ANALYSIS AND CHARACTERIZATION OF IKPESHI CLAY MINERALS CONTENT FOR INDUSTRIAL APPLICATION

BY

OKWAH AKPEPHRE GODSPOWER

(PG/ENG/1917266)

DEPARTMENT OF CHEMICAL ENGINEERING

FACULTY OF ENGINEERING

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A REEARCH PROJECT SUBMITTED BY THE DEPARTMENT OF CHEMICAL ENGINERING, FACULTY OF ENGINEERING, UNIVERSITY OF BENEIN, BENIN CITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER DEGREE OF ENGINEERING (M.ENG.) IN CHEMICAL ENGINEERING.

MARCH, 2023.

CERTIFICATION

This is to certify that, this project work was carried out by **Okwah Akpephre Godspower** under the supervision of **Dr. E. A. Oyedoh** of the Department of Chemical Engineering, University of Benin, Edo State Nigeria.

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Dr. E. A. Oyedoh   Date

Project Supervisor

……………………………………………..   …………………………

Dr. Dr. E. A. Oyedoh   Date

Head of Department

………………………………   ………………………….

External Examiner   Date

DEDICATION

I deeply appreciate God Almighty. I also dedicate the work to my wife Mrs. Eruke Godpower and my late daughter Uruemuoghene Hephizibah Godspower. I also dedicate to my late parents Mr. Fredrick Okwah and Mrs. Veronica Okwah.

I will also like to dedicate this work to my late immediate younger brother (David Okwah) and all of my siblings.

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I personally acknowledge God who made it possible for me to get to this stage of my life.

My supervisor, who was always there for me whenever I called for any necessary assistance may the good Lord bless you Ma (**Dr. Mrs. E.A. Oyedoh).**

I will never forget to thank God for my late parents Mr. Fredrick Okwah and Mrs. Veronica Okwah, My wife Mrs. Eruke Godspower, my sidings (Barr. Austin Okwah, Mrs. Christiana Otobo, Mr. Onome Okwah, Barr Moses Okwah and Helen Okwah and I do acknowledge my late brother David Okwah and My Late Daughter Hephzibah Godspower- Okwah who in their own measures contributed immensely towards this project.

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I will not forget to show appreciation to my colleagues, classmates as well.

ABSTRACT

For its bio- and environmentally friendly properties, low cost, and relative abundance, clay has become increasingly relevant and used. Based on their components and layer patterns, clay minerals have a variety of morphological and physicochemical characteristics., in addition to its well-established uses in adsorbent development, water treatment, and construction. In order to determine whether clay samples from the Ikpeshi town in the Akoko-Edo LGA could be used in an industrial process, its physical and chemical characteristics were examined. The study involved the analysis of elemental content, mineral constituent, functional groups of compounds content, surface morphology, and thermal stability with EDXRF, XRD, FTIR, SEM, BET and TGA respectively. Results revealed that the sample was kaolinite with SiO_2 45.116 wt%, and Al_2O_3 20.39 wt% as the most predominant elements. Wave numbers of 909.47043cm^{-1} to 998.92654cm^{-1} with bold peaks revealed the presence of SiO_4^{-4}. The overall study revealed kaolinite characteristics and strong thermal stability thus possesses properties for clay suitable for lining furnace kilns.

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CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Clay is a natural mineral that is found in solid form on the surface of the earth. It mostly consists of silica, alumina, water, and worn rock (Murray, 1999). The phrase "clay minerals" describes a group of minerals that play a significant role in the distinctive characteristics of loam rocks, including kaolins, clays, soils, shales, and bentonite. In their natural state, clays are a heterogeneous mixture of finely scattered minerals like quartz, feldspars, calcite, and pyrites (Jovanovi & Tatjana, 2012). Clay minerals are among the most important, if not the most important, minerals used in industry.

It is a byproduct of the earth's surface being weathered by geological processes. Clay is made up of extremely small particles. As a result of aluminum (Al_2O_3), silica (SiO_2), and water (H_2O), pure clay is also known as hydrous aluminum silicate and has the chemical formula Al_2O_3, $2SiO_2$, and H_2O. Any ceramic or pottery bodies must contain clay as a basic component. It is the hydrated aluminum silicate [$Al_2O_3.2SiO_2.2H_2O$]. A common, affordable, and widely-present mineral in nature is clay. It can be broken up, combined with water, and formed into many shapes and forms. Clay is a material that feels chilly to the touch, is soft, flexible, and impressionable.

On the potter's wheel, it can be thrown as well as pounded, shaped, flattened, rolled, pitched, coiled, crushed, pulled, and squeezed. Clay can be molded to create both large and little delicate sculptural or architectural creations. Clay is thought to be a fine-grained combination of several minerals that comes together with water to form a plastic mass. They could be categorized based on the qualities or composition of the underlying minerals. These hydrous aluminosilicates, which are often colored by iron oxides or hydroxides, are common in soils and sedimentary rocks. The main component of this substance is kaolinite ($Al_2O_32SiO_22H_2O$).

Natural inorganic materials known as clay minerals have well-known structural adsorption, rheological, and thermal characteristics. These materials were initially hydrophilic due to the hydroxyl (-OH) groups on their surfaces, which may connect water molecules quickly (Aramide et al., 2014; Orodu, 2017). Clay minerals are part of a category of minerals that are incredibly important because of properties like plasticity, hydration, and catalytic capabilities. Clay minerals find useful applications in many sectors due to their specific qualities like plasticity, hydration, and catalytic capabilities. Chemistry, pharmacy, refractory technology, ceramics, and agriculture are some of the industries that use clay minerals. For a long time, clay materials have been utilized for the adsorption of anions like nitrates, phosphates, and sulfates, heavy metals, color molecules, herbicides, and gases like SO_2 (Mokwa et al., 2019). Clay responds to shape, drying, burning, blending, and combining as well. Clay becomes hard, thick, rock-like, long-lasting, and permanent when it is burnt. The necessity for excellent handling skill and the prevention of improper handling are crucial when creating anything out of this modest material. Commercially available catalysts include clays or clay-modified catalysts. Their surface characteristics make them particularly important minerals, and their reactivity makes them suitable for industrial applications and environmental management. Because of their acidity, high surface area, and cation exchange capacity (CEC), clay minerals are useful as adsorbents, supports, and catalysts for hazardous compounds.

Because they are primarily composed of layers (structures that resemble sheets), these minerals are known as phyllosilicates (Maciver et al., 2020).

Little particle size, hardness, high plasticity, appropriate shrinkage, extreme refractoriness, and the ability to paint the surface are only a few
of the physical qualities of clays (Khitam et al., 2015). Clays have a wide variety of uses due to their , adsorption, ion exchange, swelling and enormous surface areas. Clays have been used as catalysts ever since the petrochemical and refining industries first emerged. Clays that had been acid-modified were used in the first hydrocracking process, which was developed more than 80 years ago. Although they are still used today, zeolites and aluminosilicates (Perego & Carati, 2008; Zimmermann & Haranczyk, 2016). Large in surface area and absorbent, these clay minerals.

When dried, clay can harden and demonstrate elasticity over a range of water contents (H. Murray, 2002). The distribution of particle sizes, the shape of the particles, the amount of clay, the amount of moisture, the heterogeneity of the soil matrix, the density between the soil matrix and metal contaminants, the magnetic properties, and the hydrophobic properties of the particle surface all have an impact on how effective adsorption is (Nweke et al., 2007). Heavy metals have a variety of sorption properties, and the mechanisms are a function of the adsorbents. The order of selectivity for different metals varies between adsorbent clays.

1.2 Statement of the Problem

Thermo gravimetric analysis was only used to calculate a sample's mass as a function of temperature. The sample loses mass as a result of the volatilization of a liquid breakdown product or the evolution of an inert gas. As each subsequent step of breakdown takes place, the thermogram shows a sequence of plateaus of diminishing mass. Figure 4.5 depicts a close-up of the desorption part of the curve.

It shows two weight loss zones that, when combined, represent the desorption of ammonia molecules that are weakly linked to weak acid sites and strongly attached to strongly acidic sites, respectively. The TGA derivative curve's peak minimum represents the temperature at which desorption from mildly acidic sites stops and desorption from strongly acidic sites starts. The strong and weak acid sites identified in the sample under study might be counted quantitatively as a result of this knowledge. The temperature at which the exothermic peak associated with lattice collapse emerged in the DTA curve was utilized to define the thermal stability of clay as a function of the Si/Al ratio, cation type ($La^{3+,}$ $Ca^{2+,}$ or Na^{+}), and degree of ion exchange (Majchrzak-Kucba, 2013). DTA also examined the hydrothermal stability (thermal) of the clay sample (USY). It was believed that the temperature of crystal collapse started at the beginning of the exothermic DTA peak (Figure 4.5).

1.3 Aim and Objective

In order to determine the most appropriate industrial application, a chemical as well as physical analysis of the sample was conducted on a virgin soil sample from the Ikpeshi community in the Edo state. The study's objectives include the following:

1. To ascertain the clay sample's capacity for cation exchange
2. Use an X-Ray Fluorescence fitted with an Energy Dispersive Spectrometer to ascertain the elemental makeup.
3. To use a Fourier, Transform Infrared spectrometer to identify the functional groups of the chemicals present.
4. To find out the amount of solid minerals present using the X-Ray Diffractometer.

1.4 Study Relevant

Although deposits of clay abound in Nigeria and possesses numerous indigenous uses, its physiochemical characteristics for these uses have been studied less. Numerous applications of clay, both those that have been documented and others that are characterized as traditional uses devoid of prior scientific understanding, best demonstrate its significance. Clay is utilized in Nigeria for many different things, including geophagy, modern pottery, construction, and water filtration. There are many different clay deposits, and each one contains special features which can be focused to a peculiar industrial use.

Chapter Two

Literature Review

2.1 Definition of Clay and Clays Minerals

Agricola defined the term of "clay" in 1546. (November et al., 2011). The foundations of plasticity, particle size, and fire hardening were mostly kept, but it has undergone numerous revisions since then. Clay is an earth material made primarily of tiny hydrous aluminum silicate and other mineral particles that is flexible when wet but becomes hard when burnt (Hidayat et al. 2020). According to its chemical makeup, it is a crystalline form of aluminum silicate that includes additional impurities. Quartz flakes, zircon, apatite, granite, and other minerals are possible secondary components of clay. Iron hydroxides are frequently added as admixtures to clays. Clays may also include an organic material rock with trace quantities of manganese . There are four main groups of clays based on their mineralogical composition: kaolinite ($Al_4(OH)_8Si_4O_{10}$), Montmorillonite (hydrated silicates of Aluminum, Magnesium, and sodium), illite (hydrated silicates of Aluminum, Magnesium, iron and sodium), and haloizit ($Al_4(OH)_8Si_4O_{10}4H2O$). Within each of these groups, there are several subgroups. (Maciver et al., 2020). Bentonite clay is a subset of montmorillonite. Clays play a significant part in modern industry today because of their many valuable features, including high capillarity, distinctive rheological properties, hardness, plasticity, thixotropy, a high degree of swelling, and a high degree of efficiency for M^+ cation exchange. Water in high volumes can be absorbed by clay thanks to its high capillary and porosity. Certain clays have a feature called thixotropy that causes them to become more viscous when kneaded., kneading also improves the ability to shape materials because of a change in the electrical makeup of the clay's surface layers,

- One essential property of clay minerals that enables a broad range of applications in the disciplines of geotechnical engineering, environmental engineering, and other industrial uses is their capacity to swell. A high degree of efficiency for M^+ cation exchange results from unequal charge in the clay morphology that arises because of the swapping of Al^{3+} for Si4+ in the tetrahedral sheets, Mg^{2+} for Al^{3+} cations for octahedral sheets. Aside the features, other advantages of clay are listed below:
- They can be found nearby.
- Their mining, processing, shipping, and upkeep don't require a lot of energy.
- They don't emit any noxious gases, irritate the skin, have no chemical additions, are not electrostatic, and don't absorb radiation that is damaging to people's health.
- Environmentally friendly clay additions (e.g., straw, wood waste, sand, etc.).
- It help create a comfortable indoor environment by absorbing moisture that is then released into the space under various situations, controlling the indoor temperature by cooling in the dry season and heating in the wet, and absorbing odours.
- The stability and toughness of clay construction materials are almost limitless.
- Products made with clay don't need extra thermal insulation.

2.1.1 Identification of Clay Minerals

Some of the methods used in identifying clay minerals include: X-ray analysis, dehydration curves, differential thermal analysis, optical, electron microscope, chemical analysis and cation-exchange capacity determinations. The optical method is one of the oldest means of studying clay minerals. It involves the use of refractive indices which are not especially well adapted to soil colloids. The indices are an average for a mixture of minerals which are usually present in the soil. X-ray analysis is considered the most accurate means of identification . Some difficulty is involved in differentiating Illite or Hydrous Mica diffraction patterns from those of Montmorillonite.

Dehydration involves the loss of chemically held water in the clay lattice upon heating. This test is not accurate for quantitative estimation of clay minerals. Differential thermal analysis is the study of the exothermic and endothermic reaction of clays when they are being gradually heated. Each clay mineral has its characteristic thermal curve. Quantitative determination can be made by comparing the intensity of the thermal pips with known ·standards of mixtures of the clay minerals.

2.2 Clays and its Minerals

Clay naturallyexist as a substance that is mostly made up of fine-grained minerals, is typically pliable at the right water concentrations, and hardens when dried or burnt. Clay typically contains phyllosilicates, but it may also contain additional substances that give it fluidity and cause it to harden when dried or burnt (Qadrouh et al., 2013).

The phrases "clays" and "clay minerals" are frequently used interchangeably. A natural clay might not include even one clay mineral. It might contain impurities like calcite, quartz, feldspars, iron oxides, etc. that don't belong to the clay mineral family. Clay minerals, which consist of continuous two-dimensional tetrahedral sheets with composition T_2O_5 (T=Si, Al, Be, etc.), are included in the phyllosilicate class of minerals. Three of the four corners of a tetrahedron are shared, and the fourth corner can point in any direction. In the unit structure, tetrahedral sheets are joined to octahedral sheets, coordinated sets of cations, or single cations (Mamudu et al., 2020).

They comprise sheets of connected tetrahedrons and octahedrons that are joined together by chemical bonds to form layers because they are "layered silicates" (Figure 2.1). For instance, a 1:1 type layer structure is created when one octahedral sheet and one tetrahedral sheet stack together. Clay minerals are categorized based on the various cations that may be found in their octahedral sheets and the sorts of layer that they have (Table 2.1). Smectites are clay minerals from the 2:1 layer category (two tetrahedral sheets and one octahedral sheet), while montmorillonites are a variety of smectite group clay minerals.

Montmorillonites are the most frequently used clay minerals for processing due to their high swelling and cation exchange capacities. Since the Stone Age, people have been mining clays and clay minerals; presently, they are ranked as one of the most significant raw materials used in the manufacturing and environmental industries. There are only a few particular geologic environments where clays and clay minerals can be found. It is possible to determine the formation's surroundings using geothermal fields, volcanic deposits, soil horizons, continental and marine sediments, and weathering rock formations (Khitam et al., 2015). Clay minerals can be classified as "detrital," which describes the movement and sedimentation of material from a distance, or "residual," which describes in-situ alteration of the parent rock brought on by changes in pressure, temperature, and/or pH. Those are all secondary minerals that form as a result of the breakdown and chemical deterioration of pre-existing rocks. Carbonates, non crystalline iron oxides, and primary clay minerals are also converted into more stable clay minerals during diagnosis, primarily by dissolution and recrystallization, from common silicate components including quartz, feldspars, and volcanic glasses (Novembre et al., 2011).

The majority of the minerals in clay are hydrous aluminum silicates, which have active sites on their surface.

Clay is a mixture of minerals that is stable at high temperatures and becomes hard and stiff when dried. Because clay materials are biocompatible, they can be used to adsorb biological substances (like quercetin) and deliver them to the human body for therapeutic cancer treatment.

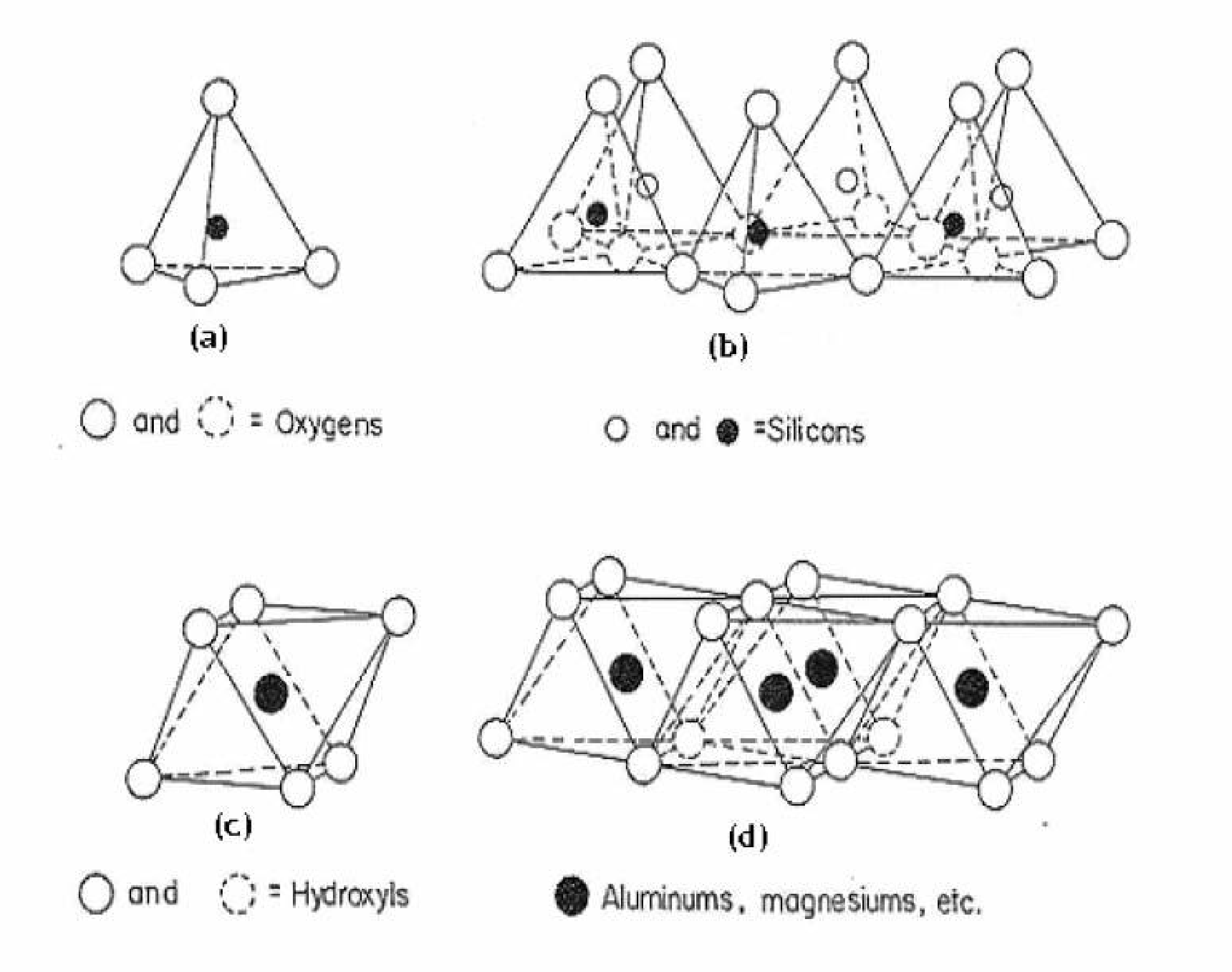


Figure 2.1. Clay minerals' tetrahedral and octahedral sheet structures include the following: (a) a single tetrahedral unit; (b) the sheet structure of the tetrahedral units; (c) a single octahedral unit; and (d) the sheet structure of the octahedral units. (Grim, 1953)

2.2.1 Clay Structure

A clay mineral's characteristics are determined by both its composition and structure (both physical and chemical properties). Clays' behavior as regards both their chemical and physical features is determined by their connections to adsorbent and/or catalytic qualities in the process industries. How they act is determined by the size and makeup of their external surface, which is modified by suitable procedures like acid and heat (Murray, 2002; Singla et al. 2012).Certain clays can be modified with acids and heat to boost their catalytic and adsorbent activity. But as clays undergo stronger and more extensive modification, activity declines. They have a lot of promise for chemical processing. We present the chemical make-up of many natural clays in Table 2.1.

Table 2.1: chemical components of many types of natural clay (H. H. Murray, 1999)

Natural Clays	Elemental Composition (wt%)								
	SO_2	Al_2O_3	Fe_2O_3	TiO_2	Loss on ignition	N_2O	K_2O	CaO	MgO
Kaolinite	53.70	43.60	2.00	0.10	-	-	0.50	-	-
Halloysite	46.86	34.10	2.27	2.72	12.60	0.05	0.80	0.13	0.08
Bentonite	50.08	17.40	6.00	-	20.32	1.39	0.84	0.28	3.95
Montmorillonite	65.34	12.89	2.38	0.52	8.06	0.53	1.54	0.24	0.95
Vermiculite	39.00	12.00	8.00	-	-	-	4.00	3.00	20.00
Attapulgite	58.38	9.50	-	0.56	-	-	-	0.40	12.10
Sepiolite	55.21	0.43	0.15	0.05	19.21	0.10.	0.15	0.20	24.26

2.2.2 Kaolin

One of the most important commercial clay minerals, kaolin, has the chemical composition Al2Si2O5(OH)4. Theoretically, the oxides are composed of Al_2O_3 (39.53%), SiO_2, and H_2O (13.94%). 2017;

Kyriakogona et al. One kaolin tetrahedral layer and one alumina octahedral sheet are joined by oxygen atoms. Kaolin is a layered silicate mineral. Because there is less substitution in the kaolin layer, it has a lower surface area and surface charge than smectites, palygorskite, and sepiolite (Mamudu et al., 2020). According to the chemical formula, Si4+ is not substituted by Al^{3+} in the layers of a tetrahedron, and Al^{3+} is not changed by other ions in the layers of an octahedron (Na+, K^+, $Zn^{2+,}$ $Mg^{2+,}$ $Ca^{2+,}$ etc.). (2015) Hosseini and Ahmadi. Kaolinite, the most available kaolin mineral, is also a typical clay mineral, however there aren't many occurrences that are both reasonably pure and practical for trade. Due to its unique physical-chemical properties, kaolinite is relevant in a variety of uses. Because of its less reactive nature and inclusion in the bulk of industrial formulations, this explains lots of its significant uses. Furthermore, kaolin contains some other minerals like dickite, nacrite, etc. Rarely occurring minerals dickite and nacrite are frequently associated with kaolinite in deposits of hydrothermal origin (Khitam et al. 2015; Kyriakogona et al. 2017b). Tetrahedral SiO_4 sheets with Al^{3+} acting as the octahedral cation make up the 1:1 layered structure of kaolinite. Within the boundaries of the octahedral sheet, the two hydroxyl groups situated below and above the two Al atoms form a center hexagonal distribution in a single plane. Despite the fact that the aforementioned is true, the aforementioned is not true for the aforementioned. Table 2.2 shows the percentage of publications on the main kinds of natural clays as of 2021.

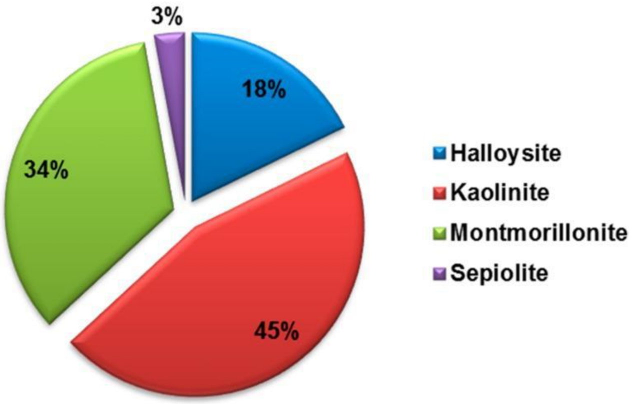


Figure 2.2: Comparing the quantity of academic papers on Halloysite, Kaolinite, Montmorillonite, and Sepiolite. Using the SciFinder Scholar search engine, papers as of February 2021 were analyzed for data.

2.1.3 Smectite

Due to the fact that they are composed of an octahedral core sheet and two tetrahedral silica sheets, smectite minerals are categorized as 2:1 layer minerals (H. H. Murray, 1999). The montmorillonite (smectite clay mineral group) is the most prevalent type of clay used in pillaring procedures. The basic unit framework of this class of clay is shown in Figures 3 and 4 below to consist of two tetrahedral Silica sheets that are separated by an octahedral sheet of Al or Mg. Ca-montmorillonite, saponite (Mg), montmorillonite, nontronite (Fe), beidellite (Al), and hectorite are the minerals that make up smectite (Li). .Smectite is present as tiny particles, 0.5 micrometers or smaller. The main component of bentonite, a term used in the context of rocks, is smectite. It has been said that bentonite is clay made from limpid rock. Fe is found in octahedral sites in clay minerals belonging to the smectite and vermiculite groups. Other transition elements frequently engulf this site, taking the place of other cations. This gives the minerals its colours(green, yellow, or brown), rendering them unsuitable for use in the manaufacture of fine porcelain.Illites can also exhibit a wide range of light hues (Agbaire and Obi, 2009). Grim and Guven's definition of bentonite (Kafashi et al., 2017) stated that it is any form of smectite clay in which the manner of extraction is not mentioned. The most common types of bentonite used in industries are Na-montmorillonite or Ca-montmorillonite, along with a much lower amount of saponite and hectorite.

2.1.3 Palygorskite

A hydrated Mg-Al silicate substance having the chemical formula $(Mg, Al)_5Si_8O_2(OH)2(H_2O)_4.4H_2O$ is referred to as palygorskite (H. H. Murray, 1999). This mineral has an inverted chain-like structure made of two silica tetrahedral chains connected by oxygen(octahedral) and hydroxyl groups consisting Al and Mg ions. This consistently occurring, extended inverted tetrahedral shape results in channels that run through it. This mineral's elongated shape and structure gave it special colloidal properties, most notably a high concentration resistance to electrolytes (palygorskite). The diameter of the elongated particles is roughly 0.01 m, and the length variations range from 1 to 10m.Due to the form and size, there is a high surface area and high porosity when thermally activated (H. H. Murray, 1999). The properties of a few non man made clays are shown in Table 2.2.

Table 2.2: Physicochemical and morphological characteristics of clays (Usha-Devi *et al.*, 2015)

Kaolin	**Smectite**	**Palygorskite**
1:1 layer	2:1 layer	2:1 layer inverted
White or near white	Tan, olive green, white	Light tan
Little substitution	Octahedral and tetrahedral substitution	Octahedral substitution
Minimal layer charge	High layer charge	Moderate layer charge
Low base exchange capacity	High BEC	Moderate BEC
Pseudo hexagonal flakes	Thin flakes and laths	Elongate
Low surface area	Very high surface area	High surface area

Very low absorption capacity	High absorption capacity	High absorption capacity
Low viscosity	Very high viscosity	High viscosity

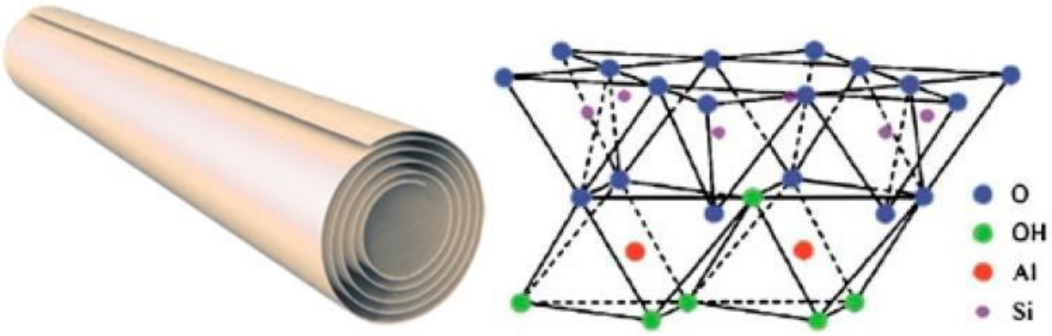


Figure 2.3: A Montmorillonite clay mineral's structure showing the oxygen atoms and hydroxyl groups. The tetrahedral state in the oxygen framework is occasionally engulfed by silicon as well as aluminum. Octahedral positions may be occupied by either aluminum, magnesium, iron, or lithium. The interlayer exchangeable cation is represented by the formula Mn+ xH2O. (Uddin, 2008).

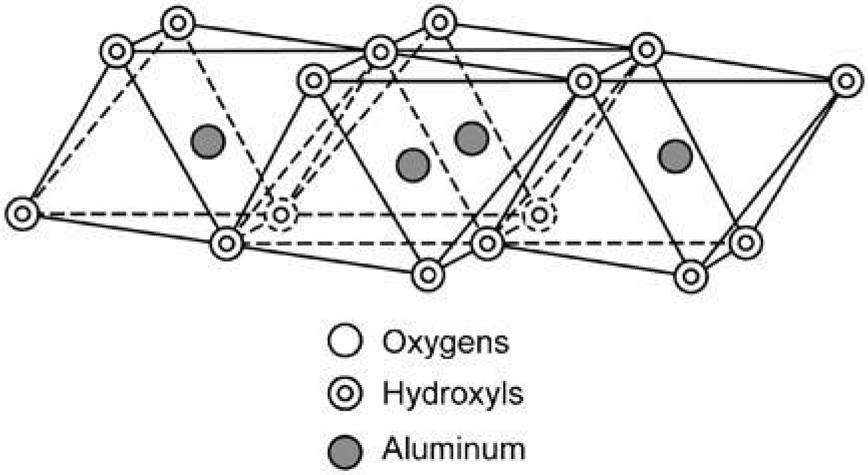


Figure 2.4: Structure of clay; octahedral sheet (Fukue et al., 1999).

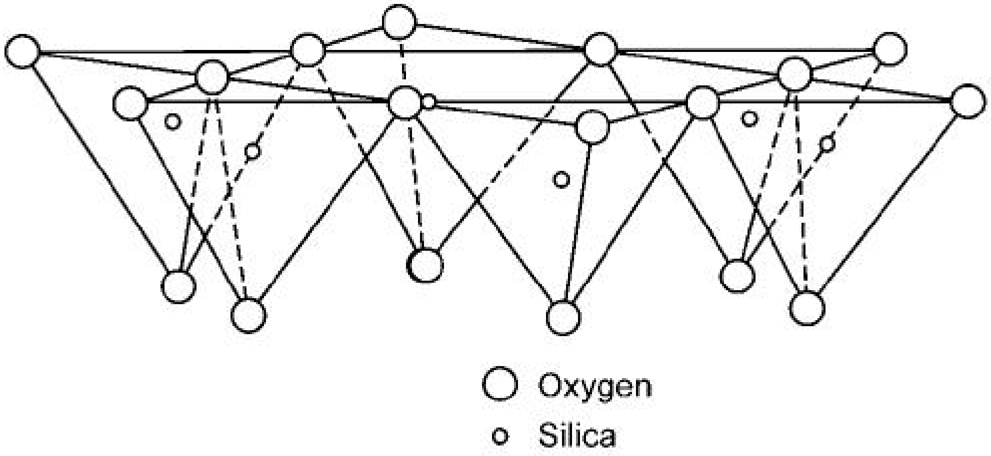


Figure 2.5: Structure of clay; tetrahedral sheet (Fukue et al., 1999).

2.2 Applications of clay

Clays have been used widely in human society since prehistoric times because they are easily accessible in practically every region on Earth that is livable and because of their undeniable distinguishing characteristics. Clay materials has wide applications in the construction of (muddy) in addition to the manufacture of bricks and pottery. The usage of clay and clay minerals has increased recently, and they are gradually replacing metals in a variety of industries as better, more affordable, and environmentally friendly alternatives (Stechemesser & Dobiá, 2005; Valtchev et al., 2009). Catalysts that are used economically are clays or refined clay catalysts. Clays are used in a wide variety of processes due to their adsorption, swelling, ion exchange, and enhanced surface areas. When the petrochemical and petroleum refining industries initially began to develop, clays were used as catalysts (Kovo & Edoga, 2005; Olaremu, 2021). Significant amounts of clay annuallyare utilized in a variety of applications. Kaolinite has the composition(chemical) $Al_2O_3.2SiO_2.2H_2O$.

One sheet of silica tetrahedral and one sheet of alumina octahedral material make up each layer of the 1:1 uncharged dioctahedral structure. It can be utilized as a nascence material for the creation of zeolite A with ease because its Si/Al ratio is close to unity (Van-Dang et al., 2021).Alumina, a substitute for bauxite, has been produced using refined kaolinitic clay.Kaolin is used extensively in the creation of functional filler, paper, fiberglass, and ceramics. The mineral kaolinite, with the chemical formula $A1_2Si_2O_5(OH)_4$, is one of the frequent byproducts of weathering in many subtropical and tropical soils. It also contains a large number of accessory minerals, including carbonates, feldspars, and hematite. The two-layered planar hydrous phyllosilicate minerals known as kaolin include kaolinite (Valeev et al., 2016; Mgbemere et al., 2017). In addition to construction, the clay minerals are used in process industries, agriculture, environmental cleanup and geology,. There are numerous and diverse uses for clays in various industries, as well as for their derivatives.The properties of the clay minerals present in it, are defined by the traits of the internal frameworks and chemical compositions of those clay minerals, dictated the sustainability of clay in a given industry. The dearth or absence of transition elements with high coloring qualities that would facilitate the utilization of kaolinite-rich clays in the production of superior porcelain. Clay minerals occur with extremely small grain sizes and have high surface activity as a result of their structural features, making them suitable as fillers in the rubber-producing industries (Nweke et al., 2007).

2.2.1 Applications of Clay in Water Treatment

Water is a crucial requirement for human sustainability. Because they are not broken down by nature, heavy metals are among the most poisonous and destructive contaminants. Heavy metal cadmium (Cd) is produced during mining operations, volcanic eruptions, soil erosion, and the industrial waste products leather, textiles, batteries, paints, and insecticides. Long-term exposure to high quantities of heavy metals can be harmful to both people and ecosystems (Kayode et al., 2019).Together with other clay ore, kaolinite is being used to treat water. In an acidic environment, hydrogen ions (H+) released from the edge of the layer framework promote the adsorption of heavy metal ions like Pb(II), Cu(II), Hg(II), and Cd(II), forming aqueous matrices (Chukwujike et al., 2015). Water pollution is a metaphor for a sudden crisis. A typical adsorbent used to remove dangerous pollutants from wastewater is activated carbon. Despite its efficiency, activated carbon is still rather pricey (Ademiluyi, 2012). Water treatment is becoming a significant industry on a global scale. The sector is divided into the treatment of industrial process water, potable water, and wastewater. The adsorption process is a notable and effective method for cleaning polluted water (Udeagbara et al., 2021). Pollutant removal from water is a necessary process that is growing increasingly significant as industrial activity increases. Because to the regular occurrence of these metals in waste streams from various sectors, the destruction of heavy metals including cadmium, lead, nickel, chromium, iron, zinc, and copper from aqueous solutions is essential. The demand for water and the urgent need for improved water quality are both growing because of the increase expansion in world human growth. End-users are exposed to significant risk because the heavy metals in the waste streams can be advantageously absorbed by marine animals and directly into human food chains. The architectures, applications, and workings of clay nano-adsorbent for water treatment were examined by Pandey et al. in 2017. Wastewater from numerous industrial operations is the principal cause of contamination in natural water bodies. Fresh drinking water is a vital requirement for a disease free human population.

Each day, there is a significant increase in the release of dangerous compounds into water bodies. Yet, the widespread presence of unwanted contaminant in clean water around the earth has been hastened by the quick increase in the usage of harmful compounds for various reasons. They held the opinion that nanotechnology is crucial to the current environmental efforts being made to clean up environmental toxins. The potential for using nano particles in wastewater treatment is enormous. Its particular properties, including having an increased surface area, can be effectively used to remove harmful metal ions, ill-causing microorganisms, and both organic and inorganic solutes from water. Water purification is aided by the characteristics of nano clays that have been discovered to be highly effective and efficient. Several researchers have extensively studied the use of clay minerals as adsorbents for the adsorption of numerous harmful substances, including heavy metals, dyes, antibiotics, biocide compounds, and other organic molecules (Kumar *et al.,* 2013; Mgbemere *et al.,* 2017; Mgbemere *et al.*, 2019).The use of organoclays in wastewater treatment applications has been very successful. In a number of situations when the water that needs to be treated contains a substantial level of acid or oil and grease, organo-clays have shown to be superior to all other water treatment technologies. The use of organoclay for cleansing process water and acid on offshore platforms is a commercial practice around the world. The commercialization of the uses of organo-clay in the treatment of wastewater is a new, successful technique due to the growing carcinogenic consequences of trihalomethane formerly used in wastewater treatment (Mamudu et al., 2020). The soil that forms as a result of volcanic rocks weathering is known as andisol soil, and it is found all over Indonesia. Good characteristics of allophone adsorbent include porosity, absorption, and strong cation exchange.

Allophone has been employed in numerous investigations as an adsorbent with comparatively good efficiency. Clays and allophone can be mixed because they both have similar adsorbent qualities.

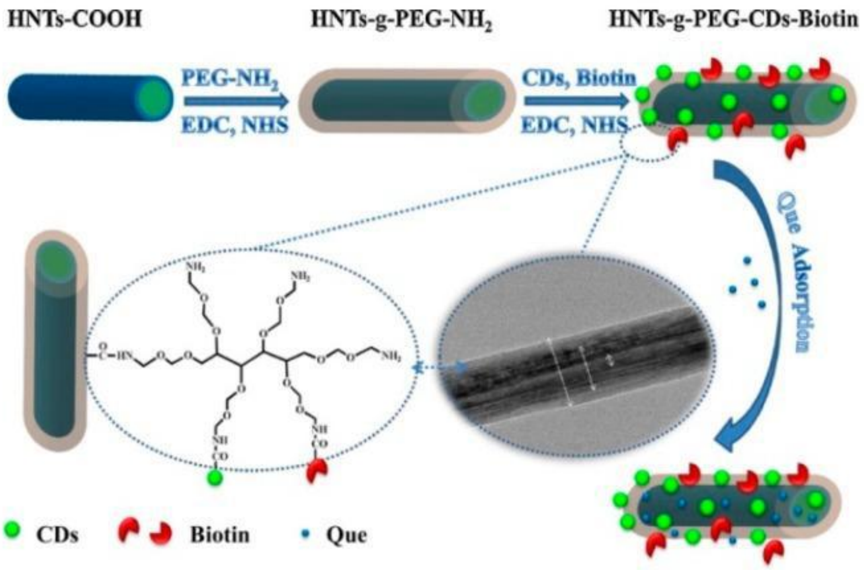


Figure 2.6: HNTs-g-PEG-CDs-structure Biotin's and synthesis are shown schematically, and then the material is adsorbed (Fukue et al., 1999)

2.2.2 Applications of Clay in Ceramics and Nanotechnology

Dey et al., (2016) reviewed the use of clay ceramics and nanotechnology in the treatment of water (2013). Their investigation emphasized the various technologies utilized to treat water pollutants. Explanation of the various types of clays that are used frequently and their benefits for water filtration and nanotechnology. Using nanotechnology, water filtration systems can be made more effective. Because of their increased surface-to-volume ratios and vast aspect ratios, these nanomaterials have a lot of active sites that can help remove contaminants more effectively through adsorption, microbial disinfection, and photo catalysis. In addition to or instead of other macro materials, nano materials can be used in developing water systems.

Yet, during macro construction, the pollutant removal effectiveness of the nano material can be significantly diminished. Therefore, research should be done to develop methods that can be used to construct nanomaterials without affecting their effectiveness (Nweke et al., 2007). According to Awasthi et al. (2019), bacterial pathogens and the heavy metal cadmium (Cd) were removed from drinking water using clays and andisol adsorbent. The ratio of andisol to clay (60:40), the calcination temperature, and the contact time all affect the capacity of Cd ions to bind to surfaces in solution models. These factors are also related to the 60-minute contact time. By reducing the amount of cadmium metal ions in water by 98.9% and the bacteria that generate drinkable water, the ceramic filter made of Andisol and clay proved effective (Awasthi et al., 2019).

2.2.2.1 Construction Structural Products: Bricks and Tiles

Bricks and tiles dominate the structural clay products used in Nigeria's building sector. It is clear that the low flexibility of kaolin clay minerals makes them ideal for the manufacture of structural goods. Due to its appropriateness, clay deposits in Anfoega,that contain Kaolin in large deposits, are utilized by the building sector. For the successful manufacturing of bricks, polymeric clays in the proper ratios with non-clay elements have been used. Clay minerals have acceptable characteristics for structural products. Clay's applicability for structural products may also be improved via composite compositions.

2.2.3 Applications of Clay in Purificationof Water

As a result of high capacity of clay minerals for cation exchange, their composites can increase the quality of water by removing metals and other organic and inorganic pollutants. The main causes of water pollution that renders water unfit for residential use are the presence of organic compounds and heavy metal ions (As, Pb, and Zn).

Additional research in this field aims to create materials made of clay that can filter and destroy the majority of contaminating organic molecules. For instance, the coming together of clay and lime eliminated about 70% of the pigment that makes water to become discolored. Using Na-montmorillonite intercalated with dodecylamine, it has been shown that the adsorptive characteristics of clay are crucial because of their use in isolation of strong metals.It can increase the electrostatic attraction between the surface of aluminosilicate clay minerals and the metal ions, adding to the adsorption properties of these clays, and the rate of metal ion adsorption by clay minerals is inversely related to the surface area of the clay material (Awasthi et al., 2019). As a result of the presence of polyvalent metals, Ca^{2+} and Mg^{2+}, such a process has been exploited in the filtration of hard water.

2.2.4 Applications of Clay in Soil Fertility

The majority of soil fertility issues are caused by a transfer of chemical species. The issue typically emerges because receptors are unable to take in chemical species that are transferred. Remediation of soil for agricultural use can be carried out by the proper donation and receiving of cations (K^+, Na^+, etc.) and anions (NO^{3-}, PO_4^{3-}, etc.) to the suitable surface. Clay mineral's capacity for ionic exchange determines a clay material's capacity to remediate soil (Figure 2.7). In other words, the clay mineral's capability to repair the soil via transfer of species(chemical) increases with its capacity for ionic exchange. The various clay mineral forms have different exchange properties. The desired application affects the rate of adsorption. Weathering, erosion, and sedimentation create clay mineral deposits. These clays can exchange the necessary cations. Cations and anions are prepared for the exchange in soil fertilizer design (Kome et al., 2019).

Smectite group clay minerals like bentonite have charged surfaces which enhances ionic exchange. In soil, colloidal clay minerals exhibit strong levels of viscosity, flexibility, and impermeability. Clay's impermeability prevents fertilizers from swelling, which encourages their fair usage in amending the soil for farming. By encouraging aeration, it also improves soil fertility and regulates soil temperature and heat exchange. Clays that expand e.g,smectites, increases drying rate, which raises pH of soil for the advantage of plants development. For environmental cleanup of soil, clay materials with a high electrostatic surface can be employed. For cleaning up contaminated regions, clay materials' adsorptive and crack-resistant qualities are essential. Plastic and non-leaching soils are used in landfills. Moreover, abandoned farms in Ghana can be restored using these local clays.

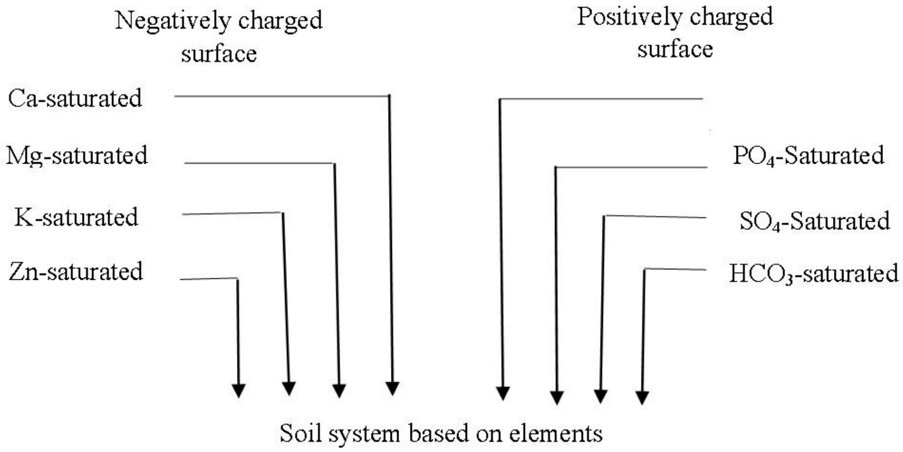


Figure 2.7 Soil additive elements in exchangeable form (Kome et al., 2019; Osuji et al., 2007)

2.2.5 Application of Clay in Nuclear Waste Disposal

Chemical toxicity of radioactive materials poses serious health hazards. Nuclear reactors dispose of radioactive materials at high levels.

The radioactive waste is placed in metal containers and buried well beneath the surface. The current single barrier system should be replaced with a multi-barrier compartment system, it is suggested. Multi-barrier systems provide containment security and stop potential leakage into drains. Clays like smectites, which have demonstrated strong swelling power to act as sealants and water permeability, have significant adsorptive potentials that enable them to bind with other materials in order to prevent leaching. So, the use of multi-barrier system made of clay and metals(canister) would be advantageous to efficiently contain high-level radioactive waste materials. For years, clay made from natural materials and metals created artificially restrict hazardous radioactive waste to save the ecology. Immobilizing radioactive waste is made possible by the enduring mechanical strength of clay-cement composite (Agbaire, et al., 2009; Dimitar et al., 2018). When compared to cement and other materials, a cement and clay mixture has comparable trustworthy sorption competence to stop the leachability of radioactive waste. Radioactive waste disposal and long-term storage may require more stringent procedures. Disposal of radioactive waste or their safe storage depends on immobilization.

2.2.6 Application of Clay in Healthcare

Natural clays that have been processed are utilized to make pharmaceuticals and other products with health benefits. The physical and chemical features, i.e., single ionic charge carrier and tiny particle size, are improved by natural clay treatment, which increases their suitability for a particular usage. The primary variables determining the usage of clay in cosmetic, pharmaceutical, food packaging, and other health applications are its chemical and structural characteristics.

Impurities prevent clay from having the optimum properties for health applications. Some ionic attachments to the surface and interlayer elements may have unfavorable biological effects. Clay minerals contain impurities that may be harmful to biological systems, including zirconium,arsenide, vanadium, lead, lithium, etc. Clay minerals' therapeutic benefits have long been understood. Those who are geophagic and pregnant women in particular ingest them in large quantities. Clay contains minerals including iron, calcium, and zinc that are beneficial to health (Hosseini & Ahmadi, 2015). These clays do, however, include potentially harmful elements like Pb, As, Hg, and Cd because they are typically not treated. Unknowingly, these harmful substances have an impact on people's health. Biomedical applications and food packaging may fall within the category of clay mineral health applications.

2.2.7 Applications of Clay in Biomedical

The biomedical application categories of pharmacokinetics and cosmetics include the development and manufacture of pharmaceutical products and medical equipment. Clay materials have an advantageous adsorptive and surface area. Also, because of their low toxicity and biocompatibility, these materials can be applied in the majority of cosmetic, pharmaceutical and drug delivery applications. Moreover, the clay materials contains anti-inflammatory, antimicrobial and other beneficial characteristics. They are contained in pharmaceuticals used to treat gastrointestinal, diarrhoeal, and other medical problems. It has been stated that the proper administration of bentonite (a form of smectite clay) can treat conditions like itching, chicken pox, etc. and improve the absorption of healing medications. Bentonite is also utilized in wound healing to treat muscular injury as well as cuts, bruises, and wounds. Furthermore, clay-based compounds are used in cosmetics.

They assist in preserving oil-in-water emulsions. They also serve as blemish covers and deterrents to sweat. It makes the skin opaque against UV rays and cleans out skin pores of pollutants. The strength of hydrogels is increased when clays and polymers are combined. Hydrogels can be used in tissue engineering to create new tissues, cartilages, and certain cells, as well as for drug delivery. To improve bone formation in vitro, Murray (2002) employed clay minerals from the Northern Area of Nigeria. Alternately, clay minerals might prevent bone development. Clay materials have a great capacity for exchanging ions. Clays' ability to exchange ions is used in medicine delivery to transport the right ionic medications. Medicines are placed onto the surface of the clay particles using a variety of bonding and attaching techniques. Drug delivery uses also make use of the hollow character of tubular clays such allophanes, imogolites, and halloysites. In the biological system, matching ions or charged surfaces accept the medications. The most common way that pharmaceuticals interact with clay mineral particles is by ionic exchange. When a clay mineral particle has a constant charge or a charge that is pH-controlled, the clay-drug ion exchange is feasible. Clay minerals with a cation charge include smectites and vermiculites (Li et al., 2020). With amines or heterocyclic functional groups, they typically interact. Charges in allophanes, imogolites, and aluminum oxides depend on pH. In many cases, they interact with carboxylates. Drugs with high molecular weight are typically unionized and then bound via adsorption. By electrostatic adsorption, the chymotrypsin medication created a contact with the mineral particles of montmorillonite clay. Hydrogen bonding and Van der Waals forces of contact allow neutrally charged clays to form hydrophobic interactions with medicines. Clay minerals' surfaces successfully use hydrogen bonds to bind to DNA and RNA (Mamudu et al., 2020). Drug agglomeration onto clay mineral particle surfaces is influenced by drug concentration, pH, temperature, electrolyte concentration, valence charge, and dielectric constant.

2.2.8 Applications of Clay in Clothing and Paints

It is anticipated that textiles would become more dye-able and of higher material quality. It is necessary for the fabric businesses to improve apparel properties like thermal deterioration and flame sensitivity. Compared to raw textiles, textiles coated with a thin coating of nanoclay offer better properties. Furthermore, bentonite, acid, and electrolyte nanoclay admixtures improve the dye-ability of fabrics. By favorable ion exchange and hydrogen bonding, nanoclay interacts with direct and basic dye. Water content is increased by nanoclay. With more dye color diffusion, this improves the quality of paint. Paints, which are essentially oil emulsions, have been discovered to have increased stability when using clays (Uddin, 2008; Awasthi et al., 2019).Due to their adsorptive nature, clays in emulsions absorb water to prevent water from penetrating the paint and causing paint to degrade.

2.2.9 Applications of Clay in Detergents

A desired detergent should have the capacity to suspend fats and emulsify them. Metallic earth ions, including Ca^{2+} and Mg^{2+}, prevent detergents from working electrically and from entering fabrics. Clay's propensity to attach to metal ions as a result of ion exchange increases the capacity of detergents to wash clothes. When clay is used in detergents, its ion exchange,large surface area,and adsorption properties produce important qualities like light foam and lather, adsorption of impurities from fiber, ion exchange to soften hard water, detergent dissolution for fiber penetration and agglomeration of fats resulting in their suspension from foam.

2.2.10 Applications of Clay in Energy

Supply innovative methods continue to be investigated for a more sustainable option to fulfill demands that are expanding. A sizeable share of overall energy consumption is made up of cooling and heating loads for homes. When combined with adsorptive materials like bentonite, phase transition materials like hydrated salt, fatty acids, and paraffin can store heat in latent form. In comparison to buildings made of different materials, such a composite has a good rate of heat transfer that increases heat per unit volume. For electrical carriers, excellent insulation is necessary. It has been discovered that clay can effectively insulate electrical carriers. Groundings for electrical systems have about 0 V. Researchers have looked into clay-based compounds to enhance electrical grounding.Na_2CO_3, $MgSO_4$, $MgCO_3$, and Na_2CO_3 in combination with clay minerals are anticipated to enhance electrical grounding.

2.2.11 Applications of Clay in Petroleum

The only factors considered while selecting catalysts for catalysis applications were regeneration capacity, distinctive microporous structure, cost, and thermal stability. Zeolite catalyst is frequently used by modern refineries during the catalytic cracking process. It is difficult or practically impossible for a catalyst to carry out all necessary reactions in cracking, much like with all other single catalysts used in the petroleum sector. However, based on this restriction, a technology that is developing in the refinery is the doping of current materials with other elements used as the catalyst to generate a new material with wholly different properties for enhanced functionality (Mamudu et al., 2020). The liquid form of petroleum that is produced spontaneously and is made up of underground hydrocarbons is known as crude oil.It is mainly found along with natural gases. Other materials include solid hydrocarbon substances i.e.,asphalt and waxes, as well as saltwater. Crude oil refineries are majorly designed to yield transportation fuels (mainly gasoline, diesel as well as kerosene), with economically vital side manufacture of starting materials for the petrochemical industry, chiefly light olefins (i.e.,ethylene, propylene, butenes, etc) and BTX. The aforementioned are the feedstock commonly used in petrochemical industries (Mamudu et al., 2020; Tago et al., 2012). Presently, the usage of new materials as catalysts' support is one of the many efforts directed at improving the activity of catalysts.The introduction of porous materials as fillers and supports, particularly clay and zeolite, in viable Fluid Catalytic Cracking (FCC) catalysts for several industrial procedures in the early 1960s was one of the most significant advancements in the history of catalytic cracking. Zeolite catalysts were highly profitable, cost-effective, and environmentally friendly because they replaced hazardous mineral acids and catalysts containing chloro, improved reaction selectivity and yields, improved product quality, prolonged the lifespan of the catalytic system, and simultaneously reduced energy consumption (Liu et al., 2007; Peng et al., 2020).

2.2.12 Application of Clay as Adsorbent

Adsorption is the main industrial separation technique used to clean effluent media. It entailed transferring mass through a solid substance that can selectively remove components that are dissolved from solution that is aqueous due to the dissolved solute's attraction to its surface. Thus, involves the buildup of concentrated chemicals at a surface or the interphase during the interphase. The removal of dye from aqueous solutions is a common use for this detachment process. Adsorption is specifically used in the industries of food, plastics, dyeing, leather, paper and cosmetic where water recovery is essential. A thorough application of the adsorbent's discretion is of utmost necessity in order to achieve and maintain the effective recovery of the proper water quality (Kumar et al., 2013).Together with other clay minerals, kaolinite is being used to treat water. In an acidic environment, hydrogen ions (H^+) released from the layer framework edge promote the adsorption of heavy metal ions like Cu(II), Hg(II), and Pb(II), which then form aqueous matrices. The abundance and toxicity of heavy metals in the environment are the only factors contributing to the severity of the environmental problem. Many health issues in both people and animals have resulted from the persistence of heavy metals in aquatic habitats, such as Pb (II), Cd (II), and Cr (VI) etc..Large areas of water and land have been contaminated by inorganic pollutants, such as pesticides, fertilizers, sludge, and municipal trash, which are primarily made up of heavy metals. Because they are carcinogens, heavy metals pose a serious risk to the health of all living things. The utilization of clay, a finely fragmented naturally occurring raw material, as a powerful adsorbent to the presence of trace heavy metal ions in aqueous solution for more than 10 years has garnered a lot of interest. Because of their low cost and been readily available in nature, both natural and manufactured clay minerals may be the necessary alternative adsorbents for removing dye. Sepiolite, kaolin, and synthetic talc are clay minerals that have been effectively used to remove dye.Acid Orange and Reactive Red were removed using synthetic talc, while Brilliant Green and Reactive Blue were removed using sepiolite and kaolinite, respectively (Awasthi et al., 2019). In a solution, heavy metals can exist as free ions or complexes with both organic and inorganic ligands.

Many efforts are made to apply inexpensive adsorbents such slag, clay-based materials, biosorbents, and agricultural by-products in order to lower production costs. The majority of clay-based adsorbents are cheap, easily accessible materials that offer a reasonable substitute for conventional treatment. Clay's large surface area and porous structure make it useful for both heavy metal adsorption and liquid absorption (Barrer, 1982).

2.2.13 Application of Clay in Ceramics

The ceramics industry has been greatly impacted by the characterization and analysis of clay. Heavy clay goods are generally considered to be structural clay products, that are primarily used in the construction sector. For instance, it has been discovered that the composition and chemical characteristics of ceramics affect their structural integrity. Further studies have demonstrated that clay may be molded, improving its cohesive qualities and flexibility while preventing excessive cracking and fracture. Clays used to create structural items should be carbonates free as these ions swells and cause cracks to occur. Data from study has shown that clay swelling may contribute to the expansion of ceramic goods during firing. This is in line with other researchers' findings from around the world that clay minerals' qualities for ceramic products need to be extensively defined in order to guide product design. Based on this, it has been discovered that more effective and better ceramic products are being made by utilizing different ways to eliminate the swelling effect of moderate bloating and shrinking.

2.2.14 Application of Clay in Concrete

When pozzolans mix with calcium hydroxide $Ca(OH)_2$ in the presence of water, they develop Cementous characteristics.

It was also said that adjustments to pozzolana clay increase the overall strength of concrete material. Pozzolana clays are capable of partially replacing Ordinary Portland Cement (OPC) in concretes due to their tiny, uniform particle sizes, that enable denser packing for water tightness. According to research, a 25% pozzolana clay binder can be added to concrete components in order to provide the best strength possible. 64 A comparison of pozzolan and OPC demonstrates that the combination of the two led to gains in strength (Figure 2.8).

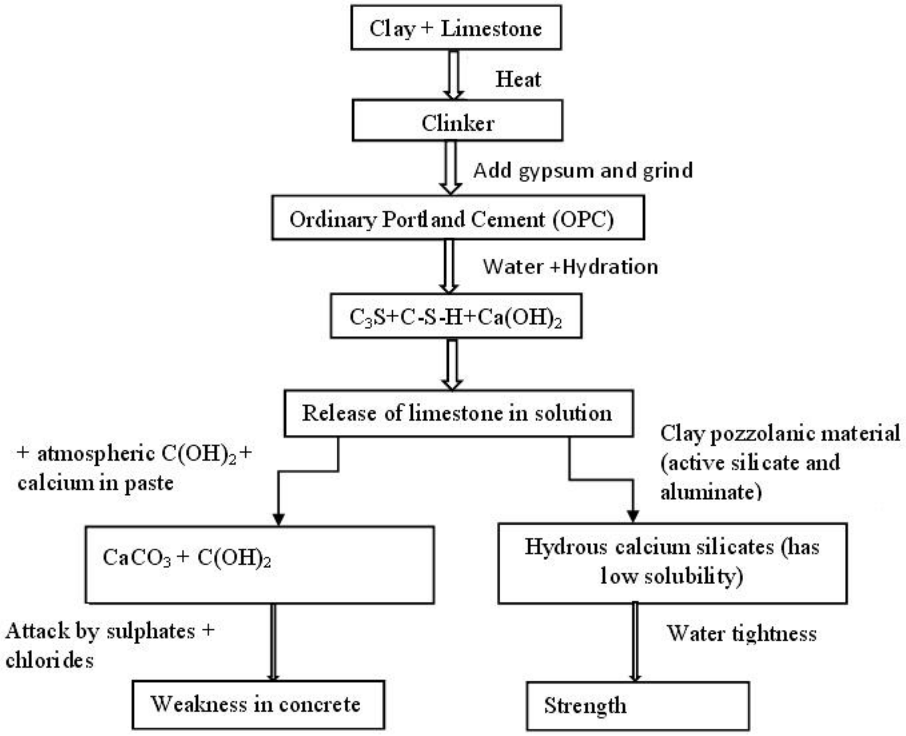


Figure 2.8 A schematic of the reaction between cement and pozzolana clay

2.2.15 Application of Clay in Environmental Remediation and Protection

Backup plans are good idea to have in case something goes wrong. Clay has the appropriate properties for safeguarding and recovering valuable environmental resources like water and land, including cation exchange capability, catalysis, adsorption, huge surface area, swelling ability of clay minerals and high permeability

2.3 Identification of Clay Minerals

Some of the methods used in identifying clay minerals include: X-ray analysis, dehydration curves, differential thermal analysis, optical, electron microscope, chemical analysis and cation-exchange capacity determinations. The optical method is one of the oldest means of studying clay minerals (14). It involves the use of refractive indices which are not especially well adapted to soil colloids. The indices are an average for a mixture of minerals which are usually present in the soil. X-ray analysis is considered tl:'B most accurate means of identification (24). Some difficulty is involved in differentiating Illite or Hydrous Mica diffraction patterns from those of Montmorillonite (18).

Dehydration involves the loss of chemically held water in the clay lattice upon heating (24). This test is not accurate for quantitative estimation of clay minerals. Differential thermal analysis is the study of the exothermic and endothermic reaction of clays when they are being gradually heated (27). Each clay mineral has its characteristic thermal curve. Quantitative determination can be made by comparing the intensity of the thermal "pips" with known ·standards of mixtures of the clay minerals.

2.3.1 Methods of Clay Identification

Ethylene glycol retention: Dyal and Hendricks introduced a simple gravimetric method for measuring external surface, and, by difference, internal surface, and total surface, of clays based on their retention of ethyleneglycol. The only clay minerals that form definite solvates with polar molecules between the structural layers are Montmorillonite, Vermiculiteand Endellite.

The latter two minerals are not too important as constituents of the soil colloid. One molecule of ethylene glycol displaces two molecules of water and forms a two layer solvate, in the presence of excess solvent, between the lattice units in Montmorillonite. Ethylene glycol does not displace exchange ions, but does assume a single layer configuration on theplane of the claysurface. The glycol is held to the clay by an attraction in the nature of a C-H•• •O bond between methylene groups and theoxygen surface of the clay.

Dyal and Hendricks (2001) added an excess amount of ethylene glycol t oa dried sample of clay and gravimetrically determined the retained glycolafter distillation of the glycol-clay _under vacuum for periods of sixteen to twenty-four hours. The distillation left a two-layer glycol solvate between the lattice units and a one layer solvate on the outside top of the clay particles. Similarly other clay sample was heated to 600°C for four hours. This treatment resulted in the destruction of the interlayer swelling. Under distillation with glycol, these clay particles retained only a one-layer glycol configuration on the external surface. Therefore, total glycol retention (total surface) minus external glycol retention (external surface) equals internal glycol retention, hence the amount of interlayer swelling. The results can be normalized against a known sample of Montmorillonite, and the values obtained applied as an index of the percentage of Montmorillonite type clay in the colloidal fraction of the sample. Mica-like clay minerals may have interlayer swelling to the extent of about ten per cent of that of Montmorillonite. Kaolinite has very low glycol retention due to a small surface area and no interlayer swelling.

2.3.2 Modified Clays (Organoclays)

Alkali and alkaline earth metal exchangeable cations are found on the negatively charged surfaces of clay minerals.

When a cation in a clay's interlayer is replaced with an cation (organic) in an aqueous media, the clay is referred to as being "organoclay" (Figure 2.9). The onium ions may be arranged in a pseudo-trimolecular layer, monolayer, lateral bilayer or tilted paraffin structure parallel to the clay surface depending on the charge density of the clay, as shown in Figure 2.9.

Quarternary ammonium cations of the general form [(CH3)3NR]+ or [(CH3)2NRR']+, where R and R' are hydrocarbon groups, are frequently used in the preparation of organoclays (Inam, 2006). In the experiments, it was discovered that the HDTMA+ tail group had a stronger affinity for the clay exchange sites than other surfactants. As a result, the research uses HDTMA+ as the surfactantmost

commonly.

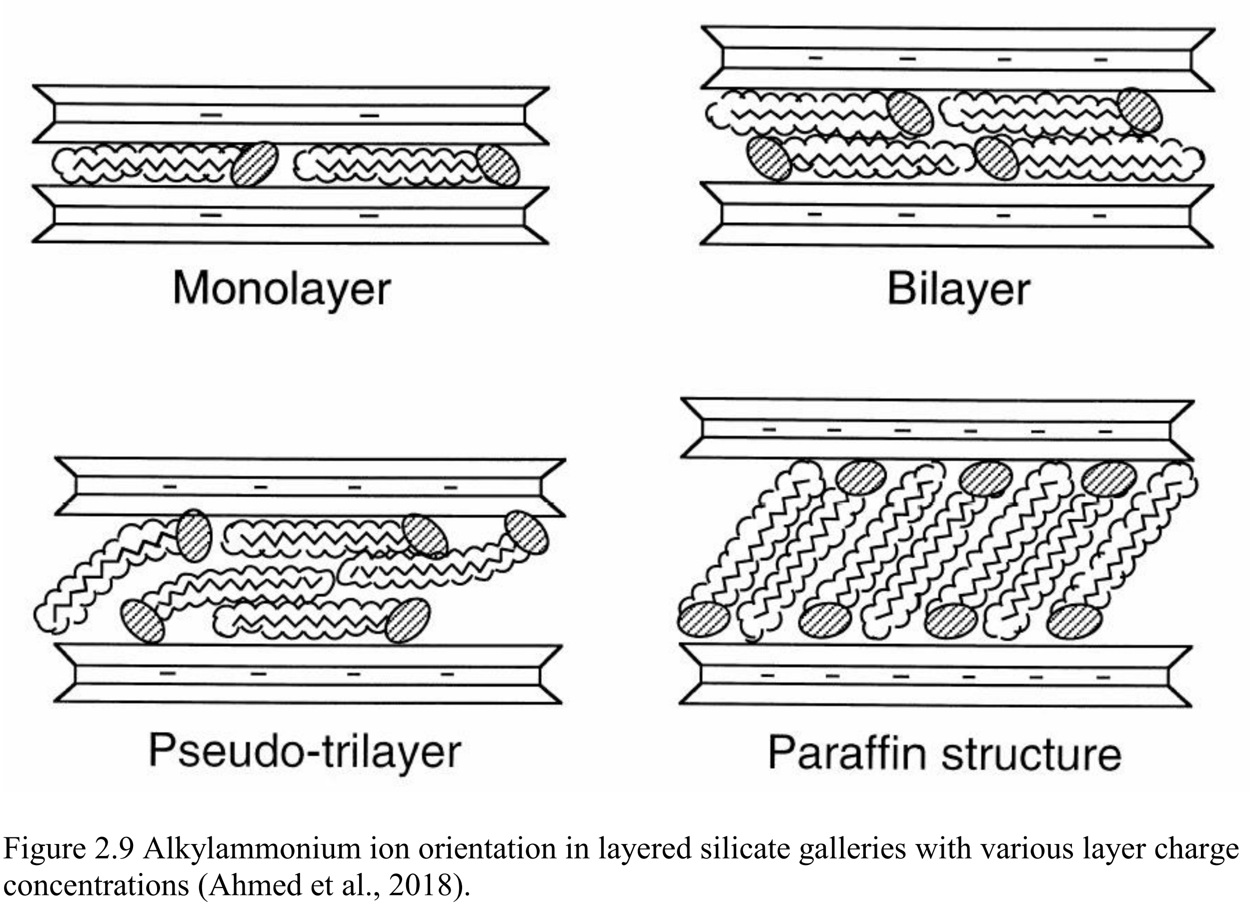


Figure 2.9 Alkylammonium ion orientation in layered silicate galleries with various layer charge concentrations (Ahmed et al., 2018).

Organoclays can be created by exchanging the hydrated exchangeable cations of clay (usually bentonite) with various types of quaternary ammonium cations (Xu et al., 1995). Depending on the property associated with the organic cation (size and/or composition), the surfaces of the clay mineral become less hydrophilic and more hydrophobic, providing improved sorption properties of nonpolar organics compared to the original clay (Xu et al., 1997). Ion exchange with alkylammonium ions is a well-known method to make clay minerals and clays dispersible in organic solvents and to render them compatible with hydrophobic materials in compounding processes (Bergaya and Lagaly, 2001).

2.4 The Clay Minerals

Mineralogical examination of clays reveals that the majority of clays fit into three main series: Kaolinite, Montmorillonite, and Illite or Hydrous Mica, according to November et al. (2011). Of the three most prevalent soil types, i.e. (sand, silt, and clay), the particle size of a natural soil typically ranges by several orders of magnitude. The fractions (fine and coarse) are two distinct classifications of a soil's grain-size distribution. Any particles greater than 0.0075 mm in diameter are classified as "coarse grained" in a soil, whereas smaller particles are classified as "fine grained". Typically, silt and clay make up the soil's fine-grained portion. Clay consists of particles that are smaller than 2 m in diameter (Nweke et al., 2007).This statement has a few exceptions because certain clay particles have diameters greater than 2 m. Clay minerals and clay sized particles have thus been designated as two distinct phrases to be utilized when referring to clays by Owabor and Ogunbor (2007). Net negative surface charge, plasticity when mixed with water, and high resistance to weathering and small particle size are the features that are used to identify clay minerals.

Cationic octahedral and tetrahedral sheets make up clay minerals. Although the composition of the octahedral sheets may vary, the aluminum or magnesium cation is most obviously the dominant ion. Gibbsite and Brucite sheets, which are composed primarily of aluminum and magnesium, respectively (Valeev et al., 2016). A clay mineral's tetrahedral component is usually always composed of silica and oxygen (Moshoeshoe et al., 2017). Each of the three aforementioned clay construction pieces is depicted in Figure 2.10 in more detail. One method for separating clay minerals from one another is to measure the basal spacing of each individual clay mineral (Singla et al., 2012). The "001" or "d-spacing" of the crystalline structure is referred to as the "basal spacing" of a clay mineral (Figure 2.11).

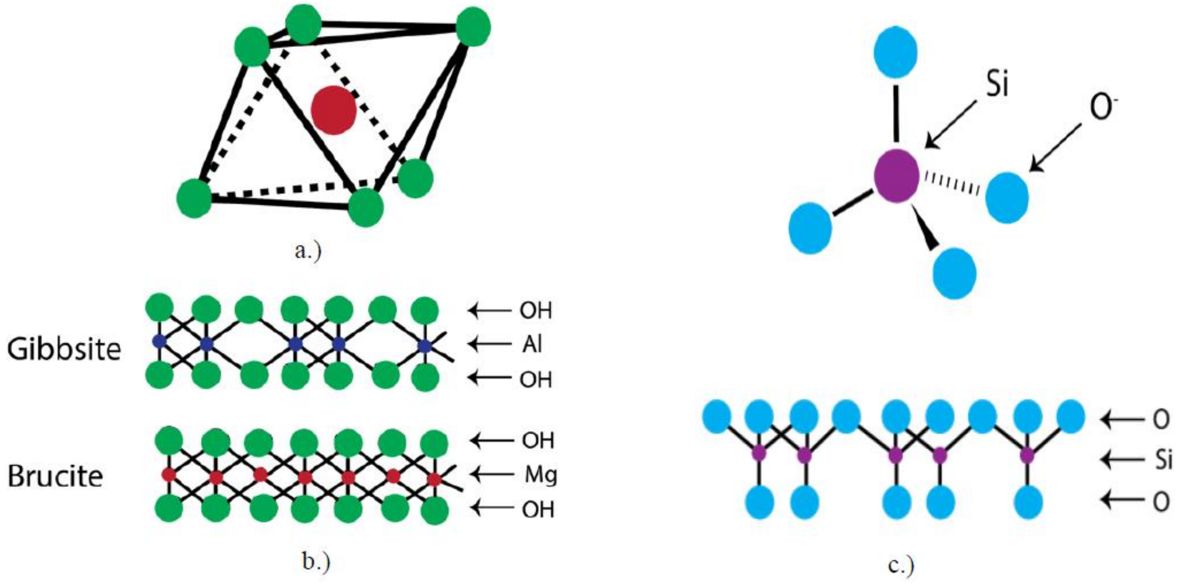


Figure 2.10: The three components that make up clay minerals are (a) a standard octahedral shape, (b) sheets of brucite lattice, and gibbsite lattice (c) a typical silica tetrahedral lattice.

The phyllosilicate mineral family includes all clay minerals. The type of clay mineral is determined by the distinct stackings of the various crystalline structures above,

the amount of isomorphic substitution (to be explained later), and the linkages between each succeeding layer (Ye et al., 2019).

2.4.1 Kaolinite

With a composition of $Al_4Si_4O._{10}$ (OH)s, kaolinite proper is the most prevalent member of this group (Putzolu et al., 2018). Dickite and Nacrite are other Kaolinite class members with comparable compositions but various crystallographic shapes. Anausite, a different group member from kaolinite, is distinguished because of it possessing greater Si and a smaller Al concentration. Halloysite is closely linked to kaolinite, according to Ross and Kerr (Jl), although it has a unique x-ray pattern and dehydration curve. The Gibbsite layer (aluminum in octahedral coordination) and the Si-0 layer appear to make up Kaolinite's structural unit (silica in tetrahedral coordination). Among the minerals in this group are saponite, Beidellite, Nontronite, and Montmorillonite proper.Al_2Si_4O $(OH)_2.xH_2O$ is the chemical formula for true montmorillonite, and magnesium is typically present. Beidellite contains more aluminum and less silicon, which may indicate that some of the Si^{+4} in the silica tetrahedral sheets has been replaced by AliJ. Some of the Al in the gibbsite layer of nontronite has been replaced by Fe43. Magnesium has completely supplanted aluminum in saponite.

Al_2Si_4O $(OH)_2$.xH2O is the chemical formula of true montmorillonite, which typically contains magnesium. Because to its lower silicon and higher aluminum concentration, Beidellite may have replaced some of the Si^{+4} in the silica tetrahedral sheets with AliJ. The gibbsite layer's Al is partially replaced by Fe43 in nontronite. All of the aluminum in saponite has been swapped out for magnesium.

2.4.2 Montmorillonite

The structural components of montmorillonite are two sheets of tetrahedral silica groups sandwiched between one gibbsite layer. H_2O is present between the structural components, which serves to weakly hold them together. The same three constituents of illite also make up montmorillonite, which is also a 2:1 phyllosilicate. As shown in Figure 2.2c, the basal spacing of montmorillonite is not constant but ranges from 0.9 to 2 nm. The interlayer linkages between the mineralogical units of these three minerals constitute one of their key distinctions. Van der Waals forces and strong hydrogen bonds hold the links in kaolinite together.

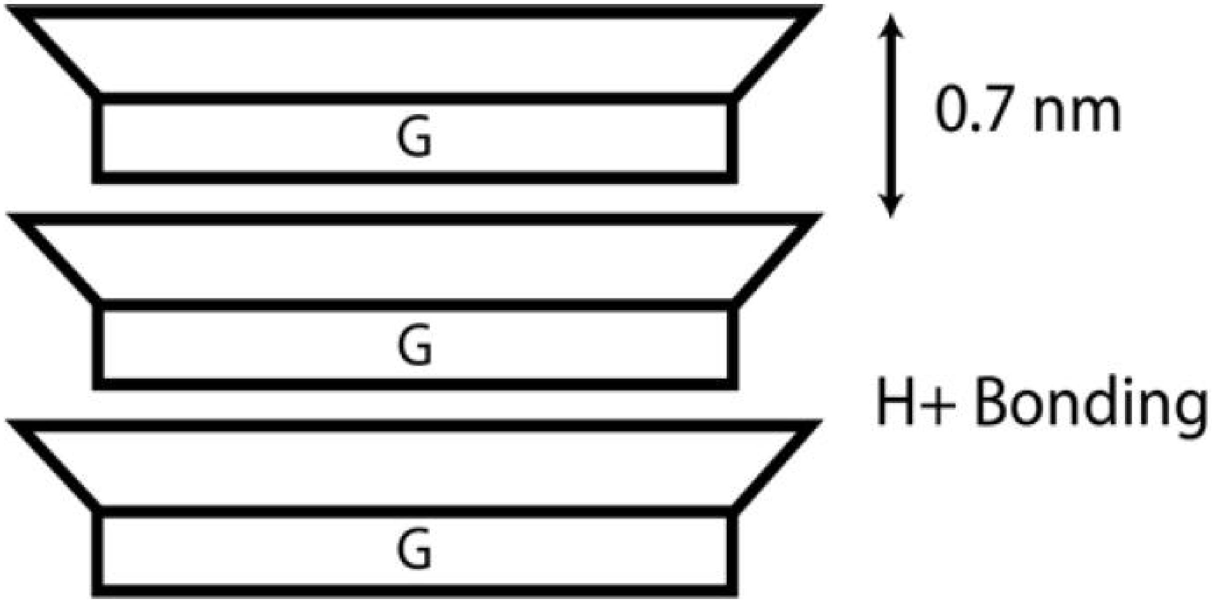
2.4.3 Illite

Illite has a structure that falls in between Muscovite and Montmorillonite. In that it likewise have one sheet of gibbsite sandwiched between two sheets of tetrahedral silica groups, it is comparable to montmorillonite. The interlayer ion that creates a solid link between the Si-O layers is potassium. The goal is to stop water from adhering and reduce the interlayer ions' potential for base exchange. According to Aramide et al. (2014), illite is composed of $KA_{l2}ALSi_3O_{10}(OH)_2.xH2O$.

Because of the cationic bonds created by the potassium ions that are present between each layer, illite also exhibits strong interlayer bonding. Only Van der Waals forces are present between each layer in montmorillonite, which has incredibly weak interlayer connections.Because of its weak bonds and high isomorphic substitution, montmorillonite is easily penetrated by water and other interlayer cations, changing the interlayer spacing.

On the other hand, the interlayer spacing of kaolinite and illite is mostly unaffected by hydration due to the strong interlayer connections between subsequent links in these minerals.

Geotechnical engineers typically refer to only three clay minerals, namely kaolinite, illite, and smectite, in spite of the fact that the fact that there are many others (montmorillonite). These three clay minerals have diverse behaviors and traits, but they all have a platy structure with clearly defined cleavage planes (Usha Devi et al., 2015). Illustrations of these three typical clay minerals can be found in Figure 2.2.



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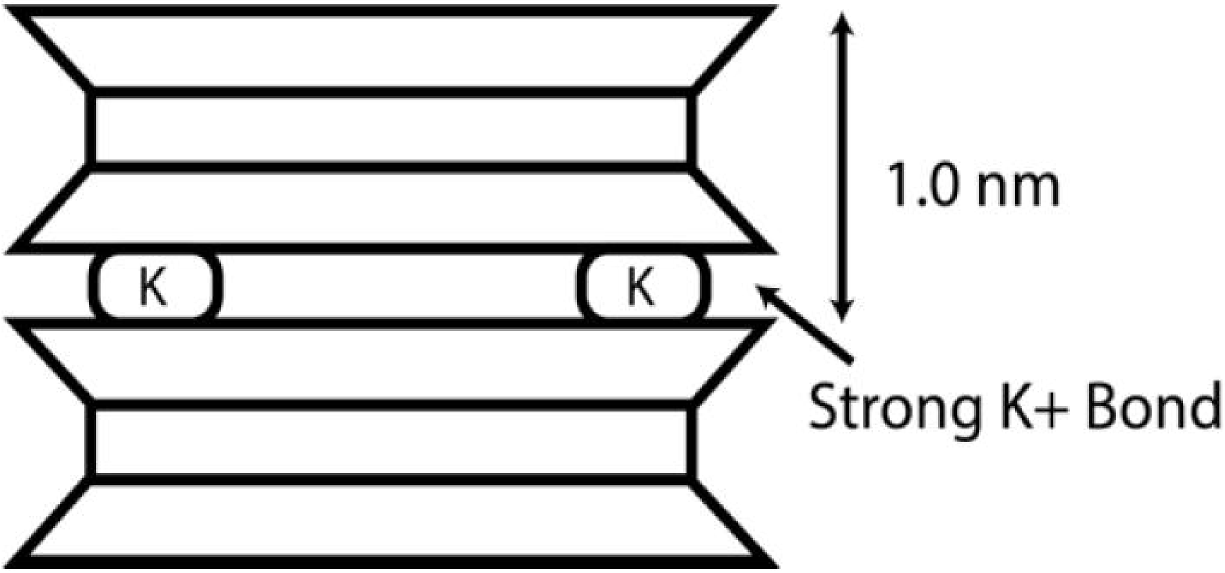

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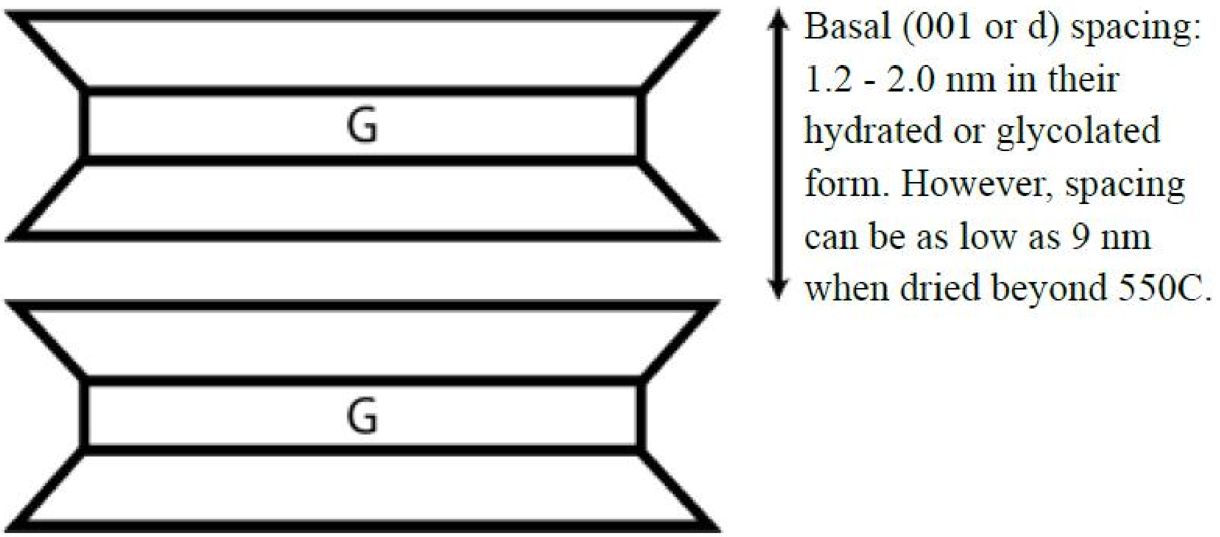


2(c

Figure 2.11(A) The kaolinite mineral's structure. (b) The illite mineral's structure. (c) The makeup of a mineral called montmorillonite.

2.5 Intercalation and Exfoliation Mechanisms in Clay Minerals

Minerals (clay) should have even distributed throughout the complex structure in order for nano composite to be created,

Clay minerals must first be rendered organophilic to ensure polymer-clay compatibility, after which they must be intercalated with these polymers and exfoliated into the polymer matrix.

A well-ordered multilayer morphology build up with alternating polymeric and inorganic layers may be seen in an intercalated nanocomposite (Figure 2.12), where one (and occasionally more than one) extended polymer chain is intercalated between the silicate layers (Ferrarini et al., 2016). Exfoliated nanocomposites (Figure 2.12) are characterized by a lack of attraction between each di-layer segment, that accounts for the inability of these materials to maintain a consistent layer space.Nevertheless, only a small number of clay layer stacks that are evenly spread throughout the polymer matrix fall under this category of exfoliated nanocomposites. Most frequently, exfoliated clay/polymer nanocomposites are sought after for their highly improved qualities due to the uniform dispersion of clay layers and the substantial interface area between clay and polymer. An exfoliated nanocomposite typically has a substantially lower clay concentration than an intercalated nanocomposite (Usha Devi et al., 2015).

The increase in tensile characteristics, as well as improved barrier properties, reduced solvent uptake, higher thermal stability, and flame retardance, can be seen as a result of nanolayer exfoliation. Instead of aggregating as tactoids or merely intercalating, clay nanolayers must be uniformly disseminated (exfoliated) in the polymer matrix for genuine nanocomposites (Usha Devi et al., 2015).

In an intercalated nanocomposite, the clay interlayer gap is fixed. On the other hand, clay silicate loading in an exfoliated nanocomposite determines the average gallery height. Ordered exfoliated nanocomposites can be recognized by X-ray diffraction, but disordered exfoliated nanocomposites are X-ray amorphous (Khitam et al., 2015).

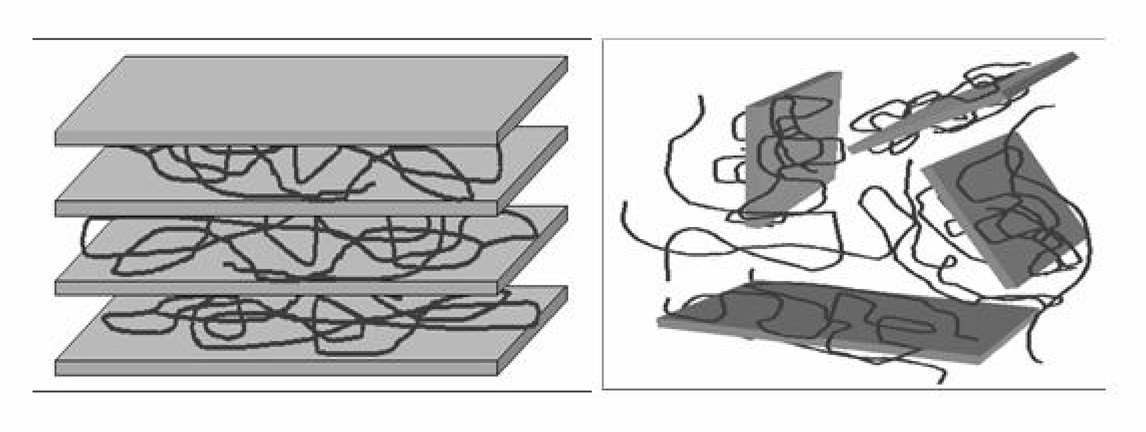
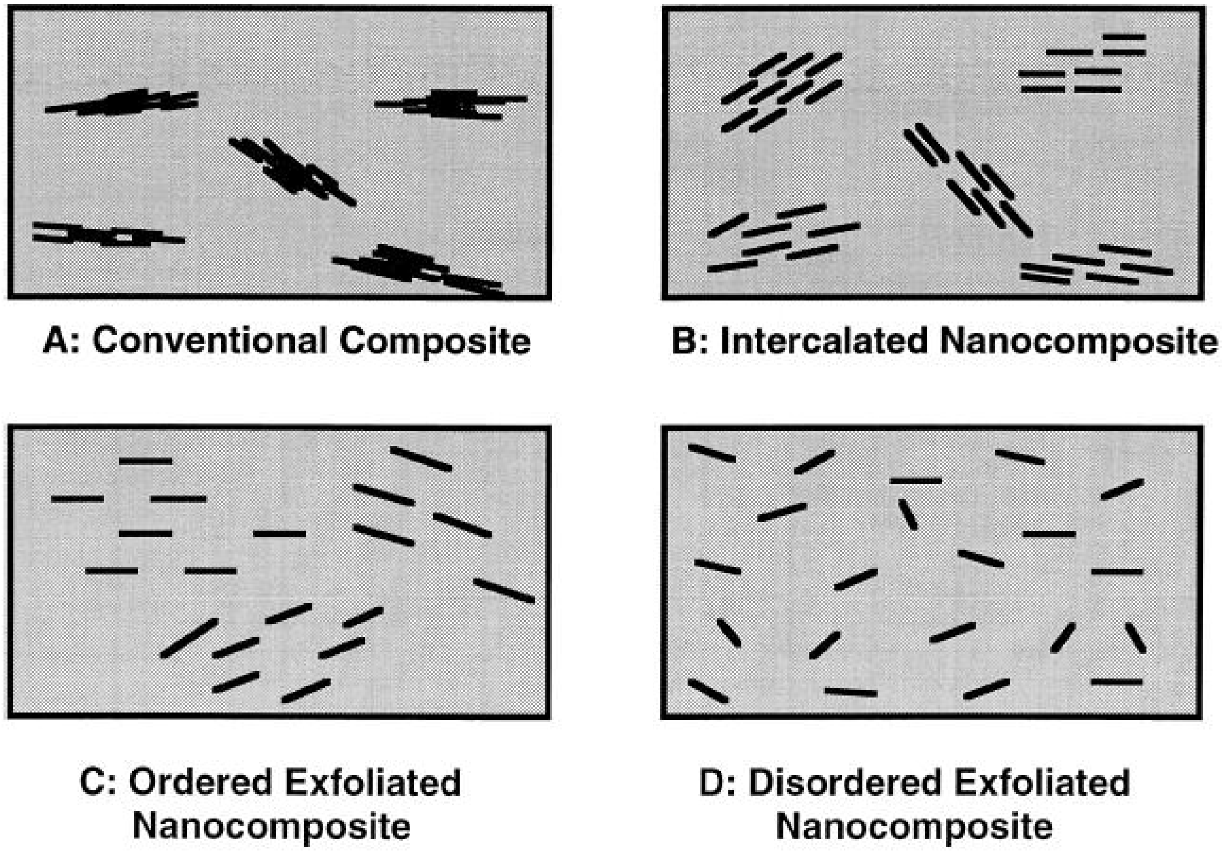


Figure 2.12. Two forms of thermodynamically feasible polymer/clay nanocomposites are illustrated schematically. The silicate layers' galleries are penetrated and enlarged in the intercalated system, seen on the left. Right: the exfoliated or delaminated system, in which distinct silicate layers are scattered throughout the matrix of a polymer (Usha Devi et al., 2015).


A: Conventional Composite

B: Intercalated Nanocomposite

C: Ordered Exfoliated Nanocomposite

D: Disordered Exfoliated Nanocomposite

Figure 2.13. Diagrams showing a conventional, an intercalated, an ordered exfoliated, and a disordered exfoliated polymer-clay nanocomposite are shown in (A), (B), (C), and (D), respectively (Usha Devi et al., 2015).

The polarity of the top of the clay is matched with the polarity of the polymer by the substitution of organic onium ions for inorganic exchange cations on the gallery surfaces of smectite clays. This also widens the clay galleries (Figure 2.14). This characteristic makes it easier for either the polymer precursors or the manufactured polymer to enter the gallery area (intercalate). Several configurations of the onium ions are possible depending on the charge density of the clay and the onium ion surfactant (Usha Devi et al., 2015).

The vertical orientation of the long chain alkylammonium in the solvated intercalates, however, determines the gallery height without regards to the starting charge density of the clay and the orientations of the gallery long chain alkylammonium ions. The intercalated polymer precursor species are represented by ellipses with cross-hatching (Figure 2.14).

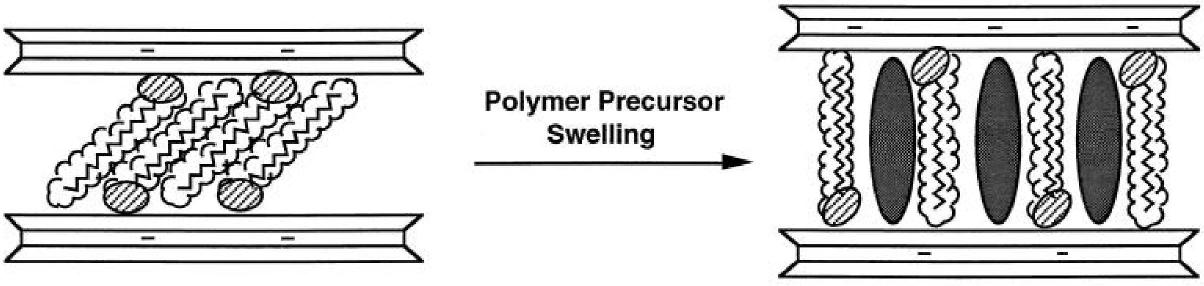


Figure 2.14. suggested model for the expansion of clay that has been alkylated and swapped for a parafin by polymer precursors.

For a permeant to traverse the nanocomposite, the impervious clay layers require a difficult route (Figure 2.15). The impeded diffusion paths across the nanocomposite contribute to the improved barrier properties, chemical resistance, reduced solvent uptake, and flame retardance of clay-polymer nanocomposites (Le Baron et al., 1999).

2.6 The Role of Isomorphic Substitution and Cation Exchange Capacity

Cations with a lower valence replace cations that are already present in the crystalline structure of a clay mineral during the process of isomorphic substitution (Mitchell & Soga, 2005). Depending on the particular clay mineral, isomorphic substitution results in a different amount of substitutions. In the silica sheet of a clay mineral, isomorphic substitution frequently occurs when part of the silicon ($Si^{4+)}$ cations are swapped out for trivalent cations like aluminum ($Al^{3+)}$ or iron III ($Fe^{3+).}$

It is typical for divalent cations like magnesium (Mg^{2+}), iron II (Fe^{2+}), or manganese (Mn^{2+}) to replace an Al^{3+} ion in the octahedral sheets. It is commonly known that isomorphic replacements produce a net negative charge on the surface of clay particles since this phenomena has been extensively researched (Li et al., 2020; Ramesh & Reddy, 2011). The net negative surface charge on a clay mineral can be used to determine the extent of isomorphic substitution in that material. When clay particles are added to a cationic solution, the adsorption of cations balances the negative surface charge on a clay mineral. As a result, the degree of isomorphic substitution for a particular clay mineral can also be used to predict how the mineral will be affected by electrolytes in solution. The term "Cation Exchange Capacity" (CEC) is used to describe the amount of exchangeable cations (Diale et al., 2011). In order to measure CEC, milliequivalents per 100 grams (mEq/100g) of dried clay are frequently used.

Table 2.3 provides typical CEC and specific surface area (SSA) values for kaolinite, illite, and montmorillonite. As seen, the SSA rises as CEC rises. It is unknown whether isomorphic substitution occurs in kaolinite minerals because it has not been adequately measured. Kaolinite's involvement in isomorphic replacement is questionable, although it has been shown that the mineral still has a tiny negative surface charge of 3 to 15 mEq/100g (Garrison, 2004; Mitchell & Soga, 2005).A technique of isomorphic substitution that would result in such a low CEC value might include exchanging one Al3+ ion for every 400th Si4+ ion (Mitchell & Soga, 2005). Illite exhibits a distinct mechanism of isomorphic substitution in contrast to kaolinite. Al^{3+} ions can take the place of Si^{4+} ions in the silica sheet. Illite has a CEC in the range of 10 to 40 mEq/100g thanks to this clearly established isomorphic replacement process.

All smectitic minerals, including montmorillonite, experience significant isomorphic replacement. Aluminum has the potential to replace up to 15% of Si^{4+} ions. Several other divalent cations can take the place of the Al^{3+} ions in the octahedral sheets of montmorillonite. Aluminum ion replacement can range from occasional to total replacement(Aramide et al., 2014; Gabelica et al., 1984; Novembre et al., 2011). The high CEC values of 80 to 150 mEq/100g are a result of the significant amount of isomorphic substitution that results in a significant negative charge on the surface of the montmorillonite minerals.

Table 2.3: a list of typical clay mineral properties(Awasthi et al., 2019)

Clay Mineral	**Specific Surface Area (m2/g)**	**D Spacing (nm)**	**Bond Type**	**CEC (mEq /100g)**
Kaolinite	10-201	0.721	Secondary Valence + Hydrogen Bonds2	3-151
Illite	65-1001	1.01	Secondary Valence + Potassium Linkages2	10-401
Montmorillonite	50-1201	Minimum of 0.962,3	Secondary Valence + Exchangeable Ion Linkages2	80-1501

2.7 Clay-Water-Electrolyte Interaction

The structure, bonding methods, and essential characteristics of kaolinite, illite, and montmorillonite have been briefly discussed in the preceding sections. These underlying principles of each clay mineral control how they behave when exposed to water. The mechanisms of cation selectivity and clay mineral hydration have been the subject of extensive research (Ayodele et al., 2012).

The methods applied for the hydration of a clay mineral are examined in the literature in the section that follows.

2.7.1 Interlayer Swelling

One broad definition of interlayer swelling in montmorillonite is the way water is been taken up between the silicate sheets of the clay material. The amount of water in montmorillonite is increased during this procedure to a maximum of roughly 0.5 grams of water per gram of clay (Usha Devi et al., 2015). It was discovered that the interlayer spacing of montmorillonite changed stepwise from 0.96 nm to 2.0 nm during interlayer hydration. There are four (4) distinct layers of hydration with a 0.25 nm thickness each throughout this range of swelling. The interlayer gap was discovered to be significantly affected by the valence and hydrated radius of the cations present in the hydrating fluid.According to Norrish (1954b), polyvalent ions as well as ions with a higher hydrated radius often create interlayer spacings that are bigger than those of monovalent ions.

(Murtaza et al., n.d.) noted that a "osmotic" phase would follow this first "hydration" phase, but only in the presence of monovalent cations. Norrish and Quirk noted interlayer spacings greater than 4.0 nm during the osmotic phase. They discovered a correlation between the interlayer spacing and the bulk solution normality, which is shown in Equation 2.4.1, where N is the bulk solution normality and d is the interlayer spacing in angstroms.

$$1/\sqrt{N}=d \qquad (2.4.1)$$

Cation selectivity and interlayer swelling are significantly influenced by the effects of layer charge. The charge that results from isomorphic substitution on a clay's surface is known as layer charge.

The level of interlayer swelling inside each of the four layers described by Norrish (1954) may be considered to be an unique "stage" of swelling since each degree of swelling in the initial hydration phase of montmorillonite can be conceived of as discrete. As a result, the ion selectivity will vary with each stage of swelling, resulting in a dominant ionic composition within the interlayer. The layer charge of the clay will be affected by changes to the interlayer composition of the soil. By following this reasoning, a feedback loop (Figure 2.15) is created, which results in a circular pattern.

A hypothesis put forth by Laird (1996) that has been utilized to explain the discrepancy in experimental data is shown in Figure 2.15. Maes & Cremers discovered that an increase in layer charge led to a larger affinity for Ca^{2+} in a montmorillonite that exchanged calcium (Ca^{2+}) cations for sodium (Na^{+}) cations. The findings were believed to suggest that polyvalent ions were more advantageous as layer charge increased. In contrast, a study by Sawhney found that as layer charge increased, the affinity for Ca^{2+} while exchanging K^{+} cations for Ca^{2+} cations dropped. Ion selectivity and valence-related arguments are presented in these two studies in conflict.

According to the paradigm put forth by Laird (2006), the interlayer will exhibit preference for the ion of greater valence in the exchange of cations with identical hydrated radii, such as a Na+ - Ca2+ exchange. Based on the idea of potential energies, Laird's model presupposes that every phase has unique energy needs. As a result, for ions with identical hydrated radii, sorbing an ion of greater valence has a poorer net energy balance than sorbing an ion with a similar valence but smaller hydrated radii.

Alternately, a rise in layer charge will make the clay more receptive to the small, weakly hydrated cation when an ion with a hydrated radius that is weak is present. The one which has a lesser water content radius will be chosen since sorbing an ion with a larger hydrated radius would need more energy.

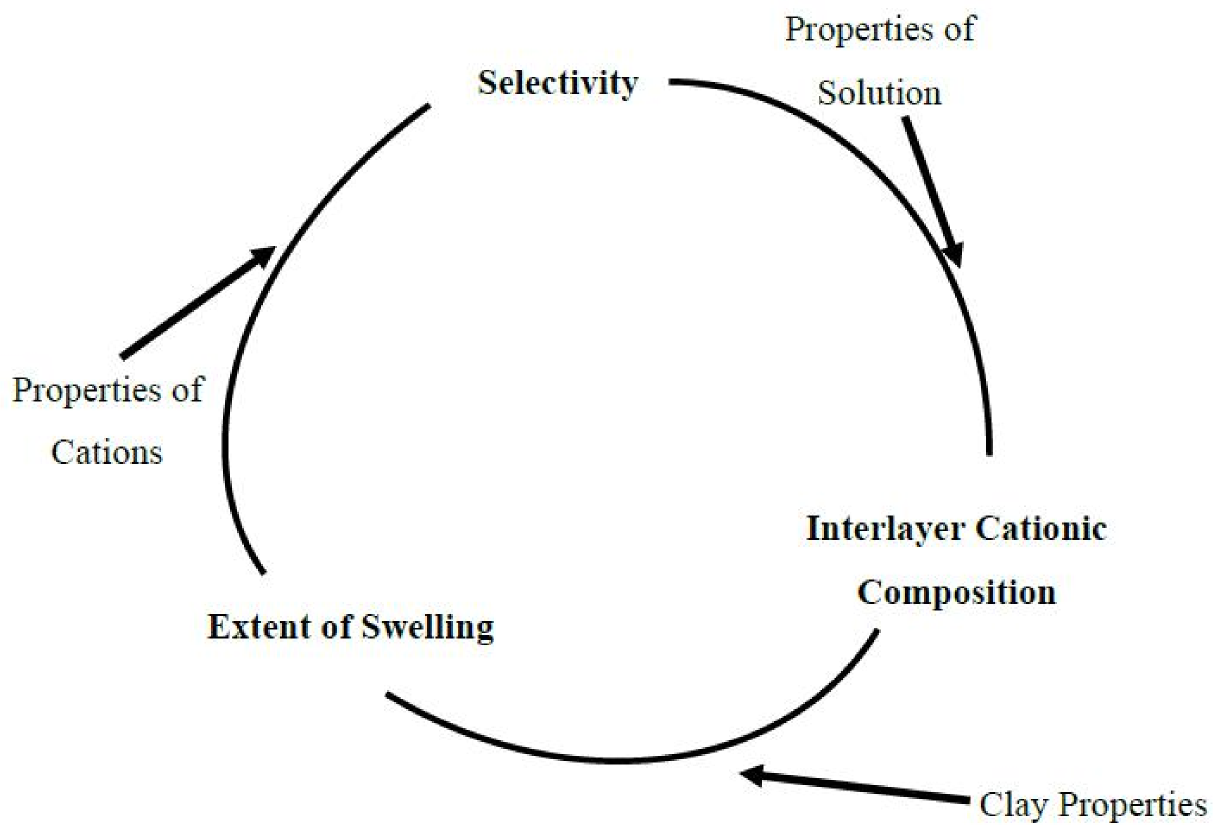


Figure 2.15: Interlayer selectivity feedback loop

It has been established that the permeability and swelling properties of montmorillonite are dominated by the friendship between bound water (water contained within the interlayer) and free water. This relationship also demonstrates the impact that various cation species have on the potential(swell) and conductivity(hydraulic) of bentonites. All of these research came to the conclusion that monovalent ions were more affected by ion species than polyvalent ions. The behavior of geosynthetic clay liners over the long term was predicted by Benson and Meer (2009) using a variable they defined as the ratio of monovalent to divalent molar concentrations (GCLs).

The findings of their study showed that an affinity for Ca^{2+} ions was indicated with rising bulk solution concentration (and consequently lowering layer charge).

The ion concentration, valence, and hydrated radius size are all factors that affect the interlayer swelling of the montmorillonite mineral, according to the aforementioned publications as well as the model put forward by Laird (1996). Also, it was demonstrated that a number of macroscopically visible behaviors of montmorillonite, including swell potential and permeability, are dominated by the composition of the interlayer.

2.7.2 Diffused Double Layer Swelling

DDL swelling, in contrast to interlayer swelling, occurs in all clay minerals. The negative charge and SSA of a clay mineral have a direct impact on the thickness of the DDL (Calisto et al., 2019). Consequently, compared to kaolinite and illite, the mineral montmorillonite can create DDLs that are significantly thicker. The negative charge that is imbedded on the surface of the clay attracts cations from the bulk porewater solution, which are then drawn back by the anions in the bulk solution to form the DDL. Although having significant shortcomings in its capacity to explain the function cations play related to the behavior of smectitic clays in solution, the Gouy-Chapman hypothesis is still the most popular model used to predict Its behavior.The four basic presumptions serve as the foundation for Gouy-Chapman theory:

1. Ions inside the DDL are point charges that don't interact with one another;
2. Charge is uniformly distributed on the surface of clay particles;
3. The particle's surfacesize is large in comparison to the thickness of the DDL; and
4. The medium (pore fluid) permittivityis unaffected by the location of the surface of the particle.

According to the first premise of the Gouy-Chapman theory, a clay platelet's surface can have an endless number of ions. This distribution of ions is called a Maxwell Boltzmann distribution. Because of this, when the concentration of electrolytes in the bulk solution is greater than 0.001 M, the theory is no longer viable for describing the interaction between clay and water (Sposito, 2004).

Several scientists have created specific formulas that relate the density of ions close to a surface of the clay and the Layer thickness (1/K). The DLVO hypothesis, which is named after its authors Boris Derjaguin and Lev Landau, Evert Verwey, and Theodoor Overbeek, is the current name for this enlarged Gouy-Chapman model (Mitchell & Soga, 2005). The equation describing the DDL thickness is shown below in

$$\frac{1}{K} = \left(\frac{\epsilon k T}{8\pi e_c^2 v^2 n}\right)^{1/2} \tag{2.4.2}$$

Where

$1/K =$ DDL thickness

$\epsilon =$ pore fluid dielectric constant (80.4)

k = Boltzmann constant (1.38 x 10^{-16} J°K^{-1})

T= temperature (°K)

$n =$ bulk solution molarity x (6.02 x 10^{23} mol^{-1}) x 10^{-3}

ec = electron charge (4.803 x 10^{-10} esu)

v = cation valence

The consideration of ahydrated radius of cation was made possible by Stern theory (1924), which effectively addressed the problems of Gouy-Chapman theory. He proposed that the negatively clay particles charge surface are covered in a hard coating of ions, as depicted in Figure 2.16. This layer, which resembles a solid structure, has about the same thickness as the hydrated cation's radius over the clay platelet's surface. The phrase "rigid-like" is often used to describe the cations within this layer since the thickness of this layer is constant, despite thermal motion causing the cations along a clay platelet's surface to be continually changing. The "Stern layer" is a fitting moniker for this layer of tightly bound cations. Stern theory-based equations.

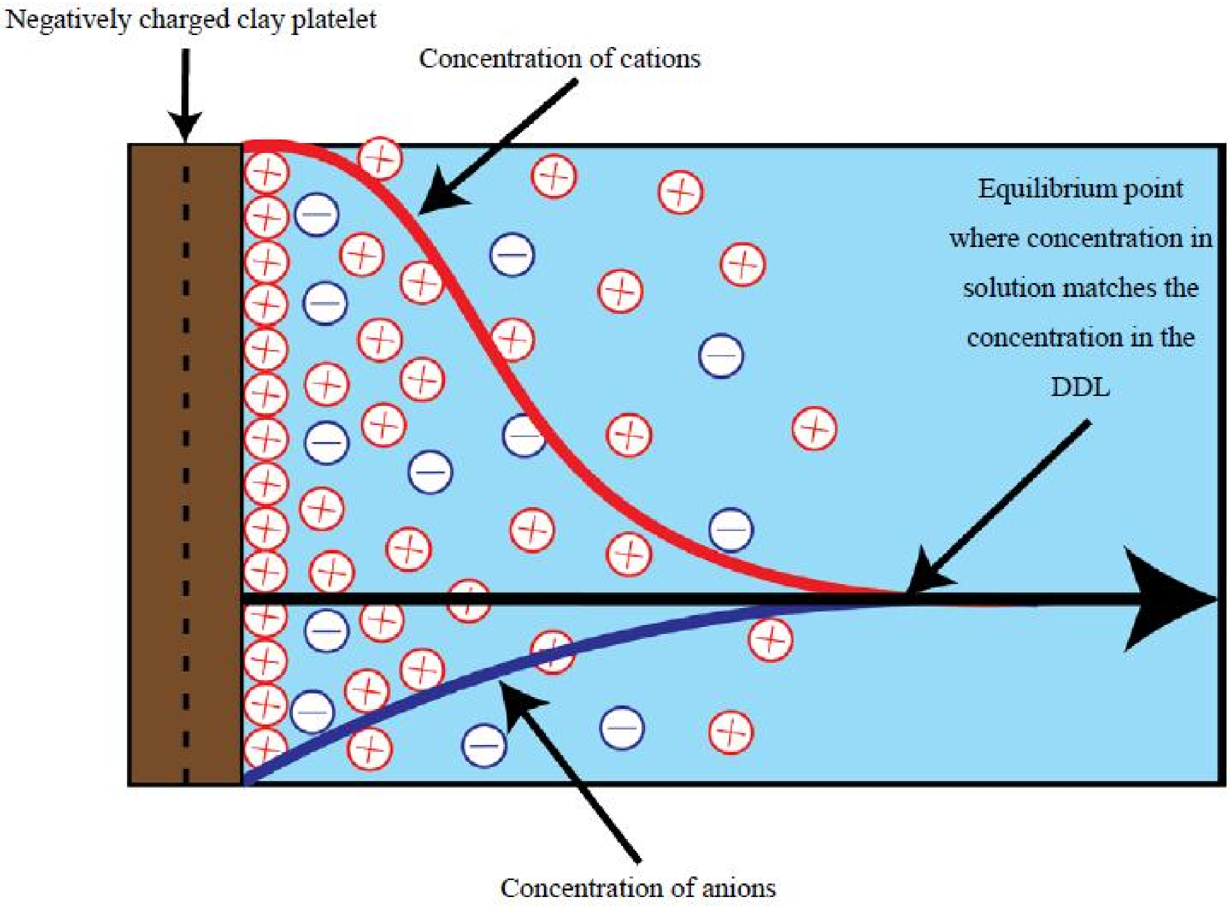


Figure 2.16: The Gouy-Chapman-Stern theory's prediction for how cations and anions are distributed inside the DDL. modified from (Powoe et al., 2021).

A method for measuring the repulsive pressures that develop between interacting DDLs of clay particles under Gouy-Chapman theory has been examined by numerous researchers. Bolt provided the Gouy-Chapman theory's first known analysis of repulsive tensions between clay particles (1956). The "Osmotic Pressure theory" that Bolt created was based on the Gouy-Chapman theory. The Layer surrounding a clay particle functions as a semi-permeable membrane in the osmotic pressure theory. In order for the pressure difference in the central planes between clay platelets and the bulk pore solution to equal that of the applied load when a load is applied to soil, a specific volume of fluid must exit the system. The Intrinsic repulsive forces between clay particles are thought to be equal to the difference in osmotic pressure between the system and the bulk pore solution. Bolt's hypothesis makes the fundamental premise that clay particles are organized in parallel plates. This presumption frequently causes differences between theoretically predicted values for repulsive pressures and experimentally measured ones.

Equations 2.4.3 through 2.4.6 present the suggested equation for calculating the repulsive pressures between clay particles. The chosen notation is in line with Balasubramonian

$$R = 2C_o rT(\cosh y_c - 1) \quad (2.4.3)$$

For $y_c < 1$:

$$y_c = 2\ln\,(\cosh\Delta + 1)/(\cosh\Delta - 1) \quad (2.4.4)$$

For $y_c > 1$:

$$y_c = 2\ln\,(\frac{\pi}{\Delta}) \quad (2.4.5)$$

$$\Delta = K(x_o + d) \quad (2.4.6)$$

And K = Eq. 2.4.2.

And K = Eq. 2.4.2.

Where:

R = repulsive pressure between particles

C0 = ion concentration of bulk solution (molar concentration x 10-3)

r = universal gas constant (85 kg-cm/mol/°K)

$xxoo$ = the distance from the surface of infinite charge density to a surface at which the charge density is equal to that of the soil of interest (equivalent to 4/*v,* where *v* is the valence of the cation, as given by Balasubramonian, 1972)

d = interparticle half space $(\frac{e}{SSA} x\ G)$, where e is void ratio and G is the specific gravity of the soil

Sridharan & Choudhury (2002) recognized successful applications for forecasting the behavior of Na-montmorillonites treated with pure Na^+;

however, theoretical solutions have not been as successful in forecasting the repulsive forces of naturally occurring montmorillonite soils that have been hydrated in a solution with other species of cations. In addition to the problems with the Gouy-Chapman theory already mentioned, the following conclusions and problems emerge when comparing the theoretical presumptions with reality:

- Presumption thatplates of clays are parallelly organized and spaced at regular intervals is frequently false.
- Fabric and structure are crucial since the separation distance between clay plates and void ratio are not only dependent on stress.
- Swelling pressure obtained will be more than what is expected by the diffuse double layer theory due to hydration forces as the particle closeness increases as a result of applied stresses

Chapter Three

Materials and Methods

3.1MATERIALS

The major material used for this work is the clay sample obtained from Ikpeshi town in Akoko-Edo LGA, Edo State.. The clay sample was collected from a spot at about 20cm deep.

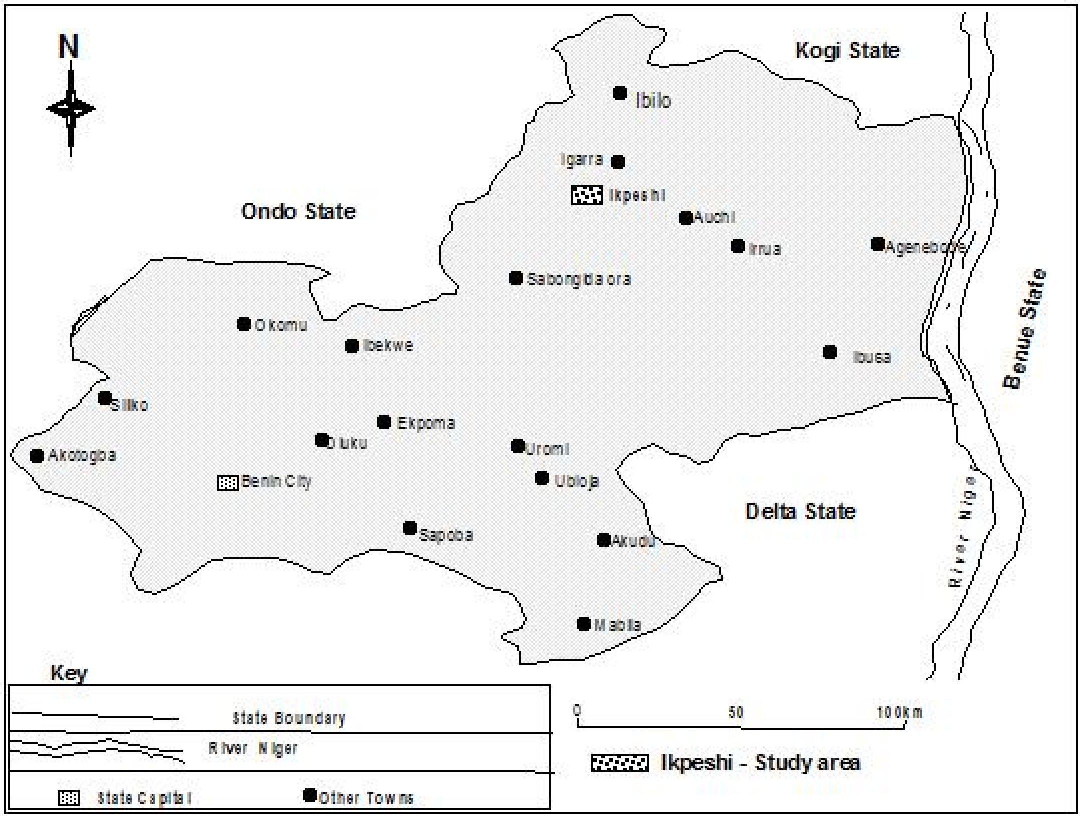


Figure 3.1: Map of Edo State showing Ikpeshi Town

3.1.1 Chemical and Reagents

The reagents and chemicals used in this work were analytical grade laboratory reagent and were obtained in the highest possible purity. The properties of the chemicals and reagents are listed below and they were obtained in a high analytical grade and mainly used in the synthesis of biosurfactant;

- sodium hydrogen surfite; 99.8% pure, produced by JHD, Shatou, Guondghuo China.
- Aluminum oxide; 90.5% pure, produced by JHD, Shatou, Guondghuo China.
- Sodium Hydroxide; 96% pure, produced by CDH, New Delhi, India.
- Sulphuric acid; 98% pure, produced by Fisons, Loughborough England.
- Ethanol; 99.7% pure, produced by JHD, Shatou, Guondghuo China.

3.1.2 Apparatus Used in Experiments

The equipment used in this study include:

Property	**Equipment**	**Manufacturer**
Drying	Vacutherm VT 6025 Air-Dry Vacuum Oven	Thermo Scientific NJ, USA
Calcination	SX-5-12 Electric Muffle Furnace	PEC Medical, US.
Density	SVM 3000 50milliliter Density Bottles	Anton Paar, UK
Functional groups	Fourier Transform Infrared (FTIR) Cary 630 Spectroscopy.	Agilent Technologies, Scientific, CA, USA
Elements/oxides composition	Energy Dispersive X-Ray Fluorescence ARL QUANT'X EDXRF.	Thermo Fisher Scientific, USA
Structural morphology	Thermo Scientific, X-Ray Diffractometer (XRD). Shimadzu XRD-6000 powder diffractometer with Cu Kα-ray radiation (λ = 0.154nm) (40 kV, 40 mA)	Thermo Fisher Scientific, USA
Surface morphology	Scanning Electron Microscope (SEM). BC43 Benchtop Confocal Microscope.	Oxford Instrument, England
Surface Area, Pore Size and pore volume	Brunauer-Emmett-Teller (BET). NovaWin version 11.03	Quantachrome Instrument
Differential Thermal Analysis	Thermo-gravimetric (TG) TGA-55	TA InstrumentNew Castle, England

Analysis		

3.2 Clay Pretreatment Procedure

Clay sample was crushed and sundried to remove loose moisture and sieved with a 100µm mesh to remove unwanted materials such as plant roots. The sieved sample was thus kept in a sealed container until further use.

Figure 3.1 Clay sample preparation process. A) Raw clay sample. B) Crushed clay sample C) Sieved clay sample.

3.2.1 Beneficiation of Clay

Clay sample was beneficiated by soaking in distilled water for 72 hours in a 2L conical flask, intermittently agitating with an overhead stirrer/homogenizer, and daily decanting of the suspended impurities. After being put through a 100-micron sieve, the mixture was allowed to settle for 24 hours. To remove the more reactive phases of bauxite metakaolin, the beneficiated kaolin clay was centrifuged, air dried for roughly 48 hours, and then calcined for roughly 6 hours at a temperature of about 600°C. After that, the supernatant was decanted. The metal oxide composition of the beneficiated samples was investigated using X-ray fluorescence.

3.2.3 Determination of Cation Exchange Capacity

Approximately 25.0g of soil had been added to a 500 mL Erlenmeyer flask. 125 mL of 1M NH_4OAc were added, thoroughly mixed, and then allowed to stand for 24 hours. With a 5.5 cm Separating funnel and retentive moist filter paper, move the dirt. If the filtrate is not clear, refilter through debris. The soil was gently rinsed with NH_4OAc four times in increments of 25ml, allowing each addition to filter through while guarding against the soil drying out or cracking. The leachate was discarded after determining the exchangeable cations. After being diluted to 250 cc, the leachate can be examined for exchangeable cations.

To get rid of extra saturating solution, the soil was washed eight times with 95% ethanol. A sufficient amount was added to cover the soil's surface, and then more was added once it had a chance to settle. The receiving flask was cleaned after the leachate was dumped. The adsorbed NH_4 was removed from the soil by slowly and thoroughly leaching it with eight separate applications of 25ml of 1M KCl. The leachate was then added to a 250 ml volumetric flask and diluted to mark with KCl after the soil had been removed. Methyl red was used as an indicator during the titration with 0.1M HCl to measure the concentration of NH_4-N. To account for any NH_4-N contamination in this reagent, also calculate the amount of NH_4-N in the initial potassium chloride extraction .

Calculations:

Where

NH_4-N is reported in mg N/L:

CEC (cmolc/kg) = $(NH_4\text{-}N_{\text{in extract}} - NH_4\text{-}N_{\text{in blank}})/14$

Where.

NH_4-N is reported in mg NH_4/L:

CEC (cmolc/kg) = (NH_4-$N_{\text{in extract}}$ - NH_4-$N_{\text{in blank}}$)/18

3.3.5 Determination of Moisture Content

The method reported by (Okop & Ekpo, 2012) and (Pollution Control Agency - Adam Sekely & McLain, 2008) was used. The moisture content of the soil sample was quantitatively determined by oven drying method at 110^0C for 1 hour. 5g of soil was weighed in a crucible using the electronic mass balance. The weight of the crucible and oil obtained together was placed in an oven at 110 degrees. At time intervals of 10 minutes, the crucible with soil was taken out and weighed with a new mass for both oil and crucible obtained. The process was continued till constant weight of the soil was obtained respectively.

The moisture content was calculated using the following equation;

$$\%Moisture = \frac{W_m - W_d}{W_m} \times 100$$

W_m = weight of moist sample

W_d = weight of dry sample

3.3.6 Determination of Soil-pH and Electrical Conductivity (EC) (USDA, 2003)

The negative logarithm of the hydrogen concentration is the pH value of an aqueous solution. Using a desktop pH meter, ion activity was monitored. In a soil to water extract ratio of 1:10, soil pH is measured. Each soil sample weighed five grams (5.0 g),also distilled water(50ml) was included to each sample cell.

The dirt lump was mixed to create a homogeneous slurry, and then pH (Jenway 3015 model) and EC (Jenway 4010 model) probes were inserted into the sample, respectively. Once the sample had stabilized at 30oC, the pH was measured.

3.4 Clay Mineralogy Test by X-Ray Diffraction

The Saskatchewan Research Council conducted a semi-oriented quantitative XRD analysis (SRC). Their procedure involved selecting a random 0.5 g aliquot from each specified pre-ground material. In a sealed room heated to 60°C, each sample was glycolated for a whole night. To determine the optimal orientation of the clay particles, sample powders were backpacked into a holder(stainless) in a circular motion. The minimal sample thickness was 1 mm, which is sufficient width for XRD utilizing a Cu source to consider it infinitely thick. Cu K radiation was used to irradiate the samples in an X-ray diffractometer called a Bruker D4 Endeavor. Samples were measured with a 0.02° step size and 0.35 second dwell time in the range of 3.0 to 70° 2.The Jade software suite was used for analysis of the data.

3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used at a higher magnification on a piece of clay. A concentrated stream of high-energy electrons was employed in (SEM) to produce different signals on the top of clay sample. A two-dimensional image was created to show spatial variations in feature such as texture, chemical characterization and material orientation using the SEM data obtained within a chosen region of the specimen top(surface). The SEM met the following requirements:

Materials investigated include solid inorganic materials such as metals and polymers; magnification ranges from 5x to 50,000x; specimen sizes to the level of to 200 mm in length and 80 mm in height; qualitative and semi-quantitative results from SEM analysis with EDS;

3.5 Functional Group Determination by Fourier transform Infra-red spectroscopy

Results were obtained using FTIR, or Fourier transform infrared spectroscopy (Model: Varian 3600; Range: 12000-100 cm^{-1}), for successive ethanol extracts as well as for isolated chemicals. The sample (1 to 2 mg) and KBr (3 to 4 mg) were combined to form a pellet, which was subsequently seen in the FTIR instrument at various incoming wavelengths.

The functional groups of the remaining components were examined using FTIR. The powdered sample was combined with potassium bromide in a pellet (KBr pellet). The substance was subjected to infrared light with a wavelength range of 10,000 to 100 cm-1 by the FTIR instrument, some of which passed through and part of which was absorbed. The absorbed radiation was converted into vibrational energy and/orrotational by the molecules of the samples. The resulting signal at the detector has a spectrum that frequently falls between 4000 cm^{-1} and 400 cm^{-1}, indicating the chemical fingerprint of the material (Fing et al., 2012). Hence, each molecule or chemical structure leaves a distinct spectral fingerprint behind (Wang and Weller, 2006).

3.6 Procedure of The Brunauer-Emmett-Teller (BET) Analysis

The N_2 gas adsorption and desorption isotherms were used to determine the porous characteristics. We used a Micromeritics Tristar V4.02 BET analyzer to assess the catalysts' surface area, pore size, and pore volume. In order to remove moisture, 200 mg of the sample were degassed at 200°C for two hours under nitrogen flow prior to conducting nitrogen adsorption tests based on the standard method of nitrogen adsorption at -196°C. The Specific Surface Area (SSA), the Por Volume(PV) and Pore Size(PS) distribution were all computed applying the BJH method using the maximum adsorption at a relative pressure of 0.999. The surface area and volume of the micropores were calculated using the t-plot method.

3.7 EDXRF Analytical Procedure

Thermo Scientific's ARL QUANT'X EDXRF Spectrometer was used to determine the chemical and elemental components of the specimen. Thermo Fisher Scientific standard reference material, Montana soil SRM 2710, was used for the EDXRF analysis, which was carried out according to protocol. With the help of a mortar and pestle, the sample was first ground into a fine powder. A sample holder was filled with 2g of the sample after it was weighed, and cotton wool was placed over the top to stop it from spraying. The sample holder's bottom is made of the thermoplastic polypropylene.

The samples were placed in sample carriers that were vacuumed for 10 minutes to eliminate air and moisture before being placed into an XRF Spectrometer with an Energy Dispersive Spectrometer for chemical analysis. To get the chemical analysis results in oxides, the method was calibrated using geological calibration of oxides in a vacuum. The EDXRF spectrometer ran the sample for a total of 10 minutes before the results were received.

3.8. X-Ray Diffraction Analysis Procedure

The sample's crystalline phase was identified using the X-Ray Diffraction (XRD) technique. Using an analytical X-Pert Pro diffractometer with Cu K monochromatic radiation, the kind of phases and the quantity of phases present in the sample were detected qualitatively and quantitatively. The average bulk composition of the tested sample was calculated following coarse crushing and homogenization. The powdered sample was then treated with the sample preparation block, crushed in the flat sample holder, and set on the sample stage in the XRD cabinet to create a flat, smooth surface. The reflection-transmission spinner stage with theta-theta settings was used for the study. The two-theta beginning position was 4 degrees, and the two-theta finishing position was 75 degrees, with an average speed of 8.67 seconds and a two-theta step of 0.026261. 40mA of tube current and 45VA of tension were present. A 5mm Width Mask, a Programmable Divergent Slit, and the Gonio Scan were used. At each rotation of the sample and detector, the amount of X-rays that were diffracted was continually measured. if they were to be part of the process and required to be part of the program and required to...-p..a.:, a and a a.. s. The peak positions overlap at low values of 2, even though each peak is composed of two independent reflections (K1 and K2), with K2 appearing as a hump on the side of K1.

3.9 Thermo-Gravimetry Analysis

The sample was warmed in order to remove adsorbed water and other volatile substances. The sample was heated to 500 °C once more at a heating rate of 10 °C/min and kept there isothermally for roughly 5–10 minutes until a constant mass was attained. After that, the furnace was set to cool to 100 °C and be left to rebalance.

The furnace purge was stopped from the gas containing the base to the gas that was inert.

A weight rise was observed while the base was absorbed for around 10 minutes, during which time a constant mass was gained. The sample lost mass as the basic molecules that had been physiosorbed to the surface began to desorbs when the furnace purge was turned back on and the temperature increased to 100°C in an inert environment. At a temperature of 100 oC, the physiosorbed base molecules were allowed to continue to desorb for about an hour, or until the sample mass stabilized. After all the physiosorbed base molecules were released, the remaining base molecules were then eliminated by increasing the temperature. It was heated to a maximum temperature of 600 °C at a pace of 10 °C per minute.At least two locations of weight loss were visible in acidic zeolites. The early mass loss is assumed to be caused by desorption from weakly acidic sites, whereas the mass loss that begins at higher temperatures (about 250°C) is thought to be caused by desorption from highly acidic sites.

Chapter Four

Result and Discussion

4.1 Physical and Chemical Properties

Physical characteristics of the clay sample revealed a low (12.79%) moisture content. 3.25 percent of water absorption. The three samples can be utilized to make refractory bricks, as demonstrated by this. A brick is more resistant to damage from freezing if its water absorption is less than 3.25%. For some Nigerian clays, like kankara clay, which has a specific gravity value of 2.810g/cm3, the specific gravity value compares quite favorably.

The average electrical conductivity was 36 S/cm (0.036 dS/m). According to Agbai et al. (2022), this number positions the soil less than four (4), which is non-saline, suggesting that there is no harm to crops and no blockage to the soil structure. The clay has low activity and can be highly weathered, according to the low CEC. As a result of the production of particles(coarse) that promote weak combination , heavily worn ground(soil) are more prone to erosion.

Table 4.1 Physical Properties of Cay Sample

Property	**Unit**	**Value**
pH	–	6.35
Bulk Density	g/cm^3	2.28
Porosity	%	29.84
Moisture Content	%	12.79
Water Absorption	%	3.25
E. C.	µS/cm	36
C. E. C.	cmolc/kg	17.52

4.2 Results of FTIR Analysis of Clay Sample

Results from the FTIR spectrum showed absorption between 3622.97 cm-1 and 685.83 cm-1 (Figure 4.1). The IR spectra of silicate ions (SiO_4^{-4}) showed two distinct, long peaks between 998.926 cm-1 and 909.47 cm^{-1} (Table 4.2). The presence of alkynes is undeniably confirmed by a large peak in the IR spectra between 2643 cm-1 and 1707 cm-1 for acidic groups (3233.2 cm-1 and 2363.4 cm^{-1} for carboxylic acids), and 3140.2 cm^{-1}. The presence of (C - Cl) and (C - Br) groups attributed to aliphatic chloro compounds and aliphatic bromo compounds, respectively, in the clay samples was indicated by stretched peaks at 752.92cm^{-1} to 685.83cm^{-1}.

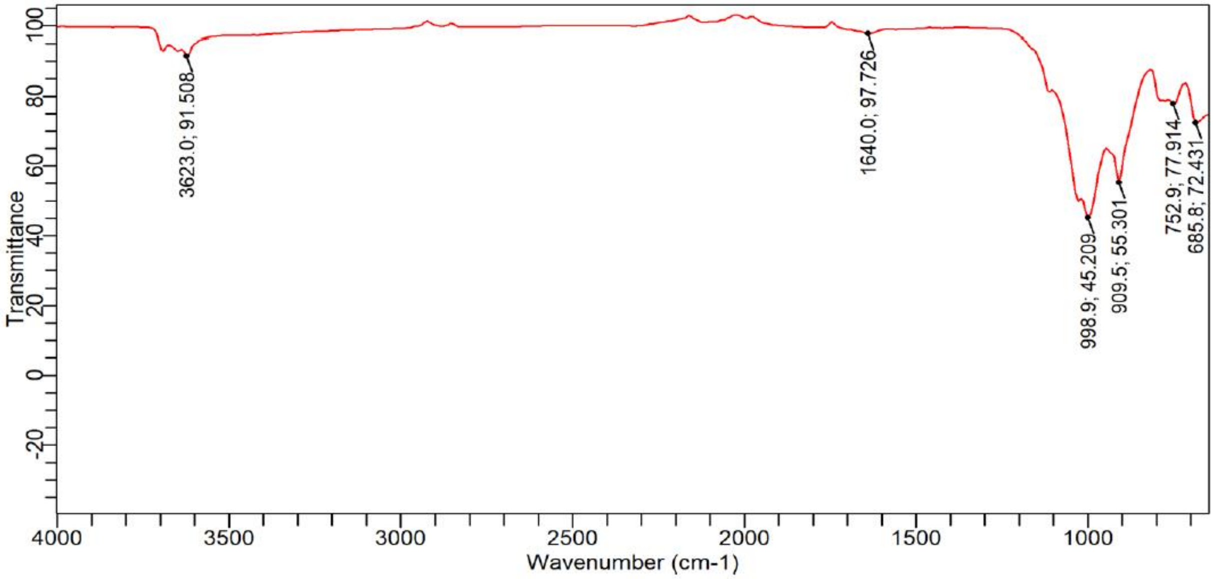


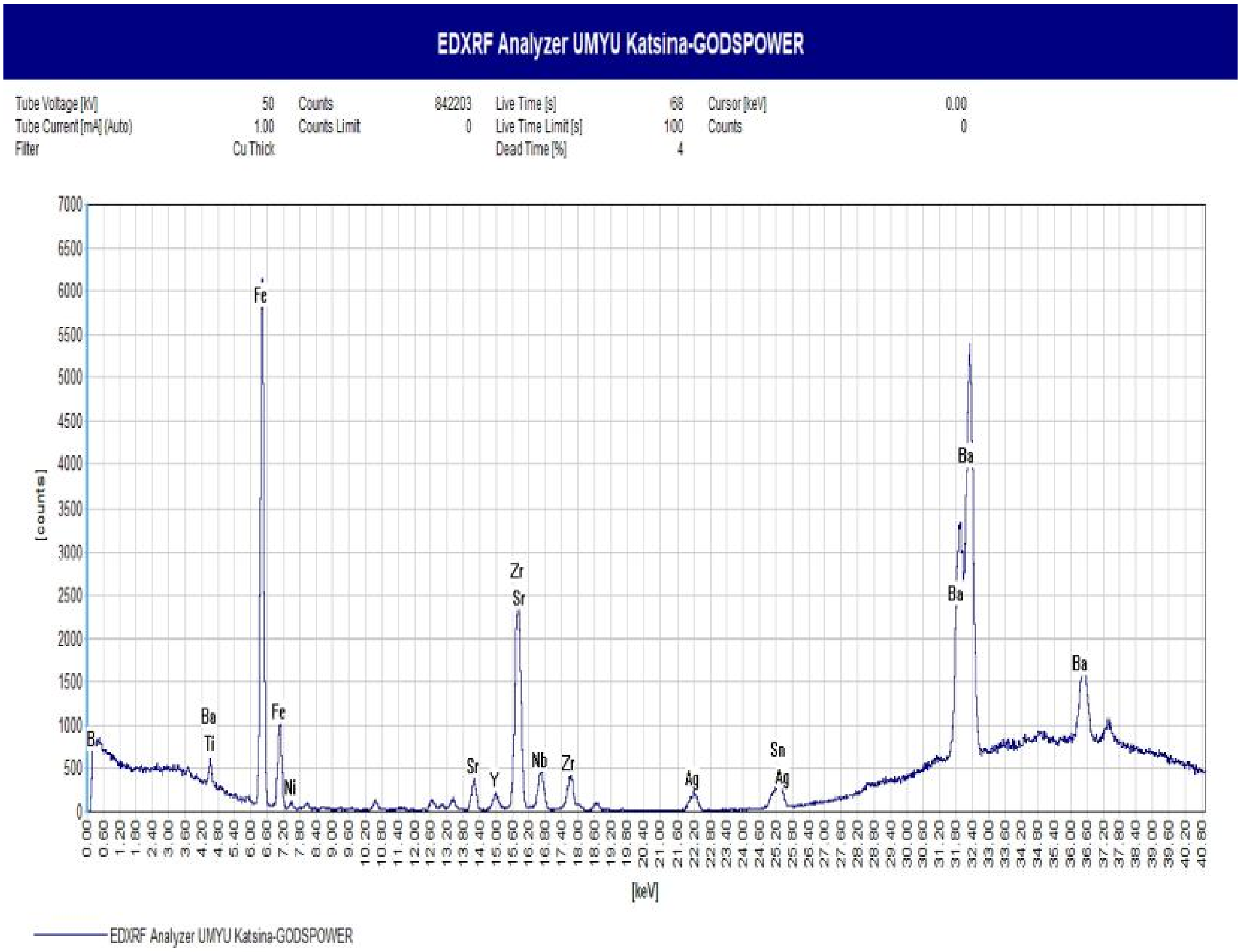
Figure 4.1 FTIR Spectrum of sample analysis

Table 4.2 Results of FTIR analysis on clay sample

Peak Number	**Wavenumber (cm^{-1})**	**Intensity**	**Functional Group**	**Comment**
1	685.83016	72.43086	C– Br, stretch	Aliphatic bromo compounds,
2	752.92224	77.91423	C– Cl, stretch	Aliphatic chloro compounds
3	909.47043	55.30056	SiO_4^{-4}	Silicate ion
4	998.92654	45.20918	SiO_4^{-4}	Silicate ion
5	1640.02865	97.72610	-C=N-	Open-chain imino
6	3622.97238	91.50831	OH	Secondary alcohol

4.3 Results of EDXRF Analysis of Clay Sample

The purpose of the XRF study was to determine the chemical makeup of the clay and any potential chemical alterations brought on by treatment.Figure 4.2 shows the result.. While other oxides including magnesium oxide, calcium oxide, etc are found in small quantity, clay contains silica, which is present in significant numbers. The compositions and maxima of the elements contained are provided in Table 4.2. Similarly, Table 4.3 reveals the most abundant substance to be silicon (45.116%), aluminum (20.39%), iron (3.2628%), and magnesium (2.61%).



Tube Voltage [KV]	50	Counts	842203	Live Time [s]	168	Cursor [keV]	0.00
Tube Current [mA] (Auto)	1.00	Counts Limit	0	Live Time Limit [s]	100	Counts	0
Filter	Cu Thick			Dead Time [%]	4		

Figure 4.2 EXDRF analysis spectrum of clay sample

Table 4.3 Elemental composition of clay sample

Element	Concentration (%)	Peak(cps/mA
Silicon	45.116	3306
Aluminum	20.39	317
Iron	3.2628	12254
Magnesium	2.61	3
Tin	2.108	11
Titanium	0.9718	3452
strontium	0.7731	40
Cerium	0.6519	49
Calcium	0.5381	804
Tantalum	0.47338	5
Manganese	0.2858	860
Sulphur	0.1746	92
Phosphorus	0.1589	35

4.4 Results of XRD Analysis of Clay Sample

The impact of the treatment on structural alterations in the clay material was uncovered using the X-ray diffraction method. Figure 4.3 shows both the original and experimented kaolin samples' XRD patterns. The mother sample displays sharply accurate reflections at 2 values of 120 and 250, which translate to d values of 7.154. Reflections of [001] can be seen at these summits.

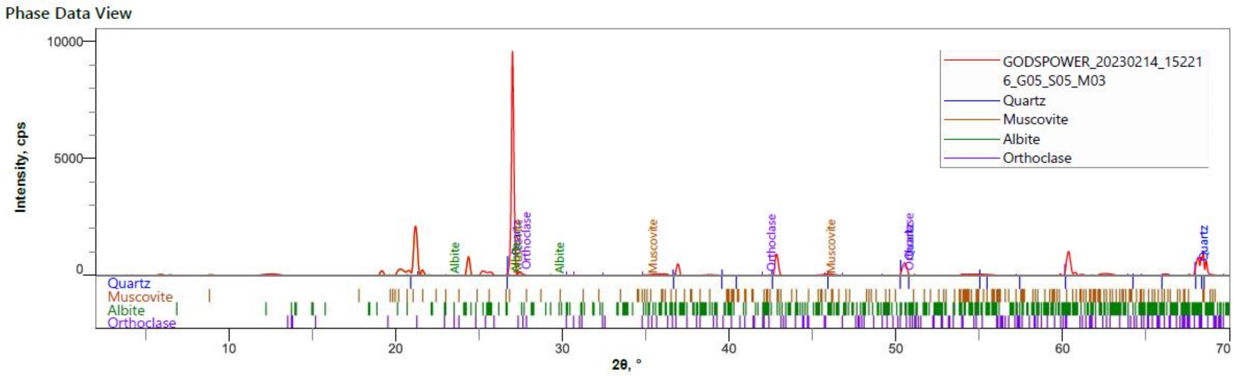


Figure 4.3 XRD pattern of clay sample

Impact of the treatment on structural alterations in the clay material was uncovered using the X-ray diffraction method. Figure 4.3 shows both the original and experimented kaolin specimen XRD patterns. The parent clay displays sharply defined reflections at 2 values of 120 and 250, which translate to d values of 7.154. Reflections of [001] can be seen at these summits.

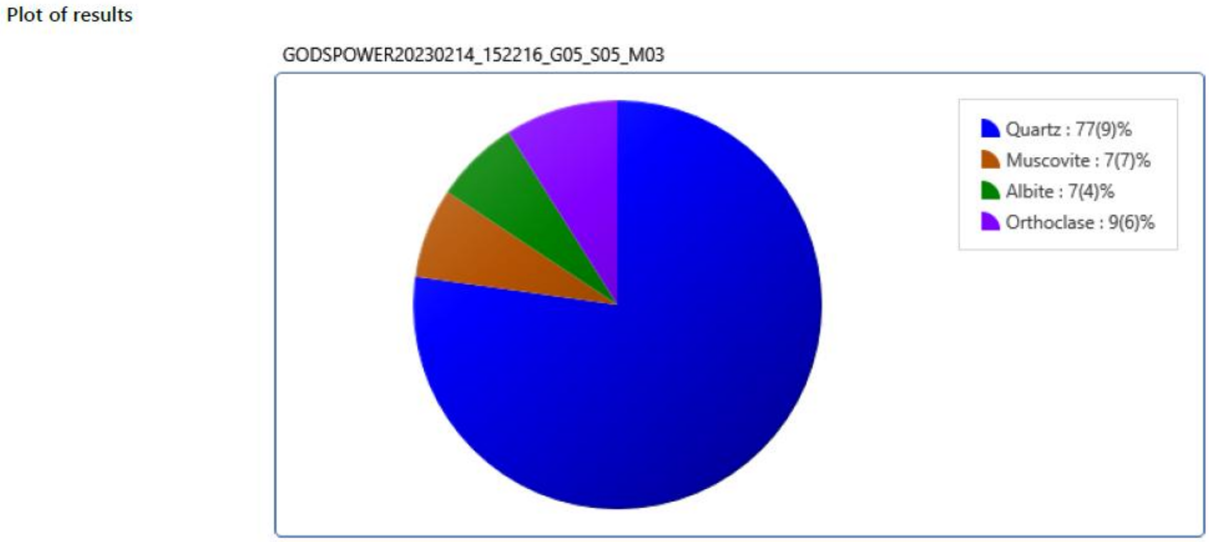


Figure 4.4 Plots of XRD results

Because of the clay mineral's silica to aluminum concentration ratio, Table 4.4 demonstrates that it can be used to synthesize a zeolite of the faujasite type. Quartz makes up the majority of the clay's composition, with minor elements of Muscovite, Albite, and Orthoclae. The study found that quartz had the highest relative amount of minerals contained in the clay sample. The analysis's findings indicate that the tested clay is ball clay.

Table 4.4 Results of The Quantitative Analysis

Name	**Formulae**	**Distinction Figure**	**Space Group**
Quartz	SiO_2	1.688	154 : P3221
Muscovite	$K\ Al_2(Si_3Al)O\ 10(OH.F)_2$	3.199	15 : C12/c1
Albite	$Na\ Al\ Si_3\ O_8$	3.168	2 : P-1
Orthoclase	$Al_2O_3\ .\ K_2\ 6SiO_2$	3.211	12 : C12/m1

4.5 Results of TGA Analysis of Clay Sample

Thermogravimetric analysis was only used to calculate a sample's mass as a function of temperature. The sample loses mass as a result of the volatilization of a liquid breakdown product or the evolution of an inert gas. As each subsequent step of breakdown takes place, the thermogram shows a sequence of plateaus of diminishing mass. Figure 4.5 depicts a close-up of the chemidesorption part of the curve. It shows two weight loss zones that, when combined, represent the desorption of ammonia molecules that are weakly linked to weak acid sites and strongly attached to strongly acidic sites, respectively. The TGA derivative curve's peak minimum represents the temperature at which desorption from mildly acidic sites stops and desorption from strongly acidic sites starts. The strong and weak acid sites identified in the sample under study might be counted quantitatively as a result of this knowledge. The temperature at which the exothermic peak associated with lattice collapse emerged in the DTA curve was utilized to define the thermal stability of clay as a function of the Si/Al ratio, cation type (La3+, Ca2+, or Na+), and degree of ion exchange (Majchrzak-Kucba, 2013). DTA also examined the hydrothermal thermal stability of the clay sample (USY). It was believed that the temperature of crystal collapse started at the beginning of the exothermic DTA peak (Figure 4.5).

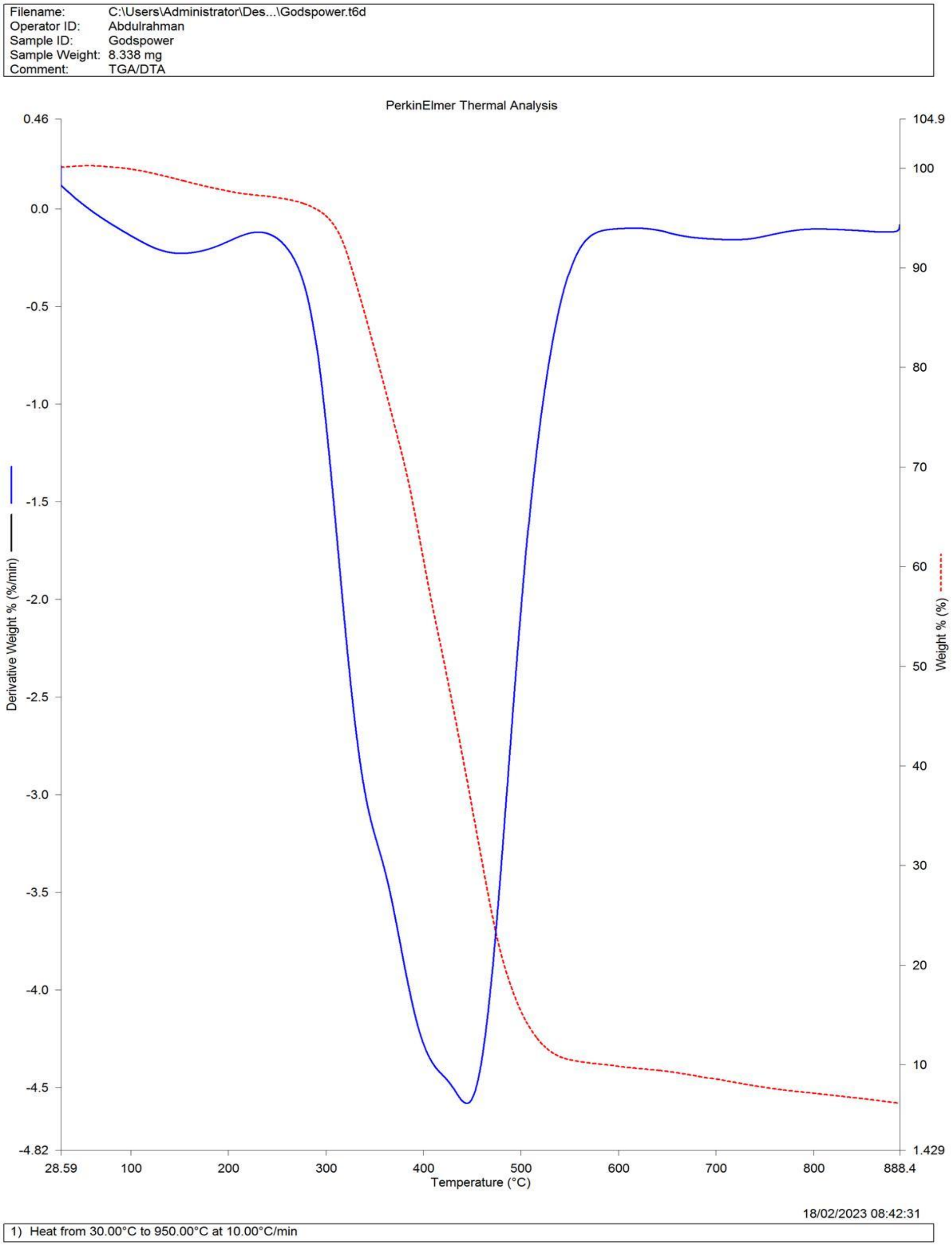


Figure 4.5 TGA/DTA curves of specimen

4.6 Results SEM Analysis on Clay Sample

Figure 4.1 shows a micrograph of the catalyst that was created using SEM images at 1500x magnifications. The sample revealed spherical particles in the 20-m range that were largely homogenous. The morphologies of these particles' surfaces, which were rough and angular, made it easier to distinguish between the crystal and the amorphous.

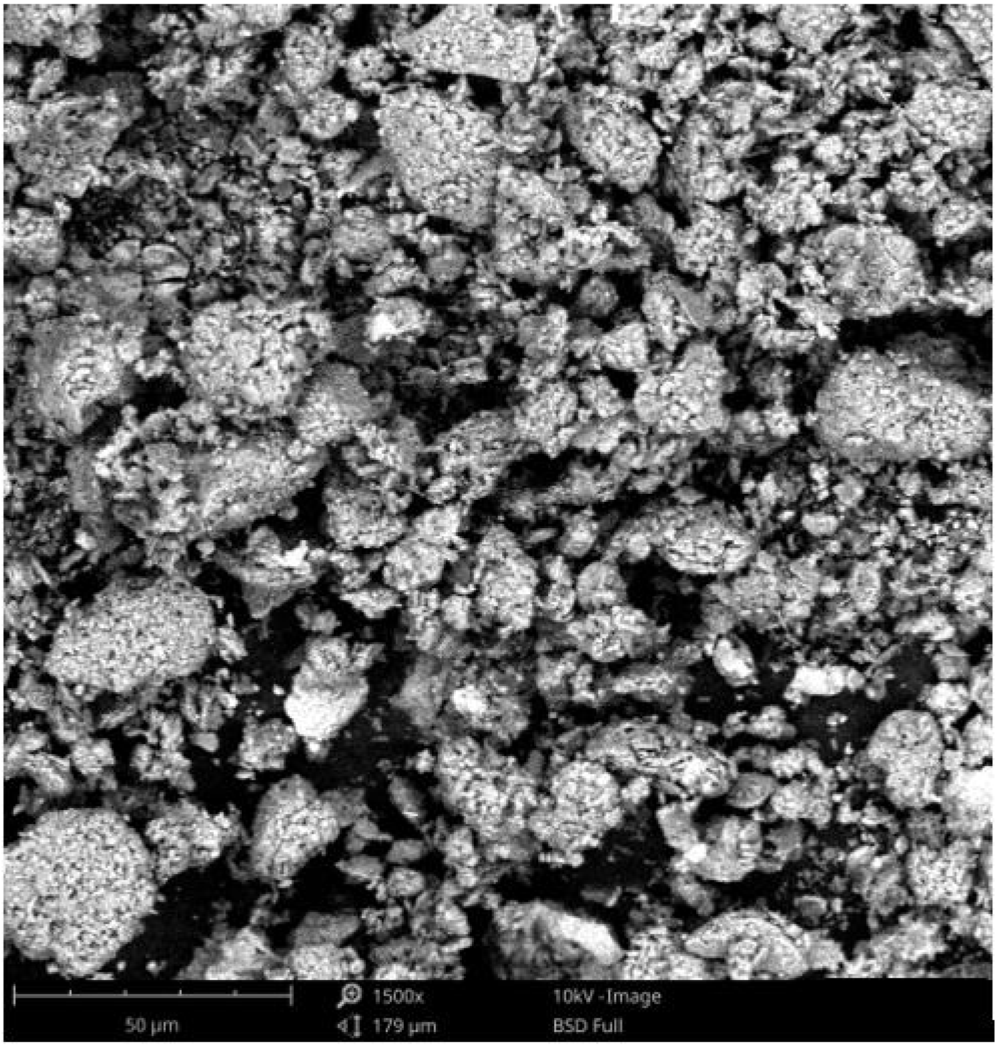
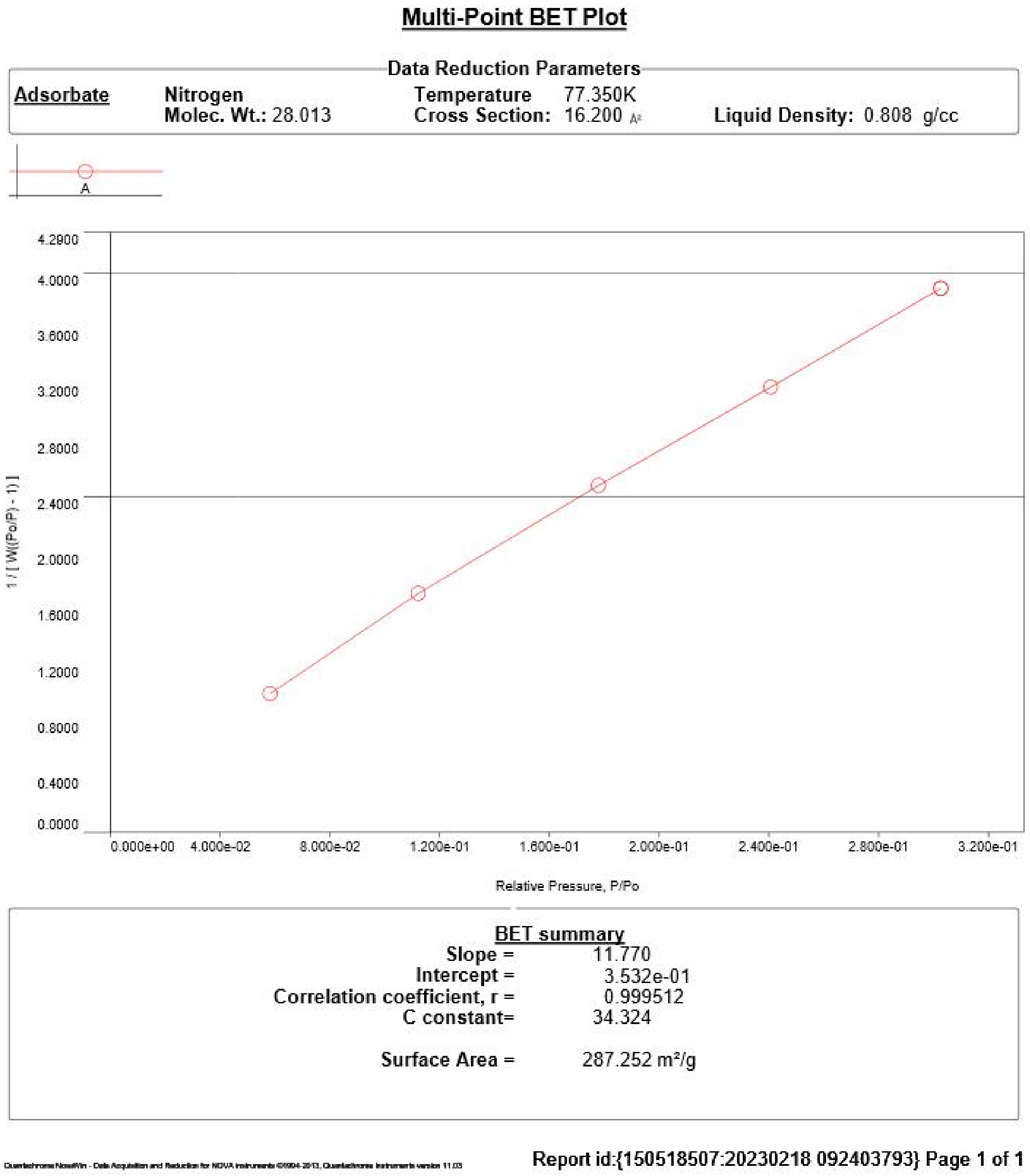


Figure 4.6 SEM micrograph of clay sample

4.7 Results BET Analysis on Clay Sample

Results of BET analysis revealed pore sizes, thepore volume with the surface area of the particles of clay sample. Results of multi-point BET analysis plot revealedthe surface area of the sample was 287.252m^2/g while the DA method gave the pore diameter to be 214nm. The pore diameter according to BJH was 3.108nm with surface area as 290.370m^2/g and pore volume as 0.140cc/g.

Table 4.4 Multi-Point BET Point



Multi-Point BET Plot

Data Reduction Parameters

Adsorbate **Nitrogen**
Molec. Wt.: 28.013
Temperature 77.350K
Cross Section: 16.200 Å²
Liquid Density: 0.808 g/cc

BET summary

Slope = 11.770
Intercept = 3.532e-01
Correlation coefficient, r = 0.999512
C constant= 34.324

Surface Area = 287.252 m²/g

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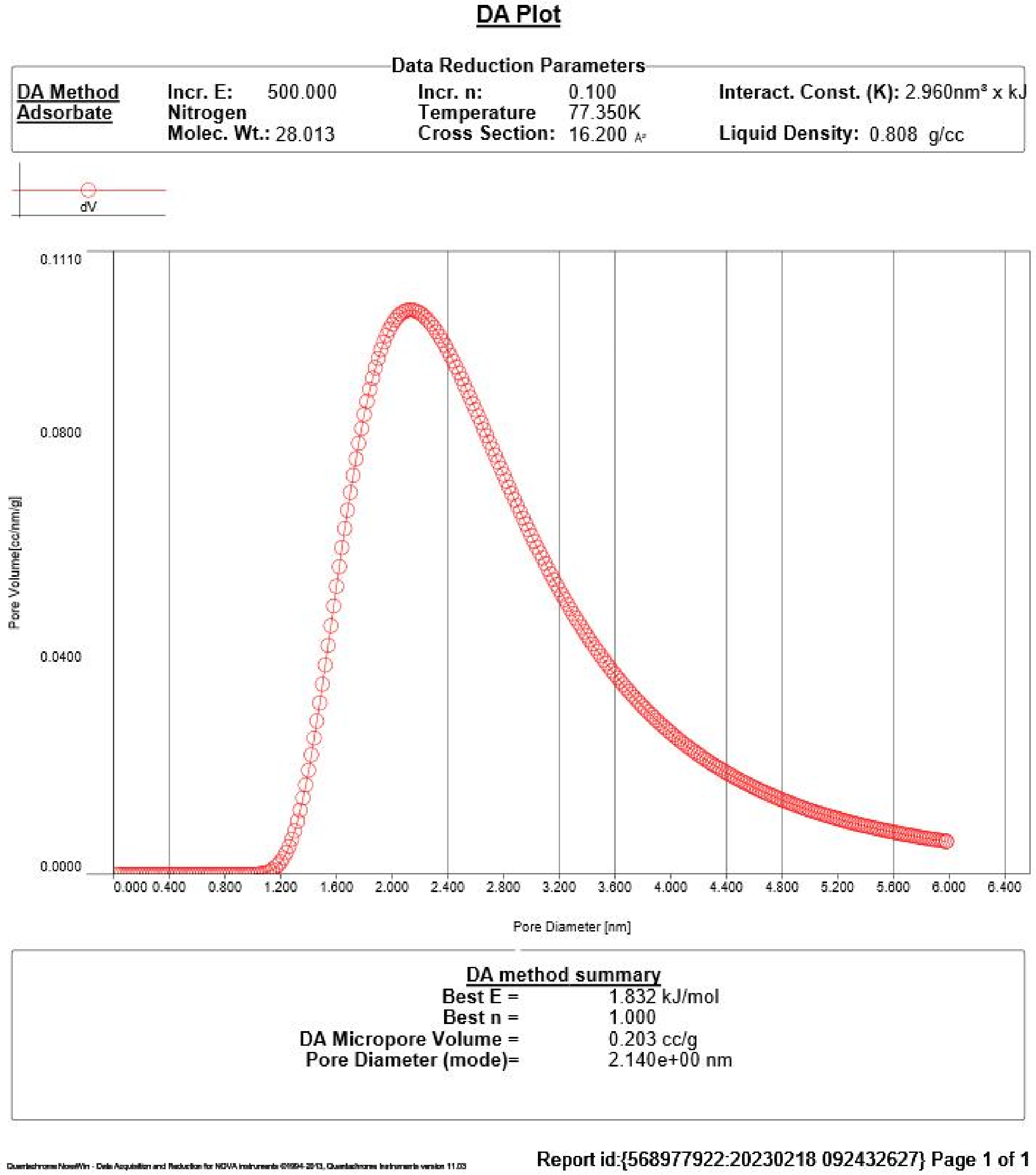
Table 4.5 The DA Plot



DA Plot

Data Reduction Parameters

DA Method	**Incr. E:**	500.000	**Incr. n:**	0.100	**Interact. Const. (K):** 2.960nm³ x kJ
Adsorbate	**Nitrogen**		**Temperature**	77.350K	
	Molec. Wt.:	28.013	**Cross Section:**	16.200 Å²	**Liquid Density:** 0.808 g/cc

DA method summary

Best E = 1.832 kJ/mol
Best n = 1.000
DA Micropore Volume = 0.203 cc/g
Pore Diameter (mode)= 2.140e+00 nm

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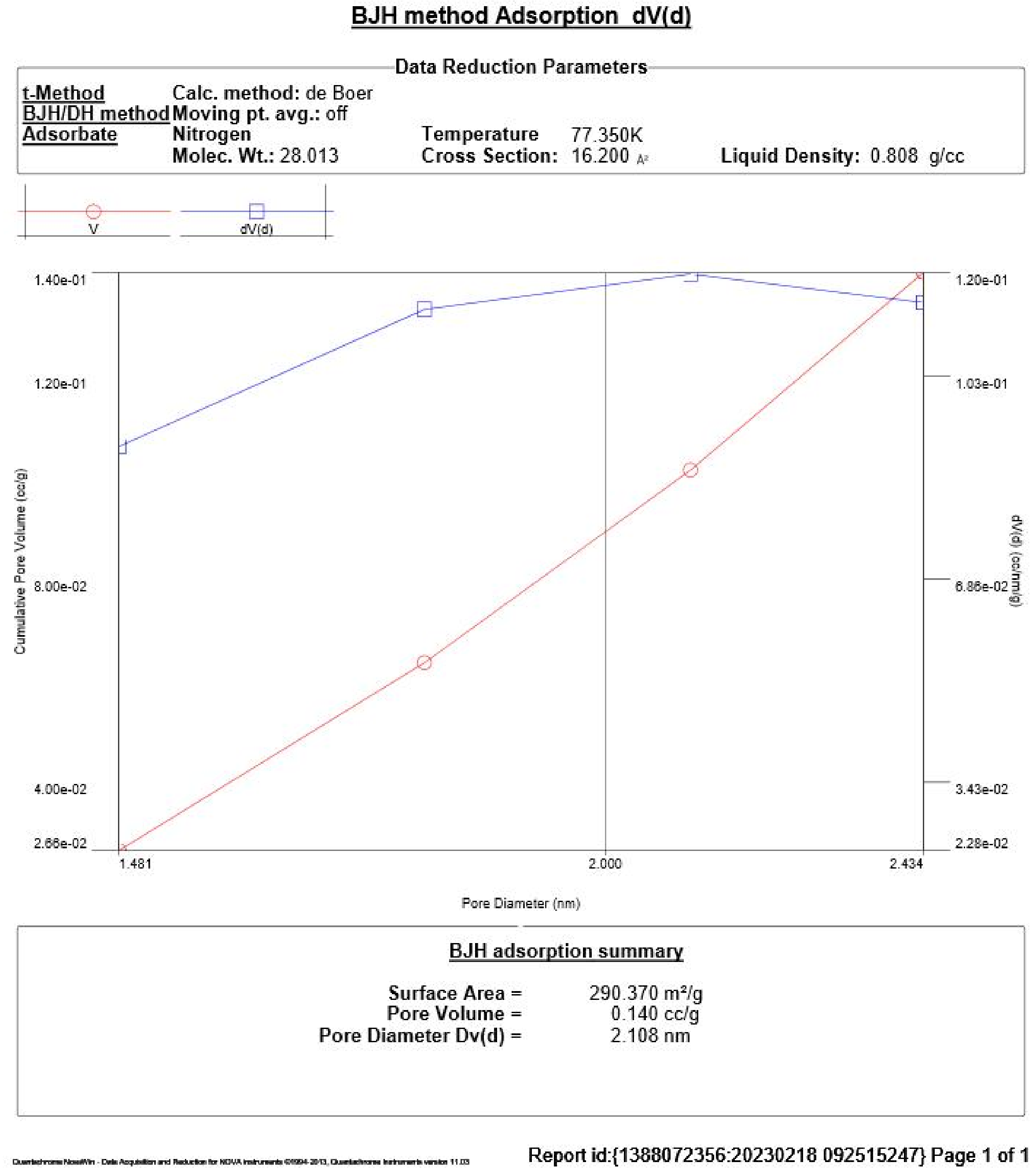
Table 4.6 The BJH Method of Adsorption



BJH method Adsorption dV(d)

Data Reduction Parameters

t-Method Calc. method: de Boer
BJH/DH method Moving pt. avg.: off
Adsorbate Nitrogen Temperature 77.350K
Molec. Wt.: 28.013 Cross Section: 16.200 Å² Liquid Density: 0.808 g/cc

BJH adsorption summary

Surface Area = 290.370 m²/g
Pore Volume = 0.140 cc/g
Pore Diameter Dv(d) = 2.108 nm

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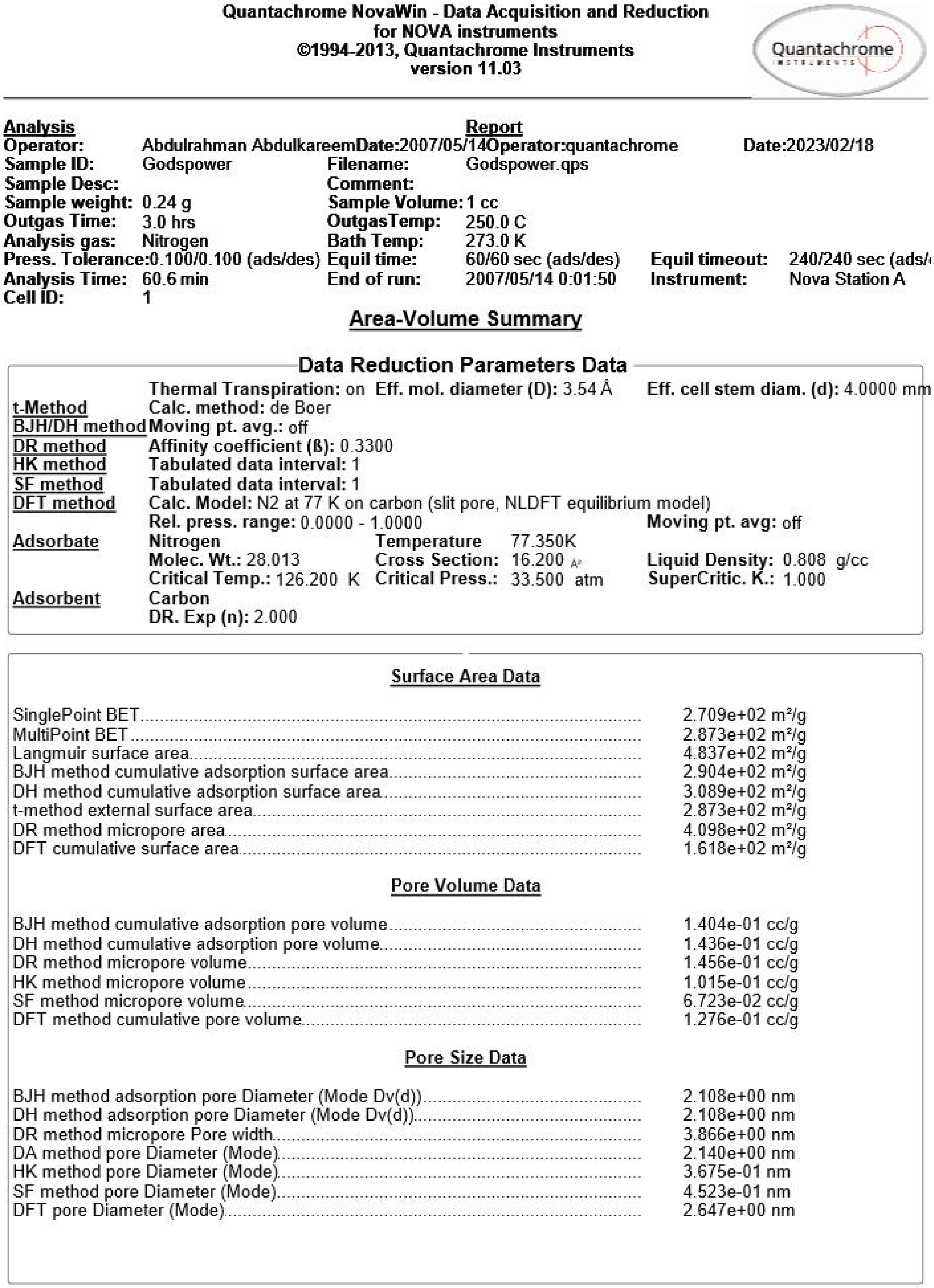
Table 4.7 The BET Area, volume and pore summery



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Analysis **Report**
Operator: Abdulrahman Abdulkareem**Date:**2007/05/14**Operator:**quantachrome **Date:**2023/02/18
Sample ID: Godspower **Filename:** Godspower.qps
Sample Desc: **Comment:**
Sample weight: 0.24 g **Sample Volume:** 1 cc
Outgas Time: 3.0 hrs **OutgasTemp:** 250.0 C
Analysis gas: Nitrogen **Bath Temp:** 273.0 K
Press. Tolerance:0.100/0.100 (ads/des) **Equil time:** 60/60 sec (ads/des) **Equil timeout:** 240/240 sec (ads/
Analysis Time: 60.6 min **End of run:** 2007/05/14 0:01:50 **Instrument:** Nova Station A
Cell ID: 1

Area-Volume Summary

Data Reduction Parameters Data

Thermal Transpiration: on **Eff. mol. diameter (D):** 3.54 Å **Eff. cell stem diam. (d):** 4.0000 mm
t-Method **Calc. method:** de Boer
BJH/DH method **Moving pt. avg.:** off
DR method **Affinity coefficient (ß):** 0.3300
HK method **Tabulated data interval:** 1
SF method **Tabulated data interval:** 1
DFT method **Calc. Model:** N2 at 77 K on carbon (slit pore, NLDFT equilibrium model)
Rel. press. range: 0.0000 - 1.0000 **Moving pt. avg:** off
Adsorbate **Nitrogen** **Temperature** 77.350K
Molec. Wt.: 28.013 **Cross Section:** 16.200 Å² **Liquid Density:** 0.808 g/cc
Critical Temp.: 126.200 K **Critical Press.:** 33.500 atm **SuperCritic. K.:** 1.000
Adsorbent **Carbon**
DR. Exp (n): 2.000

Surface Area Data

SinglePoint BET	2.709e+02 m²/g
MultiPoint BET	2.873e+02 m²/g
Langmuir surface area	4.837e+02 m²/g
BJH method cumulative adsorption surface area	2.904e+02 m²/g
DH method cumulative adsorption surface area	3.089e+02 m²/g
t-method external surface area	2.873e+02 m²/g
DR method micropore area	4.098e+02 m²/g
DFT cumulative surface area	1.618e+02 m²/g

Pore Volume Data

BJH method cumulative adsorption pore volume	1.404e-01 cc/g
DH method cumulative adsorption pore volume	1.436e-01 cc/g
DR method micropore volume	1.456e-01 cc/g
HK method micropore volume	1.015e-01 cc/g
SF method micropore volume	6.723e-02 cc/g
DFT method cumulative pore volume	1.276e-01 cc/g

Pore Size Data

BJH method adsorption pore Diameter (Mode Dv(d))	2.108e+00 nm
DH method adsorption pore Diameter (Mode Dv(d))	2.108e+00 nm
DR method micropore Pore width	3.866e+00 nm
DA method pore Diameter (Mode)	2.140e+00 nm
HK method pore Diameter (Mode)	3.675e-01 nm
SF method pore Diameter (Mode)	4.523e-01 nm
DFT pore Diameter (Mode)	2.647e+00 nm

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 FINDINGS AND CONCLUSION

The physical and chemical investigation of the clay sample showed that it included a sizable amount of silica and alumina. The sample clearly belongs to the category of kaolinite and ball clay, as a result. After calcining at a temperature of 900^{o}C, the clay samples' color changes from white to light brown. Chemical properties revealed a high silica concentration, making them suitable for the manufacture of zeolite X and Y. The sample revealed spherical particles in the 20-m range that were largely homogenous. Two lengthy and distinct peaks in the analysis's IR spectra, between 998.926 cm^{-1} and 909.47 cm^{-1}, showed silicate ions.

5.2 Recommendation

Using in-situ soil analysis techniques is one of the greatest ways to analyze soil, however it moves slowly in locations like deep-seated landslides. Traditional geotechnical engineering solutions are very challenging and expensive because of the expansive nature and deep positions of the shear planes linked to these landslides.

Kaolinite, montmorillonite, sepiolites, and halloysite are the most common clay minerals. The development of appropriate clay-based composites and their use as carriers for the delivery of drugs and the sustained release of biological active species, as well as on better adsorbents for water purification and effective catalysts, should be the main objectives of future research on the use of clay minerals. Clay surfaces can be modified through supramolecular interactions or covalent alterations, which offers amazing potentials and environmentally friendly approaches to create effective and one-of-a-kind nanomaterials with better biological, morphological, and physicochemical features.The completion of Ikpeshi clay treatment field trials should be another goal of future study. This method has to have its efficacy fully established before it can be used as a therapy option.

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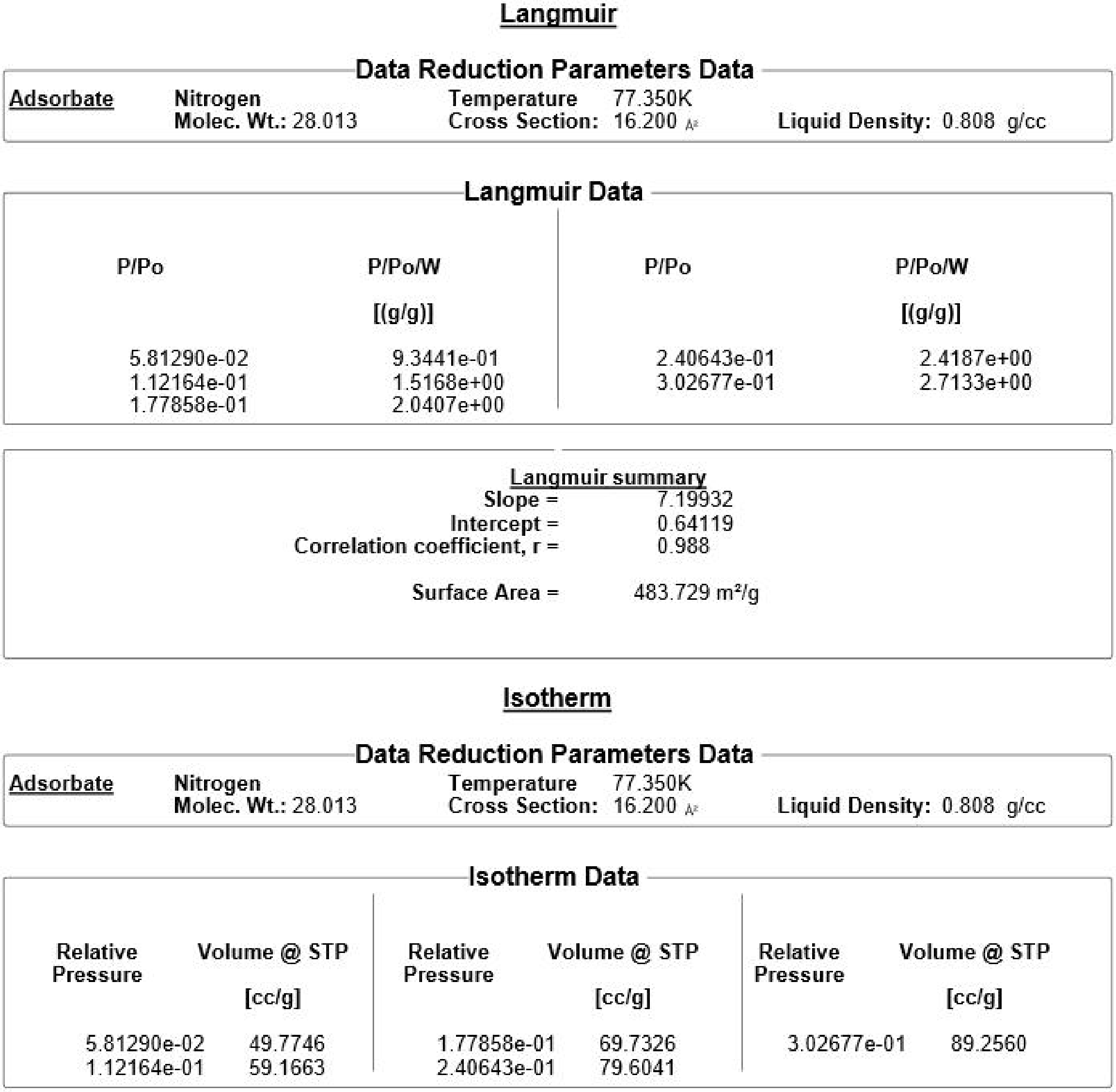
APPENDIX

Table 4.7 The Langmuir Method



Langmuir

Data Reduction Parameters Data

Adsorbate **Nitrogen**
Molec. Wt.: 28.013
Temperature 77.350K
Cross Section: 16.200 Å^2
Liquid Density: 0.808 g/cc

Langmuir Data

P/Po	P/Po/W [(g/g)]	P/Po	P/Po/W [(g/g)]
5.81290e-02	9.3441e-01	2.40643e-01	2.4187e+00
1.12164e-01	1.5168e+00	3.02677e-01	2.7133e+00
1.77858e-01	2.0407e+00		

Langmuir summary
Slope = 7.19932
Intercept = 0.64119
Correlation coefficient, r = 0.988

Surface Area = 483.729 m^2/g

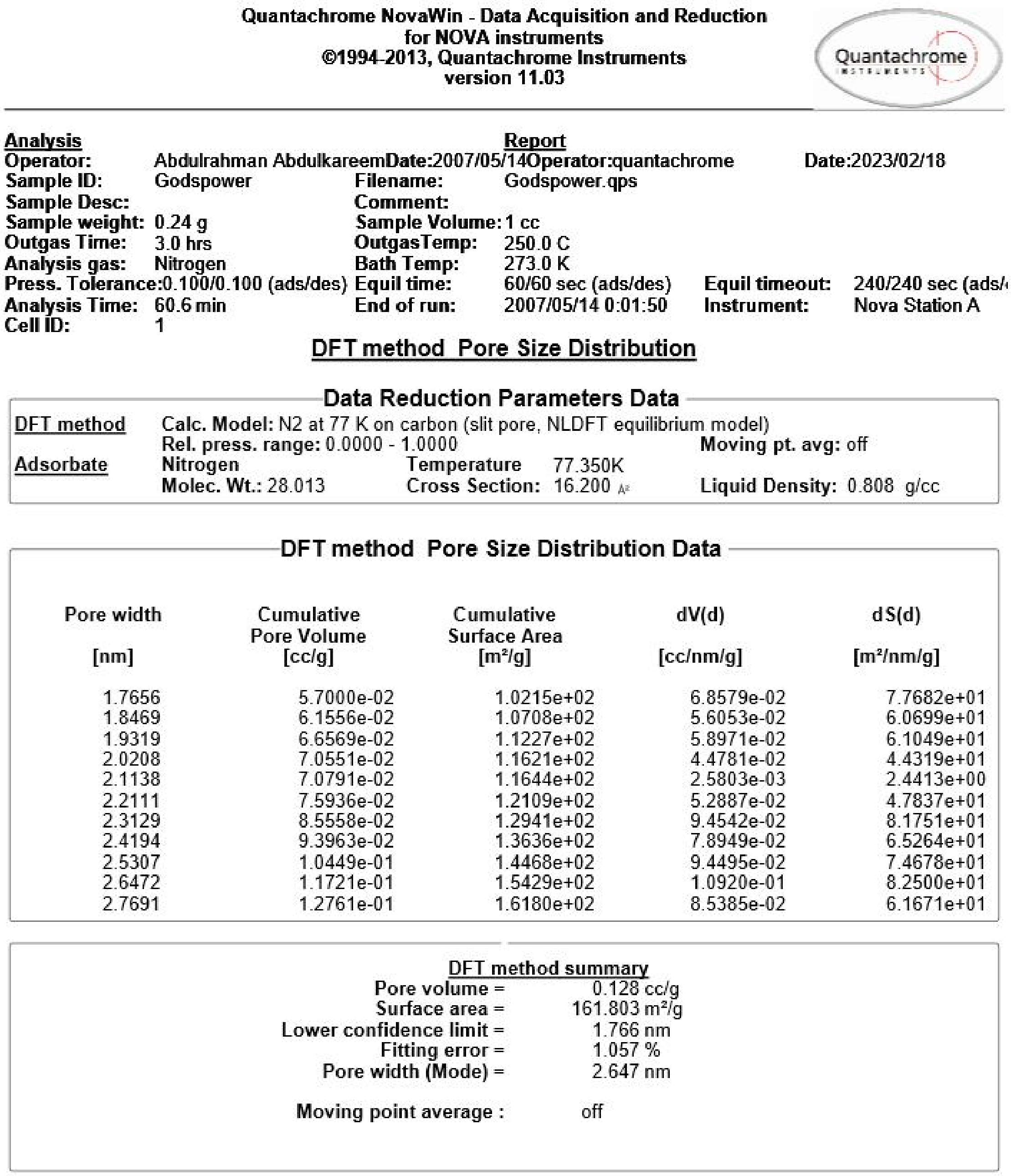
Isotherm

Data Reduction Parameters Data

Adsorbate **Nitrogen**
Molec. Wt.: 28.013
Temperature 77.350K
Cross Section: 16.200 Å^2
Liquid Density: 0.808 g/cc

Isotherm Data

Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]
5.81290e-02	49.7746	1.77858e-01	69.7326	3.02677e-01	89.2560
1.12164e-01	59.1663	2.40643e-01	79.6041		



Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
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version 11.03

Analysis **Report**
Operator: Abdulrahman Abdulkareem**Date:**2007/05/14**Operator:**quantachrome **Date:**2023/02/18
Sample ID: Godspower **Filename:** Godspower.qps
Sample Desc: **Comment:**
Sample weight: 0.24 g **Sample Volume:** 1 cc
Outgas Time: 3.0 hrs **OutgasTemp:** 250.0 C
Analysis gas: Nitrogen **Bath Temp:** 273.0 K
Press. Tolerance:0.100/0.100 (ads/des) **Equil time:** 60/60 sec (ads/des) **Equil timeout:** 240/240 sec (ads/
Analysis Time: 60.6 min **End of run:** 2007/05/14 0:01:50 **Instrument:** Nova Station A
Cell ID: 1

DFT method Pore Size Distribution

Data Reduction Parameters Data

DFT method **Calc. Model:** N2 at 77 K on carbon (slit pore, NLDFT equilibrium model)
Rel. press. range: 0.0000 - 1.0000 **Moving pt. avg:** off
Adsorbate Nitrogen **Temperature** 77.350K
Molec. Wt.: 28.013 **Cross Section:** 16.200 Å² **Liquid Density:** 0.808 g/cc

DFT method Pore Size Distribution Data

Pore width [nm]	Cumulative Pore Volume [cc/g]	Cumulative Surface Area [m²/g]	dV(d) [cc/nm/g]	dS(d) [m²/nm/g]
1.7656	5.7000e-02	1.0215e+02	6.8579e-02	7.7682e+01
1.8469	6.1556e-02	1.0708e+02	5.6053e-02	6.0699e+01
1.9319	6.6569e-02	1.1227e+02	5.8971e-02	6.1049e+01
2.0208	7.0551e-02	1.1621e+02	4.4781e-02	4.4319e+01
2.1138	7.0791e-02	1.1644e+02	2.5803e-03	2.4413e+00
2.2111	7.5936e-02	1.2109e+02	5.2887e-02	4.7837e+01
2.3129	8.5558e-02	1.2941e+02	9.4542e-02	8.1751e+01
2.4194	9.3963e-02	1.3636e+02	7.8949e-02	6.5264e+01
2.5307	1.0449e-01	1.4468e+02	9.4495e-02	7.4678e+01
2.6472	1.1721e-01	1.5429e+02	1.0920e-01	8.2500e+01
2.7691	1.2761e-01	1.6180e+02	8.5385e-02	6.1671e+01

DFT method summary

Pore volume = 0.128 cc/g
Surface area = 161.803 m²/g
Lower confidence limit = 1.766 nm
Fitting error = 1.057 %
Pore width (Mode) = 2.647 nm

Moving point average : off

Table 4.8 The DR Method of BET Analysis

Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
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Analysis			**Report**		
Operator:	Abdulrahman Abdulkareem**Date:**2007/05/14		**Operator:**quantachrome		**Date:**2023/02/18
Sample ID:	Godspower	**Filename:**	Godspower.qps		
Sample Desc:		**Comment:**			
Sample weight:	0.24 g	**Sample Volume:**	1 cc		
Outgas Time:	3.0 hrs	**OutgasTemp:**	250.0 C		
Analysis gas:	Nitrogen	**Bath Temp:**	273.0 K		
Press. Tolerance:	0.100/0.100 (ads/des)	**Equil time:**	60/60 sec (ads/des)	**Equil timeout:**	240/240 sec (ads/
Analysis Time:	60.6 min	**End of run:**	2007/05/14 0:01:50	**Instrument:**	Nova Station A
Cell ID:	1				

DR method

Data Reduction Parameters Data

DR method	**Affinity coefficient (ß):** 0.3300				
Adsorbate	**Nitrogen**	**Temperature**	77.350K		
	Molec. Wt.: 28.013	**Cross Section:**	16.200 Å^2	**Liquid Density:**	0.808 g/cc
	Critical Temp.: 126.200 K	**Critical Press.:**	33.500 atm	**SuperCritic. K.:**	1.000
Adsorbent	Carbon				
	DR. Exp (n): 2.000				

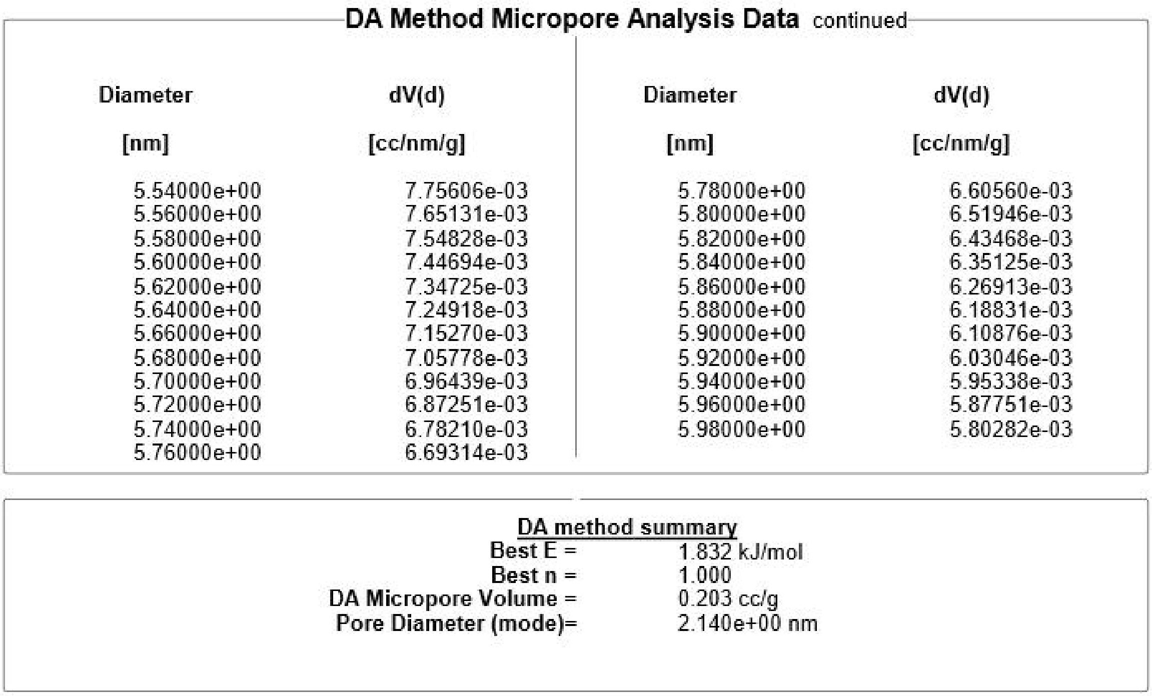
DR method Data

Log2(P/Po)	Weight Adsorbed [(g)]	Log2(P/Po)	Weight Adsorbed [(g)]
1.526725e+00	1.4930e-02	3.826991e-01	2.3878e-02
9.027784e-01	1.7747e-02	2.693824e-01	2.6773e-02
5.623899e-01	2.0917e-02		

DR method summary

Slope = -1.935e-01
Intercept = 2.824e-02
Correlation Coefficient = 0.9703

Average Pore width = 3.866nm
Adsorption energy = 6.725 kJ/mol
Micropore volume = 0.146 cc/g
Micropore surface area = 409.792 m^2/g



DA Method Micropore Analysis Data continued

Diameter [nm]	dV(d) [cc/nm/g]	Diameter [nm]	dV(d) [cc/nm/g]
5.54000e+00	7.75606e-03	5.78000e+00	6.60560e-03
5.56000e+00	7.65131e-03	5.80000e+00	6.51946e-03
5.58000e+00	7.54828e-03	5.82000e+00	6.43468e-03
5.60000e+00	7.44694e-03	5.84000e+00	6.35125e-03
5.62000e+00	7.34725e-03	5.86000e+00	6.26913e-03
5.64000e+00	7.24918e-03	5.88000e+00	6.18831e-03
5.66000e+00	7.15270e-03	5.90000e+00	6.10876e-03
5.68000e+00	7.05778e-03	5.92000e+00	6.03046e-03
5.70000e+00	6.96439e-03	5.94000e+00	5.95338e-03
5.72000e+00	6.87251e-03	5.96000e+00	5.87751e-03
5.74000e+00	6.78210e-03	5.98000e+00	5.80282e-03
5.76000e+00	6.69314e-03		

DA method summary

Best E =	1.832 kJ/mol
Best n =	1.000
DA Micropore Volume =	0.203 cc/g
Pore Diameter (mode)=	2.140e+00 nm