

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
KUMASI, GHANA

SYNTHESIS AND CHARACTERIZATION OF ZEOLITES FROM BAUXITE
AND KAOLIN: APPLICATION TO THE REMOVAL OF HEAVY METALS
FROM MINING WASTEWATER

By

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A Thesis submitted to the Department of Physics,
College of Science

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

(Materials Science)

OCTOBER 2016

DECLARATION

I hereby declare that this submission is my own work towards the PhD and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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DEDICATION

To God and Family

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ABSTRACT

Different types of zeolites were synthesized from bauxite and kaolin under varying experimental conditions such as aging time, crystallization time, alkaline source concentration and silicon-to-aluminum (Si/Al) ratio and their effects on the type of zeolite produced were investigated. The synthesized zeolites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive xray spectroscopy (EDX) and Fourier transformed infrared spectroscopy (FTIR) analytical techniques. Consequently, the capacity of the zeolites in removing heavy metals such as copper (Cu^{2+}), chromium (Cr^{6+}), iron (Fe^{2+}), lead (Pb^{2+}) and zinc (Zn^{2+}) from simulated and real mine wastewater samples were investigated using a batch system. The results obtained showed that no or short aging (0 – 6 hours) of slurries prior to crystallization favored the formation of linde type A (LTA) zeolite whilst aging slurries for twenty four (24) hours resulted in the formation of faujasite (FAU) type zeolites. Aging beyond twenty four hours produced amorphous products. Crystallization times of 3, 5, 24 and 96 hours produced linde type A (LTA), linde type X (LTX), linde type Y (LTY) and analcime (ANA) with traces of sodalite in most cases. Increasing Si/Al ratio of the reactants ($1 \leq \text{Si/Al} \leq 3$) produced zeolites LTA, LTX and LTY. Alkalinity of sodium hydroxide (NaOH) mineralizer produced zeolite LTA at lower concentrations and sodalite at higher concentrations. Increasing alkalinity resulted in higher crystallinity with a resulting decrease in crystalline size of the zeolite particles. For simulated mine wastewater sample with single heavy metal cation, the removal efficiency of all zeolites was highest for Pb^{2+} (99 %) and least for Cr^{6+} (4 %). The efficiency of zeolites was in the order $A < X < Y$. Similar trend was observed for simulated mine wastewater samples with mixed metal systems. Removal of Pb^{2+} was reduced in the mixed metal systems due to counter effect of the other cations. Both zeolite LTX and LTY showed higher removal efficiency than zeolite LTA due to the availability of greater ion exchange sites and their larger pore diameter as compared to zeolite LTA. The results also showed good agreement with zeolites produced from high grade reagents. The results indicated that the zeolites were able to remove the heavy metals to limits below EPA and WHO recommended values. Hence, zeolites produced from bauxite and kaolin provides a cost-effective technology for the treatment of mine wastewaters.

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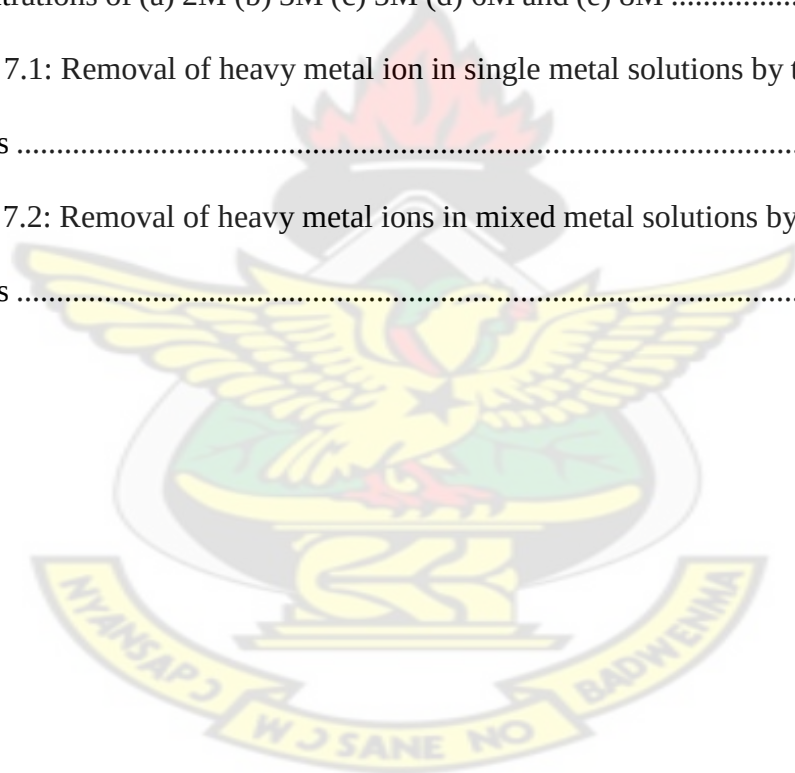
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LIST OF ABBREVIATIONS

AFK	Anfoega kaolin
Al	Aluminium
BZA	Bauxite and kaolin zeolite A
BZX	Bauxite and kaolin zeolite X
BZY	Bauxite and kaolin zeolite Y
Cr	Chromium
Cu	Copper
DF	Dry fusion
EDX	Energy dispersive x-ray
FAU	Faujasite framework
FD	Framework density
Fe	Iron
FTIR	Fourier transform infrared
HS	Hydroxysodalite
HT	Hydrothermal
ICDD	International Centre for Diffraction Data
IZA	International Zeolite Association
LOI	Loss of ignition
LTA	Linde Type A
mg/l	milligram per litre
MK	Metakaolin
NaOH	Sodium Hydroxide
nm	nanometres Pb
	Lead
PS	Pore struture
Q	Quartz
SBU	Secondary building units
SEM	Scanning electron microscopy
Si	Silicon
Si/Al	Silica to Alumina ratio
SOD	Sodalite framework
TGA	Thermo gravimetric analysis
WK	Wassa kaolin

XRD X-ray diffraction

Zn Zinc

ACKNOWLEDGEMENTS

For the various lessons learnt, for the strength to go on and the ability to come this far, I am forever grateful to God almighty for helping me accomplish this feat.

I wish to express my most sincere appreciation to my supervisor Dr. Bright KwakyeAwuah for his commitment, encouragement, dedication and day to day monitoring to ensure the success of this project. In addition to academic research, his advice in diverse fields was incredibly helpful. I would also like to thank Dr. Buamah of Civil Engineering and Dr. Leonard Amekudzi of Physics Department for their encouragements.

I would also like to thank Prof Craig Williams of University of Wolverhampton for his help and support during my stay in the University of Wolverhampton and the contributions he gave at all times.

All members of the Zeolite Research Group, KNUST became family as far as this work is concerned. It was such a blessing to have you (Esther, Dorcas, Sarah, Obed and Linus). Not forgetting Akyana and Victor Irorere. I thank Bernard Owusu Assimeng for taking time off his schedule to proof read this work; your suggestions and contributions were very helpful.

A tonne of appreciation goes to Michael Appiah-Kusi for his help in all reading and software materials and Franklin Boateng for his help during wastewater sampling in the Obuasi municipality.

I am grateful to the technical team both at Environmental Quality Lab, KNUST and School of Applied Sciences, University of Wolverhampton for their assistance in the use of equipment in line with the project.

To my family, who have been a pillar of support all through my academic career and to all and sundry who contributed directly and indirectly to my success story, I am grateful.

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CHAPTER 1: INTRODUCTION 1.1 Background

Ceramic materials are usually more resistant to high temperature and harsh environments compared to metals and polymers. They are hard but brittle and can be porous or non-porous. The porosity of a material affects certain properties such as elasticity and flexural strength. Porous materials offer a large surface area for some industrial applications and have low density for use as sensors, filters and catalysts (Rivas Cardona, 2011). The varying degrees of porosity have been studied as a means of classification.

Zeolites are usually considered microporous (Kozo *et al.*, 2013). They make the most important group in the microporous family. Typically, the term —zeolite refers to a crystalline aluminosilicate or silica polymorph based on corner sharing TO_4 (T = Si and Al) tetrahedral forming a three-dimensional four connected framework with uniformly sized pores of molecular dimensions (Xu *et al.*, 2007; Yin, 2009). Their porous property has provided it with diverse applications in many different fields. Applications of zeolites include water treatment, ion exchange, detergent production, agriculture, catalysis, construction process, petrochemical cracking and separation of gases and solvents. Other properties such as its uniform openings or shape, catalytic activity, varying chemical composition, mobile cation and hydrophobicity or hydrophilicity allows the zeolite to act as multifunctional materials in many industrial applications such as in adsorption, water treatment and ion exchange (Flanigen *et al.*, 2010; Kulpranthipanja, 2010; Kovo and Edoga, 2005).

In 1756, the first discovery of natural zeolites was documented. However, many natural zeolites have been discovered worldwide in recent times and with increasing attention to the application of these natural species. Following their discovery 200 years later by Cronstedt, zeolite minerals were known to occur normally as fine

crystals in small amounts lining the cavities of basaltic rocks or as a mixture of different zeolites in volcanic rocks (Mistry, 2005). In the 1940s, a number of zeolites with low Si/Al ratios were synthesized hydrothermally by imitating the geothermal formation of natural zeolites (Xu *et al.*, 2007). This was in an attempt to meet the high demands of zeolite needs in the industries, synthetic ones were produced besides the natural ones which take years to form.

In comparing synthetic zeolites with natural zeolites, synthetic zeolites have higher purity, uniformity of pore sizes and greater ion-exchange capabilities giving them a higher advantage in most applications. However, natural zeolites are preferred when high quality is not preferred since synthetic zeolites have a higher cost disadvantage with high quality.

Laboratory synthesis of zeolites is performed by hydrothermal means, usually with a silica source (e.g. colloidal silica, fumed silica, and metasilicate), aluminum source (sodium aluminate, aluminium hydroxide) and an alkali source combined with water in a closed system and heated (between 50 – 200 °C) under constant pressure. The hydrothermal reaction is characterized by the gradual transformation of the amorphous aluminosilicate hydrogel to the final crystalline aluminosilicate zeolites (Severance, 2014).

Chemical reagents (analytical and industrial grade) used in synthesis of zeolites come at an expensive price posing a limiting factor to explorative studies. An approach to this problem is the replacement with inexpensive raw materials. These raw materials are naturally occurring and abundant. Examples include fly ash, coal ash, volcanic glasses, kaolin and clay minerals. Successful synthesis of zeolites from these has been

reported by many scientists: kaolinite (Kovo, 2011; Rios, 2008; Lee *et al.*, 2002; Chandrasekhar and Pramada, 1999; Murat *et al.*, 1992;), montmorillonite (Lee *et al.*, 2002), bentonite (Ruiz *et al.*, 1997; de la Villa *et al.*, 2001; Ramirez *et al.*, 2002), halloysite (Gualtieri, 2001), interstratified illite– smectite (Baccouhe *et al.*, 1998).

Producing high quality zeolite is a challenging task. Reproducibility of zeolites and zeolite membrane systems is one factor contributing to the challenge. Successful sustaining efforts to design more reproducible synthesis protocols is required and it is widely acknowledged that the cost of production must also be addressed if zeolites are to be commercially realized.

In addition to synthesizing new structures, a few of the primary research frontiers in zeolite science aim at chemical control over the composition, crystal morphology and the crystallite size. Further exploration is likely to impact the performance of the materials in traditional applications like catalysis and separation (Severance, 2014). Investigation into zeolite synthesis and structure characteristics of zeolite can give a better understanding into the structure and how it can be related to the properties of interest. A search for novel synthetic routes and new structures that are similar to naturally occurring zeolites is ongoing due to demand for increased performance in various areas.

Studies into zeolite synthesis using kaolin as the principal raw material and occasionally extra reagents to vary the composition of the final product have been reported intensively. However, zeolite synthesis from bauxite and kaolin only using the hydrothermal method has not been reported. Given that Ghana is the third largest producer of bauxite in Africa as well as possessing large deposits of kaolin, these

resources are abundant and easily accessible. Exploring their use in zeolite production would be of immense benefit to the country. Thus the study is focused on the bauxite and kaolin to synthesize zeolites by developing a novel but reproducible protocol at a reduced cost. In addition, the synthesized product will be used to address the menace of water pollution caused by small scale miners. Recent water treatment technologies are energy and cost intensive.

1.2 Mining in Ghana

Zeolite technology in Ghana comes at a prime time when illegal mining has taken a surge. Ghana happens to be the second (2nd) leading producer of gold in Africa.

Long before the advent of Ghana's colonial masters, artisanal scale mining (ASM) has been long practiced. The miners use rudimentary tools in the exploitation of gold. Illegal mining is conducted on every possible land or water body where they anticipate finding gold. With the nomadic nature of their activities, they leave in their trail polluted water bodies, craters and destroying natural resources extensively (Ghana Chamber of Mines report 2012). Major problems that arise from mining activities include displacement of people, loss of livelihood, health hazards, economic disparity and frustrations. Diseases such as malaria, skin rashes and schistosomiasis are some of the vector borne diseases prevalent in such areas (Asamoah-Boateng, 2009)

The Ghana Water Company and other stakeholders have predicted an impending catastrophe regarding the rate at which its water bodies are being destroyed predominantly through illegal mining activities in the country. The cost of treating water to make it potable will increase drastically as water treatment companies would be obliged to intensify its processing plant with high cost clarifiers. The volume of potable water accessible nationwide will reduce sharply eventually (Ghana Chamber of Mines report 2012).

Pollution of surface and ground waters with heavy metals by miners renders a shortage of water accessible to both plants and animal sustenance. Such waters are unsafe for use by human beings as they cause fatal conditions. Most water treatment technologies such as reverse osmosis, electrodialysis, membrane separation and filtration are very expensive. The use of zeolite for water treatment has been studied immensely and its cost effectiveness is an advantage that should be considered.

1.3 Objectives and Scope of the Study

This research seeks to investigate the possibility of producing zeolites from bauxite and kaolin using low temperatures by developing novel protocols that would be reproducible in subsequent works. This study should enable investigations of the types of zeolites that form from specific raw materials under different conditions and the interacting influence of different factors.

The main objective of this research is to synthesize relatively low cost zeolites from bauxite and kaolin and investigate their potential in removing heavy metals from mining wastewater.

The specific objectives of this project are to:

- i. Develop a novel protocol to synthesize zeolites using bauxite and kaolin as starting materials using the hydrothermal process
- ii. Study the effect of varying Si and Al ratio and concentration of the raw materials on the type of zeolite formed
- iii. Study the characteristic features of the synthetic zeolite produced (i.e. phase identification, morphology and physico-chemical) by XRD, SEM,

FTIR and TGA techniques iv. Determine optimum conditions for the production of the zeolitic material with high cation exchange capacity from kaolin and bauxite will be established

v. Evaluate the potential of the synthesized zeolite in its capacity to remove heavy metals from mining wastewater

1.4 Outline

This thesis is organized as follows:

In Chapter One, a description of zeolites to present a general overview and its properties is given. We related the importance of zeolite structure in technological fields and environmental applications to solving pollution caused by artisanal mining in Ghana. Chapter Two serves as a study into zeolites based on discovery, structure, properties and application. It further discusses the process of synthesis and materials used. This then leads to the review of raw materials basically bauxite and kaolin which were used in this work.

Theoretical understanding on zeolite characterizations are presented in Chapter Three. Principles upon which these techniques operate are explained. Ion exchange and adsorption phenomena in zeolites are also presented. These were studied to provide insight to what happens in the zeolite structure. Descriptions of the different adsorption isotherms are also presented.

Chapter Four presents the methodology and experimental activities that were undertaken in relation to the project. Syntheses of zeolites were performed at different times and temperatures and for different kaolins. Effect of the various parameters was investigated. In Chapter Five, the results of the experimental work are presented. The influence of each of the parameters on the results is mentioned. A discussion based on

the results is given describing how they were affected and conditions to avoid during synthesis and scaling up procedures is presented in Chapter Six.

Chapter Seven is the application chapter. Here, zeolites synthesized are used to treat mine wastewater. Heavy metals which are present are removed using the different types of zeolites synthesized in the previous chapter. Lead, copper, zinc, chromium and iron were considered. Removal efficiencies and equilibrium values were determined. Various Adsorption models were evaluated.

Conclusions and recommendations pertaining to the study are mentioned in Chapter Eight.

CHAPTER 2: LITERATURE REVIEW 2.1 History of Zeolites

Zeolite (originated from the word —*zeos* meaning boils and —*lithos* meaning —stone) was discovered by a Swedish mineralogist Axel F. Cronstedt, in the year 1756, a name he coined from observing steam emanate from the mineral upon heating it (Kulprathipanja, 2010). This property led to the discovery of several other zeolites. He identified zeolites as a new group of minerals made up of hydrated aluminosilicates of alkali and alkaline earths (Ibrahim, 2007).

The era between 1777 and 1800s saw several authors describing the properties of zeolite minerals. Deville in 1862 reported the first hydrothermal synthesis of levynite. The conception of the zeolite structure to be made up of open spongy framework was developed after Friedel in 1896 observed liquids such as benzene, alcohol and chloroform were retained by the zeolite (van Bekkum *et al.*, (2001); Kulprathipanja, 2010).

In the 19th century, natural zeolites were recognized for their microporous property; their usefulness in adsorption and ion exchange as well as a number of laboratory syntheses was reported. Weigel and Steinhoff in 1925 described the first molecular sieving effect of zeolites (van Bekkum *et al.*, 2001). However, documentation of reliable characterization techniques were absent hence early synthesis work remains unsubstantiated making experimental reproducibility arduous.

The usage of X-ray diffraction technique for identifying synthesized mineral was first described by Leonard in 1927. This motivated Taylor and Pauling to accurately describe the first single crystal structure of zeolite in 1930 (Kulprathipanja, 2010).

Richard Barrer in the mid-1930s to 1940s brought ground-breaking work in zeolite synthesis and adsorption. Barrer began by investigating the conversion of known mineral phases under the action of a strong salt solution at raised temperatures (Barrer, 1948). The first classification of the zeolite pertaining to that era based on molecular size considerations was done by Barrer. A report on the first definitive synthesis of zeolite Mordenite and a novel synthetic zeolite was provided in 1948. Milton, in 1949, led the use of more reactive alkali-metal aluminosilicate gels at low temperatures (100 °C) and autogenous pressure (Milton., 1989; Flanigen *et al.*, 2010; Kulprathipanja, 2010; Ozdemir and Piskin, 2013). He had successfully prepared zeolites A, B (now Na-P) and C (hydroxysodalite) together with a crystalline impurity designated X by the end of year 1949 (Ibrahim, 2007; Kulprathipanja, 2010; Mainganye, 2012). Milton *et al.*, by 1953 had synthesized twenty (20) zeolites including fourteen (14) unknown as natural mineral (Mainganye, 2012). The golden age of zeolite development, i.e. the period between 1954 to early 1980, saw massive exploration of zeolites with high, medium and low Si/Al ratios (Xu *et al.*, 2007).

Deposits of natural zeolites found worldwide have been documented extensively. Areas with large deposits include Australia, Argentina, Bulgaria, China, Cuba, Korea, Ukraine, USA, Japan, Jordan, Hungary, Slovakia, USA, South Africa, Turkey, Italy, Germany, Iran, Indonesia, and parts of Russia. There is a wide variation in the purity, chemical composition, size of crystal, porosity, pore diameter and other properties that determine the adsorption capacity and ion exchange capacity of zeolites from different deposits (Shoumkova, 2011).

2.2 Structure

Zeolites are a group of naturally occurring crystalline inorganic microporous aluminosilicate materials. Zeolite framework typical consists of a complex three dimensional structure with adsorption, large cation exchange capacities and hydration-dehydration properties (van Straaten, 2002). The pores in a zeolite crystal are of molecular dimension. Zeolites are characterised by a net negative charge on the crystal which allows it to take up cations by ion exchange. The frameworks are chemically and thermally stable.

Zeolites are a system of channels, windows or cages of molecular dimensions. Basically, zeolite frameworks consist of silicon and aluminium atoms, so-called Tatoms, and oxygen in the crystal lattice. The presence of aluminium atoms in the framework creates a negatively charged framework that is compensated by the addition of non-framework cations, such as sodium, calcium or potassium. Four oxygen atoms surround the T-atoms forming a tetrahedron. The framework of zeolite usually comprises a three-dimensional crystalline structure with cavities and channels in the diverse directions that allow for some properties like ion-exchange and reversible dehydration (Garcia Sanchez, 2011).

Out of about the fifty (50) different species of this mineral group known, analcime, chabazite, clinoptilolite-heulandite, erionite, ferrierite, laumontite, mordenite and phillipsite have been identified as the eight zeolite minerals that make up the major part of volcanic sedimentary deposits (Cansever, 2004; van Straaten, 2002). Each structure of these minerals is unique but they all possess large open channels within their crystal structure that creates a large void space for ion exchange and adsorption purposes. Internally, the surface area of these channels sum up to several hundred square meters per gram of zeolite. This makes zeolites very effective in the ion exchange process (Cansever, 2004; Mumpton, 1984).

Three classification schemes are widely used currently for zeolite structures, i.e. classification based on: framework density (FD), secondary building units (SBUs) and pore structure (PS) (Auerbach *et al.*, 2003; Baerlocher *et al.*, 2007; Musyoka, 2009). Two of these as cited in Rios (2008), depend on specific defined features of the crystal structure, whilst the third classification is linked with historical basis, assigning zeolites with similar properties into the same category (Ambruster and Gunter, 2001).

Zeolites classification on the basis of their framework structure has identified a number of structures. 176 unique zeolite framework types have been approved and assigned a 3-letter code by the Structure Commission of the IZA (IZA-SC). These codes originate from the names of the type material, i.e. the species first used to establish the structure type (Baerlocher *et al.*, 2007). For instance, the code FAU represents the Faujasite type that includes zeolite X and Y, SOD for Sodalite and LTA for Linde type A.

The basic or primary building unit (PBU) for the framework in a zeolite is a TO_4 tetrahedron where the central T - atom is typically Si or Al and the peripheral atoms

are O (Figure 2.1). The primary building unit generates a lattice, a periodic array of identical building blocks of recurring units called secondary building unit (SBU).

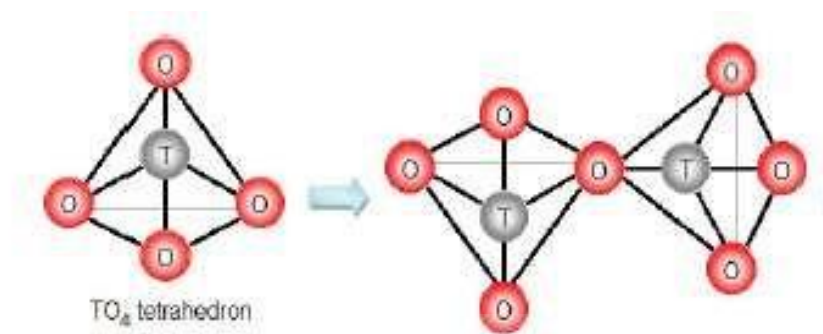


Figure 2.1: The primary building blocks of zeolite (adapted from Rivas, 2011)
The zeolite structure is defined by the SBU as its main unit with the exception of the water and cation in the framework (Feng *et al.*, 1996; Parodi, 2009; Kulprathipanja, 2010; Kovo, 2011). These secondary building units consist of 4, 6 and 8-membered single rings, 4-4, 6-6 and 8-8 member double rings, and 4-1, 5-1 and 4-4-1 branched rings (Jacob, 1998; Kwakye-Awuah, 2008).

The SBUs have the tendency of controlling the zeolite morphology. Different combinations of the same SBU can generate numerous distinctive structures from the smaller ring units, e.g. by joining the D4R, S6R and S8R will model the results in LTA-type zeolite (Garcia Sanchez, 2011). The number of observed SBU's (Figure 2.2) increased from 20 in 2001 to 23 in 2007 (Baerlocher *et al.*, 2007).

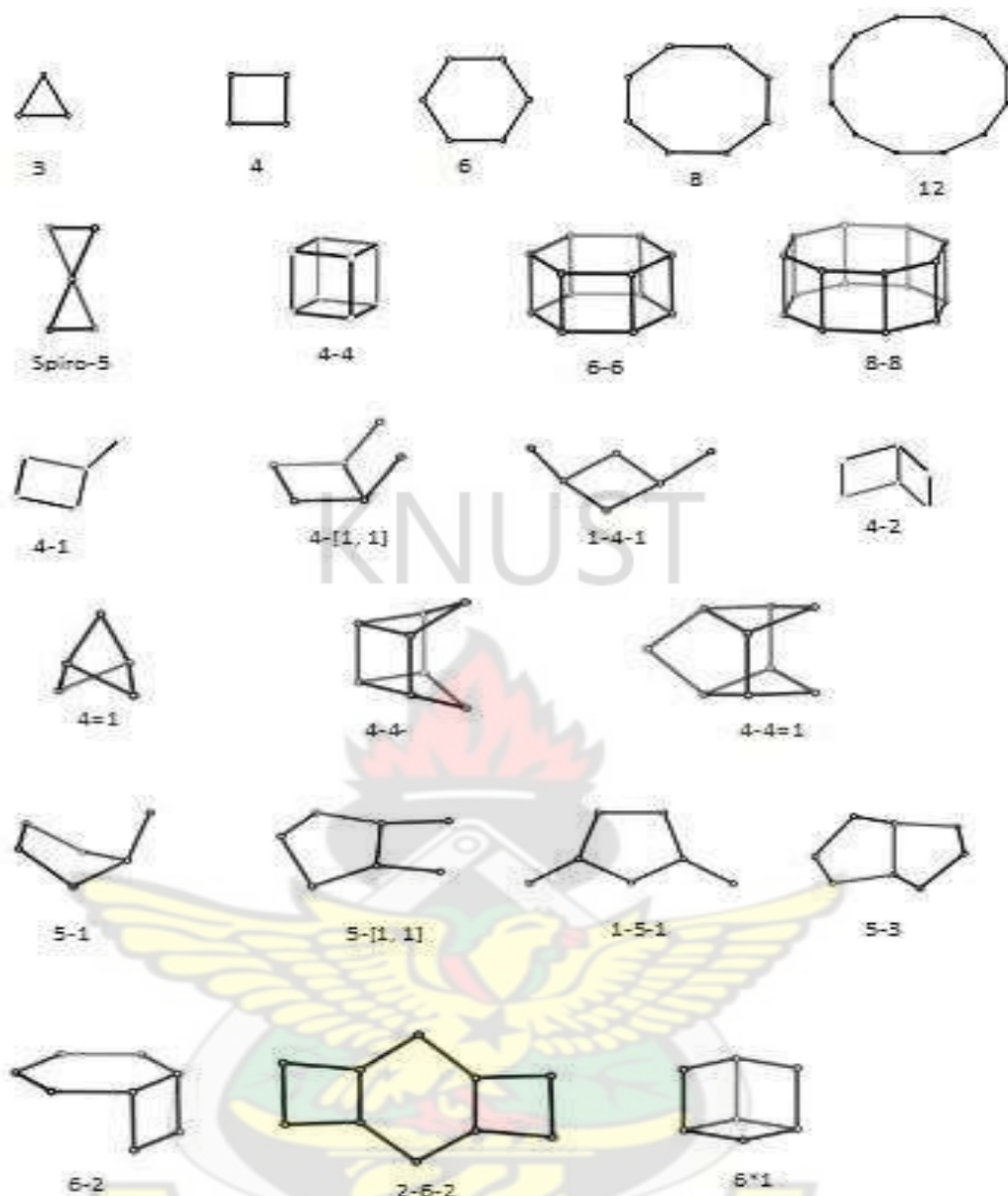


Figure 2.2: The secondary building units (SBUs) in zeolites with their codes (Baerlocher *et al.*, 2007)

The entry to the channels and cavities inside a zeolite is through a $[T-O]_n$ ring, known as a window, where n is the number of tetrahedra in the window. The ring dimensions depend of the number of tetrahedra that form it as shown in Figure 2.3. A limitation is placed on the size of the particle that is allowed to pass through the channels and cavities and hence ‘the sieving effect’ (Garcia Sanchez, 2011). The structure of each is portrayed by its own array of channels, cavities and their connectivity. Some zeolites

have a single large cavity or cage, openings to cylindrical channels, which are interconnected in one, two or three dimensions (Allendorf *et al.*, 2009; Garcia Sanchez, 2011).

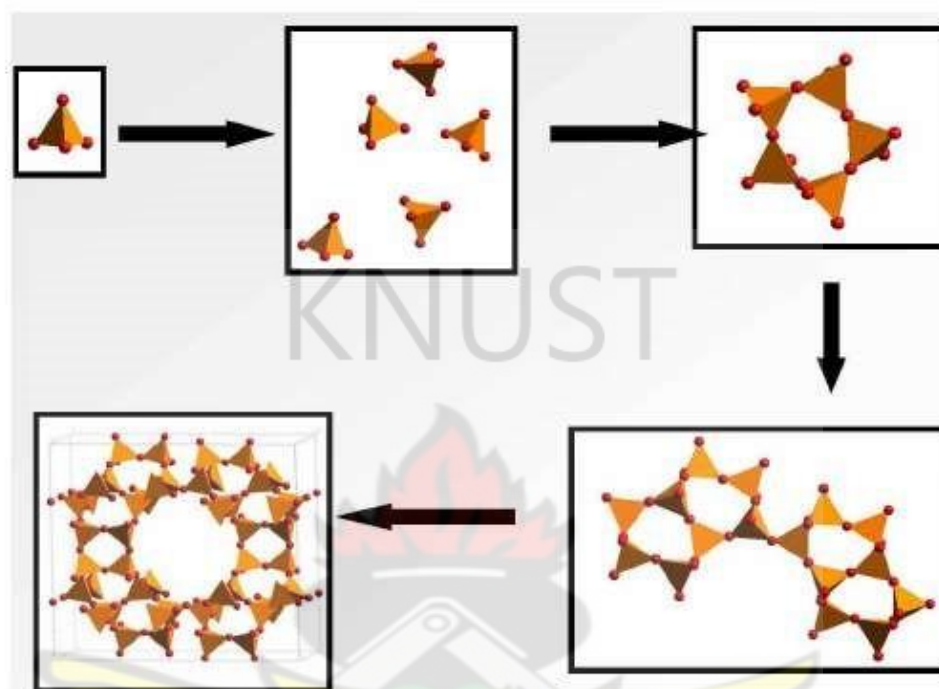


Figure 2.3: The coordination of primary building blocks to form the zeolite structure with pores (Parodi, 2009).

Zeolites have a uniform pore structure determined by the crystal structure with known pore diameter channels between 3 and 10 Å. The channels may be circular or elliptical, tubular or containing periodic cavities and straight or zigzag (Ohrman, 2000; Von-Kiti, 2012). Classification of zeolites taking into account their pore openings and the dimensionality of their channels is recognized. Three categories have been outlined using this feature:

- I. small pore zeolites such as Linde type A (LTA), Sodalite (SOD) and Gismodine (GIS) containing 8 MR pores and diameter of about 4 Å,
- II. medium pore zeolites have 10 MR and pore diameter of approximately 5.5 Å with MFI being an example; and

III. large pore zeolites formed with 12 MR pore with a 7.5 Å diameter such as Mordenite (MOR), BEA and Faujasite (FAU)-type zeolite.

In recent times, an extra-large pore zeolite category has been added with 14 MR pores and diameter higher than 9 Å, such as Cloverite or VPI-5 with 18 MR. Extra-large pore limited to 20 MR systems (Figure 2.4).

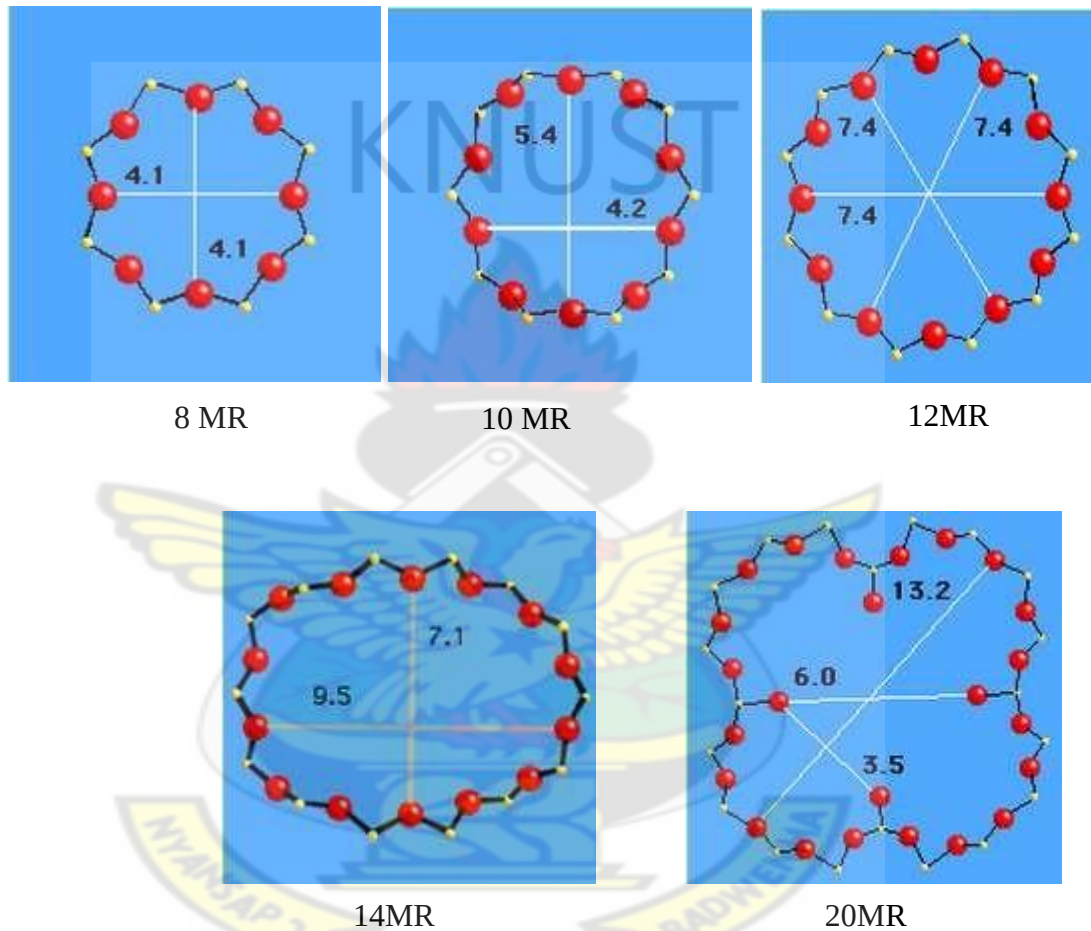
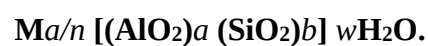


Figure 2.4: Different pore openings in zeolites each showing the number of membered rings (adapted from IZA website)

The chemical formula of zeolites with cation, is:



The part of the formula within parentheses represents the framework composition. M is the exchangeable cation of valence n . — w ” is the number of water molecules

present in a unit cell and $-a''$ the number of Al atoms per unit cell, usually $1 \leq b/a \leq 5$. The values of the variables $-a''$ and $-b''$ depend upon the structure. The total number of tetrahedra in a unit cell is the sum $(a+b)$ (Akdeniz, 1999; Garcia Sanchez, 2012).

Based on the value of Si/Al ratio, zeolites are categorized into high, middle, and less silica which determine their stability at different pH values (Flanigen *et al.*, 1991). They are low, intermediate and high silica zeolites (Flanigen, 1980). The low silica zeolites represent highly heterogeneous surface with a strongly hydrophilic surface selectivity which is hydrophobic in the high silica zeolites (Jacobs *et al.*, 2001). The acidity tends to increase in strength with increasing Si/Al ratio till maximum values are reached at Si/Al ratio of about 6 to 7 (Kovatcheva-Ninova and Dimitrova, 2002; Polatoglu, 2005).

2.3 Properties

2.3.1 Adsorption

Adsorption refers to the uptake of gases or liquid molecules of mixtures to the surface of solids. It is a separation process during which specific components of one phase of a fluid are transferred onto the surface of a solid adsorbent (Inglezakis and Pouloupoulos, 2006).

Zeolites are unique adsorbent materials, characterized by 20 % to 50 % void volumes and possessing internal surface areas of several hundred thousand square meters per kilogram (Flynn, 1994). The adsorption mechanism in zeolites is dependent on several factors. These include pore size, exchangeable ion and physical and chemical composition of the zeolite that is being used as the adsorbate. Molecules of kinetic diameter larger than the diameter of the pores cannot access the windows and enter the

canal system of the zeolite, due to its —molecular sieving effect. Dehydration and heating affects the molecular sieve property (Breck, 1974). Distortions in the lattice usually produced by heat increases the void volume of the channels, while dehydration causes a cation interchange and subsequently change the charge distribution inside the structure.

The selectivity of an adsorbate over others depends mainly on polarity of both adsorbent and adsorbate. This factor controls which molecules will be adsorbed on the zeolite. In zeolites, the Si/Al ratio is the parameter that governs the polarity. Zeolites with low Si/Al ratio have an increased polarity thus making it hydrophilic.

Uses of zeolite for adsorption purposes include drying, purification and separation. They have the ability to remove water to very low partial pressures, and very effective as desiccant, capable of containing more than 25 wt% water. They are also able to remove volatile organic chemicals from air streams, separation isomers and mixed gases. Zeolite LTA especially, is used for separation of N₂ and CO₂ from air, taking advantage of the different polarities of the two types of molecules (Barthomeuf, 1996; Kwakye-Awuah, 2008; Kovo, 2011; Garcia Sanchez, 2011).

2.3.2 Catalysis

Catalysis plays an essential role in most chemical industries. It is an essential phenomenon where a very small quantity of a catalyst is able to convert thousands or millions of times more their own weight of chemicals. Some of the most important processes are the production of fuels and petroleum products from crude oil, the production of ammonia, all kinds of plastics and the production of pharmaceuticals.

Zeolites are most suited for catalysis due to the presence of acid sites on the network and the possibility of introducing new acid sites (Garcia Sanchez, 2011). These acid sites are created due to the difference in valency of the cations. The charges created in

the framework when part of the silicon atoms is substituted by aluminium which has to be compensated by protons. The protons form the Bronsted sites making it behave similar to protons in acidic solution (Schuring, 2002).

Furthermore, zeolites can be used as support for active metals or reagents, or as catalysts for selective catalytic acid both for the transition state selectivity and for the exclusion of competing reactants depending on the diameter of the molecule (Garcia Sanchez, 2011; Labik, 2012). They also have been used as oxidation catalysts. Reactions can occur within the pores of the zeolite to allow for greater control of the product (Kwaky-Awuah, 2008). The major industrial application areas include: petroleum refining, synfuels production, and petrochemical production. Synthetic zeolites are the most important catalysts in petrochemical refineries (Flanigen *et al.*, 1991; Kwaky-Awuah, 2008).

2.3.3 Ion exchange

The ion exchange property of zeolites allows them to be used as water softeners, detergents and soaps. It is the property that allows the replacement of cation held in the zeolite framework by an external ion present in a bulk solution (Dyer, 1987). The cation-exchange selectivity depends on framework topology, ion size and shape, charge density on the anion framework, ion valence and electrolyte concentration in aqueous phase (Barrer *et al.*, 1978). The ion exchange property is due to the isomorphous substitution of Si^{4+} by Al^{3+} in the framework creating a net negative charge which causes an imbalance in the structure (Parodi, 2009). Hydrated cations located within the pores of the zeolite are weakly bound and readily exchangeable with other cations when in an aqueous medium (Garcia Sanchez, 2011). To balance this excess of negative charges, cations such Na^+ , K^+ and Ca^{2+} are introduced into the zeolite structures. These cations can be easily exchanged with others, giving the zeolite

a high ion exchange capacity. The catalytic or molecular sieve properties can also be modified by introducing other metal cations into the zeolite (Breck, 1974). Organic cations can also be used as in dye production. The use of zeolites for removal of heavy metals and other water pollutants have also been reported (Zorpas, 2000; Shevade and Ford, 2004; Rahmani and Mahvi, 2006).

2.4 Applications

One or the other unique properties of zeolite has given it enormous application worldwide. Their applications are still burgeoning in new research areas and fields. The biggest advantage of zeolites is that their properties are easy modified for specific needs in many technological fields and environmental applications. Major areas of zeolite application include petrochemical cracking treatment of certain diseases, use in the construction and agriculture industry. Both natural and synthetic zeolites are used in wastewater treatment. Pollution of water is caused by industrial and domestic activities as well as natural occurrences. Industrial activities such as mining, electroplating, tannery, etc. are examples of pollution acts. Zeolites have been studied extensively for heavy metals immobilization from natural or industrial water. The removal efficiency of heavy metal cations depends on the type of zeolite, dosage and grain size of zeolite, contact time, pH, temperature, initial metal concentration and to a significant extent to the presence of competitive ions (Shoumkova, 2011).

Zeolites are an ideal material to be used for catalysis in green chemistry due his high chemical and thermal stability. A large number of zeolites undergo dehydration and can be heated up to 1200 K without any major alteration in their crystal structure, a preferred advantage for many industrial applications. Zeolites offer a good control in the reaction selectivity that saves feed cost. They can be used at mild temperatures and pressures, reducing the operating cost. The use of zeolites also reduces waste stream,

saving treatment cost (Garcia Sanchez 2011). Zeolites utilize their ion exchange ability to function as additives in detergent production replacing phosphate. Phosphates are known to cause irreparable damage on most water bodies. In detergents, they act as water softeners as the sodium ions in the zeolite (e.g. LTA) are exchanged for calcium (Ca) and magnesium (Mg) ions in the water. The ion exchange property helps to support mineral nutrition and moisture retention when zeolites are used as fertilizers as they control pH and humidity (Garcia Sanchez 2011). Zeolites are also used chiefly in Fluid Catalytic Cracking (FCC), usually zeolites Y and ZSM-5. They serve as catalysts in cracking and hydro-cracking of hydrocarbons in the petrochemical industry.

Zeolites are regarded effective materials for the adsorption and selective separation of carbon dioxide, for the removal of carbon dioxide, water and sulphur compounds from natural gas streams and hydrogen purification (Garcia Sanchez, 2011). Zeolites are optimal ion-exchange beds for purification of drinking water and environmental decontamination of heavy and radioactive metals. They are also used for the separation and purification of radioisotopes of Cs and Sr (Payra and Dutta, 2003). Zeolites have also been found useful for adsorption refrigeration and as thermal collectors (Omisanya *et al.*, 2012).

Recent applications of zeolites in modern processes include: optic and electronics, bio-catalysis, synthesis of nanostructure catalyst, odor removers, plastic additives and drug release (Chantawong and Harvey, 2003; Payra and Dutta, 2003; Kovo, 2011).

2.5 Synthesis

Zeolites can be natural or synthetic with more than 150 zeolite types synthesized and 40 naturally occurring zeolites known (Szostak, 1989). Natural zeolites are formed from volcanic ash whilst synthetic zeolites are produced mainly in the laboratory (Atta *et al.*, 2007; Kwakye-Awuah, 2008; Rios, 2008; Mainganye, 2012; Von-Kiti, 2012).

After their discovery, zeolites were tailored for specific applications with different compositions, properties and structures. Differences in zeolites also occur from varying methodologies depending on the Si/Al ratio of the starting reactants. The IZA has several publications, books and monographs outlining zeolite synthesis (Breck, 1974; Barrer, 1982; Jacobs and Martens, 1987; Szostak, 1989). Synthetic zeolites and other molecular sieves are important products to a number of companies in the catalysis and adsorption areas and numerous applications both emerging and well established, are encouraging the industrial synthesis of the materials (Kulprathipanja, 2010). Ribeiro, (1984) as cited in Htay (2008) reviewed the preparation of zeolites for water purification, waste and wastewater treatment.

Zeolite synthesis is usually via hydrothermal technique. In recent times, synthesis can be either solvothermal, hydrothermal or ionothermal. Ionothermal synthesis is the use of ionic liquids as both solvent and potential template (structure directing agent) in the preparation of zeolites and inorganic hybrids (Parnham and Morris 2007). Ionic liquids are termed organic solvents with high polarity and pre-organised structure (Kovo, 2011). The solvothermal synthesis route was developed by Xu and coworkers in 1980. This method uses alcohols and amines with different structures and properties. The organic molecule acts a template in the reaction. Solvothermal synthesis is used for the preparation of ALPOs. Hydrothermal synthesis refers to the formation of materials

in a primarily aqueous solvent (Kulprathipanja, 2010). The water solubilizes the components of the reagent mixture to varying degrees. Hydrothermal syntheses are broadly divided into sub-critical reactions in which the reaction temperature is mild within 100 °C to 240 °C and super critical reactions whereby the reaction temperature can reach up to 1000 °C. Most zeolite syntheses however are performed at mild temperature and constant pressure. Hydrothermal and solvothermal syntheses reactions are more widely used and serve as the core of synthetic chemistry for the modification and preparation of porous materials (Kulpranthipanja, 2010). The physical and chemical properties of reactants are significantly changed under hydrothermal and solvothermal conditions (Cejka *et al.*, 2010; Xu *et al.*, 2007). The classic alkaline hydrothermal synthesis however, has been enhanced by using more complex treatments, which include an alkaline fusion step prior to hydrothermal treatment, the application of microwave-assisted zeolite synthesis and the synthesis of zeolites under molten conditions without any addition of water (Querol *et al.*, 1999; Rios *et al.*, 2008; Williams and Roberts, 2009; Rios *et al.*, 2012).

According to Davis and Lobo (1992), zeolite synthesis involves several reaction steps, molecular level self-organization, nucleation, aggregation, crystallization and growth (Wong *et al.*, 2001; Cejka *et al.*, 2010). De Moor (1998) provided important information towards the understanding of the initial formative stage of zeolite using powerful in situ characterization techniques.

Zeolite syntheses have been accounted for by two theories: (i) solid-solid transformation and (ii) solution crystallisation mechanism. In a solid-solid transformation mechanism, zeolite crystallization occurs directly from the amorphous gel to the crystalline phase (Zhdanov, 1971). However, the solution crystallization mechanism requires nuclei formation and growth in the liquid phase (Kwakye-Awuah,

2008; Occelli and Kessler, 1997). Equilibrium has been proposed to exist between the solid-gel phase and the solution, and that nucleation occurs in the solution. Whilst the gel dissolves continuously, the dissolved species are transported to the nuclei crystals in the solution. During zeolite formation by either of the two transformations, there is evidence to indicate that both types of transformation often times simultaneously. Crystallization of zeolites can occur in a single-solution system containing no secondary solid-gel phase (Kwakye-Awuah, 2008; Ueda and Koizumi, 1979; Brinker and Scherer, 1990).

However, zeolite synthesis is addressed in two major steps: (i) nucleation and (ii) crystallization.

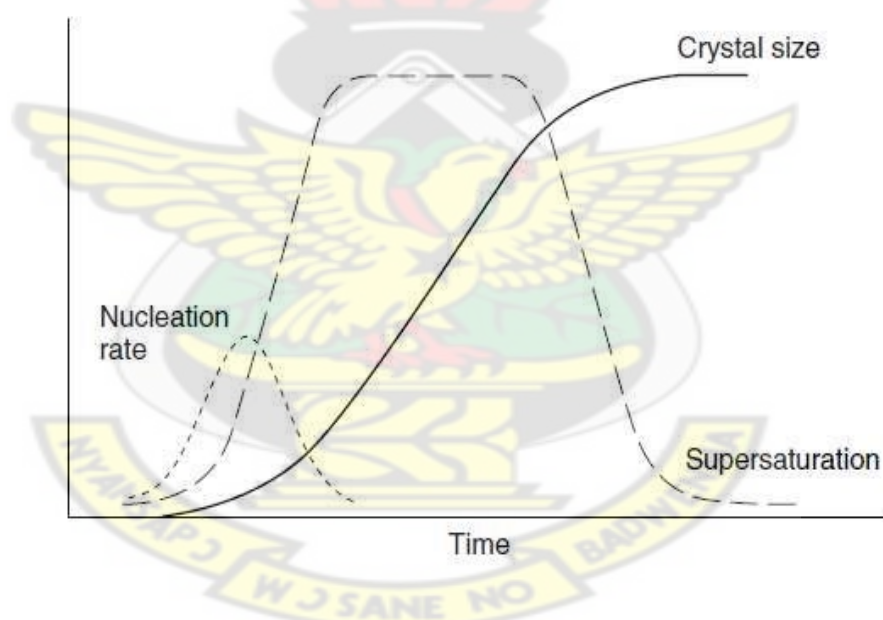


Figure 2.5: A representation of the nucleation, growth and supersaturation rates as a function of time (Cubillas and Anderson, 2010)

Nucleation

Nucleation is a process where small aggregates of precursors give rise to nuclei (embryos), which become larger with time (Szostak, 1989). Nucleation is the ratelimiting step and is consistent with studies that report addition of seed crystals

decrease the induction time (Singh, 2003; Auerbach *et al.*, 2003). Nucleation occurs usually at elevated temperatures. A gel is formed in the reaction process and the species in solution rearrange forming a continuous changing phase of monomers and clusters (Karge and Weitcamp, 2008). Crystallization occurs after nucleation (van Bekkum *et al.*, 2001). As shown in Figure 2.6, nucleation occurs after an induction time with the growth rate occurring steadily until all the nutrients are depleted. Supersaturation, is however not easily identified and other factors have been studied to have an effect on it.

Crystallization mechanism

Crystallization involves the formation of the zeolite crystals. A way to express zeolite crystallization is to view it as a process with multiple pathways. Pathways for a specific framework may be intertwined with another path that leads to a different zeolite framework (Singh and Dutta, 2003). However, the crystallization process according to Xu *et al.*, (2007), consists of four steps:

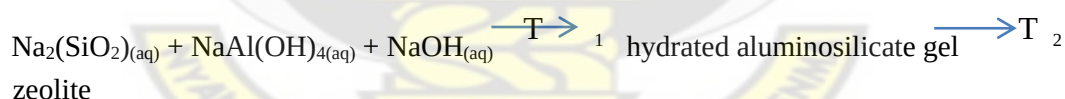
- condensation of polysilicate and aluminate anions;
- nucleation of zeolites
- growth of nuclei and
- crystal growth of zeolites (secondary nucleation).

Zeolite crystallization studies are important as a means of optimizing industrial production of zeolites and to acquire information about the mechanisms involved during nucleation and crystal growth (Ko and Ahn, 2004). The crystallization begins with an inhomogeneous gel, produced from a silica and alumina source. This is added to water under high pH conditions created by OH ion concentration. Factors such as overall composition, time, temperature, and other history-dependent factors are

parameters that affect zeolite crystallization (Ko and Ahn, 2004; Dyer, 1987; Kwakye-Awuah, 2008). A full understanding of the effects of each of these parameters on a particular zeolite is not known as it is a complicated process.

2.5.1 Factors Considered In Zeolite Synthesis

As cited in Kulprathipanja (2010) by Bedard (2010), the order of mixing the reagents into the final slurry or gel can be critical. One order of mixing may give coarse slurry while a reversed order of mixing of the same reagents may give a thick gel. Tamer (2006) also emphasized that the important point in the synthesis process is the preparation of the synthesis mixture. Variations that occur in process parameters change the product properties and the resultant products. The composition, the homogeneity of the synthesis mixture, chemical nature of the reactants, the template molecule, crystallization temperature and the period and pH of the system, recovery of final product (washing, drying and calcination) are some of the primary factors affecting the zeolite synthesis (Tamer, 2006; Xu *et al.*, 2007; Von-Kiti, 2012). A summary of the process can be represented as:



where T_1 is the aging temperature / time

T_2 is the crystallization temperature / time

2.5.1.1 Reaction or gel composition

A large number of silica and alumina oxide bearing components are used in zeolite synthesis. Silica source includes aqueous sodium silicate solution, water glass, precipitated, colloidal, or fumed silica, sodium metasilicate,

tetramethylorthosilicate, tetraethylorthosilicate and certain mineral silicates such as clays and kaolin (Taylor, 2007; Kulprathipanja, 2008). Alumina is obtained in the form of sodium aluminate, aluminium hydroxide, aluminum sulfate solution, pseudo boehmite, aluminum nitrate, and aluminum alkoxides. Additional alkali is added as hydroxide or as halide salts, while organic amines and/or alkylammonium species are added as neat amines, solutions of hydroxides, or halide salts.

In a general zeolite synthesis, sodium aluminate and sodium silicate solutions are prepared separately. The two solutions are mixed together following the recommended mixing order and agitation level, resulting in the formation of an initial zeolite gel. In some instances, this initial gel is aged at an intermediate temperature for some time to allow evolution of the gel chemistry and perhaps initial nucleation of the system. The reaction mixture is then digested at a higher temperature usually between 50 and 200 °C for a prescribed time until the desired level of product crystallinity is reached (Kulprathipanja, 2010).

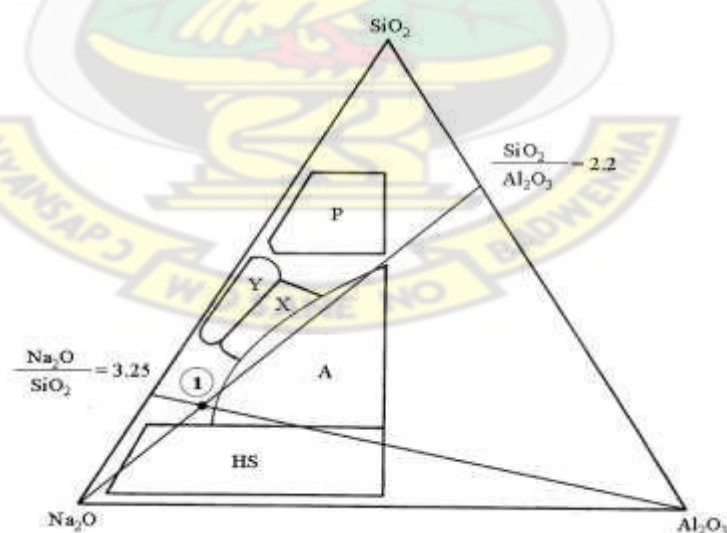


Figure 2.6: Composition diagram for a $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system showing the conditions necessary for the formation of certain zeolites (Garcia-Soto *et al.*, 2013)

The Si/Al ratio is a factor arising from the amounts of the reactants. This parameter

determines the structure and composition of the resulting product. There is however no quantitative correlation between the Si/Al ratio of the batch or starting composition and that of the product. The Si/Al ratio in the precursor gel is always greater than in the final product. Zeolite A (LTA) and hydroxysodalite (SOD) which have a low Si/Al ratios can be crystallized from low Si/Al ratio parent mixture with strong alkalinity. An opposite can be said for mordenite (MOR) which is synthesized from high Si/Al ratio with weak alkalinity (Xu *et al.*, 2007).

Another distinct feature of synthesis is the wide use of templates or directing agents. Structure Directing Agents (SDAs) or templates are used during zeolite synthesis to improve crystallization by influencing the structure of the specific zeolite targeted. Templating occurs when inorganic or organic molecule organizes the oxide tetrahedral into a particular geometric topology around itself and provides the initial building block for a particular structure during the gelation or nucleation process of zeolite synthesis (Kovo, 2011). The discovery of SDAs has aided in the preparation of nearly 100 different silicate frameworks. Activity of SDAs have been extensively studied (Rios, 2008). Some SDAs are reported to have similar structure as the final expected zeolite (Wong *et al.*, 2001).

2.5.1.2 Temperature

Temperature is an important parameter in zeolite synthesis during nucleation, aging and crystallization. It is known to have an effect on crystallization kinetics, zeolite phase, polymeric state of silicates, the dissolution and transformation of the gel. Temperature variations have been used to study the growth process, optimize yields, and alter morphology (Auerbach *et al.*, 2003). An increase in temperature results in an increase in the nucleation and the growth rate of crystals (Elliot and Zhang, 2005). The rate of crystallization has been studied to be directly proportional to temperature whilst

the rate of nucleation is inversely proportional to temperature. However, since crystallization and nucleation processes are carried out simultaneously for large periods of time, the operating temperature needs to be optimized for maximum yield (Kwakye-Awuah, 2008).

It has been observed that water or other solvents can be activated under high temperature conditions due to subcritical and super critical environments.

Zeolite synthesis is carried out at temperatures below 350 °C. A few exceptions however exist (Szostak, 1989). Crystallization performed at low temperature for a particular zeolite results in relatively long synthesis. It is therefore preferable to control crystallization temperature during hydrothermal synthesis. Studies have shown that zeolites A, Pc, X, Y, Chabazite and Gmelinite could be crystallized from the synthesis system $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ when crystallization temperature is in the range of 100 – 150 °C; small pore zeolites between 200 – 300 °C and very small pore zeolites like Analcime at temperatures above 300 °C (Xu *et al.*, 2007).

Low or ambient temperature aging can increase the rate of nucleation from the parent mixture implying a low temperature reaction. In some cases, aging is carried out at an intermediate temperature for a time to allow for evolution (Xu *et al.*, 2007; Kulprathipanja, 2010).

2.5.1.3 Time

Time factor is of importance in zeolite synthesis. This is because during crystallization, the parameter must be adjusted to minimise the production of other phases whilst also minimizing the time needed to obtain the desired crystalline phase (Georgiev *et al.*, 2009; Petrov and Michalov, 2012). Under different times, the same reactants may yield different products. The reaction gel is considered metastable

changes as time progresses forming the primary and secondary gel. Over time, the gel dissociates into two phases (liquid phase and crystalline solid phase) using density of the states in the mixture.

2.5.1.4 Aging

Aging is the period between the formation of a homogeneous gel and the start of crystallization. Zeolite aging influences the induction period, crystallization process and the purity of the final product as well as the type and sizes of the zeolite formed (Xu *et al.*, 2007). Several reports have affirmed the importance of aging on the nucleation and kinetics of zeolite growth. Hydrogel aging causes reduction of the reaction time and decreasing the size of the end product (Palcic *et al.*, 2012).

Aging increases the number of nuclei present in the synthesis mixture and the growth rate of crystals (Auerbach *et al.*, 2003). The aging process is necessary for the synthesis of both high and low silica zeolites. Depending on Si/Al ratios, the time needed for the formation of a stable gel may be long or short. As cited in Kovo (2011), aging of aluminosilicate gel at room temperature results in an increase in the silica to alumina ratio (Julide *et al.*, 2002). This is because it enhances the incorporation of more silica into the zeolite framework at low alkalinity levels. The study by Ginter and coworkers also confirmed that prolonged aging leads to insertion of additional silica into aluminosilicate solid and this increased the number of smaller nuclei reacting giving better and higher yield of zeolite NaY (Kovo, 2010). Thus the purpose of aging is to adjust synthesis conditions such as temperature and time to assist the transformation of the gel to the zeolite structure and speed up the nucleation process (Xu *et al.*, 2007).

2.6 Zeolites from Raw Materials

Synthetic zeolites are preferred over natural ones because they have less impurity and also because they can be tailored to suit the application for which it is intended. However, the cost of chemical reagents serves as a limiting factor by increasing cost of the synthesized product. Synthetic zeolites have been attempted from cheaper raw materials. Raw materials considered include clay minerals, diatomite, coal fly ash, volcanic glasses, perlite, high silica bauxite or shale, municipal solid waste incineration ashes and industrial slags. Several procedures and reports concerning these raw materials have been presented.

Chantawong & Harvey (2003) synthesized zeolite A from kaolin by hydrothermal treatment with various concentrations of NaOH solutions (0.5- 4 N) crystallized at 100 °C for 1 to 5 hours. Solid to liquid ratio was 1 gram metakaolin to 20 milliliter NaOH solution. The best crystallinity of zeolite was obtained at 2N NaOH solution with 4 hours.

Ugal *et al.*, (2010) studied the preparation of zeolite 4A from Iraqi kaolin. Metakaolinite was treated with 8M sodium hydroxide solution with a solid: liquid ratio of 1: 5 at 90 °C for 4 hours. The obtained zeolite powder was mixed with 15 % raw metakaolinite, and calcined for 4 hours at 500 °C. A number of studies have investigated the effects of varying the silica source while maintaining the other reaction parameters constant. It was observed that the use of different silica sources significantly influenced the synthesis results, in which products were obtained with different amounts of a zeolite impurity phase, different conversion rates and different particle sizes (Alves *et al.*, 2013).

Using coal fly ash, Querol *et al.*, (2007) synthesized zeolite Na-P1 with high ion exchange capacity using 2 and 3M alkali concentrations. Experiments were carried out

in a reactor with regulated temperature and pressure. Mainganye (2012) also obtained zeolite Na-P1 and zeolite A using South African fly ash via two methods. Parameters such as effect of stirring (speed and stirrer type), effect of aging and effect of fly ash composition were investigated in the study.

Successful zeolite synthesis from rice husk ash has been reported by Anggoro and Purbasari (2009) who obtained zeolite Y after extracting silica from calcined rice husk. Optimization conditions according to their study was using 20 % silicate to 10 % alumina and crystallizing for 48 hours at 100 °C. Bhavornthanayod and Rungrojchaipon (2009), synthesized zeolite A from rice husk ash using hydrothermal treatment with crystallization times between 15 minutes and 4 hours.

2.7 Bauxite

Bauxite is a generic term for a number of aluminium hydroxides like Gibbsite, boehmite and to a lesser extent diaspor, the main aluminous minerals. Bauxite is sometimes structureless, granular or earthy, pisolitic and concretionary, massive or stratified or largely pseudomorphous after the parent rock (Eggleton, 2001). It may occur in places as a derivative of the original rock or may be transported and deposited in a sedimentary formation. It is produced under subtropical to tropical climate conditions by prolonged weathering and leaching of silica from aluminium bearing rocks (Ruan, 2005)

Discovery of bauxite was done by Berthier in 1821 from Les Beaux south eastern France hence their name —*beauxite* which was changed to —*bauxite* by Sante-Claire Deville in 1861. Liebrich, in 1892 was the first to include lateritic weathering products rich in gibbsite in bauxite definition which he found on basalts of the Vogelsberg in Germany.

Laterites are found in tropical deposits consisting of hydrous aluminium and ferric oxides in residual soils. The term —lateritel was first introduced by F. Buchanan in 1807 to describe ferruginous earth rock an observation he made when travelling to India. Generally, laterites have a variable composition and purity but are usually valuable sources of aluminium and iron.

Bauxite is of twofold interest firstly due to its economic importance and secondly to the scope it affords for scientific exploration. With these two reasons, the vast application of bauxite in various industries can be emphasized.

2.7.1 Classification of Bauxite

Three different classification routes have been given to bauxite (Valeton, 1972):

1. On genetic principle
 - a. Bauxite on igneous rocks
 - b. Bauxite on sediments: Carbonate or clastic strata
2. According to geological age
 - a. Palaeozoic bauxite
 - b. Mesozoic bauxite
 - c. Cenozoic Bauxite
3. Based on mineralogical composition
 - a. Gibbsite
 - b. Boehmite
 - c. Diaspore

Table 2.1: Worldwide distribution of bauxite resources

North America	South America	Europe	Asia	Africa	Australia
USA	Brazil	Austria	China	Ghana	Australia
Jamaica	Venezuela	France	India	Guinea	
Haiti	Guyana	Germany	Indonesia	Mozambique	
Dominican Rep	Fr. Guiana	Hungary	Malaysia	Zimbabwe	
	Surinam	Italy	Philippines	Sierra Leone	
		Romania	Sarawak		
		Russia	Turkey		
		Spain			
		Fr. Yugoslavia			

2.7.2 Bauxite in Ghana

Ghana is a major producer of bauxite being the third largest producer in Africa.

Accordingly to the 2012 report on the mining industry by the Ghana Chamber of Mines, the Ghana Bauxite Company recorded a significant increase in bauxite shipments by 88% from a value of 400,069 tonnes in 2011 to 752,771 tonnes in 2012 (GCM.org). The report further stated that, the increase in volumes contributed to a significant increase in the corresponding mineral revenue by about 113 % from US\$ 13,406,433 the year earlier to 28,495,592 in 2012 (eiti.org; GCM report, 2012).

Bauxite was first discovered in Ghana by Sir Albert Kitson in 1914 with high grade deposits (61 % alumina, 9 % Fe₂O₃) at the top of Mt. Ejuanema, about 2600 feet high above sea level.

It is recorded that by the end of 1922 all the major Ghanaian deposits had been discovered. Several deposits have been landmarked in Ghana with varying grades of ore but with chief occurrences at Sefwi Bekwai (Awaso), Aya-Nyinahin, Kibi and at Mt. Ejuanema. However, exploration and mining works started in the 1940s. Awaso was chosen over the other towns for development because it had a favorable and convenient location for easier access to means of transport and its unsuitability for

human habitation. An open pit operation at Awaso was fully set up in 1943. Schellmen (1983) recorded shipping values of above 100,000 tonnes of ore each year by rail to the Takoradi harbour (Akabzaa, 2001). Operations in terms of mining and exporting are still ongoing. Ghana Bauxite Company (GBC) is the only company mining bauxite in the country at Awaso. Apart from the million tonnes (estimated 19 million tonnes) of bauxite at Awaso, there are large deposits of bauxite at Nyinahin and Kibi which remain unexploited (GEPC, 2010). Reserves at Nyinahin are estimated at about 168 million tonnes (Cooper, 1936).

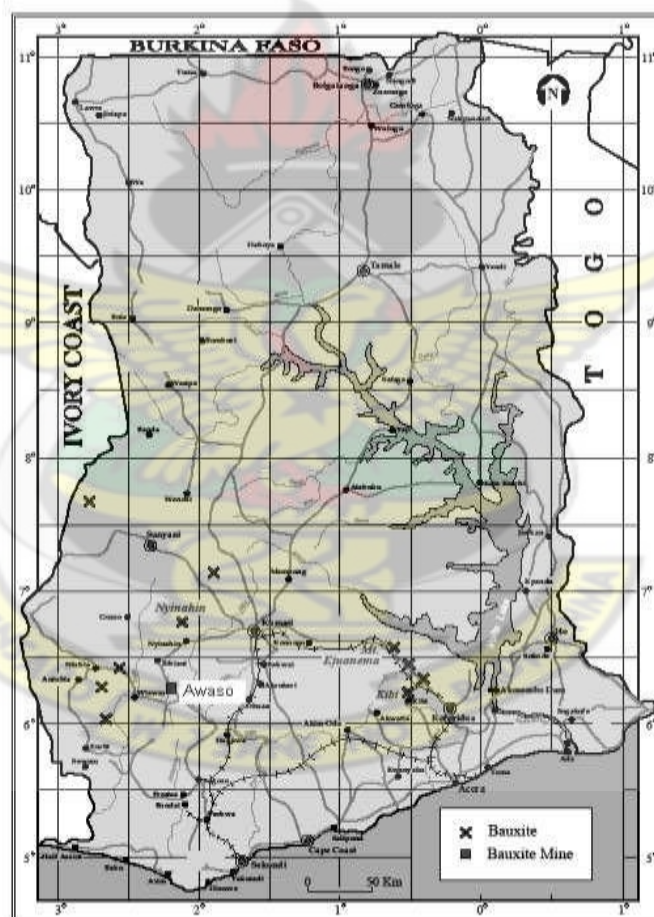


Figure 2.7: Ghanaian bauxite deposits and Awaso bauxite mine location (Momade, 2009)

Total bauxite resource in Ghana was estimated at 780 million tonnes by the International Bauxite Association in 1977 (Patterson *et al.*, 1986). Bauxite deposits at

Asafo occur in hills east of the Bia River, 65 km north of Wiawso and about 165 km along the road to Dunkwa. With a thickness of 7.5 – 11.5 m, it is estimated to contain 25 million tonnes of bauxite reserve. Mt Ejuanema bauxite deposits are at an altitude of about 750 m along the escarpment of the Kwahu plateau. The town is 3 km away from Nkawkaw and 180 km from the Tema Harbour. Deposits as estimated by Cooper (1936) was only about 4 million tonnes but of high grade. A road was constructed from the source to the Nkawkaw railway station in an attempt to mine the resource (Bracewell, 1962).

The bauxite deposits at the Kibi – Atewa range district are estimated to be between 152 – 180 million tonnes (Kesse, 1985). The deposits situated on the flat topped summits of low mountains, has the best grade bauxite. Low grade bauxite is also associated with some of the better deposits and occurs on the plateau (Patterson *et al.*, 1986).

The Awaso deposits have been reported to have very low iron content with some deposits having an iron content of 4.1 – 6 % as Fe₂O₃. This deposit was deemed a possible raw material for local production of alum. The mineralogy of Awaso bauxite as investigated by Trashliev and Stefanov (1974) found the bauxite to be chiefly gibbsite which occurred in both crystalline and cryptocrystalline forms.

Boehmite was found in marginal amount and mainly in a lighter colour.

Table 2.2: Chemical analysis of some bauxite deposits in Ghana (Acquah, 1999)

Composition	Nyinahin	Mt. Sup	Atewa	Sefwi Bekwai (Awaso)

SiO₂	2.5	0.64	1.85	0.40
Al₂O₃	44.5	60.68	50.7	61.08
Fe₂O₃	26.8	4.2	16.56	4.1
TiO₂	1-8	1.11	3.05	0.87
H₂O	-	32.17	-	32.23
CaO	-	0.33	-	0.25
V₂O₃	-	0.004	-	0.02
LOI	24.1	-	27.1	-

Lateritic bauxites generally reflect the chemical composition (including rare earth elements) of the original parent rock. The presence of reactive silica in bauxite, greater than 8 %wt (Al/Si = 6.25) renders it uneconomic. Other solid components of bauxite e.g. quartz, Fe hydroxides, TiO₂, etc. can dissolve with the aluminium phases. Large amounts of impurities if present in the bauxite ore can reduce the efficiency of the Bayer process significantly.

2.7.3 Mineralogy

The ore minerals in bauxite comprise gibbsite (Al₂O₃.3H₂O), boehmite (Al₂O₃.H₂O) and diaspor (Al₂O₃.H₂O). Although chemically both boehmite and diaspor have the same composition, boehmite is a secondary mineral formed due to dehydration of gibbsite and is softer than diaspor which is a product of metamorphism and is usually not suitable for metal recovery.

Other compounds or components deleterious to alumina production are clay (mainly kaolinite), iron oxides, quartz, titanium oxide, water and a variety of other minerals.

Bauxite occurs in a number of textural forms. They are usually the colour of iron oxides, red to brown or yellow but when organic material is present they may be black or dark green. It has a hardness of 1-3 on the Moh's scale and specific gravity of 2 – 2.5 (Gow and Lozej, 1993).

Table 2.3: Bauxite mineral properties (Habashi, 1980)

Property	Gibbsite	Boehmite	Diaspore
Formula	$\text{Al}(\text{OH})_3$	$\text{AlO}(\text{OH})$	$\text{AlO}(\text{OH})$
$\text{Al}_2\text{O}_3:\text{H}_2\text{O}$	1:3	1:1	1:1
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Specific gravity	2.42	3.01	3.44
Refractive index	1.568	1.649	1.702
Temperature of rapid dehydration	150 °C	350 °C	450 °C

2.7.3.1 Gibbsite

Gibbsite, also known as hydrargillite, is an aluminium hydroxide mineral of the oxides and the hydroxide group with structural formula $[\text{Al}(\text{OH})_3]$ or $[\gamma\text{-Al}(\text{OH})_3]$ (Kloprogee *et al.*, 2006). It is a monoclinic mineral usually located in areas with hot rainy climate and a dry period (Dominguez *et al.*, 2001). It is the chief mineral in tropical bauxites. Gibbsite can also be found in large amounts in various bauxite deposits differing in purity and extension.

Gibbsite structure is made up by the stacking of octahedral sheets of aluminium hydroxide. Each layer consists of octahedrally (six fold) coordinated Al^{3+} cations

sandwiched between two closed pack layers of OH⁻. Within the gibbsite structure, two thirds of the octahedrally coordinated sites between the oxygen layers are occupied by cations. Regarded as being built of octahedra linked laterally, the layers are shared at the edges. The network formed may be described by an orthogonal (pseudo-hexagonal) with cell parameters $a \sim 8.6 \text{ \AA}$ and $b \sim 5 \text{ \AA}$ ($a \sqrt{3}$) (Ruan, 2005).

The oxygen layers in gibbsite are in the sequence of hexagonal close packing ABBAABBA.... In the ideal structure of gibbsite, oxygens at the bottom of the layer lie directly above oxygens at the top of the layer below as seen in Figure 2.8.

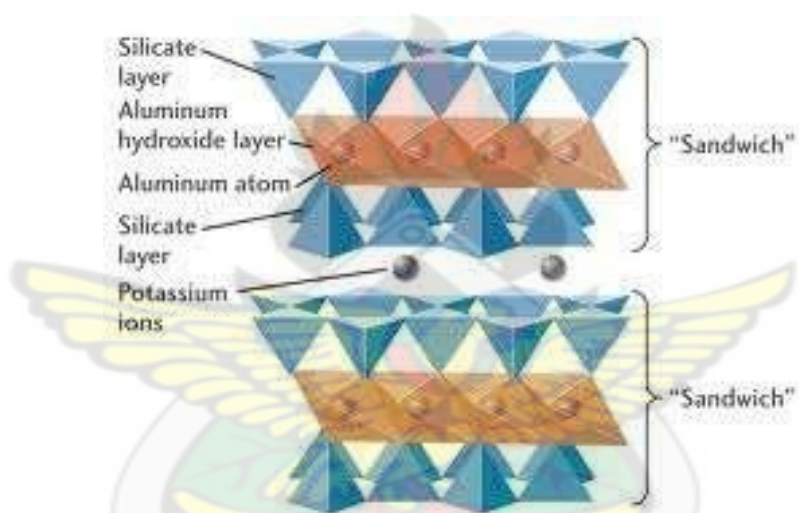


Figure 2.8: A diagram showing the gibbsite structure

Because Al is a trivalent cation, each of the hydroxyl is bonded to only 2Al and thus only two thirds of the available octahedral sites are occupied.

Heating gibbsite produces γ - alumina usually with boehmite formation as an intermediate stage. Gibbsite is the stable form at lower temperature in the $\text{Al}_2\text{O}_3 - \text{H}_2\text{O}$ system; at higher temperatures, diaspore is the stable phase. However, boehmite exist in a metastable form at about 450°C with corundum being the stable phase.

2.7.3.2 Diaspore

Diaspores are formed with light metamorphism of boehmite. It is dimorphous with boehmite, i.e. has the same chemical composition but different crystal structure. It does not contain a hydroxyl group (OH) but has cationic hydrogen (H^+) in twofold coordination with the oxygen atoms (Figure 2.9). They are sometimes gray or yellowish white in colour and have either a transparent or semi transparent appearance. Diaspore, a minor constituent in many bauxites has the formula: $\alpha-AlOOH$. Only few deposits of large amounts of diasporite are known. Genesis of diasporite is usually favored by thermal action or low metamorphism .

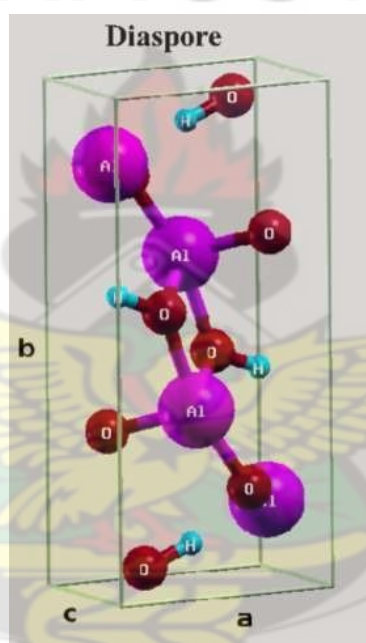


Figure 2.9: Structure of diasporite

2.7.3.3 Boehmite

With a formula $\gamma-AlOOH$, boehmite deposits are situated in mostly subtropical regions. Boehmite particle size is smaller compared to that of gibbsite (Kloprogge *et al.*, 2006). It is usually found in association with gibbsite and diasporite.

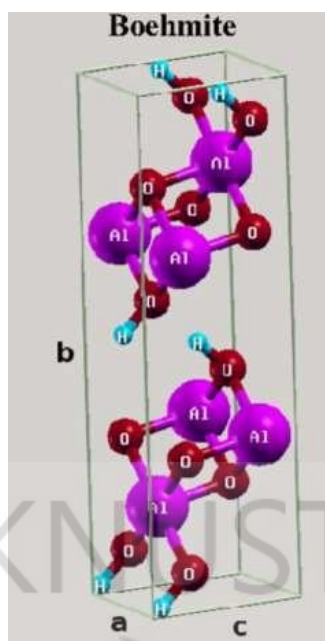


Figure 2.10: Structure of boehmite

Boehmite is isostructural with lepidocrocite (γ – FeOOH) (Ruan *et al.*, 2002). The structure of boehmite is made up of layers of oxygen in octahedral sequence with partially filled with Al cations (Figure 2.10). The sheets comprise of chains of octahedral. The three oxygen layers are stacked in a way that the double octahedral layer is in cubic close packing (Ruan, 2005; Klopogge *et al.*, 2006). A slight variation is observed in boehmite and diaspor. The differences in oxygen packing are coherent with the nature of the two polymorphs of AlO(OH) upon dehydration in that diaspor produces α -alumina (trigonal) and boehmite produces γ – alumina possessing the cubic structure of a spinel (Ruan, 2005).

The stacking of the layers has the hydroxyl groups of one layer are located over the depression between the hydroxyl groups in the adjacent layer (Klopogge *et al.*, 2006).

2.7.4 Alumina Production

Practically, most of the alumina produced commercially by bauxite is obtained via a process patented by Karl Joset Bayer in the year 1888. During the Bayer process, the

aluminium-bearing minerals in bauxite -gibbsite, boehmite and are diaspoire are separated from the insoluble components (mostly oxides) by dissolving them in a solution of sodium hydroxide (NaOH) at high temperature and pressure and then separating the resulting sodium aluminate (NaAlO_2) solution.

Alumina extraction from bauxite by the Bayer process requires an efficient digestion process. Bauxite digestion is influenced by temperature-pressure conditions, the liquor concentration, and bauxite mineralogy and charge quantity. The efficiency of the Bayer process to a large extent depends on the digestion process.

Parameters for digestion and precipitation depend on the nature of bauxite. When bauxite is predominantly gibbsite, the digestion can be carried out relatively low temperature- atmospheric digestion at 105 °C (low pressure digestion at 140 – 145 °C). For boehmite bauxite, high temperature digestion at 240 -245 °C is preferred. High pressure digestion (235 -245 °C) is used for boehmite and diaspoire. It has been observed that, among the alumina – bearing minerals in bauxite, gibbsite, has maximum solubility in caustic soda, followed by boehmite and then diaspoire.

Bauxite containing 8 % - 15 % reactive silica maybe processed by either a soda sintering process that is used directly on the high – silica bauxite or by a combination of Bayer – sinter process. Red mud is the final waste of the Bayer process. Red mud is usually the solid waste from the caustic soda leaching process. The red mud usually contains large quantity of alkali and aluminosilicate so it's potentially available to prepare inorganic polymeric materials by geopolymerisation process (Ye *et al.*, 2012).

Red mud can be permanently disposed off or used:

- in ceramic industry as an additive to make special ceramics,
- dewatered (ferro-alumina) as a raw material in cement manufacture,
- leached to produce TiO_2 ,
- in cement industry (Lafarge plants),

- in building material industry as a raw material in manufacture of building and pavement blocks and road surfacing,
- micronized and calcined as a pigment,
- in agriculture to improve soil quality, spread on the ground to lower the rate of phosphorus leaching by rainwater, etc. (Cablik, 2007).

2.8 Clays

Clays are layered aluminosilicates which have strong bonds within layers but weak bonds between layers (Fahrenholtz, 2008). They are fine grained (particle size $\sim 2 \mu\text{m}$) and vary greatly in their water and impurities in their composition. They are plastic when wet and hard when fired. Clay minerals are used widely for decorative and industrial purposes. These applications arise from the fact that they are locally available, fairly easy to acquire, harmless to human health, stable and recyclable (Savic *et al.*, 2014).

Clays are classified into several groups, kaolinite being the most common. Other groups include montmorillonite, illite, smectite, talc and vermiculite. Each group differs from the other in terms of structural layers arrangement when compared to each other observed through X-ray powder diffraction and their composition (Brindley, 1955; Murray 2006).

2.8.1 Kaolinite

Kaolin is a type of clay whose major mineral component is kaolinite. Kaolinite has a chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. In mineral form, it is expressed as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. They can also contain appreciable amounts of other clay minerals such as quartz, mica, feldspar, illite, hematite and heavy metals such as titanium oxide (TiO_2) and iron oxide (Fe_2O_3) as well as other potential coloring impurities (Fahrenholtz, 2008). It has a hardness of 1.5 on the Mohs' scale.

Kaolinite has a structure built of SiO_4 in the tetrahedral sheet bonded to similar $\text{Al}(\text{OH})_4$ octahedral sheet to form the silica gibbsite layer (S/G layer). The repetition of the layer in the resulting structure comprises alternating octahedral (O) and tetrahedral (T) sheets in stacking order or by isomorphous substitution of cations e.g. Mg^{2+} and Fe^{3+} into the octahedral sheets (Shackelford and Doremus, 2008). The sheets of kaolinite are a single T and O i.e. 1:1 layer which are continuous in the *a*- and *b*-axis directions and are stacked one above the other in the *c*-axis (Figure 2.11) (Murray, 2006). A unit layer is about 7.13 Å thick and has a triclinic crystal system.

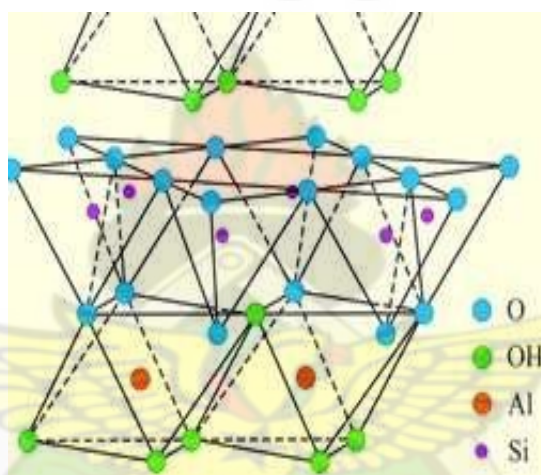


Figure 2.11: Structure of kaolinite showing the layers

Like all clays, bonding within each repeat unit is covalent (strong) whilst bonding between units is relatively weak allowing the layers to separate in excess of water or under mechanical load.

Kaolin, in the natural state is less reactive i.e. chemically inert over a pH range of 4.9, low electrical and heat conductivity, hydrophilic and easily dispersed in water (Murray, 2006). It is made reactive through dehydroxylation or a process called metakaolinization. Metakaolinization implies the removal or loss of the Hydroxyl group. When kaolin is heated, a series of transformations occur. This is accompanied by the rearrangement of the octahedral layer to the tetrahedral orientation in the calcined clay (Kovo and Edoga, 2005). Calcination has been undertaken at different

temperatures and different times. The process occurs between the temperatures of 550 – 600 °C. The metakaolin phase is disordered and metastable. When metakaolin is heated to 935 – 950 °C, a more stable phase is achieved. Aluminium-silicon spinel is produced. Also known as γ -alumina, the phase yields mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) at 1050 °C.

Some major applications of kaolin include the production of the following: paper, paint, ceramics, rubber, ink, plastics, fiberglass, Portland cement and as a catalyst. Minor uses however, include cosmetic production, use in adhesive, chalk and crayons, enamels, fertilizer, fluoride adsorption, food additives and medicinal and pharmaceutical purposes.

2.8.2 Deposits in Ghana

The Geological Survey Department of Ghana, by 1985 had conducted extensive study of clay deposits and discovered that clay exists in commercially exploitable quantities in most districts in the country (Kesse, 1985; Sarfo-Ansah, 2010). An estimate of between 500 – 600 million cubic tonnes of clay resource has been recorded in Ghana (Hammond, 1997). Towns identified with deposits include: Abonku, Anfoega, Ekon, Fomena, Kibi, Kpeve, Saltpond, Teleko Bokasso and Wassa (Figure 2.12). Major uses of the resource in Ghana are for brick production, tiles and medicinal purposes (Kokoroko, 1993; Hammond, 1997; Mohammed, 2011).

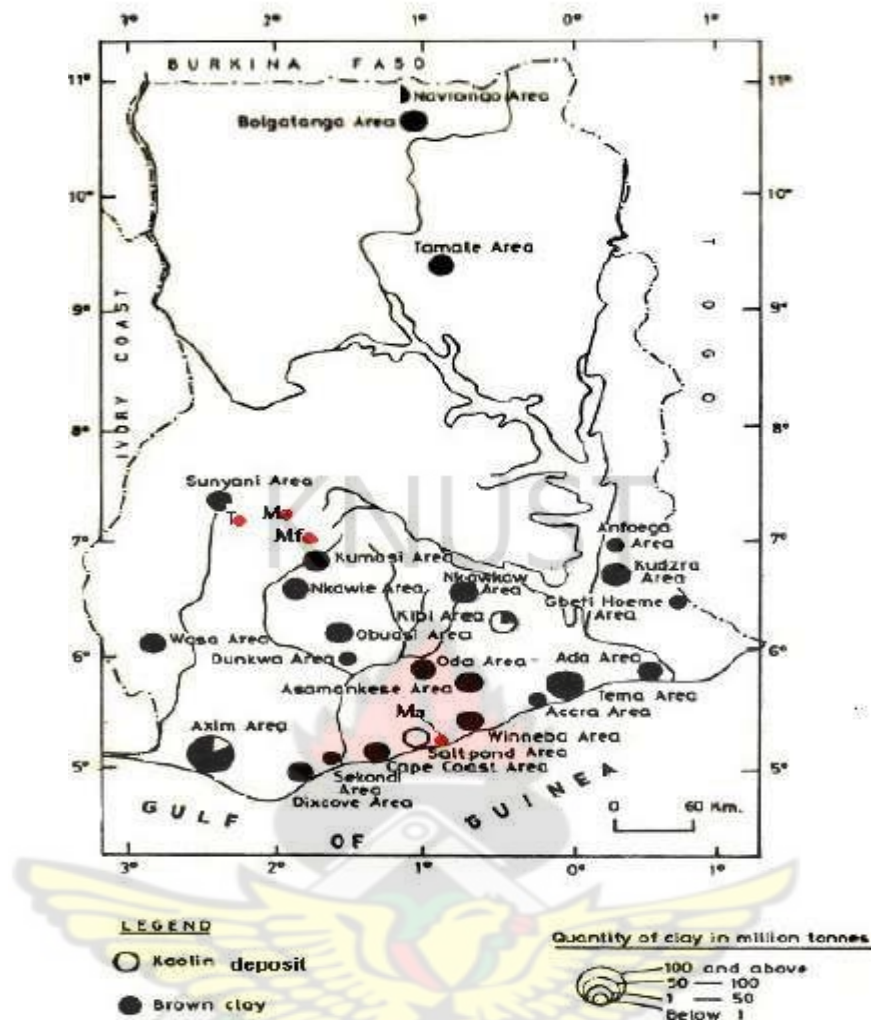


Figure 2.12: Map of Ghana showing clay and kaolin deposits

2.8.3 Synthesis of Zeolites from Kaolin

Metakaolin is observed to be a defective phase. Breck (1974) stated that it is known to be more reactive and hence possible as a starting material for the synthesis of zeolite. The primary raw materials used to manufacture zeolites are silica and alumina and these are among the most abundant mineral components on earth (ausihem.org). The zeolite formation process occurs through hydrothermal crystallization methods and this also includes the application of suitable pretreatments such grinding, acid washing, calcination and fusion with additives of the starting materials (Shoumkova, 2011).

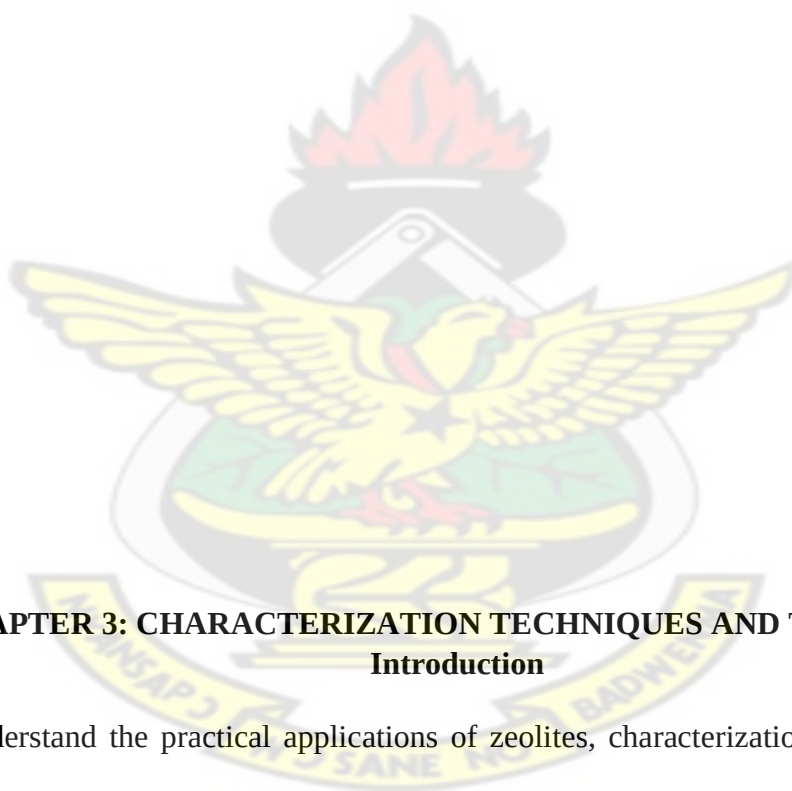
Successful zeolite syntheses from kaolin and kaolinitic materials have been reported in recent years and in different locations of the world. Some include studies and the types of zeolite include: zeolite A (Kwakye-Awuah *et al.*, (2014); Zhu *et al.*, (2011); Kovo and Holmes, (2010); Cristobal *et al.*, (2010); Rios *et al.*, (2009); Mostafa *et al.*, (2011); Covarrubias *et al.*, (2006); Chantawong and Harvey (2003); Chandrasekhar (1996); Murray *et al.*, (1992)), zeolite X (Kwakye-Awuah *et al.*, (2014); Wibowo *et al.*, (2010); Rios *et al.*, (2010); Mohammed *et al.*, (2010); Covarrubias *et al.*, (2006); Chandrasekhar and Pramada, (2004); Akolekar *et al.*, (1997)), zeolite Y (Liu *et al.*, (2003)), zeolite P (Meftah *et al.*, (2009); Rios *et al.*, (2009)) and zeolite N (Mickannon *et al.*, (2010)).

Rios *et al.*, (2012) synthesized zeolite X and P with the addition of extra silica to the procedure. They also synthesized Sodalite and Cancrinite (Rios *et al.*, 2012). Numerous variations and protocols have also been used to achieve zeolites. Rees and Chandrasekhar (1993) synthesized zeolite using hydrothermal reaction in fluoride media. Zeolite production from waste kaolin was performed by Alberti *et al.* (1994). The difficulty in finding natural kaolins free of impurities has been reported by Basaldella *et al.*, (1998). Basaldella *et al.*, (1998) stated that the concentration of impurities in raw kaolins used in the synthesis of zeolite A reduces the established specifications required for detergent production such as crystallinity, particle size distribution, exchange capacity and whiteness.

Murat *et al.*, (1992) proposed that the kinetics of zeolite crystallization from kaolin can be affected by Fe impurities existing in the clay sample. Further investigations performed by Madani *et al.* (1990) stated that the Al co-ordination number in the raw material played an important role in zeolite conversion from kaolins (Basaldella,

1998).

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CHAPTER 3: CHARACTERIZATION TECHNIQUES AND THEORY 3.1

Introduction

To understand the practical applications of zeolites, characterization is required to serve as an efficient tool to provide understanding into the underlying principles of operation and properties of zeolites.

This chapter presents the techniques that are used in the study with particular emphasis to their theory, advantages and distinctiveness of each in describing zeolites. Explicit understanding of the ion exchange and adsorption properties are also discussed.

3.2 Characterization Techniques

Characterization is essential in order to empathize the phenomena occurred in any system. The characterization of zeolites provides information about the physicochemical properties, its crystal structure and morphology. A number of techniques are available for characterization. The following techniques relative to the study are presented: X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive x-ray analysis (EDX) and Fourier Transform Infra-Red spectroscopy (FTIR).

3.2.1 X-Ray Diffraction (XRD)

The properties of materials are directly related to their crystal structure. Significant difference exists between crystalline and non-crystalline materials even with the same composition. X-ray diffraction is used for structure determination of crystalline materials, its purity, crystallite size and crystallinity of the sample. It also provides information about the quantitative determination of relative amounts of compounds in the crystalline zeolite (Ewing, 1985; Kulprathipanja, 2010). Information provided by XRD can be used for phase identification of known phases by comparing them to a database of previously indexed patterns maintained by the International Centre for Diffraction Data (ICDD). It can also be used for structural refinements on previously collected unknown phases.

XRD is a probing technique which gives information about the relative positions of atoms in the structure and hence determines the unit cell parameters and thus its unit cell volume. Powder X-ray diffraction measurements use $\text{CuK}\alpha$ radiations.

3.2.1.1 Diffraction principle

A monochromatic beam of X-rays strikes a finely powdered sample that, ideally, has crystals randomly arranged in every possible orientation. In such a powder sample, the various lattice planes are also present in every possible orientation. For each set of planes, some crystals must be oriented at the Bragg angle, θ , to the incident beam and thus, diffraction occurs for these crystals and planes (West, 1987). The incident x-ray photons on the sample are scattered. The scattering can either be coherent (in phase) – no change in the energy and wavelength of the outgoing photon (same as incident photon) - or incoherent (out of phase) – produces a change in wavelength and energy. The intensity of the emergent rays is recorded as a function of the deflection angle.

The X-ray diffraction technique is based on the Bragg's Law. The Bragg approach to diffraction is to regard crystals as built up of layers or planes such that each acts as a semi-transparent mirror (West, 1987). Some of the X-rays are reflected of a plane with the angle of reflection equal to the angle of incidence, but the rest are transmitted to be subsequently reflected by succeeding planes as in Figure3.1.

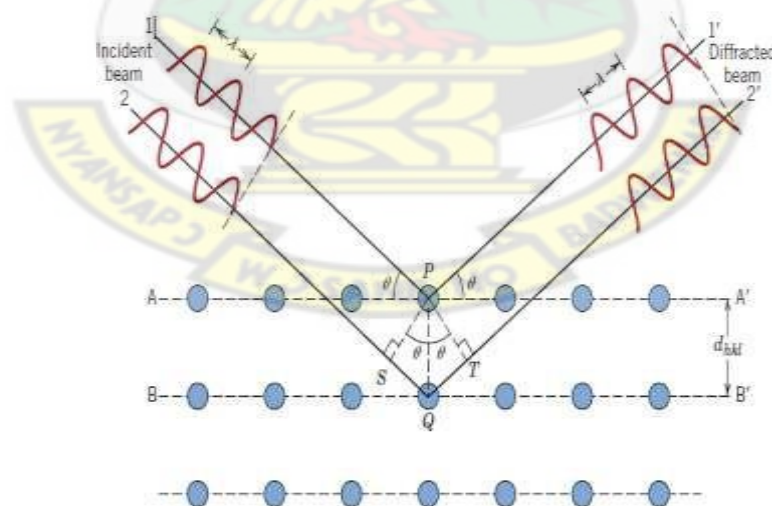


Figure 3.1: Diffraction of x-rays by planes of atoms showing Bragg's angle (Callister, 2006)

The general relationship between the wavelengths of incidence X-rays, angle of incidence and spacing between the crystal lattice planes of atoms is known as Bragg's law:

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.1)$$

Where:

n is an integer, λ is the

wavelength d is the

lattice spacing and θ is

the deflection angle

For crystals with cubic system, having lattice parameters $a = b = c$ and angles

$\alpha = \beta = \gamma = 90^\circ$, the interplanar spacing d and lattice parameter can be expressed as:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3.2)$$

For orthorhombic unit cell, the lattice parameters $a \neq b \neq c$ and angles $\alpha = \beta = \gamma = 90^\circ$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (3.3)$$

However, for a tetragonal unit cell, lattice parameters $a = b \neq c$ and angles $\alpha = \beta = \gamma = 90^\circ$

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (3.4)$$

XRD powder patterns can also be used to estimate the crystallite size in a powder sample. The particle size has been observed to decrease with broadening of the reflections in the XRD pattern. This correlation is used in Scherrer's equation to calculate the particle size.

$$\tau = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (3.5)$$

Where K is the shape factor (K=1 for spherical particles) is the X-ray wavelength

β is the line width at half the maximum (FWHM) and

θ is the Bragg's angle

Determination of particle size using Scherrer's equation can be affected however by multiple factors beside the crystallite size that contributes to broadening of the reflections in XRD patterns. Scherrer's equation underestimates the particle size of partially intergrown crystallites when compared with electron microscopy analysis.

The crystallinity of a sample can also be deduced from the XRD pattern. Materials with an amount of amorphous impurity will have lower reflection intensities relative to a purely crystalline material. To determine the crystallinity of such, XRD can be collected for the analysed sample and for a highly crystalline external reference sample of the same crystal structure. After a background correction, the intensities or areas or similar reflections of the analysed sample (I_s) and the reference (I_{ref}) can be compared and relative crystallinity, (C_{rel}) calculated (Petushkov, 2011):

$$C_{rel} = \frac{I_s}{I_{ref}} \times 100\% \quad (3.6)$$

In estimating zeolite crystallinity (% crystallinity), the sum of integral peak intensities of the synthesized zeolite sample is compared to the sum of integral peak intensities of the reference zeolite (ASTM, 2003).

3.2.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy provides information about the surface morphology. In scanning electron microscopy, the focused electron beam scans the specimen surface and backscattered or secondary electrons are then amplified and collected at the detector (see Figure 3.2). The electron gun generates a beam of electrons from a cathode or filament usually made of tungsten. The electrons escape at high voltage from the filament. The final size of the beam is controlled by the electron lenses. Scan coils make the beam scan over the sample or target. When the electrons hit the target, they collide with electrons in the inner atomic shells. Back scattered and secondary electrons that escape from the sample are detected. If there is no detection, the image will be black (Ohrman, 2000; Willis *et al.*, 2002).

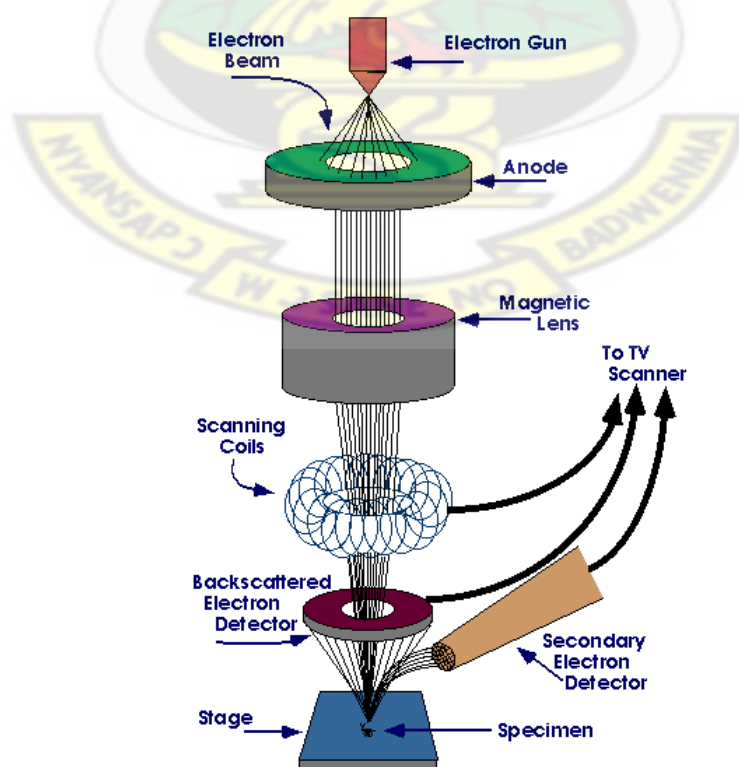


Figure 3.2: Schematic diagram of SEM (<https://www.purdue.edu/>)

The surface of zeolite is nonconductive. It consists of atoms with low atomic numbers and it tends to collect the charge acquired from the electron beam. This results in scanning faults and image artifacts. Hence zeolite samples are sputter coated with gold, carbon or platinum in a thin layer (100 – 1000 Å) of the conductive material. The presence of gold clusters on the zeolite surface may make the surface morphology study more difficult in the case of nanocrystals. A balance between the surface conductivity and the conductive film thickness is usually considered (Petushkov, 2011; Panchal, 2011).

The SEM has several advantages over traditional microscopes. The advantages of SEM include high-resolution imaging, greater depth of field and much greater magnification which provides textural information. Since SEM uses electromagnets rather than lenses, the degree of magnification can be easily controlled.

3.2.3 Energy Dispersive X-Ray Spectroscopy (EDX)

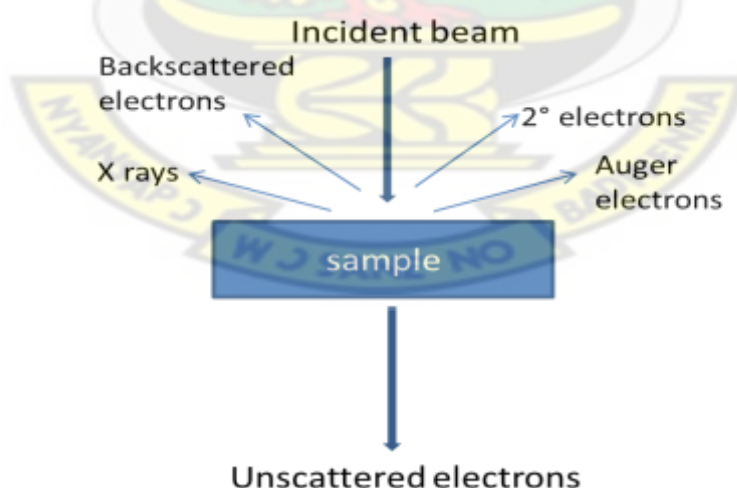


Figure 3.3: Interaction of an incident beam with sample with emission of x-ray photons

EDX is used in conjunction with a scanning electron microscope (SEM) (Kwaky-

Awuah, 2008). It provides chemical analysis in area as small as 1 μm . It allows for additional advantage of being able to obtain the elemental composition of small objects or surfaces. The EDX works by detecting x-rays that are produced by a sample placed in an electric beam (Marshall *et al.*, 2015). An incident beam excites an electron in an inner shell, ejecting it from the shell while creating an electron hole in the electron's position. An electron from an outer, higher-energy shell then fills the hole. An energy difference is created between the higher-energy shell and the lower energy shell. The excited electric beam subsequently discharges the excess energy in the form of x-rays. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. The energy of the x-ray is a characteristic of the atoms that produced them, forming peaks in the spectrum. Individual elements may have one or more peaks associated with them.

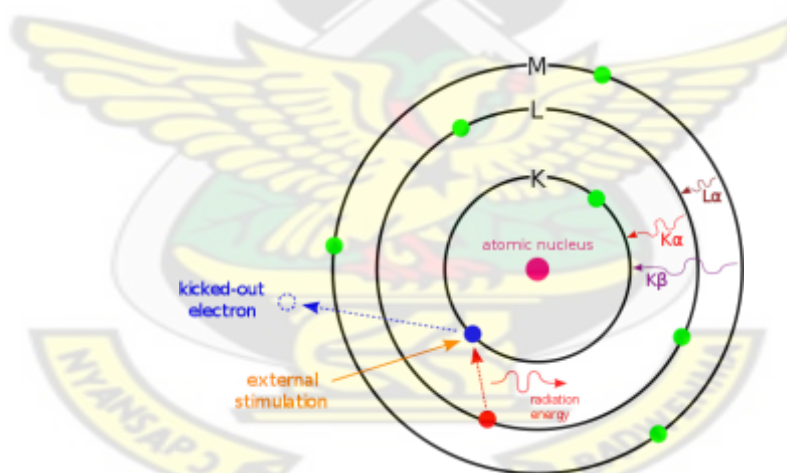


Figure 3.4: An image of electrons in the different energy levels (Muso, 2007)

This method is generally used for qualitative analyses of sample composition as the errors can be large for light atoms. In addition, emission from different shells of different elements can overlap creating a problem for some samples.

3.2.4 Fourier Transform Infra-Red Spectroscopy (FTIR)

Infrared spectroscopy as cited by Panchal (2011) is non-destructive technique for material analysis which has been used in the laboratory for several years. Infrared spectroscopy deals with the interaction of infrared radiation with matter as a function of photon frequency. FTIR provides specific information about the vibration and rotation of the chemical bonding and molecular structures, making it suitable for investigating organic materials and some inorganic materials. An infrared spectrum is the fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations existing in the bonds of the atoms which make up the material (Caltech.edu). Since each material comprises a unique combination of atoms, two compounds cannot produce the exact same infrared spectrum. Infrared spectroscopy therefore produces a positive identification (qualitative analysis) of every distinct material. The peak size in the spectrum is a direct representation of the amount of material present. Infrared is an ideal tool for quantitative analysis due to the use of recent software algorithms.

The IR region in the electromagnetic spectrum (Figure 3.5) is mostly divided into three smaller regions namely: near - infrared ($400 - 10 \text{ cm}^{-1}$), mid - infrared ($4000 - 400 \text{ cm}^{-1}$), and far - infrared ($14000 - 4000 \text{ cm}^{-1}$). Infrared photons have enough energy causing groups of atoms to vibrate with respect to the bonds that connect them. Similar to electronic transitions, these vibrational transitions correlate to specific energies, and molecules absorb infrared radiation only at particular wavelengths and frequencies. When exposed to infrared radiation, chemical bonds vibrate at characteristic frequencies. This is because the radiations are absorbed at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency gives a spectrum that can be used to identify functional groups and compounds.

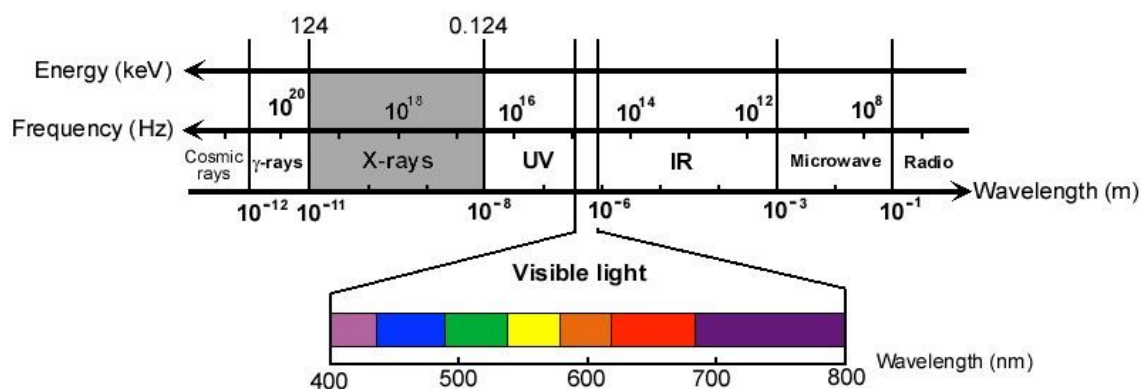


Figure 3.5: The electromagnetic spectrum

Impurities are also able to produce their own unique bands in infrared region. Concentration of impurities and their bonding with the host materials are determined by spectral measurements. To make identification, decoding or translating the individual frequencies is required as the measured interferogram signal cannot be interpreted directly (Caltech.edu). This is accomplished using a well-known mathematical technique called the Fourier Transform. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

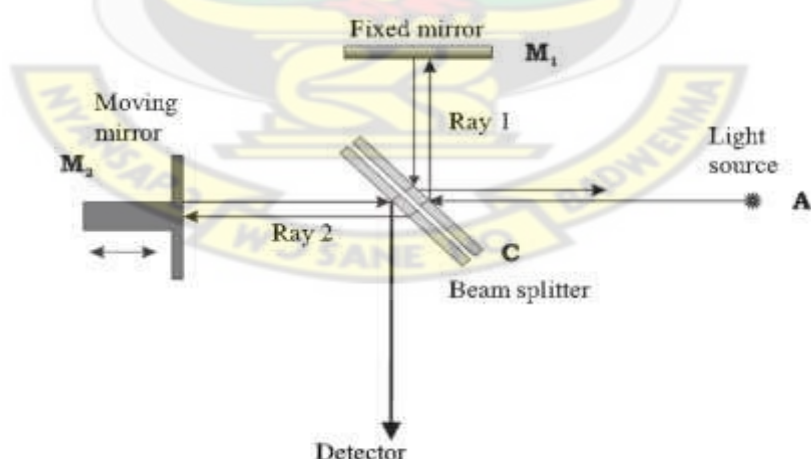


Figure 3.6: A representation of the Michelson interferometer

The Michelson interferometer serves as the basis of a FTIR spectrometer where one of the two mirrors is fixed and a second one moves intermittently with constant

velocity (Figure 3.6). The interferometer comprises of two mirrors, a detector and a beam splitter. Radiation from the IR source is directed to the beam splitter which splits the beam into two parts. The reflected part is directed to the fixed mirror and the transmitted part to the moving mirror which moves to and fro. An interference pattern is created when the two beams combine. The combination is constructive (when they arrive at the detector in phase) and destructive (when they arrive out of phase due to the moving mirror). The interference is called the interferogram is recorded at the IR detector which counts the incoming signal dependent on the optical path difference and converts it to a digital signal (analogue-to-digital converter) (Sampson, 2010.)

To achieve the infrared spectrum, the detector signal is transmitted to a computer which carries out the Fourier transformation which converts the interferogram into a single beam spectrum (intensity as a function of wavenumber or wavelength). A reference or background single beam spectrum is collected without the sample. The sample single beam spectrum is then compared to the background single beam spectrum to produce a transmittance spectrum.

The transmittance spectrum can be converted to absorbance by taking the negative log₁₀ of the data points. Transmittance (T) is the ratio of radiant power (I) transmitted by the sample to the radiant power (I_0) incident on the sample.

Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance.

$$A = \log_{10} \frac{1}{T} = -\log_{10} T = -\log_{10} \frac{I}{I_0} \quad (3.7)$$

The source of light used in a Fourier transform spectrometer is polychromatic. Each frequency gives rise to a cosine shape signal and the resulting interferogram is the sum of all the intensities.

Mathematically, the detector signal and the interferogram are related to the spectrum by:

$$I(x) = \int_{-\infty}^{\infty} B(\nu) \cos(\pi \nu x) d\nu \quad (3.8)$$

Where $I(x)$ is the intensity of the beam measured at the detector and x , the displacement of the movable mirror. $B(\nu)$ represents the intensity of the spectrum as a function of the wavenumber ν . The spectrum is obtained through the inverse Fourier transform of the above relation and is given by:

$$B(\nu) = \int_{-\infty}^{\infty} I(x) \cos(\pi \nu x) dx \quad (3.9)$$

FTIR method is used in obtaining information about the structure, channel size and cation substitution in the tetrahedral sites of the zeolite minerals. Corresponding infrared bands to certain structural groups in the various framework is used as its interpretation (Breck, 1974). The FTIR measures vibrations caused by internal stretching of the framework tetrahedra and vibrations related to the external linkages between the tetrahedral. The bands occurring in the FTIR spectra of zeolites can be characterized as follows:

Some bands are attributed to presence of zeolite water. The three typical bands observed are as follows: the broad band, characteristic of hydrogen-bonded OH to oxygen ions at about 3440 cm^{-1} , the sharp band typical of isolated OH stretching vibration at 3619 cm^{-1} , and the usual bending vibration of water at 1640 cm^{-1} (Cansever Erdogan, 2011). Bands due to pseudo-lattice vibrations are found in the region $500\text{--}800 \text{ cm}^{-1}$. These vibrations are insensitive to the nature of the channel cations, as well as to the Si/Al ratio (Cansever, 2004).

Table 3.1 Infrared Assignment table for zeolites (Mozgawa, 2000)

Infra-red Assignment	Theoretical band range wavenumber (cm^{-1})
----------------------	--

Internal vibrations due to asymmetric stretching	1250 - 950
External T–O linkages due to asymmetric stretching	1150 - 1050
External T–O linkages due to symmetric stretching	820 - 750
Internal vibrations due to symmetric stretching	720 - 650
External T–O linkages due to double ring	650 - 500
Internal vibrations due to T – O bending	500 - 420
External T–O linkages due to pore openings	420 - 300

3.2.5 Thermogravimetric Analysis (TGA)

Thermo gravimetric Analysis is an analytical method which measures the changes in weight of a material as a function of time or temperature beneath a controlled atmosphere such as air, nitrogen, oxygen, or specialty atmosphere. The main uses of this technique include measurement of thermal stability materials, moisture and solvent contents and the individual composition of substances in a material.

Applications of TGA include investigations into residual solvent content, carbon black content, decomposition temperature, moisture content of organic and inorganic materials, oxidative stability, performance stability, etc.(photometrics.net).

3.2.5.1 Operational principle

Thermal analysis usually involves a group of techniques in which a property or more of the material is evaluated whilst subjecting it to a controlled temperature programme.

Variations to the programme can include

- Constant heating or cooling rate ($dT/dt = \square$)
- Holding the sample isothermally ($\square = 0$)
- A modulated temperature programme may be used where a sinusoidal or other alteration is superimposed onto the underlying heating rate (Haines, 2002).

The technique is carried out by gradually elevating the temperature of a sample in a furnace whilst its weight is measured on an analytical balance that is situated outside the furnace as depicted in Figure 3.7. Mass loss is observed if a volatile component is present in the sample being studied. TGA records change in mass from dehydration, decomposition, and oxidation of a sample with time and temperature.

Typical thermogravimetric curves are provided for specific materials and chemical compounds due to unique sequence from physicochemical reactions occurring over specific temperature ranges and heating rates. These unique characteristics are related to the molecular structure of the sample. The weight of the sample is plotted against the temperature or time to illustrate thermal transitions in the materials.

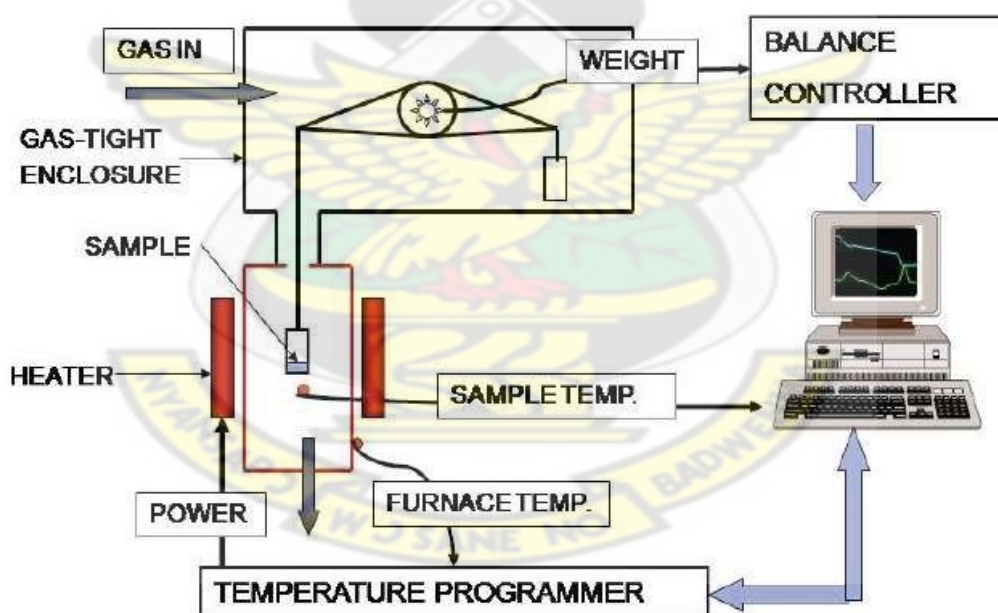


Figure 3.7: A schematic representation of thermogravimetric analyser

3.3 Ion Exchange

The ion exchange process is a reversible phenomenon where ions are replaced with a similarly charged ion. It is usually between a solid material and a solution without permanently altering the structure of the solid (Helfferich, 1962; Sherry, 2003; Alchin,

1998; Kumar and Jain, 2013). The ion exchange process bears similarities with the sorption process which involves dissolved species being taken up by the solid. The main distinguishing feature between the two however, is that the ion exchange phenomenon is a stoichiometric process where every ion that is removed from solution is replaced by an equal amount of different ions of the same sign (Figure 3.8) (Rios 2008). The sorption process on the other hand signifies that a solute is taken up without it being replaced by any ion.

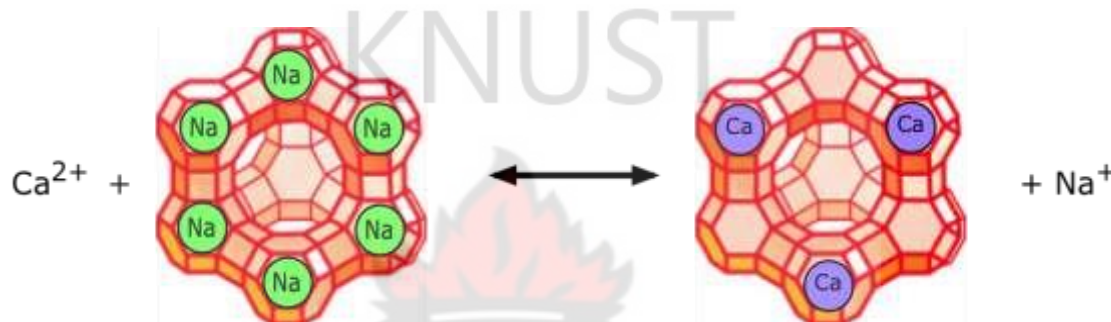


Figure 3.8: A pictorial representation of the ion exchange process (<http://www.chem1.com/CQ/>)

The ion exchange process can be expressed as

$$\propto B_s^{\beta+} + \beta A_z^{\alpha+} \leftrightarrow \alpha B_z^{\beta+} + \beta A_s^{\alpha+} \quad (3.10)$$

Where zeolite (z) is initially in the A form and that the counter ion in the solution (s) is B. α and β are the charges of the exchange cations B and A respectively.

The reaction proceeds until equilibrium is reached (Breck, 1974; Polatoglu, 2005). Both the zeolite and the solution in equilibrium possess both competing counter ion species, A and B. The cations in the zeolite channels are free to move within and in the external solution phase (Polatoglu, 2005).

Exchangers with negatively charged groups are cationic and attract positive ions. Anionic exchangers on the other hand are positively charged and attract negative ions. Zeolites are highly selective cation exchangers making them useful in several

applications including ammonium and heavy metal removal from water and wastewater.

The ion exchange behaviour of zeolites is directly connected to the framework type and to any related structural changes that take place during the ion exchange process. The ion exchange capacity of a zeolite is therefore dependent on the chemical composition i.e. low Si/Al ratios have higher ion exchange capacities (AlvarezAyuso *et al.*, 2003).

The possibility of metal substitution into the zeolite framework has been reviewed by many researchers with factors being attributed to the type of cation being exchanged, size and charge, nature, strength of any cation co-ordination complex; location of cations in the zeolite (Figure 3.9); concentration of the cation exchange solution, etc (Kumar, 2013). Consequently, because of their three dimensional framework, most zeolites do not undergo swelling or shrinking with ion exchange (Pitcher, 2002).

Cation exchange capacity of zeolites also strongly depends on charge of the ion, ionic radius and degree of hydration. Ionic charge and hydration enthalpy are related, in that a higher charge shows a higher enthalpy (Cansever, 2004). A large ion charge/size ratio results in an increase in the hydration energy. Increasing the ionic radius, results in a decrease in the hydration enthalpy.

Eisenman (1962) describes selectivity sequence of ion binding in ion channels as sole function of electrostatics and dehydration. Selectivity of the exchangeable cations can be accounted for in terms of their hydration free energies and their energies of electrostatic interaction with fixed anions in the zeolite. The free energy of ion exchange reaction can be separated into two parts:

- i. The difference between the free energy of the ions in the zeolite
- ii. The free energy differences of the hydration of the ions in the solution

(Cansever Erdogan, 2011).

The presence of a strong electrostatic field in the zeolite will cause the difference between the free energy of ions in the zeolite to be great hence preferring smaller ions. Zeolites with high framework charge and correspondingly low Si/Al ratio are observed to have strong electrostatic fields whilst weak electrostatic fields, associated with high Si/Al ratio prefer weakly hydrated cations. Low Si/Al ratio produces a weak anionic field within the zeolite.

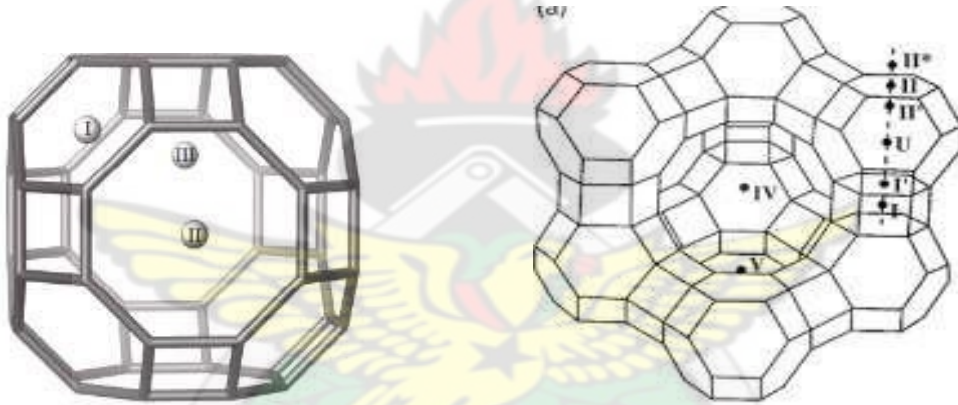


Figure 3.9: Exchangeable cation sites in LTA and FAU framework

3.3.1 Ion Exchange Equilibrium

Ion exchange equilibrium can be characterized by the ion exchange isotherm. Ion exchange isotherm shows the ionic composition of the ion exchanger as a function of the experimental conditions. It is plotted in terms of the equivalent fractions of exchanging ion in solution and in zeolite phase by keeping total solution normality constant. The equivalent fractions of the exchanging cation in solution, (A_s) and zeolite, (A_z) can be given by:

$$A_s = \frac{\alpha m_s^A}{\alpha m_s^A + \beta m_s^B} \quad (3.11)$$

$$A_z = \frac{\text{number equivalents of exchanging cation A}}{\text{total equivalents of cations in the zeolite}} \quad (3.12)$$

Where m_s^A and m_s^B are the concentrations of the respective ions in the equilibrium solution and $\square$ and $\square$ are the charges of the exchange cations B and A respectively.

Hence $(A_s + B_s) = 1$; $(A_z + B_z) = 1$

As stated in Kwakye-Awuah (2008), the cation exchange capacity (CEC) as defined by Ertl *et al.*, (1999) is the magnitude of cation exchange written as:

$$CEC = \frac{\text{number of equivalents of exchanging cation}}{\text{total number of equivalent cations in the zeolite}} = \frac{N_c}{A_m} \quad (3.13)$$

3.4 Adsorption Process

The adsorption process involves molecules in solution to adhere to the surface of a solid. The adsorbent is the surface on which adsorption occurs whilst the adsorbate is the molecules to be adsorbed. Basically, adsorption is a surface phenomenon. The presence of residual or unequal forces occurring on the surface of the solid or liquid phase allows for adsorption. The even nature of the forces creates a form of bonding between the adsorbent and adsorbate. Two types of bonding have been observed:

1. Physisorption – bonds an ion to a surface by electrostatic (Van der Waal) forces. These bonds are usually weak and reversible. It leads to the formation of a multilayer of adsorbate on the adsorbent (Asare-Mensah, 2011).
2. Chemisorption – chemical bonds are formed between the adsorbent and adsorbate. They are mostly irreversible except under extreme conditions. This type of adsorption changes the nature of the adsorbate. It also leads to the formation of a monolayer of adsorbate on the adsorbent as the molecules are restricted to the reactive area of the surface on the adsorbent.

Adsorption process is used in diverse fields. However, the process is affected by the following factors: nature of the adsorbent, effect of temperature, pressure and the surface area of the adsorbent.

The adsorption properties of the zeolites are strongly dependent on framework composition. Small ions and molecules can pass through the zeolite channels, but large ions and molecules are excluded.

Physisorption is used mainly to determine the surface area and pore architecture of zeolite, kaolin and other porous material. Six types according to IUPAC classification are the main isotherms resulting from physical adsorption. The shape of the isotherm is established to be the characteristic of the micropore filling of the adsorption (Kovo, 2011).

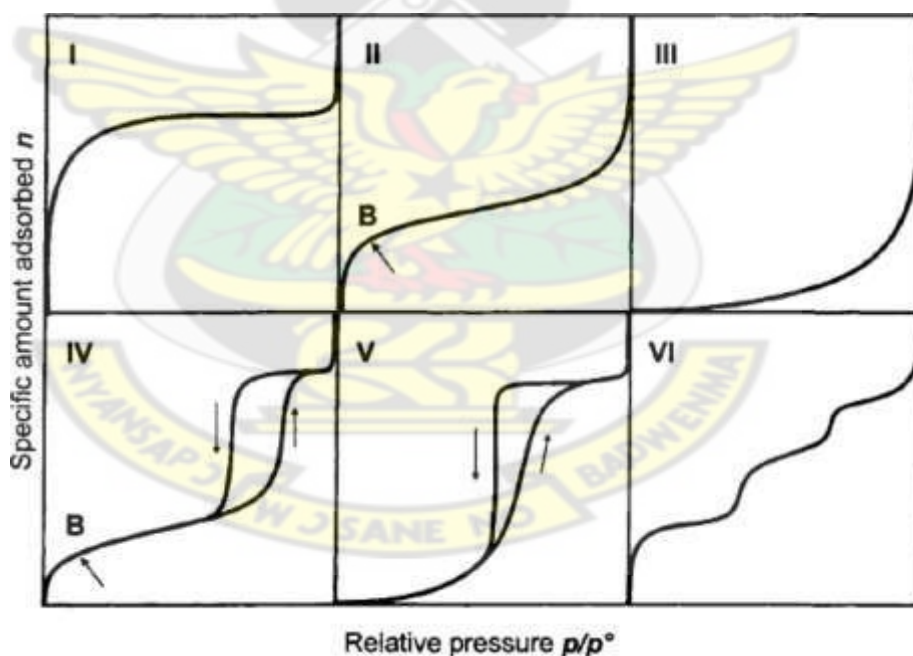


Figure 3.10: The six adsorption isotherms arising from physisorption

3.4.1 Adsorption Isotherms

Adsorption isotherms can be constructed by ascertaining the uptake of adsorbate by an adsorbent for a specific system at a particular temperature and then applying some

form of model to the experimental data. Adsorption isotherm can be defined as a functional expression for the variation of the adsorbate by the adsorbent in the bulk solution at constant temperature (Sharma, 2012). The description of the equilibrium state is a representation of the dynamic behaviour of any adsorbate to the adsorbent (Islam, 2008). The parameters obtained from the isotherm models serve as the basis for adsorption mechanisms, the surface property and affinities of the surface (Foo and Hameed, 2010). A number of the relationships were formulated to model gas adsorption in porous media but they can also be applied to the adsorption of liquids (Whitehead, 2000).

3.4.1.1 Langmuir isotherm

Developed in 1916 by Irving Langmuir, this isotherm was postulated on rational basis. It assumes that an adsorbent surface consists of identical and energetically equivalent sites and each adsorbate molecule occupies only one site. This forms a monolayer and the adsorption cannot advance beyond coverage. It is also assumed that the adsorbate species on neighbouring sites do not interact with each other and there is no movement of adsorbed adsorbate. The Langmuir isotherm can be expressed as:

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (3.14)$$

It can also be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3.15)$$

Where:

q_e is the concentration of sorbate in liquid phase at equilibrium

C_e is the concentration of sorbate in liquid phase at equilibrium

q_m is the maximum sorption capacity (mg/g)

b is the Langmuir constant (L/mg)

A plot of C_e/q_e against C_e gives a straight line. The Langmuir constant b and q_m are obtained from the intercept and slope of the graph respectively.

Introducing the dimensionless equilibrium factor R_L , the characteristic of the Langmuir isotherm can be written as:

$$R_L = \frac{1}{1 + bC_o} \quad (3.16)$$

Where C_o is the highest initial concentration

The value of R_L indicates the shape of the isotherm:

$R_L > 1$ unfavourable; $R_L = 1$ linear; $0 < R_L < 1$ favourable; $R_L = 0$ reversible

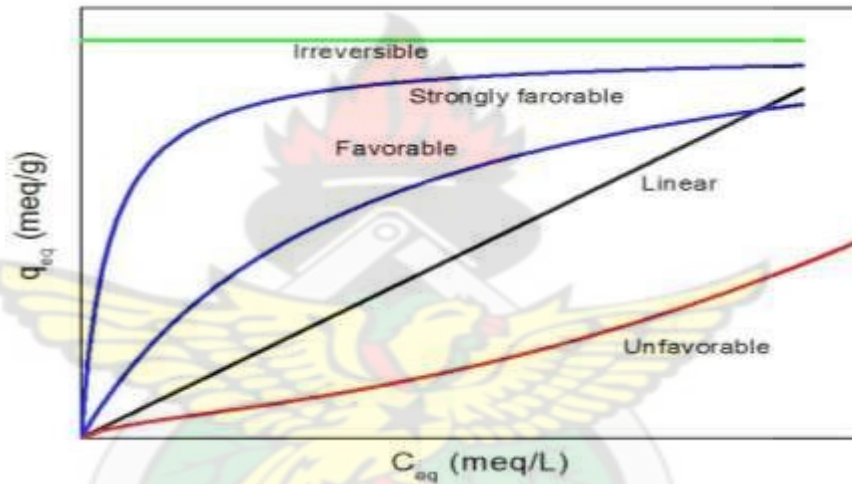


Figure 3.11: A graphical representation of the Langmuir isotherm

3.4.1.2 Freundlich isotherm

The Freundlich isotherm is the earliest known relationship used to describe the nonideal and reversible adsorption for a heterogeneous surface consisting of several sites. This isotherm is derived empirically. The model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over a heterogeneous surface (Foo and Hameed, 2010; Cansever Erdogan, 2011; Shahbeig, *et al.*, 2013). The Freundlich isotherm can be expressed as:

$$q_e = k_F C_e^{\frac{1}{n}} \quad (3.17)$$

Linearly,

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (3.18)$$

q_e is the concentration of sorbate in liquid phase at equilibrium in mg/g

C_e is the concentration of sorbate in liquid phase at equilibrium in mg/L

k_F is the Freundlich constant n is the adsorption intensity

The constant n represents the deviation from linearity of adsorption as follows:

n value	Significance
n=1	Linear
n<1	Sorption process chemical
n>1	Sorption favourable Process physical

A plot of $\log C_e$ against $\log q_e$ gives an almost straight line with the slope and intercept evaluated to determine n and k_F (Ho and Ofomaja, 2005; Asare-Mensah, 2011; Ziyath, 2012; Rahman, 2014).

CHAPTER 4: METHODOLOGY

This chapter provides the details of the procedures followed to achieve the objectives of this work. The experimental and analytical techniques used throughout the study, describing the materials and tests are addressed in this section. An outline of the activities is as follows:

- Equipment and materials used
- Sampling of kaolin and bauxite
- Zeolite synthesis
- Characterization

4.1 Equipment and Materials

Chemical reagent used chiefly was sodium hydroxide (NaOH, Analar grade). Distilled water was processed from an A8S distillation plant. The pH of the distilled water used in all experiments ranged from 5.5 – 6.0 and had a conductivity value of 10 μ S. The most frequently used equipment used included an electric furnace, oven, vacuum pump, pH meter, a mesh, mortar and pestle. These equipment were all available in the Environmental laboratory, Civil Engineering department, KNUST.

4.2 Sampling of Kaolin and Bauxite

Kaolin was sampled from two different geographical locations. This was done as a means of varying the silicate source. Wassa kaolin was from a town in the Western Region, were acquired from the Ceramics department of KNUST. This was already free from impurities. The sample was however sieved to achieve an even particle size using a mesh. Kaolin obtained from Anfoega in the Volta Region, was in a rocky form. This was soaked in water to remove organic matter and then air dried at ambient temperature. The kaolin was ground into powder form using a mortar and pestle (Plate 4.1). After grinding, it was sieved with a mesh of sieve size 0.75 μ m under dry conditions.



Plate 4.1: Anfoega kaolin as obtained from source and after grinding

Chemical and mineralogical analysis using XRD and EDX analytical techniques were carried out on all kaolin samples.



Plate 4.2: Bauxite sample used in the study

Bauxite was sampled from Awaso in the Western Region particularly close to the Ghana Bauxite Company site. To obtain a uniform particle size, size separation using the 0.75 μm mesh size was conducted (Plate 4.2). The bauxite was also characterised for its elemental and chemical compositions. The results are presented in the next chapter.

4.3 Zeolite Synthesis

Investigation by various literatures has reported the conversion of raw materials such as fly ash, kaolin and waste ash into zeolite (Milton, 2005; Rios, 2008; Kovo, 2011). The possibility of obtaining zeolite from Ghanaian bauxite or kaolin only or both was investigated. Effects of various synthesis parameters were investigated whilst considering the cost effectiveness of the entire process.

4.3.1 Zeolite Synthesis from Bauxite

Zeolite synthesis was attempted from bauxite only. However, effect of calcination of the bauxite prior to alkaline fusion was considered.

4.3.1.1 Effect of calcination

10 g each of bauxite was weighed in two (2) separate crucibles. One crucible was put in a preheated furnace with a temperature of 600 °C for 30 minutes (Plate 4.3). The calcined sample was allowed to cool to room temperature. 15 g of NaOH powder was added to both the calcined and uncalcined bauxite samples and dry mixed for 30 minutes. The bauxite and NaOH mixture was heated at 600 °C for 1 hour for fusion activation. The resultant product after fusion was ground into uniform powder when it had cooled at room temperature and then weighed. A calculated amount of distilled water was added to mixture and stirred for 20 minutes to achieve homogeneous slurry. The slurry was transferred into Teflon (PTFE) containers and covered tightly for the hydrothermal reaction in an oven. The pH was measured before and after crystallization. The crystallization reaction was performed at 100 °C for 6 hours without agitation. The solid precipitates were filtered from the solution after cooling to room temperature. To obtain a pH < 9, the synthesized sample was further washed with distilled water until the pH dropped. The as-synthesized sample was subsequently dried at 100 °C overnight. Characterization in terms of XRD, SEM, EDX and FTIR were then carried out. Comparative analyses were also performed.



Plate 4.3 (a) An image showing uncalcined bauxite on the left and calcined bauxite and (b) an electrical furnace with samples ready for fusion

The molar gel composition of the reactants was as follows:

Calcined: $1.91\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 0.01\text{SiO}_2 : 51.8\text{H}_2\text{O}$

Uncalcined: $2.93\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 0.01\text{SiO}_2 : 60.3\text{H}_2\text{O}$

4.3.2 Zeolite Synthesis from Kaolin

Since kaolin in its natural state is inert, kaolin was converted to metakaolin at $600\text{ }^\circ\text{C}$ for 2 hours to make it reactive as reported by several authors in literature.



Plate 4.4: An image of the Wassa kaolin (a) before alkaline fusion (b) after fusion (c) electric furnace

30 g of the metakaolin was added to 10 g NaOH. The mixture was fused at 600 °C for 2 hours. It was allowed to cool to room temperature and 2M NaOH solution was then added to the mixture and stirred to obtain homogenous slurry. The aluminosilicate gel was then crystallized at 110 °C for 4 hours under static conditions in Teflon containers. The initial pH was measured. The as-synthesized sample was filtered and washed until the pH was less than 10 with distilled water. The sample was dried overnight in an electrical oven at 100 °C and kept in airtight bags prior to characterization.

Variations were undertaken by increasing the molar concentrations of NaOH solution (3 M, 4 M and 6 M) and the crystallization times (4 hours, 5 hours and 6 hours).



Plate 4.5: A picture of (a) beakers containing metakaolin with different molar concentrations of NaOH (b) Teflon bottles used in crystallization (c) electrical oven.

A summary of the kaolin conversion to zeolite is presented in Table 4.1:

Table 4.1: Different protocols used in synthesizing zeolites from kaolin only

Parameters	Route 1	Route 2	Route 3
Calcination temperature (°C)	600	600	600
Calcination time (hours)	2	2	2
Mass of kaolin (g)	30	28	20/ 13.2 MK
NaOH (g)	10	22	24
Method	DF, HT	HT	DF, HT
Concentration of NaOH	2M, 4M, 6M	-	-
Volume of H ₂ O (ml)	100	245	64.5
Aging time (hours)	-	12	24
Crystallization temp (°C)	110	100	80
Crystallization time (hours)	4, 5, 6	6	24

DF – dry fusion HT – Hydrothermal MK - metakaolin

4.3.3 Zeolite from Bauxite and Kaolin

4.3.3.1 Method 1

In an attempt to increase the Si/Al ratio of the zeolites as well as synthesize new zeolites, bauxite and kaolin were used as starting materials. Bauxite was considered the alumina source and kaolin, the silica source. Alkaline fusion of bauxite and kaolin was considered before hydrothermal reaction.

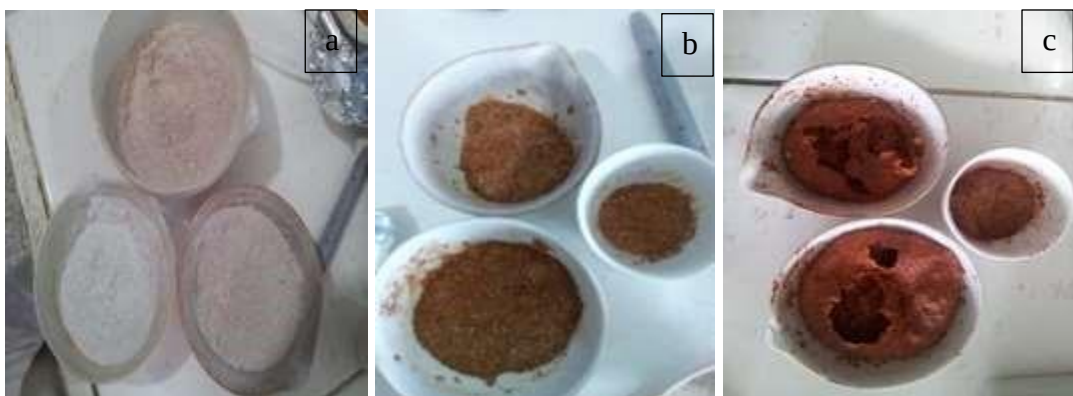


Plate 4.6: (a) Different masses of bauxite and kaolin dry mixed with NaOH (b) before and (c) after heating in a furnace

Bauxite, kaolin and sodium hydroxide were mixed in a predetermined ratio. Different masses of kaolin were considered. The mixture was fused at 600 °C for 1 hour using both WK and AFK. A skull was formed (Figure 4.6c) after heating. The fused product was cooled to room temperature in ambient air, ground and then thoroughly mixed with a volume of distilled water. The solution was then crystallized at 100 °C for 6 hours without stirring or agitation. After the crystallization time, the precipitated solids were separated by filtration and washed copiously with distilled water until pH of the filtrate was less than 9. Drying of the product was done overnight at 100 °C.

Table 4.2: Synthesis parameters using kaolin and varied bauxite using alkaline fusion method

Route	Type of kaolin	Mass of kaolin (g)	Mass of bauxite (g)	NaOH (g)	Molar composition
1	WK	30	5	1.67	$\text{Na}_2\text{O}:6.29\text{Al}_2\text{O}_3:14.6\text{SiO}_2:58.6\text{H}_2\text{O}$
2	WK	30	10	3.3	$\text{Na}_2\text{O}:3.95\text{Al}_2\text{O}_3:7.4\text{SiO}_2:32.6\text{H}_2\text{O}$
3	WK	30	15	5	$\text{Na}_2\text{O}:3.13\text{Al}_2\text{O}_3:4.88\text{SiO}_2:23.4\text{H}_2\text{O}$
4	AFK	30	5	1.67	$\text{Na}_2\text{O}:7.5 \text{ Al}_2\text{O}_3:15 \text{ SiO}_2:58.6 \text{ H}_2\text{O}$

5	AFK	30	10	3.3	$\text{Na}_2\text{O}:3.79\text{Al}_2\text{O}_3:7.64\text{SiO}_2:32.6\text{H}_2\text{O}$
6	AFK	30	15	5	$\text{Na}_2\text{O}:2.46\text{Al}_2\text{O}_3:5.05\text{SiO}_2:23.4\text{H}_2\text{O}$

4.3.3.2 Method 2

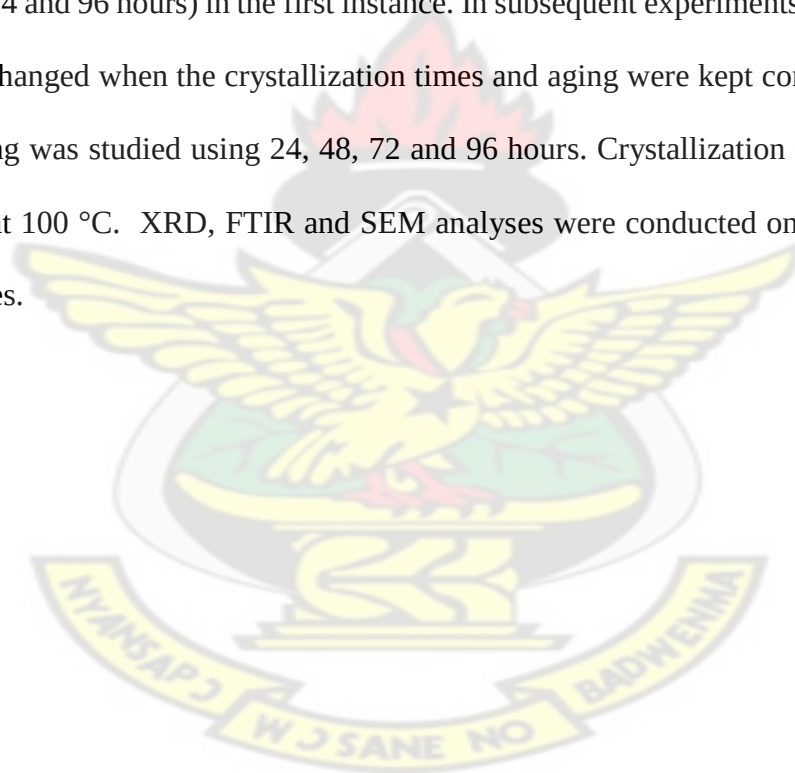
In this step, bauxite was digested using sodium hydroxide solution to form sodium aluminate. The process was carried out at 130 °C for 5 hours in an electrical oven. The sodium aluminate solution was filtered off the red mud and stored poly propylene containers. A calculated volume of the aluminate solution was added to metakaolin (calcined WK) and the mixture was stirred until homogenous slurry was formed (Plate 4.7). Parameters such as aging time and crystallization temperature were kept constant. However, the crystallization times considered were 5 hours, 18 hours and 24 hours. Variations to the procedure included fusing the metakaolin with NaOH before the addition of sodium aluminate and the addition of extra water. The crystallization times were varied between 5 and 24 hours. No aging was carried out. Crystallization temperature considered was 110 °C for 5 hours. The effect of order of mixing of the reactants on zeolite synthesis was investigated using 24 hours as crystallization time.



Plate 4.7: Slurry obtained from mixing sodium aluminate from bauxite with metakaolin

4.3.3.3 Method 3

For this method, only filtrates obtained from bauxite and kaolin were used. The process used to obtain reactants and synthesis route are presented in Figure 4.1. The solution was prepared using information from previous work and references. Investigations that were looked into were the effects of crystallization time, aging time and Si/Al ratios. The volumes of the filtrates were kept same whilst the crystallization times were varied (3, 5, 24 and 96 hours) in the first instance. In subsequent experiments, the Si/Al ratios were changed when the crystallization times and aging were kept constant. The effect of aging was studied using 24, 48, 72 and 96 hours. Crystallization temperature was fixed at 100 °C. XRD, FTIR and SEM analyses were conducted on the synthesized samples.



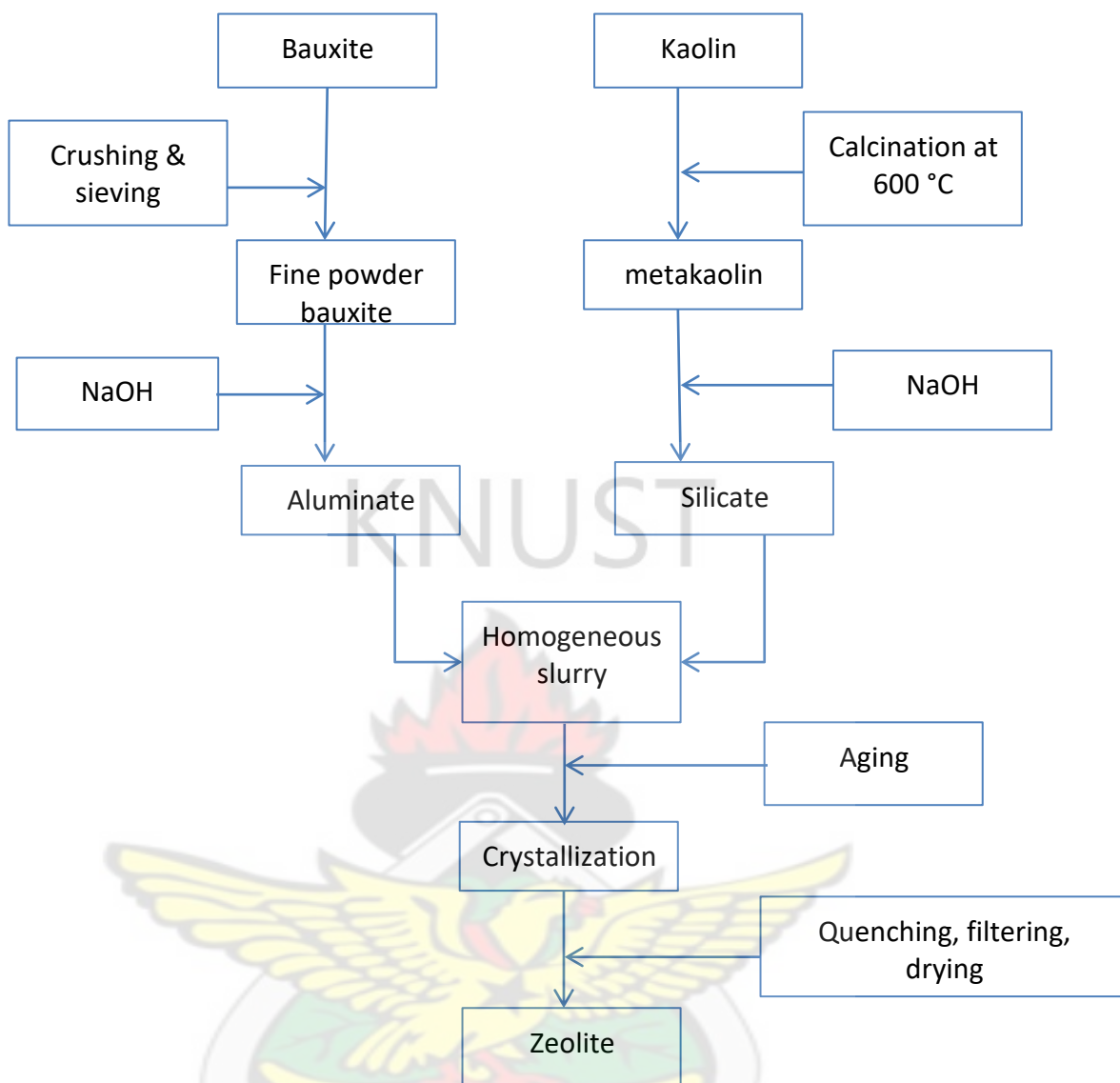


Figure 4.1: Flow chart of the zeolite synthesis process from bauxite and kaolin

4.4 Characterization

4.4.1 XRD

All XRD powder analyses were carried out at the Faculty of Science and Engineering lab, University of Wolverhampton, UK. An aluminium plate sample holder was acquired and cleaned thoroughly using acetone to remove any impurities on its surface. The samples were well ground into small, evenly sized particle powders. An amount of the powder sample was placed on flat surface of the sample holder and compressed

to achieve a smooth and levelled surface whilst filling the entire perimeter of the sample holder using a glass slab (Plate 4.8). This was ensured, as loose powder samples give poor intensities in diffraction.



Plate 4.8: Samples in aluminium plate holders being prepared for XRD analysis

A Panalytical Empyrean powder X-ray diffractometer (Plate 4.9) was used to collect data using Bragg-Brentano geometry and a slit configuration of a degree fixed divergence slit of 0.25° . The diffractometer is equipped with a $\text{CuK}\alpha$ radiation source ($\lambda=1.5406 \text{ \AA}$) and was operated at 40 mA and 40 kV. For phase identification, scans were taken from $2\theta = 5$ to 80° with a step size of 0.013° and a scan step time of 8.67 s. Rietveld analysis was then performed using Xpert HighScore plus software. Identification of each zeolite sample or compound was achieved by carefully considering the peak positions and intensities of the produced data and then searching for a mineral (reference data) that conforms to the strongest peak or peaks. For the remnant peaks, another zeolite or mineral that explains the strongest of the peak or peaks is assigned and then confirmed by looking for its peaks of lesser intensity. This was done until all peaks were identified. The data was then stored in an open format

XRDML form. Analyses of XRD data was conducted using X'pert Highscore and Matlab softwares.



Plate 4.9: PANalytical Empyrean X-ray diffractometer

Crystallinity was evaluated from the peak intensities of the samples by comparing them to the reference zeolite. Using the Scherer equation with method based on the width of the diffraction patterns, the average crystallite size was calculated using Xrays reflected in the crystalline region.

$$\text{Crystallinity \%} = \frac{\text{sum of integral peak intensities for sample}}{\text{sum of integral peak intensities for reference zeolite}} \quad (4.1)$$

$$\text{Crystallite size } \tau = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (4.2)$$

4.4.2 SEM and EDX Analysis

Using a ZEISS EVO50 scanning electron microscope (Plate 4.10) attached with Energy dispersive X-ray analyzer (EDX), the morphology of the starting materials and the as-synthesized zeolites were investigated. The SEM was operated under the following analytical conditions: accelerating voltage EHT = 20.00 kV, Signal A = SE1, WD = 4.0 – 5.5 mm. Bauxite, kaolin and zeolite powder samples were dry sprayed onto aluminium stubs using double-sided adhesive carbon discs.



Plate 4.10: ZEISS EVO50 equipment used for surface measurements

They were then coated with gold to decrease static charging during their observation under SEM conditions. Surface morphology and atomic percentage compositions for the present study were done using EDX. The samples were prepared similarly to SEM for EDX analysis. Instead of aluminium stud, a carbon sample holder was used to avoid errors in the aluminium content (Plate 4.11).



Plate 4.11: Samples gold sprayed on aluminium stubs for SEM and EDX analysis

4.4.3 FTIR

A Mattson FTIR spectrometer (Mattson Instruments, UK) equipped with a ZnSe crystal plate attached to the spectrometer with a mercury cadmium telluride A

(MCTA) detector and KBr as beam splitter was used to analyze zeolite samples (Plate 4.12). Measurements were done using 100 scans at 4 cm^{-1} resolution, units of $\log(1/R)$ (absorbance), over the mid-IR region of $1200 - 400\text{ cm}^{-1}$. An air background spectrum was collected at the start of the sample collection. A small sample of each zeolite was centred on the ZnSe plate to ensure that it covered the entire crystal surface, and a pressure clamp was used to apply pressure on the filter. The zeolite samples were analyzed three times for each sample. FTIR results were also analysed using Matlab. Crystallinity of the samples was also deduced from FTIR data.

$$\text{Crystallinity} = \frac{\text{ratio of intensity of band at 560 to the intensity of band at 620 of the sample}}{\text{ratio of intensity of band at 560 to the intensity of band at 620 of the ref sample}}$$

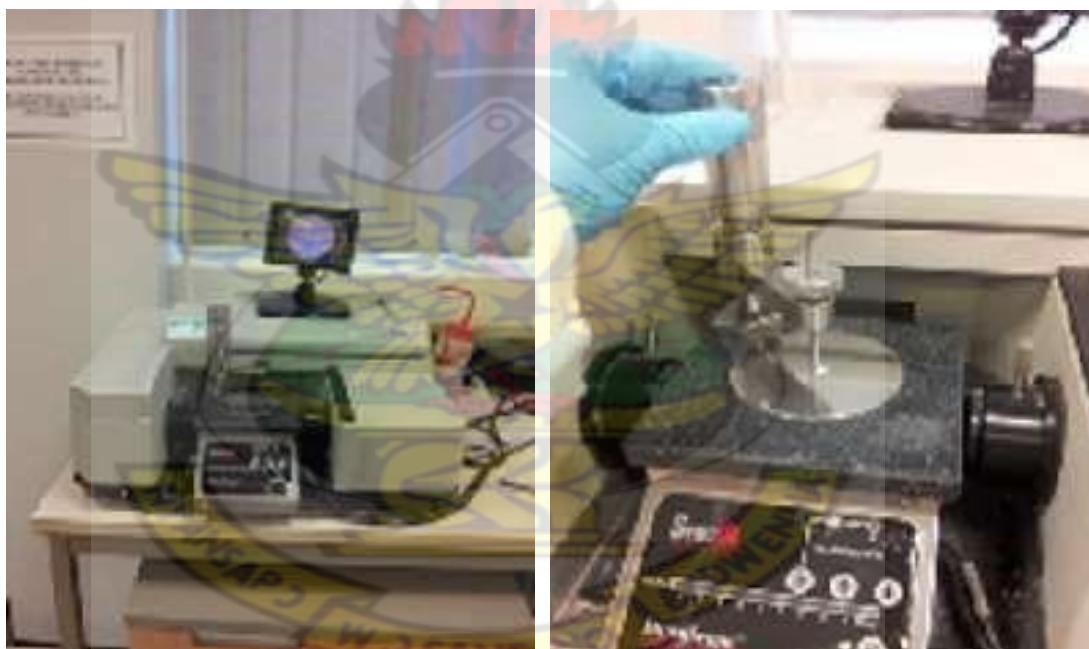


Plate 4.12: Genesis Mattson FTIR spectrometer being used to study the vibrational properties

4.4.4 TG Analysis

The TG analyses were conducted using a Perkin Elmer thermogravimetric analyser with an output interface (Plate 4.13). The raw materials were analyzed by between 25

and 900 °C, using a heating rate of 10 °C min⁻¹. The powdered sample was directly filled into a Pt-Rh crucible for the testing. An amount of between 15-20 mg was used to reduce background noise. This analytical technique was very useful to estimate the thermal stability of the synthesis products. Loss in mass and peak temperature were ascertained using TG and TGA curves (derivative TG and second derivative curves).



Plate 4.13: Perkin Elmer TGA analyser used in the study

CHAPTER 5: EXPERIMENTAL RESULTS

5.1 Characterization of Raw Materials

5.1.1 Bauxite

Bauxite was investigated for its elemental, chemical and morphological properties.

The initial elemental composition was carried out on an EDX analyser. The mineral

composition of bauxite varies depending on geological location. The EDX pattern showed a high peak for aluminium (Al) whilst the other elements Ti, Fe and K in the compound had relatively low peaks. Silicon (Si) was significantly low as well, as shown in Figure 5.1(a). The chemical composition of bauxite presented in Table (5.1) revealed that Al_2O_3 accounts for 88.6 % wt% of the total bauxite whilst TiO_2 , the next highest was 9.0 % , SiO_2 1.12 % and traces of K_2O . A high $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of 79.1 was obtained. Iron impurity was observed to be 1.3 %.

The SEM of bauxite as depicted in Figure 5.1 (b) is somewhat hexagonal but slightly distorted shape.

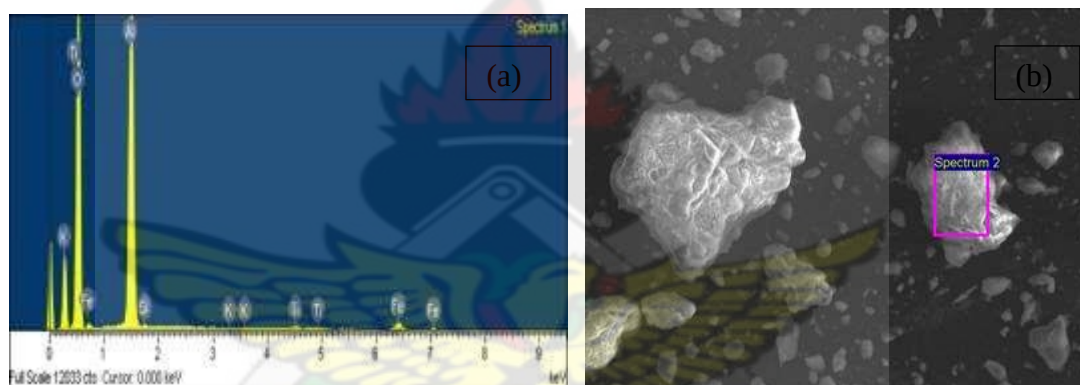


Figure 5.1 (a) EDX image of bauxite showing the peak abundance of each element.
(b) SEM image of bauxite.

The chemical composition of the bauxite used in this study is presented below:

Table 5.1 Chemical composition of bauxite in wt %	
Chemical composition	Wt %
SiO_2	1.12
Al_2O_3	88.6
K_2O	trace
TiO_2	9.0
Fe_2O_3	1.3
Na_2O	-

MgO	-
Total	100

Figures 5.2 and 5.3 show the XRD patterns of bauxite: Figure 5.2, the mineralogical composition and 5.3 presenting the peak positions. The chief mineral phase was found to be Gibbsite (99.6 %) and Rutile (0.4 %) in small proportion on performing Rietveld analysis. The XRD plot shows observable peaks between $2\theta = 15^\circ$ and 55° . A prominent peak was however observed at $2\theta = 18.25^\circ$ with a basal spacing $d(002)$ and a second high intensity peak at $2\theta = 20.29^\circ$ and its corresponding basal spacing $d(11\bar{1})$. The SEM image of bauxite shown in Figure 5.4 portrays somewhat

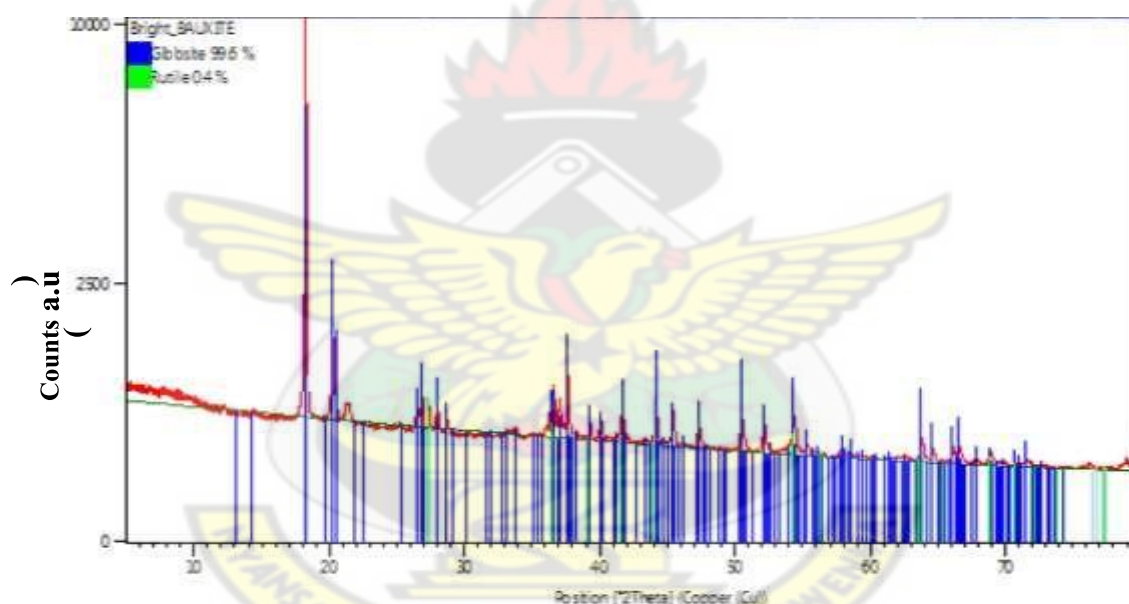


Figure 5.2 : XRD image showing the mineralogical composition of bauxite

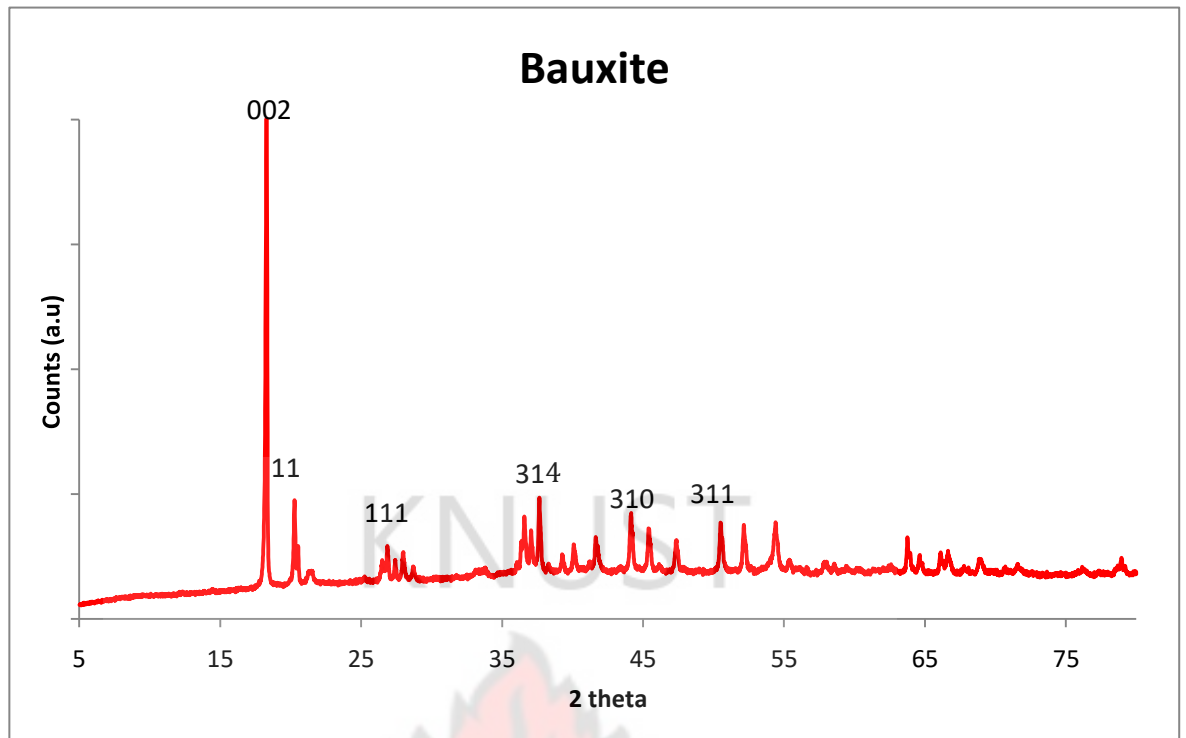


Figure 5.3: XRD plot of bauxite used in the study depicting the gibbsite positions.

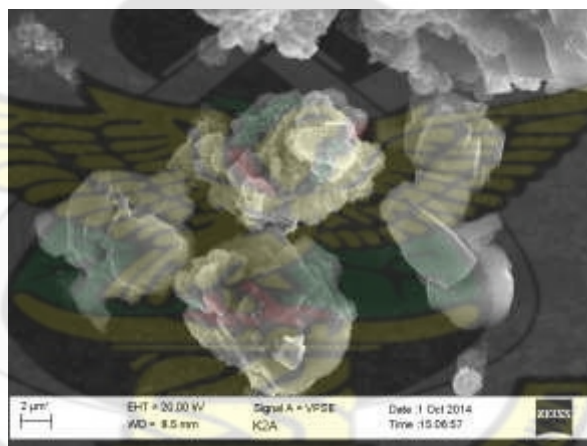


Figure 5.4: SEM micrograph of gibbsite

hexagonal shaped crystals stacked together with other small irregular crystals coexisting.

5.1.2 Kaolin

EDX analysis of the kaolins obtained exhibits the presence of Si, Al, Na and K as distinct peaks in the WK and additional Ti, Fe and Mg ions present in AFK (Figure

5.5). A relatively high Si peak is however observed in both spectra with a much higher intensity for the AFK sample. The ratio of Si/Al gives a value of approximately 1.4 and 2.0 for WK and AFK respectively. Several peaks indicating the minerals present in the sample are shown in the XRD patterns. The mineral quartz was significantly present in both samples. The percentage of kaolinite mineral was 54.8 % and 45.2 % quartz in WK. kaolinite accounted for 45.3 % of the AFK sample. It was accompanied by 50.8 % quartz mineral and 3.9 % phengite. An evaluation of the peaks indicate sharp peaks at $2\theta = 12.3^\circ$ and 24.8° for WK; 12.29° and 24.79° for AFK being the characteristic kaolinite peak (Figure 5.7 a and b).

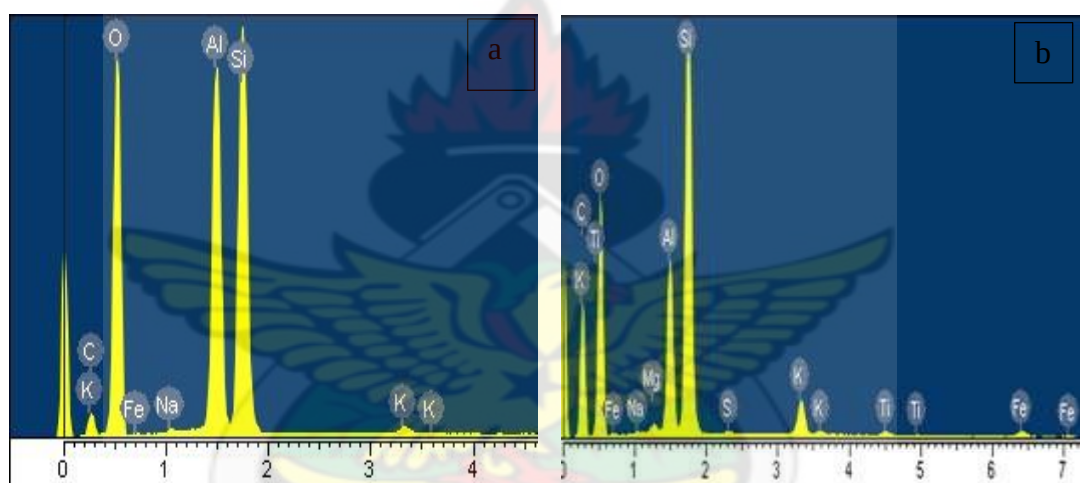


Figure 5.5: EDX spectra of (a) WK and (b) AFK showing the elemental compositions.

Quartz peaks appeared at 20.8° , 26.58° and 37.58° 2θ for both WK and AFK. The intensity of the peaks were however different in both kaolin. A phengite peak appeared at 7.86° 2θ .

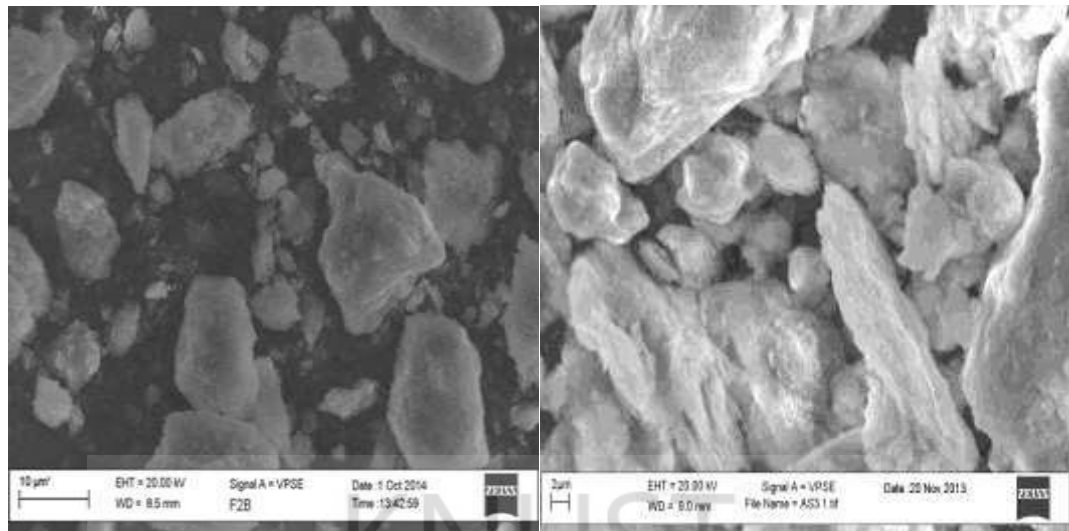


Figure 5.6: SEM micrographs for WK and AFK

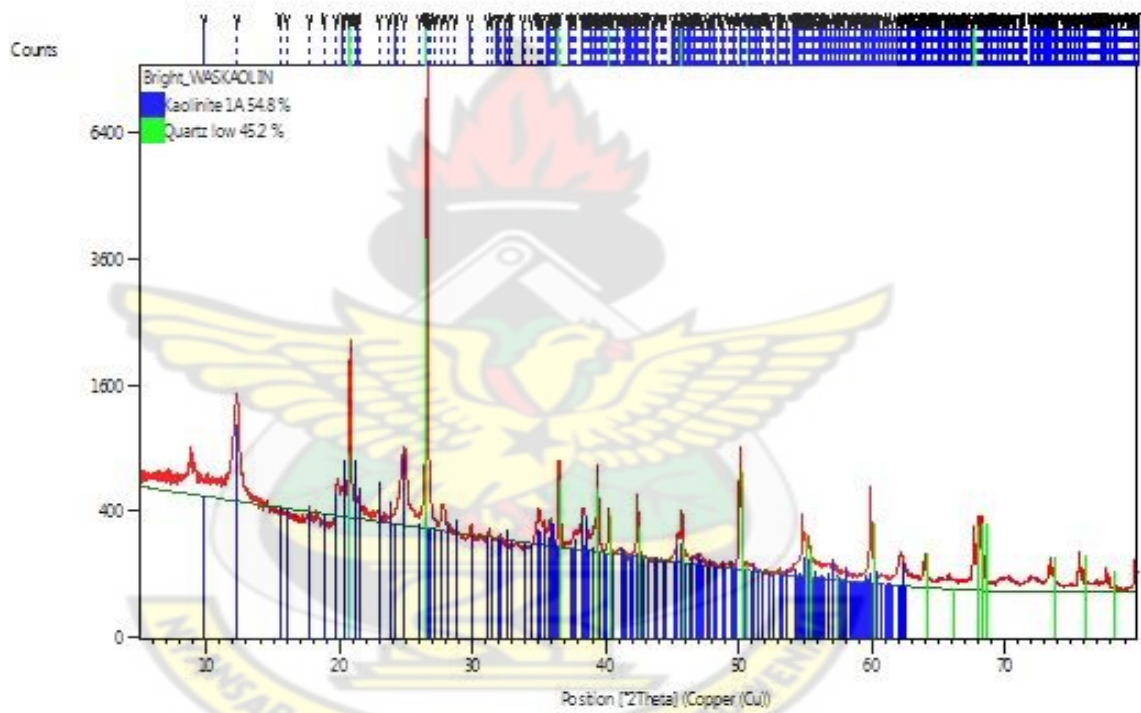


Figure 5.7a: XRD image of WK showing its mineralogical composition

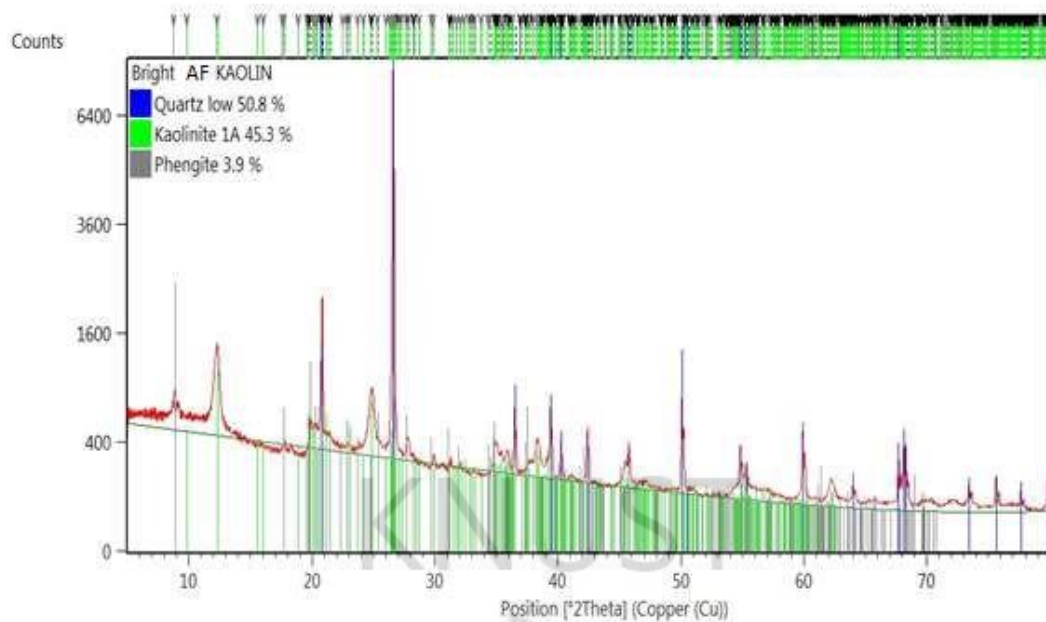


Figure 5.7b: XRD image of AFK depicting the minerals present in the sample

Similar peak positions can be observed in both samples. The basal spacing observed at d(110) and d(002) near 13° and 25° 2θ in WK are however, quite sharper in comparison to that of the AFK sample as seen in Figure 5.8.

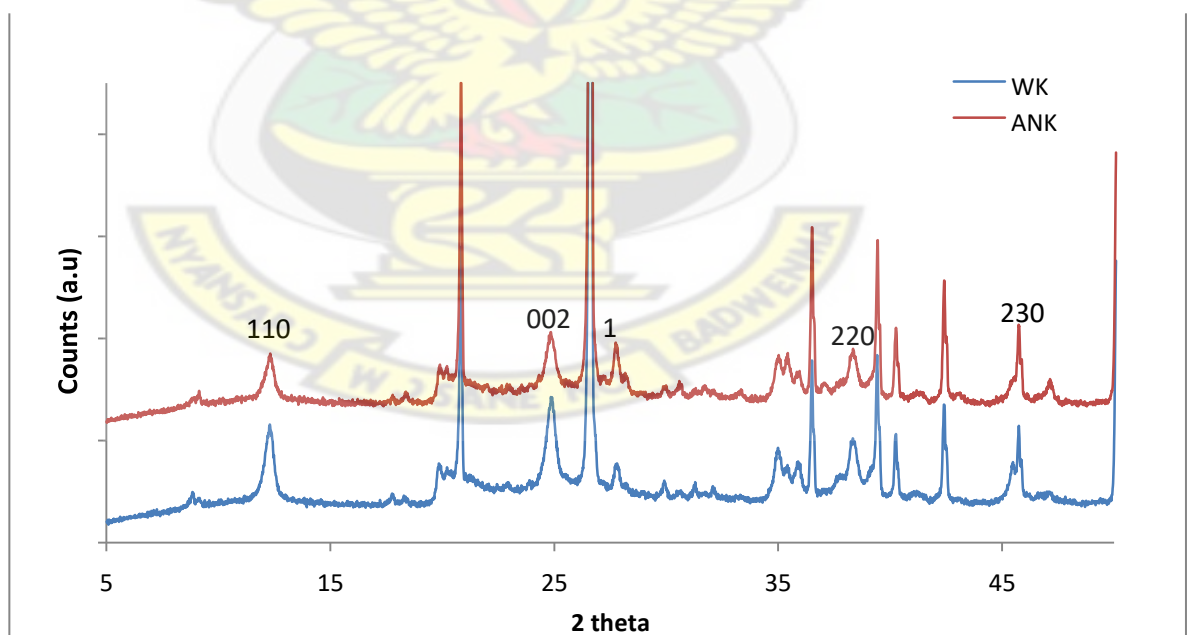


Figure 5.7c: XRD pattern for WK and AFK showing the kaolinite peak positions and their corresponding hkl values.

The SEM images of both kaolins (Figure 5.6) show plate-like sheet morphology with a hexagonal outline. The plates are observed to be flaky and loosely packed. Smaller particle sizes are also observed in the image. The AFK SEM further exhibits a coarse surface.

Table 5.2 presents the chemical composition of the kaolin samples used in the study. AFK were found to contain more impurities than the WK. No Mg or Fe bearing phase was reported for WK, however the SiO₂ value of 56.99 % was observed for the AFK sample and 62.64 % for the WK sample.

The Hinckley Index (HI) was calculated using the sum of peak heights of (1 $\bar{1}$ 0) and (1 $\bar{1}$ 1) in the region between 15° and 30° 2 θ .

Table 5.2: Chemical composition and Hinckley index of WK and AFK samples

Composition	WK	AFK
SiO ₂	56.99	69.58
Al ₂ O ₃	40.97	20.54
Fe ₂ O ₃	-	1.08
K ₂ O	0.54	5.59
Na ₂ O	1.21	0.28
MgO	-	1.98
Ti	-	0.95
Total	100	100
HI	0.95	0.98

5.1.3 FTIR of Raw Materials (Bauxite & Kaolin)

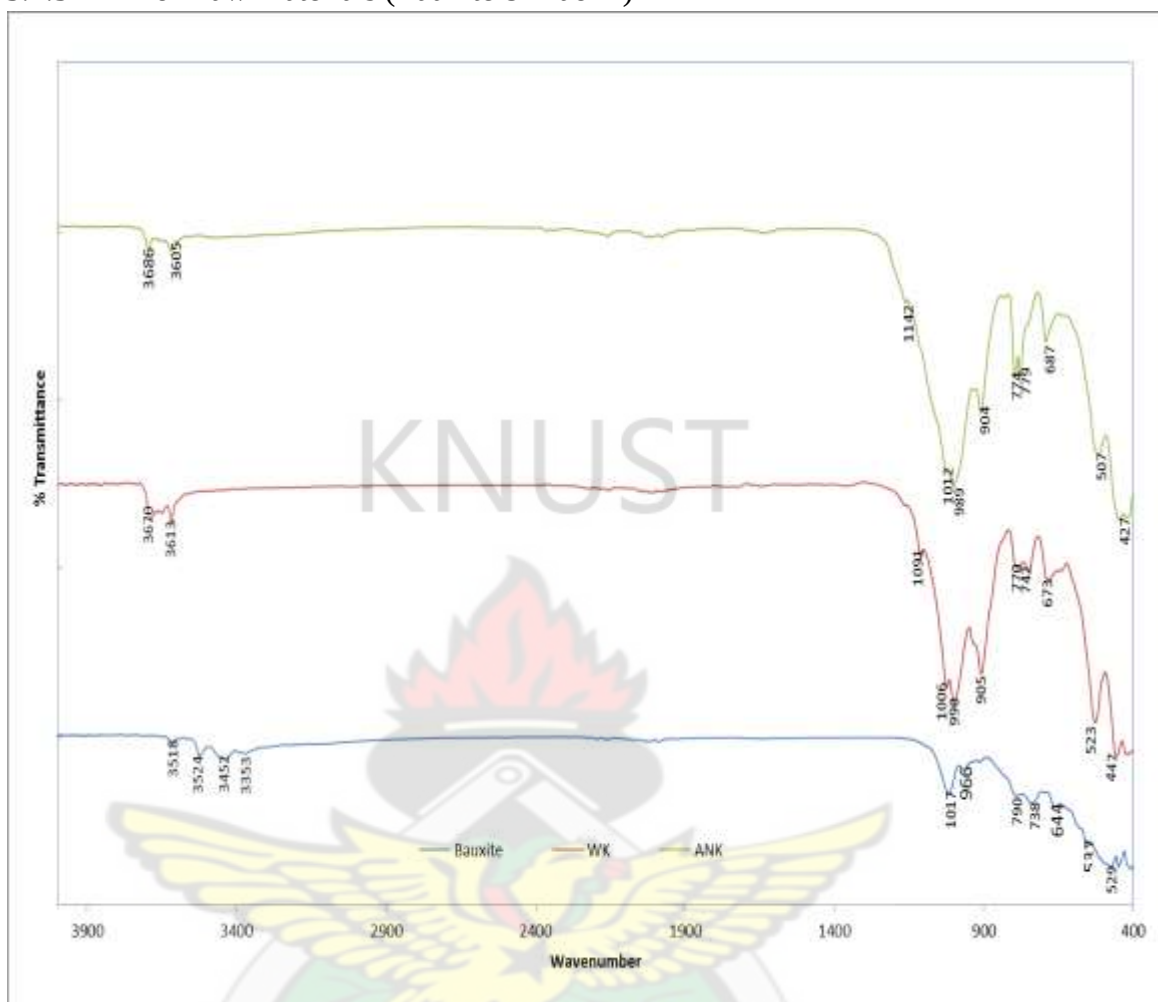


Figure 5.8: FTIR spectra of raw materials bauxite, WK and AFK samples

The FTIR plot of all raw materials is presented in Figure 5.8. The characterization was carried out between 400 and 4000 cm^{-1} . Similar plots are observed for both kaolins and bauxite. Strong bands at 3618, 3524, 3452 and 3353 cm^{-1} were observed for the bauxite. No prominent peak was observed between 3000 and 1100 cm^{-1} . A number of peaks with variable intensities were observed in the following 1200 – 400 cm^{-1} region. These included 1017, 966, 913, 790, 738, 644, 537 and 529 cm^{-1} . Similar peak positions were noted in the kaolin samples. WK recorded peaks at 3664, 3622 and 3613 cm^{-1} and AFK had peaks at 3686 and 3605 cm^{-1} . As with the bauxite, the 1200 - 400 cm^{-1} region had more strong peaks and peak positions were similar to both

kaolins. Between 1200 and 900 cm^{-1} region, five bands namely: 1108, 1024, 993, 924 and 904 cm^{-1} band positions were observed for WK whilst AFK recorded four bands: 1147, 1011, 997 and 907 cm^{-1} . The bands for bauxite compared to the kaolins were weaker for this region. In the very low frequency regions, bands were observed around 761, 743, 667, 616, 520 and 448 cm^{-1} for WK. AFK had 809, 779, 775, 679, 504 and 420 cm^{-1} as appearing bands in the low frequency region.

5.1.4 TGA Analysis of Raw Materials

The TG-DTA curve of bauxite is presented in Figure 5.9. The effect of temperature on mass change was investigated.

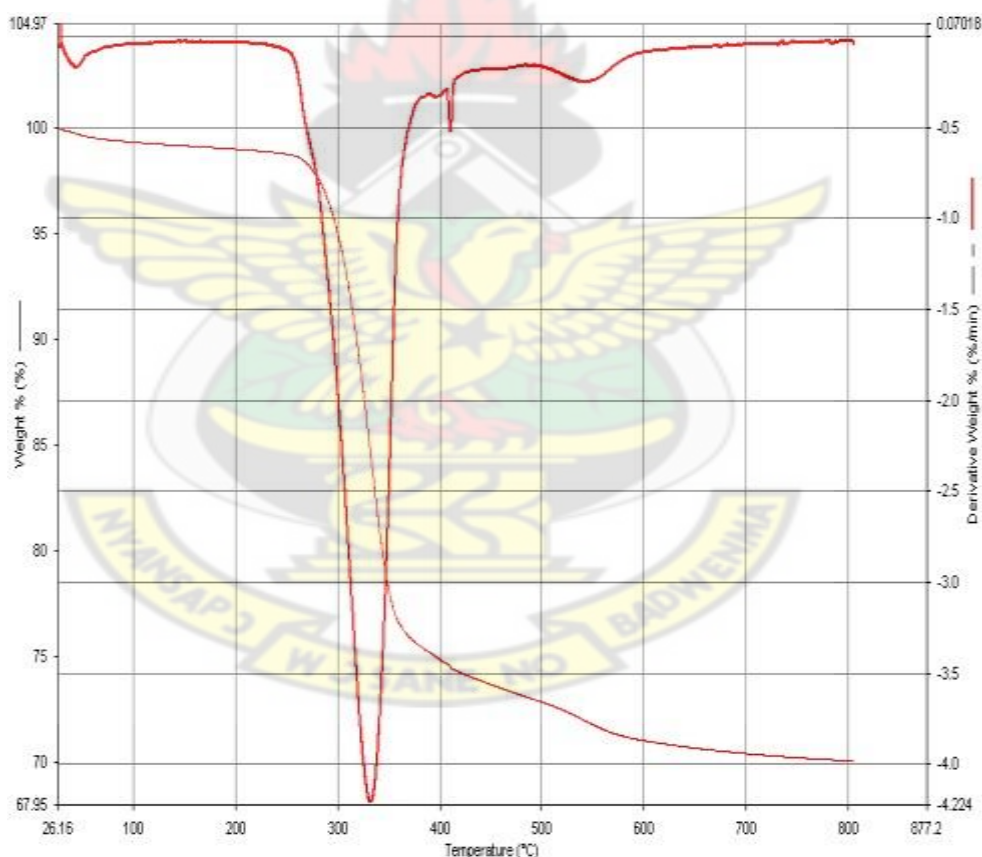


Figure 5.9: TG with DTA curves of bauxite between 25 °C and 800 °C

The TG-DTA analysis was conducted between 25 and 800 °C. The TGA curve shows a continuous weight loss due to the loss of water when heating was done up to 800 °C.

A small weight loss of the sample is noted to occur between 24 and 50 °C. In the temperature range from 100 – 300 °C, the weight loss was about 2 %. About 24.7 % of weight loss was realized at around 330 °C, with a sharp endotherm. Two small endotherms were seen around 410 and 534 °C.

The total weight loss between 350 – 700 °C was about 7 %. No noticeable weight loss was observed after 700 °C.

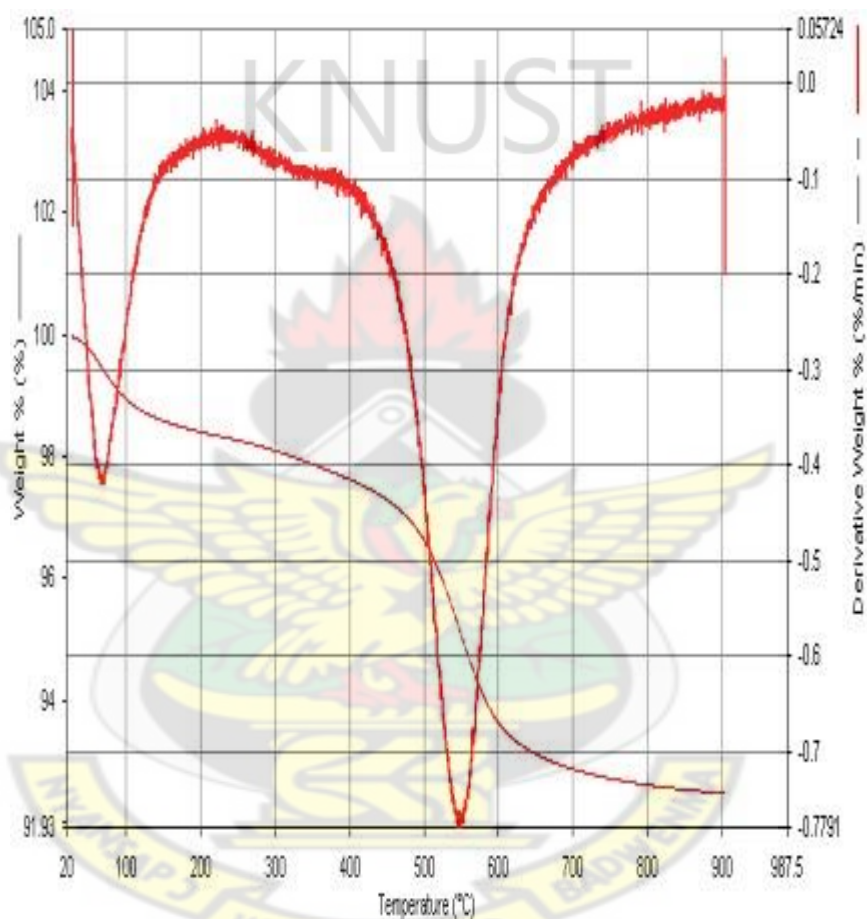


Figure 5.10: DTA-TGA curves between 20 and 900 °C for WK

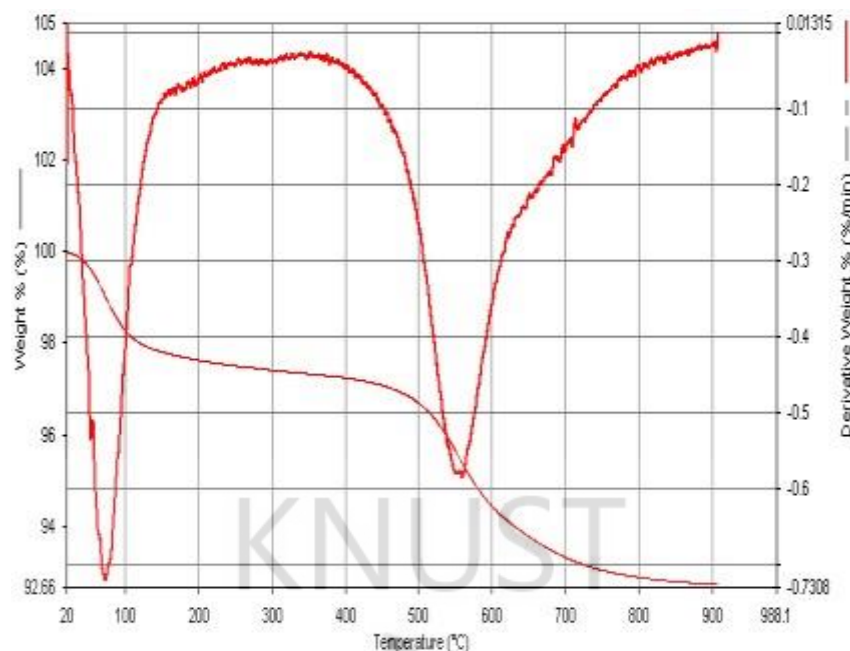


Figure 5.11: DTA-TGA curves for AFK between 20 and 900 °C

The plot exhibits two main parts: the first activity major activity occurs within the 50 – 550 °C range. The second activity, a more rapid decline in the range of 550 – 900 °C is observed. Below 100 °C, an approximately 2% weight loss was observed for AFK sample and about 0.5 % between 560 and 570 °C. WK had a 1 % weight loss below 100 °C and 1.5 % at 550 °C. A total weight loss of 9 % and 7.34 % was observed in the WK and AFK respectively.

5.2 Zeolite from Bauxite

5.2.1 Effect of Calcination

In the attempt to synthesize zeolites from bauxite, effect of calcination was investigated. The XRD patterns of the calcined and uncalcined bauxite after zeolite synthesis are presented in Figure 5.12 below.

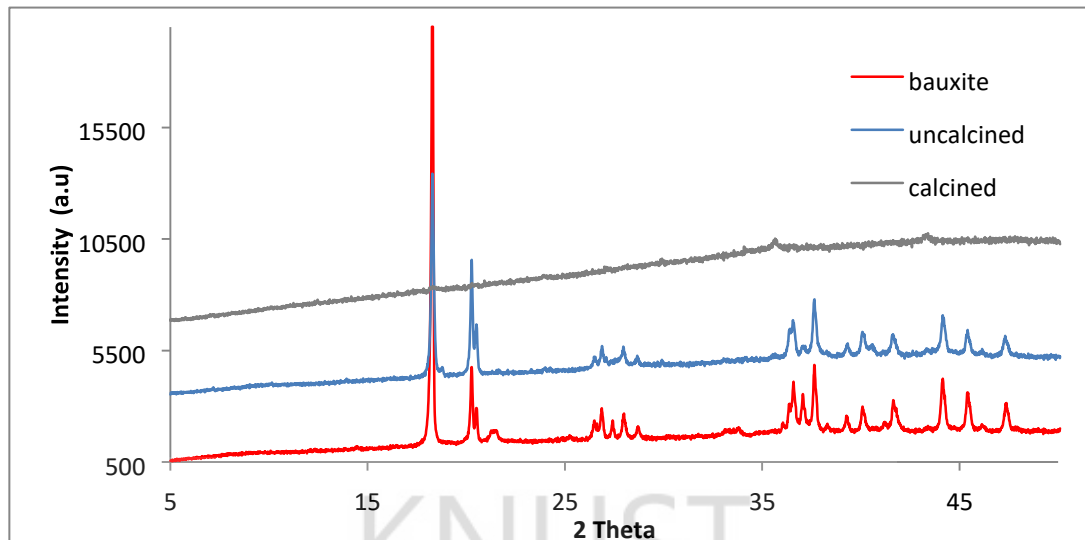
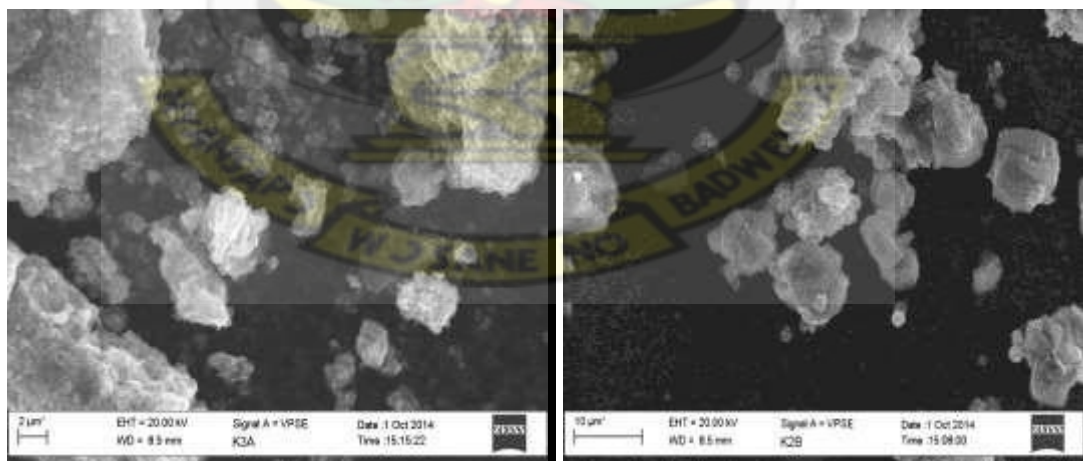


Figure 5.12: XRD patterns of as-synthesized zeolite using calcined and uncalcined bauxite

The synthesized product using the calcined bauxite has peaks similar to the original bauxite sample. The peaks are however less intense in comparison to the raw material. The XRD of the calcined bauxite after synthesis was amorphous with no distinct peak. The product obtained after synthesis using the uncalcined bauxite was Gibbsite and from the uncalcined bauxite was an unknown non-crystalline product.



(a)

(b)

Figure 5.13: SEM of products obtained using (a) calcined bauxite (b) uncalcined bauxite

The SEM of the product obtained from synthesis using calcined bauxite show no regular shape as seen in Figure 5.13 (a). This corroborates the XRD result which was amorphous. However, the SEM of the product using the uncalcined bauxite had a cluster of hexagonal shaped crystals similar to the parent material. No zeolitic phase was observed in both products.

5.3 Zeolite Synthesis from Kaolin 5.3.1

Effect of Calcination

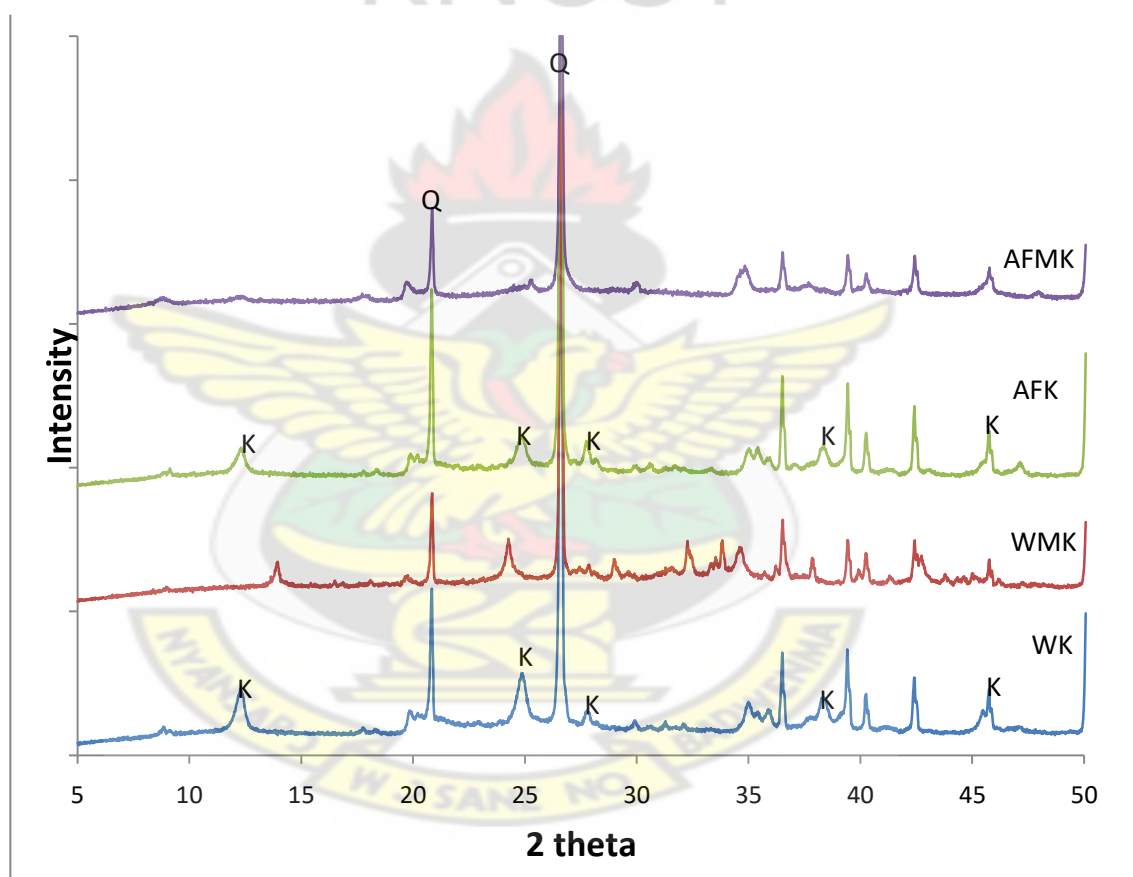


Figure 5.14: XRD patterns of raw kaolin and metakaolin obtained at 600 °C.

The effect of calcination was investigated on both kaolins. The kaolins were calcined at 600 °C for 2 hours in an electrical furnace. The loss of ignition was ascertained and the XRDs were evaluated. The XRD pattern before calcination and after calcination

of each kaolin sample is presented in Figure 5.14. The XRD patterns of the calcined sample (metakaolin) had relatively low peak intensities. The kaolinite peaks were missing in the calcined samples. New peaks, evidently absent in the raw WK sample, were observed at $2\theta = 13.8^\circ$ and at 32.2° of the calcined WK. The calcined AFK did not show any significant peaks apart from the reduced quartz phases.

5.3.2 Route 1

Using metakaolin obtained from calcination at 600°C for 2 hours as outlined in section 4.3.3.2, zeolite synthesis was attempted from WK only. The protocol involved adding NaOH solution to the metakaolin and carrying out hydrothermal synthesis at a stipulated time and temperature. Using a fixed alkali concentration of 2M NaOH solution, the crystallization time was varied at 4, 5 and 6 hours.

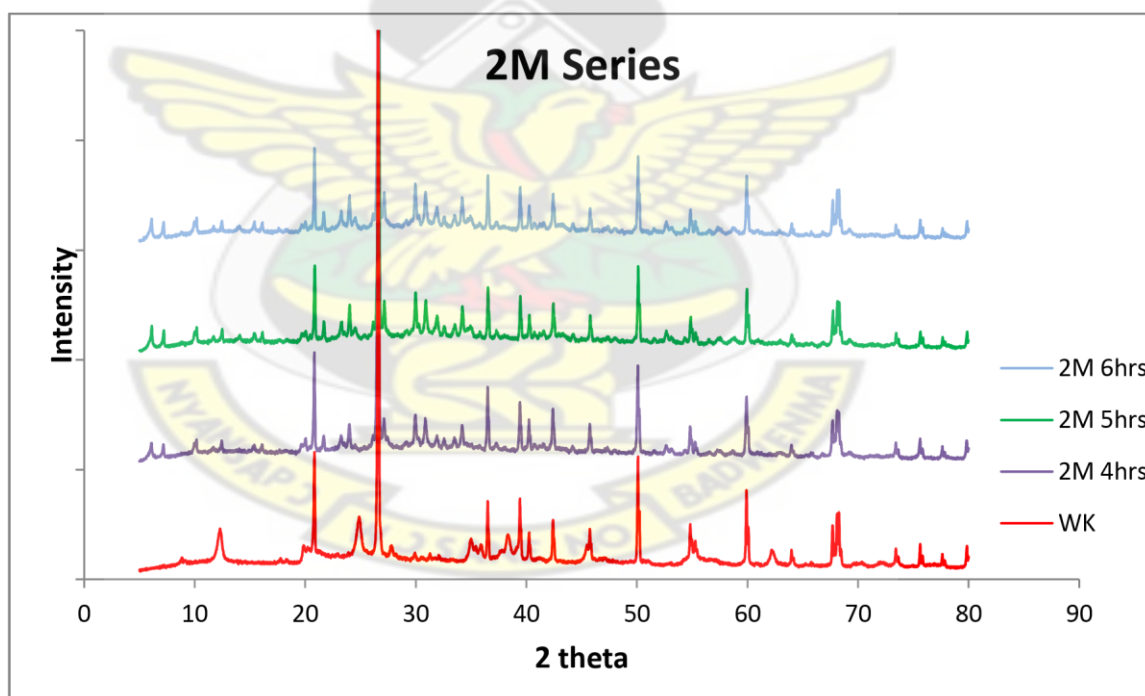


Figure 5.15: XRD plots of as-synthesized zeolites using 2M NaOH solution with varied crystallization times

The XRD of the samples synthesized at different crystallization times were compared to the parent WK sample. The peak at $2\theta = 12.4^\circ$ is absent in all variations. The peak

at $2\theta = 26^\circ$ in the parent WK sample is present but with substantially reduced intensity in the synthesized samples. The 4, 5 and 6 hour samples show similar peaks in their XRD patterns. The similar peaks observable at $2\theta = 7.08^\circ$ and 10.12° in the 2 M 4 hours, $2\theta = 7.12^\circ$ and 10.13° for 2 M 5 hours and $2\theta = 7.19^\circ$ and 10.18° for 2 M 6 hours. However, the peak intensities (Figure 5.15) are more pronounced in the 5 hour crystallization sample. Compared to the parent kaolin, all the quartz peaks ($2\theta = 26.4^\circ$, 36.5° and 50°) were still present indicating that the quartz phase was not reactive in the synthesis in all crystallization times. The mineral phases from the XRD analysis show zeolite A coexisting with quartz at all crystallization times.

In subsequent studies, the molar concentrations of NaOH were varied using 4 M and 6 M with a constant crystallization time of 5 hours. The XRD patterns show distinct variation from the parent kaolin. Comparing as-synthesized samples with each other, a lot of similarities are observed in the 4 M and 6 M NaOH concentration samples ($2\theta \sim 14^\circ$, 20.8° , 24.4° , 26.5°). Peak intensities are more prominent in the 6 M synthesized product. The 2 M synthesized sample in comparison to both the 4 M and 6 M sample has peak positions appearing at fairly different locations. A new peak appeared in both the 4 M and 6 M samples at $2\theta = 13.8^\circ$. The characteristic SOD peak at $2\theta = 14.16^\circ$ and 24.6° with d spacing $6.3 \text{ \AA}$ and $3.63 \text{ \AA}$ respectively were observed in synthesized samples. The quartz phase is observable in all reaction conditions. From the experiments, it was noted that the best results were obtained with 2 M NaOH concentration.

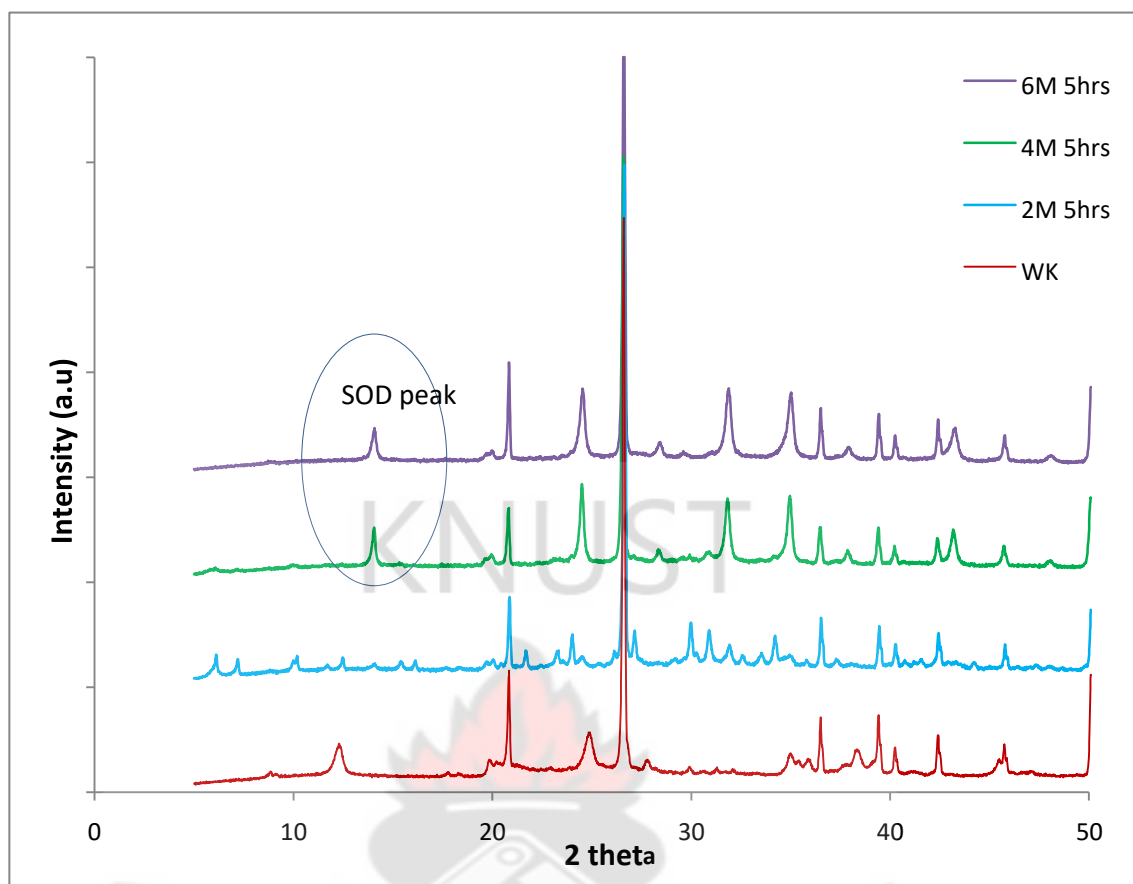


Figure 5.16: XRD patterns of 2M, 4M and 6M NaOH concentrations at 5 hours crystallization time

Table 5.3: Composition of resultant products and their crystallinity formed from varying the molar concentration of NaOH

Sample	Product	Crystallinity
2M	Zeolite A, Quartz	73.27 %
4M	Hydroxysodalite, Quartz	73.80 %
6M	Hydroxysodalite, Quartz	78.70%

SEM analysis conducted on the samples are presented in Figure 5.17. The cubic outline depicting zeolite A is clearly visible in the 2M NaOH sample. Both the 4 M and 6 M sample SEM reveal pseudo-hexagonal prisms intertwining with larger block-like crystals of sodalite. The quartz phase is also observed.

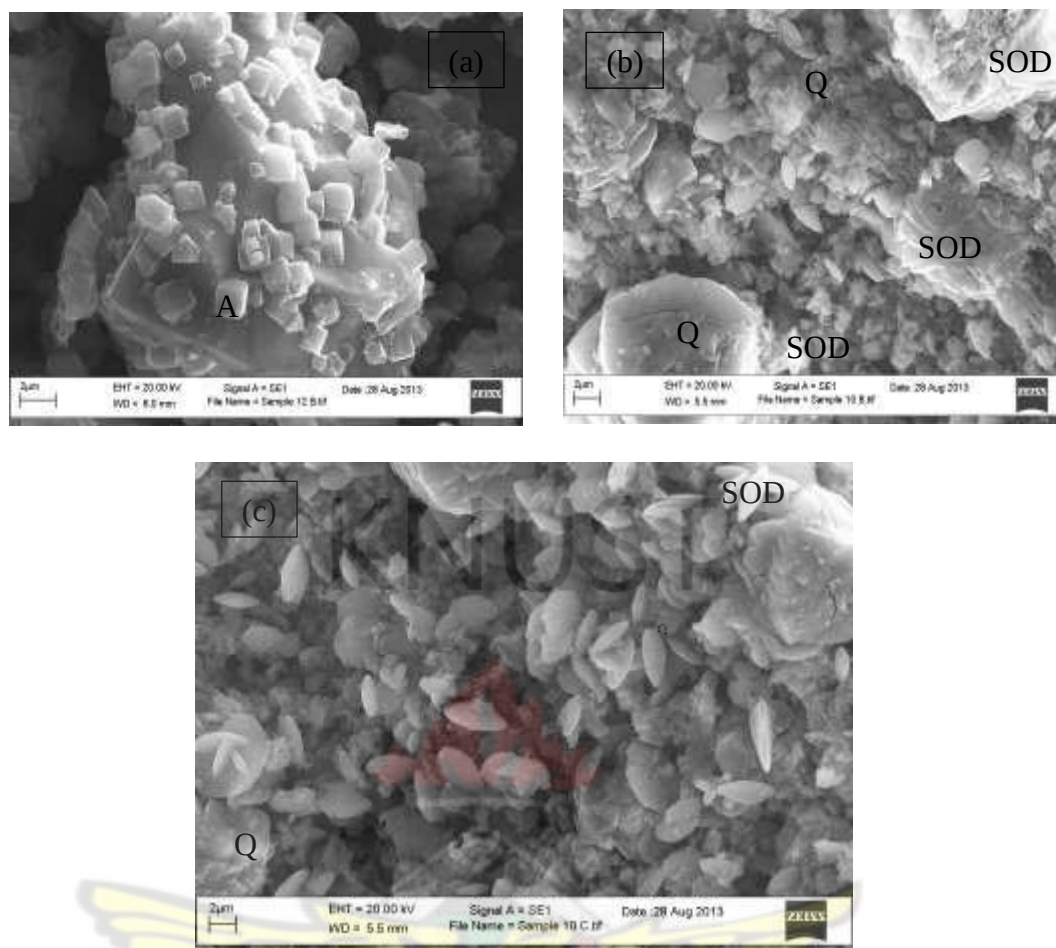


Figure 5.17: SEM images showing the products obtained from varying NaOH concentrations (a) 2M (b) 4M and (c) 6M

5.3.3 Route 2 and 3

Using WK, different protocols mentioned the previous chapter were considered. XRD patterns for routes 2 and 3 are presented in Figure 5.18. The dominant peaks for the Route 2 procedure were observed at $2\theta = 7.09^\circ$, 10.06° , 12° , 21.56° and 23.91° . The quartz phases ($2\theta = 20.7^\circ$ and 26.5°) were still dominant but slightly reduced. The as-synthesized product was found to be zeolite A and quartz.

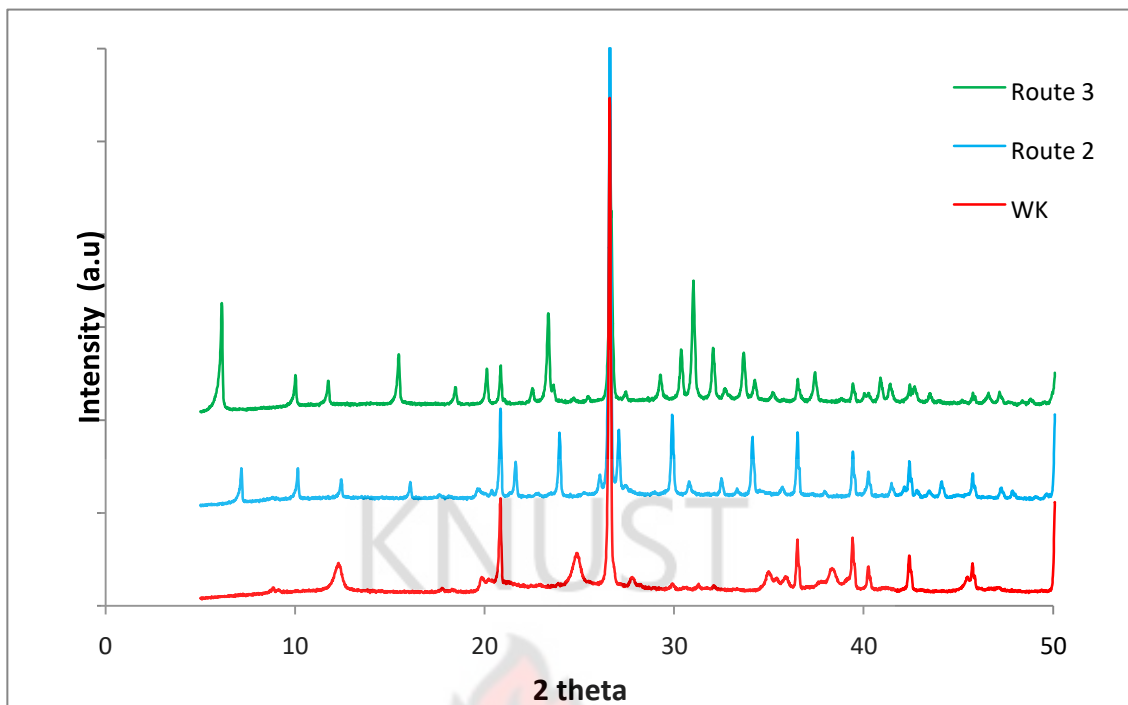


Figure 5.18: XRD patterns of as-synthesized samples using kaolin with varied procedures

Route 3 produced a crystalline compound with its first major peak at $2\theta = 6.1^\circ$ with a relatively high intensity. Subsequent prominent peaks were recorded at $2\theta = 15.4^\circ$, 23.3° and 30.99° . Compared to the parent kaolin, the quartz phase at $2\theta = 20.8^\circ$ and 26.5° were reduced significantly. The Rietveld analysis showed the mineralogical phases as 84.2 % of zeolite Na-LSX and 15.8 % quartz (Figure 5.19).

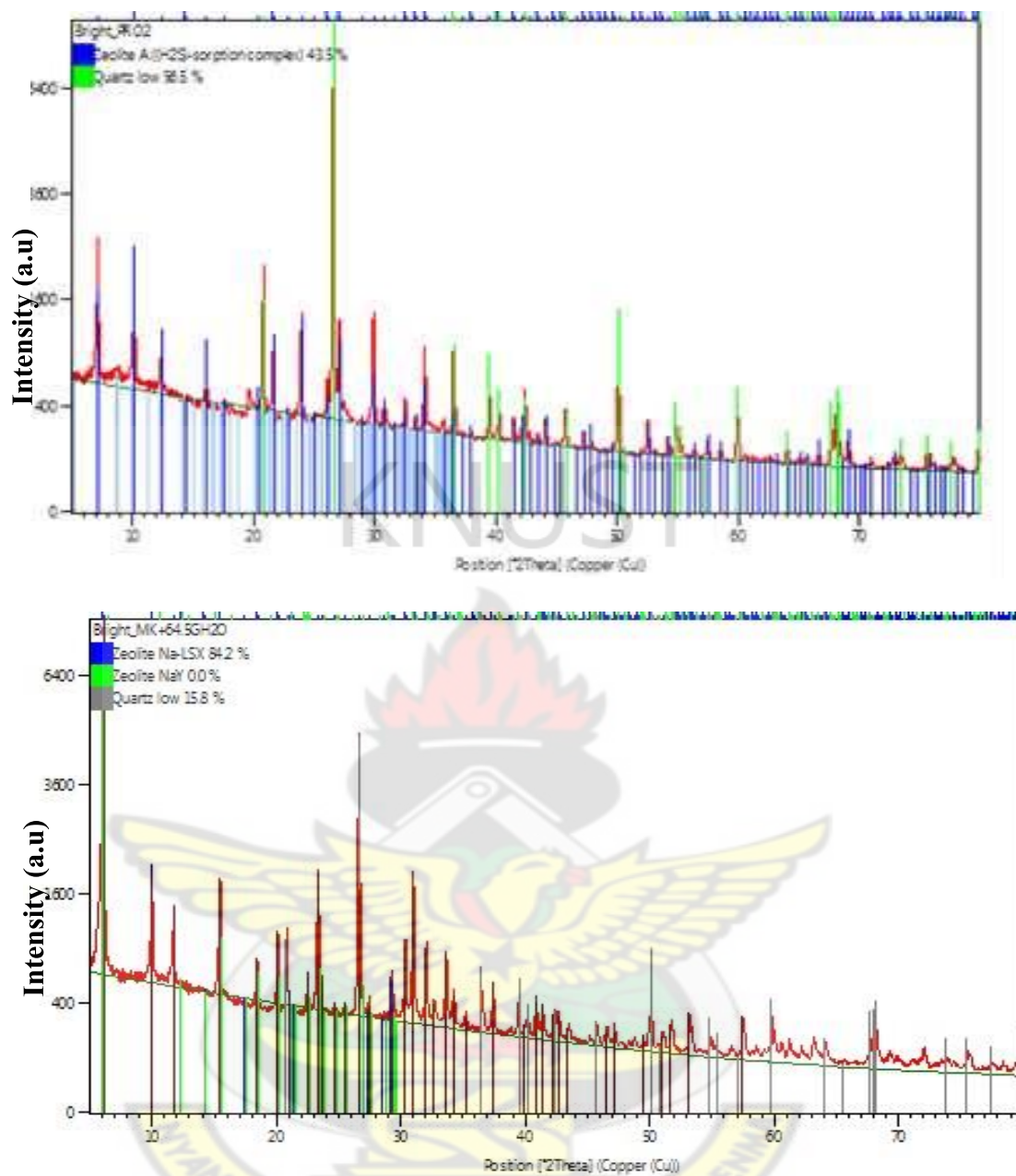


Figure 5.19: XRD patterns showing the mineralogical composition of the assynthesized product (Route 2 and 3)

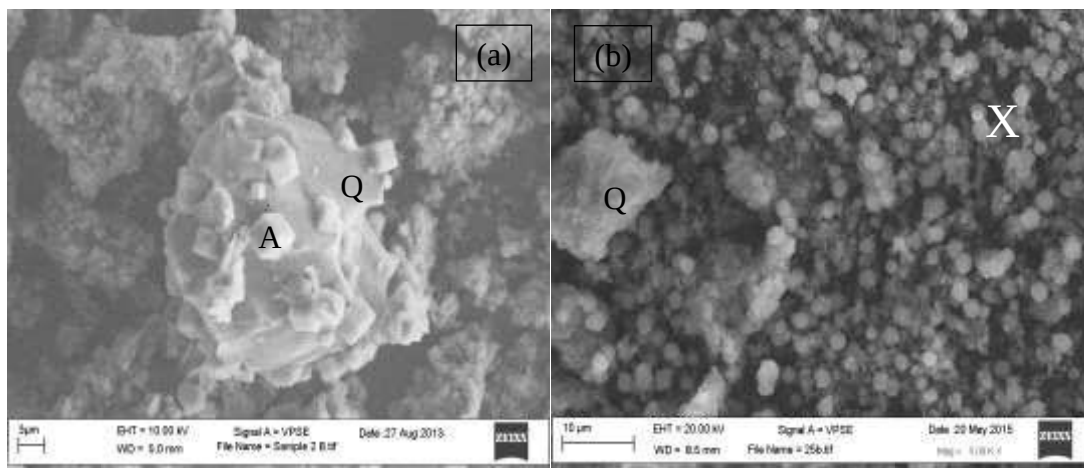


Figure 5.20: SEM images of (a) Zeolite A and quartz obtained from synthesis route 2 (b) zeolite X and quartz obtained from synthesis route 3.

The SEM images confirm the XRD results by clearly depicting the various phases present. A larger amount of quartz is observed in the product from route 2 with zeolite A crystals embedded on them. The octahedral shaped crystals observed in Figure 5.20b corresponds to the presence of zeolite X using the protocol outlined for Route 3.

5.4 Zeolite from Bauxite and Kaolin

With the aim of synthesizing new zeolitic products at low cost, bauxite was mixed with kaolin to improve the Si/Al ratio. Using a constant mass of kaolin with varying masses of bauxite, zeolite synthesis was attempted.

5.4.1 Method 1: Effect of mass of bauxite

Using 5, 10 and 15 g of bauxite to a constant mass of WK and AFK, all other synthesis parameters were kept constant. The XRD patterns of all three variations in mass had similar peak positions and intensities.

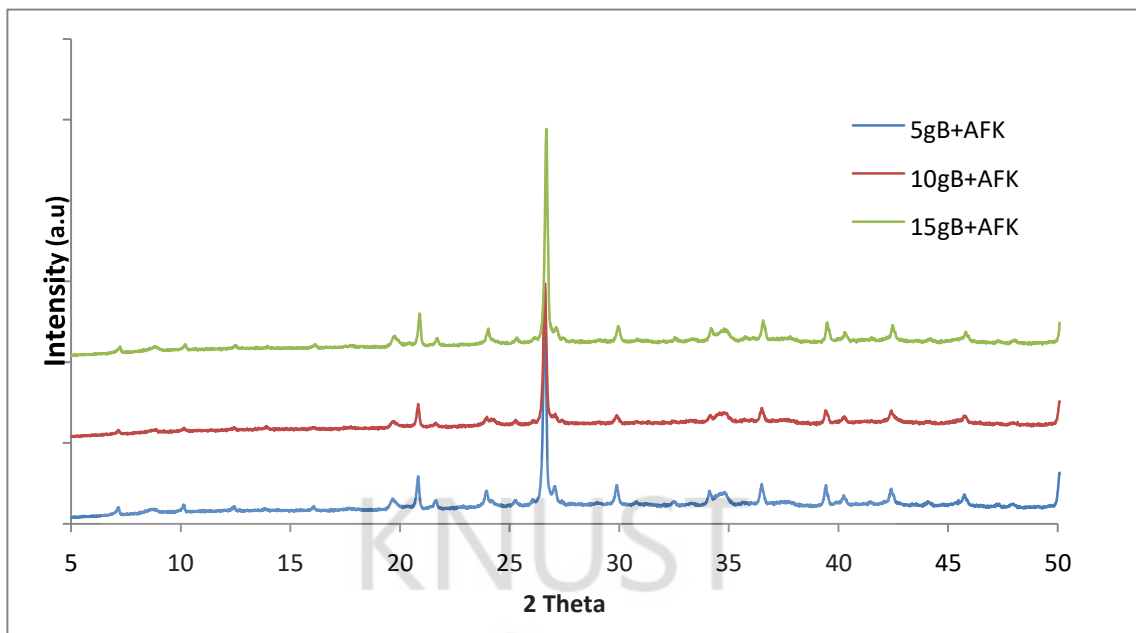


Figure 5.21a: XRD patterns of zeolites from Anfoega kaolin and different masses of bauxite

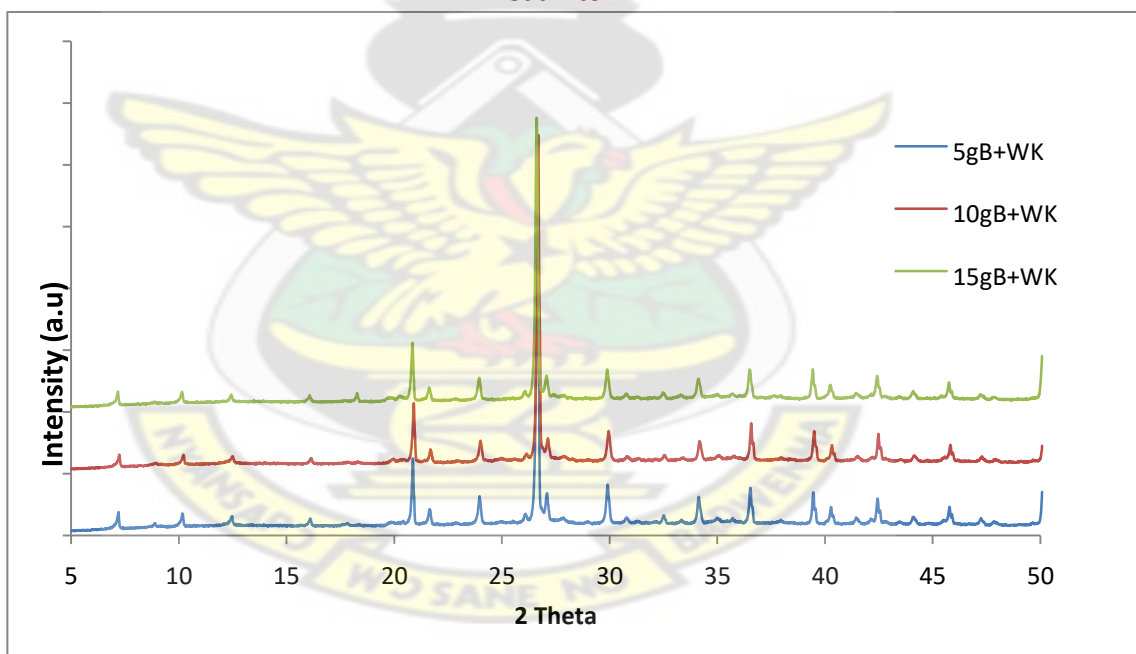


Figure 5.21b: XRD patterns of zeolites from Wassa kaolin and different masses of bauxite

Regardless of the mass of bauxite used, similar products were obtained. Zeolite A was the major zeolitic product coexisting with quartz. The quartz peaks were still dominant. Their corresponding zeolite crystallinities were low as peak intensities were

not too distinct. Analysis of the results obtained using both WK and AFK showed the similarities in both.

5.4.2 Method 2

Using the Bayer process, sodium aluminate (NaAlO_3) was extracted from the bauxite and added to metakaolin. The effect of crystallization time on zeolite synthesis using this protocol was investigated. Crystallization times of 5 hours, 18 hours and 24 hours were evaluated keeping aging time and all other factors constant. The XRD patterns show that zeolite A was formed with the different crystallization times.

Variable amounts of quartz were found in each resulting product with its peak at $2\theta = 26.5^\circ$. A peak attributed to the characteristic zeolite A was recorded at $2\theta = 7.12^\circ$. The intensity of the peaks however decreased with increasing crystallization time of the hydrothermal reaction.

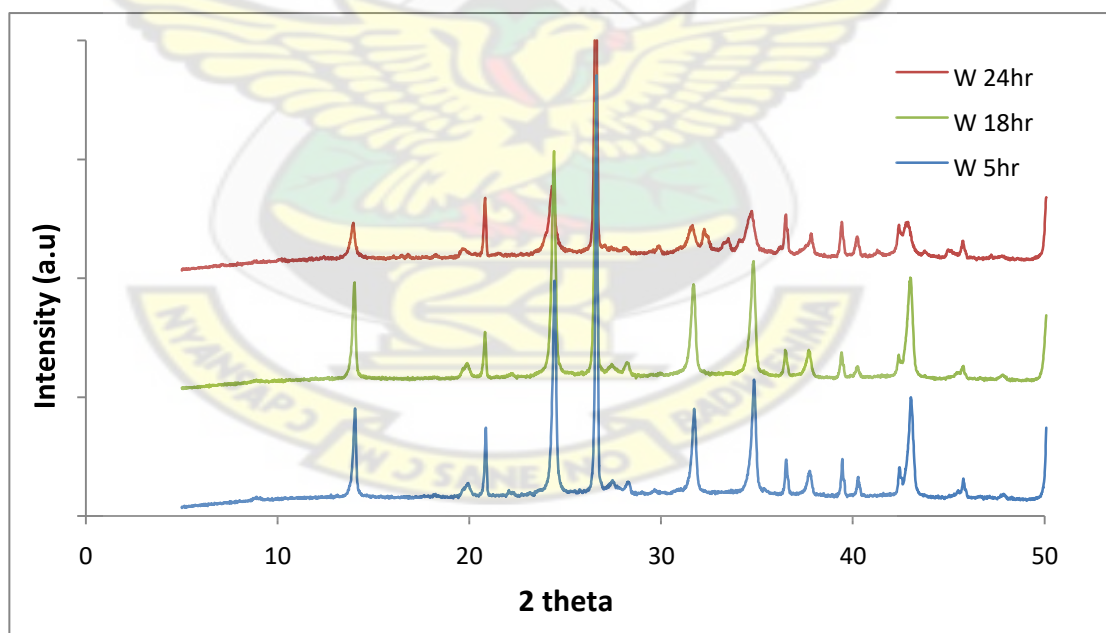


Figure 5.22: XRD patterns of as-synthesized products obtained from using aluminate solution and metakaolin at different crystallization times of 5, 18 and 24 hours.

However, the amount of zeolitic phase increased with increasing crystallization time. The results also reveal that the crystallinity of the synthesized zeolite was highest when crystallization time was 5 hours.

Apart from comparing crystallization times using sodium aluminate solution from bauxite, the order of mixing was investigated after 24 hours. Results showed similar peaks when the order of mixing was reversed. Peak positions were similar in both results but intensities were reduced in the initial protocol. Additional water to the reaction produced a different pattern as seen in Figure 5.23. The peak intensities were however very reduced. ZK-14 and quartz were the resulting products when additional water was added whilst Zeolite A and quartz were the products of the other experiments. The SEM images show cubic morphology typical of zeolite A crystals. Crystals of zeolite ZK-14 had hexagonal plate-like discs as shown in Figure 5.24c.

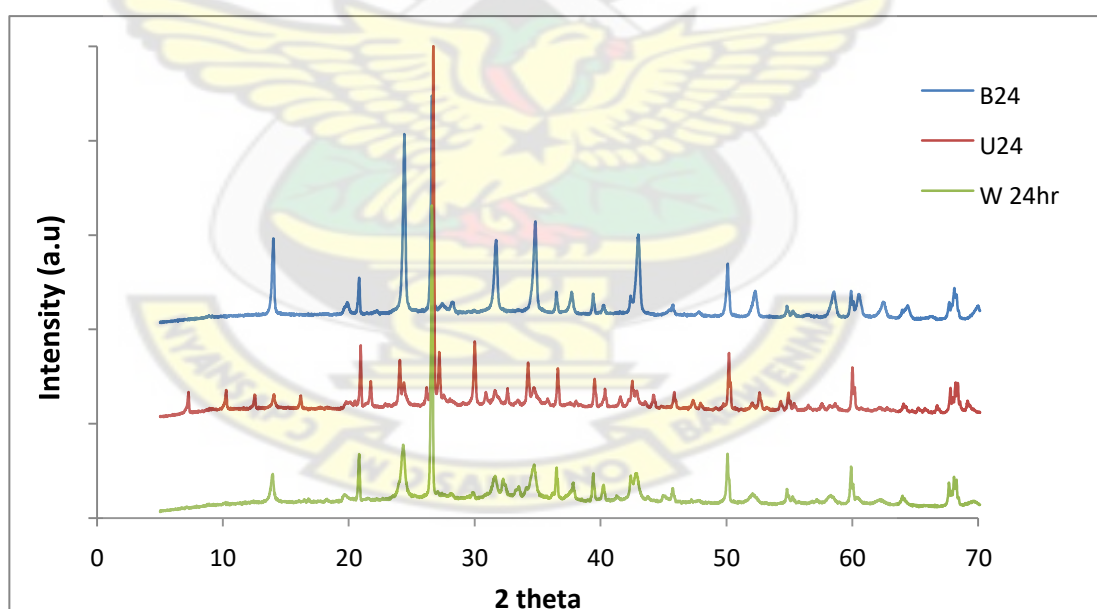


Figure 5.23: XRD patterns of as-synthesized zeolite using sodium aluminate from bauxite and metakaolin with or without additional water

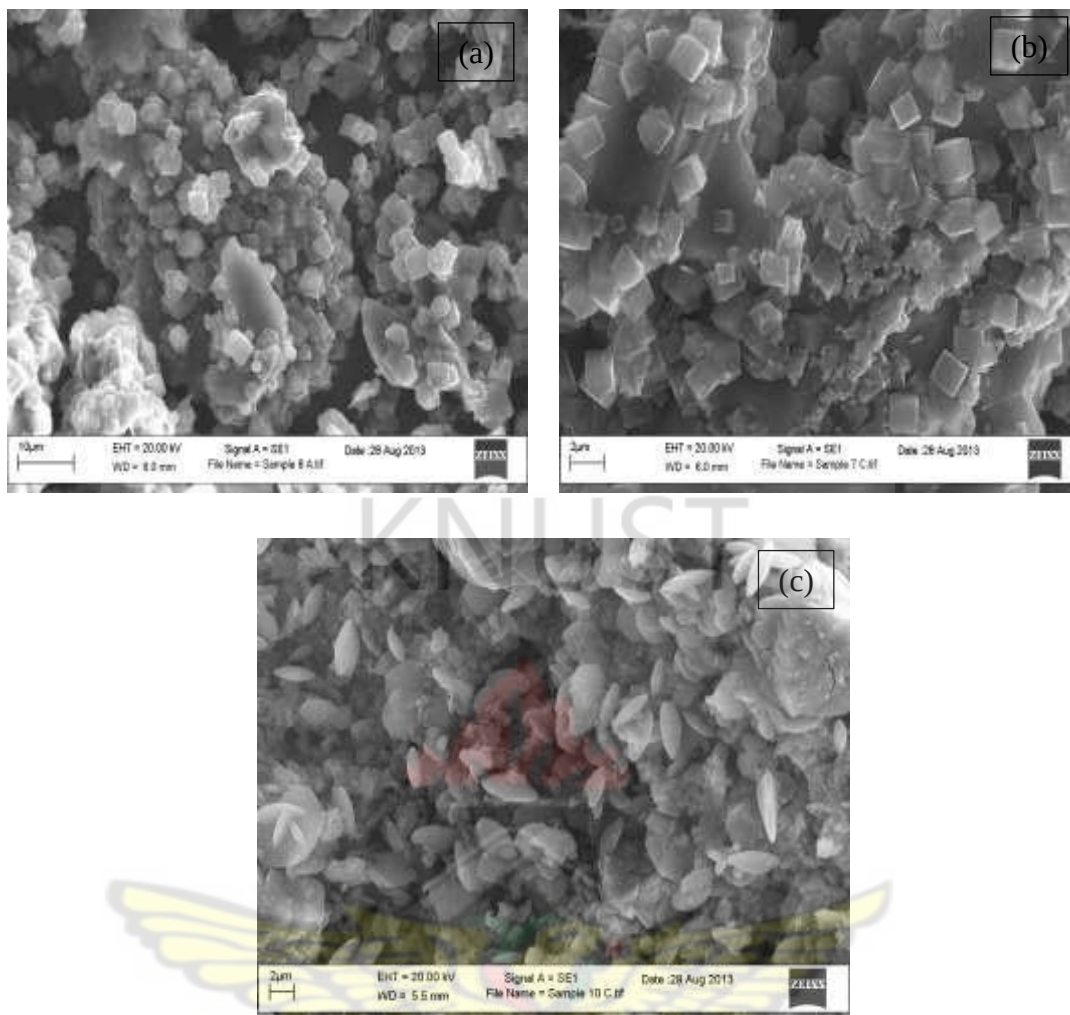


Figure 5.24: SEM images of as-synthesized zeolites from sodium aluminate solution from bauxite (a) zeolite A and quartz (b) zeolite A and quartz (c) ZK-14 and quartz crystals.

5.4.3 Method 3

5.4.3.1 Effect of varying crystallization time

Using sodium aluminate filtrate from bauxite and sodium silicate from AFK, various variations were considered. Increase in crystallization time from 3 to 96 hours was studied whilst keeping all other factors constant. The XRD, SEM EDX and FTIR analysis are presented below.

The EDX analysis of all samples of the synthesized zeolites containing Si, Al, Na and traces of K. the presence of these ions is an indicator of the recommended ions required

in a zeolite structure. The Si/Al ratios in the 3 hours and 5 hours zeolite is ~ 1 whilst that of the 24 hour zeolite is ~ 1.3 and ~ 1.2 for 96 hours.

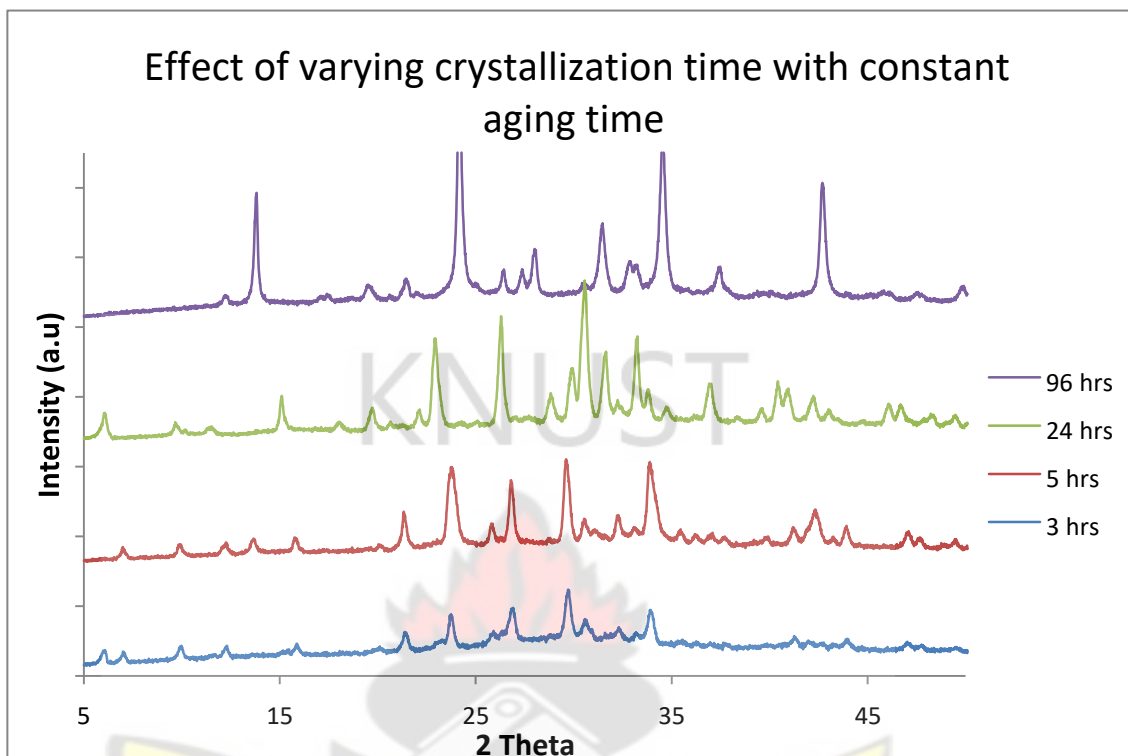


Figure 5.25: XRD patterns of zeolites with different crystallization times of 3, 5, 24 and 96 hours

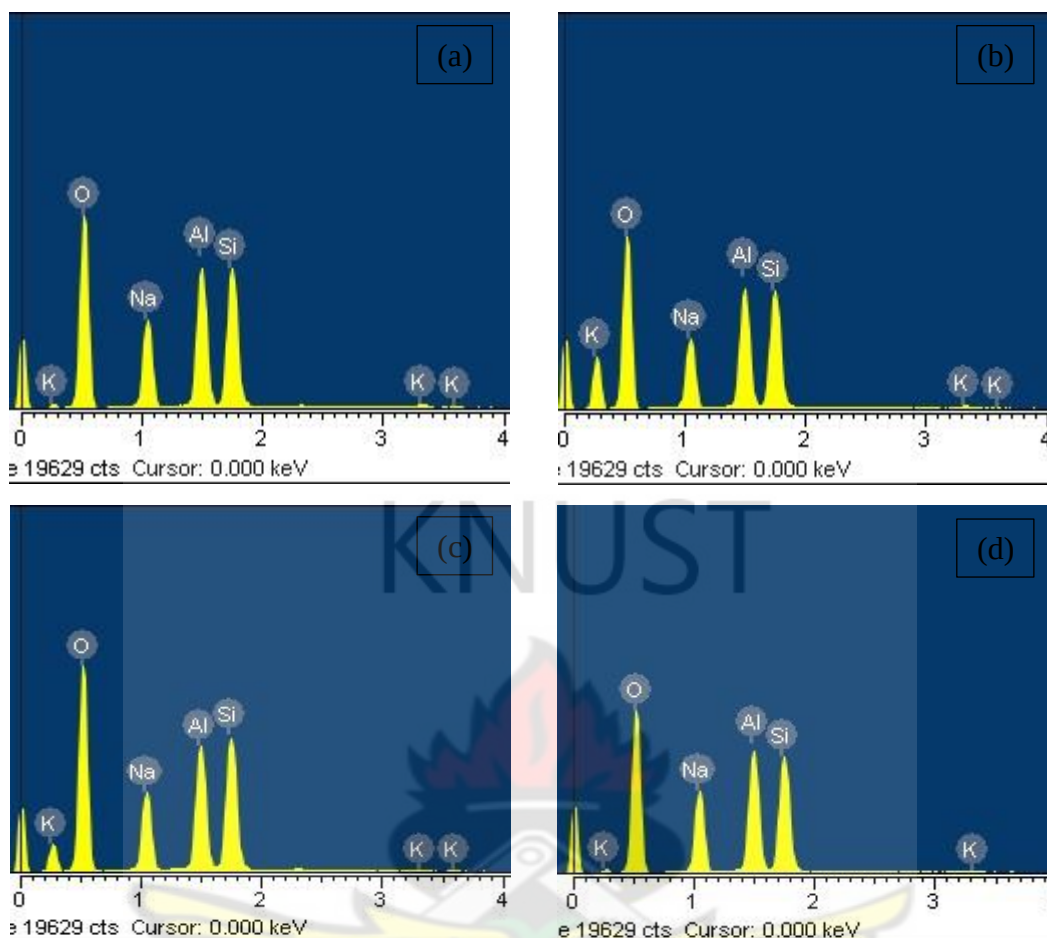


Figure 5.26: EDX spectra of synthesized products with crystallization times of (a) 3 hours (b) 5 hours (c) 24hours and (d) 96 hours

The 3 hour sample has its first at $2\theta = 5.88^\circ$. Other distinct but not too prominent peaks are observed at $2\theta = 6.94^\circ, 9.95^\circ, 12.24^\circ$ and 15.9° . The region between $2\theta = 23.5^\circ$ and 33.8° had a cluster of prominent peaks.

The 5 hours sample showed similar peak positions as the 3 hour sample. The 5 hour sample however, has more intense peaks compared to the 3 hour sample. The 24 hours sample possesses peaks at position $2\theta = 5.72^\circ, 5.73^\circ, 9.60^\circ, 9.62^\circ, 11.32^\circ, 15.03^\circ$ and 19.67° . For the 96 hours, peak intensities are observable at $2\theta = 12.25^\circ,$

13.76°, 13.79°, 13.83°, 24.11°, 24.12°, 24.17°, 24.23° and 27.94°. Peak intensities are more defined for the 96 hours sample than for the remaining 3 samples indicating very crystalline material.

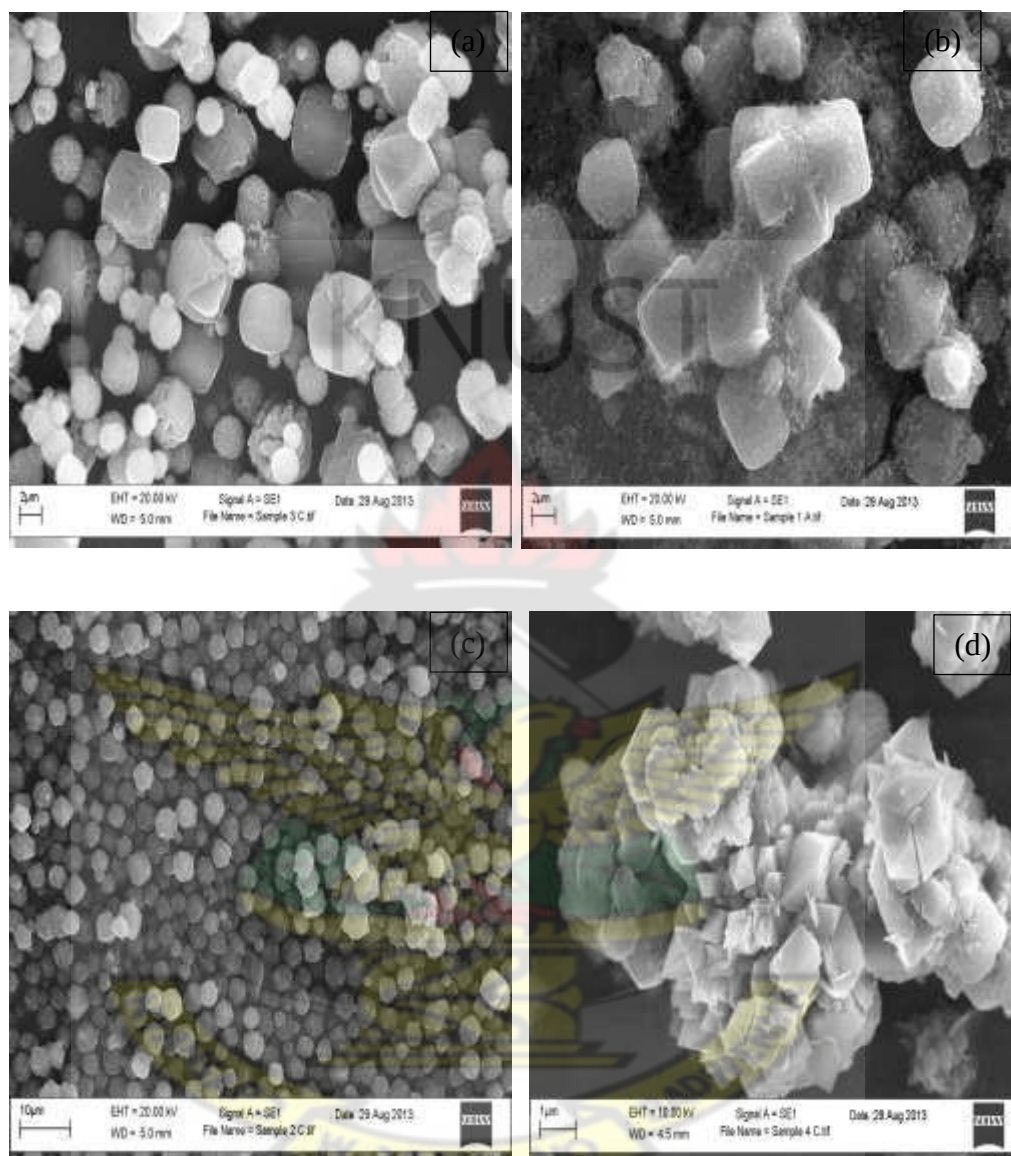


Figure 5.27: SEM images of zeolites synthesized at (a) 3 hours (b) 5 hours (c) 24 hours and (d) 96 hours

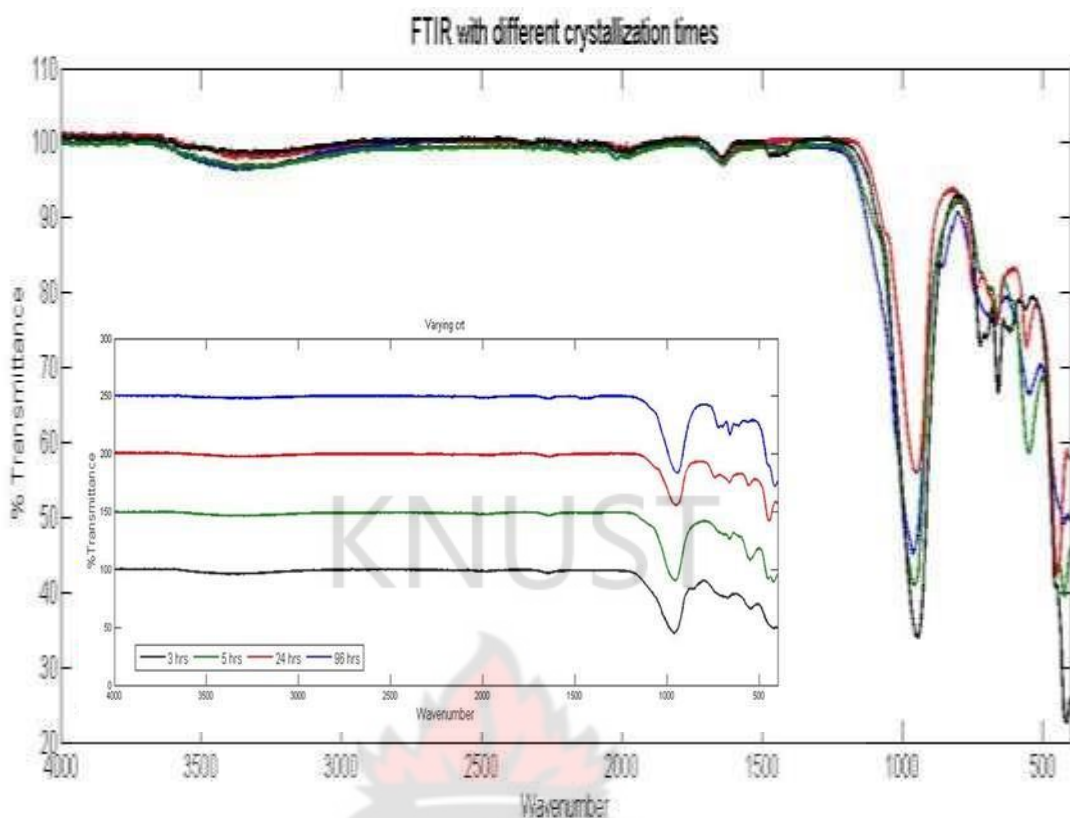


Figure 5.28: FTIR spectra of as-synthesized zeolites with different crystallization times

The mixed phases observed in the XRD analyses is corroborated by the SEM analyses. The SEM images show mixed species of a cubic formed crystals coexisting with spherical crystals with 3 hours crystallization time. Single cubic crystal cubes are observable in the SEM image after 5 hours. different particle sizes of zeolite A were however present. Octahedral shaped crystals are portrayed in the image after 24 hours. Wedge shaped crystals were observed after 96 hours of crystallization together with hexagonal discs forming an aggregate.

The FTIR spectra in Figure 5.28 show similar peak positions for all synthesized zeolites. Highest intensity is observed in the 1200 – 950 cm^{-1} region. Different band positions are observed in the 820 – 750 cm^{-1} and 650 – 500 cm^{-1} regions. Two broad

peaks are noticeable in the $500 - 420 \text{ cm}^{-1}$ for the samples synthesized at 24 and 48 hours.

5.4.3.2 Effect of varying aging time

The results obtained when a constant crystallization time of 24 hours and crystallization temperature of 105°C with varied aging times are presented. SEM and EDX analyses were not conducted on the amorphous products after XRD analysis.

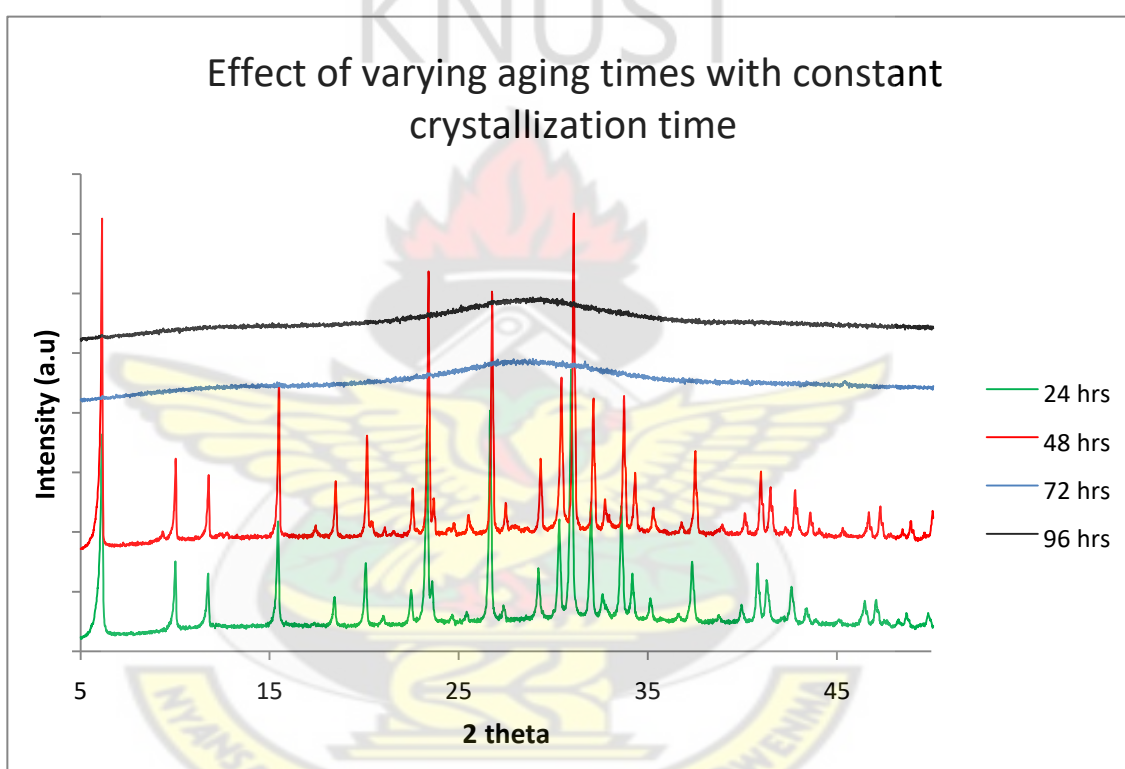


Figure 5.29: XRD patterns of as-synthesized zeolites with varied aging times

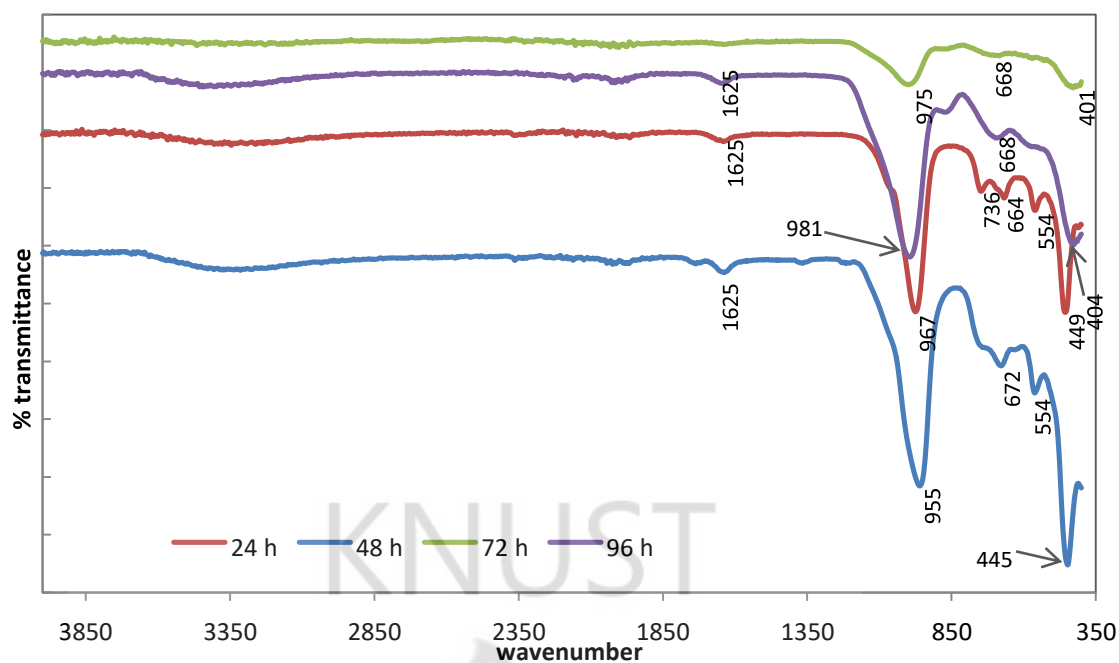


Figure 5.30: FTIR spectra of as-synthesized zeolites using different aging times but with constant crystallization time

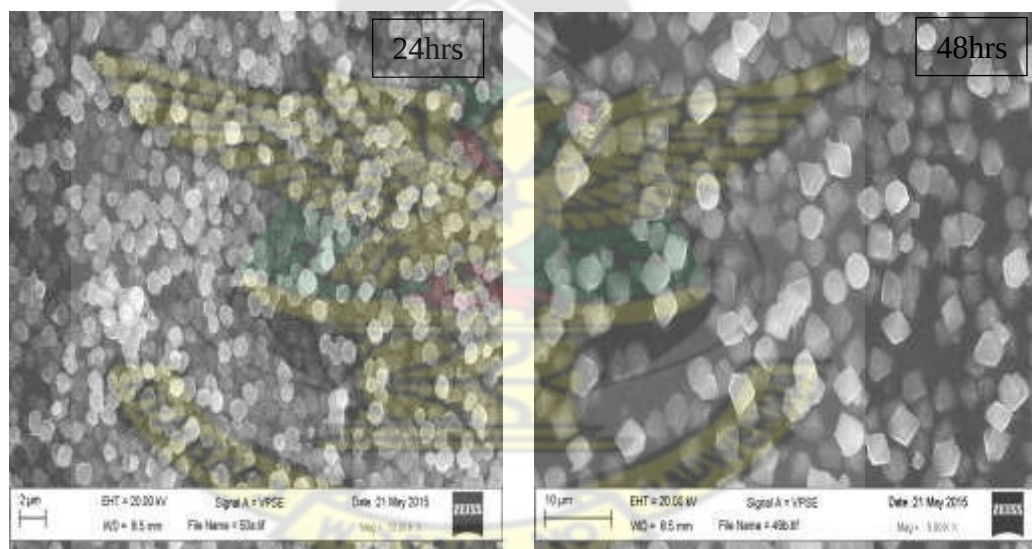


Figure 5.31: SEM images of samples aged for 24 and 48 hours

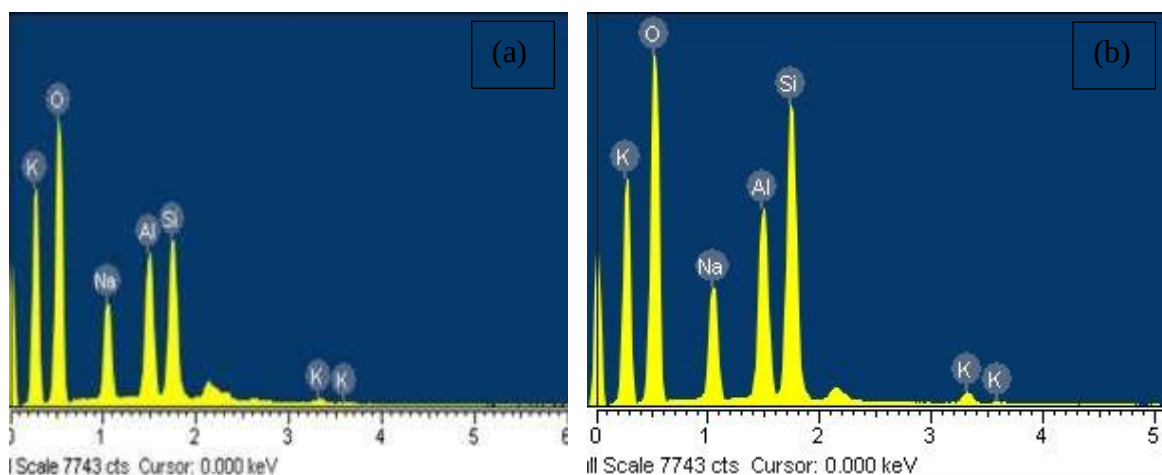


Figure 5.32: EDX analysis of as-synthesized crystalline zeolite samples using (a) 24 hours (b) 48 hours aging time

XRD results as seen in Figure 5.29 show zeolites with high peak intensities for samples synthesized after aging for 24 and 48 hours. Zeolite X was obtained after aging for 24 hours and zeolite Y after 48 hours. No quartz phase was recorded.

Similar distinct peak positions are observable in the 24 and 48 hour aging samples. No crystalline peak is observed in the 72 and 96 hours samples. Aging for 72 and 96 hours produced amorphous compounds.

FTIR studies were conducted on all the samples. An intense band occurs at 967, 955 and 981 cm^{-1} for 24, 48 and 96 hours respectively. However, a similar peak is observed in the 72 hour sample with low intensity at 975 cm^{-1} . Both the 24 and 48 hour aging samples recorded a number of bands between 750 and 400 cm^{-1} whilst the 72 and 96 hour samples recorded two peaks in that region.

SEM images of the crystalline synthesized samples exhibit multifaceted crystal shapes. A minute number of spherical crystals are also observed interspersed with the octahedral crystals. EDX analyses performed on the crystalline samples depicted the

presence of Na, Al, Si and K as the elements present. The ratio of Si/Al was 1.3 for 24 hours and 1.7 for 48 hours.

5.4.3.3 Effect of varying Si/Al ratio of reactants

Figure 5.30 shows the XRD patterns of zeolitic products obtained using a crystallization time of 24 hours whilst varying the Si/Al ratios (1, 1.8 and 2.0).

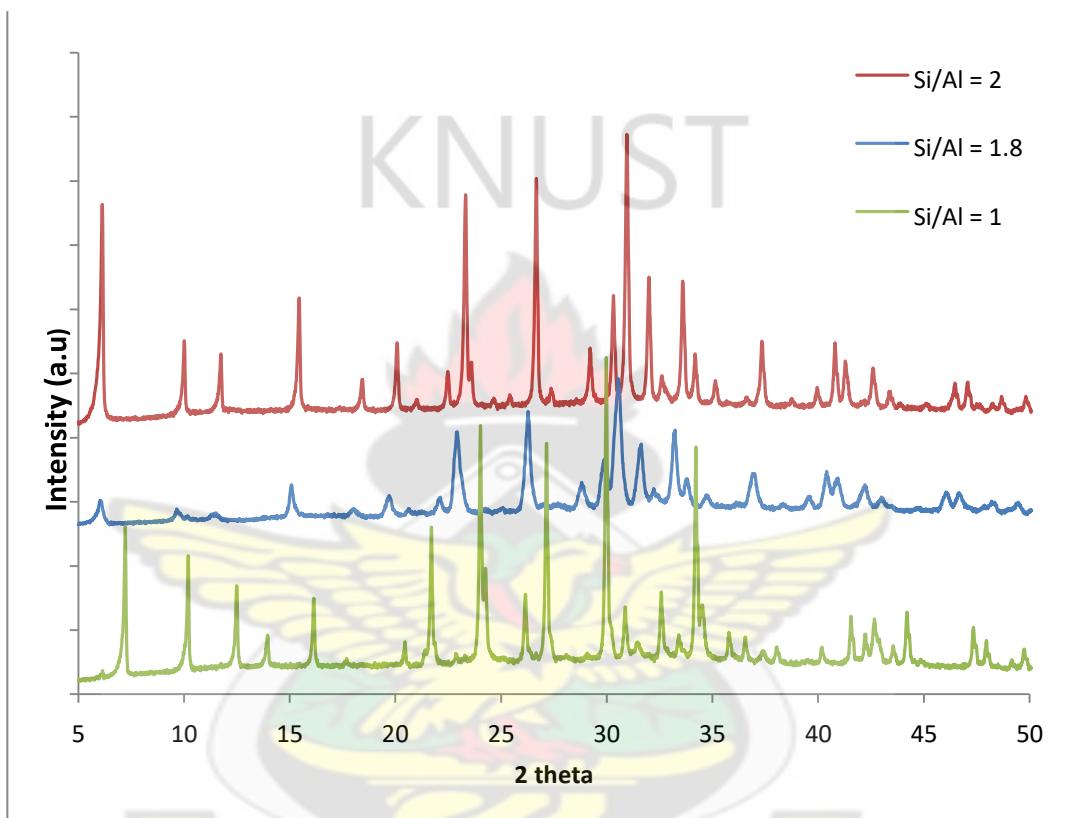


Figure 5.33: XRD patterns of the as-synthesized zeolites obtained using varied Si/Al ratios

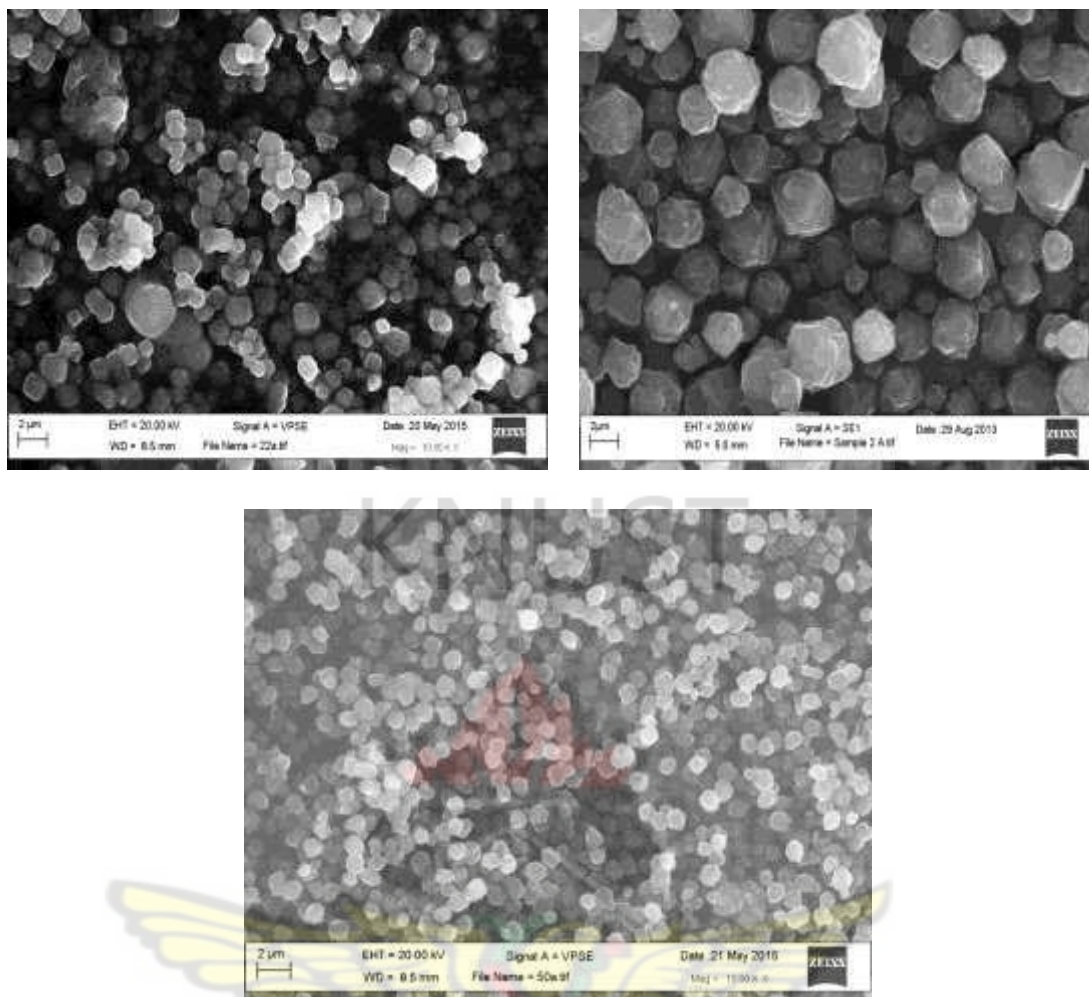


Figure 5.34: SEM images showing the products obtained when the Si/Al ratio was varied

Results obtained whilst varying Si/Al ratio with constant and aging times show crystalline products with distinct peaks. First five Peak positions are observed at $2\theta = 7.19^\circ, 10.18^\circ, 12.46^\circ, 13.38^\circ$ and 16.11° for the sample with Si/Al =1 indicating zeolite A. Similar peak positions are noticed in the samples with Si/Al = 1.8 and 2 but with very high intensity with Si/Al = 2. The first five peak positions are observed at $2\theta = 6.12^\circ, 9.98^\circ, 11.7^\circ, 15.4^\circ$ and 18.37° . These peaks are the characteristic zeolite X peaks. Increasing the Si/Al from 1 to 1.8 produced zeolite X.

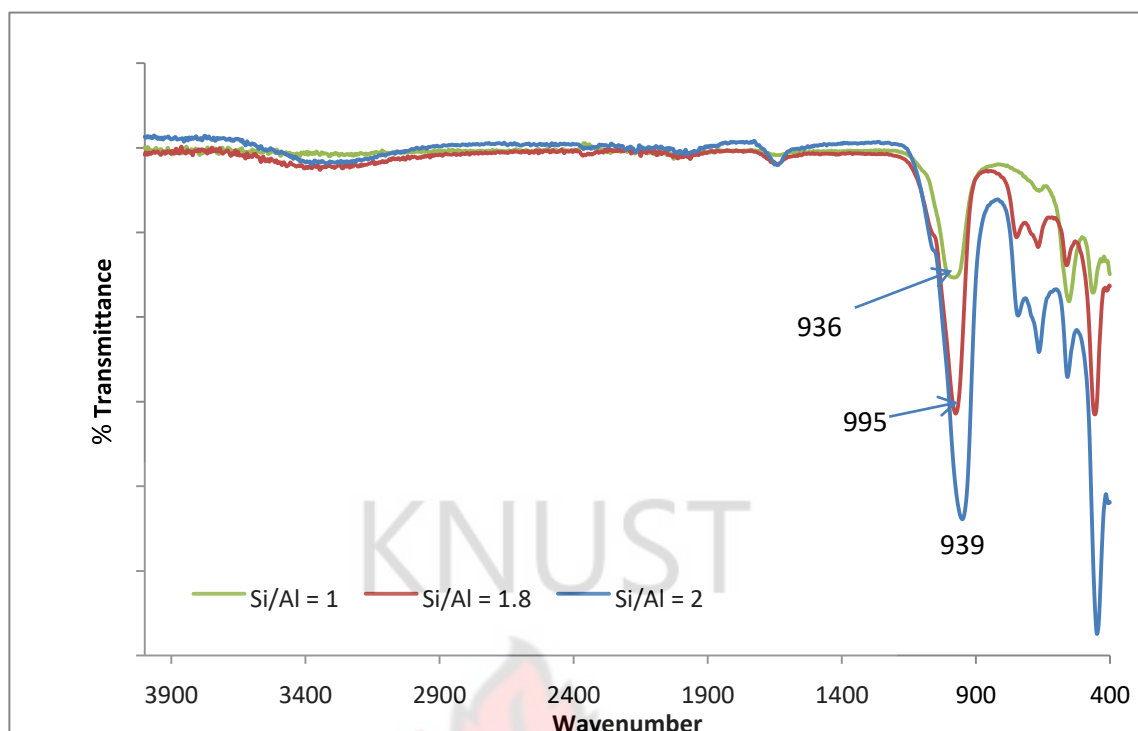


Figure 5.35: FTIR spectra of the as-synthesized product obtained after varying the Si/Al ratio of reactants

SEM images of the corresponding zeolites confirm the XRD analysis. A cubic outline was seen for the as-synthesized zeolite A, with zeolite X as the product obtained from both Si/Al = 1.8 and 2, a more distinct shape was noted in latter.

Figure 5.32 portrays the FTIR spectra of the as-synthesized. An intense band is observed at 936, 995 and 939 cm^{-1} attributed to as-symmetric stretching of internal vibrations is visible in all three products. The intensity of the bands is however reduced with decreasing Si/Al ratio. A larger number of bands are noticed in the region between 780 and 550 cm^{-1} . These bands are missing in the zeolite A product except for a band at 580 cm^{-1} .

5.4.3.4 Effect of alkali concentration

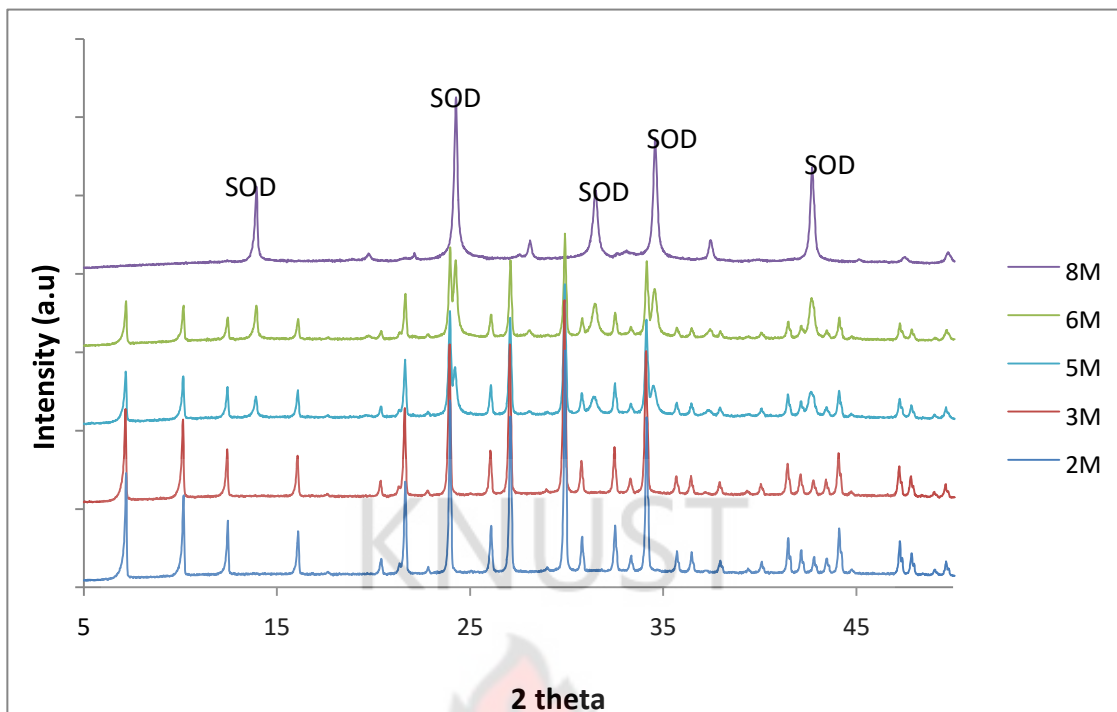


Figure 5.36: XRD patterns of as-synthesized zeolites from bauxite and kaolin filtrates with increasing alkali concentrations

The molarity of the alkali solution used in obtaining sodium aluminate from bauxite was varied (2, 3, 5, 6 and 8 M). The XRD patterns show crystalline products with distinct peaks. A similar pattern is observed in the 2 and 3 M samples. New peaks appeared with increasing molarity from 3 M to 5 M. The intensity of the peaks also observed to reduce whilst increasing molarity. A similar pattern is noticed in the 5 and 6 M samples with similar peak positions. A few peaks were detected in the 8 M sample at $2\theta = 13.87^\circ, 24.22^\circ, 31.4^\circ, 34.52^\circ$ and 42.65° . Peak positions of this sample were fairly different from the 2 and 3 M however; similar but less prominent peaks were noticeable in the 5 and 6 M products. The SEM images of the assynthesized zeolitic products using different alkali concentrations are presented in

Figure 5.37. The SEM images were acquired using a working distance (WD) = 2 μm . A cubic crystal morphology is observed in the first two samples (2 and 3 M). The 5, 6

and 8 M SEM images had needle-like crystals coexisting with hexagonal shaped discs. The particle sizes of the crystals appear to reduce with increasing alkali concentration. The EDX analyses of the samples showed the major elements to be Na, O, Si and Al in all the zeolite products (Figure 5.38). The peak intensities of the elements appeared similar in all the results. The ratios of Si/Al of the resultant products are presented in Table 5.4 below:

Table 5.4: The Si/Al and Na/Si ratio of the as-synthesized zeolites

NaOH concentration	Si/Al	Na/Si	Product
2M	~1	1.1	LTA
3M	~1	1.21	LTA
5M	1	1.37	LTA, SOD
6M	1	1.27	LTA, SOD
8M	1.06	1.08	SOD

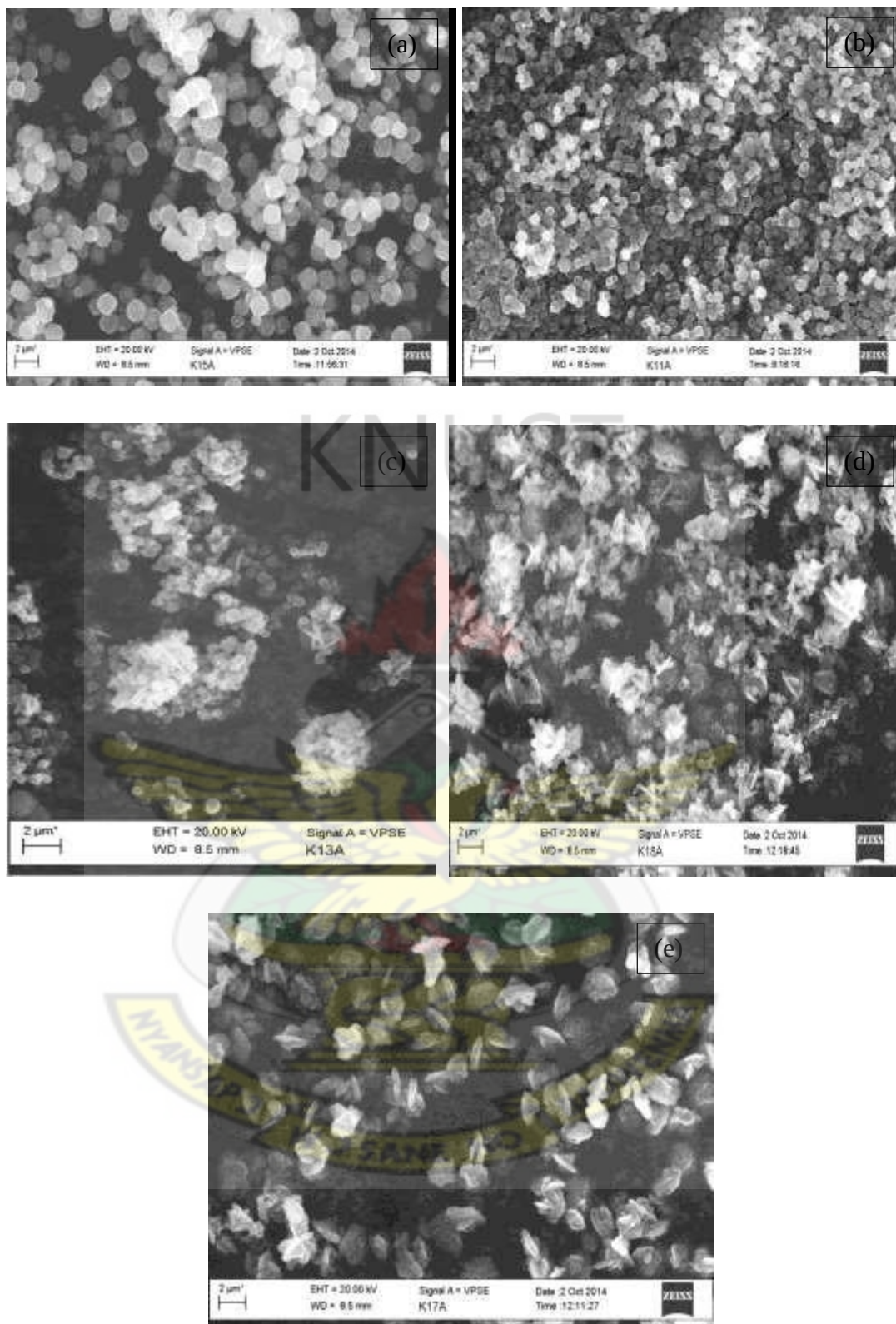


Figure 5.37: SEM images of zeolitic products obtained using (a) 2M (b) 3M (c) 5M (d) 6M and (e) 8M NaAlO_3 solution

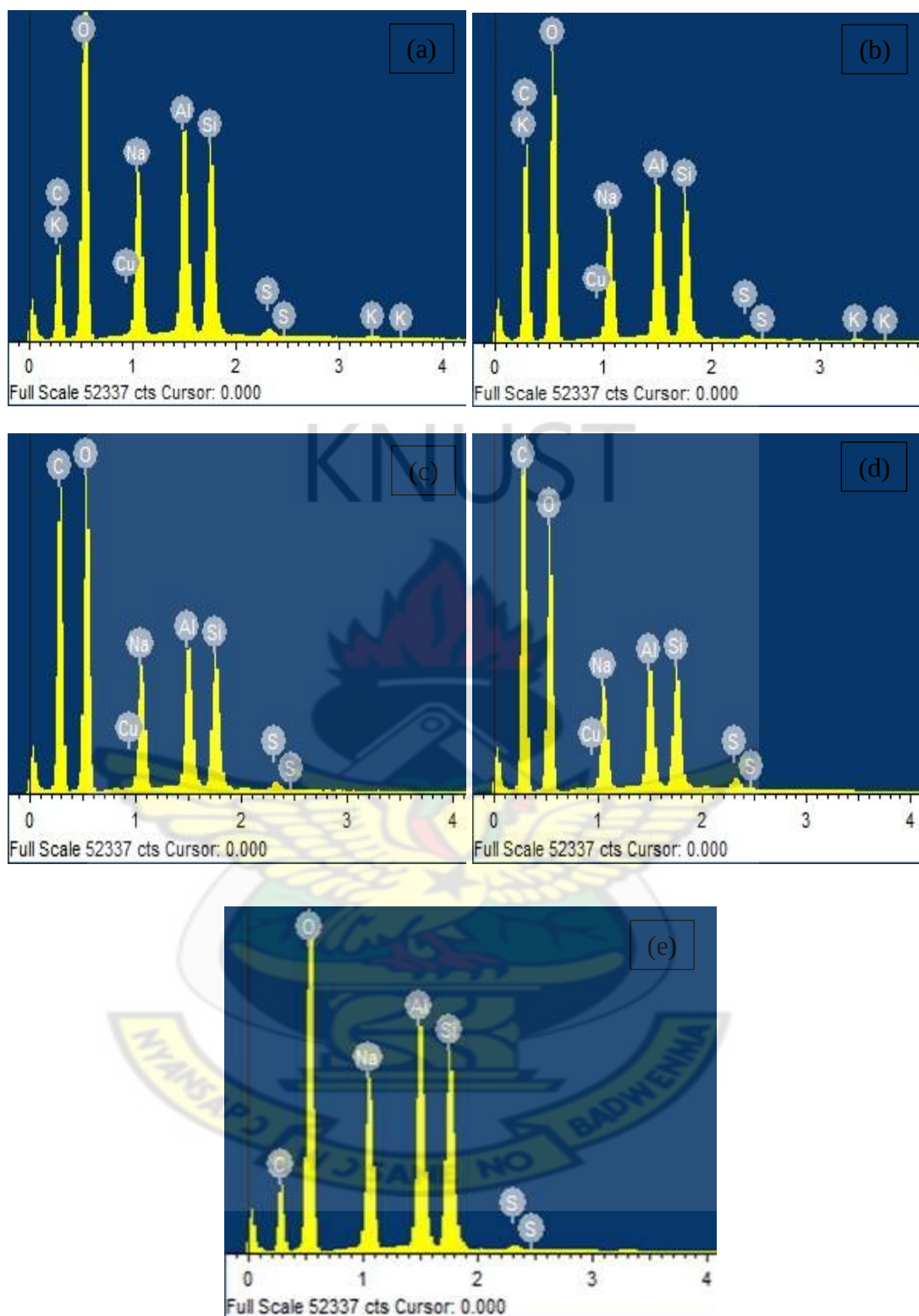


Figure 5.38: EDX spectra of the as-synthesized zeolites from different alkali concentrations of (a) 2 M (b) 3 M (c) 5 M (d) 6 M and (e) 8 M

5.4.3.5 Crystallinity and crystallite size results

The crystallinity of the synthesized samples were evaluated using both XRD and FTIR analyses. The crystallite size was deduced using the Scherer's equation (equation 3.5). The crystallinity of the samples increased slightly with increasing alkaline concentration. However, due to the mixed phases obtained with 5 M and 6 M concentrations of NaOH, the crystallinity of the products was decreased. The crystallinity values obtained from both FTIR and XRD were very similar.

Table 5.5: The crystallinity of synthesized zeolites and their crystallite sizes

Sample	% Crystallinity	% Crystallinity	Crystallite size /nm
	XRD	FTIR	
2 M	87.25	87.56	1.57
3 M	92.55	91.80	1.77
5 M	79.59	80.41	1.80
6 M	84.83	84.64	0.75
8 M	92.19	89.76	0.65

The crystallite size was found to increase with increasing alkali concentration with the formation of zeolite A. With the formation of Sodalite, the crystallite size decreased with increasing alkali concentration.

5.5 Comparing structural features

Table 5.6: Structural parameters of the synthesized zeolites

	Standard zeolite A	2 M	3 M	Standard SOD	8 M
Name	LTA	LTA	LTA	SOD	SOD
Formula	$\text{Na}_{96}\text{Si}_{96}\text{Al}_{96}\text{O}_{384}$	$\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$	$\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$	$\text{Na}_6\text{H}_2\text{Si}_6\text{Al}_6\text{O}_{24}$	$\text{Na}_6\text{H}_2\text{Si}_6\text{Al}_6\text{O}_{24}$
System	cubic	cubic	cubic	cubic	cubic
Space group	Pm-3m	Pm-3m	Pm-3m	Im-3m	P-43n
a	11.919	12.309	12.278	8.9561	8.87
b	11.919	12.309	12.278	8.9561	8.87
c	11.919	12.309	12.278	8.9561	8.87
α	90	90	90	90	90
β	90	90	90	90	90
γ	90	90	90	90	90
Density	1.42	1.69	1.53	1.67	2.3
Cell volume	1693.24	1864.95	1850.9	718.3	697.8

The structural parameters of the synthesized zeolites according to Table 5.6, possess similarities with the standard zeolite. Comparison was made for pure phased samples only. A decrease in the unit cell dimensions is observed for the 3 M sample. The crystal systems are however maintained.

CHAPTER 6: DISCUSSIONS 6.1 Characterization of Raw Materials

6.1.1 Bauxite

EDX analysis of bauxite obtained indicates an almost pure aluminous sample. The bauxite used in this study (Table 5.1) is of high grade as the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio is greater than 10. This is in agreement with most analysis carried out on bauxite from Awaso (Kesse, 1985; Acquah, 1999; Kwakye-Awuah *et al.*, 2013; Dodoo-Arhin *et al.*, 2013). The ratio of Al_2O_3 to SiO_2 was 79.1. The iron impurity reported here is relatively low compared to that reported by Acquah *et al.*, (1999) and Kwakye-Awuah *et al.*, (2013) who reported 4.3 % and 3.42 % respectively. The iron impurity is usually the source of the reddish colour portrayed by most bauxite samples. The pseudo hexagonal shape observed from the SEM is similar to the study of Ruan (2005). The distorted structure is a deviation from the ideal results in its monoclinic cell as studied by Klopogge (1999). The particles of gibbsite usually coalesce to form a cluster and this can be observed in Figure 5.4.

Results from the XRD showed Gibbsite and Rutile. The presence of these two compounds is in agreement with the results from the EDX analysis. Dodoo-Arhin *et al.*, (2013) reported Gibbsite and rutile amongst the other minerals in Awaso red mud. Analysis of the XRD peaks showed a peak with highest intensity (100 %) $2\theta = 18.25^\circ$ and $d = 4.8477 \text{ \AA}$ with (002) implying a 2nd order reflection. A second peak at (11 $\bar{1}$) with $d = 4.373 \text{ \AA}$ and intensity of 37 % agree with the reference pattern of gibbsite obtained from the ICDD and Mineral Data Publishing (2005).

Table 6.1: Peak positions and their relative intensities of theoretical gibbsite

2θ	$d/\text{\AA}$	Relative intensity

18	4.853	100
25	4.380	36
35	4.32	18

6.1.2 Kaolin

The spectra analyses of the kaolins are shown in Figure 5.5. Kaolinite and quartz are primarily the minerals present in most kaolin deposits. Differences in kaolin mineralogy are determined by geographical location and the degree of alteration by weathering and other natural processes (Murray, 2006). The magnitude of impurity associated with kaolin is unique and conditional to its location and the type of activity occurring near the deposit. Tropical and subtropical latitude kaolin bearing rocks are usually known to have a substantial amount of staining caused by ferric iron thereby giving it a red or deep pink coloration (Bloodworth *et al.*, 1993) as observed in AFK. This type of kaolin is not preferred in most industrial, economical and valued applications of kaolin since they have to be treated to remove the coloration. Chemical compositions obtained for both kaolins make them viable starting materials for the synthesis of zeolites. The relatively high SiO₂ values contained in the kaolins as depicted in the chemical composition is validated by the presence of quartz along with silica bearing mineral phases i.e. phengite and kaolinite. Depending on the SiO₂/Al₂O₃ ratio of the starting or raw material, low or high silica zeolites can be produced. WK with SiO₂/Al₂O₃ of 1.4 renders it apposite for the synthesis of low silica zeolites possessing high ion exchange capacity and high selectivity for polar molecules (Rios, 2008; Kovo, 2011). The concentration of Al however, 20.54 wt% in AFK and 34.57

wt% in WK samples are in comparison with alumina concentration in theoretical kaolin is reduced.

Table 6.2: Comparing the mineralogical composition of theoretical kaolin and kaolins used in the study

Sample	Kaolinite	Quartz	Al wt %
Theoretical kaolin	95.4	4.6	39.5
Wassa kaolin	54.8	45.2	34.57
Anfoega Kaolin	45.3	50.8	20.54

The SEM of both kaolins showed crystalline samples with slightly hexagonal outline though not as distinctive as images presented by Georgiev *et al.*, (2009) and Kovo (2011). The plates are loosely packed. Similar to other kaolinites, AFK show crystal layers in platy form with rough surfaces attributed to the presence of quartz. Particle sizes of the kaolin are seen to be varied.

Figure 5.7 (a and b) show the XRD patterns of the kaolins. Upon evaluation of the peaks, a sharp peak with an intensity of 16.28 % appears at $2\theta = 12.32^\circ$ ($d = 7.178 \text{ \AA}$) in WK sample and 19.36 % at $2\theta = 12.3^\circ$ ($d = 7.19 \text{ \AA}$). This has been identified as the first characteristic peak of kaolinite. Rios (2008) noted this peak at $2\theta = 12.34^\circ$ and Kovo (2011) at 12.335° . The second kaolinite peak reflection was observed at $2\theta = 24.84^\circ$ and 24.79° for WK and AFK respectively. Theoretical kaolin records these peaks at $2\theta = 12.46^\circ$ ($d = 7.16 \text{ \AA}$) and $2\theta = 24.8^\circ$ ($d = 3.573 \text{ \AA}$) (Bloodworth *et al.*, 1993). Quartz was characterized by its distinct reflections at $2\theta = 20.8^\circ$ and 26.58° for both samples. The peak at 26.58° ($d = 3.35 \text{ \AA}$) had the highest intensity.

Similar observations were made by Rios (2008). The phengite mineral observed in the XRD of the AFK sample had composition $(K (AlMg)SiO_{10}(OH)_2)$ as corroborated by the EDX analysis. Peak intensities of WK are observed to be stronger than AFK sample. This reduction of intensities is usually caused by impurities which tend to mask the appearance of the kaolinite peak.

The amount of order and disorder in the structure is depicted by the XRD patterns. According to Aparicio and Galan (1999), kaolins as established by the expert system, are regarded as two-phase complexes containing 14 % to 31 % wt% of a well ordered phase.

The HI of WK was 0.95. This indicates poorly ordered or poorly crystalline kaolin. Kaolins with broad X-ray peaks have a low HI hence high defect kaolins. Defects are introduced by the presence of other cations or impurities. Invariably, kaolins with low defect have sharp X-ray diffraction peaks with an HI of > 0.7 .

6.1.3 FTIR

FTIR analytical technique is usually preferable in compound or mineral identification because each mineral has a significantly different IR spectrum as each is emitted at a different frequency. The raw materials used were characterized between 400 and 4000 cm^{-1} .

Studies or reports on the IR spectra of a large number of $Al_2O_3-H_2O$ systems including gibbsite, boehmite, bayerite and nordstrandite (Ruan, 2005). In the bauxite, four strong bands were observed between 3650 and 3350 cm^{-1} . Like in most gibbsites, the bands were at 3618, 3524, 3452 and 3370 cm^{-1} . The bands in this region are usually assigned to the hydroxyl stretching frequencies. Characterization of synthetic gibbsite by Frost *et al.*, (1999) using FTIR reported the hydroxyl stretching frequencies at 3670, 3524,

3395 and 3375 cm^{-1} . Lu *et al.*, (2012) stated that a well crystallized gibbsite will typically show five OH stretching vibrations at 3620, 3527, 3464 and a double band at 3391/3373 cm^{-1} . Natural gibbsite compared to synthetic gibbsite show broader bands and not too distinct peaks even when peak observations are made in the same positions (Ruan, 2005). This difference is usually caused by short range ordering that influences the infra-red absorption spectra of gibbsite and the presence of organic or inorganic ions. Another reason attributed to the difference in the width of the bands between natural and synthetic gibbsite has been considered a factor to this is variations in the particle shape and stacking of the crystals of the natural sample (Parikh *et al.*, 2014; Balan *et al.*, 2006; Ruan, 2005; Frost *et al.*, 1999).

The 3452 cm^{-1} band has been reported to be perpendicularly polarized to the 001 plane. Polarized parallel to the $\text{Al}(\text{OH})_3$ sheets in the gibbsite structure are the bands at 3524 and 3618 cm^{-1} (Ruan, 2005). It has been suggested by Frost *et al.*, (2002) that the 3452 cm^{-1} band is linked with hydrogen bonds found within the layers whilst 3618 and 3524 cm^{-1} bands are connected to longer hydrogen bonds between OHs lying in the same plane.

The kaolinite bands at around 3670- 3620 cm^{-1} are identical to the gibbsite bands 3645, 3621 and 3451 cm^{-1} located in the hydroxyl stretching region. These characteristic bands can be observed in all kaolin samples as depicted in Table 6.3 below. This can be corroborated since kaolinite consists of Silica / Gibbsite (S/G) sheet connected by an oxygen atom at the top. Observed similarities in the FTIR band positions are attributed to the structure of both minerals. The band observed in the 3620 cm^{-1} region is attributed to the inner hydroxyls.

Table 6:3. FTIR assignment of theoretical kaolin and different kaolin samples

Assignment	Wavenumber / cm ⁻¹				
	Theoretical kaolin	Rios (2008)	Saika <i>et al.</i> , (2010)	WK	AFK
Al-O-H stretching	3670 - 56	3692	3640	3670	3687
OH stretching	3645	3618	3624	3618	3605
Si – O stretching Clay minerals	1107 - 05	1119	1179	1108	1147
	1035 - 30	1034	1038	1024	1011
	1019 - 05	1012	-	998	997
OH deformation linked to 2Al ³⁺	918 - 09	916	915	904	907
OH deformation linked to Mg ²⁺	800 -784	801	-	-	809
Si – O quartz		762	778	743	779
Si – O quartz	700 - 686	696	694	684	692
Fe – O, Fe ₂ O ₃	542 - 35	538	527	520	513
Si – O – Si bending	475 - 68	468	468	448	447

6.1.4 TGA

6.1.4.1 Bauxite

TG-DTA curve for bauxite is presented in Figure 5.9. During the thermal decomposition of gibbsite, diffusion of protons occurs and a reaction of the hydroxyl ions to form water (Kwaky-Awuah *et al.*, 2014 (b); Ruan, 2005; Frost *et al.*, 1999). A removal of the binding forces between the gibbsite strata occurs during the process thereby changing the chemical composition and density within the layers (Ruan

2005; Klopogge, 2002; Frost *et al.*, 1999).

Dehydration of gibbsite was observed in two endothermic steps occurring around 50 °C and 330 °C correspond to a total mass loss of 26.7 %. A further reduction of about 7 % in mass loss that was complete by 700 °C contributed to an overall loss of 33.7 % is achieved which is in agreement with the theoretical value of 34.6 %. The slight variation can be attributed to particle size difference, origin of the sample and the impurities present (Klopogge, 2002).

The small endotherm observed at much lower temperature (between 24 and 50 °C) is assigned to non-hydrogen bonded outer hydroxyl groups which are removed easily. Small particle sized gibbsite show one strong endothermic reaction between 199 °C and 347 °C (Frost, 2005). The DTA of coarse grained gibbsite has been reported to show an endotherm around 230 °C and another endotherm around 280 °C. The endotherm at 280 °C is attributed to the formation of boehmite under hydrothermal conditions due to retarded diffusion of water out of the large gibbsite grains. This is not observable in fine grained gibbsite particles, thus the sample used in this study can be classified as such. The strong endotherm was recorded at 330 °C. The internal porosity enlarges in the process of conversion as density increases from 2.42 to 3.98 g/cm³ due to loss of water with increasing temperature is observed.

6.1.4.2 Kaolin

The conversion of kaolin into metakaolin has been subject to diverse approaches with varying temperature and exposure time. Calcination of kaolin has been acknowledged to increase its reactivity. Several reports on kaolin dehydroxylation and the structure of kaolins afterwards have been provided. Initial TGA studies were performed on the kaolins. The TG-DTA thermograms of both WK and AFK show a weight loss pattern in the range of 25 – 900 °C.

Depending on the nature and the amount of disorder in the stacking of kaolin, water is absorbed in the pores of the surface at temperatures less than 100 °C (Frost *et al.*, 2004). The loss of weight between 100 °C and 400 °C is attributed to a dehydration process that takes place as a result of reorganisation in the octahedral layer first occurring at the OH of the process.

Dehydroxylation has been studied to occur around 400 °C – 650 °C by Kakali *et al.*, (2001) and at temperatures within 450 – 550 °C by Frost *et al.*, (2004). Dehydroxylation is the transformation of crystalline non-reactive kaolin into a noncrystalline reactive metakaolin (Rios, 2013). WK and AFK reported dehydroxylation at 450 °C and 480 °C respectively.

The DTA curves for both kaolins also indicated the endothermic peak between 500 and 600 °C and a deviation in direction afterwards with the main exothermic peak reached around 900 °C. This would indicate that at 500 – 600 °C, dehydration occurred followed by disruption of lattice structure is at a maximum. Heating the kaolins at elevated temperatures within the region of the exothermic peak would cause thermal transformation (usually from kaolinite to mullite formation) (Bhatt, 1982).

The FTIR spectra of the kaolin and metakaolin showed different peaks in their structure. The transformation of kaolinite to metakaolinite can be observed by the loss of peaks at 3618 -3370 cm⁻¹ being the stretching vibrations of hydroxyl groups present in kaolin but absent in metakaolinite. Intense bands occurred at 900 - 1200 cm⁻¹ and 430 - 520 cm⁻¹ for kaolin and 900 – 1050 cm⁻¹ and 430 – 500 cm⁻¹ for metakaolin. The first band is assigned to an asymmetric stretching mode and the second one to a bending mode of the T–O bond. All these bands are more or less dependent on the crystal structure (Kwakyee-Awuah *et al.*, 2014(b)). The loss of AlOH bands at 925 and

910 cm^{-1} , changes in the Si-O stretching bands (1002 cm^{-1} , 1019 cm^{-1}) and the reduction in intensity of Al-O-Si bands at 796 and 778 cm^{-1} further confirm the transformation and a distortion of the tetrahedral and octahedral layers. These changes are similar to those reported in other studies (Akolekar *et al.*, 1997; Zhao *et al.*, 2004; Covarrubias *et al.*, 2006). Generally the presence of Al in kaolin is required for successful zeolite synthesis.

6.2 Zeolite from Bauxite

Effect of calcination on zeolite synthesis

Alumina trihydrate (gibbsite) is converted to monohydrate at temperatures below 250 °C. The following reaction is observed:



Alumina monohydrate is converted to γ - alumina within the temperatures of 300 – 900 °C:



As realised from the corresponding TGA, the sharp endotherm at 330 °C is due to dehydration. Dehydration causes the loss of both physically adsorbed and interlayer water together with the removal of hydroxyl water from the lattices. The progressive loss of water molecules upon heating leads to the formation of numerous metastable phases with variations in their crystallographic state, grain morphology and specific surface area until the most stable form of alumina (γ - Al_2O_3) is obtained (Ray and Parya, 2014). Klopogge *et al.*, (2002) stated that dehydroxylation begins around 220 °C and it was completed around 350 °C for gibbsite.

Ray and Parya (2014), observed a loss in the crystallinity of bauxite when heated at 500 °C. Their XRD analysis revealed a semi amorphous product with peaks identified as pseudo-boehmite.

The amorphous product obtained during hydrothermal treatment with calcined bauxite could be due the transitional phase of the bauxite heat treated at 600 °C.

The uncalcined bauxite however, in a relatively stable state reacted with the NaOH to produce sodium aluminate solution. The resultant product was still gibbsite because the reaction occurred at a low temperature hence most of the gibbsite present could not react.



Zeolite synthesis proved unsuccessful with both calcined and uncalcined bauxite.

This can be attributed to the low Si/Al ratio of 0.013 of the starting material.

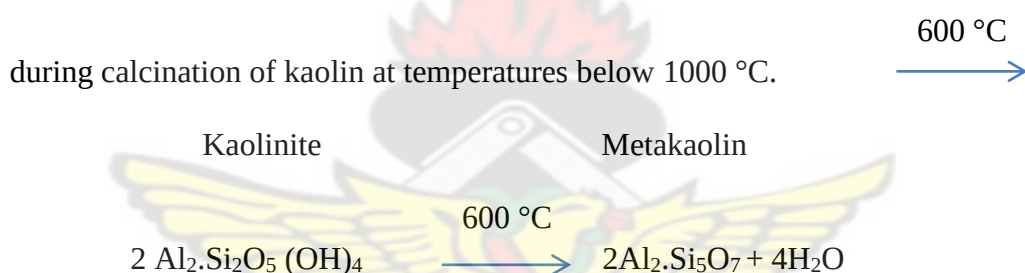
Additional silica is needed to boost the Si/Al ratio for successful zeolite synthesis. The SEM (Figure 5.11) for the calcined bauxite showed no distinct shape as compared to the uncalcined sample which had hexagonal shapes similar to the parent bauxite elucidating the fact that most of the gibbsite was still present.

6.3 Zeolite from Kaolin

6.3.1 Effect of Calcination

Kaolinite activity can be increased by altering its properties with thermal, mechanical or chemical treatment. Calcining above 550 °C, converts kaolin into metakaolin by removal of structural OH ion making it reactive. However, different temperatures and observations have been made by several researchers (Rios *et al.*, 2008; Lee *et al.*, 2002; Chandrasekhar and Pramada, 1999; Murat *et al.*, 1992).

The XRD patterns of both calcined and raw kaolin are presented in Figure 5.14. Heating kaolin distorts or destroys the crystal lattice. The metakaolin is signified by a loss in existing kaolinite peaks or reflections at (010) and (020). This is an indication of the formation of a metastable non-crystalline phase (Kovo, 2011). The non-crystalline phase has also been attributed to the removal of hydration water in the kaolinite structure. Hence according to Brindley and Nakahira (1959), metakaolin can be classified as an amorphous material possessing free silica and alumina. Akolekar *et al.*, (1997), in his study, also observed kaolinite to have a crystalline structure whilst metakaolin had a highly disordered structure. The peaks assigned to quartz were present though with reduced intensities. Similar observation was made by Kovo (2011)



The relative crystallinity of raw kaolin and metakaolin show a very large disparity in their values confirming that the process was successful.

Table 6.4: Comparing the crystallinities of kaolin and its corresponding metakaolin

Sample	% Crystallinity	
	Raw	Metakaolin
WK	79.22	39.07
AFK	85.97	49.1

Zeolite synthesis from kaolin only has been performed and reported in literature by several authors. However, the final product has been linked to the initial composition of the starting material. Kaolinite reacted with NaOH to form sodium aluminosilicate

solution with a high saturation towards its silicate content. The conversion of metakaolin to zeolite has been enumerated to consist of transformation of the metakolin into aluminosilicate gel and the subsequent fixation of Al into the lattices of the silicate ring to form the zeolite structure.



6.3.2 Effect of Alkali Concentration

Experimental results obtained show that the quartz phase was unreactive under all conditions. The insignificant to no account of reactivity of quartz observed during the synthesis of zeolites as cited by Dakalo (2005) has been reported by a number of authors. He observed stable quartz phases when working with fly ash in zeolite synthesis. However, the characteristic zeolite A peak was observed at $2\theta \sim 7.18^\circ$ and 10.17° in all of the different crystallization times considered in this study (Treacy and Higgins, 2001). Obtaining zeolite A from Wassa kaolin is agreeable since its Si/Al ratio was approximately 1.34.

Variation of the NaOH molar concentrations as seen in Figure 5.16, yielded different peak positions and intensities of the synthesized products for 2 M and 4 M. The 2 M NaOH concentration sample produced zeolite A and quartz. Quartz and hydroxysodalite coexisted in both 4 M and 6 M products from the Rietveld analysis. Increase in alkalinity from the OH is known to influence the dissolution reaction of silicates and aluminosilicates. The activation of metakaolin with higher alkaline concentration of NaOH has been observed from this study to enhance the cocrystallization of hydroxysodalite. Increased alkalinity alters the already formed zeolite phase as the NaOH further permeates the zeolite's framework resulting in its conversion into hydroxysodalite. Similar results have been reported by Mostafa *et al.*,

(2011) during their work with Egyptian kaolin. Zeolite A was obtained with 3 M NaOH solution and hydroxysodalite with higher alkali concentrations of 4 M, 6 M and 8 M. Conversion of zeolite A to hydroxysodalite or sodalite is due to the fact that zeolite A is unstable under higher alkali regions (Alkan *et al.*, 2005; Mostafa *et al.*, 2011).

Obtaining zeolite A from kaolin has been studied by many researchers using the alkaline fusion method (Rios *et al.*, 2012; Kovo, 2011; Akolekar *et al.*, 1997).

The introduction of the alkaline fusion step prior to hydrothermal treatment has been studied to have an enhancing effect on conditions employed for zeolite synthesis. Larger quantities of aluminosilicates have been observed to dissolve using this method and very effective in obtaining the silicon species from admixtures (Rios and Vargas, 2011). Compared to Routes 1 and 2, the amount of zeolite yield was higher with the Route 3 protocol. Zeolite X, amounting to 84.2 % was obtained in this study whilst Rios and Vargas (2011) reported faujasite as the zeolitic product using a similar method. Wibowo *et al.*, (2010) synthesized KNaX zeolite from kaolin using the alkaline fusion method. However, zeolite A and mica were found to co-exist with the desired product. The XRD pattern still showed the intense peak at $2\theta = 26^\circ$ indicating the presence of quartz. This is because the calcination temperature of 600 °C was not sufficient to dissolve quartz. Quartz has been studied to be reactive at temperatures exceeding 600 °C (Rios, 2008).

The cubic morphology observed in the SEM images of the synthesized zeolitic products corroborates the XRD analyses of the formation of zeolite LTA with other irregular shaped crystals belonging to the quartz phase.

Comparing the FTIR spectra of the kaolin and synthesized products (Appendix A), the absorbance bands at 1006 and 998 cm^{-1} were shifted to lower wavenumbers in the synthesized zeolite indicating an increase in Al substitution in tetrahedral sites of the silica framework of the zeolite compared to the kaolin (Breck, 1974; Rios, 2008).

In general, the FTIR spectra of the synthesized products exhibited bands between 420 and 470 cm^{-1} are attributed to T – O vibrations and between 930 and 950 cm^{-1} attributed to asymmetric stretching vibrations. Similar band positions confirm the formation of similar end products from the synthesis.

6.4 Zeolite from Bauxite and Kaolin

Distinct changes were observed in comparing the XRD patterns of the reactants to the final products with the appearance of new crystalline phases. The main product obtained from synthesis was zeolite A coexisting with quartz phase. Peak intensities corresponding to zeolite A were low and hence crystallinity was observed to be low. There was no observable difference in the XRD analysis of the samples considering the different masses of bauxite used. This can be attributed to the fact that Si/Al ratio of the reaction was low. Introducing bauxite increases the Al of the system, thereby further decreasing the Si/Al ratio, hence new zeolites cannot be anticipated from the reaction. Zhu *et al.*, (2011), investigated the synthesis of zeolite from bauxite and kaolin from China. With variations in fusion temperature and time as well as Si/Al ratio, zeolite 4A was obtained in all synthesis conditions.

With a change in the order of mixing of reactants but with same masses of reactants and synthesis parameters, relatively higher zeolite A product was obtained. Addition of bauxite to kaolin before alkali fusion did not impact any significant change to the process as the resultant zeolite was not changed. The peak intensities were more distinct and prominent with all the varied masses. The quartz phase still existed. The

increase observed in the crystallinity of the synthesized product can be attributed to higher reactivity of bauxite and kaolin realized from the alkaline fusion step. The alkaline fusion step has been reported by many researchers to boost the silica content of the mixture (Rios, 2008).

6.4.1 Effect of Varying Crystallization Time

One significant parameter that is considered during zeolite synthesis is crystallization time. Effect of crystallization time on zeolite synthesis was investigated at a constant aging time and crystallization temperature of 105 °C. The amount of zeolite material obtained with each crystallization time is presented in Table 6.5 below:

Table 6.5: Zeolites obtained from varying crystallization time

Sample	Aging time /(hours)	Crystallization time /(hours)	Product
1	24	3	Zeolite Na-LTA 62 %, Analcime 27.2 %, zeolite X 10.9 %
2	24	5	Zeolite LTA 100 %
3	24	24	Zeolite NaK-LSX 93 %, zeolite Y 7 %
4	24	96	Sodalite 72 %, zeolite ZK14 16 %, zeolite SAPO 11.7 %

Increasing the crystallization time according to Kovo (2011), provides an avenue for the alkalinity content of the system to enhance the solubility of the silicate and aluminate ions resulting in improved poly-condensation reaction between the silicate and aluminate. Generally, the crystallinity and crystal size has been studied to increase with an increase in time. Increasing the temperature of the synthesis mixture has been studied to increase the nucleation rate and the growth rate of the crystal (Younesi and Ghasemi, 2011). This implies that higher growth rates results in larger crystals at

higher crystallization temperature while lower temperature yields small particle size with a decrease in crystallization rate.

The SEM images for the various crystallization times are shown in Figure 5.26. The cubic shaped crystal corroborates the successful synthesis of zeolite LTA. The 3 hours sample had spherical shaped particles which also confirmed the presence of zeolite Analcime. Since only aluminate and silicate filtrates were used, all the zeolites recorded no quartz phases. The 24 hours SEM image showed octahedrally shaped crystals and this is known to be shape of FAU type zeolites (Treacy and Higgins, 2001). Because of the presence of different zeolitic products in the 96 hours sample, a distinct shape could not be identified from the aggregate. However, the Sodalite crystals were quite noticeable (orthorhombic shape). The transformation of zeolite LTA to FAU has been suggested to be due to the basic sodalite cages in both frameworks which form LTA with double 4-rings or FAU with double 6-rings (de Vos Burchart *et al.*, 1989).

The FTIR of all the synthesized products showed similar bands assigned to zeolites. The bands assigned to internal vibrations of asymmetric stretching ($1250 - 950\text{ cm}^{-1}$) are found to overlap around 950 cm^{-1} region. The difference in intensity between the samples (5 hours and 24 hours) in this region can be attributed to the difference in Si/Al ratio. The bands in the $950 - 1250\text{ cm}^{-1}$ have been studied to be sensitive to Si/Al ratio (Mainganye, 2012).

6.4.2 Effect of Varying Aging Time

Aging of reactants before hydrothermal treatment has been reported to enhance the process by decreasing crystallization time and increasing reaction time. To this effect, aging of reactants for 24, 48, 72 and 96 hours were considered in this study. The

solutions were all aged at room temperature. When the aging time was 24 hours, almost pure zeolite LSX was realized and with 48 hours, zeolite Y was achieved.

Nucleation of zeolite crystals is believed to occur during the aging time and remains dormant until an increase in temperature is applied (Rivas Cordona, 2011). Dissolution of silica causing the release of silicate ions is observed with aging of the reaction mixture according to Akolekar *et al.*, (1997), thus increasing the yield and crystallinity of the synthesized product. The formation of FAU is observed with long aging and LTA with short aging time (Xu *et al.*, 2007). Ogura *et al.*, (2001) stated that the aging process is necessary for the formation of FAU and also proposed that 6R and double membered rings (D6R) are the precursors of FAU and are formed in the gel phase during the aging process.

Prolonged aging of reaction gels are known to speed up nucleation hence shorter crystallization times will be required for synthesis.

Evidence of in different Si/ Al ratio of the crystalline products is depicted by the FTIR with a peak at 967 cm^{-1} for the 24 hour sample and a more intensified peak at 955 cm^{-1} for the 48 hour sample. The crystallinity of the samples is in agreeable with that of the XRD using the intensity of the bands at 554 and 449 cm^{-1} of the FTIR

6.4.3 Effect of Varying Si/Al Ratio

As observed in Figure 5.30, a Si/Al ratio of approximately 1 produced zeolite LTA. Increasing the Si/Al to 2 under the same conditions, zeolite X was obtained. An increase in Si/Al ratio of the reaction mixture changes the stability of zeolite NaA whilst favouring the formation of zeolite X (Novembre *et al.*, 2011). Akolekar *et al.*, (1997) as cited in Novembre *et al.*, (2011), achieved zeolite X at a higher Si/Al ratio of 2.5 by adding additional sodium silicate solution. The variation in crystallinity of

the zeolitic products with respect to aging as depicted by both FTIR and XRD show increased crystallinity with increasing Si/Al ratio. The intensity of the band at 955 cm^{-1} as mentioned previously increases with increasing Si/Al ratio.

6.4.4 Effect of Alkaline Concentration

2 M, 3 M, 5 M, 6 M and 8 M NaOH concentrations were used to study the effect of increasing alkali concentrations. Upon increasing the alkalinity of solution used during the synthesis of zeolites, a higher yield (mass of final product obtained) was noted to be higher. The final products obtained from reactions are presented in Table

5.4.

Generally, reaction rate increases with increasing alkaline concentration and a higher yield of the resultant product is usually observed. This is an indication that the dissolution of the solid amorphous phase increases with an increase in the concentration of alkali (Thammavong, 2003). Upon further analysis, the best condition for pure zeolite with highest yield was realized at 5M NaOH concentration at 6 hours crystallization time and $100\text{ }^{\circ}\text{C}$.

Alkan *et al.*, (2005) synthesized zeolite NaA with kaolin using hydrothermal treatment with 4M NaOH. By increasing NaOH concentrations from 4M to 8M, the ratio of hydroxysodalite formation increased in the reaction mixture. With increasing NaOH concentration, Fukui *et al.*, (2006) observed an increase hydroxysodalite proportion to a decrease in phillipsite mass. Lower mass achieved with lower NaOH can be assigned to incomplete reaction within the 24 hours crystallization time that was used.

SEM images of the 2 M and 3 M NaOH concentration samples show well defined cubic crystals confirming pure phased zeolite NaA uniform particle size. Particle size decreased with increasing alkalinity. This can be attributed to an increased nucleation

rate coupled with increased polymerization rate between the polysilicate and alumina anions at high alkali concentrations (Xu *et al.*, 2007).

The formation of sodalite at high alkali concentrations from zeolite LTA can also be explained by Ostwald's rule of succession where the first phase to crystallize from a solution will be hydrothermally least stable phase but with time, this phase will transform to a more stable and denser phase (Mainganye, 2012; Huertas, 2007).

The main band associated with the T-O asymmetric stretching vibrations provide information on the degree of crystallinity of the sample (Criado *et al.*, 2005).

The intensity of the band was low in the 950 cm^{-1} region. This means the crystallinity of this product is low. Band position appearing in slightly higher wavenumbers basically means that the Si/Al ratio of the product is higher.

6.4.5 Crystallinity and Crystallite Size

Recalling the Debye-Scherrer equation (section 3.2.1), the crystallite sizes of the particles were evaluated. The crystallite size were observed to increase with increasing aging time and decrease with increasing alkaline concentration. The crystallite sizes obtained for zeolite LTA are much larger than that of sodalite crystals. Formation of new phases or mixed phases interferes with the true crystallinity of the final product. Similar observations were made by Xu *et al.*, 2007 and Younesi and Ghasemi, 2011.

CHAPTER 7: REMOVAL OF HEAVY METALS FROM MINING WASTEWATER **7.1 Small Scale Mining**

Mining is considered an important economic endeavour which contributes to the development and livelihood of the region where it is located. It plays an important role in the economic development of the country or community bestowed with the resource, by generating revenue usually through employment opportunities and foreign exchange. It has been estimated that small scale mining contributes to 12 % of the world's total gold production (Besseah, 2011).

Before the enactment of laws to regulate the activities of the mining sector, small scale miners were reported to be operating along the coastal areas dating back to the pre-colonial era.

The art of small-scale mining in Ghana often referred to as —galamsey, is a phrase coined from —gather them and sell. It is defined by various groups mostly taking into

consideration the level of output method and the tools used in their operations as well as the people who partake in it (Adjei *et al.*, 2012).

According to Asklund and Eldvall (2005), over 150,000 persons in Ghana have been estimated to be operating illegally on concessions belonging to large scale operators, or in restricted areas (Ghana academy of arts and sciences 2003). Amalgamation is the main process used by small scale miners (Akosa *et al.*, 2002). The miners mix mercury amalgam with gold concentrate to form gold amalgam and heat it to separate the gold (Aryee *et al.* 2003).

The activity of these small scale miners causes the siltation of most streams and rivers thereby increasing the amounts of heavy metals into rivers (Plate 7.1).

Siltation of rivers reduces river conveyance and deteriorates water quality (Besseah, 2011).



Plate 7.1: A picture of water source before and after —galamsey activity in Johnkrom, Ashanti Region.

In recent times, a rise in small scale mining activities has been noticed in several communities within the middle belt of the country. Even with highlights on the advantage of small scale mining boosting the economy, the disadvantages largely outweigh the former. The disadvantages include deforestation, land degradation, lack

of basic needs, pollution of water bodies and subsequent health hazard to individuals in the communities. This in turn heightens poverty levels; distort the ecosystem thus requiring relocation of the people who are in contact with the situation.

The disadvantages of the act largely outweighs the advantages. The activities of these miners should be regulated by Environmental Protection Agencies whilst appropriate treatment methods are applied to solve the water pollution problem.

7.2 Water Pollution

Natural resources include gold, diamond, bauxite, iron, manganese, petroleum and to a great extent water. Water and other natural resources have been subject to mass exploration in all facets of human endeavour. Increase in population has been linked directly to higher demand of quality water for both economic and domestic purposes. However, the day to day activities of man cause pollution of our water bodies leading to water scarcity and health hazards to the individuals who depend on it directly. Agriculture, tannery, municipal waste and mining are a few of industrial activities that introduce pollutants into water bodies. Such pollutants can be either organic or inorganic, heavy metals and or radionuclides.

Heavy metals occur naturally and play a vital role in the metabolism of many organisms but may have inimical effect on the ecosystem and human health (Whitehead, 2000). Heavy metals are considered very toxic. They are known not to biodegrade easily and accumulate in organisms, causing a number diseases and disorders (Inglezakis *et al.*, 2002). Removal of heavy metals from polluted waters is a challenging task all over the world regarding the correct management of wastewaters for a sustainable future and cannot be overlooked.

7.3 Heavy Metal Removal Methods

Treatment of contaminated water involves the transfer of heavy metals from one state to another, reduction in metal build up or alteration of the speciation of the metal ions in solution to minimize their toxicity (Whitehead, 2000). Some methods used in heavy metal removal include the following: chemical precipitation, electrodeposition, ion exchange, membrane separation and adsorption (Rios, 2008).

Precipitation is usually by the adding of hydroxides or sulphates to the wastewater. It has a primary advantage of reduced cost and easily workable. However, it is disadvantaged in treating large volumes since considerable amount of chemical dosage is required and large amounts of sludge are generated.

Activated carbon is considered to be a very effective and competitive adsorbent for heavy metal removal. It is not a recommended choice due to high cost of production and regeneration of spent carbon (Panday *et al.*, 1985).

Ion exchange resins and methods have been used for water purification of polluted and wastewaters by several studies and industries. They are usually preferred as they possess high cation exchange capacity and reaction rates and resistant to harsh conditions or environments. Adsorbents however, which are readily available, economically feasible and can be easily regenerated are preferred.

Zeolites in recent times have found lots of usefulness in the water treatment industry. According to Rios (2008), the physico-chemical properties and unique structure of zeolites have been studied to be effective on the removal of toxic ions from wastewaters. The treatment of water and removal of heavy metals from contaminated water using both synthetic and natural zeolites have been evaluated significantly by several researchers (such as Kwakye-Awuah *et al.*, (2014a); Zendelska *et al.*, (2014);

Kabuba and Rutto (2014); Egashira *et al.*, (2012); Hani *et al.*, (2012); Ismail *et al.*, (2013); Shaheen *et al.*, (2012); Uttapan *et al.*, (2011); Qiu and Zheng (2009); Rios *et al.*, (2008); Wingenfelder *et al.*, (2005); Peric *et al.*, (2004); Erdem *et al.*, (2004); Covarribus *et al.*, (2000)).

However in this study, zeolites synthesized from bauxite and kaolin are considered to investigate its viability in removing some heavy metal ions from mine wastewater.

7.4 Heavy Metals Studied

Heavy metals as defined by Lottermoser (2007) are metals with density greater than 6 g/cm³ such as Cd, Co, Cu, Fe, Hg, In, Ni, Pb, Sn, W and Zn. Some of these metals are important to the human body to function properly (WHO, 1996). They are termed essential or non-essential depending on the bodies need for them.

Heavy metals can be grouped into four according to Asklund and Eldvall (2005); (i) metal forming hydroxides, (ii) strongly absorbing cations, (iii) cations adsorbed with average strength and (iv) weakly adsorbed cations.

Heavy metals considered in this study are discussed below:

7.4.1 Lead

Lead exists in the earth's crust in small amounts such as 15 mg/kg (Moore, 1991). It is a non-essential element and a cumulative poison in organisms. Reports of lead having a metabolism similar to Calcium (Ca²⁺), in terms of ionic radii and its bone deposition have been provided. It has a retention ability of up to 90 % in the skeleton of humans under normal conditions (Al Rashdan, 2000). It is known to cause neurological disorder in children by impairing mental development and induction of hyperacidity. Insomnia, irascibility, loss of appetite and subsequent weight loss leading to starvation are common symptoms associated with lead poisoning

(Whitehead, 2000). According to Islam (2008), it has also been linked to high blood pressure in later years, high mortality rates from cardiovascular diseases.

7.4.2 Iron

Iron is an essential element in human sustenance and nutrition. The minimum daily requirement for iron has been estimated depending on age, sex, physiological status and iron bioavailability and range from about 10 to 50 mg/day (WHO, 1996). Iron (III) hydroxide, usually with a yellow to reddish brown colouration is observed to precipitate from unstable iron (II) salts in drinking water. Iron (III) hydroxide (Fe_2O_3) is insoluble. Generally, iron (ii) maybe found in anaerobic groundwater with concentrations of several milligrams per litre (mg/l) without any discolouration. Turbidity and discolouration is noticed in systems with iron levels above 0.05 - 0.1 mg/l (Asklund and Edvall, 2005). The recommended, maximum tolerable daily intake has been marked at 2 mg/l of drinking water to prevent the human body from accumulating excess iron.

Kuma (2004) as cited in Asklund and Eldvall (2005) reported 18.3 mg/l as maximum iron levels in groundwater and 4.01 mg/l in surface water.

7.3.3 Copper

Copper exists naturally in metallic form and in a large range of organic compounds and mineral salts. It possesses a reddish- brown colour and is malleable and ductile. It is slightly soluble in water, alkaline and slightly acidic and very soluble in nitric and sulphuric acids. Copper has high thermal and electrical conductivity and corrosion resistant (EHC, 1998).

Copper is a vital element in a lot of enzymes in vegetation, humans and animals and in the development of connective tissues in mammals. Extreme copper intake

accumulates in the liver leading to its damage and biliary cirrhosis. Copper deficiency in humans causes bone ossification and anaemia. Another rare defect caused by copper is copper toxicosis with notable symptoms including nausea, vomiting, hepatic, coma and death (Whitehead, 2000). Copper exposure to aquatic life is exceedingly toxic at levels between 5 and 25 $\mu\text{g/l}$ to some fish species and invertebrates within 96 hours (Whitehead, 2000).

7.4.4 Zinc

Zinc is the 25th most abundant mineral in the earth and makes 0.02 % of the earth's crust. It is a transition element and forms complexes with variety of organic ligands (EHC, 2001). Zinc is present in most rocks in different masses. It is a micronutrient possessing many vital roles in both plants and animals. Estimated requirement of daily intake of zinc is age dependent. Many enzymes rely on as a cofactor. Zinc toxicity or poisoning is exhibited through vomiting, dizziness, severe anaemia, abdominal cramps, dehydration and lack of muscular coordination and occasionally death in larger doses. Zinc deficiency in humans' results in delay in wound healing, immune disorder, oligospermia and retarded growth. Aquatic organisms are adversely affected by elevated zinc concentrations.

7.4.5 Chromium

Chromium is vastly dispersed in the earth's crust. Chromium can be found in different oxidation states in aqueous media (Figuerido and Quintelas, 2014). Chromium (III) is a positive ion that forms hydroxides and complexes, and is adsorbed at relatively high pH values in water (WHO, 2011). Concentration of chromium in groundwater is generally low ($<1 \mu\text{g/l}$). The presence of either chromium (III) or chromium (VI) has been observed to vary appreciably in surface water. Naturally, the total chromium

content of surface water is about 0.5-2 $\mu\text{g/l}$ and the dissolved chromium content being 0.02-0.3 $\mu\text{g/l}$. Most surface waters contain between 1- 10 μg of chromium per litre (WHO, 2016). The chromium content of surface water is usually dependent on the extent of industrial activity of the area.

Generally, chromium (VI) salts are known to be more soluble than chromium (III). The amount of chromium required for adults daily is estimated to be within the range of 0.5-2 μg of absorbable chromium (III) whilst chromium in rainwater is approximately 0.2-1 $\mu\text{g/l}$ (EHC, 1988).

Harmfulness of chromium arises from its oxidation state. Current analytical methods and the variable speciation of chromium in water favour a guideline value for total chromium. The WHO (2011) guideline for chromium is set to 0.05 mg/l.

7.5 Methodology

7.5.1 Sampling

The sampling site was chosen due to the ongoing activity reported around that area and the effect on the water bodies. The collection was done at a relatively new —galamsey —site in Johnkrom, a town in the Obuasi district of the Ashanti region. It's a town with about 400 inhabitants with the predominant activity being farming and in recent times mining.

Wastewater samples were taken between the months of March and September, 2015. The Sampling was done on a monthly basis for the six (6) months period. The sample containers used were thoroughly washed with nitric acid and distilled water prior to the wastewater collection. Using a portable pH meter, the pH was measured at the source. Keeping them in a cool chest, the samples were conveyed to the laboratory for

further analysis. To keep the metals in solution, concentrated nitric acid (5 ml) was added to each 1 litre of the sample. Acidifying the sample serves a means of preservation for later analysis. This is done to minimize the adsorption of the metals onto the walls of the container. The acidified samples were preserved at 4 °C.

Considering the data acquired, synthetic mine water was produced in the laboratory to simulate the mine wastewater. Standard stock solutions were prepared from chemical reagents (Aldrich, UK) using the heavy metals present in the wastewater as a matrix. The stock solutions were appropriately labelled and stored in 1000 ml conical flasks. With the exception of Fe, all the stock solutions were prepared with concentrations higher than that of the mine wastewater (Table 7.1). Details of the calculation procedures are presented at the Appendix section.

Table 7.1: Concentration of heavy metal cations in actual and simulated wastewaters

Metal concentration/ mg l⁻¹	Actual mine wastewater	Simulated
Fe	32.7 ± 1	35.0
Cu	1.47 ± 0.5	5.0
Pb	0.012 ± 0.01	2.0
Cr	0.283 ± 0.01	0.5
Zn	0.865 ± 0.1	5.0

7.5.2 Batch Technique

To investigate the removal of heavy metals by the synthesized zeolites, the batch technique was used. Considering the type of zeolite (adsorbent), adsorbent to wastewater dosage, contact time, heavy metal concentration as the important parameters to be investigated, the experiments were conducted to comprehend the processes involved in the removal of the metals and to subsequently achieve maximum

efficiency of the system. From the various zeolites synthesized in the previous chapter, pure phased zeolite A, Na X and Y were used in the study.

The removal was undertaken using both the simulated and actual wastewater. The efficiencies of the zeolites were evaluated using single metal solutions i.e. solutions containing only one heavy metal cation as contaminant and mixed metal solutions – solutions containing all heavy metal cations previously listed. This was considered to investigate the effect of competing cation against the other in solution.

The experiments were performed in sets of 8. A solid to liquid ratio of 1:100 was considered with time intervals of 15, 30, 45, 60 and 120, 180, 240 and 1440 minutes respectively on a rotary shaker at an average speed of 200 revolutions per minute (rpm). Preliminary investigations proved this ratio to be appropriate. A constant initial metal concentration for each element was used in all studies.

The zeolite was then separated from the supernatant at the required time. The pH of the supernatant at each of these times was taken. With very small particle sizes, separation of the phases was fairly difficult. Filtration by gravity caused an increase in contact time. Hence, filtration with a vacuum unit with membrane filters was used. All experiments were conducted at room temperature. Each parameter investigated was repeated twice and thrice for very varied results. The concentrations of the individual heavy metals were determined using Hach 3900 UVis spectrophotometer.



Plate 7.2: A picture of (a) the rotary shaker and (b) UV spectrophotometer used

7.6 Results

Detailed report on the data from the monthly water collection is presented in Appendix C. The pH levels of the wastewater samples were between 5.2 and 6.5 for the different collection months. The lowest pH was noted in the month of June. This can be attributed to the large amounts of rainfall experienced for that month. Similar observation was realized by Asklund and Eldvall (2005). Generally, the pHs of all the samples were slightly acidic to neutral. According to Lottermoser (2007), surface waters are usually slightly acidic (pH ~5.6) whilst waters with pH < 5.5 achieve their acidity when sulphide minerals oxidize.

7.6.1 Mine Wastewater Analysis

The heavy metals investigated in this study were high for Fe and Cu while Pb, Zn and Cr were significantly low for all the months. Recorded values for Fe were between 24 and 37 mg/l, Pb (0.8 – 3 mg/l), Cu (0.16 – 2.84 mg/l), Cr (0.1 – 0.48 mg/l) and Zn (0.33 – 1.42 mg/l). Low metal concentrations observed during the months of May, June and July were attributed to rainfall which caused runoff of the contaminated water or dilution. The values obtained for Zn and Cu were observed to be lower than the permissible levels of the metals of the WHO report for 2012. Chromium recorded

values in this study is similar to reports by Kuma (2004) who recorded maximum levels in surface water as 0.49 mg/l.

Though no analysis was conducted to determine the composition of the soil at the sample site, the soil type was observed to be clayey. Clay soils are able to adsorb some heavy metals due to their numerous adsorption sites hence the low metal values observed for the metals.

7.6.2 Kinetic Studies

Initial treatment studies obtained by varying the mass of zeolites to a constant initial metal concentration indicated that equilibrium concentration of the metals in solution reduced with increasing zeolite mass as the removal of metal is faster from the wastewater. This phenomenon, as expressed by Gade and Pelilinan (2003) can be predicted as an increase in adsorbent dose increases the surface area and the adsorption sites of the zeolites. However, increasing the amount of zeolite increases the pH of the system above the stipulated value. Therefore for a sustained but reliable treatment of contaminated waters, the dosage that effectively removes heavy metals but within the acceptable pH limits is recommended.

For this study the zeolite to liquid ratio used for all batch experiments was 2 g: 200 ml.

7.6.2.1 *Single metal solutions*

Removal of metal ions from individual solutions is presented in Figure 7.1. The performance of each zeolite with increasing time is analysed. The removal efficiency of each metal by each zeolite was evaluated. The pH of the

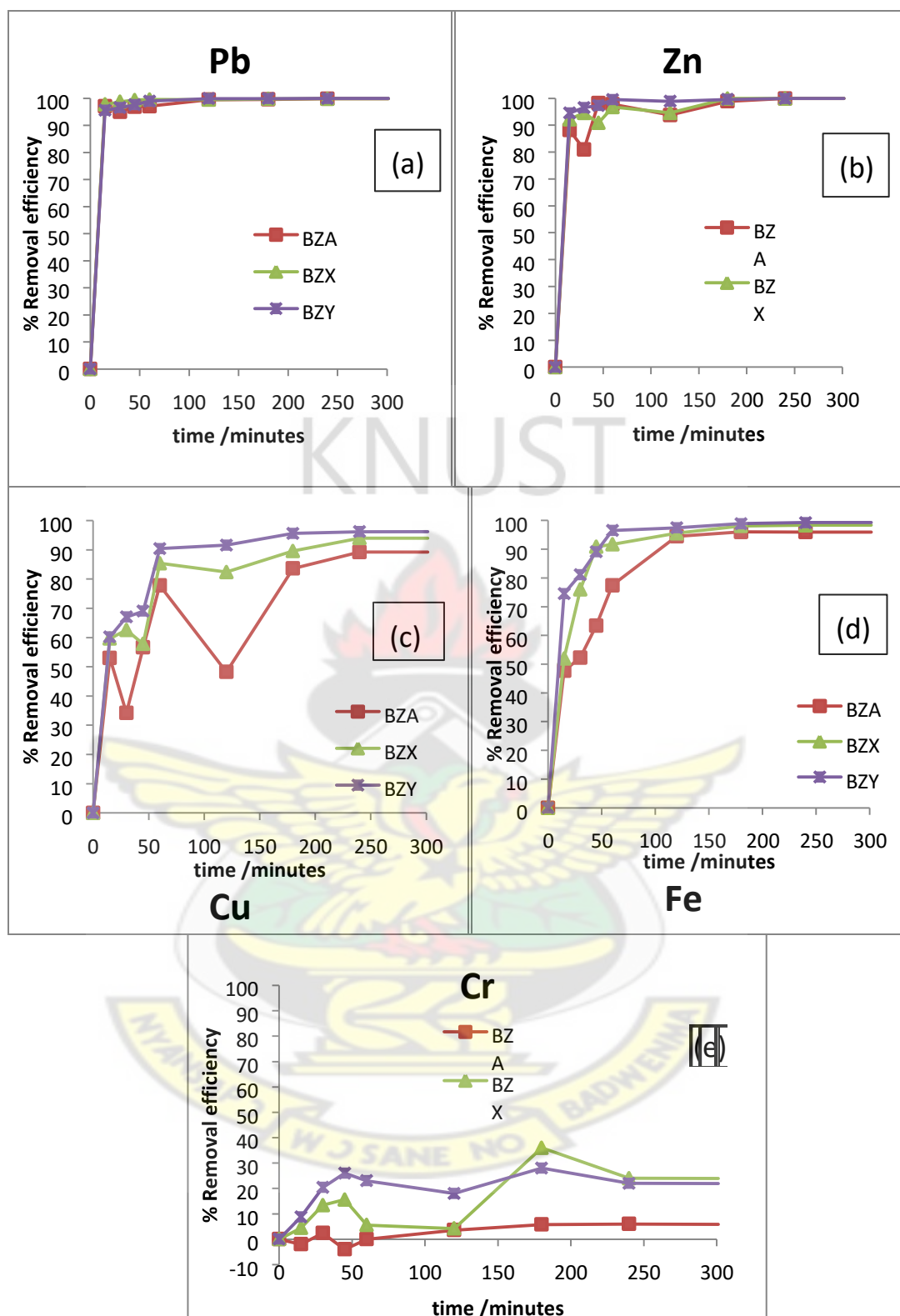


Figure 7.1: Removal of heavy metal ion in single metal solutions by the different zeolites

Lead as observed in the Figure 7.1(a) has a high removal by all three zeolites with a 97 % for zeolites A and X within the first 15 minutes of ion exchange. Zeolite Y recorded 95 % in that time. A reduction in removal by zeolite X was observed after 60 minutes. Zeolites X and Y recorded a fairly stable removal reaching up to 99.88 % and 99.95 % respectively at the end of the run (24 hours).

Zinc removal as portrayed in Figure 7.1(b) exhibits high removal after 15 minutes in all zeolites. Zeolite A shows a decrease in removal after 30 minutes. The highest removal is obtained after 180 minutes. Zeolite X and Y showed similar trend in Zn removal. A drop in removal is observed in zeolite X after 45 minutes. An increment is achieved after 60 minutes followed by a fairly stable removal until a slight fluctuation is observed after 120 minutes. Zeolite Y achieved a fairly consistent removal rate with very minimum fluctuations until the end of the experiment. The highest removal obtained for Zn was 99.96 %, 99.96 % and 99.98 % for zeolites A, X and Y respectively after 24 hours.

In the study of Cu (Figure 7.1c), a high removal was obtained after the first 15 minutes of ion exchange by all zeolites. A decrease in removal was observed after 30 minutes for zeolite A. zeolite X and Y however, recorded an increment in Cu removal after 30 minutes. Generally, Cu removal was characterized by fluctuations from 15 minutes up until 240 minutes.

47.7 %, 52 % and 74 % removal of Fe was achieved by zeolites A, X and Y during the initial 15 minutes of the experiment (Figure 7.1d). A gradual progression was observed in all the zeolites with increasing time. Highest removal was observed after 180 minutes with zeolite Y showing a greater removal capacity.

Cr was the least removed metal of the heavy metals by all the zeolites as indicated by Figure 7.1(e). The steep decrease in concentration observed in the other systems was not realised here. Cr removal was marked by severe fluctuations with very minimal reduction of its concentration. No removal was achieved by zeolite A after the first 15 minutes whilst zeolite X and Y achieved 4.4 % and 8.8 % removal. Zeolite Y recorded slight removal of Cr between 15 and 45 minutes. A drop in the removal was noticed at the end of 120 minutes. The highest removal for Cr was observed after 180 minutes but a subsequent decrease occurred afterwards. Similar trend is observed for zeolite A and X.

7.6.1.2 Effect of competing metal cations (mixed metal solutions)

The effect of competing metal ions was investigated using zeolites A, X and Y. Figure 7.2 depicts the rate of removal of each of the heavy metal ions by the individual zeolites as a function of time. As observed in the single metal solutions, the initial 15 minutes was characterised by a sharp decrease of all the metals in solution but with varied amounts. Pb removal was highest with 56 % in the first 15 minutes and 90.5 % after 240 minutes. Fe was removed similar to Pb. A steady increase is achieved between 0 and 30 minutes. A further 4 % removal was realised after 45 minutes and 5 % after 60 minutes. A reduction in Fe removal was observed at 120 minutes. Maximum Fe removal was 89.6 %. Cu removal fluctuated considerably as time progressed. Steady and maximum removal of Cu occurs after 180 minutes until the end of the experimental period. As usual, the erratic removal of metal ions is not observed in Cr. At 15 minutes, an 18 % removal of Cr was observed. This value reduced to 1.3 % after 120 minutes. At the end of the experiment, Cr removal was 15.3 % using zeolite A.

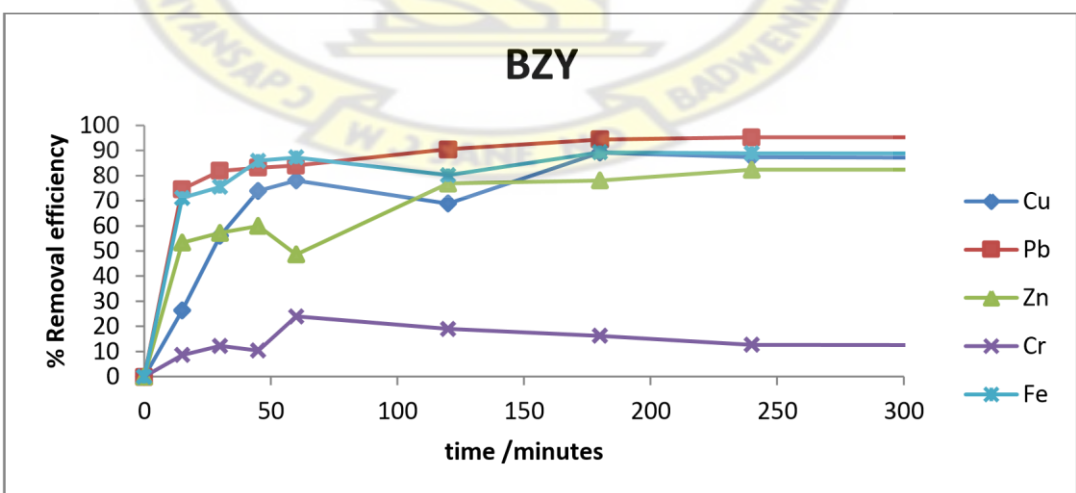
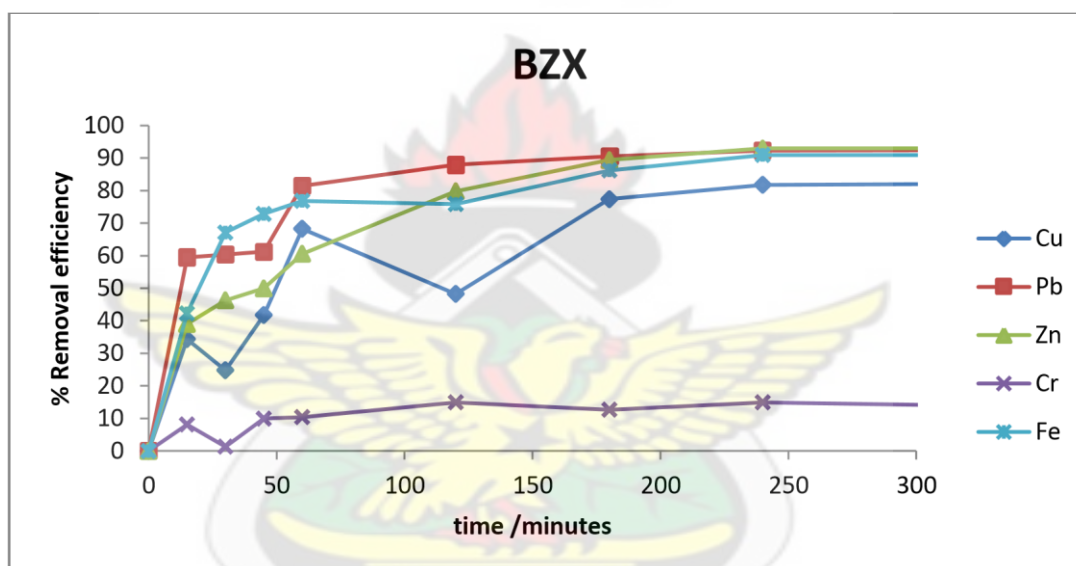
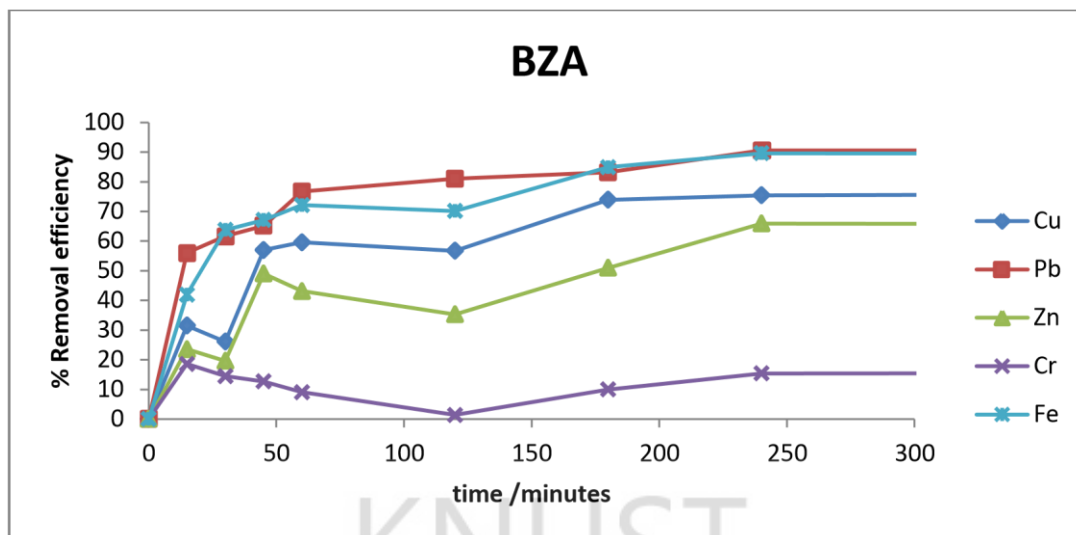


Figure 7.2: Removal of heavy metal ions in mixed metal solutions by the different zeolites

Similar behaviour for most of the metal ions removal as seen with zeolite A was observed in zeolites X and Y with a sustained decrease in concentration of Pb with time. Cu fluctuated appreciably when zeolite X was used but was however fairly stable with zeolite Y.

Cr removal was removed the least with the highest being 14.9 % for zeolite X and 23.9 % for zeolite Y.

7.7 Discussion

The pH and the amount of exchangeable cations present in the solution after the end of the experiment is a determining factor of the type of removal mechanism involved (Pitcher, 2002).

The removal of heavy metal ion with zeolite has been reported by various authors to be a result of ion exchange and/ or adsorption (Ibrahimi and Sayyadi, 2015). For metal removal occurring with pH levels around 6, ion exchange has been observed to be the dominant mechanism (Whitehead, 2000). All pH values recorded for this experiment were between 6.3 and 7.4 therefore heavy metal removal can be attributed to ion exchange reaction.

Generally, all the zeolites used in the study produced high metal removal efficiencies.

The as-synthesized zeolites from bauxite and kaolin showed low Si/Al ratios of 1.1, 1.3 and 1.5. Ion exchange capacity is higher for zeolites with high Al in their zeolite framework as more charge compensation cations will be present to preserve neutrality (Pitcher, 2002). Low Si/Al ratios are an indication of high terminal Al-OH group concentration at the mineral/ solution interface and are also hydrophilic.

Subsequently, a larger ligand exchange and improved overall performance is observed during treatment experiments of metal removal from wastewater (Misak, 2000; Semosa *et al.*, 2002; Alvarez-Ayuso *et al.*, 2003; Rios, 2008). Also, zeolites which possess low Si/Al ratios are known to hydrolyse easily in solutions (acidic conditions).

The sudden removal of heavy metal ions during the early 15 minutes of reaction can be attributed to the availability of free exchange sites on the zeolite surface which permit very rapid diffusion and exchange of the metals in the solution into the zeolites. However, the extent of metal removal depends on inherent properties of the species involved (Rios, 2008). The slow uptake observed beyond this time indicates a saturation or depletion of most of the active exchange sites. Fluctuations in removal as observed in both mixed and single solutions are usually due to different exchange sites within the zeolite frameworks. As such, as the reaction proceeds with time, some previously unreached sites with different affinities are accessed whilst other proton exchanges occur.

The most preferential ion is removed first by any zeolite. This illuminates why Cr appear to be least affected with increasing time.

The selectivity sequence revealed that the zeolites show a strong affinity for Pb in the mixed metal solution. Relative concentration of each of the metals would significantly affect the removal of each other implying that the metals are interdependent. However, if the exchange capacity of the zeolite is not exceeded, the preferred metal will be completely removed before the other competing metals. This phenomenon can be observed in all three zeolites (Figure 7.2) with Pb and Cr being the highest and least preferred ions respectively.

Low removal efficiencies are achieved when the cations in the solution cannot occupy the available ion exchange sites present in the zeolite framework. This is usually due to volume exclusion where the internal volume of the zeolite is filled with charge balancing cations.

Table 7.2: Selectivity sequence of the zeolites observed in the study

Zeolite	Single	Mixed
A	Pb > Zn > Fe > Cu > Cr	Pb > Fe > Cu > Zn > Cr
X	Pb > Fe > Cu > Zn > Cr	Pb > Fe > Cu > Zn > Cr
Y	Pb = Zn > Fe > Cu > Cr	Pb > Fe > Cu > Zn > Cr

Amongst all three zeolites, a similar selectivity sequence in metal removal was observed in the mixed metal solution. Slight variations are however noted in the removal of the metals in the single metal solutions. Common factors known to affect selectivity of a zeolite for various cations according to Sherry (1979) and Eisenman (1962) include the radius of the cation, its hydrated cationic size, the diameter of the zeolite channels and the amount of cation to zeolite framework interaction that can occur.

On the whole, heavy metal removal with zeolite A was lower compared with removal efficiencies obtained for zeolites X and Y. This can be attributed to the pore opening of Zeolite A which is relatively smaller than the pore openings of zeolites X and Y. Each zeolite is noted to contain cages interconnected to create pores. Depending on the particular zeolite structure, the pore openings of the zeolite cavities may be too small to allow large cations. The pores may consist of one type of channel having

essentially the same width. This determines the accessibility of the channel to incoming cations from the solution.

Table 7.3: Pore dimensions of the zeolites used in the study

Zeolite	Framework type	Pore
A	LTA	4.1 *4.1
X	FAU	7.4 *7.4
Y	FAU	7.4 *7.4

Theoretically, the pore opening of zeolite A will exclude hydrated divalent Cu and Zn from entering its framework. The radii of unhydrated cations are usually much smaller than its hydrated form. The ease with which a cation can shed its hydration sheathes is an additional factor in determining the selectivity of the zeolite for a specific cation. A large hydrated ion can vary its size by losing its water of hydration from the solvated ions to enable them penetrate the pores of the zeolite framework (Weitcamp and Puppe, 2013). The size of the hydration shell at a particular temperature depends on the size and charge of the anhydrous ion. The rate of ion exchange depends on the concentration of the ions of size capable of penetrating the pores of the zeolite (Kuhl, 1999). Kirov and Filizova (2012) in their study stated that the degree of ion exchange in a zeolite depends on the structural interactions particularly on the positions of the competing cations.

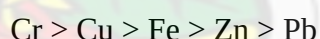
On the basis of available exchangeable sites in the zeolite framework, LTA has 3 cation sites. A fully Na-exchanged LTA with Si/Al ratio of 1 has 12 cations per alpha cavity whereas FAU can accommodate up to 48 cations in sites 1 and 2 of its

framework (Kulprathipanja, 2010). Hence obtaining a greater removal of cations for zeolite X and Y than zeolite A can be justified.

Table 7.4: Ionic and hydrated radius of cations

Cation	Unhydrated	Hydrated	Enthalpy of hydration
Pb²⁺	1.32	4.01	-1481
Fe²⁺	0.87	5.82	-1946
Zn²⁺	0.83	4.30	-2046
Cu²⁺	0.82	4.19	-2100
Cr⁶⁺	0.30	4.26	-1900

According to the size of the unhydrated radius of the cations (Table 7.4), the metal removal sequence could be predicted as:



From the table, it can be observed that the metal with the highest free hydration would prefer to remain in the solution. Hence the following sequence should have been expected:



However, both trends do not agree with the sequence observed in this study. Experimental results obtained by Whitehead (2000) using zeolite A for heavy metal removal recorded the sequence $\text{Pb} > \text{Cd} > \text{Zn} > \text{Cu} > \text{Ni}$. Observed differences can be attributed to the specifics of the synthesized zeolite and variations in the experimental

conditions and techniques used. It can be inferred that the zeolites used in the study exhibit a higher removal for metal ions with lower enthalpy of hydration. Pitcher (2002) and Zamzow and Schultz (1995) attributed the high affinity for Pb to be due to its low free energy. Yuan *et al.*, (1999) stated that the partial stripping of the hydration shells of an ion is a requirement for a cation to be able to enter the zeolite framework. This has been observed to occur readily with Pb ions (Pitcher, 2002).

It can be observed that the removal of Pb from the mixed metal solutions is not affected significantly by the presence of the other competing cations. A similar observation was made by Panayotova and Velikov (2002). It can be anticipated therefore that, the removal of the other cations could be higher with lower concentrations of Pb. The presence of Na, Ca, K and Mg however, has been studied to interfere with the removal of heavy metal ions by reducing the available ion exchange sites present in the zeolite in practical systems.

Cr was least removed in all the metal solutions by all zeolites. Mier *et al* (2001) achieved 12 % Cr^{6+} removal with Mexican clinoptilolite using a pH of 7 in their investigation. Studies on cationic metal ions removal processes indicate that Cr^{6+} removal occur differently compared with other heavy metals. Cr^{6+} is found as chromates or dichromates which are anions. The negative charge of chromate or dichromate is responsible for the poor adsorption in some mineral structures and soils thereby giving it its great mobility. Ion exchange of Cr^{6+} with zeolites is usually not successful as charge repulsion may occur from the negatively charged zeolite framework. This phenomenon has been experienced by several works (Figuerido and Quintelas, 2014). Cr^{6+} removal can be achieved by modifying the zeolite surface with

a surfactant. Cr^{3+} on the other hand is directly removed by both natural and synthetic zeolites with a wide variety of treatment methods.

7.8 Conclusion

Removal of heavy metal cations from actual and simulated mine wastewater was successful by all three zeolites synthesized from bauxite and kaolin. Removal occurs as result of ion exchange and adsorption processes with ion exchange occurring due to the weak nature of bonds between the zeolite framework and extra framework cations. Zeolite selectivity has been established for the zeolites to be due to their free hydration energy, width of their pore sizes and pH of the surrounding solution.

Pb removal was highest in both single and metal solutions with a removal efficiency or uptake of about 99 % by all zeolites in single metal solutions and 90, 94 and 96 % removal for zeolites A, X and Y respectively in the mixed systems. Cr recorded 4, 22 and 20 % removal corresponding to zeolite A, X and Y. in the mixed metal solution 16, 0.4 and 11 % removal was recorded for Cr after 24 hours run.

CHAPTER 8: OVERALL CONCLUSIONS AND RECOMMENDATIONS 8.1

Conclusions

Bauxite and kaolin are naturally occurring raw minerals whose capacity is least explored in Ghana. With the objective of synthesizing zeolites that are cost effective, these two materials were considered. The main aim of the study was to develop protocols by means of investigating the effect of various synthesis parameters on the composition of the final product.

Generally, zeolite LTA synthesis from kaolin has been reported in literature and successfully established in this study. Zeolite A was obtained using kaolin from Wassa in the Western Region and Anfoega from the Volta Regions of Ghana. Effect of synthesis parameters such as crystallization time, NaOH concentration and the fusion method were considered. Results from the study suggest that no new zeolitic product can be formed since the Si/Al ratio of the starting material is low. Consequently, production of zeolite from the bauxite alone from this study proved unsuccessful. Pure phased Zeolite LTA was not attained with hydrothermal synthesis using kaolin. The highest zeolite yield (87 %) obtained involved the alkaline fusion step prior to hydrothermal treatment. The XRD, SEM, FTIR and EDX analyses of the synthesized zeolites compares well with zeolites obtained from chemical reagents.

However, zeolite synthesis from bauxite and kaolin yielded different zeolitic products. All protocols used were developed and enhanced in the course of the study. The transformations that occurred and the phase of the resulting products were coordinated by the aging time, crystallization time, alkaline concentration and Si/Al ratio of the system. Zeolites A, X, Y, Analcime, Sodalite and ZK-14 were some of the phases achieved. Zeolite LTA was achieved with short crystallization times of 3, 5, 18 hours and a maximum aging of 24 hours. Zeolite LSX was synthesized with 24 hour aging

followed with 24 hour hydrothermal treatment whilst zeolite Y crystallized after 48 hour of aging and 24 hour crystallization. Prolonged crystallization time produced a mixed phased product. Prolonged aging times on the other hand did not yield any zeolite as the sample was amorphous. Increasing the alkaline content of the reaction mixture above 5 M introduced sodalite phase in the final product.

The cost of producing zeolites from kaolin and bauxite is greatly reduced when compared to reagent cost. It is therefore suitable to produce zeolites using lower alkalinity, shorter aging and crystallization times when working with bauxite and kaolin to further cut down cost.

Suitability and efficiency of the synthesized zeolites were evaluated by applying them to natural and simulated mine wastewater. This was targeted as a means of treating polluted waters caused by the action of galamsey operators in some communities. Using the batch technique, metal removal was found to reduce drastically in the first 15 minutes of the reaction. Removal of metal ions occurs due to ion exchange between the zeolite framework and ions in solution. However, adsorption mechanism as well as the formation of meal complexes aided the removal of the metals considered in this experiment. Metal removal was higher in the single systems than in the mixed system due to the competition between ions and relatively lower accessible sites available to them on the zeolites. Pb was removed highest by all three zeolites in both single and mixed metal solutions and Cr being the least removed. It was concluded that the ease of removal of these heavy metal cations depend on the size of their hydrated radii.

8.2 Recommendations

The following are recommended:

- Zeolite synthesis at low crystallization temperatures should be investigated as a means of further reducing the cost of synthesis to the minimum and the possible production of new zeolites.
- A mathematical model should be developed to further produce an insight as to how nucleation and crystallization occur to be able to optimize experimental conditions and synthesis parameters. This design would help both scientifically and technologically in predicting the type of zeolite that can be formed and as a means of controlling the zeolite properties.
- Bulk treatment of polluted water must be considered using column studies. However, due to the small particle size of the synthesized zeolite, pelletization as well as the use of structure directing agents to reduce their hydrophilicity should be considered.
- Since the extent of pollution depends on the intensity of activities and the natural bedrock of particular location, further analysis should be undertaken using a wider geographical location and considering other reaction mechanisms.
- For the removal of chromium and other anions in wastewater, surface modification of the zeolites using surfactants such as Hexadecyltrimethylammonium (HDTMA) bromide is recommended to improve their anion affinity.
- The use of zeolites in catalysis has been widely documented. Application of these low cost materials in this regard is highly recommended.

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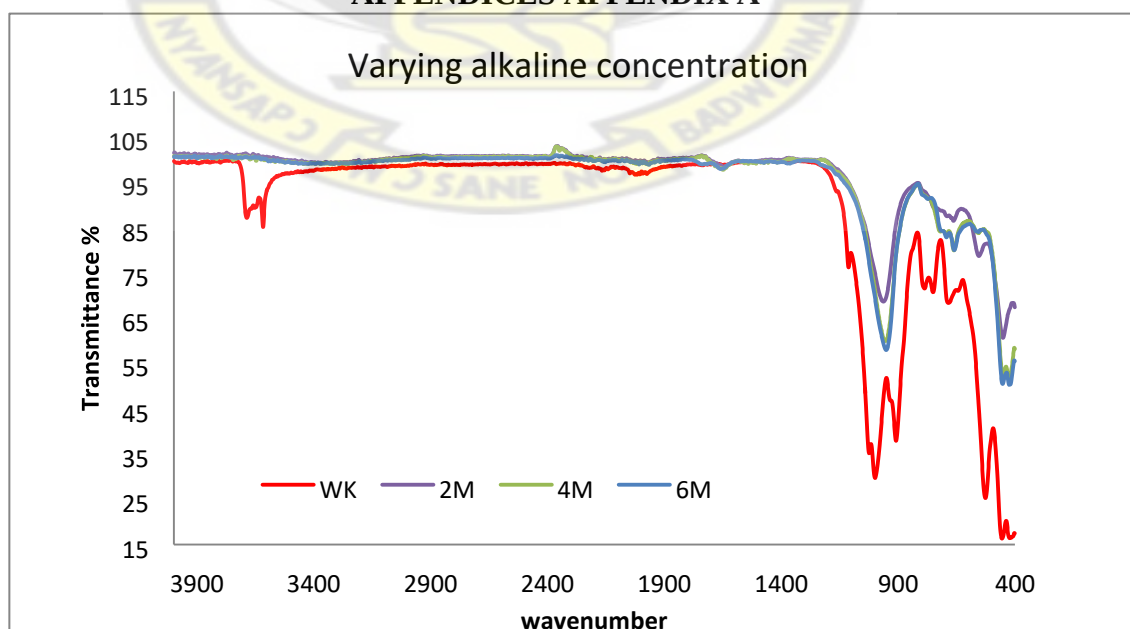
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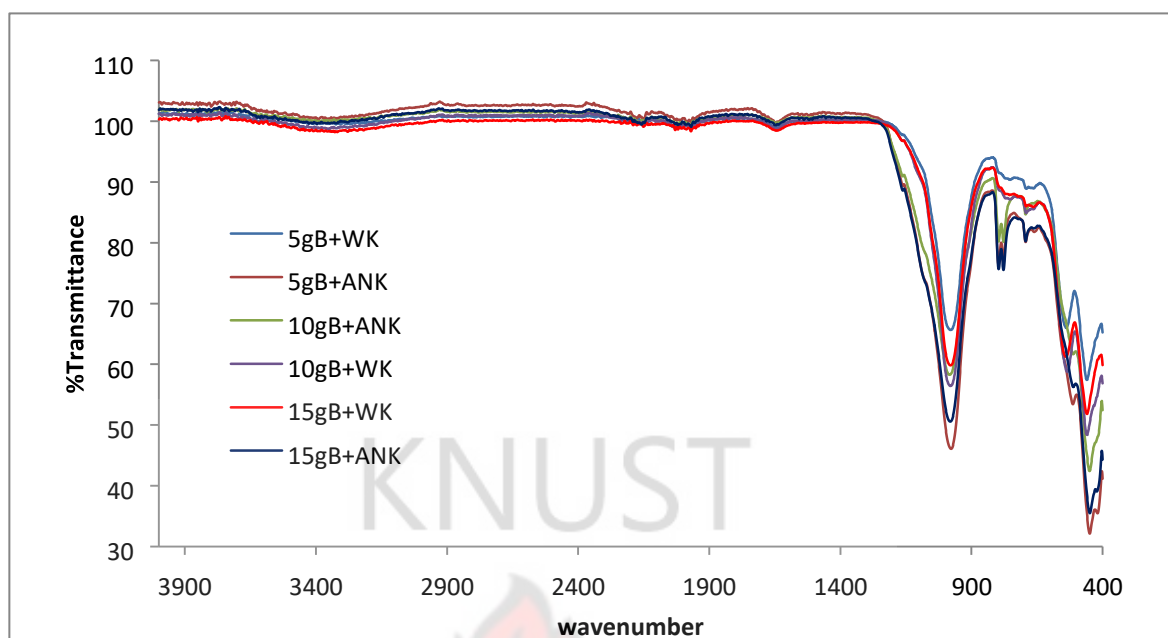
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APPENDICES APPENDIX A



FTIR spectra of zeolites from kaolin using varying alkaline concentrations



FTIR spectra of products obtained from varying mass of bauxite with the different kaolins.

APPENDIX B

COST ANALYSIS

Item	Cost per unit (GH¢)
Sodium hydroxide 500g	70
sodium aluminate 2kg	400
Sodium metasilicate 500g	120
Kaolin 50kg	40
Bauxite 50 kg	50

□ To synthesize 1kg of zeolite A from reagents using protocol adapted from Robson (2001)

Reagents	Mass/g	Cost (GH¢)
NaOH	72.3	10.122
Al ₂ O ₃	825.8	165.16
SiO ₂	1548	371.52
TOTAL (GH¢) =		546.802

□ Cost of 1 kg Zeolite A from bauxite and kaolin

Item	Mass/g	Cost (GH¢)
NaOH	400	56
Kaolin	1000	0.8
Bauxite	1000	1
Total (GH¢) =		57.8

APPENDIX C

MINE WASTEWATER TREATMENT

Monthly Water Collection Data

Month	pH	Parameters				
		Pb/mg l ⁻¹	Zn/mg l ⁻¹	Fe/mg l ⁻¹	Cr/mg l ⁻¹	Cu/mg l ⁻¹
April	6.0±0.2	0.022±0.01	1.08±0.03	35±0.05	0.31±0.02	2.84±1
May	6.3±0.1	0.011±0.01	1.20±0.02	35±0.05	0.1±0.01	0.22±0.1
June	6.5±0.1	0.013±0.01	0.33±0.10	24±0.1	0.1±0.02	0.16±0.04
July	6.5±0.1	0.016±0.02	0.33±0.05	30.4±0.2	0.43±0.04	0.46±0.03

August	7.0±0.3	0.002±0.02	1.42±0.01	35±0.1	0.28±0.02	2.34±0.2
September	7.0±0.2	0.008±0.01	0.83±0.01	37±0.01	0.48±0.03	2.84±0.5

Mine Wastewater Treatment Results

	Single Systems					
	Pb WHO= 0.05 mg/l					
Time (mins)	BZA	%	BZX	%	BZY	%
0	2	0	2	0	2	0
15	0.058	97.1	0.045	97.75	0.088	95.6
30	0.099	95.05	0.025	98.75	0.069	96.55
45	0.062	96.9	0.013	99.35	0.047	97.65
60	0.058	97.1	0.0081	99.595	0.02	99
120	0.01	99.5	0.0097	99.515	0.0018	99.91
180	0.0073	99.635	0.0041	99.795	0.0013	99.935
240	0.003	99.85	0.0027	99.865	0.001	99.95
1440	0.003	99.85	0.0025	99.875	0.0011	99.945

	Zn WHO = 2.5mg/l					
Time (mins)	BZA	%R	BZX	%R	BZY	%R
0	5	0	5	0	5	0
15	0.59	88.2	0.389	92.22	0.273	94.54
30	0.95	81	0.272	94.56	0.172	96.56
45	0.089	98.22	0.456	90.88	0.135	97.3
60	0.11	97.8	0.162	96.76	0.022	99.56
120	0.31	93.8	0.272	94.56	0.056	98.88
180	0.054	98.92	0.004	99.92	0.02	99.6
240	0.003	99.94	0.002	99.96	0.0018	99.964

1440	0.002	99.96	0.002	99.96	0.001	99.98
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	Cu WHO = 2mg/l					
Time (mins)	BZA	%R	BZX	%R	BZY	%R
0	5	0	5	0	5	0
15	2.35	53	2.02	59.6	1.99	60.2
30	3.29	34.2	1.87	62.6	1.65	67
45	2.17	56.6	2.11	57.8	1.55	69
60	1.11	77.8	0.73	85.4	0.48	90.4
120	2.59	48.2	0.88	82.4	0.42	91.6
180	0.82	83.6	0.52	89.6	0.22	95.6
240	0.54	89.2	0.3	94	0.19	96.2
1440	0.55	89	0.31	93.8	0.16	96.8

	Fe WHO = 0.3 mg/l					
Time (mins)	BZA	%R	BZX	%R	BZY	%R
0	35	0	35	0	35	0
15	18.3	47.71429	16.8	52	8.9	74.57143
30	16.7	52.28571	8.4	76	6.6	81.14286
45	12.8	63.42857	3.2	90.85714	3.8	89.14286
60	7.9	77.42857	2.9	91.71429	1.22	96.51429
120	1.93	94.48571	1.55	95.57143	0.89	97.45714
180	1.39	96.02857	0.67	98.08571	0.38	98.91429
240	1.41	95.97143	0.59	98.31429	0.25	99.28571
1440	1.43	95.91429	0.48	98.62857	0.23	99.34286

	Cr WHO = 0.1 mg/l					
Time (mins)	BZA	%R	BZX	%R	BZY	%R
0	0.5	0	0.5	0	0.5	0
15	0.51	-2	0.478	4.4	0.456	8.8
30	0.488	2.4	0.433	13.4	0.398	20.4
45	0.52	-4	0.422	15.6	0.37	26
60	0.5	0	0.472	5.6	0.385	23
120	0.482	3.6	0.479	4.2	0.41	18
180	0.471	5.8	0.32	36	0.36	28
240	0.47	6	0.38	24	0.39	22
1440	0.48	4	0.39	22	0.4	20

BZA Mixed System					
Time (mins)	Cu/mgl ⁻¹	Pb/mgl ⁻¹	Zn/mgl ⁻¹	Cr/mgl ⁻¹	Fe/mgl ⁻¹
0	4.6	2.32	5.1	2.21	29.8
15	3.15	1.02	3.9	1.8	17.3
30	3.4	0.89	4.1	1.89	10.8
45	1.98	0.81	2.6	1.93	9.8
60	1.86	0.54	2.9	2.01	8.3
120	1.99	0.44	3.3	2.18	8.9
180	1.2	0.39	2.5	1.99	4.5
240	1.13	0.22	1.74	1.87	3.1
1440	0.98	0.22	1.8	1.85	3.3

BZX Mixed System					
Time (mins)	Cu/mgl ⁻¹	Pb/mgl ⁻¹	Zn/mgl ⁻¹	Cr/mgl ⁻¹	Fe/mgl ⁻¹
0	4.6	2.32	5.1	2.21	29.8
15	3.02	0.94	3.11	2.03	17.2
30	3.46	0.92	2.74	2.18	9.8
45	2.68	0.9	3.1	1.99	8.1
60	1.46	0.43	2.01	1.98	6.9
120	2.38	0.28	1.03	1.88	7.2
180	1.04	0.22	0.54	1.93	4.11
240	0.84	0.18	0.36	1.88	2.7
1440	0.62	0.13	0.36	2.2	2.6

BZY Mixed System					
Time (mins)	Cu/mgl ⁻¹	Pb/mgl ⁻¹	Zn/mgl ⁻¹	Cr/mgl ⁻¹	Fe/mgl ⁻¹
0	4.6	2.32	5.1	2.21	29.8
15	3.39	0.59	2.38	2.02	8.6
30	2.02	0.42	2.18	1.94	7.3
45	1.2	0.39	2.04	1.98	4.2
60	1.01	0.37	2.62	1.68	3.8
120	1.43	0.22	1.18	1.79	5.9
180	0.5	0.13	1.12	1.85	3.2
240	0.58	0.11	0.9	1.93	3.3
1440	0.75	0.1	0.9	1.96	3.4