

**SYNTHESIS OF ZEOLITES AND THEIR APPLICATION TO THE
DESALINATION OF SEAWATER**

By

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DECLARATION

I VON-KITI ELIZABETH, author of the thesis ‘Synthesis of Zeolites and Their Application to the Desalination of Seawater’ hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

In this study, zeolite X and Y were synthesized hydrothermally in the laboratory at 90 °C and 100 °C respectively. The synthesized zeolites were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infra-red spectroscopy (FTIR), EDX and thermogravimetric analysis. Exchange of Ca, Mg and K for Na ions in seawater were evaluated in Linde type X and Y. The desalination capacity of both zeolite X and Y were evaluated by adding 0.5 g and 1.0 g of each zeolite to 100 ml of seawater on a rotary shaker. The kinetics of desalination was carried by taking analyte samples at 10, 15, 30, 60, 90 and 120 minutes. The results obtained showed that zeolite mass to seawater ratio of 0.5:100 yielded higher removal efficiencies. Ion exchange was carried out at room temperature. Replacement of Na cations by Ca, K and Mg in the zeolite framework was noted. The overall ion exchange selectivity of both X and Y showed preference in the order of Ca > Mg > K > Na. Removal efficiencies obtained when zeolite X was used was Ca 81.5%, Mg 75%, K 59.9% and Na 11.5%. Efficiencies obtained in the case of zeolite Y was Ca 53.9%, Mg 38.5%, K 35.5% and Na 34.5%. Silver nitrate was used to reduce chloride ions and reduce electrical conductivity. It was concluded that zeolites are efficient in the desalination of seawater. The quality of water produced was not suitable for drinking. However, it can be used for irrigation and other industrial purposes. It is suggested that, to effectively desalinate seawater, zeolites without sodium will be appropriate. Also alternate methods like the Column method could be utilized.

DEDICATION

To God Almighty, the author and finisher of my faith

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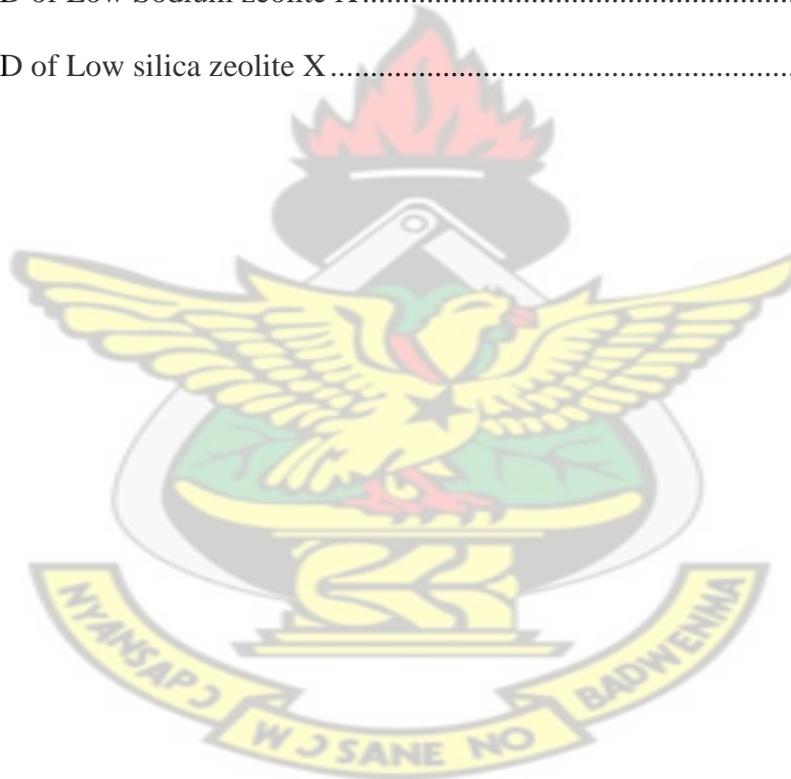
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CHAPTER ONE

INTRODUCTION

Seawater is an abundant natural resource. About 71% of the earth's surface is covered by water which is in the form of oceans, seas and ice at the poles. However, only about 3% of the water is fresh and suitable for drinking. The water of the oceans and seas is salty and thus not directly usable. In view of the world's permanently growing needs of fresh clean water, improved and economical methods for ion exchange and desalination would be very desirable.

Desalination refers to any several processes that remove excess salt and other minerals from water. Sometimes the process produces table salt as a by-product. It is used on many sea going ships and submarines (www.wikipedia.com).

Desalination processes involves removing soluble salts from seawater to render it suitable for drinking, irrigation or industrial use. Principal methods used for desalination include distillation, evaporation, electro dialysis, freezing, ion exchange and reverse osmosis. These current water desalination techniques are energy intensive and some use membranes operated at high temperatures (Cao *et al.*, 2009). Present day scientists aim at providing new and effective ways of desalination, removing anions and cations using zeolites.

Zeolites, based on their high ion exchange capacity and absorptivity can be used to reduce sodium ions in seawater by ion exchange and reused repeatedly by ion exchange with other cations (Takaaki *et al.*, 2008).

Zeolites are crystalline materials that have a composition very similar to sand, mainly comprising of Si and O₂. Zeolites have three dimensional framework of tetrahedra silica or

alumina anions strongly bonded at all corners. The zeolite structure contains (Si – O – Al) linkages that form surface pores of uniform diameter and enclose regular internal cavities and channels of discrete sizes and shapes depending on their chemical composition and crystal structure of the specific zeolite. Pore size range from about 2 to 12Å.

The enclosed cavities contain both the metal cations and water molecules. The cations are loosely bound to the lattice and thus engage in ion exchange (Sean, 2009). Their open pore structure makes them very useful for solving the mobility of toxic elements in a number of environmental applications (Belvisoet *al.*, 2009).

Zeolites are widely used in industry for water purification, as catalysts and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture. They occur naturally as minerals that are mined in some parts of the world. Others are synthetic and are made for specific uses (Bell, 2001). One hundred and fifty (150) different structures have been reported of which forty (40) are naturally occurring formed from volcanic ash (Szostak, 1989).

Zeolites are widely used because of their ion exchange capabilities of ions of interest. Studies have shown that they have the ability to function in temperatures and pH regions necessary for cost and energy effectiveness (Plesset *al.*, 2006). All this is strictly connected with their ability to exchange cations, their large surface area and their typical structural characteristics (such as porosity) which facilitate pollutant adsorption and encapsulation (Belvisoet *al.*, 2009).

1.1 BACKGROUND TO THE STUDY

With population growth coupled with unpredicted droughts in Sub-Saharan Africa water scarcity is gradually reaching alarming proportion. The need to find alternative water source(s) has become paramount. In recent times desalination techniques have been used to

desalinate sea water, brackish water or waste water. These techniques although relevant come with high cost and in some cases results in the introduction of other harmful chemicals. The high capital and energy cost requirements remain a concern in many parts of the world (Cao *et al.*, 2009)

Very recently zeolites have been considered as the best alternative to achieve high desalination rate with virtually no introduction of other harmful chemicals whilst effectively removing anions and cations in varying ways.

1.2 STATEMENT OF PROBLEM

Following their discovery, various applications of zeolites have been noted in almost all industries. Based on their structure and composition, types of zeolites can be synthesized for varying processes. Some of the processes, that is, the production of high quality fuels from crude oil, the production of ammonia, detergents, and all kinds of plastics and also production of pharmaceuticals involve their use. Ion exchange and catalytic ability of zeolites allows for their usage in industries. In this exploratory project, the desalination propensity of different zeolites will be investigated.

1.3 OBJECTIVES OF THE RESEARCH

The aim of this project is to explore the desalination capacity of laboratory-synthesized zeolites on seawater thereby making the 'treated' water drinkable or usable (at least) for industrial purposes. Specific objective(s) of this study include:

- (i) To synthesis zeolite type X and Y.
- (ii) To characterize the thermal, vibrational, morphological and elemental composition of the synthesized zeolites.
- (iii) To investigate the diffusive properties of the synthesized zeolites.
- (iv) To investigate the efficiency of the synthesized zeolites.

1.4 JUSTIFICATION OF OBJECTIVES

The use of zeolites in waste water treatment and their applications to removing harmful pollutants is well documented. In addition, zeolites are used as antimicrobial agents in Japan, the USA and in Europe. Zeolites are extensively used in industries as ion exchangers and catalysts in a large range of processes. Diffusion of ions in zeolites differs greatly from diffusion in liquids and gases due to the presence of pores that makes their framework. As the framework structures of zeolites determine the ease or speed with which substances enter or leave the active centres, a thorough study of ion exchange mechanism in zeolites is appropriate. There is little or no research on zeolites in Sub-Saharan Africa to date. Hence, this project will provide first-hand knowledge of the efficacy of zeolites in desalination of seawater.

1.5 IMPORTANCE OF THE RESEARCH

The importance of zeolites in various industries cannot be understated. The work proposed in this study will be the first of its kind in the country. Although work has been carried out on the use of zeolites in treating municipal and industrial waste waters, little is known on the efficacy of synthesized zeolites on seawater.

The results will benefit the health sector as most of the toxic compounds from the seawater will be removed. Also, it would be a viable alternative to water shortages.

1.6 OVERVIEW OF THE STUDY

This work is divided into six chapters: Chapter one introduces the work in terms of the objectives and what zeolites are. Review of literature is presented in chapter two. Chapter three explains ion exchange mechanism in zeolite with relevant equations. In chapter four, the experimental design and methodology is presented. Method of synthesis of zeolite X and Y are presented. Characterization of zeolite and ion exchange mechanism are also treated

here. Chapter five deals with the result of zeolite synthesis, characterization and results relating to ion exchange in zeolite are provided. Discussions based on these results are also analysed. Finally, chapter six concludes the work based on findings made and suggestions for future work are given.

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CHAPTER TWO

REVIEW OF LITERATURE

2.1 ZEOLITES

Zeolites are a group of hydrated aluminosilicates of the alkali or alkaline earth metals: principally sodium, potassium, magnesium, lithium, barium and calcium (Sean and Yoshio, 2009). Zeolites are inorganic porous materials having a highly regular structure of pores and chambers that allow molecules to pass through and cause others to be either excluded or broken down. Their framework is crystalline and three dimensional networks of tetrahedra silica or alumina anions strongly bonded at all corners.

The very regular structure and pore sizes give these materials a sponge-like appearance (Figure 2.1). Their pores hold water and or other molecules. Differences in zeolites arise from pore diameter, pore shape and the way these pores are interconnected. The pore size plays a significant role in the use of zeolites: allowing or prohibiting the entrance of the molecules to the system.

A negatively charged framework, due to the presence of alumina, is counter balanced by positive ions (cations) resulting in a strong electrostatic field observed on the internal surface of zeolites.

Zeolites are expressed by the formula



M representing the exchangeable cations of valence n. M may either be a Group I or II ion. X and y are the stoichiometric coefficients of the Al^{3+} and Si^{4+} in the tetrahedra (Breck, 1974).

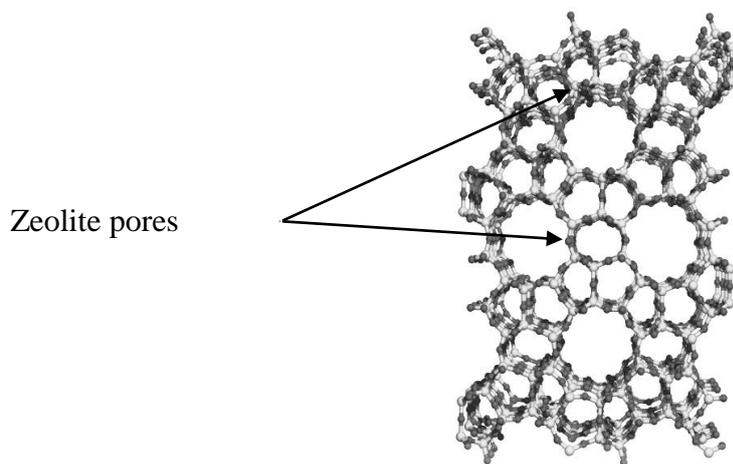


Figure 2.1: Structure of Zeolite silicalite showing its pores (Schuring, 2002).

2.2 DISCOVERY

Zeolites were discovered in 1756 by Cronstedt, a Swedish mineralogist. The name 'zeolite', he derived from Greek words 'zein and lithos' meaning 'to boil' and 'stone'. Eichhorn(1858) showed that these materials can exchange their constituent cations for others. In 1857, Damour demonstrated the hydration-dehydration properties of zeolites (van Bekkum *et al.*, 2001). Weigel and Steinhof in 1925 separated gas molecules on the basis of size once the water had been removed from the zeolite internal structure (Mumpton, 1978).

Firedel and Bull (1896) cited by Szostak (1989) proposed that the structure of dehydrated zeolites consists of open porous frameworks. As cited in Breck, (1974) the first laboratory synthesis of a zeolite is attributed to Deville, who in 1862 synthesized levynite by heating potassium silicate and sodium aluminate in a glass ampoule.

Barrer in 1938 successfully synthesized Chabazite and Mordenite, leading to an inspiring period of zeolite synthesis in the search of new approaches for the separation and purification of air (Flanigen, 2001). In 1940, low silica zeolites were synthesized. The application of low temperature hydro thermal technique facilitated the extensive industrial production of zeolites. Further discovery of significant commercial zeolite types A, X and Y was produced

by Milton and Breck between 1949 and 1959. Zeolites A and X were first synthesized in China also in the year 1959.

Zeolites were introduced as adsorbers for industrial separations and purifications in 1954. The beginning and development of molecular sieve zeolite was by Milton in 1967. He traced early discoveries and synthesis of new zeolites A, X and Y which led to their commercial applications as selective adsorbents and catalysts (van Bekkum *et al.*, 2001).

The discovery in 1957 of large deposits of relatively high purity zeolite minerals in volcanic tuffs in the western United States and in a number of other countries represents the beginning of the commercial natural zeolite era. Prior to that time there was no recognized indication that zeolite minerals with properties useful as molecular sieve materials occurred in large deposits. Commercialization of the natural zeolites chabazite, erionite, and mordenite as molecular sieve zeolites commenced in 1962 with their introduction as new adsorbent materials with improved stability characteristics. The applications of clinoptilolite in radioactive waste recovery and in waste water treatment during the same period of the 60's were based not only on superior stability characteristics but also high cation exchange selectivity for caesium, strontium, and for ammonium ion (Flanigen, 1980).

Following their discovery zeolites were found to be characterized by the following properties (Szostak, 1989; van Bekkum *et al.*, 2001):

1. catalytic properties;
2. high hydration propensity;
3. stable crystal structure when dehydrated;
4. low density and high void volume when dehydrated;
5. cation exchange and sorption properties.

Presently, the use of zeolites is known worldwide. Natural zeolites are easily exploited and used after simple processes hence have a lower cost associated with it (Xu *et al.*, 2007). Synthesized zeolites compared to natural zeolites have several advantages such as purity, uniform pore size and better ion exchange abilities.

2.3 ZEOLITE AND ZEOLITIC MATERIALS

2.3.1 Microporous and Mesoporous Materials

Porous materials are classified by their pore size into microporous and mesoporous materials. Microporous materials have pore diameters of less than 2 nm. Microporous materials are often used in laboratory environments to facilitate contaminant-free exchange of gases. Mold spores, bacteria, and other airborne contaminants will become trapped, while allowing gases to pass through the material. This allows for a sterile environment in the contained area. Zeolites are a very important member of this family (Xu *et al.*, 2007).

Mesoporous materials are those with pores in the range 20-500Å in diameter. They have huge surface areas, providing a vast number of sites where sorption processes can occur. These materials have numerous applications in catalysis, separation and many other fields. The synthesis of these materials is of considerable interest and is constantly being developed to introduce different properties (Hoets, 2001). Typical mesoporous materials include some kinds of silica and alumina that have similar sized fine mesopores. Mesoporous oxides of niobium, tantalum, titanium, zirconium, cerium and tin have also been reported.

2.3.2 Molecular Sieves

During the past half century, compounds with diverse elemental composition have been studied. Zeolite-like materials have structures similar to zeolites but other elements other than Si, Al and O are present in them. The ability to adjust the pores precisely determines the uniform openings to allow for molecules smaller than its pore diameter to be adsorbed whilst

excluding larger molecules hence the name “Molecular Sieves”. Thus zeolites, silicalites, and aluminophosphates were classified as molecular sieves. Zeolite molecular sieves have precisely uniform pore sizes and molecular dimensions between 0.3- 2.0 nanometres. This translates into a sieve-like selectivity where molecules of varying size and polarity may be readily adsorbed, slowly adsorbed or completely excluded. This selectivity, combined with a high capacity over a wide range of operating conditions, gives each zeolite molecular sieve a high level of adsorption efficacy. Molecular sieves are often utilized in the petroleum industry. Use of zeolite molecular sieves to dry, purify and separate liquids and gases prevents unwanted side reactions, helps meet product specifications, and avoids costly complications from equipment corrosion and freeze-up. Examples include carbons, glasses and oxides (van Bekkum *et al.*, 2001).

Table 2.1 Difference between molecular sieves and zeolites

Molecular Sieves	Zeolites
Composition varies and distinguishes materials on the basis of their size	Special class of molecular sieves with aluminosilicates as skeletal composition
May be crystalline, non-crystalline, paracrystalline or pillared clays	They are highly crystalline materials
Variable framework charge with porous structure	Have anionic framework with microporous and crystalline structure

2.4 STRUCTURE

Zeolites have interesting properties due to their anionic framework and exchangeable cations. Zeolite refers to a crystalline aluminosilicate with a corner sharing TO_4 ($T = Si$ or Al) tetrahedra forming a three dimensional four-connected framework with uniformly sized pores of molecular dimensions.

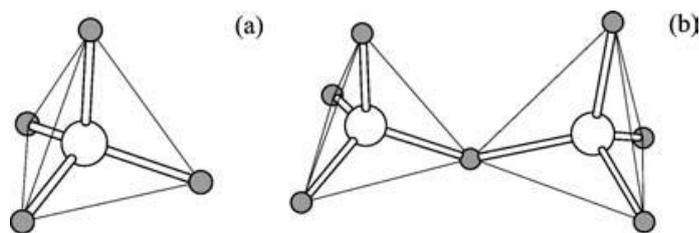


Figure 2.2: (a) TO_4 tetrahedron. (b) tetrahedra sharing a common oxygen vertex (Xu *etal.*, 2007)

As shown in Figure 2.2, the primary building unit of the zeolite structure has a central atom, silicon or aluminium with four oxygen atoms at the corners. A tetrahedron is formed with an oxygen atom being shared by two tetrahedra.

Zeolites constructed from SiO_4 and AlO_4 tetrahedra possess an anionic framework, the negative charge of which is compensated by extra framework cations. Cations in the channels can be exchanged easily hence the term exchange or extra framework cations. Si and Al are not exchanged under ordinary conditions. They are called framework cations (Top, 2001). Exchangeable cations include lithium, cadmium, lead, zinc, copper, ammonium, silver and protons (Kwakyeh- Awuah, 2008).

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.

A ring of oxygen atoms define the aperture of each channel i.e. the pore size. There may be 4, 5, 6, 8, 10 or 12 oxygen atoms in a ring. Pore size and structure of a zeolite affect the selectivity of a reaction (Hagen, 1999).

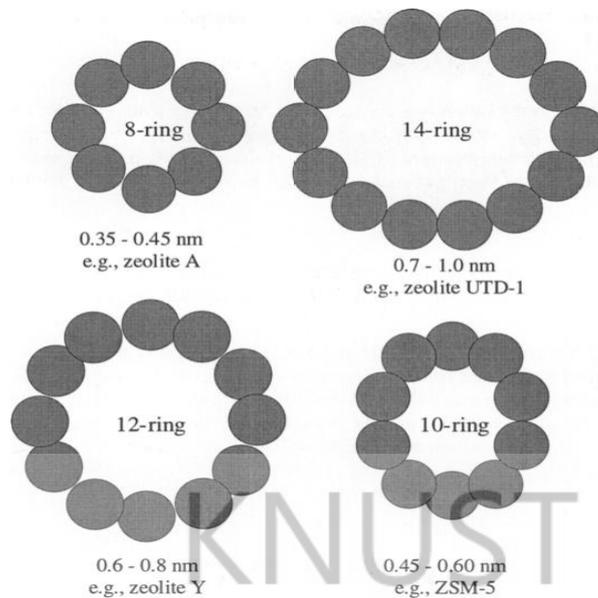


Figure 2.3: Illustration of zeolite pore sizes with oxygen atoms (van Bekkum *et al.*, 2001).

2.5 APPLICATIONS

Zeolite has a wide range of applications. Currently, the use of zeolites is recognised and used in many industries. The largest is its use in the making of detergents. Others include:

2.5.1 Gas Purification and Separation

Zeolites act as molecular sieves. They are used to purify or sweeten natural gases through the removal of impurities such as carbon dioxide, sulphur dioxide and water. In addition to upgrading natural gas, zeolites are used to separate oxygen and nitrogen in pressure swing adsorption columns.

2.5.2 Ionexchange

The enclosed cavities contain both the metal cations and water molecules. The cations are loosely bound to the lattice and thus engage in ion exchange. The water molecules can also be reversibly driven off in most zeolites. Cation exchange of zeolites is used routinely in modifying the properties of zeolite products used in adsorption and catalysis. The largest ion exchange application of zeolites is in its use as a builder for detergents.

2.5.3 Catalysis

Applications of zeolites include its use to catalyze the conversion of crude oil to more useful products such as gasoline, kerosene and other smaller hydrocarbons. Reactions involved include hydro cracking, hydro-isomerization, aromatization and dehydrogenation of cyclohexanes.

Advantage of using zeolite is that these catalysts because of their specific pores and cages not all products can be formed resulting in selectivity of the reaction i.e. fraction of desired products of all products that are formed.

Zeolites are extremely useful as catalysts for several important reactions involving organic molecules (Szostak, 1989). The most important are cracking, isomerization and hydrocarbon synthesis. Zeolites are able to promote a diverse range of catalytic reactions including acid-base and metal induced reactions; serve as acid catalysts and can be used to support active metals or reagents (Barthomeuf, 1996). Zeolites can be shape-selective catalysts either by transition state selectivity or by exclusion of competing reactants on the basis of molecular diameter (Sobolev *et al.*, 1993). They have also been used as oxidation catalysts. The reactions can take place within the pores of the zeolite, which allows a greater degree of product control (Szostak, 1989).

2.5.4 Lightweight Construction Materials

Natural zeolite can be used to prepare lightweight concrete for construction. Its porous silicate structure makes it much lighter than sand with an increased volume per tonne but with similar hardness and strength. Zeolite is free from clay which reduces the overall strength of concrete and its porous structure holds moisture which facilitates a more rapid curing of concrete. When added to Portland cement as a Pozzolan, it can reduce chloride permeability and improve workability. It reduces weight and helps moderate water content while allowing for slower drying which improves break strength.

2.5.5 Waste Water Treatment Media

Zeolites contribute to a cleaner, safer environment in a great number of ways. In fact nearly every application of zeolites has been driven by environmental concerns or plays a significant role in reducing toxic waste. As zeolites are a granular material, solid and suspended particles are trapped between the grains. The porous structure also causes colloid particles from both organic and mineral origin to be removed from the water (Szostak, 1989; Thompson, 1998). The capacity for the removal of solid particles is up to 45% greater than the capacity of sand with an equivalent particle size distribution. Certain natural zeolites have a high affinity for ammonium ions and are being used in a tertiary water treatment system

2.5.6 Radioactive Waste Treatment

Natural zeolite has a high ion exchange capacity and a particular affinity for heavy metal cations. It can absorb elements such as strontium 90, caesium 137 and other radioactive isotopes from solutions and hold them in its 3 dimensional crystal framework. Zeolites react readily with cement and glass systems thus allowing the radioactive waste to be entrapped and contained safely. Zeolites are physically robust and resistant to nuclear degradation, and they are less expensive than organic ion exchange resins.

2.5.7 Pool Filtration Media

Zeolites offer superior performance for sand and carbon filters, giving purer water and higher output rates with less maintenance required. The highly porous structure of zeolites captures particulate contamination down to 4 microns in size. Chemicals such as chlorine, algaecides and flocculants can change the pH of pool water. In addition, environmental factors as well as the quality of the fill water can create changes in the pH of a swimming pool (Dyer and White, 1999). The use of zeolites results in lower chlorine consumption and a better swimming environment in pools. Zeolites also adsorb ammonia and its compounds thus

reducing and preventing their formation (Bergero *et al.*, 1994; Dyer and White, 1999) as cited by Kwakye-Awuah (2008).

2.5.8 Fertilizer and Feed Additive

Zeolites are known to be slow release fertilisers. Plant nutrients such as nitrogen and potassium are held by the negatively charged clinoptilolite structure and released on demand. Clinoptilolite application on the daily diet of the animals reduces digestion system illnesses. Clinoptilolite addition to the feed formulation has a positive effect on the growing up of the animals.

2.5.9 Fillers

Zeolites are used as fillers in the manufacture of papers. These filler grades of zeolite have a large potential for utilization in paint and plastics industries.

2.5.10 Aquaculture

Zeolites can reduce ammonium and hydrogen sulphide levels in fish/prawn ponds, resulting in increased fish/prawn growth rates and population densities. Zeolite is an efficient ammonia remover and also provides a large surface area for nitrifying bacteria in recirculation systems. Zeolites do not only provide optical clearness of your water but also keeps it biologically clean.

2.5.11 Desalination

Desalination is a process that removes dissolved minerals from seawater, brackish water or treated waste water. The water of the oceans and seas is salty and thus not directly usable. In view of the world's permanently growing needs of fresh clean water, improved and economical methods for ion exchange and desalination would be very desirable.

Most modern ocean-going vessels create drinkable (potable) water from seawater using desalination processes such as vacuum distillation, multi-stage flash distillation, or reverse osmosis. However these processes are energy intensive.

2.5.11.1 Methods

A wide variety of desalination technologies are available to remove salts from seawater producing fresh water.

Desalination technologies fall into three categories of chemical, thermal (evaporative) and membrane based methods. Processes used in desalination include: Vapour Compression, Multistage Flash, Electrodialysis, Reverse Osmosis, Solar Distillation, Freezing, Ion Exchange, Solvent Process and others.

Large scale desalination typically uses extreme large amounts of energy and specialized infrastructure. For smaller quantities e.g. in a laboratory scale, also consecutive application of cationic and anionic exchange materials are commonly used.

Chemical Processes include liquid-liquid extraction, gas hydrate and other precipitation scheme. It is not very common. They are used in special applications such as specific feed water contamination. Membrane desalination plants produce portable water by molecular separation whilst Thermal plants work by breaking bonds between water molecules.

Membrane methods are considered cheaper and less energy intensive than the thermal methods. Reverse Osmosis (RO) and Electrodialysis (ED) are membrane methods that due to cost effectiveness and feasibility reasons have attracted greater attention.

2.5.11.1a Reverse Osmosis

In this process, water with a high salt concentration is allowed to move through a water-permeable membrane under high pressure separating the water from its dissolved

components. Based on pressure differences, the feed water and the permeate (water through the membrane), the product water is obtained.

Reverse osmosis is highly efficient in terms of the amount of water that is obtained at the end of the process. However, it requires a lot of maintenance of its systems which are sensitive to pH, oxidizers, bacteria, particulates and other foulants. Pre-treatment of the feed water is recommended to protect the membrane that is used. Reverse osmosis is the finest level of filtration available and supplies water that is safe and pleasant to use.

2.5.11.1b Electrodialysis

Electrodialysis is one of the methods used for many years. It is an electrochemical process for the separation of ions across charged membranes from one solution to another under the influence of an electrical potential difference used as a driving force. It involves forcing ions from the saltwater through ion exchange membrane under an electrical field. The salt molecule basically comprises a positive and negative ions bound together are made to separate at units called cell pairs.

This process is widely used for the production of drinking and process water from sea and brackish water, treatment of industrial effluents, recovery of useful materials from effluents and salt production.

2.5.11.1c Using Zeolites

Ion exchangers exchange one ion for another, hold it temporarily, and then release it to a regenerant solution. In an ion exchange system, undesirable ions in the water supply are replaced with more acceptable ions. For example, in a sodium zeolite softener, scale-forming calcium and magnesium ions are replaced with sodium ions.

In 1905, Gans, a German chemist, used synthetic aluminosilicate materials known as zeolites in the first ion exchange water softeners. Although aluminosilicate materials are rarely used today, the term "zeolite softener" is commonly used to describe any cation exchange process.

All natural waters contain in various concentrations dissolved salts which dissociate in water to form charged ions positively and negatively charged ions. Ion exchangers exchange one ion for another, hold it permanently and then release it to a regenerate solution. In an ion exchange system, undesirable ions in the water supply are replaced with more acceptable ions (Alchin, 2006).

Environmentally friendly methods and materials for desalination are available using ionexchangers. The desalination process effectively removes anions and cations in separate steps with minimal caustic waste generation. Similarly, zeolites can be used because of their specific ion exchange capacities. Zeolites have the ability to function in temperatures and pH regions necessary for cost and energy effectiveness. Zeolites are improved high ion exchange materials which have high ion binding capacity in particular for monovalent ions and favourable regeneration properties (Plesset *al.*, 2006).

Previous studies have shown that a series of ion-exchange column (chabazite) will most likely result in a higher removal efficiency of Na ions. The use of zeolites for water desalination has been reported by many researchers (Caputo and Pepe, 2007) with a reported reduction in contaminants of up to 99.99% using a series of zeolite columns depending on the type of zeolite and salt concentration (Ghaly and Verma,2008). Since seawater is high in sodium ions, the use of a Na-free zeolite will be recommended for the removal of sodium ions.

2.6 ZEOLITE SYNTHESIS

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. Ribeiro *et al.*, (1984) as cited in Htay (2008) reviewed the preparation of zeolites for water purification, waste and wastewater treatment. 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.

Synthetic zeolites are manufactured from water, silica (SiO_2) and alumina (Al_2O_3) containing substances under high temperatures (Breck, 1979; Barrer, 1982). Zeolites can be prepared by using various materials such as fly ash, kaolinite and rice husk. Zeolite was prepared from clay in Myanmar (Win, 2004).

Sources of silica may include fumed silica, silica sol, alkali metal silicates, alkoxides of silicon, silicic acid and other forms or suitable mixtures. Alumina may exist in the form of colloidal alumina, aluminium salts, aluminium alkoxides, aluminium hydroxides or trichlorides, sodium aluminate and other mixtures.

Synthetic zeolites can have their frameworks modified by the addition of metal cations other than aluminium and silicon in the framework. Alternatively, modification can occur by dealumination to increase the silica content thereby increasing the hydrophobic nature of the zeolite (Myat, 2003). Depending on the Al content, zeolites have different chemical and physical properties.

Zeolite synthesis involves producing a reaction mixture. Occurring in the synthesis mixture at the reaction temperature is the formation of zeolites from amorphous materials. The mixture undergoes nucleation usually at high temperature. The gel formed in the reaction process and

the species in solution rearrange from continuous changing phase of monomers and clusters. Crystallization occurs after nucleation (van Bekkum *et al.*, 2001).

In a typical aluminosilicate zeolite synthesis, sodium aluminate is dissolved in water along with some fraction of the additional sodium hydroxide that is needed for the reactant mixture. Separately, sodium silicate is mixed with the remainder of the sodium hydroxide. The two solutions are combined using the required mixing order and agitation level, resulting in the initial zeolite gel. In some cases this initial gel is aged at an intermediate temperature for a 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).

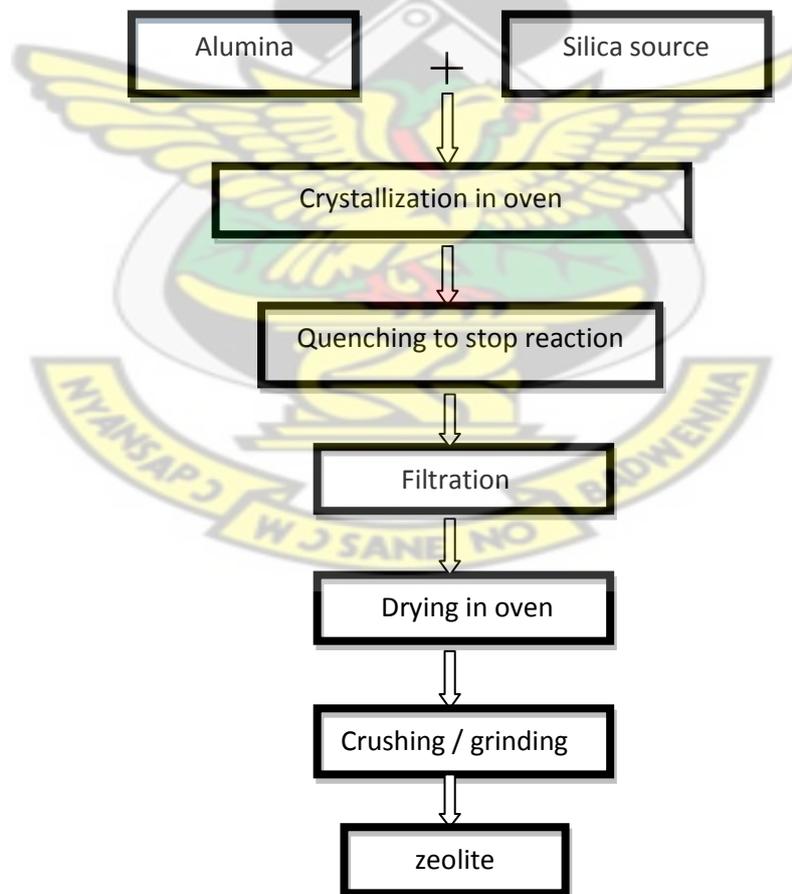


Figure 2.4: Flow Chart showing Zeolite Synthesis

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. Nadir (2006) also emphasized that the important point in the synthesis process is the preparation of the synthesis mixture. A variation occurred in process parameters changes the product properties, moreover the product. Therefore, the composition and the homogeneity of the synthesis mixture, chemical nature of the reactants, crystallization temperature and the period, the template molecule, and pH of the system are the main factors affecting the zeolite synthesis.

2.7 CHARACTERISATION

This is used to identify the crystalline product by comparing its properties to those of known standards. X-Ray diffraction, Scanning electron microscopy, thermogravimetric analysis, elemental analysis and the crystal size of the synthesized zeolite are methods used to describe a particular type of zeolite.

2.7.1. X-Ray Diffractometer (XRD)

Diffraction is a central technique for characterizing the structure of a zeolite. X-ray diffraction is commonly used to identify the presence and quantitatively determine the amount of crystalline zeolite present (Kulprathipanja, 2010). It provides the unit cell parameters of the product. X-ray diffractometer is based on the elastic scattering theory. The diffraction patterns differ for all types of zeolites. The purpose of XRD patterns is to be able to determine the unit cell parameters and thus its unit cell volume (Vedrine, 1992). Powder X-ray diffraction measurements use $\text{CuK}\alpha$ radiations to determine zeolite crystallinity. Phase identification can also be performed by XRD.

During this activity, the zeolite sample is subjected to an x-ray beam ray. The intensity of the emergent rays is recorded as a function of the deflection angle.

Using Bragg's law, i.e.

$$n\lambda = 2d \sin\theta$$

where n is an integer,

λ is the wavelength

d is the lattice spacing and

θ is the deflection angle

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For crystals with cubic symmetry e.g. FAU, the size of the unit cell a_0 can be determined from the angular positions of the reflection.

$$a_0 = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$$

hkl is an orientation indicated by the Miller's indices.

2.7.2 FTIR Spectroscopy

The method used by FTIR is similar to X-ray structural analysis (Breck, 1974). Corresponding infra red 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 tetrahedra.

The spectrometer has two mirrors, a fixed mirror and a moving mirror, a detector and a beam splitter. A radiation from the IR source is directed to the beam splitter which splits the beam into two parts, one to the fixed mirror and the other to the moving. FTIR is operated based on the principle of diffuse reflectance. An incident beams emits a spectra of both absorbance and

reflectance features. Radiations that pass through the sample are recorded by a detector. Calibrations on the detector enable radiations to be read in the form of energy signals.

2.7.3 Energy Dispersive X-ray Spectroscopy (EDX)

EDX is used in conjunction with a scanning electron microscope (SEM). 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. The electric beam excites the atoms in the sample that subsequently produce x-rays to discharge the excess energy. 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. EDX spectrum can be collected from a specific point or particle on the sample giving an analysis of a few cubic microns of the material (Healy, 2010).

2.7.4 Elemental and Thermo gravimetric Analysis

Thermal analysis is done to determine water content whilst the elemental analysis provides the amount of the cations to oxide present in a ratio. Elemental analysis can either be qualitative or quantitative.

Thermal or thermo gravimetric analysis measures the physical or chemical changes in a material. The temperature at which zeolites are dried has been suggested to have an effect on its structural characteristics (Trif *et al.*, 1993). This is usually studied through thermal analysis. Thermal analysis is usually a group of techniques in which the physical property of a substance is and/ or its reaction products are measured as a function of temperature when the substance is subjected to a controlled temperature variation (Skoog *et al.*, 1998). Data correlated gives information about properties such as thermal stability, moisture content or solvent and decomposition temperature and rate (MEEI, 2009).

2.7.5 Scanning Electron Microscopy (SEM)

Electron microscopy has played a major role in the understanding of zeolitic materials. SEM is used to determine the morphology of the zeolites. The size of zeolites studied with this apparatus is between 20nm and 20 μ m. Information gathered from the SEM picture of zeolites includes:

1. crystal form i.e. type of zeolite and crystal form and size.
2. external surface such as relative roughness.
3. purity of phase i.e. presence of other zeolite types.

The crystal size is an estimate of the crystallite size and or the aggregate particle size (Robson, 2001).

SEM consists principally of an electron gun, electron lenses, scan coils and detectors. 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).

2.8 STRUCTURES IN THIS STUDY

Several types of zeolites exist each with a unique structure as well as composition controlling properties. For the purpose of this study Zeolites X and Y will be addressed.

2.8.1 Zeolite X

Zeolite X is a member of the Faujasite family very similar to zeolite Y. It has very large microporous spaces allowing organic molecules to diffuse in and out. It possesses a three

dimensional channel structure. Pore diameter is 7.4 Å with equidimensional channels running perpendicular to each other. The sodalite cages are arranged similarly to carbon atoms in diamonds. They are joined to one another via double 6-rings, producing the supercage with four tetrahedrally oriented 12-ring pore openings. It also has an ABCABC stacking order. The Si/Al ratio of zeolite X is generally between 2.2 and 3.0 (Xu *et al.*, 2007). Zeolite X has a wide range of industrial application primarily due to the excellent stability of the crystal structure and a large pore volume and surface area (Kwaky-Awuah, 2008).

Primary cation (exchangeable cations) sites are site I in (or near) the centre of the D6R, site I' inside the sodalite on the face of the six-ring of the D6R, site II' in the sodalite cage on the six-ring connecting to the supercage, site II in the supercage on the face of the six-ring and site III in the supercage near the four rings (van Bekkum *et al.*, 2001; Kulprathipanja, 2010; Xu *et al.*, 2007). The important cation sites for interaction with adsorbed molecules are site II and III since the other sites are buried in cages accessible only through six rings. The FAU unit cell contains 16 D4R, eight sodalites and eight supercages. Sites I, I', II', II and III can accommodate 16, 32, 32, 32 and 96 respectively (Kulprathipanja, 2010).

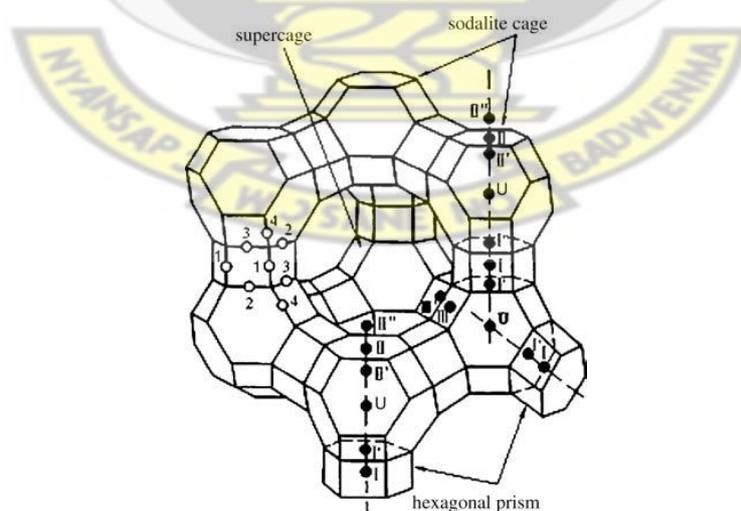


Figure 2.5: Structure of zeolite X showing exchangeable cation sites (FAU framework, Copyright 1996, Elsevier).

2.8.2 Zeolite Y

Zeolite Y exhibits the FAU (Faujasite) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y and z planes similar to each other in the x, y and z planes similar to LTA and is made of secondary building units 4, 6 and 6-6.

The pore diameter is large at 7.4\AA , aperture defined by a twelve (12) member oxygen ring and leads into a larger cavity of diameter 12\AA . The cavity is surrounded by 10 sodalite cages (truncated octahedral) connected on their hexagonal faces. Its unit cell is cubic ($a=24.7\text{\AA}$) with face diagonal-3m symmetry. Zeolite Y has a void volume fraction of 0.48 and Si/Al ratio of 2.43. It decomposes at 793°C (Herreros, 2001; Meier *et al.*, 2000; Subhash 1990).

Applications include its use as a cracking catalyst. It is used in acidic form in petroleum refinery catalytic cracking units to increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffin into gasoline grade naphtha (Subhash, 1990; Ribeiro *et al.*, 1984) as cited in Kwakye- Awuah (2008).

Zeolite Y is known to supersede X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio.

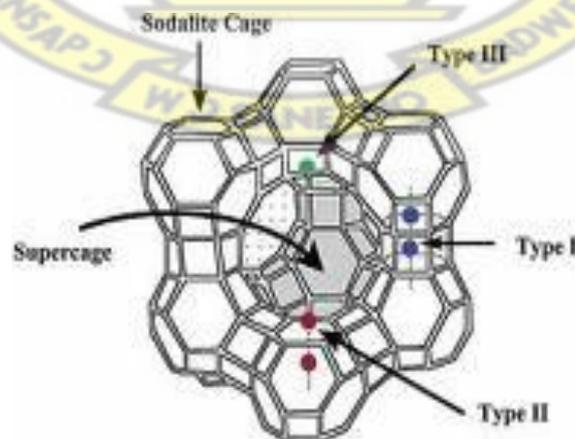


Figure 2.6: Framework structure of zeolite Y showing its exchangeable sites and cages

(www.iza.org/zeolites.html)

2.9 SEAWATER

Seawater is water from a sea or ocean. Its availability is independent of weather or climate changes and resilient to natural disasters. On average, seawater in the world's oceans has a salinity of about 3.5% (35 g/L). This means that every kilogram (roughly one litre by volume) of seawater has approximately 35 grams of dissolved salts mostly Sodium chloride. The average density of seawater at the ocean surface is 1.025 g/ml. Seawater is denser than both fresh water and pure water because the dissolved salts add mass without contributing significantly to the volume. The freezing point of sea water decreases as salt concentration increases. At a typical salinity it freezes at about $-2\text{ }^{\circ}\text{C}$ ($28.4\text{ }^{\circ}\text{F}$). Seawater is known to have the following ions: H_2O , Cl^- , Na^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , K^+ , Br , Sr and traces of others. The dissolved salts add to the mass without contributing significantly to its volume.

Although the vast majority of seawater has a negative salinity of between 3.1% and 3.8%, seawater is not uniformly saline throughout the world. Where mixing occurs with fresh water runoff from river mouths or near melting glaciers, seawater can be substantially less saline. The most saline open sea is the Red Sea, where high rates of evaporation, low precipitation and river inflow, and confined circulation result in unusually salty water.

The density of surface seawater ranges from about $1020\text{-}1029\text{ kg/m}^3$, depending on the temperature and salinity. Deep in the ocean, under high pressure, seawater can reach a density of 1050 kg/m^3 or higher. Seawater pH is limited to the range 7.5 to 8.4. The speed of sound in seawater is about 1,500 metres/second, and varies with water temperature, salinity, and pressure.

The thermal conductivity of seawater is 0.6 W/mK at 25 °C and a salinity of 35 g/kg. The thermal conductivity decreases with increasing salinity and increases with increasing temperature (www.wikipedia.com).

Table 2.2 Seawater composition (Castro and Huber, 2003)

Element	Concentration in seawater (ppt)	Percentage composition
Chloride	19.345	55.03
Sodium	10.752	30.59
Sulphate	2.701	7.68
Magnesium	1.295	3.68
Calcium	0.416	1.18
Potassium	0.396	1.11
Bicarbonate	0.145	0.41
Bromide	0.066	0.19
Borate	0.027	0.08
Strontium	0.013	0.04
Fluoride	0.001	0.003
Other	< 0.001	< 0.001

2.10 WATER DEMINERALISATION

Due to the tiny nature of the pores in zeolites, particles that are larger than the water molecules are not allowed to pass through. Salts and other materials are left behind thereby ensuring the water has a quality. The quality of water produced from the removal of ions and other pollutants has been shown to be successful.

Water demineralisation processes differ not only in the driving force but also in the water quality obtained. The energy consumption of the different methods also depends on the quality of the water produced and the feed water composition. Water deionization generally intends to produce drinking water whose composition is given below (PCA, 2005):

Table 2.3 WHO standards for drinking water (2000).

Element	Desired maximum concentration (mg/l)	Permitted maximum concentration (mg/l)	Isotonic solution in mg/l
TDS	500	1500	9000
Magnesium	30	150	-
Calcium	75	200	-
Chloride	20	60	3550 – 3800
Sulphate	200	400	-
Sodium	-	-	3050 – 3400
Potassium	-	-	150 – 210
Total content in m/mol	App. 10	App. 30	App. 150

CHAPTER THREE

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ION EXCHANGE PHENOMENA IN ZEOLITES

3.1 ION EXCHANGE PROCESS

Generally, the ion exchange process refers to the removal of ions from an aqueous solution and replaced by another ionic species. The removal of each ion in solution is substituted by an equivalent amount of the exchanger of the same sign. At equilibrium, electroneutrality is maintained in both liquid and solid (zeolite) phases (Kulprathipanja, 2010). Ion exchange occurs without any physical alteration to the ion exchange material (Alchin, 2005). It is controlled by mass transport within the pore network if it occurs in porous material. Exchangers with negatively charged groups are cationic and attract positive ions. Anionic exchangers on the other hand are positively charged and attract negative ions.

The mass action law treats the ion exchange process as chemical reactions. The cations associated with the exchange sites and those in solution are considered to be discrete entities and their concentrations can be measured separately (Chen, 1960).

One important characteristic of zeolites is its cation exchange capability. Using zeolites is advantageous especially as a low cost exchangers and the method can be cost effective.

According to Breck (1974) as stated by Top (2001), the exchange behaviour of cations in zeolites depends on:

- the nature of the cation species, the cation size, both hydrated and anhydrous and cation charge
- the temperature
- the concentration of the cation species in solution
- the anion species associated with the cation in solution
- the solvent
- the structural characteristics of the particular zeolite.

The technique effectively inserts protons and ions into the zeolites under ambient conditions and with minimal impact on the zeolites structural impact (Hadlington, 2005). Zeolites are insoluble in water but are electrically charged holding ions of opposite charge at the exchange sites. Ionic sieve properties can also occur according to Amphlett (1964) in zeolites either because of channel diameters is too small to permit the passage of certain cations or because, when the cations concerned are above a certain size, the cavity dimensions are inadequate to accommodate the number of available exchange sites.

3.2 REACTIONS AND EQUATIONS

The understanding and development of the ion exchange phenomena has been subjected to several reviews and equations with varying models.

The ion exchange process can be represented by



Where Z stands for a zeolite or a type of exchanger

A^+ and B^+ are univalent cations (mono positive ions), C^{2+} is a divalent cation.

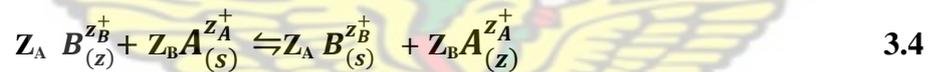
Reversible reactions are equations describing the relative concentrations (amount of material per unit volume) of the various species in equilibrium, i.e. the rate of forward reaction equal the rate of backward reaction. For the above equation

$$K_1 = \frac{[B^+][A^+Z^-]}{[A^+][B^+Z^-]} \quad K_2 = \frac{[B^+]^2 [C^{2+}Z^-]}{[C^{2+}][B^+Z^-]^2} \quad 3.3$$

K_1 and K_2 show the relationship of the materials under equilibrium.

3.2.1 Ion Exchange Equilibrium

An ion exchange reaction will proceed until equilibrium is reached. Equilibrium is a measure of the selectivity of the zeolite for one ion over the other (Top, 2001). The reversibility of the ion exchange greatly affects the behavior of ion exchange system. Typical reaction



where Z_A, Z_B are the charges of the cations A and B and the symbols 'z' and 's' refer to the zeolite and solution phases respectively. The mass action quotient or selectivity coefficient for the reaction is

$$K_m = \frac{A_{(z)}^{Z_B} B_{(s)}^{Z_A}}{B_{(s)}^{Z_A} A_{(z)}^{Z_B}} \quad 3.5$$

The equilibrium constant for the reaction in 4.4 can be written in terms of concentrations and the activity coefficient (γ_i) of the ions.

$$K_{eq} = \frac{A_{(z)}^{Z_B} B_{(s)}^{Z_A} \gamma_B^{Z_A}}{B_{(s)}^{Z_A} A_{(z)}^{Z_B} \gamma_A^{Z_B}} \quad 3.6$$

where γ_A and γ_B are the ion activity of the cations A and B in solution.

$$\text{However, } \frac{\gamma_B^{z_A}}{\gamma_A^{z_B}} = \Gamma \quad 3.7$$

$$K_{eq} = K_m \Gamma \quad 3.8$$

Γ is the activity ratio.

The main relevant properties of the ion exchanger are considered to be the equilibrium behavior and the diffusion rate through the material, expressed by solid diffusion coefficients.

The rate controlling step in ion exchange is usually either diffusion of ions within the exchanger itself or within a thin film of solution surrounding the latter depending upon the chemical and physical parameters of the system. Ion exchange has to do with the formation and breaking of bonds between ions in solution and exchange sites in a zeolite. The reaction equilibrium of the ion exchange process depends on the contact time, operating temperature and ionic concentration.

Barrer (1949) has shown that for spherical particles, the extent of exchange is governed by

$$\text{the expression: } \frac{Q_t}{Q_\infty} = \frac{2A}{V} \sqrt{\frac{D^i t}{\pi}} = \frac{6}{r} \sqrt{\frac{D^i t}{\pi}} \quad 3.9$$

Where Q_t and Q_∞ are the amounts of exchange at time t and equilibrium respectively. A , V and r are the surface area, volume and radius of the exchanger particles. The apparent diffusion coefficient varies with temperature with the Arrhenius equation

$$D^i = D_0^i \exp(-E/RT) \quad 3.10$$

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

$$\text{CEC} = \frac{\text{number of equivalents of exchanging cation}}{\text{total number of equivalents of cations in the zeolite}} = \frac{N_c}{A_m} \quad 3.11$$

The total ion exchange capacity of a zeolite has been observed to be a function of its SiO₂/Al₂O₃ mole ratio (Kulprathipanja, 2010).

3.2.2 Selectivity

Ion exchange selectivity series have been published in a number of reports and seminal works by Breck, Barrer and Sherry. Ion exchangers do not prefer all ions equally (Clifford *et al.*, 2003 as cited in Edzwald, 2011). Preference for some ions over the others is due to differing thermodynamic affinities. It is sometimes also due to the nature of the ions.

Consider equation 4.1 the selectivity coefficient for the ions A and B can also be written as

$$K_{BA} = \frac{q_B C_A}{q_A C_B} \quad 3.12$$

q_i is the molar concentration for the solid phase

C_i is the molar concentration of the liquid phase

In a homovalent exchange, the separation factor α_{ij} and the selectivity coefficient K_{ij} are equal i.e.

$$K_{BA} = \alpha_{BA} = \frac{q_B C_A}{q_A C_B} \quad 3.13$$

For exchanging cations of unequal charge, the separation factor is not the same as the selectivity coefficient. Considering equation 3.2

$$K_{BC} = \frac{q_B C_C^2}{q_C^2 C_B} \quad 3.14$$

$$\alpha_{BC} = K_{BC} \frac{q y_B}{C x_B} \quad 3.15$$

x and y are equivalent fractions of B and C

In general, higher selectivity is observed for higher charged cations. For same valence cations, ion exchange selectivity depends on the hydrated ionic radii (Kulprathipanja, 2010).

Chabazite has affinity for $K^+ \gg Na^+$ at all compositions, Basic Sodalite: $Ag^+ \gg Na^+ > Li^+ > K^+$. In Faujasite, the extent of exchange among the alkaline earth decrease in the order $Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++}$, suggesting that the hydrated ions are involved (Amphlett, 1964). Zeolite synthesis is often carried out with the type of ion exclusion in mind. It is known that if the ion exchanger shows selectivity, the distribution coefficients depend on the liquid equilibrium concentration of the incoming cation (Inglezakis *et al.*, 2004).

Selectivity of ion exchangers is an equilibrium parameter and may have several physiochemical causes. The ion exchanger as a rule prefers the cation with a higher valency, an effect that is purely electrostatic and in many cases, the smaller counter ion. On the other hand, very large complexes may be mechanically excluded by sieve action being the result of a narrow pore to accommodate incoming ions (Inglezakis *et al.*, 2004).

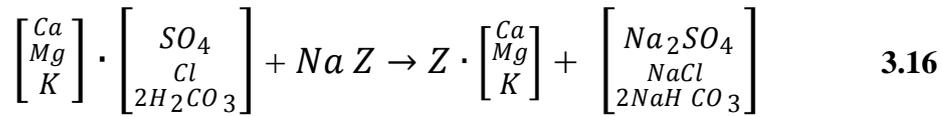
Zeolite ion exchange selectivity decreasing with ionic radii as sited in Kulprathipanja (2010)



3.3 WATER SOFTENING

The presence of magnesium ions (Mg^{2+}) and calcium ions (Ca^{2+}) in water renders the water 'hard' and difficult to use. The concentration determines the level of hardness. Seawater has large amounts of dissolved salts and hardness above 6500 milligram per litre. In the act of water softening or purification, zeolites containing sodium ions (Na^+) are applied to water to bind calcium and magnesium ions whilst releasing sodium ions thereby making the water

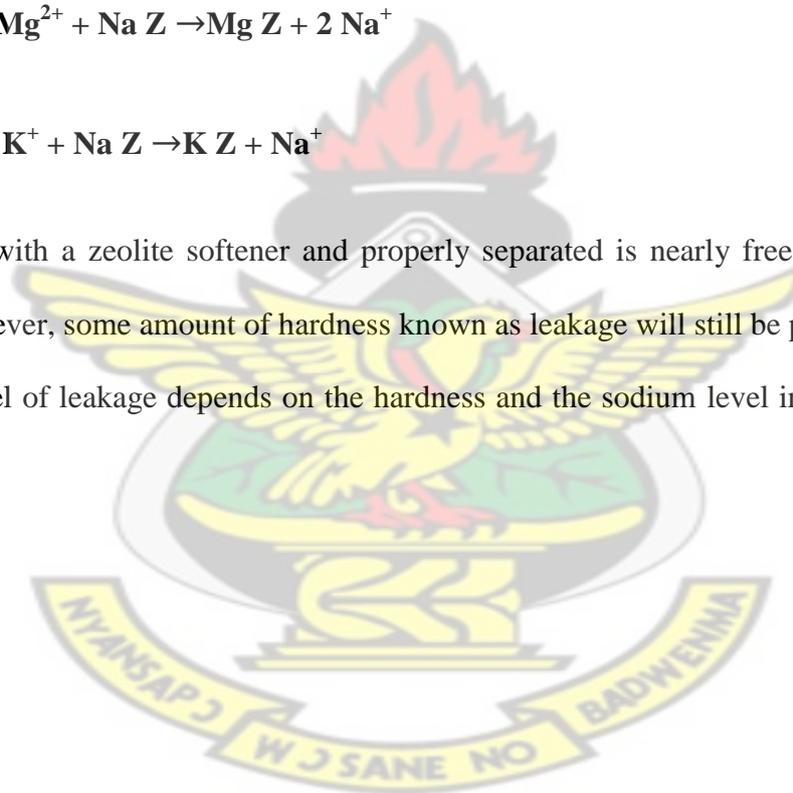
softer. Na^+ cations are loosely bound to the zeolite surfaces and can easily be exchanged as in the expression below:



The cation exchange mechanism between seawater and zeolites can further be presented as



Water treated with a zeolite softener and properly separated is nearly free from detectable hardness. However, some amount of hardness known as leakage will still be present in treated water. The level of leakage depends on the hardness and the sodium level in the supernatant (GE, 2010).



CHAPTER FOUR

METHODOLOGY AND EXPERIMENTAL STUDIES

4.1 INTRODUCTION

In this chapter, the methodology used in the synthesis of zeolites X and Y is presented. The powder form of each zeolite type after being crushed was packaged and sent to the UK for analysis. Investigation into their efficiency in desalting seawater was tested using ion equilibrium studies. Concentrations of ions before and after zeolite addition were carried out at the Council for Scientific and Industrial Research (CSIR), Kwadaso Kumasi. All other procedures were carried out in the Civil Engineering laboratory, KNUST.

Experimental work has been grouped into three parts

- Zeolite synthesis
- Structure characterization and analysis
- Kinetic Studies of desalination

4.2 REAGENTS AND APPARATUS

The following instruments were used during the research. FTIR spectrophotometer (Mattson Instrument, UK), X-ray diffractometer (Philips PW 1710), Thermal analyzer (PerkinElmer), Elemental analyzer (model 1108), SEM (LEO 435 VI), digital pH meter (pH 323), digital electrical conductivity probe, electronic balance, electrical oven, vacuum pump, thermometer and a rotary shaker (L.E.D Orbit Shaker) .

All reagents were obtained from AnalaR NORMAPUR, UK. The following reagents were used:

1. sodium hydroxide (NaOH)
2. sodium silicate (NaSiO₂)
3. alumina (Al₂O₃)
4. distilled water

4.3 ZEOLITES SYNTHESIS

4.3.1 Synthesis of Zeolite X

The synthesis of zeolite X was undertaken using the method as described by Lechert (1991) and Kacirek (1992) as cited by Robson (2001).

The reaction mixture had 100 g of sodium hydroxide (NaOH) was added to 100 g of water (H₂O) and then added to 97.5 g of alumina (Al₂O₃). The reaction was allowed to cool. 202.5 g of H₂O was added to the mixture to obtain suspension (solution 1). 219.7 g of sodium silicate (NaSiO₂) was weighed and added to 100 g of solution 1 to obtain the reaction gel. The resulting gel was stirred for 30 minutes to obtain a homogenous mixture in the form of slurry as in Figure 4.1a. The batch composition of the gel was:



This was then placed in Teflon jars tightly covered and incubated for 7 hours at a constant temperature of 95 °C. The zeolite crystals were separated from the clear solution using a vacuum pump, washed with water to lower pH whilst still filtering and the dried at 77 °C for 8 hours in an oven. The crystals were then ground in a mortar to obtain a smooth and evenly distributed powder. The zeolite sample obtained was characterized by X-ray diffraction. Its thermal stability as well as other properties was also determined.



Figure 4.1: (a) A picture of slurry obtained from the reaction mixture (b) image of mortar used in grinding and synthesized zeolite X

4.3.2 Synthesis of Zeolite Y

The method of synthesis of zeolite Y employed was that of Ginter *et al.*, (1992). It was prepared with a molar composition of:



A suspension was produced from 19.95 g of water, 4.07g sodium hydroxide and 2.09 g of alumina and stirred. 22.72 g sodium silicate solution was added to the previously prepared solution and stirred for 10 minutes to obtain the seed gel. The seed gel was allowed to age for 24 hours at room temperature. The feedstock gel was subsequently prepared by weighing 130.97 g of water, 0.14 g sodium hydroxide, and 13.09 g alumina and added to 142.43 g of sodium silicate solution and stirred. The seed gel was slowly added to the feedstock gel whilst stirring. A 30 minutes stirring yielded a smooth but light gel with an average pH of 12.35. The mixture was covered and allowed to crystallize for 7 hours in an oven at 100 °C. The resultant solution was allowed to cool. The precipitate was separated from the supernatant by filtration. The filtrate was washed with distilled water until pH was 9.8 and dried at 110 °C for 12 hours.



Figure 4.2: Electrical oven used in drying of the zeolite crystals

4.4 STRUCTURE CHARACTERIZATION AND ANALYSIS

This was used to identify the crystalline product by comparing its properties to those of known standards. In this study, XRD, SEM, thermogravimetric analysis, elemental analysis and the crystal size of the synthesized zeolite were sought. In order to know the crystal structure, crystallinity and XRD, samples were sent to the Wolverhampton University for these analyses.

Phase identification was performed by XRD as well as phase purity determined. During this activity, the zeolite sample is subjected to an x-ray beam ray. The intensity of the emergent rays is recorded as a function of the deflection angle. The distance between the crystal cells was determined. The XRD patterns were identified by comparing them with reference diffractograms.

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. Measurements were done using 100 scans at 4 cm^{-1} resolution, units of $\log(1/R)$ (absorbance), over the mid-IR region of $1200\text{-}400\text{ cm}^{-1}$. 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 three different samples.

For the EDX analysis, the sample was bombarded by the SEM's beam. The relative abundance of the emitted x-rays versus their energy was measured by the EDX detector. The energy as determined from the voltage measurement for each incident ray was sent to a computer display and further data evaluation.

Samples were then rinsed with distilled water and transported to an inductively couple plasma which is a high temperature zone. The samples were heated to different states to produce characteristic optical emissions. These emissions were separated based on their respective wavelengths and their intensities were measured. The intensities are known to be proportional to the concentration of analytes in the aqueous sample to obtain the elemental composition.

For thermogravimetric analysis, the sample was subjected to heat for a specific time. The thermally activated sample events were recorded and expressed as weight loss or weight change for the given time.

SEM was used to determine the morphology of the zeolites. The size of zeolites studied with this apparatus was between 20nm and 20 μ m. A beam of incident electrons in an electron column was generated from the SEM. An SEM image was created as the electron beam scanned the surface of the zeolite sample creating a pattern on the detector.

4.5 KINETIC STUDIES

4.5.1 Seawater Sampling

Seawater samples were obtained from different sources including Dansoman, Cape Coast, Bortianor and Takoradi in 5 litre gallons. The samples were transported to the laboratory in a

bus. The pH of the water samples was taken. At regular intervals for 3 weeks, the pH was measured. A drop in the pH was observed in seawater from Cape Coast and Takoradi after some time. Seawater from Bortianor became malodorous. However, seawater from Dansoman recorded a fairly stable pH after 3 weeks. This was probably due to the presence of beach sand deposited at the bottom of the gallon. Its scientific significance was not taken into account.

The study was carried out using seawater obtained from Dansoman, Accra. Initial pH, hardness and conductivity of the seawater sample were recorded. Analysis was done to ascertain the levels of concentration of the constituent elements. The pH of the seawater was between 7.68-7.70.

4.5.2 Batch Technique

The batch technique was utilised to monitor the effect of contact time on ion exchange. An equal volume of 100 ml of seawater was measured into six flasks. The ratio of zeolite to seawater was varied between 0.5: 100 and 1: 100. With varying time labels, the flasks were placed on a rotary shaker at an average speed of 200 rpm at room temperature.



Figure 4.3: Rotary shaker with beakers containing zeolite and seawater.

Time intervals noted included 15, 30, 60, 90, 120 minutes respectively. The zeolite was then separated from the supernatant at the required time. Each sample was filtered using Whatman Filter No.1 paper. The pH of the supernatant at each of these times was taken. Its corresponding conductivity was also measured. The concentrations of sodium, potassium, calcium and magnesium in the seawater were calculated and also determined using Atomic Absorption Spectrophotometer. All tests were repeated and only mean values were presented. The procedure was repeated using zeolite Y. The quality of the resulting filtrate was compared to standard drinking water and presented. The chloride ion concentration was reduced by the use of silver nitrate.

The percentage removal efficiency of each zeolite was determined. Levels of sodium and potassium were determined using flame photometry. Calcium and magnesium levels were sought by its absorbance.

In the first part, the mass of zeolite was varied between 0.5 g and 1 g. Zeolite mass to solution ratio was adjusted to obtain significant differences in initial and final concentrations of cations in solution. The solid ratio of 0.5: 100 was however maintained.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 INTRODUCTION

In this chapter, results and analysis based on the experimental procedure stated in the previous chapter are presented.

Synthesis and characterization of zeolite X and Y were carried out. It was observed that zeolites X and Y both show similar crystallization patterns. All analyses of elements presented here were made by atomic absorption spectrometry.

5.2 SYNTHESIS OF ZEOLITE X

Zeolite X synthesis was unsuccessful the first time. Subsequent synthesis was however successful in the production of Low silica type X zeolite. Characterisation of this zeolite was done using X-ray diffraction pattern which showed high peaks indicating full crystallization. The diffraction pattern of the synthesized zeolite is presented in the appendix section.

Low sodium zeolite X was then synthesized as stated in Section 4.3. A composition of 18 Na₂O: Al₂O₃: 4SiO₂: 325H₂O was used in the preparation. The X-ray pattern showed clearly the structure of the zeolite and gave a confirmation to the fact that the synthesis was successful.

SEM obtained was highly crystalline and very similar to those of known literature. The average crystal size of the zeolite from the SEM is about 0.5 μm.

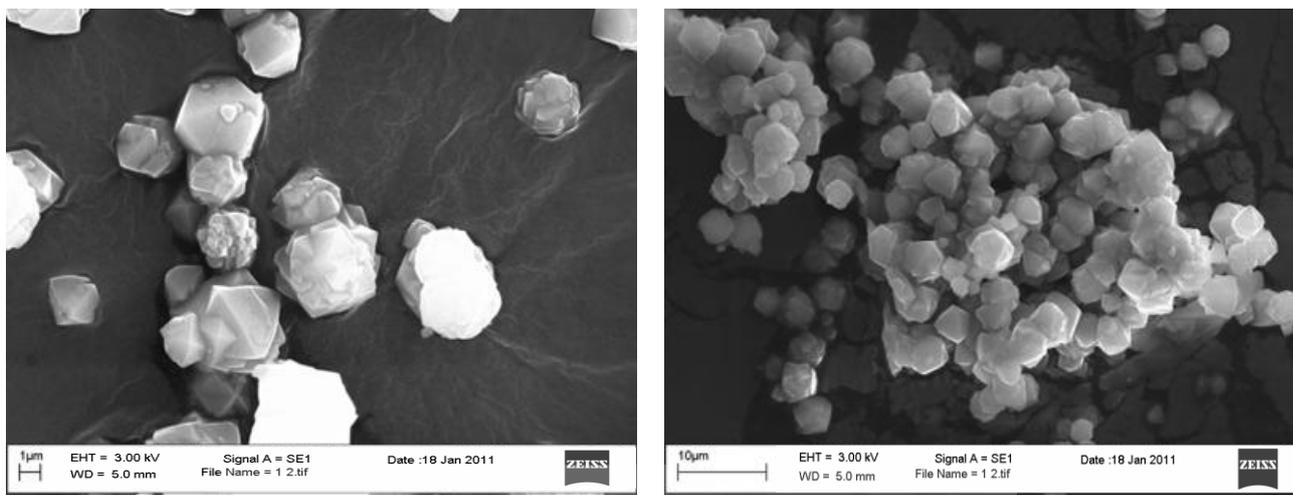


Figure 5.1: SEM micrographs showing the size of zeolite X crystals.

XRD patterns of the crystal formed are presented in the appendix. The pattern corresponds to that of Treacy and Higgins (2001). The EDX spectrum produced is presented in figure below:

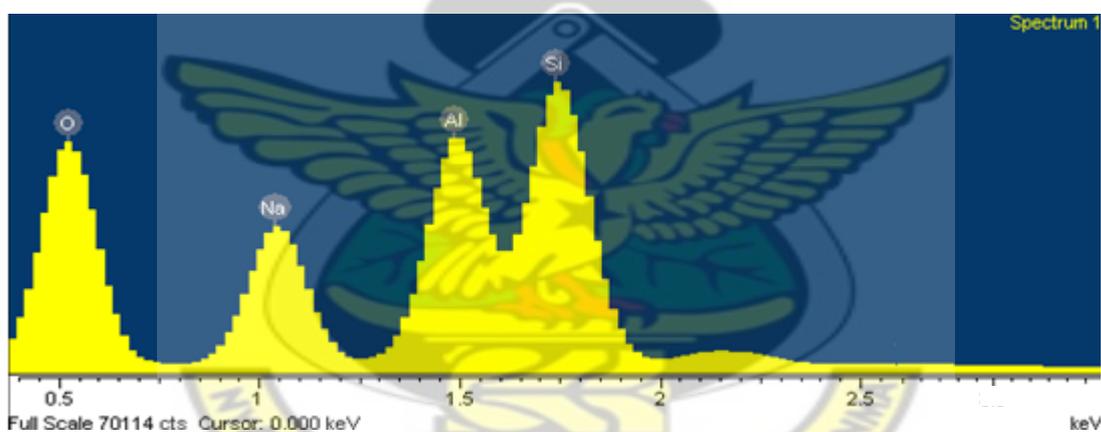


Figure 5.2: EDX spectrum showing the elemental composition of zeolite X

Elemental analysis of zeolite showed that it contained (%wt) Si = 22.6, Al = 15.2, Na = 5.3 and O = 56.9. Si to Al ratio was 1.45.

It was clear from the thermogravimetric analysis plot of zeolite X that up to 100 °C, only 58% weight loss was observed probably due to the removal of water on the surface (Figure 5.3). Further weight loss of approximately 7% occurred between 100 °C and 300 °C. An S-shaped growth curve describes an induction period followed by a rapid growth. Morphological

changes, interpreted as a successive ordering of gel as crystallization proceeds until crystal growth is permanent in the solid phase.

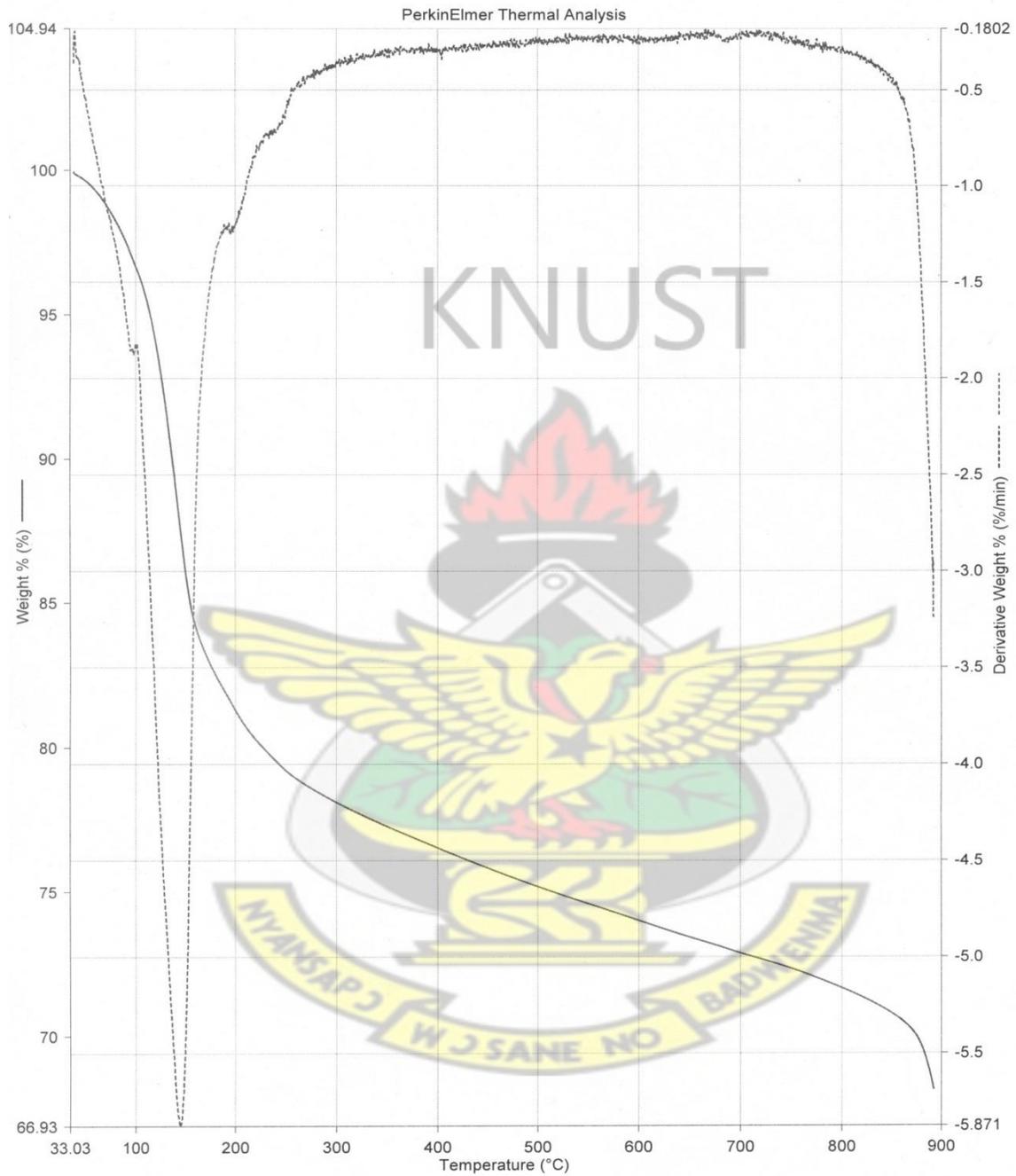


Figure 5.3: Thermogravimetric analysis plot for zeolite X for temperature 33 °C – 900 °C

Structural characterisation of the zeolite was done by FTIR to confirm the formation of the zeolite. The FTIR spectrum exhibits the characteristic peak at 975 and 1350 cm^{-1} .

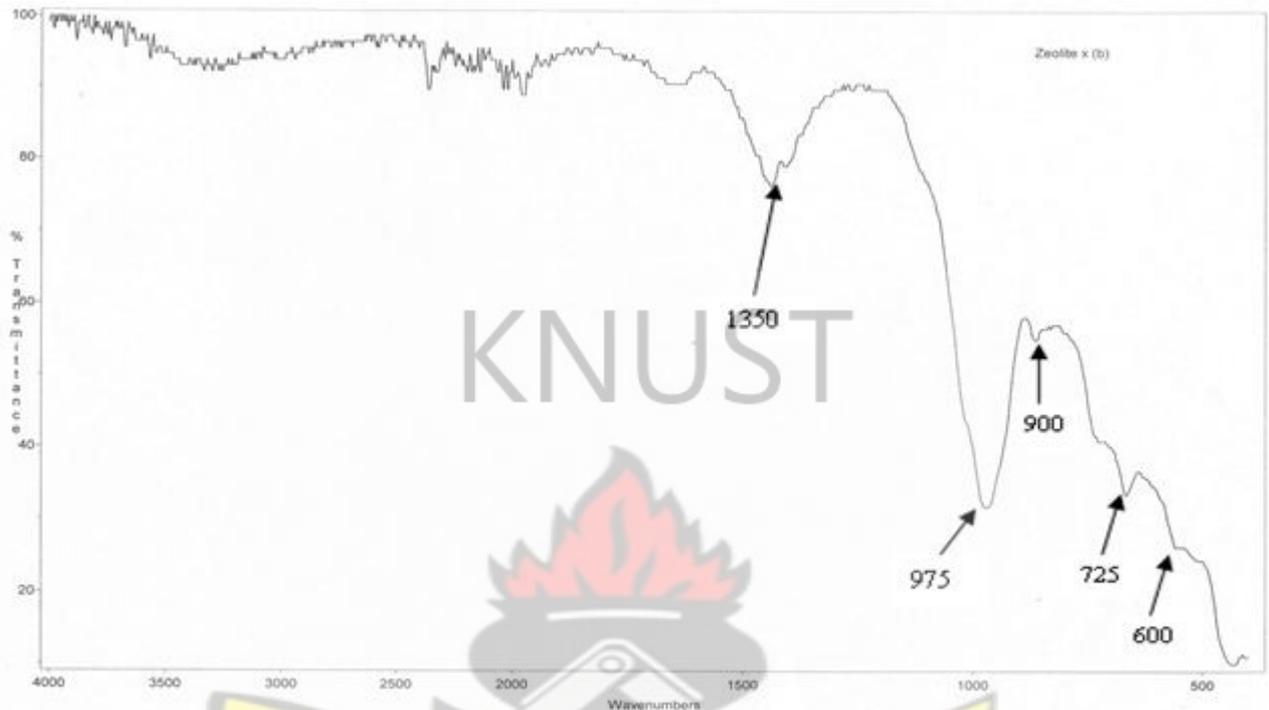


Figure 5.4: FTIR spectrum of zeolite X

Vibrational spectrum of zeolite X showed strong IR absorption in the spectral region below 1200 cm^{-1} . Strong peaks were observed at 480 cm^{-1} which shifted to 600 cm^{-1} . Other peaks were observed in the region 975 and 1600 cm^{-1} . In general the lattice modes can be divided into structure sensitive and structure intensive vibrations.

As presented in Kwakye-Awuah (2008), the general infrared assignments as proposed by Flanigen *et al.*, (1978) and Mozgawa (2000) is shown below:

Table 5.1 General infrared assignments (Flanigen *et al.*, (1978); Mozgawa (2000))

Internal Vibrations	
Asymmetric Stretch	1250 - 950
Symmetric Stretch	720 - 650
T- O Bend	500 - 420
External T –O Linkages	
Double ring	650 - 500
Pore opening	420 - 300
Symmetric Stretch	750 - 820
Asymmetric Stretch	1150 - 1050

5.3 SYNTHESIS OF ZEOLITE Y

First two synthesis of this zeolite was not successful. Powder XRD was used to determine the sample crystallinity. The formation of zeolite Y was confirmed by comparing its XRD pattern to documented diffractograms indicating an FAU structure. According to Treacy and Higgins within a range of $2\theta = 2- 50^\circ$, the first peak for zeolite Y will appear within $6-10^\circ$. The first peak was observed at $2\theta = 7^\circ$ and at 12° . Small zigzag peaks refer to the presence of amorphous material. Strong peaks represent full crystallization. There were not as many peaks as there is in the case of the reference Y. Synthesized zeolite Y gave similar SEM morphology (Figure 5.5) and FTIR spectrum pattern (Figure 5.6) to that of the referenced literature.

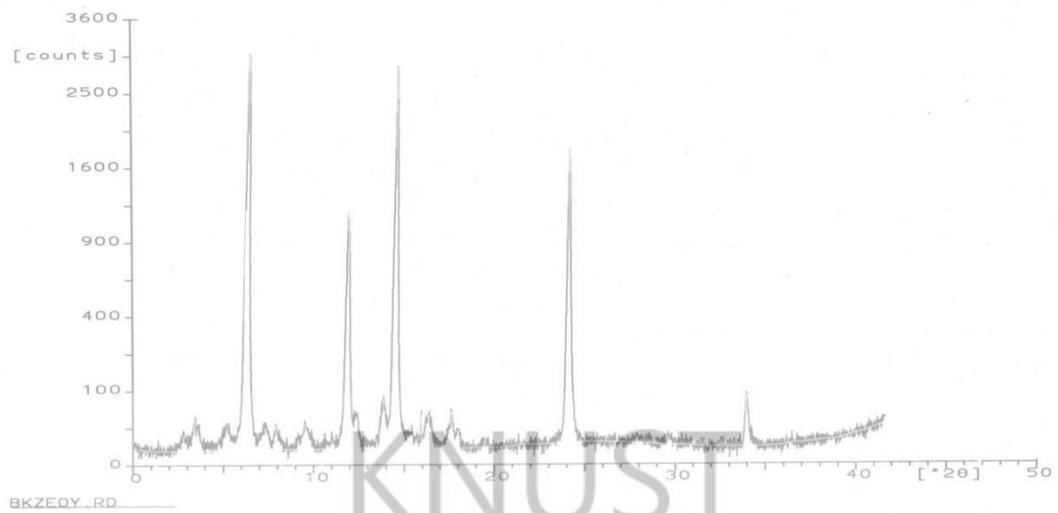


Figure 5.5: X-ray diffraction pattern of zeolite Y showing peaks for $2\theta = 0^\circ$ and 50° .

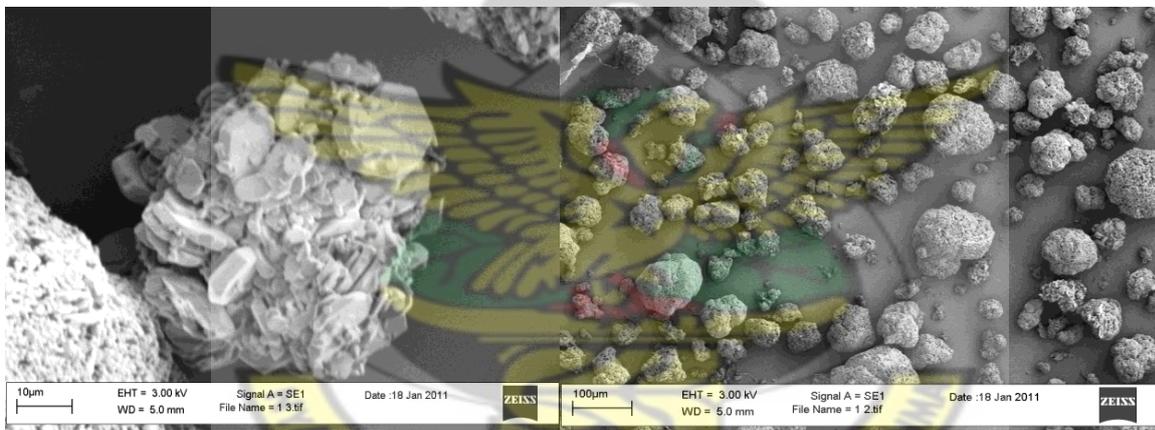


Figure 5.7: SEM of zeolite Y showing the size and nature of crystals

EDX analysis showed the peaks corresponding to the relative amounts of the elements present in zeolite Y is presented in Figure 5.8. Breakdown of elemental composition is also given as in Table 5.2.

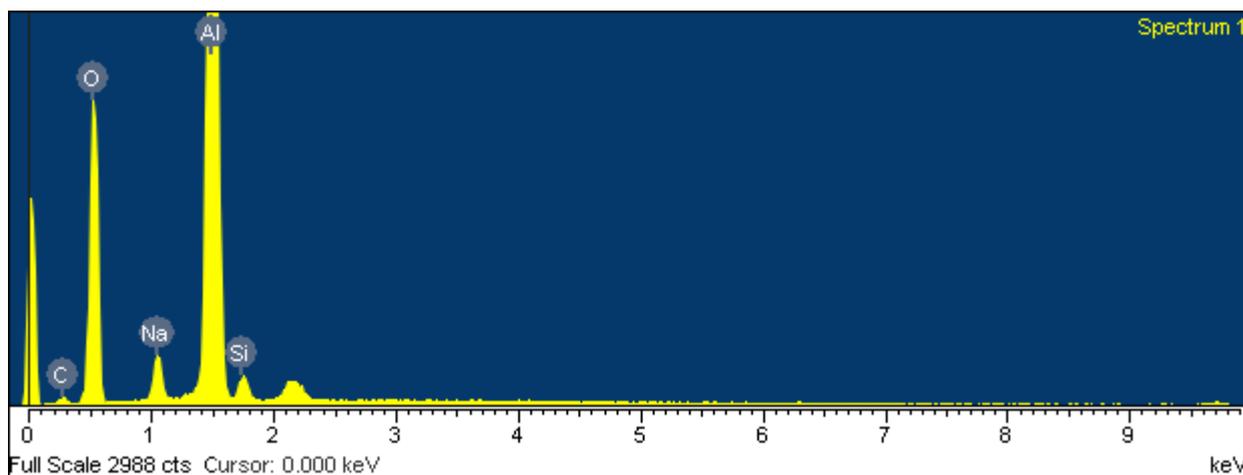


Figure 5.8: EDX spectrum of zeolite Y

Table 5.2 Elemental composition of zeolite Y

Element	Weight%	Atomic%
C K	8.46	13.18
O K	48.4	56.59
Na K	3.02	2.45
Al K	38.53	26.71
Si K	1.6	1.07
Total	100	100

The FTIR image of zeolite Y showed peaks between 450 and 1250cm^{-1} . A large broad band was observed in the 550 - 575 cm^{-1} . The bands shifted to higher frequencies of 995 and 1250 cm^{-1} respectively. The most intense bands were 570 and 1250 cm^{-1} .

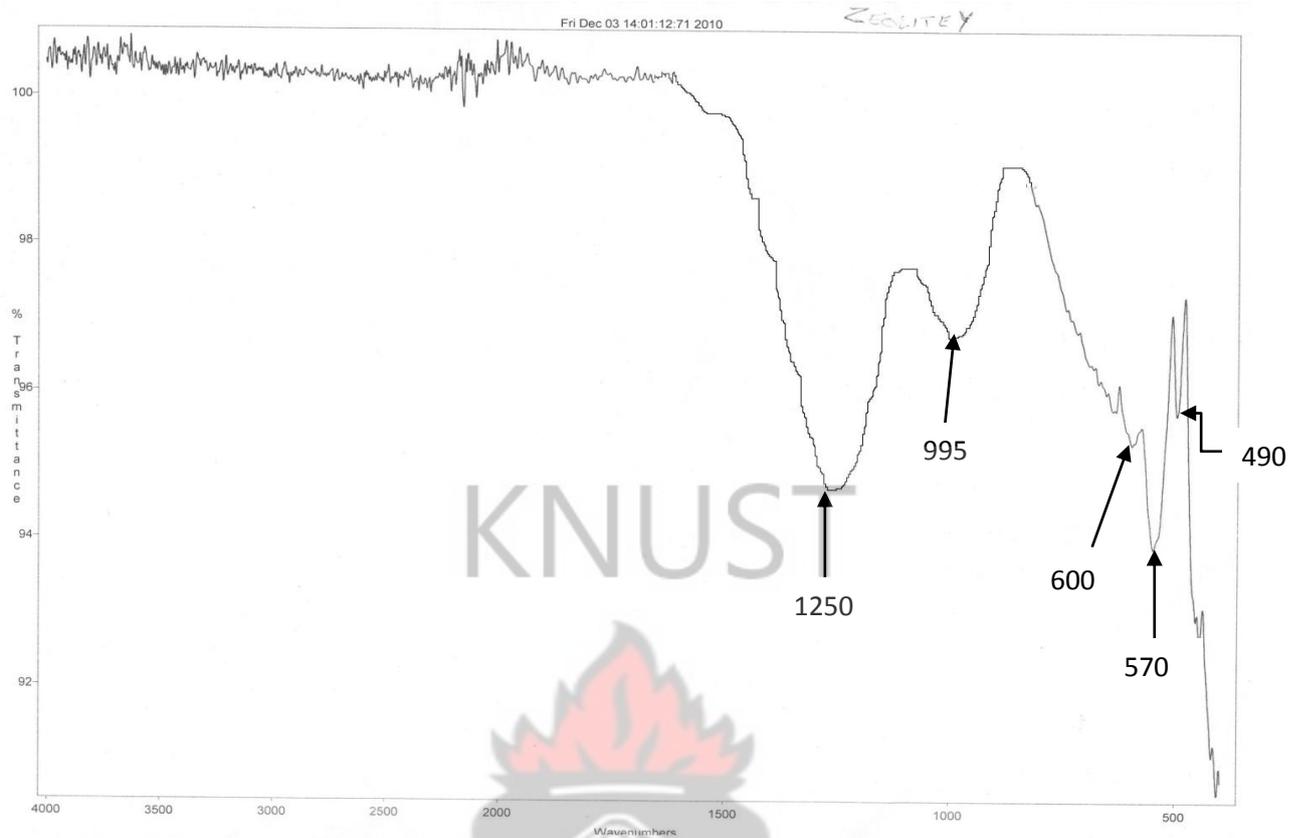


Figure 5.6: FTIR spectrum of zeolite Y

The TGA plot of zeolite Y is presented in the appendix section. The plot was between the temperature range of 0 and 800 °C. The plot showed a little loss in weight as the temperature increased with time indicating a very stable phase of the zeolite.

5.4 KINETICS

Seawater had an initial pH of 7.69 and an electrical conductivity of 12.12 mS/cm.

Preliminary analysis of seawater composition indicated the following:

Table 5.3 Average value of the various elements in seawater used

Element	Na	K	Mg	Ca
Concentration mg/l	68.51	13.36	28.47	74.72

These values were not acceptable because the standards used were not accurate. These values did not reflect the true representation of the amount of the various elements present. The electrical conductivity of the seawater ought to have been lower if the values were such.

Seawater analysis was redone. Prior to this analysis, the synthesized zeolites were added to the seawater. After the kinetics, the element removal efficiency, R % was calculated using the formula:

$$R \% = \frac{C_i - C_f}{C_i} * 100$$

where C_i is the initial concentration of element in seawater and

C_f is the concentration of the element in seawater after ion exchange with zeolite.

The results after zeolite application to seawater are presented as follows

- Effect of zeolite mass to solution ratio
- Effect of type of zeolite

5.4.1 Low Silica Type X Zeolite (LSX)

Low silica zeolite X was used to test its efficiency in the desalination of seawater. A zeolite mass to seawater ratio of 1:100 was utilised. The pH before the addition of zeolite was 7.96. Concentration of elements at the different times is presented below:

Table 5.4 pH and concentration of elements before and after the addition of LSX

TIME / min	pH	Na	K	Mg	Ca
0	7.96	4872.00	1075.15	1140.63	751.75
15	8.80	5540.85	1393.39	787.50	156.75
30	8.94	6719.76	1892.26	875.00	108.13
60	8.89	4933.51	1789.05	828.13	46.25
90	8.78	4222.40	1789.05	856.25	79.88
120	8.68	6248.20	1668.63	809.38	95.50
180	8.54	5413.34	2580.36	834.38	110.13

A considerable increase in the pH of seawater was observed. The pH increased from 7.96 to 8.80 when LSX was added for 15 minutes. This was probably due to the high pH of zeolite introduced into the seawater. The pH after 30 minutes started reducing. There was a reduction of 0.4 in the pH between 30 minutes and 180 minutes when the experiment was stopped. The pH after 180 minutes was 8.54. This pH of 8.54 was much higher than the pH of the blank of 7.96.

The concentration of the elements Sodium (Na), Potassium (K), Magnesium (Mg) and Calcium (Ca) before the addition of zeolite X was determined using AAS. Upon the addition of zeolite, their concentrations were measured again as presented in Table 5.4. The value of Na which was initially 4872 mg/l increased to 6719.76 mg/l after 30 minutes. A high reduction was observed after another 30 minutes i.e. 6719.76 – 4222.40 mg/l. A lot of activity notably occurred after every 30minutes. The value of Na in the seawater after 180minutes was 5413.34 mg/l. This amount is significantly higher than the initial level before the addition of LSX.

The same trend is observed for K, a significant increase after 30 minutes and a reduction after 30 minutes. The value then became constant between 60 and 90 minutes. The value after 180 minutes was more than twice the value when the experiment began (from 1075.15 mg/l to 2580.36 mg/l).

The case was however different for Mg and Ca. Both elements showed a decrease in their concentrations when LSX was added to the seawater. Magnesium level reduced considerably after 15 minutes. It then recorded an increase of 87.5 mg/l after another 15 minutes. Magnesium levels fluctuated until the end of the 180 minutes. The final value of 834.38 mg/l was all the same lower than the initial value of 1140.63mg/l. Calcium recorded the highest reduction compared to the other three elements. A reduction of 595mg/l from its starting value of 751.75 mg/l was achieved within the first 15 minutes. There was further reduction up till 60 minutes when an increase of 33.63 mg/l was observed. Afterwards the Ca concentration reduced again (between 120 and 180 minutes). The final concentration after 180 minutes was 110.13 mg/l.

Considering the removal efficiency Table 5.5, Na recorded negative values except for the 90 minutes interaction when a 13.33% removal was achieved. This means that its removal was unsuccessful. The amount of sodium in this type of zeolite was very high causing the sodium in the zeolite framework to leach considerably into the seawater. K recorded negative values (as low as -140%) all through the test. Potassium also leached due to this same reason. There was however no Ca or Mg in the zeolite framework, thus no leaching occurred for these two elements. The highest effective removal of Ca was after 60 minutes when 93.85% was recorded and after 15 minutes for Mg with a value of 30.96%.

The removal efficiency for individual times was calculated as follows:

Table 5.5 Removal efficiency of the various elements by LSX

TIME / min	Na	K	Mg	Ca
	Removal efficiency %			
0	0	0	0.00	0.00
15	-13.73	-29.60	30.96	79.15
30	-37.93	-76.00	23.29	85.62
60	-1.26	-66.40	27.40	93.85
90	13.33	-66.40	24.93	89.37
120	-28.25	-55.20	29.04	87.30
180	-11.11	-140.00	26.85	85.35

With high concentrations of sodium and potassium in the ‘treated’ seawater, the salinity was still high and desalination was not effective. With the reduction in Ca and Mg levels however, the hardness of seawater was reduced.

5.4.2 Low Sodium Zeolite X

With the aim of reducing the Na and K concentration in the seawater, a different type of zeolite was produced. Using the method of synthesis in Chapter 4, section 4.2.1, a composition of $18\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 4\text{SiO}_2 : 325\text{H}_2\text{O}$ was synthesized.

5.4.2.1 Effect of zeolite mass to seawater ratio (zeolite X)

Tests were carried out with zeolite to seawater ratio of 1:100 and 0.5:100. Both were carried out under the same conditions and time limits. The initial pH was 7.61 and electrical conductivity was 16.70 mS/cm.

Table 5.6(a) Ratio of 1:100 using zeolite X

TIME/mins	pH	EC	Na	K	Mg	Ca
0	7.61	16.70	2554.27	92.69	307.28	98.53
15	8.41	15.55	2162.40	78.55	260.12	83.32
30	8.44	15.00	2274.30	74.46	246.61	78.99
60	8.45	13.51	2468.80	73.35	176.69	56.59
90	8.43	11.00	2615.40	72.31	104.03	23.71
120	8.48	10.69	2652.20	70.52	101.35	19.65

Table 5.6(b) Ratio of 0.5:100 using zeolite X

TIME/mins	pH	EC	Na	K	Mg	Ca
0	7.61	16.70	2554.27	92.69	307.28	98.53
15	8.27	14.47	2795.20	83.36	276.05	88.42
30	8.35	12.43	2501.60	65.21	215.95	69.17
60	8.34	11.82	2294.83	70.01	132.52	42.44
90	8.33	10.43	2421.60	45.31	80.72	16.24
120	8.35	10.58	2472.60	37.17	76.85	18.21

The optimum pH value of 8.27 was recorded for 05:100 compared to that of 1:100 ratio of 8.41 which was higher than the initial pH. Conductivity values reduced when the zeolite was added from 16.70 to 10.69 mS/cm in Table 5.6 (a) and 16.70 to 10.43 mS/cm in table 5.6 (b). A significant decrease in elemental composition was evident in Table 5.6(b). Na reported the lowest decrease compared to the rest. Na leached in Table 5.6(a). K, Mg and Ca were reduced in terms of their concentrations.

Graphs showing the effective removal of elements using different zeolite masses.

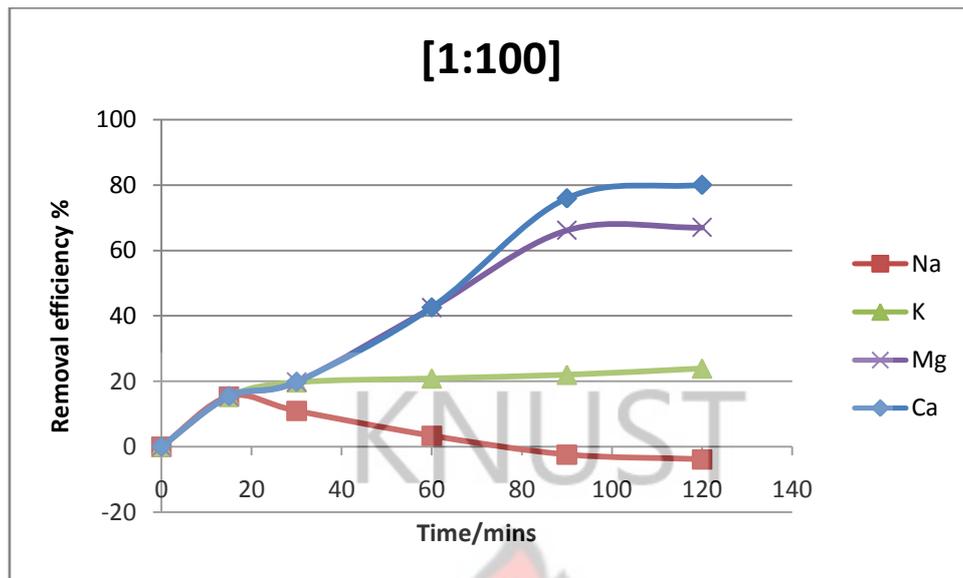


Figure 5.9(a): a graph showing removal efficiency of zeolite using a ratio of 1:100

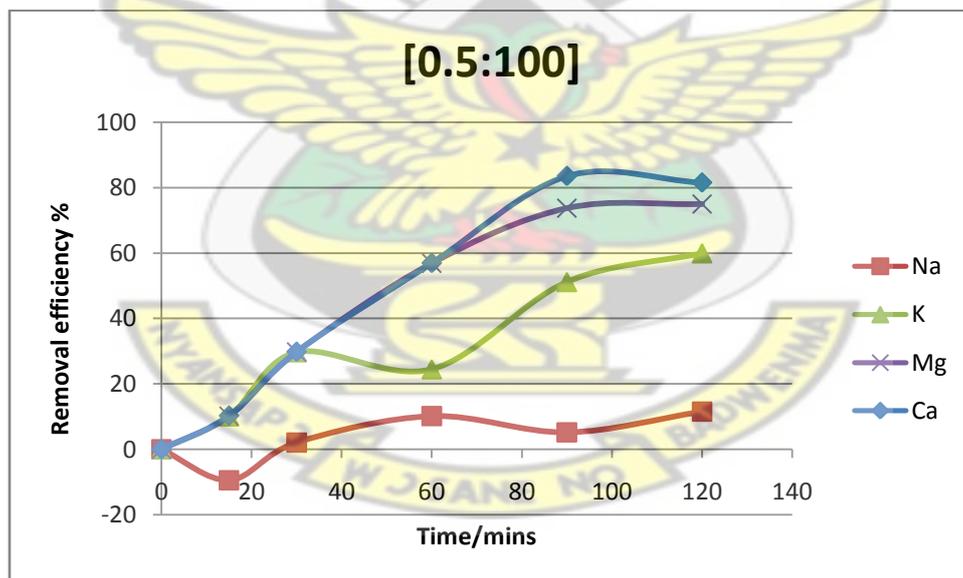


Figure 5.9(b): graph showing removal efficiency of zeolite using a ratio of 0.5:100

In Figure 5.9(a) removal or reduction of the elements in the seawater was almost proportional in the first 15 minutes of the experiment. There was steady increase in the removal efficiency in Mg and Ca. The rate of removal of K was fairly stable. The concentration of Na in the

seawater was higher at the end of the test. A similar trend was observed in Figure 5.2. A slight deviation was in K which reduced at 60 minutes and then increased again. Na leached after 15 minutes but its removal though minimal was also fairly stable.

The removal of Na was the lowest in both cases, showing occasional leakages (15.34% and 10.16%). K was removed with the highest value being 23.9% in Figure 5.1 and 59.9% in Figure 5.2. Mg and Ca were removed successfully, 67.02% and 74.99% for Mg and 80.06 and 83.51 % for Ca in Figure 5.1 and 5.2 respectively.

5.4.3 Effect of zeolite mass to solution ratio (zeolite Y)

As with zeolite X, the effect of the mass of zeolite was taken into consideration. Results are presented as:

Table 5.7a Varying mass of zeolite to seawater ratio

	ratio 0.5 :100						
Time/mins	pH	EC	TDS	Na /mg ^l ⁻¹	K / mg ^l ⁻¹	Mg / mg ^l ⁻¹	Ca / mg ^l ⁻¹
Blank	7.63	18.57	3815	2840.28	103.06	341.69	109.56
15	7.85	16.70	3925	2203.52	80.04	265.07	84.90
30	8.00	15.80	4000	1927.52	68.92	218.26	53.11
60	8.16	15.80	4080	1927.52	68.92	218.26	53.11
90	8.18	15.70	4090	1893.52	67.69	214.17	51.80
120	8.13	15.60	4065	1859.52	66.45	210.08	50.49

TIME/mins	pH	EC	TDS	Na/ mg ^l ⁻¹	K/ mg ^l ⁻¹	Mg/ mg ^l ⁻¹	Ca/ mg ^l ⁻¹
Blank	7.63	18.57	9285	2840.28	103.06	341.69	109.56
15	7.88	16.40	8200	2621.52	86.33	252.80	80.97
30	8.03	15.50	7750	2101.52	65.22	215.99	69.18
60	8.09	15.70	7850	2063.52	67.69	224.17	51.80
90	8.10	15.90	7950	1951.52	70.16	212.35	54.42
120	8.10	16.20	8100	2053.52	73.86	224.62	58.35

Table 5.7b Varying mass of zeolite to seawater ratio

The initial pH in both tests was 7.63 and electrical conductivity of 18.57 mS/cm. In both tests, the pH saw a gradual increase upon addition of zeolite Y. A total increase of 0.5 was realized in the zeolite to seawater ratio of 0.5: 100 and 0.47 in the event of 1:100. Electrical conductivity in both cases again showed a reduction. As in Table 5.7(a), the electrical conductivity was lowest at 120 minutes. It was lowest in Table 5.7 (b) at 30 minutes. The concentrations of the various elements were reduced. Table 5.7 (a) however, showed much reduction in all elements than in Table 5.7 (b). The least value in Na was recorded at 120 minutes in table 5.7 (a). It also recorded the least values for Mg and Ca at the same time. The least concentration value of K was recorded in Table 5.7 (b) after 30 minutes of ion exchange.

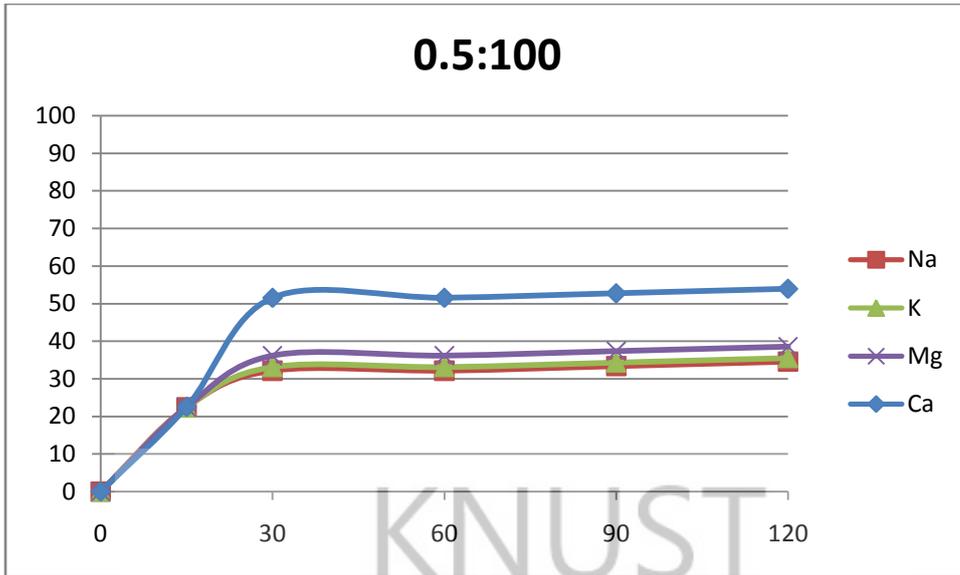


Figure 5.10(a): a graph showing the removal efficiency of elements by zeolite Y using a ratio of 0.5:100

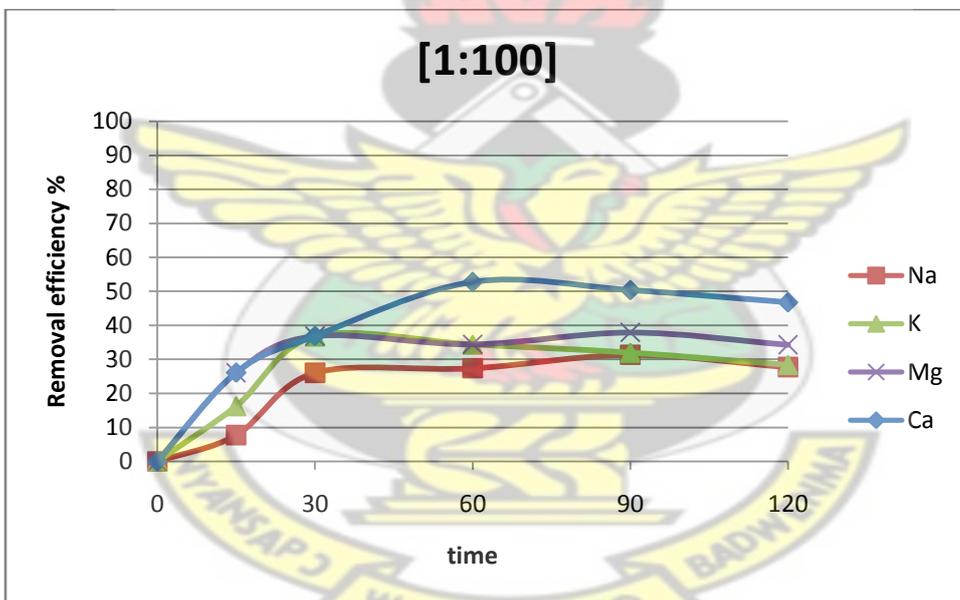


Figure 5.10(b): a graph showing the removal efficiency of elements by zeolite Y using a ratio of 1:100

Figures 5.10(a) and 5.10(b) show the removal efficiencies of zeolite Y with varying mass to seawater ratio. Figure 5.10 (a) showed a gradual rise in the effective removal of all four elements recording an almost equal value of approximately 15%. Also there was a fairly stable increase in their removal until the end of the experiment. Na and K removal was

almost the same. The highest removal efficiency of Ca was 53.9%, Mg 38.52%, K 35.52% and Na 34.53%.

In the instance of the 1:100 ratio i.e. Figure 5.10 (b), Na removal was the least successful depicting 7.7% within the first 15 minutes and 27.70% after 120 minutes. Ca was removed, the highest being 52.72% after 60 minutes but reduced to 46.74% after 120 minutes. Mg had a removal of 34.26% and K had 28.33% after 120minutes.

As was in the case of zeolite X, 0.5:100 ratio yielded better removal in terms of its efficiency in desalting seawater.

5.4.4 Effect of Type of Zeolite

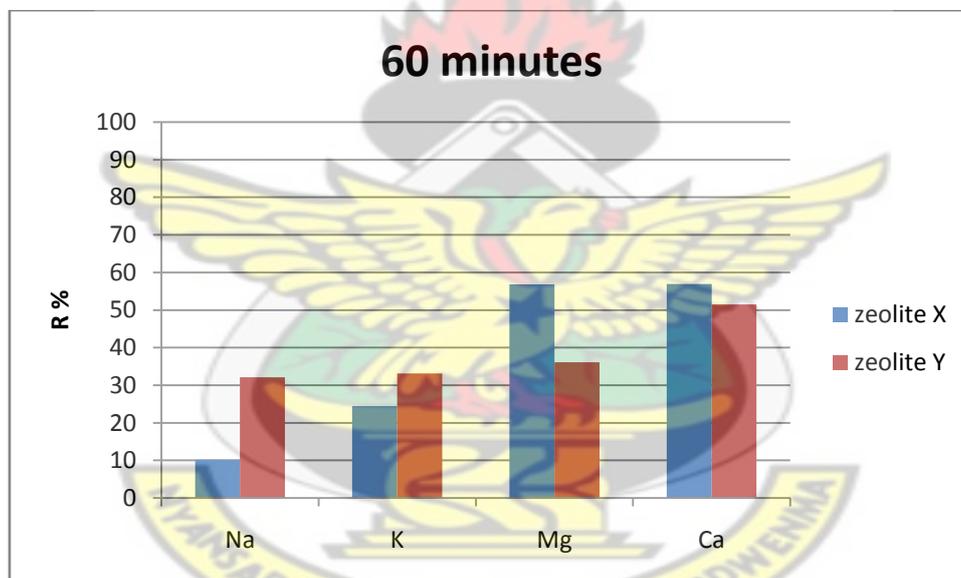


Figure 5.11(a): comparing efficiencies of zeolites X and Y at 60 minutes

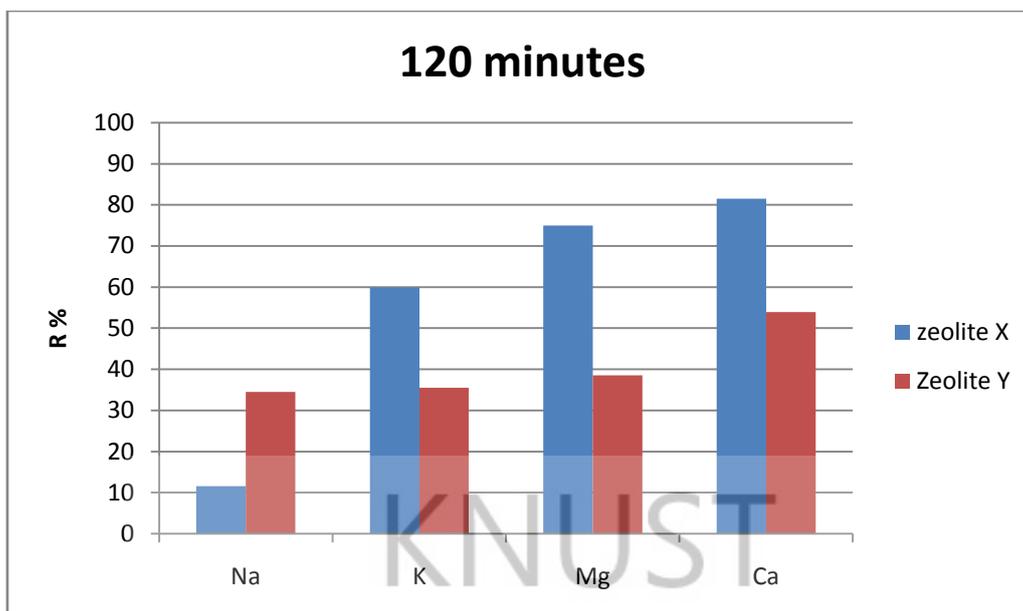


Figure 5.11(b): Comparing the efficiencies of zeolite X and Y at 120 minutes

Zeolites X and Y were compared to ascertain which of the two had a higher efficiency in the uptake of cations with the aim of desalinating seawater. Analysis showed a higher uptake of Na and K in zeolite Y than X in 60 minutes. Zeolite X however had higher values for Mg and Ca. All two zeolites had the same trend for the selectivity of cations in seawater. At 120 minutes, zeolite X showed much higher uptake of K, Mg and Ca than zeolite Y. Higher preference for Na was shown by Y than X in this case. This could be attributed to the fact that zeolite Y had less Na in its framework compared to zeolite X. All other elements were reduced more by zeolite X than zeolite Y.

5.4.5 Effect of Silver Nitrate on Ion Removal

The treated water after ion exchange did not meet the requirements of drinking water. This water was still salty because of the presence of Cl and Na ions. With the aim of making the water suitable, the amount of Cl was reduced by adding silver nitrate to the seawater. The silver nitrate reacted with the chloride ions forming a white precipitate (silver chloride). Silver nitrate was titrated against seawater to ascertain the amount of chloride present

(Mohr's titration, see appendix). The chloride ions were reduced. The seawater was then treated with zeolites. Results are presented below (Table 5.8):

Introducing silver nitrate into the seawater reduced the pH and electrical conductivity considerably. The pH was reduced by 0.97 ± 0.05 . The electrical conductivity was also reduced by 3.22 ± 0.4 mS/cm. Initial concentration of cations in seawater was: Na = 4782.40 ± 0.1 mg/l, K = 1789.05 ± 0.1 mg/l, Mg = 828.13 ± 0.1 mg/l, Ca = 751.75 ± 0.1 mg/l.

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Table 5.8 Silver chloride treatment with zeolite X and its removal efficiencies

TIME	pH	EC	TDS	Na	K	Mg	Ca	Na	K	Mg	Ca
								Removal Efficiency %			
b/4											
AgNO ₃	7.38	9.75	4875	4782.4	1789.05	828.13	751.75	0	0	0	0
after											
AgNO ₃	6.41	6.53	3265	4782.40	1789.05	828.13	751.75	0.00	0.00	0.00	0.00
15	7.30	6.20	3100	4320.00	1652.00	730.00	399.50	9.67	7.66	11.85	46.86
30	7.38	6.08	3040	3968.00	1572.50	709.00	361.00	17.03	12.10	14.39	51.98
60	7.72	6.02	3010	3550.00	1048.50	672.00	333.94	25.77	41.39	18.85	55.58
90	7.70	5.91	2955	3541.53	963.30	633.00	179.25	25.95	46.16	23.56	76.16
120	7.58	6.09	3045	4927.20	943.60	586.80	168.00	-3.03	47.26	29.14	77.65

The addition of zeolite X to the seawater saw an increment of 0.89 units to the pH within the first 15 minutes. The electrical conductivity did not increase but further reduced (from 6.53 to 6.20). A reduction in concentration was observed in all four elements between 15 minutes and 120 minutes except for Na which leached at 120 minutes. Removal efficiencies showed

high preference for Ca with 77.65%. Next was K with 47.26% and Mg with 29.14%. Na had an efficiency of -3.03% implying a leakage.

Results after treatment of the seawater with zeolite Y after the addition of silver chloride is as follows:

Table 5.9 Silver chloride treatment with zeolite Y and its removal efficiencies

TIME	pH	EC	TDS	Na	K	Mg	Ca	Na	K	Mg	Ca
								Removal Efficiency %			
b/4 AgNO ₃	7.38	9.75	4875	4782.40	1789.05	828.13	751.75	0.00	0.00	0.00	0.00
after AgNO ₃	6.41	6.53	3265	4782.40	1789.05	828.13	751.75	0.00	0.00	0.00	0.00
15	7.70	5.86	2930	4475.20	1101.33	508.00	220.05	6.42	38.44	38.66	70.73
30	7.70	5.73	2865	4859.20	1048.53	512.00	226.25	-1.61	41.39	38.17	69.90
60	7.70	5.68	2840	3426.04	835.50	547.20	154.00	28.36	53.30	33.92	79.51
90	7.70	5.66	2830	3387.20	874.80	537.30	153.25	29.17	51.10	35.12	79.61
120	7.67	5.96	2980	3387.20	796.20	486.00	154.75	29.17	55.50	41.31	79.41

An increase in pH of 1.29 units was recorded after 15 minutes when zeolite Y was added to the seawater. The pH remained constant until it reduced by 0.3 after 120 minutes. The electrical conductivity reduced considerably all through the experiment. However, after 120 minutes an increment in the conductivity was noted.

Na was reduced by 307.2 mg/l after 15 minutes. The level of Na in the seawater increased after 30 minutes. The removal of Na rose to 28.36% afterwards. The other three elements showed a similar trend though they recorded much higher efficiencies compared to Na. Zeolite Y was 79.41% effective on the removal of Ca, 55.5% for K, 41.31% for Mg and 29.17% for Na. Na did not leach when zeolite Y was used although its efficiency was low (29.17%).

5.5 DISCUSSION

5.5.1 Synthesis and Characterisation of Zeolite X and Y

The SEM images of synthesized zeolite X and Y were highly crystalline. The average crystal size for zeolite X is about 5 μ m and that of Y is 10 μ m. Crystallinity observed could be attributed to the presence of Al in the starting gel. This was confirmed by the TGA results which portrayed a highly stable zeolite. Frequencies observed in the range 500 – 1300 cm^{-1} in the FTIR indicate that SiO_4 or AlO_4 are linked. An overlap of the asymmetric vibrations of Si – O (bridging) and Si – O⁻ (non-bridging) bonds were determined by large band observed in the region of 975-995 cm^{-1} both zeolites. Symmetric stretching due to external T-O linkages occurred at 725 cm^{-1} . Vibrations assigned with the double six rings (D6R) that connect the sodalite cages occurred at 600 cm^{-1} for zeolite X. In zeolite Y characterisation, the most intense bands were 970 – 1250 cm^{-1} and 450- 500 cm^{-1} . The first is assigned to asymmetric stretching modes, the second to a bending mode of the T- O bonds. There were no bands in the region to be assigned to a symmetric stretching within the T – O tetrahedra.

Elemental analysis confirmed the presence of all the elements in their right proportions in each of the synthesized zeolite.

XRD patterns of both zeolites are highly crystalline and match those of literature. The X-ray diffraction for zeolite Y had a flat base and distinct peaks indicating a highly crystalline

product with no impurities. The purity of zeolite Y was confirmed as there was no other phases or lines present.

5.5.2 Removal of Cations

The ion exchange process in tests that were run showed an increase in the solutions pH. This occurrence is due to the removal of Calcium and magnesium and its replacement by sodium ions.

Selectivity of ions by low silica zeolite X was found to be higher for divalent cations than for monovalent cations (Sherry, 1979). Sherman (1983) in his work stated a selectivity of $K^+ > Na^+$ and $Ca^{2+} > Mg^{2+}$. This order of selectivity for cations observed in study is $Ca > Mg > K > Na$. This order of selectivity could be confirmed by the fact that zeolites prefer ions of higher charge (Sherman, 1983; Amphlett, 1964; Sherry, 1979).

The preferred counter ion is taken up by the exchanger at a higher relative rate (Helffrich, 1995). The presence of Ca^{2+} and Mg^{2+} in the seawater influence the uptake of K^+ and Na^+ . The process of cation uptake by zeolites is determined by the kinetics of adsorption. The amount of Na released into the seawater by zeolites indicates ion exchange activity. Since there was sodium in both seawater and zeolite, the effective removal of all cations was hindered. Very often, a zeolite favours the least hydrated ion while the solution phase favours the mostly hydrated ion (Sherman, 1983).

The effect of competitive cations and anions on ion exchange of heavy metals in clinoptilolite was examined by Inglezakis *et al.*, (2005). The presence of cations in the solution of the heavy metals is reducing the presence of the latter due to simultaneous exchange of cations which occupy available exchange sites in the zeolite structure. Removal of each cation is presented below:

5.5.2.1 Calcium

Calcium removal was successful recording a value of 81.5% for zeolite X and 54% for Y suggesting high affinity for the cation. Since both zeolites had no calcium in their framework, no leaching was observed. Galvan *et al.*, (2009) achieved a successful ion exchange between Ca and Na ions in their study. It was concluded in their study that, the amount of Na ions exchanged by Ca was in complete agreement with their corresponding molar balance.

5.5.2.2 Magnesium

Magnesium removal in zeolite X was lower compared with Ca with 75% removal 120 minutes. Overall removal in zeolite Y was 38.5%. There was however a decrease in the uptake of Mg ions after 60 minutes (from 32% to 15%).

5.5.2.3 Potassium

Removal of Potassium was relatively low. K level was reduced but not as significant as Ca and Mg, the highest amount being 59.9% for zeolite X and 35.52% for zeolite Y. This was attributed to the fact that due to its similar size to the Na cations, there was competition for sites. It was not possible to achieve complete ion exchange of cations especially K with Na. This was because of Na cations in the zeolite framework. However as stated by Barrer *et al.*, (1969), K is still preferred in the Faujasite framework over Na. The zeolite Phillipsites shows preference for K over Na at all temperatures. This was realised by Shibue (1981). However, the selectivity for K over Na is smaller in the higher charged zeolite than in the lower charged ones.

5.5.2.4 Sodium

Sodium removal in all zeolites was least effective. Sodium leached into the seawater. The excess Na found in the seawater was probably from the zeolite. This was because sodium was loosely attached and often easily exchangeable. Previous kinetic experiments by Dyer (1992) showed that the sodium cations initially present in zeolite channels were all replaceable by

cations studied therein. With the sodium levels increasing, the value of seawater measured after 120 minutes was 4880 mg/l. Initial concentration of Na in the seawater before the addition of zeolite X was 2444 mg/l. This rendered the seawater more salty. Values obtained for Na were negative as the ion exchange occurred for the other ions. Zeolite X however recorded its highest successful removal of Na after 120 minutes (32%).

It has been shown that many exchange reactions in zeolite X and Y fail to proceed to completion and suggestions have been made that the lack of total sodium exchange is due to difficulty of replacing residual Na cations present in the sodalite cages (Naccahe *et al.*, 1984). Sodium in the zeolite framework affects the uptake of extra sodium from the seawater. A sodium-free would be more appropriate for treating seawater.

5.5.3 Comparing zeolite X and Y

As cited in Kuronen *et al.*, (2006), highly aluminous zeolites are known to be selective to divalent cations. It was reported in the study that a higher selectivity for Sr^{2+} than K^+ in ion exchange with Na in MAX (maximum aluminium zeolite X).

The results from the studies showed that on the average, ZY had a better Na removal efficiency of 34% compared with that of zeolite X at 11.5% due to a lesser Na content in the zeolite Y framework. The low removal of sodium (Na) could be attributed to the fact that, the concentration of Na in seawater is rather high and Na in the zeolites is exchanged out for other cations. In most cases Na was observed to have leached. According to Ghaly and Verma (2008), results suggested that a series of ion-exchange column (with chabazite) was most likely required to attain a higher removal efficiency of Na ions. A two column ion-exchange system was used, the Na removal efficiency increased from 75.25- 99.79%.

Maes and Cremers (1974) studied ion exchange of divalent transition metals Co^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} on synthetic zeolite NaX and NaY. In spite of their identical crystal radius, there

was difference in their behaviour. The selectivity in the small cages depends on the occupancy and type of ion present in the big cavities and vice versa. Both zeolites had the same preference in terms of selectivity.

In his work, Lee (2007), showed the possibility of using zeolite membranes in desalination. He achieved 74.5 % ion rejection with MFI zeolite membrane in 40000 mg/l brine solution and 90% for 5500 mg/l sodium chloride solution. The method used was the cross-flow experiment. It was done by passing fluid to be treated through one or more cylindrical containers containing the zeolite membranes.

In both zeolites, the same trend was observed. However, unlike the previous test the trend was a little different. Selectivity was in the order $\text{Ca} > \text{K} > \text{Mg} > \text{Na}$.

This could be attributed to the acid introduced into the seawater. The nitrate (NO_3) ions increased the total dissolved ions. Comparing the two tables, it was realised that the removal rates though not stable were higher i.e. more efficient in Table 5.8. It was found that optimum zeolite to seawater ratio is 0.5 g to 100 ml.

In acidic solutions, pH increases as ion exchange occurs. Changes in solution pH is known to be an important factor affecting the ion exchange selectivity because the dissociation of the OH groups, the weakly acidic zeolites is sensitive to solution pH (Kuronen *et al.*, 2006). It can be inferred that anions (Cl^-) are not strong enough to inhibit the ion exchange process (Inglezakis *et al.*, 2005).

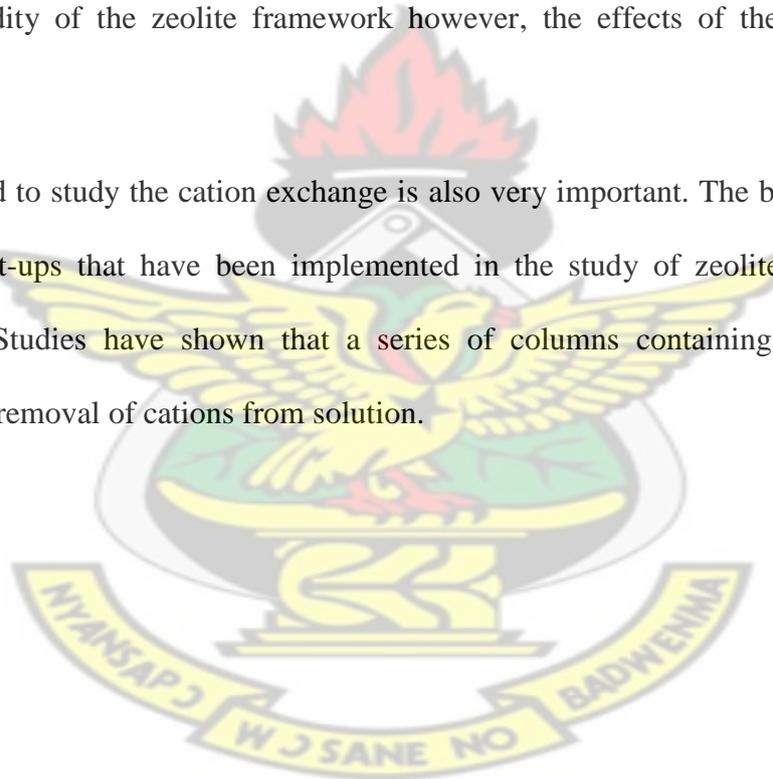
After critically observing the results, it was noted that the synthesized zeolites would be highly effective in the treatment of wastewater which has a lesser amount of sodium compared to seawater.

5.6 Other Variables Affecting Cation Exchange in Zeolites

Extensive studies have also shown that exchange selectivities in zeolites do not follow the typical rules and patterns exhibited by other organic and inorganic ion exchangers (by Csicsery as cited by Sherman, 1983). Exchange rates vary due to differences in energies required to exchange solvent molecules and may be very slow at lower temperatures.

Ion exchange selectivities and loadings on zeolites are dependent upon pH, temperature and aqueous solution chemistry. The types and concentration of anions, competing cations and complex agents can each alter the quality of ion exchange separation which can be achieved. Due to the rigidity of the zeolite framework however, the effects of these variables are minimal.

The method used to study the cation exchange is also very important. The batch, cross-flow and beds are set-ups that have been implemented in the study of zeolites (Breck, 1974; Sherry, 1979). Studies have shown that a series of columns containing zeolite is most effective for the removal of cations from solution.



CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSION

The removal of Ca, Mg and K from seawater was successful with a selective ion exchange process. Calcium had the highest removal (83.4% with zeolite X) and sodium recording the least (11%). Due to the presence of sodium in both zeolite and seawater, total desalination was not achieved. Silver nitrate achieved its purpose in being able to reduce the chloride level. The level of sodium was still higher than the acceptable amount in drinking water. However, the quality of water produced is acceptable for use in industrial plants and irrigation.

Zeolite selectivity depends on the cation size. During the ion exchange process, cations move through the pores of the zeolite mass and also through the channels of the lattice by replacing cations with Na. Based on the experimental studies, the following conclusions were made:

- Cation selectivity in Faujasite was confirmed as $Ca > Mg > K > Na$.
- Removal efficiencies obtained when zeolite X was used was Ca 81.5%, Mg 75%, K 59.9% and Na 11.5%. Efficiencies obtained in the case of zeolite Y was Ca 53.9%, Mg 38.5%, K 35.5% and Na 34.5%.
- Selectivity is higher for divalent cations than for monovalent cations in both zeolite X and Y.
- One zeolite cannot effectively remove all cations from seawater. Treating the zeolite with alternate zeolites and a combination of water treatment methods might enhance the quality of water obtained.
- The zeolite mass to seawater ratio of 0.5:100 yielded higher removal efficiencies compared to the ratio of 1:100.

6.2 RECOMMENDATIONS

Due to time and financial constraints, the scope of this work was limited. Based on the present study, some recommendations can be made for future work.

It is first of all recommended that alternative materials such as rice husks, clay and plaintain husks be used in the zeolite synthesis. A lot of work has been done in this area and has successfully produced high quality as-synthesized zeolite. This will cut down cost considerably as local materials are cheaper than purchasing chemicals.

Secondly, the synthesis of sodium-free zeolites will be recommended in the treatment of seawater to take care of the large amount of sodium in the seawater. More than one type of zeolite should be applied per seawater sample to handle any leakages left by previous zeolite.

In this study, ion exchange occurred at room temperature. Increasing the reaction temperatures would enhance the equilibrium point. Working at different temperatures will help to understand the process more as well as note the effect of temperature on the reaction and ion exchange process.

The use of alternate methods other than the batch method is highly recommended. Columns or beds could be used to measure the efficiency of zeolites and also produce a water of higher quality.

In the batch method, a long contact time may be required to reach equilibrium. Finally, it is suggested that the time of exposure should be increased to be able to determine the maximum contact time when equilibrium has been achieved.

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APPENDIX A

Table A.1 mass composition of Reagents Used in synthesis mixture of zeolite X and Y

	Zeolite X	Zeolite Y	Supplier
NaOH	100g	4.21g	AnalaR Normapur
Al ₂ O ₃	97.5g	15.18g	AnalaR Normapur
NaSiO ₃	219.7g	165.15g	AnalaR Normapur
H ₂ O	302.5g	150.92g	Self

Batch composition calculation for zeolite X synthesis

18 Na₂O: 4SiO₂ : 16 NaOH :325 H₂O

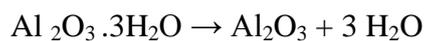
Source materials

Distilled water

Sodium Hydroxide (99+% NaOH)

Alumina trihydrate (Merck, 65% Al₂O₃)

Sodium silicate solution (27.35% SiO₂, 8.3% Na₂O, 1.37 g/ml)



Mass of Al₂O₃ = moles of Al₂O₃ x molar mass Al₂O₃

$$= 1 \text{ mole Al}_2\text{O}_3 \times 102 \text{ g/mol}$$

$$= 102 \text{ g}$$

$$\text{For } 102 \text{ g of Al}_2\text{O}_3 = 102 \text{ g Al}_2\text{O}_3 \times \frac{100 \text{ g alumina trihydrate}}{65 \text{ g Al}_2\text{O}_3}$$

$$= 156.9 \text{ g alumina}$$

$$\begin{aligned} \text{Mols of Na}_2\text{O} &= \frac{156.9 \text{ g alumina} \times 8.3 \text{ Na}_2\text{O}}{100 \text{ g alumina} \times 61.98 \text{ Na}_2\text{O}} \\ &= 0.2 \text{ mols} \end{aligned}$$

$$\begin{aligned} \text{Mass of SiO}_2 &= 1 \text{ mole SiO}_2 \times 60.086 \text{ g/mol} \\ &= 60.086 \text{ g SiO}_2 \end{aligned}$$

For 60.086 g SiO₂,

$$\begin{aligned} &= \frac{(60.086 \text{ g SiO}_2 \times 100 \text{ g Sodium silicate})}{40 \text{ g SiO}_2} \\ &= 150 \text{ g Sodium silicate} \end{aligned}$$

$$\begin{aligned} \text{Mass of NaOH} &= 1 \text{ mole NaOH} \times 39.99 \text{ g/mol} \\ &= 39.99 \text{ g NaOH} \end{aligned}$$

For 39.99 g NaOH

$$\begin{aligned} &= \frac{(39.99 \text{ g NaOH} \times 100 \text{ g sodium hydroxide})}{97 \text{ g NaOH}} \\ &= 41.227 \text{ g sodium hydroxide} \end{aligned}$$

In 41.227 g sodium hydroxide

$$\begin{aligned} &= 41.227 \text{ g sodium hydroxide} \times \frac{3 \text{ g water}}{100 \text{ g sodium hydroxide}} \times \frac{1 \text{ mole}}{18 \text{ g water}} \\ &= 0.07 \text{ mol H}_2\text{O} \end{aligned}$$

Total mass of reactants is presented in Table A.1

Values obtained during synthesis mixture are presented below

Table A.2 pH before and after crystallization values of zeolite X

zeolite X						Mean	Std Dev	Error
before	exp1	13.60	13.58	13.41	13.60	13.55	0.09	0.05
	exp2	13.32	13.35	13.39	13.41	13.37	0.04	0.02
	exp3	13.46	13.51	13.41	13.38	13.44	0.06	0.03
after								
	exp1	13.03	13.05	13.09	13.05	13.06	0.03	0.01
	exp 2	13.07	13.12	13.09	13.10	13.10	0.02	0.01
	exp3	12.76	12.83	12.62	12.62	12.71	0.11	0.05

Table A.3 pH before and after crystallization values of zeolite Y

zeolite Y										
before							Mean	Std Dev	error	
	exp1	12.83	12.84	12.85	13.02	12.87	12.67	12.84667	0.11	0.05
	exp2	11.31	11.31	11.34	11.52	11.29	11.33	11.35	0.09	0.04
	exp3	11.62	11.59	11.6	11.4	11.53	11.56	11.55	0.08	0.04
after	exp1	11.77	11.79	11.74	11.74	11.66	11.67	11.73	0.05	0.02
	exp2	11.80	11.82	11.84	11.82	11.82	11.80	11.82	0.02	0.01
	exp3	11.51	11.53	11.52	11.52	11.60	11.65	11.56	0.06	0.03

Table A.4 Changes in pH of seawater from various locations over time

	Bortianor	Cape Coast	Dansoman	Takoradi
Date	pH			
1/2/2011	7.95	7.94	7.87	7.81
16-02-11	7.90	7.88	7.87	7.68
21-02-11	7.57	7.20	7.87	7.64
25-02-11	7.32	7.16	8.00	7.61
28-02-11	7.28	7.17	7.96	7.57
03-03-11	7.28	7.35	7.96	7.49

APPENDIX B

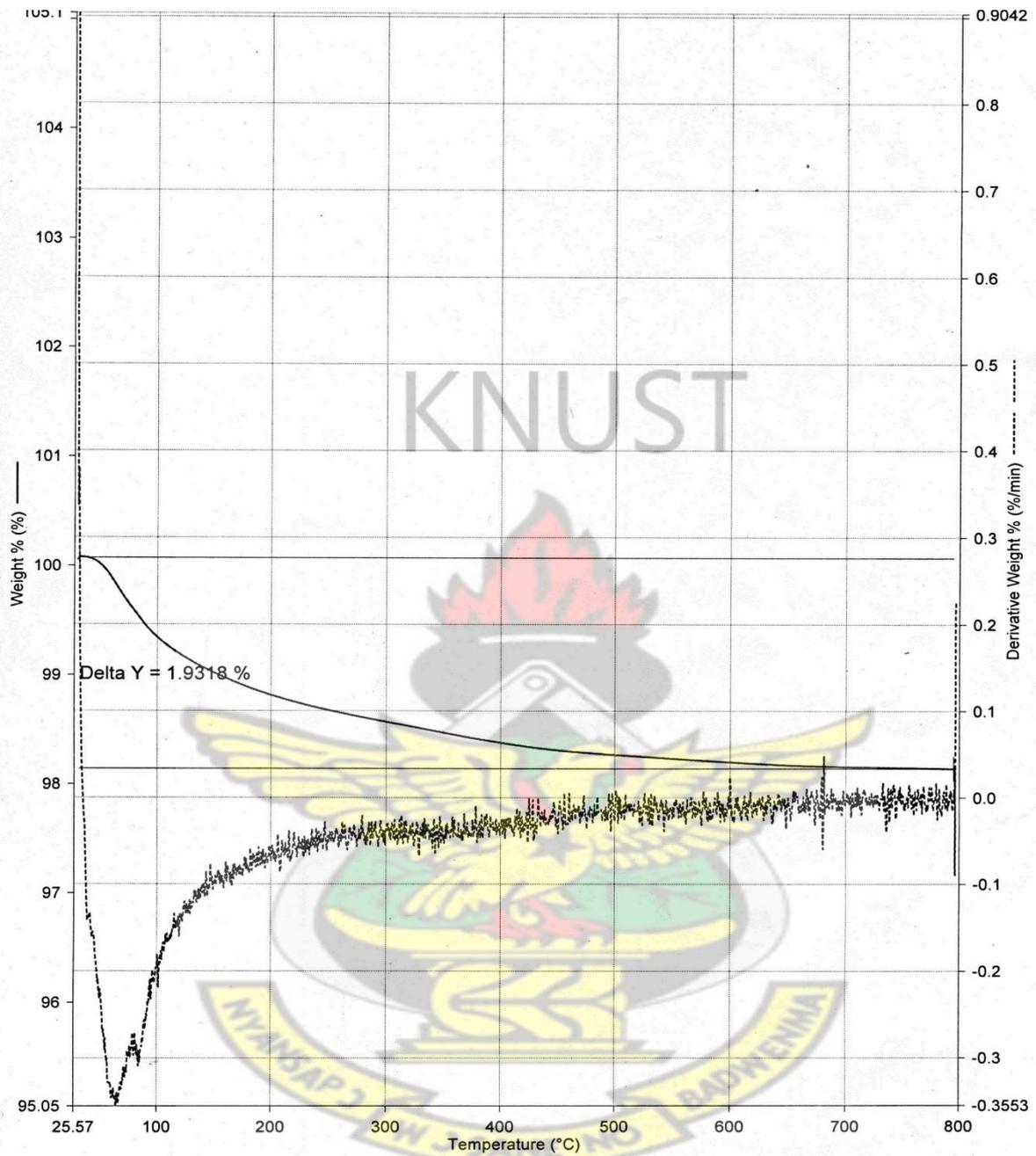


Figure A1: TGA curve of zeolite Y from 25 °C – 800 °C

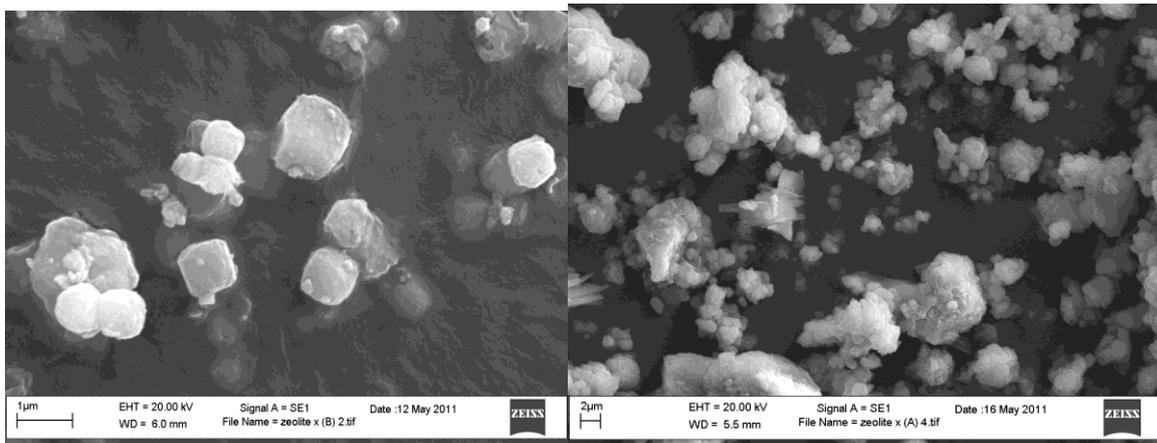


Figure A.2: SEM image of Low silica zeolite X

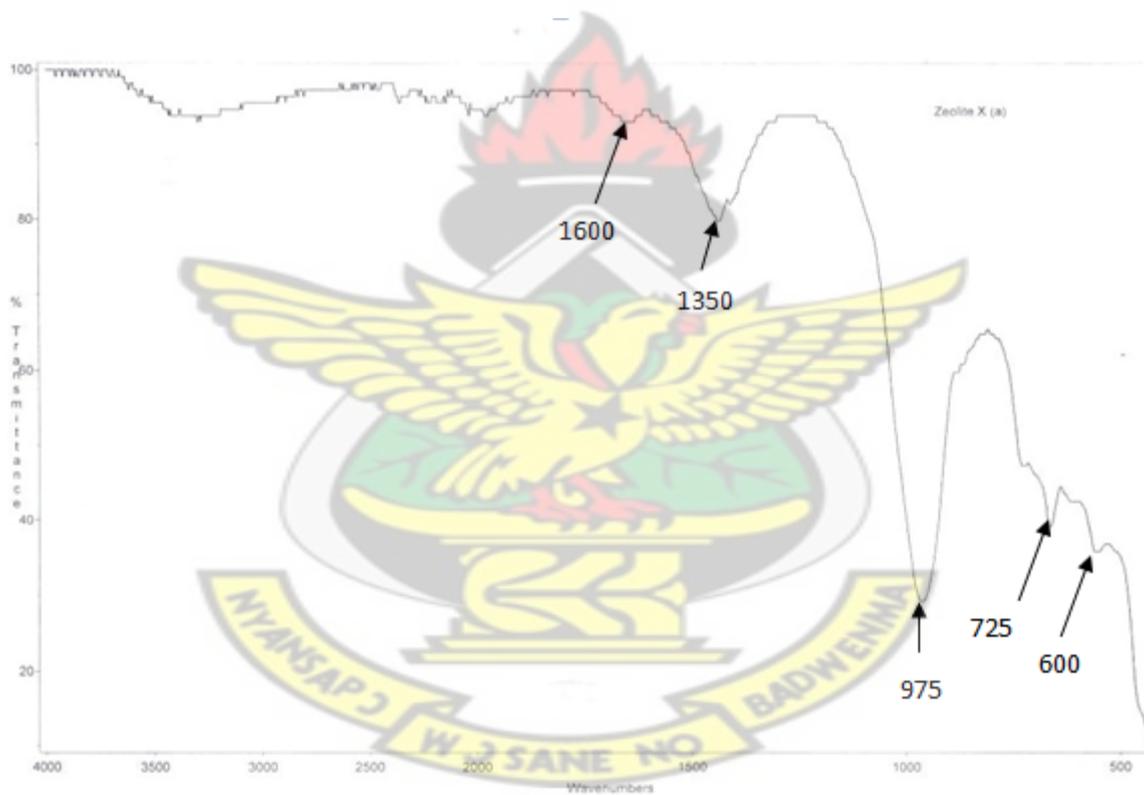


Figure A.3: FTIR image of Low silica zeolite X

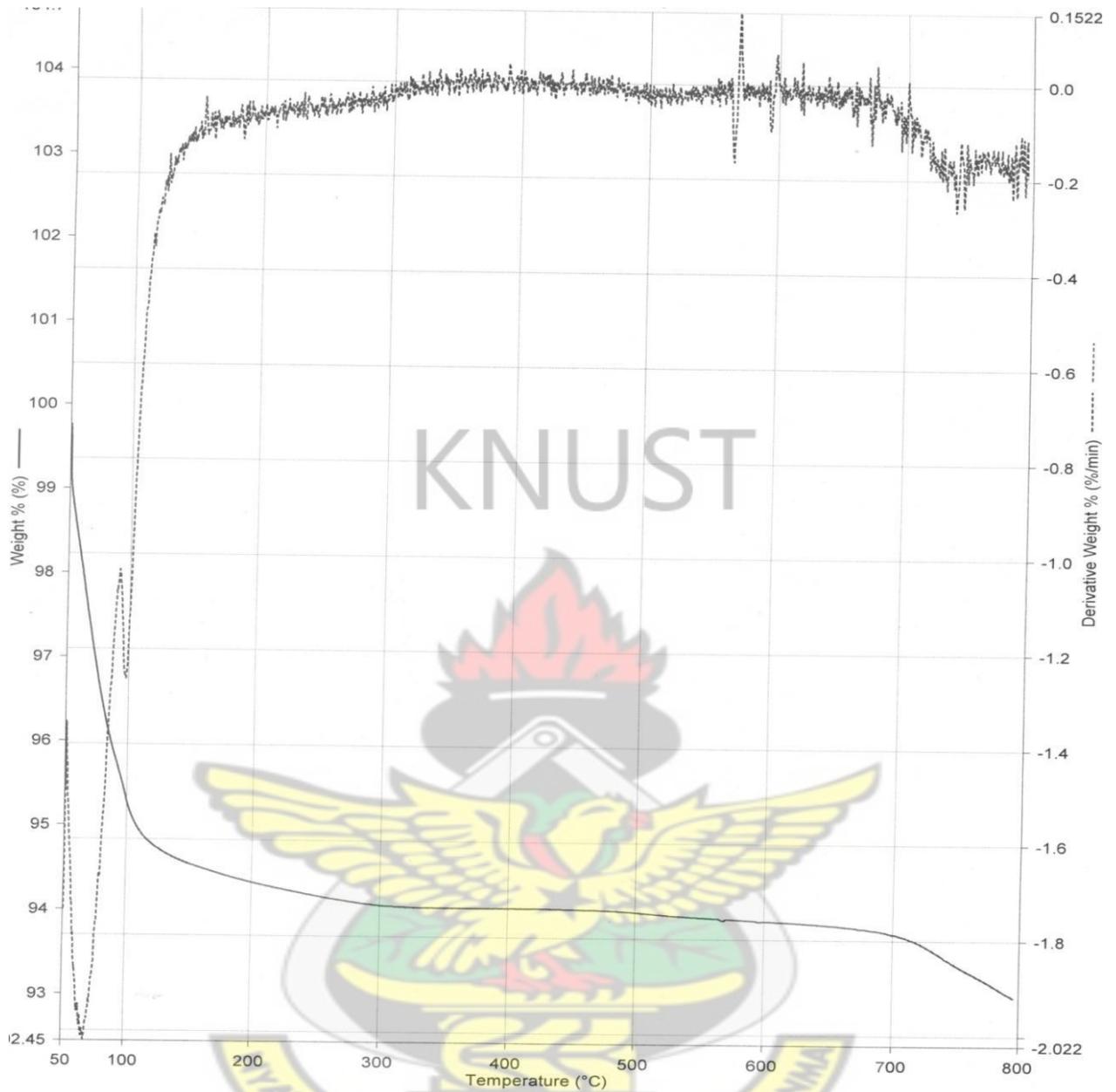


Figure A.4: Thermogravimetric analysis plot of Low Silica zeolite X from 50 °C – 800°C

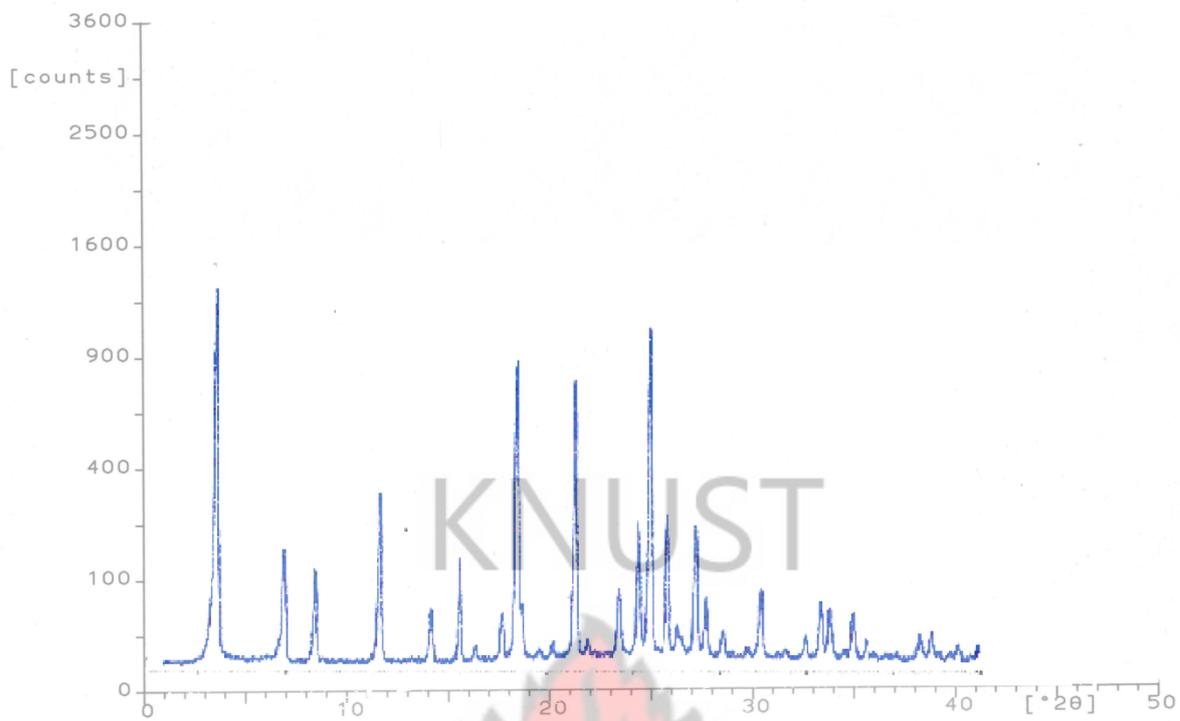


Figure A.5: XRD of Low Sodium zeolite X

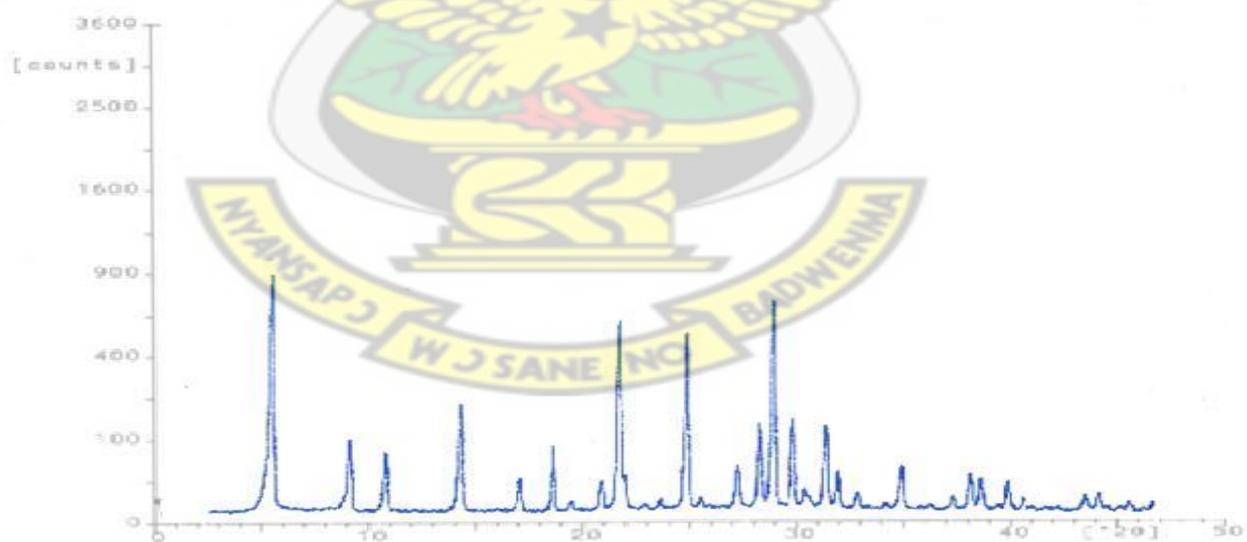


Figure A.6: XRD of Low silica zeolite X

APPENDIX C

TITRATION

Apparatus

10 and 20 ml pipettes

10 ml flask

250 ml conical flask

10 ml and 100 ml measuring cylinders

Reagents

M AgNO₃

Distilled water

0.25 M K₂CrO₄ as indicator

Reaction equation



Table B.1 Titrating silver nitrate against seawater

	1 st reading	2 nd reading	3 rd reading
Final	11.1	22.1	33.3
initial	0.00	11.1	22.1
titre	11.1	11.0	11.2

$$\text{Average titre} = \frac{(11.1+11.0+11.2)}{3}$$

$$= 11.1 \text{ cm}^3$$

$$\text{Moles of AgNO}_3 = M \text{ AgNO}_3 \times V \text{ AgNO}_3$$

$$= 0.1 \times 0.0111$$

$$= 1.11 \times 10^{-3} \text{ mols}$$

$$\text{Moles of Cl}^- = \text{moles AgNO}_3$$

$$= 1.11 \times 10^{-3} \text{ mols}$$

$$\text{Mass of chloride in solution} = \text{moles of Cl}^- \times \text{molar mass of Cl}^-$$

$$= 1.11 \times 10^{-3} \times 35.45$$

$$= 0.0393 \text{ g}$$

$$\text{Mass of Cl in undiluted seawater} = \text{mass of Cl} \times \text{dilution factor}$$

$$= 0.0393 \times 10$$

$$= 0.393 \text{ g}$$

$$\text{Chlorinity} = \frac{0.393}{21} \times 1000$$

$$= 18.7 \text{ ppt}$$

$$\text{Salinity of seawater used} = 1.80655 \times 18.7$$

$$= 33.78 \text{ ppt}$$

In the experiment, 100 ml of seawater was used in every test. 100 ml seawater contains 1.97 g of Cl ions. To neutralise the Cl ions, the above reaction was used to calculate the mass of AgNO₃ required.

$$\text{Mols of Cl} = \frac{\text{mass of Cl}}{\text{Molar mass of Cl}}$$

$$= \frac{1.97}{35.45} = 0.06 \text{ mols}$$

$$\text{But mols of Cl} = \text{mols of AgNO}_3$$

$$\text{mols of AgNO}_3 = 0.06 \text{ mols}$$

$$\text{mass of AgNO}_3 = 0.06 \text{ mols} \times 170 = 9.4 \text{ g}$$

Nitric acid with zeolite test

Table B.2 Trial test using zeolite and nitric acid

time	ZEOLITE X						Calculated Values			
	ratio 0.5:100						Na	K	Mg	Ca
	pH	EC	Na mg/l	K mg/l	Mg mg/l	Ca mg/l				
0	7.66	12.12	14782.40	3304.00	2176.00	993.40	1853.75	67.27	223.01	71.51
15	7.40	10.57	19710.40	3776.00	2496.00	1445.20	1326.12	47.97	159.52	50.70
30	7.93	10.34	13550.40	3145.60	2080.00	1148.00	1247.92	45.15	150.12	47.71
60	7.85	10.07	14320.00	3304.00	2192.00	1198.60	1156.12	41.82	139.07	44.20
90	7.80	10.05	13968.00	3145.60	2128.00	1084.00	1149.32	41.58	138.26	43.94
120	7.76	10.14	13550.40	3145.60	2016.00	1001.80	1179.92	42.69	141.94	45.11
acid +90	6.39	11.64	14628.80	3304.00	2096.00	990.60	1689.92	61.14	203.29	64.61
90 + acid	6.77	13.35	14936.00	3304.00	1968.00	926.80	2849.08	103.07	342.73	108.94
	ZEOLITE Y									
0	7.66	12.12	14782.40	3304.00	2176.00	993.40	1853.75	67.27	223.01	71.51
15	8.12	10.55	14782.40	3304.00	1952.00	916.60	1319.32	47.73	158.71	50.44
30	8.09	10.49	15091.20	3382.40	2080.00	896.60	1298.92	46.99	156.25	49.66
60	8.07	10.44	14859.20	3304.00	2096.00	926.20	1281.92	46.38	154.21	49.01
90	8.12	10.54	14782.40	3304.00	2048.00	905.40	1315.92	47.61	158.30	50.31
120	8.08	10.28	14475.20	3145.60	2032.00	880.20	1227.52	44.41	147.66	46.93
acid + 90	6.36	10.56	13243.20	2832.00	1936.00	809.00	1322.72	47.85	159.12	50.57
90 + acid	7.87	10.47	12473.60	2753.60	1888.00	803.20	1292.12	46.74	155.43	49.40



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Date:

	Na mg/l	K mg/l	Mg mg/l	Ca mg/l
Blank	4872.00	1075.15	1140.63	751.75
X ₁	5540.85	1393.39	787.50	156.75
X ₂	6719.76	1892.26	875.00	108.13
X ₃	4933.51	1789.05	828.13	46.25
X ₄	4222.40	1789.05	856.25	79.88
X ₅	6248.20	1668.63	809.38	95.50
X ₆	5413.34	2580.36	834.38	110.13
Y ₁	8959.68	928.93	1059.38	794.00
Y ₂	5305.07	1221.37	1171.88	721.50
Y ₃	8606.01	1169.76	1193.75	741.38
Y ₄	7780.77	1169.76	1084.38	619.00
Y ₅	4833.51	860.12	1078.13	601.75
Y ₆	4951.40	963.33	962.50	584.75



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	Na mg/l	K mg/l	Mg mg/l	Ca mg/l
Blank	2554.27	92.69	307.28	98.53
X1	2162.40	78.55	260.12	83.32
X2	2468.80	73.35	246.69	78.59
X3	2615.10	72.35	170.03	56.59
X4	2452.20	16.43	101.40	23.71
Blank	2554.27	92.69	307.28	98.53
X5	2795.20	83.36	215.95	69.17
X6	2201.60	70.01	132.52	42.44
X7	2421.60	45.31	80.72	16.24
X8	2472.60	37.17	76.85	18.21



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Date:

	Na mg/l	K mg/l	Mg mg/l	Ca mg/l
Blank	2840.28	103.06	341.688	109.56
Y1	1761.52	63.98	211.9	67.87
Y2	1795.52	65.22	215.99	69.18
Y3	1863.52	67.69	224.17	71.80
Y4	1931.52	70.16	232.35	74.42
Y5	2033.52	73.86	244.62	78.35
Blank	2840.28	103.06	341.69	109.56
Y6	3474.48	126.21	417.96	133.87
Y7	1897.52	68.92	228.26	73.11
Y8	1897.52	68.92	228.26	73.11
Y9	1863.52	67.69	224.17	71.80
Y10	1829.52	66.45	220.08	70.49



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	Na mg/l	K mg/l	Mg mg/l	Ca mg/l
Blank	4782.40	1789.05	828.13	751.75
X1	4320.00	1652.00	730.00	399.50
X2	3968.00	1572.50	709.00	361.00
X3	3550.00	1048.50	672.00	333.94
X4	3541.53	963.30	633.00	179.25
X5	4927.20	943.60	586.80	168.00
Y1	4475.20	1101.33	508.00	220.05
Y2	4859.20	1048.53	512.00	226.25
Y3	3426.04	835.50	547.2	154.00
Y4	3387.20	874.80	537.30	153.25
Y5	3387.20	796.20	486.00	154.75