3443.05 cm^{-1} : O-H stretch. The appearance of the strong peak at 2275.11 cm^{-1} and 1648.23 cm^{-1} for the intercalated kaolin can be attributed to the O-H stretching vibration which was caused by the intercalation. OH peak is good for adsorption. The assignment of band was made as reported by Bharska and Gopalakrishnarao (2010).

4.1.2 Brunauer-Emmet Teller (BET) Surface Area

BET method is used for determination of the surface area of most porous material. Total surface area is an important parameter since it determines the accessibility of the active site to probing molecules (Warwick, 2013). Surface area of non-intercalated and intercalated kaolin are carried out by nitrogen adsorption which is generally known to refer to the enrichment of one or more of a component between two bulk phases. One of the phases must be solid (adsorbent) and the other phase fluid (gas or liquid) which is the adsorbate. Nitrogen is usually the preferred adsorptive material because of quadra-pole moment that is permanent and it is responsible for the formation of well defined monolayer on most surfaces.

The result showed that the surface area for the non- intercalated kaolin was $2.4298 \pm 0.0014 \text{ m}^2/\text{g}$ while that of the intercalated kaolin was $16.1716 \pm 0.0323 \text{ m}^2/\text{g}$. This is in accordance with that found in similar kaolin as reported in the literature (specific surface area for kaolin $5\text{-}20 \text{ m}^2/\text{g}$) (Aras *et al.*, 2007).

4.1.3: X-ray Diffraction Analysis

The XRD gives a unique fingerprint of samples under consideration and it is used for confirming the structural characteristics of a sample. (Kovo, 2011). The starting and the intercalated kaolin were analyzed with the aid of the XRD. The result is presented in figure 4.3 and 4.4



2 theta (degree)

FIG 4.4: XRD Pattern for intercalated Kaolin

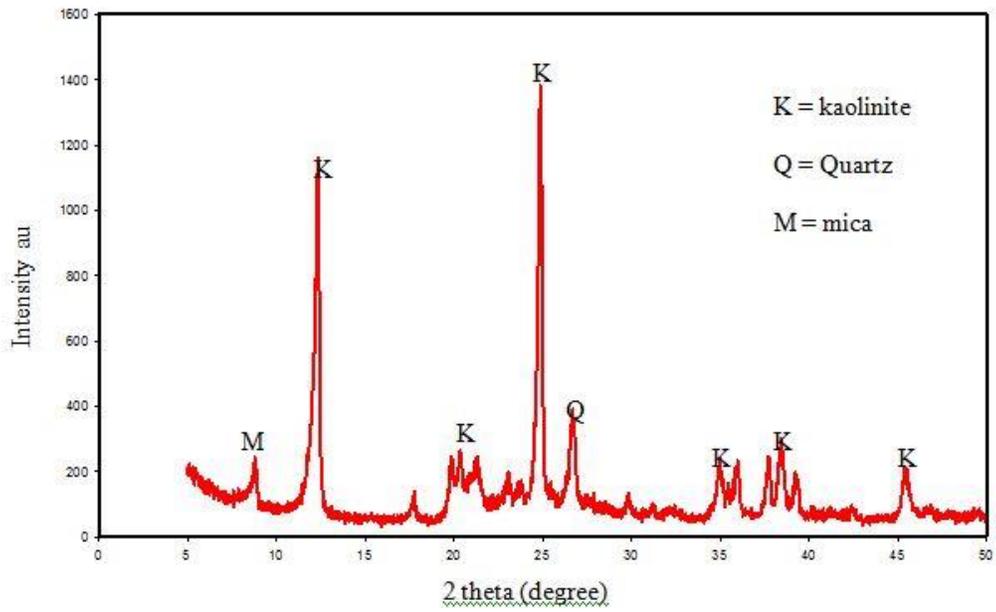


FIG 4.5: XRD pattern of Watts Blake Bearne (WBB) kaolin

4.1.4 SEM Analysis

Kaolin is a mineral with a double-layer structure comprising of Si-O tetrahedron and Al-O tetrahedron ($\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$) (Aras *et al.*, 2007). The results for the SEM images of the non-intercalated and intercalated kaolin are presented in figures 4.6, 4.7, 4.8 and 4.9.

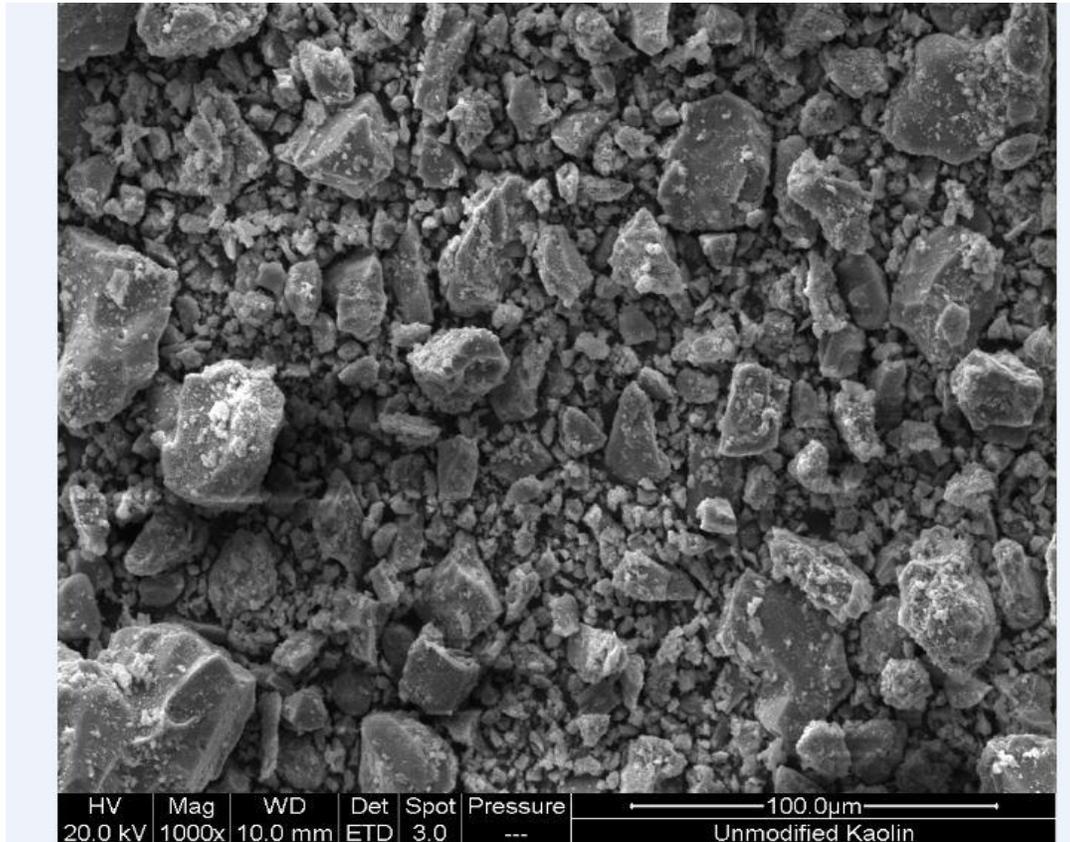


Fig 4.6: SEM Image for non-intercalated Kaolin at 1000x Magnitude

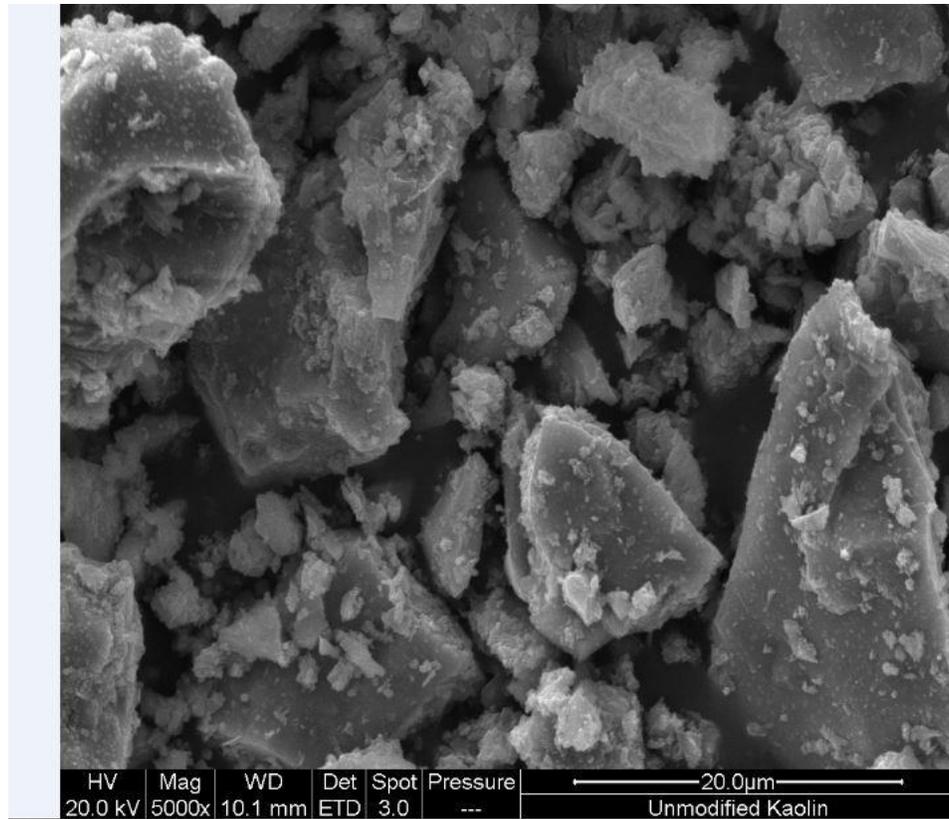


Fig 4.7: SEM Image of non- intercalated Kaolin at 5000x Magnitude

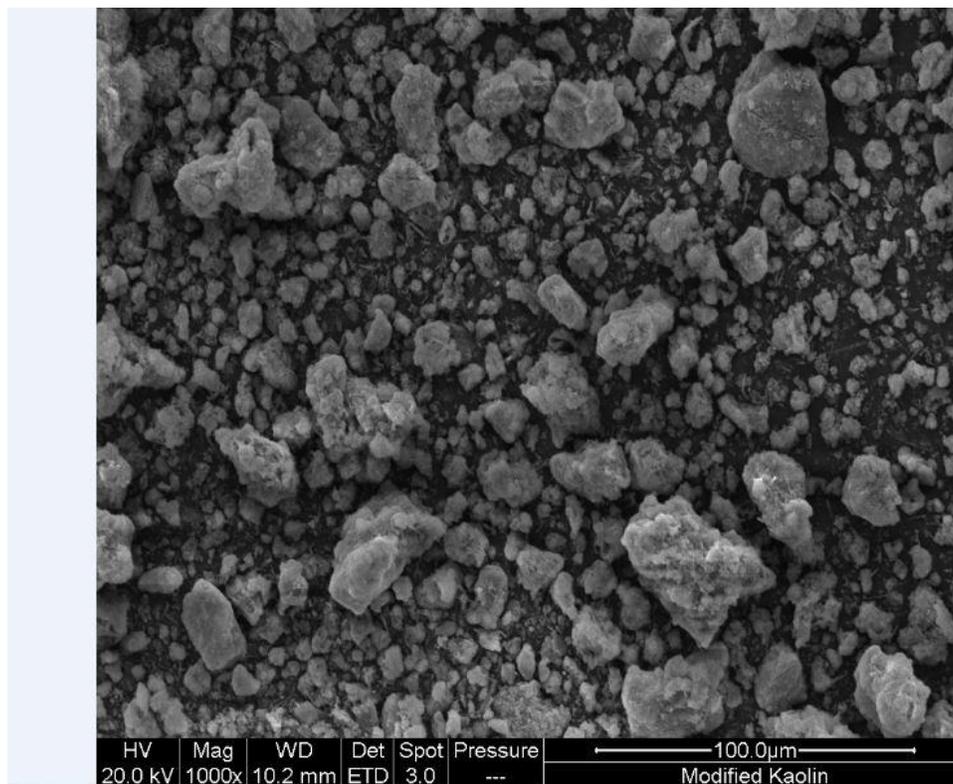


Fig 4.8: SEM Image for intercalated Kaolin at 1000x Magnitude

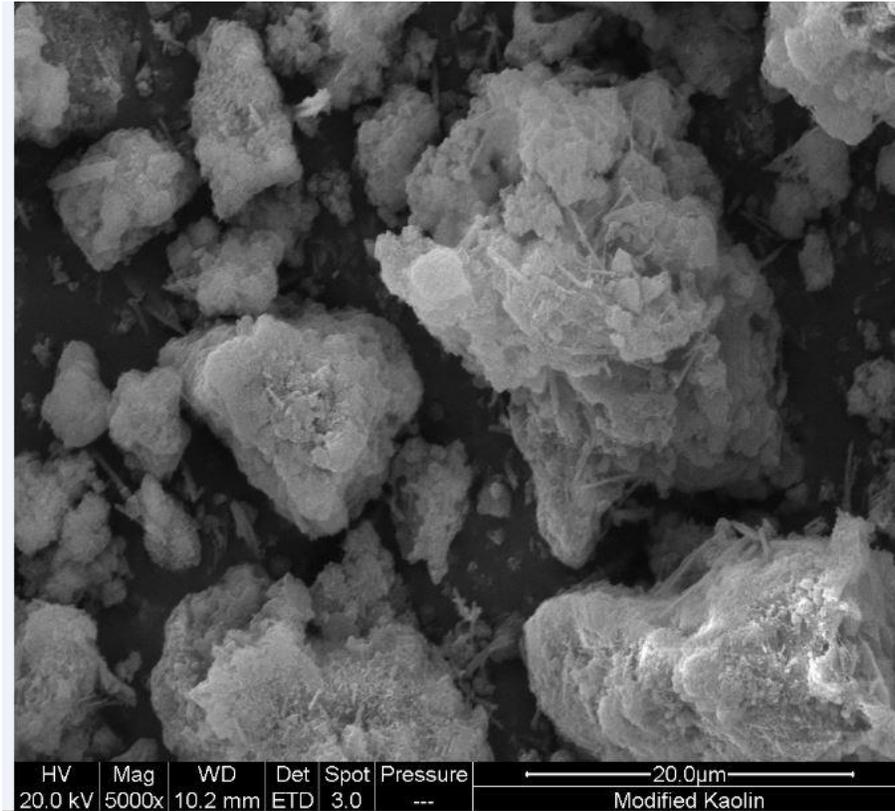


Fig 4.9: SEM Image for intercalated Kaolin at 5000x Magnitude

The SEM was used to identify the morphology of the kaolin samples as depicted in (Figure 4.6 - 4.9). The non-intercalated kaolin shows platelets features. The intercalated kaolin also shows platelets features with growth on the surface as a result of the intercalation process. The images reveal a proper crystallized particle with pseudo-hexagonal platelet shape as reported for other kaolin in the literature by Rue and Ott, (1974).

4.1.5. EDAX (Energy Dispersive X-ray Analysis) Analysis

The EDAX which is an x-ray technique was used for the identification of the elemental composition of kaolin as depicted in Figure 4.10-4.11.

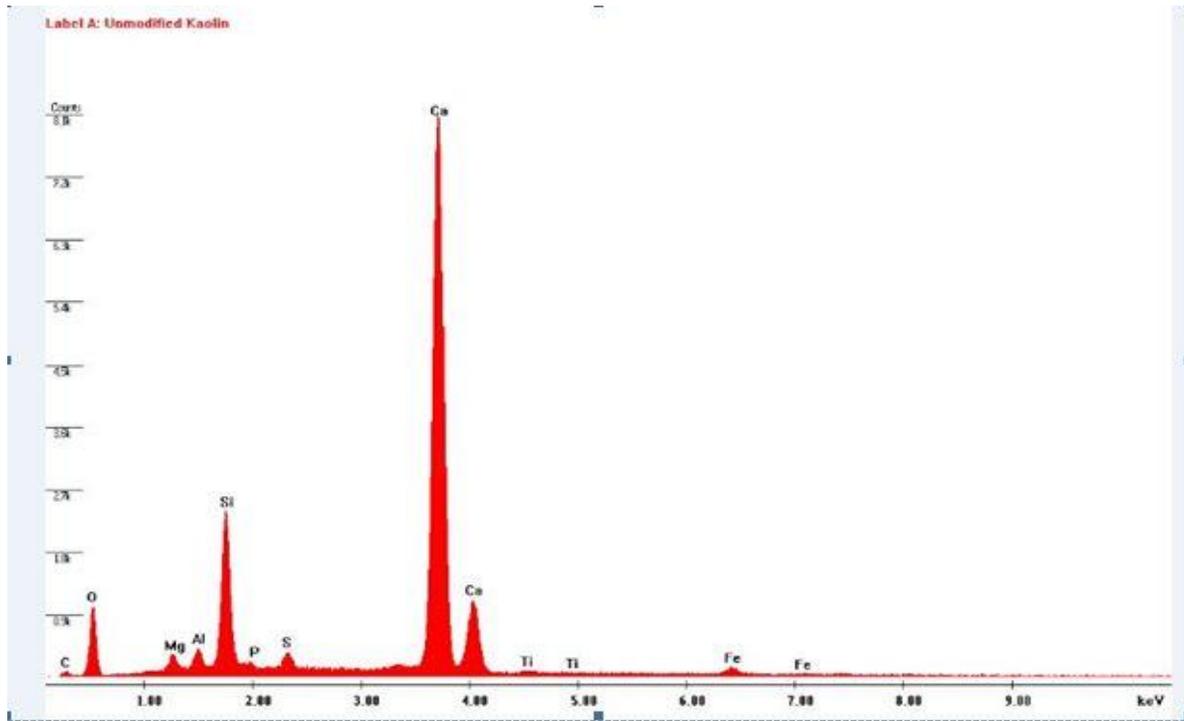


Fig 4.10: EDAX for non-intercalated kaolin

C:\Images 2013\Kovo\19-6-13\Modified Kaolin.spc

Label A: Modified Kaolin

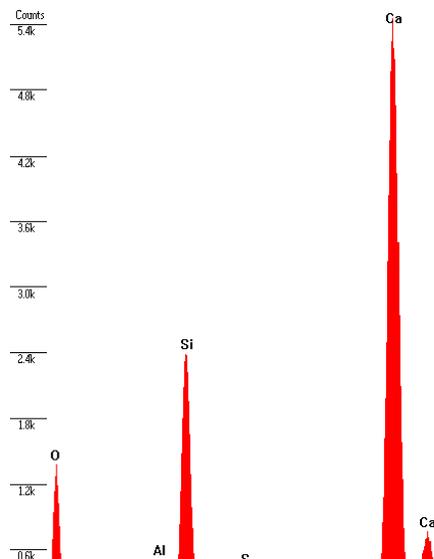


Fig 4.11: EDAX for intercalated kaolin

Figures 4.10 and 4.11 are the data generated by EDAX analysis consisting of spectra showing peaks corresponding to the elements which makes up the true composition of the analyzed kaolin. Accelerating voltage of 20keV was used for the analysis. All the elements present in both non-intercalated and intercalated revealed light elements emitting X-rays of K-series only. The concentrations of the elements (in wt%) for the non-intercalated kaolin are Ti (0.23), S (1.22), Ca (40.55), C (2.23), O (27.53), Mg (1.59), Al (1.78), Si (10.40), and P (0.37) while that of intercalated kaolin (in wt%) are Ti (0.42), S (1.91), Ca (52.70), C (2.63), O (35.05), Mg(1.72), Al (2.52), Si (12.25) and P (0.89). The result showed that the intercalation process increased the concentrations of the elements in the intercalated kaolin.

4.2 Adsorption study

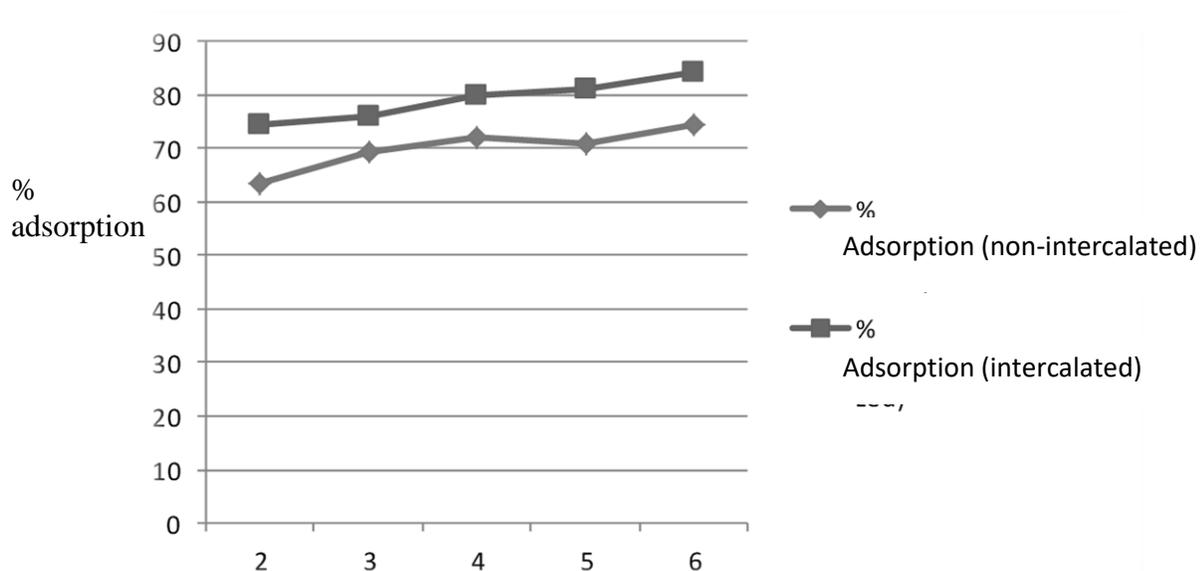
The adsorption study was carried out in both batch and continuous process.

4.2.1 Batch Studies

The batch studies were carried out in ambient temperature. The results of the conditions for the experiment are presented in Tables 4.1- 4.4 and Figures 4.10-4.13.

Table 4.1: Effect of pH on % adsorption of chromium ion on intercalated and non-intercalated kaolin

pH	Final concentration (non- intercalated) (mg/L)	Final concentration (intercalated) (mg/L)	% adsorption (non- intercalated)	% adsorption (intercalated)
2	14.5550	10.1829	63.6	74.5
3	12.3312	9.5163	69.2	76.2
4	11.1414	8.0498	72.1	79.9
5	11.6696	7.5768	70.8	81.01
6	10.1980	6.3543	74.5	84.1



pH

Fig 4.12: Effect of pH on adsorption of chromium ion on intercalated and non- intercalated kaolin

The effect of pH on adsorption of chromium on intercalated and non-intercalated kaolin is presented in fig 4.12. pH is an important parameter in metal adsorption process. Changes in the effect of pH occur due to the type of adsorbent used, its behavior in the solution and the type of ions adsorbed. The removal efficiency increases throughout with increase in pH for the intercalated kaolin, the removal efficiency also increases to a pH of 4 for the non- intercalated, reduced at pH of 5 and later increased at the pH of 6. The highest removal efficiency in the chromium adsorption with both intercalated and non-intercalated kaolin was obtained at a pH of 6 with % adsorption of 84.1 and 74.5 respectively. The intercalated kaolin gave the highest removal efficiency with a value of 84.1%

Table 4.2: Effect of time on % adsorption of Cr metal ion on intercalated and non-intercalated kaolin

Time (min)	Final concentration (intercalated) (mg/L)	Final concentration (non-intercalated) (mg/L)	% adsorption (non-intercalated)	% adsorption (intercalated)
30	9.1516	9.9440	75.14	77.1
45	9.6497	9.9716	75.1	75.9
60	17.1259	13.1287	67.2	57.2

90	10.7892	9.9943	75	73.03
120	11.8004	10.3565	74.1	70.5

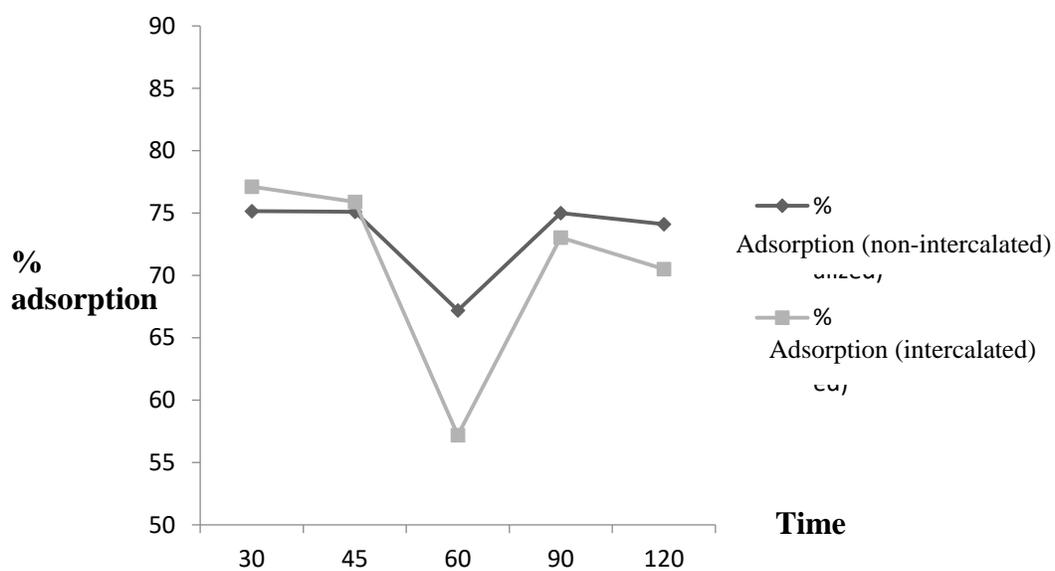


Fig 4.13: Effect of time on adsorption of chromium ion on intercalated and non- intercalated kaolin

The effect of time on adsorption of chromium ion on intercalated and non- intercalated kaolin is presented in Figure 4.13. It can be observed that instant adsorption took place at the initial stage

in both processes. Due to the time required for the equilibrium to be reached, a gradual decrease in the adsorption process is observed in both cases. The maximum adsorption of chromium by the intercalated kaolin was 77.1% in 30mins and 75.14% in the non- intercalated kaolin. Equilibrium can be attained after some time or can occur almost immediately as 30mins in both cases. This shows that high removal efficiency of chromium can be obtained at short time period of 30mins.

Table 4.3: Effect of adsorbent dose on % adsorption of chromium ion on intercalated and non-intercalated kaolin

Adsorbent dose (g)	Final concentration (intercalated) (mg/L)	Final concentration (non-intercalated) (mg/L)	% adsorption (intercalated)	% adsorption (non-intercalated)
0.2	8.1353	9.4031	79.7	76.5
0.3	9.2119	9.9389	77	75.2
0.4	7.8586	8.9604	80.4	77.6
0.5	8.1856	9.6798	79.5	75.8
0.6	10.4898	9.9515	73.8	75.1



**%
adsorption**

Adsorption (intercalated)

Adsorption (non-intercalated)

Adsorbent dose

Fig 4.14: Effect of adsorbent dose on adsorption of chromium ion on intercalated and non-intercalated kaolin

The effect of adsorbent dose on adsorption of chromium ion in intercalated and non-intercalated kaolin is presented in Figure 4.14. The maximum adsorption of chromium occurs at a dosage of 0.4 g in both cases with 80.4% in the intercalated kaolin and 77.6% in the non-intercalated one. This shows that 0.4 g of the adsorbent is the optimum that can be used in chromium removal.

Table 4.4 Effect of concentration of adsorbate on % adsorption of chromium ion on intercalated and non-intercalated kaolin

Adsorbate conc. (mg/L)	Final concentration (intercalated) (mg/L)	Final concentration (non-intercalated) (mg/L)	% adsorption (intercalated)	% adsorption (non-intercalated)
40	9.4710	9.6144	76.3	76
50	14.2632	13.7148	71.5	72.6
60	16.1498	14.8468	73.1	75.3
70	16.3460	16.8793	76.6	75.9
80	11.7979	18.2377	85.3	77.2

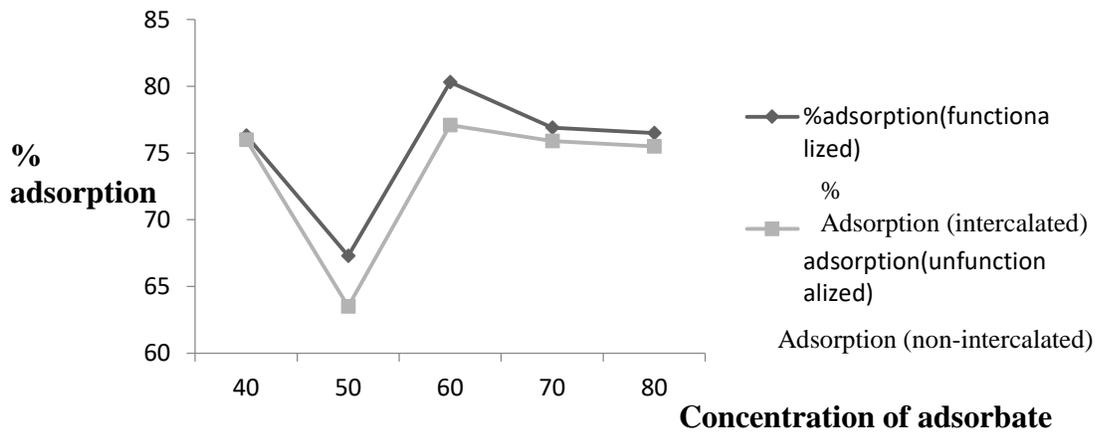


Fig 4.15: Effect of concentration of adsorbate on adsorption of chromium ion on intercalated and non-intercalated kaolin

The effect of concentration of adsorbate on adsorption of chromium ion on intercalated and non-intercalated kaolin is presented in Figure 4.15. The maximum adsorption efficiency obtained was at 80mg/L in both cases and decreases with increase in the concentration of the adsorbate. Hence, the % adsorption of chromium is dependent on the initial concentration.

4.2.2 Column Adsorption Study

A column adsorption study was carried out in a glass column. The study was used to determine the breakthrough curve for the adsorption of chromium unto intercalated kaolin. The result is presented in Figure 4.16.

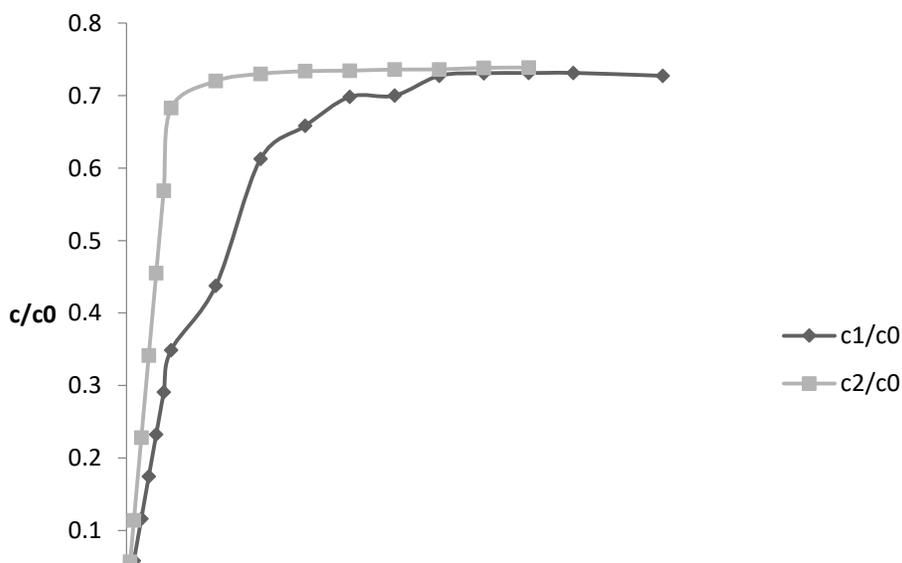


Fig 4.16: Effect of Flow Rate on Breakthrough Time

Where

c_0 is the inlet concentration of the adsorbate at 20mg/L

c_1 is the outlet concentration of the adsorbate at 6mg/L

c_2 is the outlet concentration of the adsorbate at 10mg/L

Figure 4.14 shows the effect of flow rate on the adsorption of chromium by intercalated kaolin.

The breakthrough curves were developed for 6mL/min for c_1 and 10mL/min for c_2 . The outlet concentration of the adsorbate was zero at the early stage of the experiment, but increases gradually with increase in time until saturation point was reached. The breakthrough occurred faster and the breakpoint time decreased at a higher flow rate. This is as a result of long residence time of the adsorbate in the column leading to minimized contact time between the adsorbate and the adsorbent. (Sivakumar and Palanissamy, 2009).

4.3 Equilibrium Isotherm

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equilibrium isotherms were used to compare the experimental equilibrium adsorption data.

4.3.1 Langmuir Isotherm

It is usually used to describe adsorption of solute from a liquid solution and it is perhaps the best of all the isotherms which describes adsorption. (Dada *et al*, 2012). It assumes that adsorption takes place at specific homogenous sites within the adsorbent. It can be represented as

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (4.1)$$

This can be written in linear form as

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (4.2)$$

Where

C_e is the equilibrium concentration of the adsorbate in mg/L

q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium in mg/g

Q_0 is the maximum monolayer coverage capacity in mg/g

K_L is the Langmuir isotherm constant in L/mg

The values of Q_0 and K_L were obtained from the slope and intercept of the Langmuir plot of $1/q_e$ against $1/C_e$ (Figure 4.16). The Langmuir isotherm essential features can be expressed in terms of equilibrium parameter R_L which is a dimensionless constant referred to as equilibrium parameter or separation factor. (Dada *et al.*, 2012)

$$R_L = \frac{1}{1 + (1 + K_L C_0)} \quad (4.3)$$

Where C_0 is the initial concentration

K_L is a constant which is related to the energy of adsorption

R_L indicates the adsorption nature which can be unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. (Dada *et al.*, 2012)

But

$$q_e = \frac{(C_o - C_e)V}{m} \quad (4.4)$$

Where

C_o (mg/L) is the initial metal ion concentration

C_e (mg/L) is the equilibrium concentration of metal ion in the solution

m (g) is the mass of adsorbent

V (L) is the volume of metal ion solution

Mass of the adsorbent used=0.4g

Volume of metal ion solution used=100ml=0.1L

The parameters for plotting and the linear plot of Langmuir Isotherm are shown on Table 4.5 and Figure 4.17 respectively.

Table 4.5 Parameters for plotting Langmuir isotherm

S/No	C_o (mg/L)	C_e (mg/L)	Q_e	$1/q_e$	$1/C_e$
1	40	9.4710	7.6323	0.1310	0.1056
2	50	14.2632	8.9342	0.1119	0.0701
3	60	16.1498	10.9626	0.0912	0.0619

4	70	16.3460	13.4135	0.0746	0.0612
5	80	11.7979	17.0505	0.0586	0.0848

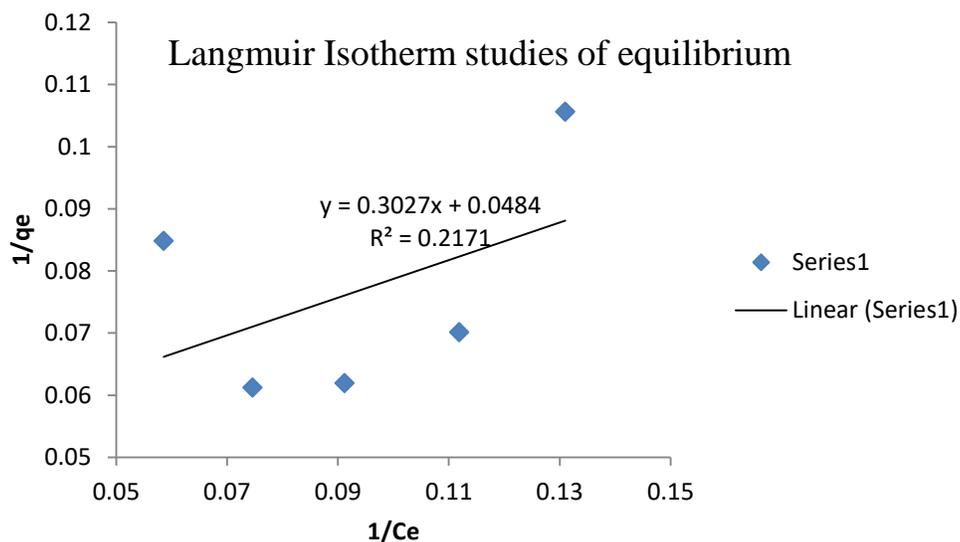


Fig 4.17: Linear plot for Langmuir isotherm

From the calculated data, the maximum monolayer coverage capacity was 20.66mg/g, the Langmuir isotherm constant was found to be 0.16L/mg and the separation factor was found to be 0.12. Since the value of R_L is greater than zero but less than 1, it implies that Langmuir Isotherm is favorable. (Bhattacharyya and Gupta, 2008). Also, the coefficient of determination R^2 was found to be 0.217.

4.3.2 Freundlich Isotherm

This isotherm is usually used in describing a heterogeneous surface of the adsorption characteristics. (Tan, Ahmad, Hameed, 2009). It is represented as

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (4.5)$$

Where K_f is the Freundlich Isotherm constant in mg/g

Q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium in mg/g

C_e is the equilibrium concentration of the adsorbate in mg/L

n is the adsorption intensity

In linear form, it can be written as

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (4.6)$$

K_f , represents an approximate indicator of adsorption capacity while $1/n$ represents a function of the strength of adsorption in the adsorption process (Dada *et al.*, 2012). The parameters for plotting and the linear plot of Freundlich Isotherm are shown on Table 4.6 and Figure 4.18 respectively.

Table 4.6: Parameters for plotting Freundlich adsorption isotherm

S/No	Ce	qe	Log qe	LogCe
1	9.4710	7.6323	0.8827	0.9764
2	14.2632	8.9342	0.9511	1.1542
3	16.1498	10.9626	1.0399	1.2082
4	16.3460	13.4135	1.1275	1.2134
5	11.7979	17.0505	1.2317	1.0718

Freundlich Isotherm Studies of equilibrium

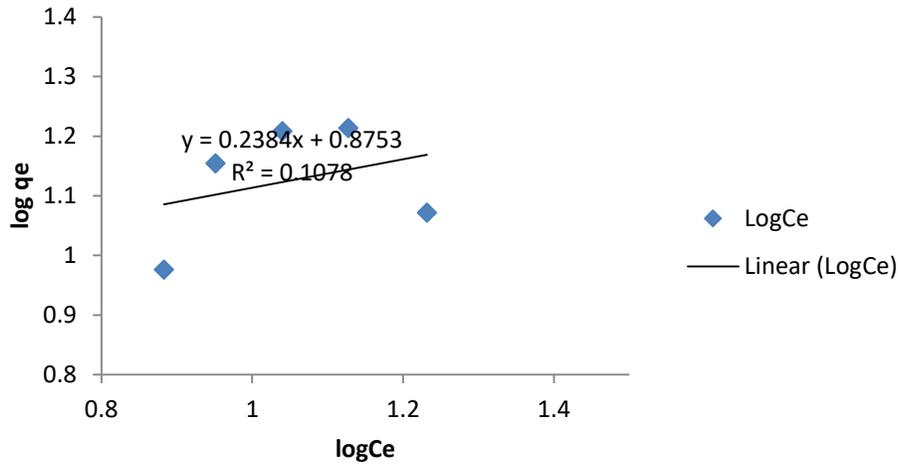


Fig 4.18: Linear plot for Freundlich Isotherm

The smaller the $1/n$, the greater the expected heterogeneity which reduces to a linear adsorption isotherm when $1/n=1$. If n is between 1 and 10; it implies a favourable sorption process. (Dada *et al.*, 2012)

From the plot (Figure 4.18), $1/n$ is 0.2384, $n=4.19$ which indicates that Freundlich isotherm is also favourable. The coefficient of determination R^2 was found to be 0.1078.

4.3.3 Temkin Isotherm

This isotherm has a factor that considers the interactions of adsorbent-adsorbate. This model assumes that the heat of adsorption of all molecules in the layer decreases linearly rather than logarithmic with coverage. Constants were determined from the slope and intercept by plotting q_e (quantity adsorbed) against $\ln C_e$ (Nunes *et al.*, 2009; Hameed, 2009). It is given as

$$q_e = \frac{RT}{b} \ln(A_T C_e) \quad (4.7)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b}\right) \ln C_e \quad (4.8)$$

$$B = \frac{RT}{b_T} \quad (4.9)$$

$$q_e = B \ln A_T + B \ln C_e \quad (4.10)$$

Where A_T is Temkin Isotherm equilibrium binding constant in L/g

b_T is the Temkin Isotherm constant

R is the universal gas constant (8.314J/mol/K)

T is temperature at 300K

B is a constant related to heat of sorption in J/mol (Dada *et al.*, 2012)

Table 4.7: Parameters for plotting Temkin Adsorption Isotherm

S/No	Co(mg/L)	Ce(mg/L)	Qe	logCe
1	40	9.4710	7.6323	0.9764
2	50	14.2632	8.9342	1.1542
3	60	16.1498	10.9626	1.2082
4	70	16.3460	13.4135	1.2134
5	80	11.7979	17.0505	1.0718

Temkin Isotherm Studies of Equilibrium

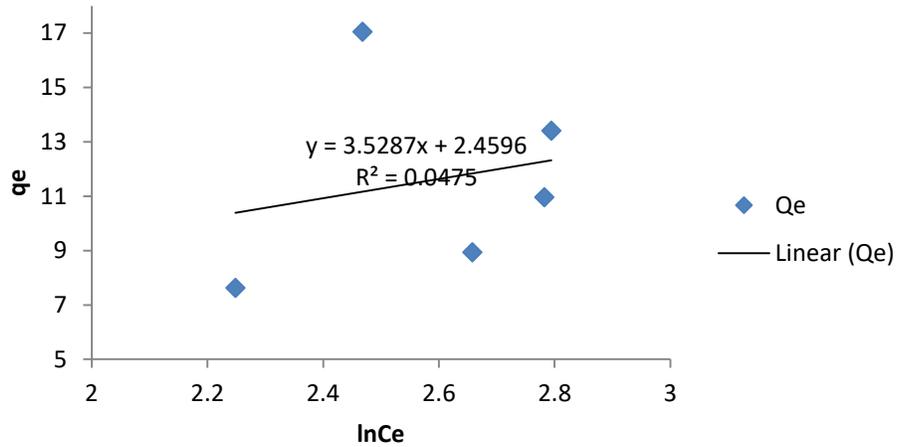


Fig 4.19: Linear Plot for Temkin Isotherm

The linear plot for Temkin Isotherm (Figure 4.19) gave a much lower value of coefficient of determination, $R^2=0.0475$. A_T was found to be 2.01L/g while B was found to be 3.53J/mol, this indicates that the heat of sorption is a physical adsorption process.

4.3.4 Dubinin –Radushkevich Isotherm

The isotherm stated that the characteristic sorption curve is related to the porous structure of the sorbent. It is expressed as

$$q_e = q_D \exp\left(-B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \quad (4.11)$$

It can be written in linear form as

$$\ln q_e = \ln q_D - B_D \left(RT \ln\left(1 + \frac{1}{C_e}\right)\right)^2 \quad (4.12)$$

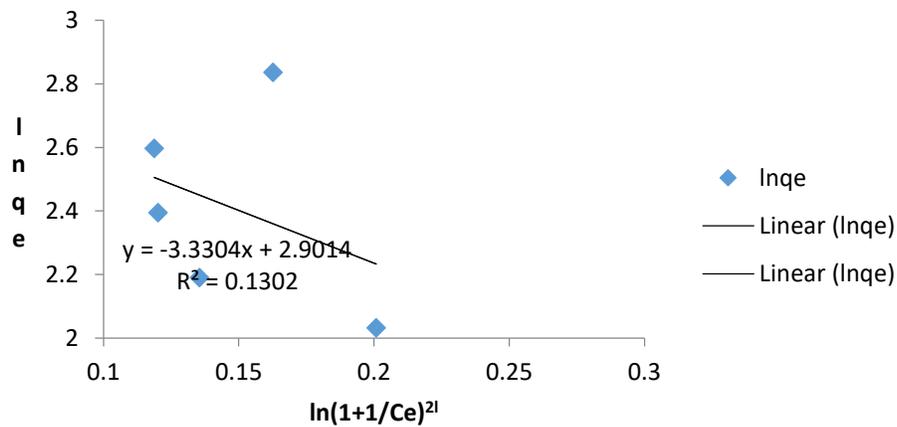
E_D is the apparent energy and it can be computed using

$$E_D = \sqrt{1/2} B_D \quad (4.13)$$

where K and C_e the adsorbate equilibrium concentration in mg/L, B_D is the isotherm constant, q_e is the amount of adsorbate in the adsorbate in the adsorbent at equilibrium (mg/g), R is the gas constant (8.314J/molK) and T is the absolute temperature.(Dada *et al.*, 2012).

Table 4.8: Parameters for plotting Dubinin-Radushkevich isotherm

Q_e	$\ln q_e$	$C_e(\text{mg/L})$	$(1+1/C_e)^2$	$\ln(1+1/C_e)^2$
7.6323	2.0323	9.4710	1.2223	0.2008
8.9342	2.1899	14.2632	1.1451	0.1355
10.9626	2.3945	16.1498	1.1277	0.1202
13.4135	2.5963	16.3460	1.1261	0.1188
17.0505	2.8362	11.7979	1.1767	0.1627



4.20: Linear Plot for Dubinin Radushkevich Isotherm

From the linear plot, (figure 4.20) q_D was determined to be 18.1996mg/g, the mean free energy, E is a parameter used for prediction of the type of adsorption process, $<8\text{KJ/mol}$ indicates physisorption process (Monika *et al.*,2009).

E was found to be 0.97KJ/mol which signifies a physisorption process. R^2 for linear plot was found to be 0.1302.

Table 4.9: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherm constants for the adsorption of Chromium unto functionalized Kaolin

Metal Ion	Langmuir Isotherm					Freundlich Isotherm				
	Q_o (mg/g)	K_L (L/mg)	R_L	R^2		1/n	N	K_f	R^2	
Cr	20.66	0.16	0.12	Linear	0.2171	0.2384	4.19	7.50	Linear	0.1078
	Temkin Isotherm					Dubinin-Radushkevich Isothermal				
	A_T	b_T	B	R^2		q_D (mg/g)	B_D (mol ² / kJ ²)	E (KJ/ mol)	R^2	
	2.01	706.8	3.53	Linear	0.0475	18.1996	5.35×10^{-7}	0.97	Linear	0.1302

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the study, the pH of the adsorbate, concentration of the adsorbate, contact time and adsorbent dose are highly responsible for chromium removal from aqueous solution. Also, the mechanism of adsorption onto kaolin was deduced to be physisorption. The coefficient of determination for the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms were low, this might be as a result of the process condition e.g. temperature that was not considered. However, Langmuir adsorption still gave the best fit. The breakthrough occurred faster and the breakpoint time decreased at a higher flow rate for the column study.

It can therefore be concluded that the adsorption capacity of kaolin was improved through phosphate intercalation which makes it very effective in removal of chromium from aqueous solution.

5.2 Recommendations

It can be recommended that the operation parameters for the batch process should be optimized in order to determine the best condition. Also, models can be developed using the parameters obtained to validate results of other experiment. Peristaltic pump is a necessity for column studies

and should be made available in the laboratories. The problem of pressure build up within the column should be critically examined when researching into column studies using kaolin as the adsorbents

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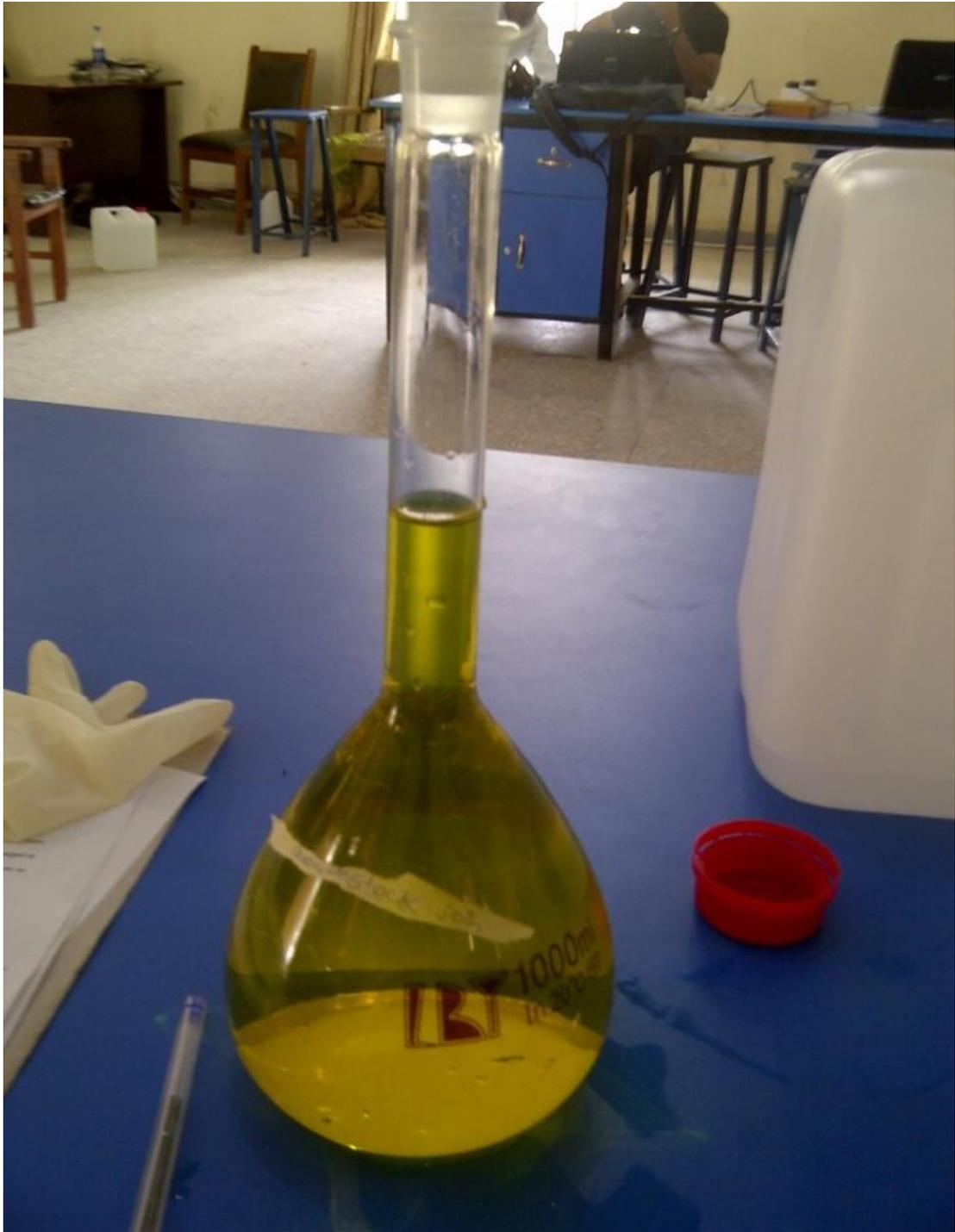
APPENDICES



APPENDIX 1: pH Adjustment of the Sample



APPENDIX 2: Intercalated Kaolin



APPENDIX 3: Chromium Stock Solution



APPENDIX 4: Experimental Set Up for Column Adsorption Process

