A LEGACY OF LEADERSHIP: A SPECIAL ISSUE HONOURING THE TENURE OF OUR VICE CHANCELLOR,
PROFESSOR ARMAYA'U HAMISU BICHI, *OON, FASN, FFS, FNSAP*

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KAOLINITE CLAY AS GREEN AND SUSTAINABLE RAW MATERIAL FOR ZEOLITES PRODUCTION: A REVIEW

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ABSTRACT

This review explored the potential of kaolinite clay as a green and sustainable raw material for the production of zeolites. Clay is a naturally abundant and inexpensive mineral, with unique properties that make it an ideal precursor for zeolite synthesis. The review discussed the properties and applications of clay minerals, as well as the preparations and applications of metakaolin, the thermally activated form of kaolinite clay. Furthermore, the review delved into the properties, structures, types, and methods of preparation of zeolites from metakaolin. Applications of zeolites in various fields, including catalysis, adsorption, and environmental remediation were highlighted. Moreover, the various characterization methods for zeolites including X-ray diffraction, scanning electron microscopy, X-ray fluorescence (XRF) and nitrogen adsorption-desorption analysis were also discussed. Obviously, the review have provided a comprehensive understanding of the potential of kaolinite clay as a sustainable raw material for zeolite production. Findings of the study will not only advance the understanding of zeolite production from kaolinite clay, but will also promote their industrial applications.

Keywords: Applications, Characterization, Clay minerals, Kaolinite clay, Zeolites

INTRODUCTION

Clay minerals are group of hydrous aluminum silicates which play a vital role in various natural processes and industrial applications. Formed primarily by the weathering of igneous and metamorphic rocks, clay minerals are characterized by their fine particle size, plate-like morphology, and layered structure (Ajibola *et al.* 2018). Their unique physical and chemical properties, such as high surface area, cation exchange capacity, and plasticity, make them essential components in soil formation, environmental interactions, and material science. Understanding clay minerals is crucial for a wide range of fields, including geology, agriculture, and engineering (Augustyn, 2020).

The primary types of clay minerals include kaolinite, illite, and smectite, each with distinct structural characteristics and properties. Kaolinite, a 1:1 layer silicate, consists of alternating silica tetrahedral and alumina octahedral. Its low plasticity and non-swelling behavior make it particularly valuable in ceramics and paper production (Augustyn, 2020). Illite, on the other hand, is a 2:1 layer silicate that exhibits moderate cation exchange capacity and is commonly found in sedimentary environments (Sutherland, 2014). Smectite, another 2:1 layer silicate, is known for its significant swelling capacity and high cation exchange capacity, making it useful in applications such as drilling fluids and environmental remediation (Murray, 2020).

The properties of clay minerals significantly influence their behavior in various contexts. Their cation exchange capacity (CEC) determines their ability to retain and exchange essential nutrients, which is critical for soil fertility and plant growth (Yue *et al.*, 2018; He *et al.*, 2021). Additionally, the plasticity of clay minerals affects their usability in construction and ceramics. The adsorption properties of these minerals allow their interaction with different ions and molecules, making them effective in environmental applications for contaminant removal and soil stabilization (Murray, 2006).

In recent years, the applicability of clay minerals has extended to the production of zeolites, which are important materials in ion exchange processes and catalysis. Clay minerals, especially kaolinite, serve as precursors for zeolite synthesis due to their silica and alumina content. Transformation of clay minerals into zeolites involves processes for instance calcination and alkaline activation, followed by hydrothermal crystallization (Lam & Rivera, 2006). This conversion not only highlights the versatility of clay minerals but also underscores their importance in developing sustainable materials and technologies.

Structure and composition of clay minerals

Clay minerals are vital component of the earth that play a crucial role in numerous geological and environmental processes. They are largely classified into two types based on their structural arrangement: 1:1 layer silicates and 2:1 layer silicates. The 1:1 layer silicates, such as kaolinite, comprise a single tetrahedral silica layer bonded to one octahedral alumina layer. This simple arrangement offers low plasticity and minimal swelling, making the kaolinite suitable for uses in ceramics, paper, and as a filler in various products (Wu *et al.,* 2020). In contrast, the 2:1 layer silicates including smectite and illite have two tetrahedral layers surrounding a central octahedral layer. This configuration promotes a more complex arrangement that enhances their cation exchange capacity (CEC) and swelling properties, making them particularly valuable in agriculture and environmental applications (Wu *et al.*, 2020).

The composition of clay minerals is primarily made up of silica (SiO_2), alumina (Al_2O_3), and water (H_2O), along with various metal oxides and hydroxides. The presence of isomorphic substitution within the tetrahedral and octahedral layers leads to charge imbalances, which are compensated by cations such as sodium, potassium, and calcium. This characteristic significantly influences the reactivity of clay minerals, allowing them to retain and exchange nutrients in soil, thus enhancing soil fertility (Mignoni *et al.*, 2008; Mohamed *et al.*, 2008; Reed & Breck, 1956). Furthermore, the ability of clay minerals to absorb water between their layers contributes to their swelling behavior, which can impact soil structure and stability in various environmental contexts (Wu *et al.*, 2020).

Understanding the structure and composition of clay minerals is essential for harnessing their properties in numerous applications. In environmental remediation, for instance, clay minerals can adsorb pollutants and heavy metals, playing a critical role in soil and water purification (Kodama, 2020). Additionally, their layered structure allows for the intercalation of various ions and molecules, enabling the development of advanced materials like zeolites, which are used in catalysis and gas separation (Ugochukwu, 2019). As research continues to explore the diverse functionalities of clay minerals, their significance in both natural ecosystems and engineered solutions becomes increasingly apparent, highlighting their importance in sustainable development and environmental management.

Tetrahedral sheet

The primary atom that dominates the structure of the tetrahedral sheet is present in the form of a silicon cation, specifically Si^{4+}. This tetrahedral sheet serves as a fundamental building block and consists of a single silicon atom that is encircled by four oxygen atoms, collectively referred to as silica tetrahedral. The formation of the tetrahedral sheet occurs through the sharing of three oxygen atoms from each tetrahedron with three adjacent tetrahedral (Verbung & Baveye, 2014).

These shared oxygen atoms are termed basal oxygen atoms, and they play a crucial role in connecting pairs of tetrahedral, effectively arranging them in a planar configuration (Figure 1). In contrast, the fourth oxygen atom remains unshared and forms bonds with other polyhedral elements, which are identified as apical oxygen atoms. The apical oxygen atoms are situated in a distinct plane, creating a link between the tetrahedral sheet and the octahedral sheet, as referenced in source. Notably, since there is only one apical oxygen atom associated with each tetrahedron, each tetrahedron is able to share a corner with an octahedron within the octahedral sheet (Verbung & Baveye, 2014). Furthermore, the tetrahedral sheet exhibits a negative charge, which arises from the process of isomorphic substitution. In this process, aluminum ions (Al^{3+}) substitute for some silicon ions (Si^{4+}), leading to a deficiency in positive charge within the tetrahedral sheet. The most common cations found in this tetrahedral structure include Si^{4+}, Al^{3+}, and Fe^{3+}.

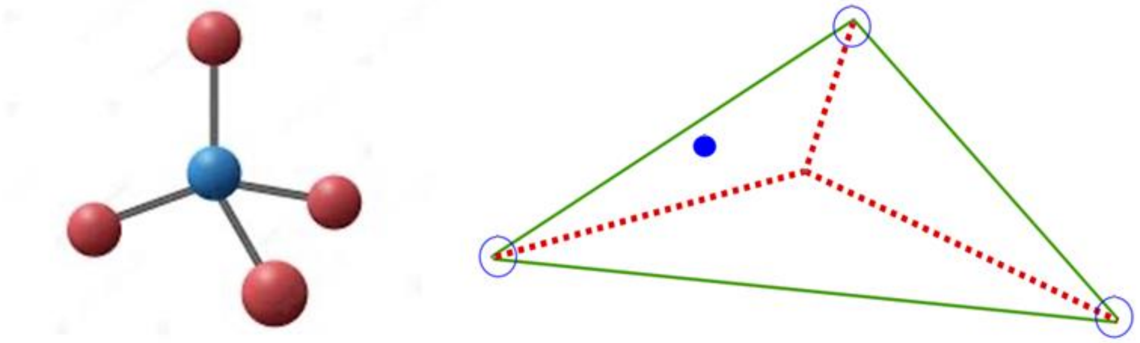

Figure 1: Tetrahedral arrangement of atoms

Octahedral sheet

The atoms that play most essential role in the structure of octahedral sheets are predominantly aluminum ions (Al^{3+}) and magnesium ions (Mg^{2+}). These ions are coordinated by six oxygen atoms or hydroxyl groups, which together form a geometric configuration called an octahedron, characterized by an eight-sided shape (Figure 2). It is necessary to understand that octahedral sheets can manifest in two different structural forms namely dioctahedral sheets and trioctahedral sheets (Karpinski & Szkodo, 2015).

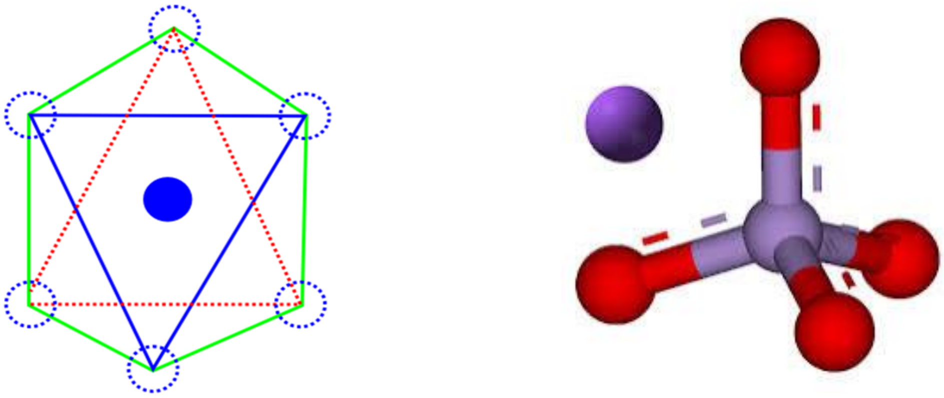

Figure 2: Octahedral arrangement of atoms

When aluminum carrying a charge of three positive valences is incorporated into the octahedral sheet, it is observed that only two-thirds of the available sites within this structure are filled. This partial occupancy is significant because it allows for the balancing of electrical charges throughout the sheet, which finally leads to the formation of what is referred to as a dioctahedral sheet. Conversely, when magnesium, which possesses two positive charges valences, is present in the structure, all three positions within the octahedral structure are fully occupied. This complete filling is required to maintain charge balance, resulting in the creation of a trioctahedral sheet (Ogunniyi & Adeyemi, 2020).

Thus, in the context of the dioctahedral sheet, Al^{3+} functions as the main dominating atom. Formula of the unit cell for this configuration is represented as $Al_2(OH)_6$. This formula is abbreviated to its stoichiometric equivalent, $Al(OH)_3$, which specifies two aluminum ions are coordinated with a total of six oxygen or hydroxyl ions.

In the case of the trioctahedral sheet, the main dominating atom is Mg^{2+}. Here, three magnesium ions are coordinated with six oxygen or hydroxyl ions. The unit cell formula for this structural arrangement is expressed as $Mg_3(OH)_6$, which can also be written as $Mg(OH)_2$ (Ogunniyi & Adeyemi, 2020). Noteworthy minerals that are associated with these octahedral structures include gibbsite or hydrargillite, which is a specific type of hydrous aluminum oxide represented by the formula $Al_2(OH)_6$ or $Al_2O_3•3H_2O$, and brucite, which is recognized as the hydrous oxide of magnesium and is represented by the formula $Mg(OH)_2$. These minerals are frequently discussed in academic literature concerning clay chemistry, mineralogy, and structural analysis. The formation of the octahedral sheet is achieved through the sharing of two oxygen atoms from each individual octahedron as various octahedral are linked together horizontally (Ogunniyi & Adeyemi, 2020).

Crystal structure

The crystal structure of clay minerals is primarily characterized by their layered arrangement, which significantly influences their physical and chemical properties. Clay minerals belong to the phyllosilicate group and are composed of alternating tetrahedral and octahedral sheets (Cherif *et al.*, 2018). The tetrahedral sheets consist of silicon-oxygen tetrahedra, while the octahedral sheets are typically formed from aluminum or magnesium cations coordinated by oxygen or hydroxyl groups. This unique structure creates a two-dimensional sheet-like formation that is essential for understanding the behavior of clay minerals in various environments (Cherif *et al.*, 2018).

Different types of clay minerals can be categorized based on their structural characteristics. For instance, kaolinite is a 1:1 clay mineral, comprising one tetrahedral layer and one octahedral layer per unit cell, with hydrogen bonds providing stability (Orodu, 2017). In contrast, illite is classified as a 2:1 clay mineral, consisting of two tetrahedral layers and one octahedral layer, with potassium ions occupying the interlayer space, enhancing its structural integrity. Montmorillonite, another 2:1 clay mineral, is notable for its expandable layers that can accommodate water and cations, resulting in significant swelling and plasticity, which are advantageous for various applications (Aroke *et al.*, 2013).

The interlayer space between the sheets of clay minerals is crucial in determining their properties, as it can host water molecules, cations, and other small molecules. This ability to expand or contract in response to moisture is particularly important in agriculture and construction, where moisture retention and stability are essential (Orodu, 2017). The crystal symmetry of clay minerals typically falls within monoclinic or triclinic systems, and the unit cell parameters are vital for understanding their characteristics. The unique properties derived from the crystal structure of clay minerals make them invaluable in numerous applications, including enhancing soil fertility, improving water retention, and serving as key components in environmental engineering for waste containment (Maigari *et al.*, 2015).

Mineral structure

The structure of clay minerals is characterized by a unique layered arrangement that significantly influences their physical and chemical properties. Clay minerals belong to the phyllosilicate group, which features alternating tetrahedral and octahedral sheets. In the tetrahedral sheets, silicon ions (Si^{4+}) are surrounded by four oxygen ions (O^{2-}), forming a tetrahedral geometry (Mokwa *et al.*, 2019). These tetrahedral are arranged in a two-dimensional plane, sharing oxygen atoms with adjacent tetrahedral. The octahedral sheets comprise of metal cations, for example aluminum (Al^{3+}) or magnesium (Mg^{2+}), coordinated via six oxygen or hydroxyl (OH) groups, forming the octahedral structure. The tetrahedral and octahedral sheets combination together forms the basic building blocks of clay minerals (Ammann, 2003).

Clay minerals are classified into two primary categories based on their layer structures, which are 1:1 and 2:1 clay minerals. The 1:1 clay minerals including the kaolinite, comprise of one tetrahedral sheet bonded to one octahedral sheet (Mokwa *et al.,* 2019). This configuration results in strong hydrogen bonding between layers, contributing to kaolinite's stability and low expansion capacity. In contrast, 2:1 clay minerals, like illite and montmorillonite, consist of two tetrahedral sheets surrounding one octahedral sheet. This arrangement allows for greater flexibility and expansion, particularly in montmorillonite, which can absorb water and cations between its layers, leading to significant swelling and varying plasticity. These structural differences play a crucial role in determining the minerals' reactivity and usability in various applications (Maigari *et al.*, 2015).

The interlayer space between the sheets of clay minerals is critical for their properties, as it can accommodate water molecules and cations, which influence the mineral's behavior in different environments. The ability of clay minerals to expand or contract in response to moisture is particularly important in fields such as agriculture, construction, and environmental engineering (Aroke *et al.*, 2013). Additionally, the crystal symmetry of clay minerals typically falls within monoclinic or triclinic systems, with variations in unit cell dimensions affecting their physical characteristics, such as plasticity, adsorption capacity, and thermal stability. Overall, the mineral structure of clay minerals is fundamental to their diverse applications and interactions in both natural and engineered systems (Aroke *et al.,* 2013).

Characteristics of clay minerals

Clay minerals are unambiguous due to their special characteristics (Christopher *et al.,* 2012). Therefore, some of the clay mineral characteristics which are well defined have been reported.

Layered structure

Clay minerals are primarily composed of silicate sheets arranged in a layered structure, which is pivotal to their unique properties. These sheets are formed from two types of tetrahedral and octahedral arrangements. In the tetrahedral sheet, silicon (Si^{4+}) atoms are surrounded by four oxygen (O^{2-}) atoms, creating a tetrahedron shape (Olaremu, 2021). This tetrahedral sheet can bond with an octahedral sheet, which comprises metal cations commonly aluminum (Al^{3+}) or magnesium (Mg^{2+}) coordinated by six oxygen or hydroxyl (OH) groups, forming an octahedron. The bonding between these sheets can be either strong covalent bonds or weaker van der Waals forces, depending on the type of clay mineral

(Olaremu, 2021).The arrangement of these sheets determines whether the mineral is classified as a 1:1 type (like kaolinite, which has one tetrahedral and one octahedral sheet) or a 2:1 type (like montmorillonite, which has two tetrahedral sheets surrounding one octahedral sheet). This layered structure is crucial for understanding the physical and chemical behavior of clay minerals, influencing their thermal properties, mechanical strength, and interactions with other substances (Olaremu, 2021).

Plasticity and workability

Plasticity is a defining characteristic of many clay minerals, particularly when mixed with water. The water molecules penetrate the interlayer spaces, reducing friction between the layers and allowing them to slide over one another (Ogunniyi & Adeyemi 2020). This property is essential for various applications, such as ceramics, where the ability to mold and shape the material is critical. The degree of plasticity varies among different clay types; for instance, montmorillonite exhibits high plasticity and can be deformed extensively without breaking, making it ideal for applications like drilling muds and sealants (Ogunniyi & Adeyemi 2020). Conversely, kaolinite has lower plasticity, which limits its use in certain applications. The workability of clay also depends on factors such as moisture content, particle size, and mineral composition, making it necessary to tailor processing methods for specific uses in pottery, construction, and other industries (Ogunniyi & Adeyemi 2020).

Cation exchange capacity (CEC)

Cation exchange capacity is a key property of clay minerals, reflecting their ability to attract and hold positively charged ions (cations) on their surface (Gebremariam & Marchetti 2018). This property is crucial for soil fertility, as it enables clay minerals to retain essential nutrients like calcium, magnesium, potassium, and sodium, which are vital for plant growth. The CEC of clay minerals can vary widely; for example, smectites have a high CEC due to their large surface area and the presence of exchangeable cations in their interlayer spaces (Gebremariam & Marchetti 2018). This high CEC allows smectites to improve soil structure, enhance nutrient retention, and influence soil pH. Understanding CEC is vital for agricultural practices, as it affects fertilization strategies and soil management. Additionally, CEC plays a significant role in environmental contexts, such as the immobilization of heavy metals and contaminants in soils (Gebremariam & Marchetti 2018).

Swelling and shrinkage

Certain clay minerals, particularly smectites like montmorillonite, exhibit significant swelling when they absorb water between their layers. This phenomenon occurs because water molecules infiltrate the interlayer spaces, causing the layers to expand and increase in volume (Olaremu, 2021). This swelling can be several times the original volume of the dry clay, making it useful in applications such as drilling fluids, where it helps to stabilize boreholes. However, this property also poses challenges; when the clay dries, it can shrink dramatically, leading to the formation of cracks and potential instability in structures built on or with these materials (Olaremu, 2021). Understanding the swelling and shrinkage behavior of clay minerals is crucial in geotechnical engineering, where soil movement can impact foundations, roads, and earth structures. Engineers must consider these properties when designing structures to mitigate potential damage (Olaremu, 2021).

Adsorption properties

Clay minerals possess a high surface area and a complex surface chemistry, enabling them to adsorb a wide variety of substances, including water, nutrients, organic compounds, and pollutants. The adsorption capacity is influenced by several factors, including the mineral's charge, surface area, and the nature of the adsorbate (Aroke *et al.,* 2013). For example, clays can effectively capture heavy metals, pesticides, and other contaminants, making them valuable in environmental remediation efforts (Aroke *et al.,* 2013). The ability to retain moisture and nutrients enhances agricultural productivity by improving soil quality and water retention. Additionally, clays are often used in water treatment processes, where they help remove impurities and clarify water. The adsorption properties of clay minerals are also critical in industrial applications, such as catalysis, where they can facilitate chemical reactions by providing a surface for reactants to interact (Aroke *et al.,* 2013).

Thermal stability

The thermal stability of clay minerals varies widely, impacting their behavior in high-temperature applications. Some clay minerals, like kaolinite, are highly thermally stable and can withstand elevated temperatures without undergoing significant structural changes (Melo *et al.,* 2019). This stability makes kaolinite suitable for use in ceramics and refractory materials, where high-temperature resistance is essential. In contrast, smectites like montmorillonite may lose water and undergo structural transformations when subjected to high temperatures, affecting their physical properties (Melo *et al.,* 2019). Understanding the thermal stability of clay minerals is crucial for industries that rely on firing processes, such as ceramics, bricks, and tiles. Additionally, thermal stability is important in environmental contexts, where the behavior of clay minerals at elevated temperatures can influence soil stability and contaminant behavior (Melo *et al.,* 2019).

Color and appearance

Clay minerals can exhibit a diverse range of colors, influenced by their mineral composition and the presence of impurities. For example, iron oxides can impart reddish or yellowish hues, while pure kaolinite is typically white (Deniz, 2015; Melo *et al.,* 2019). The color of clay minerals can affect their aesthetic qualities in ceramics and pottery, influencing consumer preferences and marketability. Additionally, color can serve as an indicator of certain properties, such as the mineral’s oxidation state or the presence of specific elements (Deniz, 2015). In geological contexts, the color of clay can provide insights into the environment of formation and the processes that have affected the mineral over time. Understanding the color and appearance of clay minerals is essential for both artistic applications and scientific investigations (Melo *et al.,* 2019).

Types of clay minerals

Kaolinite

Kaolinite is a 1:1 clay mineral, consisting of one tetrahedral sheet and one octahedral sheet, with the chemical formula $Al_2Si_2O_5(OH)_4$. This mineral typically forms through the weathering of feldspar and other silicate minerals in acidic conditions, often found in sedimentary environments (Deniz, 2015). Kaolinite is characterized by its white or pale yellow color, low plasticity, and fine particle size. It exhibits thermal stability, retaining its structure at high temperatures, making it ideal for ceramic applications. In terms of uses, kaolinite is widely utilized in ceramics and pottery, contributing to the production of porcelain and stoneware due to its fine texture and whiteness (Deniz, 2015). Additionally, it serves as a filler in paper production, enhancing brightness and opacity, and is also found in cosmetics, where its absorbent properties are beneficial for skin care products.

Smectite

Smectites are 2:1 clay minerals characterized by two tetrahedral sheets surrounding one octahedral sheet, with a general formula of $(Na,Ca)_5(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$. These minerals typically form from the alteration of volcanic ash and are commonly found in sedimentary environments (Maigari *et al.,* 2015). A distinctive feature of smectites is their high swelling capacity; they can absorb significant amounts of water between their layers, leading to expansion several times their original volume (Maigari *et al.,* 2015). This property, combined with a very high cation exchange capacity (CEC), allows smectites to retain nutrients effectively. The high plasticity of smectites makes them easily moldable, making them suitable for various applications. In industry, smectites are used in drilling fluids for oil and gas extraction to stabilize boreholes and cool drill bits. They also serve as effective sealants to prevent water seepage in landfills and ponds, and their absorbent nature makes them a popular choice for cat litter (Maigari *et al.,* 2015).

Illite

Illite is a 2:1 clay mineral that shares similarities with smectite but contains potassium ions (K^+) in its interlayer structure, which restricts swelling. Its formula is $KAl_2(AlSi_3O_{10})(OH)_2 \cdot nH_2O$. Illite typically forms from the weathering of feldspar and other minerals in soils, particularly in temperate climates (Bahgaat *et al.,* 2019). This mineral exhibits moderate swelling properties, less than smectites but more than kaolinite, and has a moderate cation exchange capacity (CEC), allowing for some nutrient retention (Deniz, 2015). Illite is often gray, brown, or greenish in color, reflecting its mineral content. In agriculture, illite plays a crucial role in soil fertility, helping to retain moisture and nutrients. Additionally, it is used in various industrial applications, including ceramics and as a filler in paints and plastics, where its properties contribute to product performance (Bahgaat *et al.,* 2019).

Chlorite

Chlorite minerals are generally classified as 2:1:1 type, consisting of two tetrahedral sheets, one octahedral sheet, and an additional octahedral layer. Their general formula is $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$ (Abdulkareem & Ojo, 2022). Chlorites typically form in metamorphic environments and are often associated with other minerals like biotite and garnet. These minerals are characterized by their green color, which is often due to iron content, and they generally exhibit non-expanding properties, making them stable and useful in construction (Abdulkareem & Ojo, 2022; Deniz, 2015). Chlorites have a lower cation exchange capacity (CEC) compared to smectites and illites, which limits their nutrient retention capabilities. In terms of uses, chlorites are commonly employed in the production of ceramics, tiles, and bricks, as well as in various industrial applications, including the manufacture of rubber and plastics (Deniz, 2015).

Vermiculite

Vermiculite is a 2:1 clay mineral known for its ability to expand significantly when heated. Its chemical formula is $(Mg,Fe)_3(AlSi_4O_{10})(OH)_2 \cdot 4H_2O$. Vermiculite typically forms from the weathering of biotite and other minerals, often in arid environments. One of its most remarkable properties is its high swelling capacity when heated, resulting in a lightweight, porous material that is highly useful in various applications (Abdulkareem & Ojo, 2022; Deniz, 2015; Olaremu, 2021). Vermiculite also possesses a very high cation exchange capacity (CEC), allowing it to effectively retain nutrients and moisture. In horticulture, vermiculite is commonly used as a soil amendment to improve aeration and moisture retention, promoting healthy plant growth. Additionally, its insulating properties make it valuable in building materials for thermal insulation, contributing to energy efficiency in construction (Deniz, 2015). Table 1 lists the different types of minerals found in clay.

Table 1: Types of clay minerals and their properties (Deniz, 2015)

Type	Structure	Swelling	Cation Exchange Capacity (CEC)	Common uses
Kaolinite	1:1	Non-expanding	Low	Ceramics, paper, fillers
Smectite	2:1	High	High	Drilling fluids, sealants, cat litter
Illite	2:1	Moderate	Moderate	Soil, agriculture, fillers
Chlorite	2:1:1	Non-expanding	Low	Ceramics, industrial applications
Vermiculite	2:1	High (when heated)	High	Soil amendment, insulation

Applications of clay minerals

Clay minerals are naturally occurring, fine-grained minerals that have various applications, demonstrating their importance both in industrial processes and consumer products. Their uses are highlighted in the following sections.

Ceramics and pottery

Clay minerals, particularly kaolinite and ball clay, are foundational to the ceramics industry, which encompasses a wide range of products from everyday tableware to high-tech ceramics used in electronics. Kaolinite, known for its fine particle size and purity, contributes to the whiteness and translucency of porcelain, making it highly sought after for premium ceramic products (Velde, 2020). The plasticity of these clays allows artisans and manufacturers to shape them into intricate designs, while their thermal stability ensures that finished products can withstand the high temperatures encountered during the firing process. This firing not only solidifies the structure but also enhances the strength and durability of the ceramics. Additionally, the ability of these clays to form strong bonds upon firing is crucial for producing items that can endure regular use, such as dishes and tiles (Velde, 2020). The versatility of clay in ceramics also extends to artistic applications, where sculptors utilize various clays for their unique textures and colors (Velde, 2020).

Paper production

In the paper industry, clay minerals like kaolinite, calcium carbonate, and talc are extensively used as fillers and coating pigments. These minerals significantly enhance the brightness, opacity, and smoothness of paper, which is essential for high-quality printing (Oke *et al.,* 2020). Kaolinite, in particular, is favored for its ability to improve the aesthetic qualities of paper, making it more appealing for magazines, brochures, and art prints. The fine particle size of kaolinite allows it to fill voids between cellulose fibers, resulting in a denser and more durable sheet (Oke *et al.,* 2020). Furthermore, the use of clay in coatings creates a smooth surface that enhances printability, ensuring that inks adhere well and produce vibrant colors. This not only improves the visual appeal of printed materials but also increases their resistance to wear and tear. The incorporation of clay in paper production can also contribute to sustainability efforts, as it can reduce the need for more expensive wood pulp and improve the overall cost-effectiveness of manufacturing processes (Oke *et al.,* 2020).

Agriculture

Clay minerals play a pivotal role in enhancing soil health and fertility, making them invaluable in agricultural practices. Minerals such as illite and vermiculite contribute to improved soil structure by promoting aeration and water retention, which are essential for healthy plant growth (Velde, 2020). Vermiculite has a high cation exchange capacity (CEC), allowing it to retain essential nutrients like potassium, magnesium, and calcium, making them available to plants over time. This nutrient retention is vital for sustaining crop yields and improving soil fertility, particularly in nutrient-poor soils (Velde, 2020). The addition of clay minerals can also help mitigate soil erosion and improve moisture retention, especially in arid regions, thereby enhancing agricultural productivity. Moreover, the use of clay minerals as soil amendments can improve soil pH and microbial activity, further promoting plant health and resilience against pests and diseases. As a result, farmers and agronomists often incorporate clay minerals into their soil management practices to enhance productivity and promote sustainable agricultural practices (Velde, 2020).

Construction and building materials

In the construction industry, clay minerals such as bentonite and kaolinite are widely utilized for various applications, from foundational materials to finishing products. Bentonite, with its unique swelling properties, is particularly valued for its ability to create impermeable barriers, making it ideal for sealing and waterproofing applications in landfills, ponds, and basements. Its use in drilling mud is crucial for stabilizing boreholes during construction and excavation, preventing collapses and ensuring safety (Oke *et al.,* 2020). Additionally, clay minerals are essential in the production of bricks, tiles, and other building materials. The plasticity of these clays allows for easy shaping and molding, while their thermal properties contribute to the durability and longevity of the finished products. Clay bricks and tiles provide excellent insulation, reducing heating and cooling costs in buildings and enhancing energy efficiency (Oke *et al.,* 2020; Velde, 2020). The aesthetic qualities of clay products, available in various colors and textures, make them popular choices for architectural design, contributing to both functionality and visual appeal in construction projects (Velde, 2020).

Pharmaceuticals

Certain clay minerals, including bentonite and halloysite, find applications in the pharmaceutical industry as excipients in drug formulations. Their unique properties can aid in drug delivery, stabilization, and controlled release of active ingredients (Babalola *et al.,* 2017). For example, halloysite's tubular structure allows for the encapsulation of drugs, enhancing their bioavailability and effectiveness while minimizing side effects. Bentonite is often used as a suspending agent in liquid formulations, ensuring that active ingredients remain evenly distributed and stable over time (Babalola *et al.,* 2017). These clays are appreciated for their biocompatibility and safety, making them appropriate for use in various medicinal applications, including topical treatments, oral medications, and carriers for medical drugs. The ability of clay minerals to improve the performance of pharmaceutical products underscores their significance in healthcare and medicine (Babalola *et al.,* 2017).

Kaolin

Kaolin, otherwise known as china clay, is a naturally occurring clay mineral largely composed of kaolinite, a layered silicate mineral. It is formed through the weathering and decomposition of feldspar-rich rocks, particularly granite, over millions of years. Renowned for its fine particle size, whiteness, and low shrink-swell capacity, kaolin has become a crucial raw material in various industries. Its unique properties make it highly sought after for applications ranging from ceramics and paper production to cosmetics and pharmaceuticals (Hakeem *et al.,* 2018).

The name is derived from the Chinese word "Kaoling," which denotes high-quality clay discovered in the Jingdezhen region, historically significant for porcelain production. The mineral's characteristics, such as its plasticity when wet and its ability to retain shape when fired, have made it indispensable in the creation of fine ceramics and pottery (Bahgaat *et al.* 2020; Ajibola *et al.,* 2018; Santander *et al.,* 2013). Besides its traditional uses, kaolin is increasingly recognized for its environmental benefits, such as its role in soil amendment and its applications in sustainable building materials. As industries continue to seek eco-friendly alternatives, kaolin’s versatility and natural origin position it as a valuable resource in the modern economy (Hakeem *et al.,* 2018). This introduction highlights the significance of kaolin in various sectors, showcasing its importance as both a functional and aesthetic material.

Structure and composition of kaolin

Mineral composition

The primary component of kaolin is the kaolinite, a clay mineral with the chemical formula $Al_2Si_2O_5(OH)_4$. Kaolinite mineral is formed through the weathering of feldspar-rich rocks, predominantly granite, in acidic conditions via a process of hydrolysis (Petrov & Michalev, 2012; Hakeem *et al.,* 2018; Ajibola *et al.,* 2018). During this process, feldspar breaks down releasing aluminum and silica which recombine to form kaolinite. Other than kaolinite, kaolin may contain other minerals such as illite and montmorillonite, which can influence its properties (Hakeem *et al.,* 2018). Illite, for example, has a similar layered structure but contains potassium ions between the layers, enhancing the plasticity of kaolin (Petrov & Michalev, 2012). Montmorillonite, known for its high swelling capacity, can also be present, affecting water retention and plasticity. Quartz, often found as a non-clay impurity, can influence the overall physical characteristics of kaolin, such as its density and flow properties (Petrov & Michalev, 2012).

Layered structure

The structure of kaolinite is characterized by its unique layered arrangement. Each unit of kaolinite consists of a tetrahedral layer of silica bonded to an octahedral layer of alumina. The tetrahedral layer is formed by silicon atoms coordinated with four oxygen atoms, creating a flat sheet (Ajibola *et al.,* 2018). In contrast, the octahedral layer consists of aluminum atoms surrounded by hydroxyl groups and oxygen, forming a second sheet. These two layers are held together primarily by hydrogen bonds, which are relatively weak, allowing the layers to slide over one another (Petrov & Michalev, 2012). This layered structure is essential for kaolin's plasticity; when water is added, the layers can separate and absorb moisture, making the clay moldable. The weak bonding also allows for easy shaping and reshaping, which is critical in ceramics and pottery production (Petrov & Michalev, 2012).

Crystal morphology

Kaolin typically exhibits a distinctive crystal morphology characterized by platy or flaky crystals. These thin, flat plates result from the layered structure and can vary in size, impacting the clay's properties (Pereira *et al.,* 2018). The platy morphology provides kaolin with a high surface area, which enhances its reactivity and effectiveness in various applications. The size of the kaolinite crystals can influence their brightness and plasticity; finer particles tend to have better workability and higher whiteness. Additionally, kaolin can aggregate into larger masses, which can affect its processing behavior (Pereira *et al.,* 2018). The degree of aggregation is important in industrial applications, as it influences flow properties during mixing and molding processes.

Metakaolin

Metakaolin is a highly reactive pozzolanic material produced through the calcination of kaolin clay, typically at temperatures ranging from 500 to 800 °C (Parthasarathy & Narayanan, 2014). This thermal treatment alters the crystalline structure of kaolinite, converting it into an amorphous form that significantly enhances its reactivity. The resulting metakaolin possesses a fine particle size and a high surface area, which are critical factors that contribute to its effectiveness as a supplementary cementitious material (Parthasarathy & Narayanan, 2014). The amorphous nature of metakaolin allows it to readily react with calcium hydroxide in the presence of water, forming additional calcium silicate hydrates. This reaction not only improves the mechanical properties of concrete but also enhances its durability and resistance to environmental factors (Parthasarathy & Narayanan, 2014).

The incorporation of metakaolin into concrete and cement formulations has gained popularity due to its numerous benefits (Maciver *et al.,* 2020). By replacing a portion of Portland cement with metakaolin, concrete can achieve higher compressive strength, reduced permeability, and improved resistance to chemical attacks, such as sulfates and chlorides (Maciver *et al.,* 2020). These properties make metakaolin particularly valuable in high-performance concrete applications, where structural integrity and longevity are paramount. Metakaolin helps mitigate issues related to efflorescence and enhances the aesthetic qualities of concrete by contributing to a smoother finish and improved color consistency (Maciver *et al.,* 2020).

Physical properties of metakaolin

Fine particle size

Metakaolin typically has a particle size ranging from 1 to 20 micrometers (Pereira *et al.,* 2018). This fine particle size significantly increases the surface area available for chemical reactions, allowing metakaolin to react more efficiently with calcium hydroxide in cementitious mixtures. The increased surface area not only enhances the pozzolanic activity but also contributes to improved workability, making it easier to mix and apply in construction applications (Pereira *et al.,* 2018).

Amorphous structure

The calcination process transforms the crystalline structure of kaolin clay into an amorphous form. This amorphous nature is crucial for metakaolin's pozzolanic activity, as it allows for more effective reactions with calcium hydroxide, leading to the formation of additional calcium silicate hydrates (Pereira *et al.,* 2018). These hydrates are essential for increasing the strength and durability of concrete, making metakaolin an important additive for high-performance concrete.

Low bulk density

Metakaolin has a lower bulk density compared to traditional Portland cement (Pereira *et al.,* 2018). This characteristic allows for the formulation of lighter concrete mixtures, which can be advantageous in construction where weight reduction is desired. Lighter concrete can lead to lower transportation costs and reduced structural load on foundations, making it an appealing option for various building application (Hakeem et al, 2018).

Excellent thermal stability

Metakaolin exhibits high thermal stability, meaning it maintains its performance characteristics even at elevated temperatures. This property is particularly beneficial in applications where concrete may be exposed to high heat, such as in industrial settings or fire-resistant structures (Hakeem *et al.,* 2018). The ability to withstand high temperatures without degrading ensures that metakaolin enhanced concrete remains reliable and effective under challenging conditions. Low shrinkage

One of the most important properties of metakaolin is its low shrinkage behavior. When incorporated into concrete, metakaolin helps minimize the risk of cracking that can occur as the material dries and cures (Hakeem *et al.,* 2018). This reduction in shrinkage not only enhances the aesthetic quality of the finished product but also contributes to the overall longevity and durability of concrete structures, making them more resilient to environmental stresses.

Chemical properties of metakaolin

Silica (SiO_2)

Metakaolin typically contains about 50-60% silica. This high silica content is crucial because silica forms the backbone of zeolite structures, contributing to their framework. The availability of silica during the synthesis process allows for the formation of various zeolitic structures, which can have different pore sizes and functionalities depending on the intended application (Karthik *et al.,* 2017).

Alumina (Al_2O_3)

Metakaolin usually contains around 30-40% alumina. The presence of alumina is vital as it influences the ion-exchange capacity of the zeolite, a key property that determines its effectiveness in applications such as catalysis, adsorption, and ion exchange processes. The Si/Al ratio can significantly affect the type of zeolite formed, impacting its stability and performance (Kadri *et al.,* 2011). Table 2 shows the results from different spectroscopic methods of determination of Si/Al ratio (Ma *et al.,* 2021).

Reactivity

The amorphous nature of metakaolin, resulting from its calcination, enhances its reactivity compared to crystalline kaolinite. This increased reactivity is essential during hydrothermal synthesis, where metakaolin can dissolve in alkaline solutions, releasing silica and alumina into the solution. This dissolution is a critical step in zeolite formation, allowing for the reorganization of these components into zeolitic frameworks. The reactivity can also be influenced by the temperature and duration of calcination, which can optimize the properties of the metakaolin for zeolite synthesis (Kadri *et al.*, 2011).

pH and alkalinity

The pH of the synthesis medium plays a significant role in the formation of zeolites from metakaolin. An alkaline environment, often achieved by adding sodium hydroxide (NaOH) or potassium hydroxide (KOH), is necessary to facilitate the dissolution of silica and alumina. The optimal pH range (typically between 10 and 14) promotes the hydrolysis of metakaolin and the subsequent precipitation of zeolite structures (Karthik *et al.*, 2017). The pH can also affect the morphology and crystallinity of the zeolites formed, influencing their practical applications. Effect of sodium hydroxide solution on synthesis of zeolites from pure kaolin is shown in Figure 3.

Table 2: Results of Si/Al ratios from different spectroscopic methods (Ma *et al.*, 2021)

No.	Zeolites	Framework code	Wavenumber (cm^{-1})	Si/A1 ratio		
				IR[a]	ICP-OES	XRF
1.	K-F	EDI	973	0.98	1.26	1.02
2.	Cs-ABW	ABW	985	1.53	1.03	1.13
3.	Na-EMT	EMT	980	1.30	1.16	1.18
4.	K-W	MER	992	1.85	2.30	2.19
5.	K-L	LTL	1023	3.27	3.20	2.93
6.	K-J	LTJ	987	1.62	1.86	1.77
7.	Na-Mordenite	MOR	1059	4.92	4.93	4.88
8.	Na-X	FAU	977	1.16	1.16	1.18
9.	Na-Y	FAU	996	2.03	1.98	2.13
10.	Na-EMC-2	EMT	1035	3.82	3.76	3.71
11.	Hydroxysodalite	SOD	983	1.44	1.10	1.14
12.	Na-A	LTA	952	0.02	1.04	0.98
13.	Heulandite	HEU	1026	3.41	3.50	3.48
14.	Brewsterite	BRE	1012	2.77	3.00	2.91
15.	Na-LSX	FAU	973	0.98	0.98	1.03
16.	Offretite	OFF	1037	3.91	3.89	3.76
17.	Na-P	GIS	983	1.44	1.35	1.44
18.	Na-BEA	*BEA	1083	6.02	15.1	15.0
19.	Na-ZSM-5	MFI	1088	6.25	13.5	12.2

Thermal stability

Metakaolin is stable at elevated temperatures, which is advantageous during the synthesis process. Its thermal stability ensures that the structural integrity of the metakaolin is maintained while allowing for the necessary heat treatment to promote zeolite crystallization (Karthik *et al.*, 2017; Hakeem *et al.*, 2018). The ability to withstand high temperatures without significant degradation is crucial for processes that involve prolonged heating, such as hydrothermal synthesis. This stability also allows for the potential reuse of metakaolin in multiple synthesis cycles, enhancing its economic viability (Karthik *et al.*, 2017).

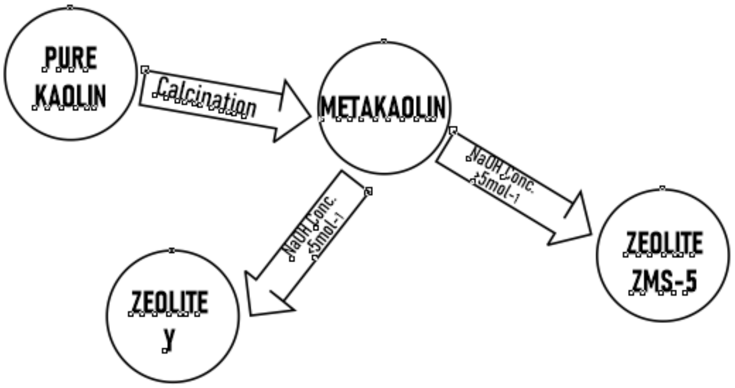

Figure 3: Effect of NaOH of concentration on pure kaolin and metakaolin

Surface area and porosity

The calcination of kaolinite to produce metakaolin increases its surface area, often exceeding 200 m²/g (Hakeem *et al.*, 2018). This high surface area provides more active sites for reactions during zeolite synthesis, promoting higher yields and better-quality zeolites. The porosity of metakaolin also increases, allowing for greater penetration of reactants during synthesis (Babalola *et al.*, 2017). The increased surface area and porosity can lead to enhanced adsorption properties in the final zeolite product, making them suitable for various industrial applications, such as water purification and gas separation (Babalola *et al.*, 2017).

Structural composition of metakaolin

Metakaolin is a dehydroxylated form of kaolinite and exhibits distinct structural characteristics that differentiate it from its precursor. Understanding its structural composition is key to appreciating its applications in various fields (Karthik *et al.,* 2017).

Amorphous structure

Metakaolin is primarily amorphous meaning it lacks a long-range ordered crystalline structure. This arises from the thermal treatment of kaolinite, where the crystalline lattice is disrupted during dehydroxylation (600 to 900 °C) (Hakeem et.al, 2018; Karthik *et al.,* 2017). The resulting amorphous structure provides a high surface area, enhancing reactivity and making it suitable for applications like pozzolanic reactions in cement (Karthik *et al.,* 2017).

Layered arrangement

Metakaolin does not retain the full layered structure of kaolinite, it is derived from the original 1:1 layer configuration of kaolinite, consisting of one tetrahedral silica layer and one octahedral alumina layer. During calcination, the layers lose hydroxyl groups and water, leading to a more disordered arrangement (Karthik *et al.,* 2017).

Particle morphology

Metakaolin consists of fine particles, typically ranging from a few micrometers to sub-micrometer sizes. This fine particle size increases the surface area available for chemical reactions and enhances the material's overall reactivity. The morphology of metakaolin particles can vary, with some exhibiting spherical shapes while others may appear more irregular (Karthik *et al.,* 2017). This variation can depend on the specific calcination conditions, such as temperature and duration.

Chemical bonding and functional groups

Metakaolin is predominantly amorphous, some residual hydroxyl groups may remain on the surface of the particles. These groups contribute to the hydrophilicity of metakaolin, allowing it to absorb moisture and participate in chemical reactions. The structural framework of metakaolin consists of interconnected silica and alumina tetrahedral (Karthik *et al.,* 2017). This framework is crucial for the material's reactivity and its ability to form bonds with other compounds during processes like cement hydration.

Thermal stability and phase changes

Metakaolin exhibits good thermal stability, which is important for its performance in high-temperature applications. The amorphous nature allows it to withstand elevated temperatures without significant degradation, making it suitable for various industrial processes. The transition from kaolinite to metakaolin involves significant changes in the structural arrangement of silica and alumina (Khatib *et al.,* 2014). This transformation is characterized by the loss of structural water and the rearrangement of the atomic framework, leading to the amorphous state.

Preparation of metakaolin

Metakaolin is a highly reactive pozzolanic material derived from the thermal treatment of kaolinite clay. The preparation process involves several detailed steps, each critical to achieving the desired properties of the final product.

Raw material selection

The preparation of metakaolin begins with the selection of high-quality kaolinite clay, primarily composed of the mineral kaolinite ($Al_2Si_2O_5(OH)_4$). This clay is typically found in sedimentary deposits and is often sourced from weathered granite or other geological formations rich in kaolinite (Khatib *et al.,* 2009b). The purity and mineral composition of the raw material are vital, as impurities such as quartz, feldspar, and iron oxides can adversely affect the quality of the resulting metakaolin. To ensure the selected kaolinite meets the required specifications, it undergoes characterization using techniques like X-ray fluorescence (XRF) and X-ray diffraction (XRD), which help identify its mineral content and assess its suitability for metakaolin production (Khatib *et al.*, 2014).

Pre-treatment

Once the raw kaolinite is collected, it undergoes pre-treatment to prepare it for calcination. The first step in this phase is grinding the kaolinite into a fine powder. The grinding process increases the surface area of the clay, which is crucial for achieving uniform heating during calcination. The target particle size is typically less than 100 micrometers, ensuring optimal reactivity (Khatib *et al.,* 2009b). Following grinding, the kaolinite is sieved to remove larger particles, further ensuring uniformity. This step is essential, as a consistent particle size contributes to better performance in the subsequent calcination process (Khatib *et al.,* 2014).

Calcination process

The core of metakaolin preparation lies in the calcination process, where the pre-treated kaolinite is subjected to control heating in a furnace. The temperature is typically set between 600 °C and 800 °C, depending on the preferred properties of the metakaolin and the specific characteristics of the raw material. At high temperatures, kaolinite undergoes dehydroxylation, losing hydroxyl groups and water (Khatib & Adams, 2016). Such change is represented by the chemical reaction in Equation 1 (Khatib & Ahmadeen, 2016).

$$(Al_2Si_2O_5).(OH)_4 \rightarrow 2Al_2Si_2O_7 + 2H_2O \qquad (1)$$

The result of this reaction is metakaolin ($Al_2Si_2O_7$), which is predominantly amorphous. This amorphous structure enhances the material's reactivity compared to the original kaolinite, making it suitable for various applications, especially in construction.

Cooling and collection

After the calcination process, the metakaolin must be cooled gradually to room temperature. Controlled cooling is crucial to avoid thermal shock, which can lead to structural damage and micro-cracking in the material. Once cooled, the metakaolin is collected for further processing or immediate use (Khatib & Adams, 2016). This step ensures that the material retains its desired properties and is ready for characterization or application in various industrial processes.

Post-treatment

Post-treatment may involve additional milling of the metakaolin to achieve the desired fineness and uniformity. This step is significant, as finer metakaolin particles generally exhibit enhanced reactivity, which can improve their performance in applications like cement and concrete. After milling, the final product undergoes various characterization techniques to confirm its properties (Khatib & Ahmadeen, 2016). Techniques such as X-ray diffraction (XRD) are used to verify the amorphous nature of the metakaolin and identify any residual crystalline phases. Scanning electron microscopy

(SEM) helps analyze the particle morphology and size distribution, while specific surface area analysis (BET method) measures the surface area, which is a critical factor influencing reactivity and performance (Khatib *et al.,*2014).

Additional chemical reactions

Metakaolin exhibits pozzolanic properties, allowing it to react with calcium hydroxide (produced during cement hydration) to form additional cementitious compounds. This pozzolanic reaction can be represented as shown in Equation 2 (Khatib & Ahmadeen, 2016).

$$Al_2Si_2O_7 + 2Ca(OH)_2 \rightarrow Ca_2Al_2SiO_7 + 2H_2O \quad (2)$$

This reaction enhances the strength and durability of cement-based materials. Additionally, when mixed with water and calcium hydroxide, metakaolin contributes to the formation of calcium silicate hydrates (C-S-H), which are crucial for improving the mechanical properties of concrete.

Zeolite

Zeolites are a unique group of naturally occurring and synthetic hydrated aluminosilicate minerals characterized by their porous crystalline structures. Composed mainly of silicon (Si) and aluminum (Al), these minerals possess a framework that includes channels and cavities, allowing them to accommodate cations and small molecules. Their distinctive properties, such as high surface area and significant ion-exchange capacity, make zeolites valuable in various industrial applications (Ren *et al.,* 2018).

The structure of zeolites consists of a three-dimensional network of tetrahedra formed by silicon and aluminum atoms, bonded by oxygen. The ratio of silicon to aluminum influences the zeolite's properties and classification. Natural zeolites, like clinoptilolite and mordenite, are found in volcanic rocks, while synthetic zeolites, such as zeolite A and ZSM-5, are engineered for specific uses. These materials are widely utilized in catalysis, gas separation, and ion-exchange processes (Sen *et al.,* 2018). Zeolites have diverse applications across multiple industries. They serve as catalysts in petrochemical processes and are effective adsorbents for gases and liquids, making them essential in air and water purification. Additionally, their ability to exchange cations is beneficial in water treatment and agriculture, where they enhance soil fertility. As research continues, zeolites remain a significant focus in materials science, demonstrating their versatility and importance (Ma *et al.,* 2010).

Physical properties of zeolite

Zeolites are a unique class of minerals with several distinctive physical properties that enhance their functionality across various applications. Understanding these properties is essential for leveraging zeolites in fields such as catalysis, environmental science, and agriculture (Bhatia, 2020).

Porosity and surface area

One of the most critical physical properties of zeolites is their high porosity, characterized by a well-defined network of pores and channels. This porous structure results in a high specific surface area, typically ranging from 300 to 800 m²/g, although some synthetic zeolites can exceed this range (Jiang *et al.,* 2018). The pore sizes generally fall between 3 to 10 angstroms, allowing for selective adsorption of molecules based on size and shape. This property is particularly useful in applications such as gas separation, where zeolites can selectively trap specific gases while allowing others to pass through (Hern´andez-Palomares &Espejel-Ayala 2022).

Ion-exchange capacity

Zeolites possess significant ion-exchange capacity due to the presence of cations in their structure, such as sodium, potassium, calcium, and magnesium. The negative charge resulting from the substitution of aluminum for silicon in the tetrahedral framework creates sites for cation exchange. This allows zeolites to effectively remove unwanted ions from solutions, making them valuable in water treatment, soil enhancement, and agricultural applications (Musyoka *et al.,* 2014). The ability to exchange cations also enables zeolites to play a crucial role in controlling nutrient availability in soils, improving plant growth.

Thermal stability and chemical resistance

Zeolites are known for their remarkable thermal stability, often maintaining their structural integrity at temperatures up to 600 °C or more, depending on the specific type of zeolite (Zhao *et al.,* 2014). This thermal stability is essential for their use in catalytic processes and high-temperature applications. Additionally, zeolites exhibit good chemical resistance to acids and bases, which allows them to withstand harsh environments without significant degradation. This property is particularly advantageous in industrial processes where zeolites are exposed to aggressive chemicals (Garshabi *et al.,* 2017).

Chemical properties of zeolite

Zeolites are renowned for their unique chemical properties, which contribute to their versatility in various applications, including catalysis, ion exchange, and environmental remediation (Mohiuddin *et al.,* 2016). Understanding these properties is crucial for optimizing their use in industrial and scientific fields.

Ion exchange capacity

One of the most significant chemical properties of zeolites is their ion-exchange capacity. Zeolites can exchange cations in their structure, such as sodium, potassium, calcium, and magnesium, with other cations in solution. This property is vital for applications in water treatment and soil amendment, as zeolites can remove harmful ions and replace them with beneficial ones, enhancing soil fertility (Mohiuddin*et al.,* 2016). The efficiency of ion exchange is influenced by factors such as the type of zeolite, the concentration of ions, and the pH of the solution (Joseph *et al.,* 2020).

Acid-base properties

Zeolites exhibit distinct acid-base properties, which are crucial for their catalytic activity. The presence of acidic sites on the zeolite framework allows them to act as solid acids, facilitating various catalytic reactions, such as hydrocracking and isomerization (Zones *et al.,* 2020). The strength and density of these acidic sites can be modified through ion exchange and dealumination, enabling the tailoring of zeolite properties for specific catalytic applications (Zones *et al.,* 2020). This tunability makes zeolites valuable in the petrochemical industry and for biomass conversion processes.

Stability in harsh conditions

Zeolites demonstrate remarkable stability under harsh chemical conditions, including exposure to acids, bases, and high temperatures. This stability is essential for their use in catalytic processes and environmental applications (Artillo *et al.,* 2023). Recent studies have shown that specific modifications, such as the incorporation of metal ions or the synthesis of hierarchical structures, can enhance their chemical resistance and catalytic performance (Djeffal *et al.,* 2017). This resilience allows zeolites to maintain their structural integrity while effectively catalyzing reactions or adsorbing pollutants.

Structure and composition of zeolite

Zeolites are crystalline aluminosilicates characterized by a unique framework structure composed of interconnected tetrahedra. Their structural and compositional properties are fundamental to their functionality in various applications, including catalysis, ion exchange, and environmental remediation (Mezni *et al.,* 2011).

Framework structure

The basic structure of zeolites consists of a three-dimensional framework formed by SiO_4 and AlO_4 tetrahedral. Each tetrahedron is made up of a central silicon or aluminum atom surrounded by four oxygen atoms. The tetrahedra are linked together by sharing oxygen atoms, which creates a robust framework. The presence of aluminum in the structure introduces a negative charge due to the lower valency of aluminum compared to silicon. To maintain charge balance within the framework, cations such as sodium (Na^+), potassium (K^+), or calcium (Ca^{2+}) are incorporated into the voids of the structure (Djeffal *et al.,* 2017).

This framework can vary in topology, leading to a multitude of zeolite types, each with distinct properties. The specific arrangement of tetrahedral results in various pore sizes and shapes, which are crucial for the selective adsorption and catalytic activities of zeolites. For instance, the framework type determines whether a zeolite is more suitable for separating small molecules or larger ones, impacting its application in gas separation and catalysis.

Composition

The general chemical formula for zeolites can be represented as: $Mn(AlO_2).n(SiO_2)_m.x(H_2O)$.

In this formula, M represents the cations that balance the negative charge from the aluminum, while n and m denote the number of tetrahedral units of aluminum and silicon, respectively. The variable x indicates the number of water molecules associated with the zeolite structure, which can be crucial for its stability and reactivity (He *et al.,* 2021).

The Si/Al ratio is a critical factor influencing the properties of zeolites. A higher Si/Al ratio generally leads to increased thermal stability and reduced acidity, making the zeolite suitable for applications requiring high thermal resistance, such as catalytic processes (Hong *et al.,* 2020). Conversely, zeolites with lower Si/Al ratios exhibit stronger acidic properties, beneficial for catalytic reactions that require acidic sites.

Pore structure and size

Zeolites are distinguished by their diverse pore structures, which can be categorized based on dimensionality. The 1D (Channel-type) zeolites contain linear channels that facilitate the passage of molecules in one direction. An example is zeolite A, which is commonly used in detergents and water softening. The 2D (Layer-type) zeolites feature two-dimensional arrays of pores, allowing for more complex molecular interactions. Mordenite is a classic example, often utilized in gas separation and adsorption processes (Djeffal *et al.,* 2017). Lastly, the 3D (Cage-type) zeolites exhibit a three-dimensional network of interconnected voids, such as faujasite, which is extensively used in catalytic cracking in the petrochemical industry.

The pore sizes of zeolites typically range from 3 to 10 angstroms, allowing selective adsorption according to molecular size and shape. This selectivity is critical in certain applications like gas separation, in which zeolites can preferentially adsorb particular gases in exclusion of others (Oshima *et al.,* 2020). The ability to modify pore sizes and structures through synthetic methods permits for the design of zeolites for specific industrial applications, enhancing their utility in modern chemistry.

Types of zeolite

Zeolites are categorized based on their framework structure, chemical composition, and pore size. Each type possesses unique properties that make them suitable for various applications. Below is a more comprehensive overview of the different types of zeolites (Bao *et al.,* 2018).

Natural zeolites

Natural zeolites form through geological processes, primarily from volcanic ash, and are often found in sedimentary deposits. They have been used for centuries in various applications due to their unique properties and are categorized as follows: i) Clinoptiloliteis one of the most abundant natural zeolites with a high cation-exchange capacity, making it valuable in agriculture for improving soil quality and enhancing nutrient retention. It can be used in water treatment to remove heavy metal and ammonium ions, attributable to its ability to selectively exchange ions (Choo *et al.,*2022); ii) Mordenite is recognized for its great thermal stability and resistance to acidic environments. Mordenite zeolite has a distinctive channel structure which allows for efficient gas adsorption. It is commonly used in industrial applications for gas separation processes, such as removing water vapor from gases; iii) Chabazite zeolite has a smaller pore size compared to the others, making it very effective in ion-exchange processes. Chabazite is frequently utilized in applications involving the elimination of ammonium from wastewater and in the manufacture of fertilizers (Choo *et al.,* 2022).

Synthetic zeolites

Synthetic zeolites are engineered in laboratories, allowing for precise control over their properties, including pore size, acidity, and thermal stability. They are extensively used in industrial applications as a result of their well-tailored characteristics. For instance, Zeolite A (LTA) is commonly used in detergents and water softening since it has an excellent ion-exchange capacity (Chebude & Díaz 2015). It softens hard water by effectively removing calcium and magnesium ions. Its crystalline structure allows the encapsulation of water molecules, enhancing its performance in cleaning applications.

Zeolite X (FAU) is known for its high adsorption capacity and is typically used in petrochemical processes, particularly in the separation of hydrocarbons. Its large pore size enables it to adsorb larger molecules, making it suitable for applications like gas purification and catalytic cracking (Ayoola *et al.,* 2018). Similar to Zeolite X but with a different Si/Al ratio, Zeolite Y is extensively used in the petroleum industry for catalytic cracking processes. Its high thermal stability and large surface area enhance its effectiveness in breaking down large hydrocarbons into more valuable products (Ayoola *et al.,* 2018; Chebude & Díaz, 2015).

Synthesis of zeolite

The synthesis of zeolites is a process that creates their unique crystalline structures. The most common method used is hydrothermal synthesis, but there are several techniques available. Each method involves specific materials and conditions to achieve the desired type of zeolite.

Hydrothermal Synthesis

Hydrothermal synthesis is the primary method for producing synthetic zeolites. In this process, a mixture of silica and alumina sources, along with alkali metal hydroxides and water, is prepared. Common silica sources include sodium silicate, while aluminum sources can be aluminum hydroxide (Sivalingam & Sen 2019). The mixture is combined to form a gel, with specific ratios of these materials determining the final zeolite's properties. Once the gel is prepared, it is placed in a sealed container called an autoclave. The autoclave is heated to high temperatures, usually between 100 and 200 °C, under pressure for several hours or even days. This heating allows the gel to undergo chemical reactions that lead to the formation of zeolite crystals (Watanabe *et al.*, 2015). After crystallization, the zeolite is filtered, washed to remove any unreacted materials, and dried. Sometimes, it undergoes ion-exchange to improve its properties. Figure 4 shows the synthetic route to Zeolite A.

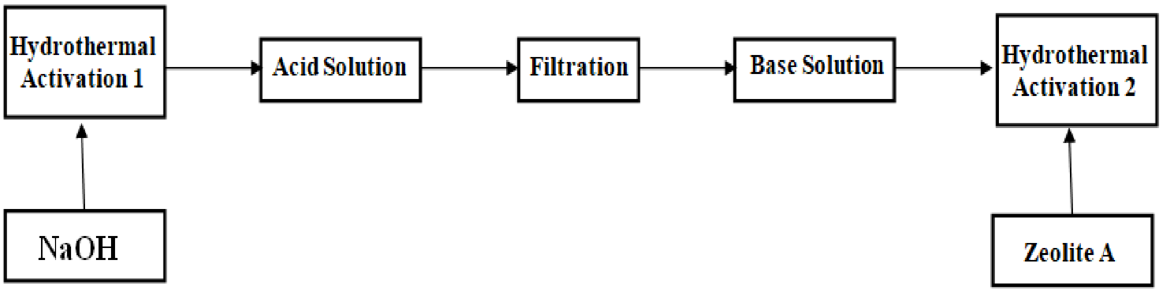

Figure 4: Experimental Flowchart of Synthesized Zeolite A

Solvothermal synthesis

Solvothermal synthesis is similar to hydrothermal synthesis but uses organic solvents instead of water. This method can produce different types of zeolites and is useful for creating zeolites with specific characteristics. In this process, solvents like alcohols are mixed with the silica and alumina sources.The mixture is then placed in a sealed reactor and heated under pressure (Watanabe *et al.,* 2015). The choice of solvent and the heating conditions can significantly affect the crystallization process and the final structure of the zeolite. This method allows for more flexibility in synthesizing zeolites tailored to particular applications.

Template-assisted synthesis

Template-assisted synthesis involves using organic templates or structure-directing agents to guide the formation of zeolite frameworks. These templates are often quaternary ammonium compounds or other organic molecules that fit within the zeolite structure during synthesis. They help shape the arrangement of the framework. After the zeolite forms, the templates are removed through heating or solvent extraction. This method allows for the production of zeolites with specific pore sizes and shapes, which can enhance their performance in various applications (Sivalingam & Sen 2019). Figure 5 represents the synthetic route to Zeolite Y.

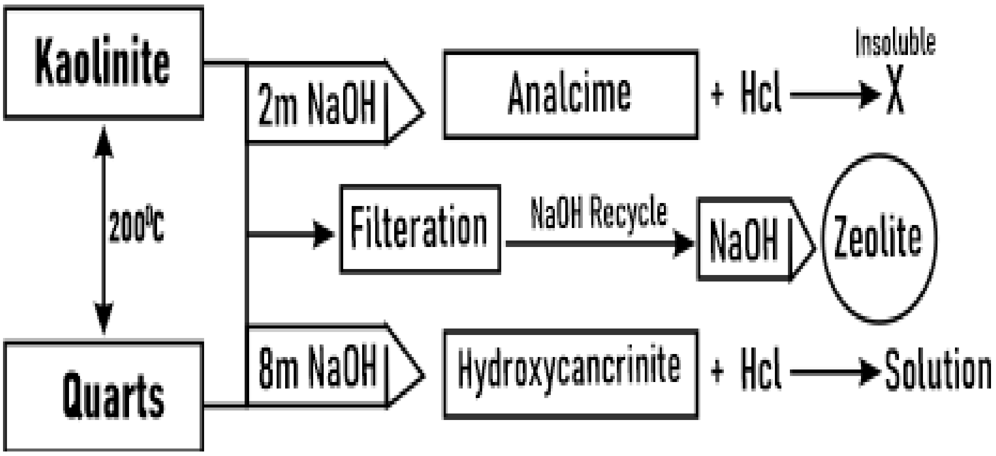

Figure 5: Synthesis Flowchart of Zeolite Y

Microwave-assisted synthesis

Microwave-assisted synthesis is an innovative technique that uses microwave energy to promote zeolite crystallization. This method can significantly reduce the time and energy needed for synthesis. In this process, the gel mixture is placed in a microwave reactor, where it is exposed to microwave radiation. The rapid heating and uniform temperature distribution help speed up the crystallization process (Sivalingam & Sen 2019). This method is becoming increasingly popular due to its efficiency and ability to produce high-quality zeolites in shorter time frames.

Applications of zeolites

Catalysis

Zeolites play a crucial role in the petrochemical industry as catalysts. Their unique porous structure allows them to facilitate important chemical reactions, such as catalytic cracking and hydrocracking. These processes convert large hydrocarbon molecules into smaller, more valuable products like gasoline and diesel. The ability of zeolites to selectively adsorb and react with specific molecules makes them highly effective in refining processes, enhancing efficiency and product quality (Yang *et al.*, 2017).

Adsorption and separation

Zeolites are renowned for their adsorption capabilities due to their molecular sieve properties. They can selectively trap and separate molecules based on size and polarity, making them ideal for applications in air and water purification. For instance, zeolites can effectively remove volatile organic compounds (VOCs) from industrial emissions and heavy metals from wastewater. Their high surface area and ion-exchange capacity contribute to their effectiveness in these environmental cleanup processes (Yue *et al.,* 2018).

Agriculture

In agricultural settings, zeolites are used to improve soil quality and enhance nutrient retention. They help retain moisture in the soil, reducing the need for frequent irrigation. Additionally, zeolites can slowly release nutrients, acting as a natural fertilizer. This slow-release mechanism leads to better crop yields and healthier plants, making zeolites a valuable resource for sustainable farming practices (Abdullah *et al.,* 2016).

Animal feed

Zeolites are incorporated into animal feed as dietary additives. They help detoxify feed by binding harmful substances and improving overall digestion in livestock. By enhancing nutrient absorption, zeolites contribute to better growth rates and overall health of animals. This application is particularly important in the livestock industry, where feed quality directly impacts productivity and animal welfare (Abdullah *et al.,* 2016).

Environmental remediation

Zeolites are effective tools for environmental remediation, particularly in treating contaminated soils and groundwater. Their ability to adsorb heavy metals, ammonium ions, and other pollutants makes them suitable for cleaning up hazardous waste sites. By trapping these harmful substances, zeolites help restore contaminated environments, protecting ecosystems and public health (Yang *et al.,* 2017).

Construction materials

In the construction industry, zeolites are added to materials such as concrete to enhance their properties. They improve durability, chemical resistance, and thermal insulation. Additionally, incorporating zeolites can reduce the environmental impact of cement production by lowering the amount of Portland cement needed. This contributes to more sustainable building practices and helps reduce carbon emissions associated with construction (Yang *et al.,* 2017). Figure 6 illustrates the applications of zeolite in various industries.

Method of characterization of kaolin and zeolites

Kaolin and zeolite are two important mineral materials with diverse applications across various industries, including agriculture, environmental remediation, construction, and catalysis. Their unique physical and chemical properties make them valuable resources in both industrial and research settings. To fully harness their potential, it is essential to characterize these materials comprehensively (Akinruli *et al.,* 2021). Characterization involves a range of analytical techniques that provide insights into their structural, chemical, and physical properties.

Understanding the characteristics of kaolin and zeolite not only aids in identifying their suitability for specific applications but also enhances the ability to optimize their performance. By employing various methods, researchers can determine aspects such as mineral composition, particle size, surface area, thermal stability, and reactivity. This knowledge is crucial for developing innovative solutions and improving existing processes in fields ranging from agriculture to environmental science. The following sections outline the most common methods used for the characterization of kaolin and zeolite, detailing their principles, applications, and outcomes (Bessa *et al.,* 2017).

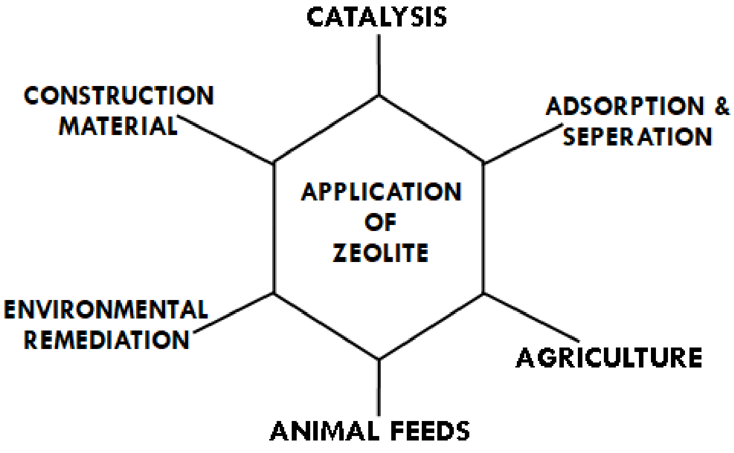

Figure 6: Industrial applications of zeolites

X-ray Diffraction (XRD)

X-ray diffraction is a fundamental technique for identifying the crystalline structure of minerals. When X-rays are directed at a crystalline material, they are scattered in specific directions based on the arrangement of atoms within the crystal lattice. This scattering produces a diffraction pattern unique to each mineral. XRD is particularly useful for determining the mineral phases present in kaolin and zeolite samples, assessing crystallinity, and identifying specific minerals such as kaolinite, illite, or various types of zeolites. By analyzing the resulting diffraction patterns, researchers can calculate lattice parameters and identify impurities or mixed phases, providing essential information for both academic and industrial applications (Bessa *et al.,* 2017). Figure 7 shows the XRD patterns of Zeolites synthesized by ultrasonic-assisted hydrothermal synthesis (Ng *et al.,* 2019).

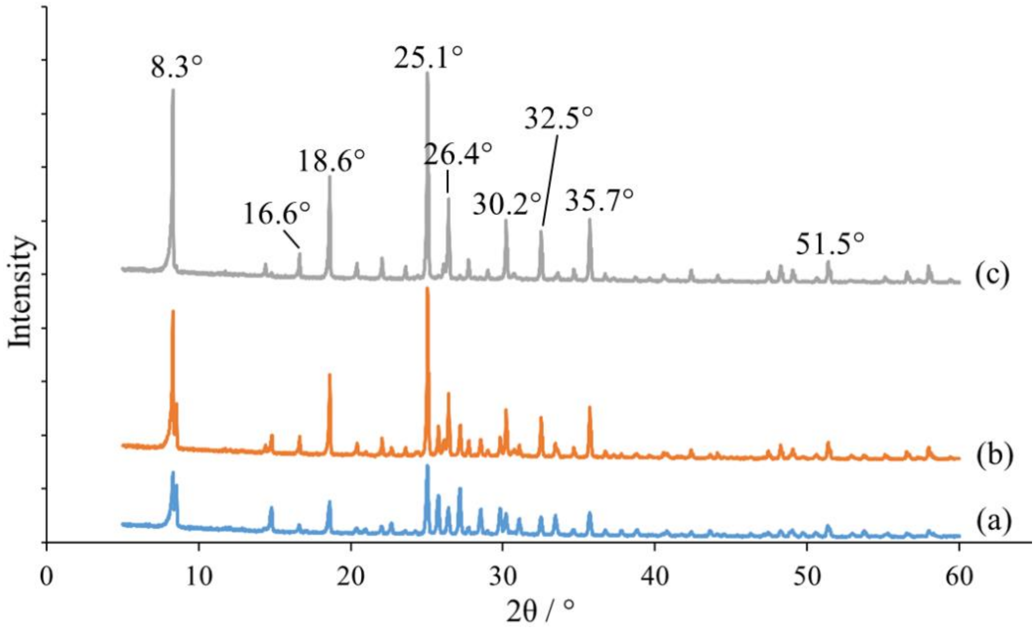

Figure 7: XRD patterns of zeolites synthesized by ultrasonic-assisted hydrothermal process at 30, 60 and 120 min respectively (Ng *et al.,* 2019)

X-ray fluorescence (XRF)

X-ray fluorescence provides detailed information about the elemental composition of kaolin and zeolite. In XRF, the sample is irradiated with X-rays, causing the elements to emit characteristic fluorescent X-rays that can be detected and quantified. This analysis identifies major and trace elements, which affect the physical and chemical properties of these minerals. Understanding the elemental composition is crucial for predicting how kaolin and zeolite will behave in different applications, from catalysis and water purification to their use in construction materials (Bhatia, 2020).

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful technique used to identify functional groups and molecular structures within kaolin and zeolite. This method measures the absorbance of infrared light by the sample, which corresponds to the vibrational transitions of molecular bonds. FTIR can distinguish between different mineral forms and detect functional groups such as hydroxyl (–OH) and silicate (Si-O) bonds, which are crucial for understanding the reactivity of these materials. The resulting spectra provide insight into the chemical composition and structural characteristics of the minerals, allowing researchers to assess their potential applications in various fields, including catalysis and environmental remediation (Bhatia, 2020). Figure 8 illustrates the FTIR spectra of zeolites prepared by hydrothermal synthesis (Krongkrachang *et al.,* 2019).

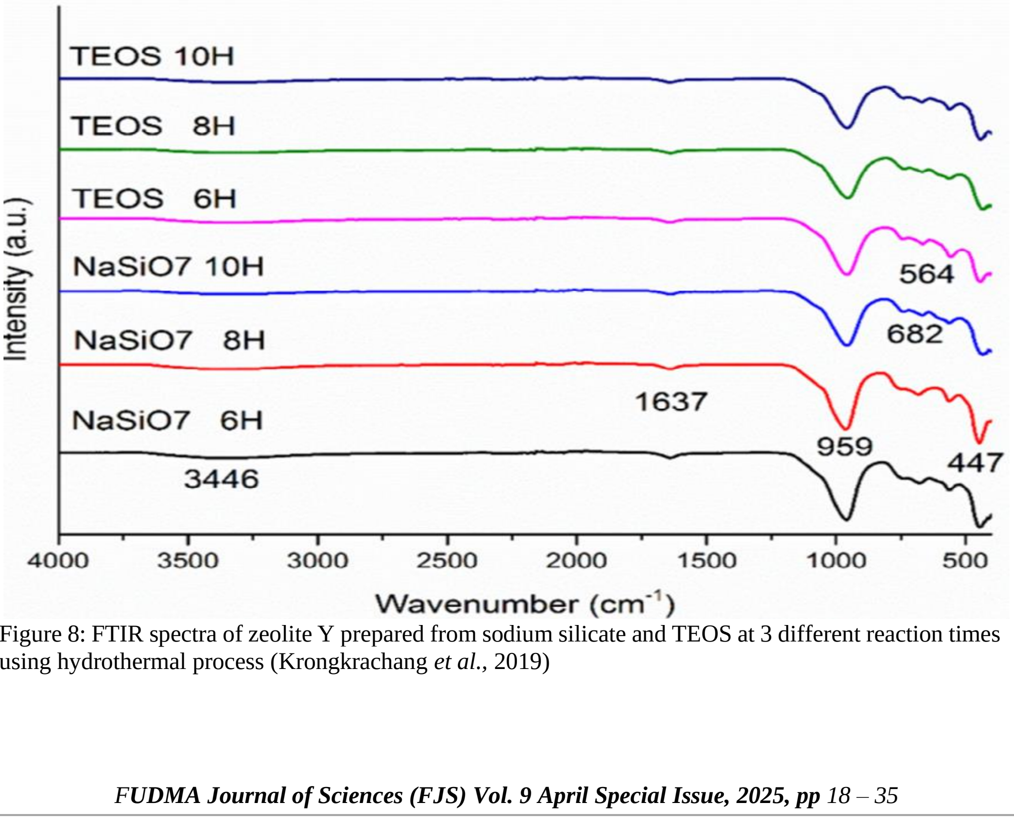

Figure 8: FTIR spectra of zeolite Y prepared from sodium silicate and TEOS at 3 different reaction times using hydrothermal process (Krongkrachang *et al.,* 2019)

Scanning Electron Microscopy (SEM)

Scanning electron microscopy offers high-resolution images of sample surfaces, revealing intricate morphological details. In this technique, a focused beam of electrons scans the surface of the sample, producing images based on the interaction of electrons with the material. SEM is particularly valuable for analyzing particle size, shape, and surface texture of kaolin and zeolite. It can also reveal agglomeration and porosity, which are important for understanding the material's behavior in various applications. Additionally, when coupled with Energy Dispersive X-ray Spectroscopy (EDX), SEM can provide elemental composition data, helping to identify the presence of specific elements and their distribution within the material (Bhatia, 2020).

CONCLUSION

The potential of kaolinite clay as a green and sustainable raw material for the synthesis of zeolites has been thoroughly examined in this research. Kaolinite clay is the ideal precursor for zeolite synthesis because of its unique properties, including its natural abundance, affordability, and environmental friendliness. The characteristics and uses of clay minerals, plus the preparation and uses of metakaolin, the thermally activated form of kaolinite clay have been covered in the review. Additionally, the review has examined the characteristics, compositions, types, and synthesis processes of zeolites from metakaolin, emphasizing their uses in a number of industries, such as environmental remediation, adsorption, and catalysis. Future research should concentrate on increasing the production of different types of zeolites from kaolinite clay and investigate its feasibility for commercial use. Researchers should also look at new uses.

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