KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI,

GHANA

Removal of Fluoride from Water Using Surfactant Modified

Synthetic Zeolites

By

Obed Asiedu (BSc Chemistry)

A Thesis Submitted to the Department of Civil Engineering,

College of Engineering,

in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

Water Supply and Environmental Sanitation

MAY 2016

DECLARATION

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

Student:

Obed Asiedu   ……………………….   ………………

(PG 9727513)   Signature   Date

Certified by:

Dr. R. A. Buamah
                                    …………………...   ………………
(Supervisor)   Signature   Date

Certified by:

Prof. Y. A. Tuffour
                                    …………………….   ………………
(Head of Department)   Signature   Date

DEDICATION

For my parents, Mr. and Mrs. Asiedu…again.

More than ever.

ABSTRACT

Although fluoride is beneficial in preventing dental caries, long term consumption of drinking water contaminated with high levels of fluoride (above 1.5 mg/L) could cause teeth mottling. Extreme concentrations may result in severe health conditions such as skeletal fluorosis and even crippling fluorosis. The removal of fluoride from water using synthetic zeolites modified with a cationic surfactant was studied using a batch system. The zeolites employed as adsorbents in the study, zeolite Na-LSX and zeolite Na-LTA, were synthesized from locally available clay materials. A third synthetic zeolite nicknamed zeolite ZR (containing both Na-LSX and Na-LTA phases) was synthesized using only reagent-grade chemicals. Hexadecyltrimethylammonium (HDTMA) bromide surfactant

was used to modify the zeolites in order to improve their fluoride removal potential. The XRay Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX) and Fourier Infrared Spectroscopy (FTIR) techniques used to characterize the zeolites confirmed the surface modification by the HDTMA surfactant molecules. Moreover, the characterization confirmed that the structural integrity of the zeolites remained intact after the surface modification. Varying process conditions including surfactant dosage, modification reaction time and pH of the batch processes were investigated to determine the optimal conditions for fluoride uptake. From the batch experiments, fluoride adsorption was found to be highly pH dependent. Zeolite Na-LSX was found to be the best performing adsorbent at a pH of 5.5. Increase in solution pH from 5.5 to 7.5 significantly reduced fluoride removal efficiency (86 % to 15 %). No appreciable removal was observed above pH of 7.5. The best performing HDTMA surfactant dosage was found to be 5 g surfactant/L for all the zeolite types. Fluoride removal performance of modified zeolites increased with increasing modification reaction time from 2 hours until 24 hours, beyond which performance relatively declined.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CEC	Cation Exchange Capacity
CFC	Chlorofluorocarbon
CMC	Critical Micelle Concentration
CTAB	Cetrimonium bromide
ECEC	External Cation Exchange Capacity
EDX	Energy Dispersive X-ray Analysis
F^-	Fluoride

FTIR	Fourier Transform Infra-red Spectra
HDTMA-Br	Hexadecyltrimethylammonium bromide
IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
IZA	International Zeolite Association
Na-LSX	Sodium Low Silica X
Na-LTA	Sodium Linde Type A
NEERI	National Environment Engineering Research Institute
NO_3^-	Nitrite
NO_{32-}	Nitrate
PO_{43-}	Phosphate
SEM	Scanning Electron Microscopy
Si/Al	Silica Alumina ratio
SMZ	Surfactant Modified Zeolite
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
XRD	X-ray Diffraction
ZR	Reagent only zeolite

ACKNOWLEDGEMENTS

CHAPTER 1:

INTRODUCTION

1.1   Background

The growth of population and the concomitant increase in different industrial and agricultural activities has resulted in the substantial rise of both fresh water consumption and wastewater production. This has led to the contamination of both surface and ground waters. In many developed and developing countries, fresh water demand has already exceeded its supply (UNEP-Nairobi, 2006). In view of this, effective treatment is required in order to produce drinking water of high quality for human consumption.

Fresh water and drinking water contaminated by anionic constituents such as nitrate, nitrite, phosphates, fluoride, arsenates, chromate, sulphate, bicarbonate etc. are a menace to both human health and environmental safety. Fluoride is beneficial in preventing dental caries in smaller concentrations. Meanwhile, prolong consumption of drinking water polluted by excessive concentrations of fluoride (above 1.5 mg/L) may cause teeth mottling. Extreme fluoride concentrations may as well result in severe health conditions such as skeletal fluorosis (3 – 6 mg/L) and crippling fluorosis (above 10 mg/L) (Buamah *et al.*, 2013; Edmunds & Smedley, 1996). According to the WHO, high levels of nitrate levels in drinking water above the acceptable limit of 50 mg/L may cause methemoglobenemia or blue baby syndrome especially in infants. Moreover industrial effluents polluted with nitrate and phosphates cause eutrophication in receiving water bodies. The adverse effect includes: the reduction of aquatic biodiversity (e.g. poisoning of aquatic animals), hindrance to mobility and the decreased aesthetic quality of surface waters (Volterra *et al.*, 2002).

Various conventional removal techniques have been developed to reduce the amount of anionic components from polluted water. Defluoridation techniques refer to the methods of water treatment that reduce the concentration of fluoride in the water in order to make it safe for human consumption. These methods include: adsorption, coagulation, membrane processes, precipitation, electrolytic treatment, ion-exchange etc. Meanwhile, the adsorption process is used predominantly. This is because the adsorption process presents satisfactory results and seems to be a more desirable method in terms of its cost advantage, simplicity of design and operation (Habuda-Stanić *et al.*, 2014). In view of this, several researchers are bent on finding adsorptive materials that are relatively cheaper and have better filter features, more stable, accessible and environmentally friendly.

Since their advent, zeolites have aroused a lot of scientific interest due to their high adsorption and ion-exchange capacities (Gholikandi *et al.*, 2010). Their unique properties have made them useful in a wide range of industrial applications such as adsorbents, ion exchangers, catalysts, and molecular sieves. They have also been found useful in a significant number of water treatment processes such as water softening and purification from toxins, odours, heavy metals, radioactive species, ammonia, dissolved or emulsified organic substances (Shoumkova, 2011). The most common synthetic zeolites used for industrial applications include zeolite A, X, Y, and ZMS-5 (Bogdanov *et al.*, 2009).

Principally, the raw materials used to synthesize zeolites are obtained from silica and alumina sources. These minerals are among the most abundant mineral compounds on earth. The potential to supply raw materials for zeolite synthesis is therefore nearly unlimited (Shoumkova, 2011). Aside rocks, coal fly ash, natural clinker, bauxite, municipal waste incinerated ash, and rice husk ash etc., the kaolin mineral from clays is

predominantly used as the silica and alumina source for zeolite synthesis (Kovo, 2011). This is due to its high content in silica and alumina, which easily dissolve to produce zeolite under hydrothermal and alkaline conditions (Shoumkova, 2011). In view of this, the study employs locally available clays (kaolin mineral) from the Anfoega (Volta Region) and Wassa (Western Region) communities of Ghana to hydrothermally synthesize, respectively, sodium Linde Type A (Na-LTA) and sodium Low Silica X (NaLSX) zeolites.

Uniquely most natural and synthetic zeolites have high selectivity for cations and have therefore found wide applications in water purification, mainly in the uptakee of heavy metal pollutants, ammonia, and radioactive species (Bogdanov *et al.*, 2009; Mehdizadeh *et al.*, 2014). However, the net negative charge on the zeolitic frameworks affords them little or no affinity for anions removal in aqueous solutions (Hrenovic *et al.*, 2010.; Wang & Peng, 2010; Shoumkova, 2011). The residual negative charges consequently repel the negatively charged anions such as fluoride in solution (Mohammadi *et al.*, 2012; Masukume *et al.*, 2010; Srdjan *et al.*, 2012). As a result, applications involving zeolites to remove pollutant anions (e.g. nitrate, nitrite, phosphates, fluoride, arsenates, chromate, bicarbonate etc.) from drinking and waste water only becomes feasible provided that the zeolitic adsorbent receive adequate pretreatment (or modification) to transform the negatively charged surface to a positive surface (Aghaii *et al.*, 2013; Thanos *et al.*, n.d.). According to Wang & Peng (2010), the surface modification of both natural and synthetic zeolites can be achieved through acid treatment, ion exchange, and surfactant modification. The use of cationic surfactants (e.g. hexadecyltrimethylammonium bromide or HDTMA-Br) to modify zeolites in particular, greatly increase the adsorption potency and affinity for anions removal in aqueous solution (Margeta *et al.*, 2013; Wang & Peng, 2010).

Several researchers (including Aghaii *et al.*, 2013; Masukume *et al.*, 2010 etc.) that employed surfactant modified zeolites (SMZs) to immobilize anion pollutants in aqueous media focused on enhancing their adsorption capacities and efficiencies. Therefore, factors that influence anion removal from water including the kind of zeolite employed, modification reaction time, pH, presence of competitive ions, initial concentration of pollutant, temperature, the amount of zeolite and surfactant loading and particle size of zeolite (Margeta *et al.*, 2013; Shoumkova, 2011) are being investigated. Nonetheless, the use of surfactant modified Na-LSX and Na-LTA zeolites to remove fluoride from aqueous solutions under altering process conditions such as varying surfactant load and contact time for modification, and pH have not been extensively investigated. This study seeks to investigate the effects that these varying batch process conditions have on the fluoride removal potential of the modified zeolites.

1.2   Problem Statement

Fluoride is an important micronutrient useful for the calcification of the dental enamel and formation of bones. Low concentration of fluoride (between 0.5 – 1.5 mg/L) in drinking water is beneficial for bone development and prevention of dental caries in humans. However, chronic ingestion of concentrations above 1.5 mg/L have been linked to the development of dental fluorosis and in severe cases (between 3 and 6 mg/L), skeletal fluorosis (Edmunds & Smedley, 1996) in humans. As cited by Buamah *et al*. (2013), protracted consumption of fluoride contaminated drinking water above 10 mg/L may give rise to crippling fluorosis (WHO, 2008).

In the greater parts of the Northern Regions of Ghana, groundwater is largely the major source of freshwater for domestic, livestock and agricultural activities. The incidence of

4

dental fluorosis amongst children has been attributed to the excessive levels of fluoride in their drinking water. In the Bongo district to be specific, a study by Frempong *et al.* (2013) revealed that 63.0 % of children in the Bongo township and less than 10.0 % in its neighboring villages were affected by dental fluorosis. Apambire *et al.*, (1997), Salifu *et al.* (2012) and Buamah *et al*. (2013) found fluoride concentrations ranging between 0.11 and 11.6 mg/L in some groundwater in the Upper Regions of Ghana. A report by the British Geological Survey (2000) revealed that the geologically dominant granite bedrock of the Bongo district and neighboring towns has interspersed Birimian meta-igneous rocks and minerals such as amphiboles, biotites and apatites that contain high concentrations of fluoride and other halides. These fluoride bearing rocks upon weathering reacts with rainfall to seep dissolved fluoride into the ground waters (Smedley *et al.*, 2002).

In order to curb dental fluorosis and the health threats presented by fluoride contamination in such deprived areas, the use of cheap, locally available, environmentally friendly, sustainable and effective treatment techniques cannot be overstated. Indigenous adsorption media such as laterite and wood charcoal have been used to treat fluoride. Nonetheless, the use of synthesized zeolites from locally available clay materials, with high adsorption and ion exchange capacities could serve as a viable alternative to treat fluoride contamination in drinking water.

In Ghana, most industries discharge their effluent wastewater into receiving water bodies without adequate treatment. The problem could be partly attributed to the lack of costeffective treatment techniques (Djaisi & Bulley, 2015; Kagya, 2011). Asare-Donkor *et al.* (2013), Bedu-Addo *et al.* (2013) and Gyasi *et al.* (2014) reported high concentrations of phosphates (3.54 to 30 mg/L of P) at effluent disposal sites of several industries within

the Kumasi and Accra metropolis. Disposal of industrial wastewater contaminated with anionic constituents such as nitrate, nitrite and phosphate are a cause for concern. It has been known that these oxyanions are the main cause of eutrophication in surface waters (Volterra *et al.*, 2002). Their adverse environmental effects include hypoxia whereby oxygen in the water gets depleted. This occurrence may result in the death of aquatic animals and thus decrease biodiversity. Moreover, algal bloom and weed growth reduce the aesthetic value of fresh waters (Volterra *et al.*, 2002). In order to reduce these environmental threats, modified zeolites with high adsorption and ion exchange capacities could be synthesized and applied to treat anions like nitrate and phosphates from industrial effluents before being discharged into receiving water bodies.

1.3   Justification

In developing countries like Ghana, it would be prudent if drinking water and wastewater treatment techniques employ the use of simpler, cost-effective and locally available materials. Zeolites have been reported to possess high adsorption and ion exchange capacities and environmentally friendly (Bowman, 2003; Margeta *et al*., 2013; Shoumkova, 2011). The synthesis of synthetic zeolites from locally available clay materials and their eventual application as defluoridation adsorbents could help curb the potential health hazards posed by fluoride contamination in drinking water. Zeolites could serve as efficient alternative adsorbent materials to defluoridate water and reduce cases of dental and skeletal fluorosis in the Bongo districts of Ghana and beyond. In view of this, an investigation into zeolites synthesis and their application as effective defluoridation materials is of immense importance.

6

Moreover, the ability to apply surfactant modified zeolites to remove other anions such as nitrate and phosphates from industrial wastewater effluents will help reduce algal bloom, weed growth, fish poisoning and restore biodiversity in surface waters.

1.4 Research Objectives

The goal of this research is to investigate the effectiveness of surfactant-modified zeolites to remove contaminant anions from water.

The specific objectives are:

- To synthesize sodium Low Silica X and sodium Linde Type A zeolites from clay and modify the zeolites with HexadecylTrimethylAmmoniumBromide (HDTMA-Br) surfactant

- To characterize the synthesized and modified zeolites

- To determine the fluoride removal potential of the modified zeolites under varying process conditions (surfactant load, contact time and pH) using batch experiments

1.5 Scope of Study

This research employs laboratory scale experiments to investigate fluoride removal capacities of zeolites. Model water was prepared in the laboratory and used to simulate the ground water quality from the Bongo district (Northern region). This water quality data (as shown in Appendix Table A1) was reported by Buamah *et al.* (2013).

The investigation is restricted to the use of only synthesized zeolite sodium Linde Type A (Na-LTA) and sodium Low Silica X (Na-LSX) as defluoridation materials in laboratory scale fluoride removal experiments.

CHAPTER 2:

LITERATURE REVIEW

2.1   Importance of Water

An estimated two-thirds of the arth's surface and some of its subsurface is covered by water. Water is vital to all life forms and its role in the processes and functioning of the Earth's ecosystems is critical (USEPA, 1993).

Water is the common element that links the different ecosystems of the world. The forest environments of the interior mountains link up with the bays and estuaries of the coasts. Water transports food, nutrients as well as biologically essential materials and organisms. Apart from moving, diluting and removing wastes, water cools organisms and the land. This maintains the climatic settings to support and sustain life forms. By way of cooling and movement water provides energy to the ecosystems thus saving the energy that organisms and ecosystems would otherwise need to utilize (USEPA, 1993).

People of all walks of life depend on water to grow food, generate power, cool the machines of industry, carry wastes, and much more. Personally, people use water for bath and clean themselves. Other uses include drinking, cooking, gardening, and recreation. Water also provides habitat for fresh and salt water living resources.

Saltwater forms approximately 97 % of the Earth's oceans and salt lakes. The remaining 3 percent is fresh water locked up in ice caps and glaciers. About a fraction of the fresh water (0.3 %) is accessible, and roughly 98 % of this quantity is stored as groundwater. The rest is water in streams and lakes, stored in the soil, and in the atmosphere (Vandas *et al.,* 2002).

2.2 Water Pollution

Water pollution is any chemical, physical or biological change in the quality of water that either makes it unsuitable for the desired use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Water is polluted or impaired by either anthropogenic activities or natural phenomena. Sources of natural pollution includes: volcanoes, algae blooms, storms, earthquakes etc. In the current era of rapid economic growth, water is getting more polluted due to industrialization in addition to geogenic contamination (Balkis, 2012).

2.2.1 Sources of water pollution

Water pollution is predominantly caused by anthropogenic activities. Various natural sources also add to the pollution of water. Mainly, the sources of water pollution are grouped into either point or nonpoint source. Nonpoint source pollution emanates from many dispersed sources. Nonpoint source pollution is caused by the movement of rainfall or snowmelt over and through the ground. Runoffs from rainfall picks up both natural and human-made pollutants and deposit them into rivers, lakes, coastal waters, wetlands and even underground sources of drinking water (USEPA, n.d.). The United States Environmental Protection Agency (USEPA) reports nonpoint pollutants to include the following:

- Excess fertilizers, insecticides from agricultural lands, herbicides and residential areas
- Grease, oil and toxic chemicals from urban runoff and energy production
- Sediment from poorly managed construction sites, crop and forest lands, and eroding stream banks
- Salt from irrigation practices and acid drainage from deserted mines

10

- Bacteria and nutrients from livestock, pet wastes, and defective septic systems ☐ Pollutants resulting from atmospheric accumulation and hydromodification.

According to the USEPA, nonpoint source pollution is the leading cause of water pollution. The effects of nonpoint source pollutants on specific waters vary and may not always be fully assessed. However, these pollutants have harmful effects on drinking water supplies, recreation, fisheries, and wildlife.

Pollution from point sources implies discrete conveyances for instance pipes or manmade ditches. These include industrial discharges, sewer discharges and oil spills. Industrial wastewater contains (both organic and inorganic) toxic chemicals and metals.

Improper effluent disposal practices by most industries result in contamination of raw water supplies. Several industries that employ large amounts of water for processing have the ability to pollute the waterways. These industries improperly discharge their waste water without adequate pretreatment into receiving streams and rivers. Moreover stored wastes from these industries could seep into nearby water sources. Other sources of water contamination may include deep well injection and improper disposal of wastes in surface impoundments (Olajumoke *et al.*, 2010; Pederson, 1997).

Organic wastes include solvents and cleaning fluids, pesticide residues, dissolved residue from fruit and vegetables, lignin from pulp and paper etc. Industrial effluents may also contain inorganic wastes such as brine salts, fluoride, phosphates, nitrates, nitrites, sulphates, and metals.

2.3   Fluoride Contamination in Water

Fluorine is a common element that occurs as a diatomic gas in its elemental form; has a valence number of 1 and an oxidation state of -1. It is the most electronegative and reactive of all the elements therefore elemental fluorine does not occur in nature but is found as fluoride in mineral complexes (Fordyce *et al.*, 2007; Khandare, 2013). Fluoride compounds are abundant in the earth's crust   . 6-0.09 %) and found in rocks, soils, salt,

and sea water almost all fresh and ground waters at varying concentrations. The geological chemistry of rock types at an area is a major contributory factor to the fluoride concentrations in its groundwater. Volcanic and granite rocks as well as geothermally active areas and tectonically active regions are liable to high fluoride concentrations. Therefore, some rock types present a higher potential risk than others (Khandare, 2013). Fluoride exists in a number of minerals of which fluorite (CaF_2), fluorapatite ($Ca_5F(PO_4)_3$), cryolite (Na_3AlF_6), phosphorite and amphiboles are the most common (Singh & Maheshwari, 2001; Umarani & Ramu, 2014).

Fluoride is one of the known natural contaminants of ground water resources globally (Murugan & Subramanian, 2006). Predominantly, the cause of high fluoride in groundwater is geogenic, being as a result of the dissolution and weathering of the abovenamed fluoride bearing minerals as well as the soil of the earth's crust.

In addition to the natural geological sources for fluoride leachate into groundwaters, several anthropogenic sources also contribute to fluoride pollution to a great extent. Major contributions are from industries that manufacture biocides, fertilizers and aluminum. Aluminium production industries employ inorganic fluorine compounds in most of their synthesis whereas the steel and glass fiber industries utilize these compounds as flux.

Fluorine compounds may get released into the environment during the production of phosphate fertilizer (which contain an average of 3.8 % fluorine), bricks, ceramics, and tiles. The municipal water fluoridation schemes utilizing fluorosilicic acid, sodium fluoride and sodium hexafluorosilicate may pose fluoride contamination threats if not given proper attention (IARC, 1982; IPCS, 2002).

The mechanism of mobilization or the fate of fluoride in the environment has been summarized in Figure 2-1.
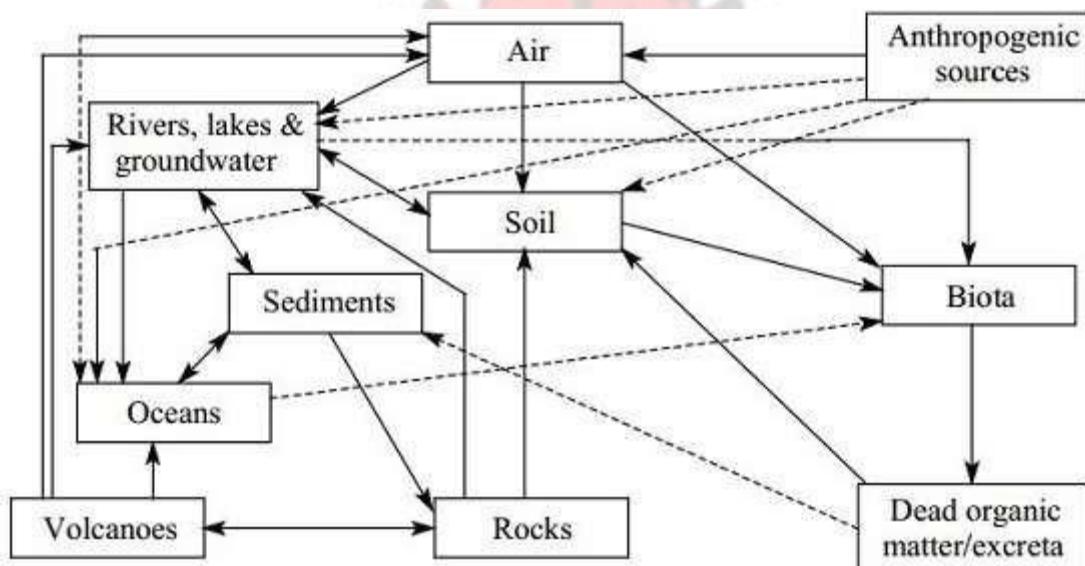
Figure 2–1: Cycling of fluoride through the biogeosphere (IPCS & WHO, 2002)

Contamination from fluoride in drinking water for regions and countries around the world is well documented. The high variability in the fluoride concentrations in the environment is largely due to the presence of certain rock types or minerals or water (Fordyce, 2007; Khandare, 2013, British Geological Survey, 2000). Most notably, the arid parts of northern China, Sri Lanka, India, West Africa (Ghana, Senegal, Ivory

Coast), North Africa (Algeria), South Africa, East African Rift (Kenya, Uganda, Tanzania, Ethiopia), northern Mexico and central Argentina are some of the worst affected areas (see Figure 2–2). High concentrations can also be found locally in many parts of the world (WHO, 2011; Khandare, 2013).

In the northern arid regions of Ghana, a report by the British Geological Survey (2000) revealed that the geologically dominant granite bedrock of the Bongo district and its neighboring towns have interspersed Birimian meta-igneous rocks and minerals such as amphiboles, biotites and apatites that contain high concentrations of fluoride and other halides. These fluoride bearing rocks upon weathering reacts with rainfall to seep dissolved fluoride into the ground waters (Smedley *et al.*, 2002).

Figure 2–2: World map showing regions with high levels of fluoride in the groundwater (Appropedia.org, 2013)

2.4   Factors that affect fluoride concentration in groundwater

The concentration of fluoride in ground water is affected mainly by the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the surrounding temperature, the action of other chemical elements and intensity of weathering. Moreover, pH, solubility of fluorine-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-) and contact time of water with a particular geological formation also play roles (Khandare, 2013).

Even though it has been observed that issues with fluoride tend to occur where the element is most abundant in the host rocks, contact time with the host aquifer and solubility of the main fluoride-bearing mineral fluorite ($CaF2$) are determining factors for the fluoride concentration. Besides, waters that are rich in sodium, potassium and chloride but poor in calcium have a tendency to contain high concentrations of fluoride (Fordyce, 2007). According to Khandare (2013), a high fluoride concentration is often associated with neutral to alkaline pHs, low concentration of calcium but high sodium and bicarbonate concentrations. Aside all the factors given, arid climatic conditions coupled with deep tubewells usually present high concentrations of fluoride in water (British Geological Survey, 2000; Khandare, 2013).

2.5   Route of Fluoride Exposure and Ingestion in Human

Humans are exposed to fluoride through both natural and anthropogenic sources. Thus, fluoride may enter the human body via the inhalation of air, consumption of food and water. However, the main medium by which it enters the body is via drinking water (Fordyce *et al.*, 2007; IPCS & WHO, 2002). Approximately, 80% of ingested fluoride is excreted mainly in the urine. Nonetheless the remainder is assimilated into body tissues and later on

15

released very slowly. The recurrent or continuous exposure to fluoride therefore causes build-up of fluoride in the body. Studies have found that lack of calcium, vitamins and protein in the diet enhances the adverse health effects of fluoride. The absorption of fluoride from water by humans and their dietary calcium intake have also been found to be inversely related. Besides, gastrointestinal fluoride absorption can be reduced by high concentrations of other cations such as magnesium and aluminium that form insoluble complexes with fluoride (Fordyce *et al*., 2007).

2.6   Impact of Fluoride on Human Health

Estimates are not well founded, but more than 200 million people worldwide are thought to be consuming water with fluoride in excess of the WHO recommended value (1.5 mg/L). Most are in developing countries where groundwater is markedly susceptible to fluoride contamination. About half of the 30 countries identified with serious fluoride problems worldwide are from Africa (Smedley *et al*., 2002).

In most instances, studies on fluoride in drinking water have concentrated on its excessive levels (i.e. contamination above the WHO guideline of 1.5 mg fluoride/L concentration). Despite this, fluoride is an essential element in the human diet. Deficiency in fluoride has long been linked to the incidence of dental caries (Smedley *et al.*, 2002) particularly in children. Studies on the post-eruptive stage of tooth formation in children up to 12 years old was thought to accelerate the mineralization and can enter the mineral lattice forming fluorapatite, which is stronger (less soluble) than hydroxylapatite (Fordyce *et al*., 2007). Owing to the slim margin between the beneficial effects of fluoride and the incidence of dental fluorosis, it is imperative to ensure a suitable balance between the two (Fawell *et al.*, 2006).

Figure 2–3: (Left) Child with teeth mottled with fluorosis (Smedley *et al.*, 2002)

(Right) Child with skeletal fluorosis (Appropedia.org, 2013)

It has been documented that both deficiency and excess of fluoride in the human diet can have harmful effects. Yet, it is the excesses that are now of most concern since fluoride deficiencies can be minimized by using fluoridated toothpastes (and water fluoridation as most developed countries practice). Health issues linked with too much fluoride intake have also been extensively reported. According to Fordyce *et al*., (2007), a link between teeth mottling and excess fluoride levels in drinking water was established and proved by Smith *et al.* (1931). Dental fluorosis, as it is called, is an irregular calcification disorder of the enamel-forming cells. Fluoride concentration in excess of 1.5 to 3.0 mg/L has been linked to this condition (WHO, 2011). Dental fluorosis is not life threatening, yet can negatively affect the quality of life as poor dental health threatens social lifestyle. In some developing countries dental fluorosis can affect a woman's ability to marry (Smedley *et al.*, 2002). Several cases of dental fluorosis (Gopal & Ghosh, 1985; IPCS &

WHO, 2002; Frempong *et al.*, 2013, etc.), associated with the consumption of drinking water containing elevated levels of fluoride have been, and continue to be reported. More so, chronic ingestion of fluoride concentrations between 3 to 6 mg/l can lead to skeletal fluorosis; a condition characterized by severe pain and stiffness of the backbone in addition to pain in the joints. As cited by Buamah *et al.*, (2013) and Smedley *et al.* (2002), prolonged consumption of drinking water with levels of fluoride above 10 mg/L may give rise to an even severe condition called crippling fluorosis (see Figure 2–3). In practice, there is no clear cut linkage between the concentrations and observed disease. This varies from region to region and may depend on added factors, particularly climactic conditions, age and nutrition.

2.7   Guidelines and Standards for Fluoride in Drinking Water

The World Health Organization (WHO) (2011) guideline value for fluoride in drinking water is 1.5 mg/L. This recommended value is not fixed but intended to be adapted to take into account the prevailing local conditions (e.g. diet, water consumption etc.). The standard in both China and India is 1 mg/L. In the US where municipal or community fluoridation of drinking water is practiced, the USEPA sets a maximum allowable limit for fluoride in community drinking water at 4 ppm and a secondary limit (i.e., nonenforceable guideline) at 2 ppm (Edmunds & Smedley, 1996; Smedley *et al.*, 2002). Tanzania adopts 4 mg/L as the national standard. This national standard is an improvement from the temporary 8 mg/L standard used before 2009 (Kupaza, 2013). The rather high standard reflected the struggles with compliance in a country with extreme fluoride concentrations (10 – 46 mg/L) and problems with water scarcity (Gumbo & Mkongo, 1995). Ghana adopts

the WHO guideline of 1.5 mg/L as the national standard for drinking water. Table 2-1 shows the guideline values of WHO and some countries.

Table 2–1: Regulations and Guidelines for Fluoride in Drinking Water from a Number of Organizations and Countries

(Edmunds & Smedley, 1996; Smedley *et al.*, 2002)

Organization or country (date)	Name	Fluoride concentration (mg L^{-1})
WHO (1993)	Guideline value	1.5
EU (1998)	Maximum permissible value	1.5
USA (1999)	Secondary (recommended) standard	2
USA (1999)	Maximum contaminant level (MCL)	4
Australia (2012)	Recommended Range	0.6—1.1
Australia (2012)	Maximum value	1.5
Ghana	National standard	1.5
Tanzania (1974)	Temporary national standard	8
Tanzania (2009)	National standard	4
Canada	National standard	1.5
India (1998)	National standard	1
China	National standard	1

2.8   Measuring Fluoride

Ion selective electrode such as fluoride selective electrode is often used in measuring fluoride concentrations in aqueous media. This method provides a reliable way of testing water for fluoride concentrations in the lab. However, fluoride measurements in the field face several challenges. The technique makes it possible to measure total dissolved fluoride in its free and/or bound forms. A lanthanum fluoride crystal (LaF$_6$) fitted inside the electrode detects the difference in electro-potential when in contact with fluoride ions. Several other methods such as the calorimetric tests have been developed to test for fluoride concentrations in the field (Appropedia.org, 2013). Colorimetric methods are susceptible

to interferences from substances such as high concentrations of $CaCO_3$, aluminium (Al^{3+}), chloride (Cl^-), turbidity, colour, (Fe^{3+}), hexamethaphosphate ($NaPO_3)_6$, phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}) in the sample. Though the calorimetric methods are not as accurate as the electrode tests, they are helpful in evaluating if a body of water is safe for consumption (Brossok *et al.*, 1987).

2.9   Defluoridation Techniques

Defluoridation techniques refer to methods of water treatment that reduce the concentration of fluoride in the water in order to make it safe for human consumption. Two options are available: (a) the central treatment of water at source and (b) the treatment of water at the point of use (i.e. at the household level). Developed countries usually adopt treatment at the source. This involves large scale defluoridation schemes whereby skilled personnel supervise at treatment head works. Decentralized level treatment is usually adopted at the community, village or household level (Lyengar, 2002).

Generally, defluoridation techniques fall under the following categories: precipitation and coagulation, ion-exchange, membrane separation (reverse osmosis), electrodialysis and adsorption (Bhatnagar, Kumar, & Sillanpää, 2011; Habuda-Stanić *et al.*, 2014; Meenakshi & Maheshwari, 2006; Renuka & Pushpanji, 2013). Table 2-2 shows the advantages and disadvantages of the various techniques employed in fluoride removal.

2.9.1   Ion-exchange

The use of ion-exchange to remove fluoride from water involves the application of a synthetic anion exchange resin. During the process, the fluoride contaminated water is

made to pass through the resins packed in a column. The fluoride removal uptake proceeds according to the following reaction:

$$Matrix\text{-}NR_3{}^+Cl^- + F^- \rightarrow Matrix\text{-}NR_3{}^+F^- + Cl^-$$
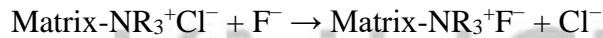
Where: $-NR_3{}^+$ is the ion exchange group, Cl^- is the chloride exchangeable ion and F^- is the fluoride ion.

The fluoride (F^-) in the water substitutes the chloride (Cl^-) in the resins and the defluoridated water is received at an outlet. The process proceeds until all the free sites on the resin are occupied. The fluoride saturated resin could then be regenerated for reuse by backwashing with dissolved supersaturated sodium chloride salt solution (Khandare, 2013; Meenakshi & Maheshwari, 2006).

2.9.2 Membrane separation (RO & Electrodialysis)

In the physical RO process, pressure is applied on the feed water to force it through a semipermeable membrane leaving the fluoride contaminated salts behind. The pressure applied on the membrane is relative to the size of the pollutants left behind (Renuka & Pushpanji, 2013).

Electrodialysis is an electrochemical separation process whereby ions are separated via a semipermeable membrane by applying a potential gradient. The electrical charges on the fluoride ions allow them to be driven through the membranes fabricated from ion exchange polymers. The membranes used in electrodialysis for fluoride treatment have the potential to selectively transport the negatively charged fluoride ions and reject opposite ions ―lectrodialysis ‖ n.d. .

RO and electrodialysis are very efficient; however, their expensive cost amongst others renders them inappropriate for use in developing countries (Renuka & Pushpanji, 2013; Meenakshi & Maheshwari, 2006).

2.9.3 Precipitation and coagulation technique

Precipitation methods employ the addition of coagulant and coagulant aids to precipitate sparingly soluble salts of fluoride as fluorapatite. A well-known defluoridation technique that uses this method is the Nalgonda technique.

The Nalgonda technique is widely used for defluoridation of water in developing countries such as India, Kenya, Senegal, Tanzania and rural China (Bhatnagar *et al.*, 2011; Lyengar, 2002) at both domestic and community levels (Lyengar, 2002). This technique was developed by the National Environmental Engineering Research Institute

(NEERI) in India (1975) in response to fluorosis concerns in the endemic village of Nalgonda and its surrounding areas (Suneetha *et al.*, 2008; Appropedia.org, 2013).

During the process, prescribed quantities of lime, alum and bleaching powder are added to the raw water, followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection (Lyengar, 2002). Lime and alum are the most commonly used coagulants. Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride. The formation of fluoride precipitate follows this reaction:

$$Ca(OH)_2 + 2F^- \rightarrow aF_2 + 2OH^-$$
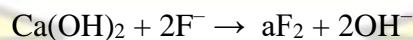
The ensuing step involves the addition of alum that causes coagulation. The addition of bleaching powder also ensures disinfection during the process (Bhatnagar *et al*., 2011; Gopal & Ghosh, 1985; Meenakshi & Maheshwari, 2006; Renuka & Pushpanji, 2013).

The drawbacks of this technique (as given in Table 2-2) have also been reported by few researchers to include: e.g. high residual aluminium and sulfate concentration; requiring regular attendant for chemical dosing; producing large volume of sludge etc.

Table 2–2: Comparison of fluoride removal technologies (Habuda-Stanić *et al.*, 2014)

Technology	Advantages	Disadvantages
Coagulation/precipitation: *calcium hydroxide; aluminum hydroxide*	High efficiency; commercially available chemical	Expensive, efficiency depends of pH and presence of co-ions in water, adjustment and readjustment of pH is required, elevated residual aluminum concentration, formation of sludge with high amount of toxic aluminum fluoride complex and high amount of retained water (sludge dewatering is required prior disposal)
Membrane filtration: *reverse osmosis; nanofiltration*	High efficiency; remove other contaminates	High capital high running and maintenance costs toxic waste water produced
Electrochemical treatments: *dialysis; electro-dialysis; electro-coagulation*	High efficiency; high selectivity	High cost during installation and maintenance
Ion-exchange: *Strong basic anion-exchange resin with quaternary ammonium functional groups*	High efficiency	Expensive, vulnerable to interfering ions (sulfate, phosphate, chloride, bicarbonate, *etc.*), replacement of media after multiple regenerations, used media present toxic solid waste, regeneration creates toxic liquid waste, efficiency highly pH-dependent
Adsorptive materials: *activated alumina; activated carbons; other natural and synthetic adsorbents*	Greater accessibility, low cost, simple operation, availability of wide range of adsorbents	High efficiency often demand adjustment and readjustment of pH, some common water ions can interfere fluoride adsorption

2.10 Fluoride Removal by Adsorption

Adsorption process occurs when a liquid or gas solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). The adsorbates are held there by weak intermolecular forces (Habuda-Stanić *et al.*, 2014; Varadan, 2010).

Adsorption is one important technique in fluoride removal from aqueous solutions. The adsorption methods utilize the passage of the fluoride containing water through a contact

bed. However, the viability of adsorption techniques is greatly dependent on the quality and development of adsorptive materials (Smittakorn *et al.,* 2010). Adsorption process for fluoride uptake has been explored widely and offers satisfactory results especially with mineral-based and/or surface modified adsorbents. Moreover, it seems to be a more attractive method for the removal of fluoride in terms of cost, simplicity of design and operation (Bhatnagar *et al.*, 2011).

A wide variety of both conventional and non-conventional adsorbent materials have been tested in the past to find out an efficient and economical defluoridating agent. Activated carbons, activated alumina, activated aluminum coated silica gel, bauxite, calcite, fly ash, bone charcoal, brick powder, red soil, laterite, pumice stone, red mud etc. have been reported. Moreover, plant materials such as seed extracts of *Moringa oleifera*, Tamarind seeds, serpentine, activated rice husk etc. have also been reported in literature. Other natural and synthetic materials have also been tested to remove fluoride from water: zeolites, chitin and chitosan derivatives, algal and fungal biomass (Bhatnagar *et al.*, 2011; Habuda-Stanić *et al.*, 2014; Lyengar, 2002; Renuka & Pushpanji, 2013; Sajidu, Masamba, Thole, & Mwatseteza, 2008; Singh & Maheshwari, 2001). However according to Habuda-Stanić *et al.* (2014), Meenakshi & Maheshwari (2006) and Renuka & Pushpanji (2013), the most commonly used and highly tested adsorbents were activated alumina, activated carbon and bone char.

2.10.1 Activated alumina, activated carbon and bone char

Activated alumina is an adsorbent of aluminium oxide (Al_2O_3) prepared from the calcination or dehydration (300-600°C) of aluminium hydroxides. The adsorption process works best at narrow pH of 5 to 6. Activated alumina can remove fluoride up to 90 %.

24

Therefore it is being publicized in several rural areas by volunteer organizations funded by UNICEF or other support agencies to offer safe drinking water (Meenakshi & Maheshwari, 2006).

Though activated alumina is an efficient adsorbent for fluoride removal from drinking water, it has limited regeneration capacity and slow rate of adsorption. Hence, modified activated alumina has been tested to increase its adsorption rate (Rafique *et al.*, 2013).

According to Meenakshi & Maheshwari (2006), the use of activated carbon (activated charcoal) to remove fluoride was first investigated by Mckee and Johnston (1934). Their research reported good results achieved by powdered activated carbon. Bandewar *et al.* (2015) and Poudyal & Babel (2015) also demonstrated the successful use of activated charcoal for fluoride uptake using fixed bed studies. Activated carbon has therefore become very common adsorbent for defluoridation because of its high surface area and high adsorption capacity. Nonetheless, it is expensive and necessitates frequent regeneration (Apreutesei *et al.*, 2008).

The use of bone char to defluoridate fluoride from water has been reported to be effective. Smittakorn *et al.,* (2010) reports removal of fluoride by adsorption onto bone char to have been used successfully in several countries, including India and Tanzania. Bone char comprises of ground animal bones that have been charred using calcination or pyrolysis to eliminate all organic matter. The major constituents of bone charcoal are calcium phosphate, calcium carbonate and activated carbon. The technique normally involves passing the contaminated water through a bone char packed column. The fluoride removal mechanism involves the substitution of carbonate of the bone char by fluoride ion in solution (Lyengar, 2002).

The use of bone char for water treatment comes with several limitations. Renuka & Pushpanji (2013) reported that bone char harbors bacteria and hence becomes unhygienic. Again, it is a sensitive techniques that requires much attention during charring and water treatment process. Moreover, the use of bone char may invite cultural and religious objections.

2.10.2 Natural adsorbents

Various naturally occurring materials have been investigated as adsorbents for the removal of fluoride from water. Clay minerals have a special position among the natural and low-cost adsorbents (Worch, 2012). Fired or calcined brick pieces and mud pot from soils and clays, respectively, have been reported to be effective filters for fluoride removal. The soils and clays used in the manufacture contain aluminium oxide (Al_2O_3). During burning operation in the kiln, they get activated and adsorb excess fluoride when raw water is passed through (Renuka & Pushpanji, 2013).

Other low-cost natural adsorbents such as coal based sorbents, bauxite waste, raw laterite, montmorillonite, bentonite clay, zeolites etc. have been evaluated and used for the defluoridation of aqueous solutions (Bhatnagar *et al.*, 2011; Sajidu *et al.*, 2008; Sujana & Anand, 2011; Worch, 2012). Bhatnagar *et al.* (2011) further reports biosorbents such as chitin and chitosan-derivatives as emerging techniques for water treatment.

2.11   Other Anionic Pollutants in Water (NO_3^{2-}, NO_2^-, PO_4^{3-})

It has been known that the oxyanions; nitrates, nitrites and phosphates are the main cause of eutrophication in surface waters. These anions may pose the following detrimental effects to the environment: hypoxia or the exhaustion of oxygen in the water, which may

kill aquatic animals, decrease biodiversity and aesthetic value of fresh waters (Volterra *et al.*, 2002).

Nitrate and nitrite occur naturally as ions forming part of the nitrogen cycle. The level of nitrate is found to be normally low in surface and ground water. Meanwhile nitrate concentrations in agricultural and industrial wastewaters are often characterized by very high concentrations, which could cause human health threats and eutrophication. According to WHO, (2011) high concentrations of nitrite and nitrate (well above the guideline values of 3 mg/L and 50 mg/L respectively) in drinking water are the major cause of a condition called methaemoglobinaemia or blue baby syndrome in infants. High levels of nitrate and nitrite have also been linked to cause cyanosis and, at higher concentrations, asphyxia in humans. As cited by WHO (2011), the United States National Research Council found some suggestion of an association between high nitrate intake and gastric and/or oesophageal cancer (NAS, 1981) however no convincing evidence was found due to the inadequacy of the data available.

In Ghana, most industries discharge their wastewater directly into water bodies without pre-treatment (Djaisi & Bulley, 2015; Kagya, 2011). Kagya (2011) attributed this problem to the lack of cost-effective wastewater treatment techniques. Therefore, the need to treat industrial effluents to acceptable standards with simpler and cost-effective treatment techniques cannot be overstated especially for a developing country like Ghana. The guideline values for effluent discharge into receiving waters is 50 mg/L and 2.0 mg/L P for nitrate and phosphates respectively (E.P.A. Ghana, 2000). Nitrite is also pegged at 3.0 mg/L by WHO. In their works, Asare-Donkor *et al*., (2013) found high concentrations of phosphates (5.2 to 30 mg/L) at sampling points of streams close to industries within the

Kumasi Metropolis. Bedu-Addo *et al.,* (2013) and Gyasi *et al.* (2014) also recorded high levels of phosphate (3.54 to 27.3 mg/L) in wastewater effluents of two breweries within the same metropolis.

Chemical analysis on wastewater effluents of some industries in the Kumasi Metropolis discharging directly into surface waters contained high concentrations of nitrate and phosphate. Levels of these anionic pollutants generally exceeded the limits set by the Ghana nvironmental Protection Agency's Guidelines for effluent disposal. Gyasi *et al.* (2014) found high levels of phosphate (11.11 to 27.3±0.1 mg/L) in the effluent of a brewery company that discharges into the Sisa stream. Bedu-Addo *et al.* (2013) also reported 3.54 ± 0.79 mg/L of phosphate above the limit (2 mg/L) set by the Ghana EPA for industrial discharge into surface waters. Moreover, chemical analysis by AsareDonkor *et al.* (2013) on four major rivers (Wiwi, Sisa, Oda and Subin) at sampling points close to industries in the Kumasi Metropolis also recorded high levels of phosphate ranging between 5.2 ± 0.065 to 30 ± 1.53 mg/L. Among other reasons, the high levels of phosphates and nitrate were mostly attributed to the lack of cost-effective wastewater treatment technologies in the industries. Thus, pollutants could not be treated to acceptable levels before discharge into receiving water bodies.

2.12   Zeolites

Zeolites are microporous crystalline solid structures made of silicon, aluminum and oxygen that form a framework with cavities and channels. Cations, water and/or small molecules may reside within these cavities and channels (Bell, 2001). Principally, the alkali or alkaline earth metal cations usually attached to the zeolite structure are sodium, potassium, magnesium, lithium, barium and calcium (Davis & Inoguchi, 2013).

The Swedish mineralogist Axel Fredrick Cronstedt is given the honour to have discovered stilbite in 1756. He observed that a large amount of steam was obtained upon heating. Therefore this material was named ―zeolite‖ which stems from classical Greek where ζεω zeo means ―to boil‖ and λἰθος lithos means ―stone‖ (Kulprathipanja, 2010).

The structure of zeolites can be denoted by this general chemical formula:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O$$

Where n represents the charge of the exchangeable cation M, and the values of x, y and z depend on the type of zeolite. The total number of tetrahedra in a unit cell is the sum of x and y (Georgiev *et al.,* 2009; Kulprathipanja, 2010; Shoumkova, 2011).

2.12.1 Structure

The aluminosilicate crystals of zeolites consist of an open and complex three dimensional framework structures built of SiO_4 and AlO_4 tetrahedra interconnected to each other by sharing all the O atoms to form ordered intra-crystalline spaces and channels of molecular dimensions (see Figure 2–4). This framework coordination is a characteristic feature of zeolites (Bell, 2001). The tetrahedra are connected together at their corners to give a rich mixture of beautiful uniform structures. The framework structure may contain connected cages, voids or channels, which are big enough to allow small molecules to enter with pore sizes varying between 4-12 Å. The large cavities justifies the consistent low specific density of these compounds (Bell, 2001; Peskov, 2010).

Figure 2– 4: (a) Chemical structure of zeolite unit and (b) Primary building unit of zeolite structure (Bogdanov *et al.*, 2009)
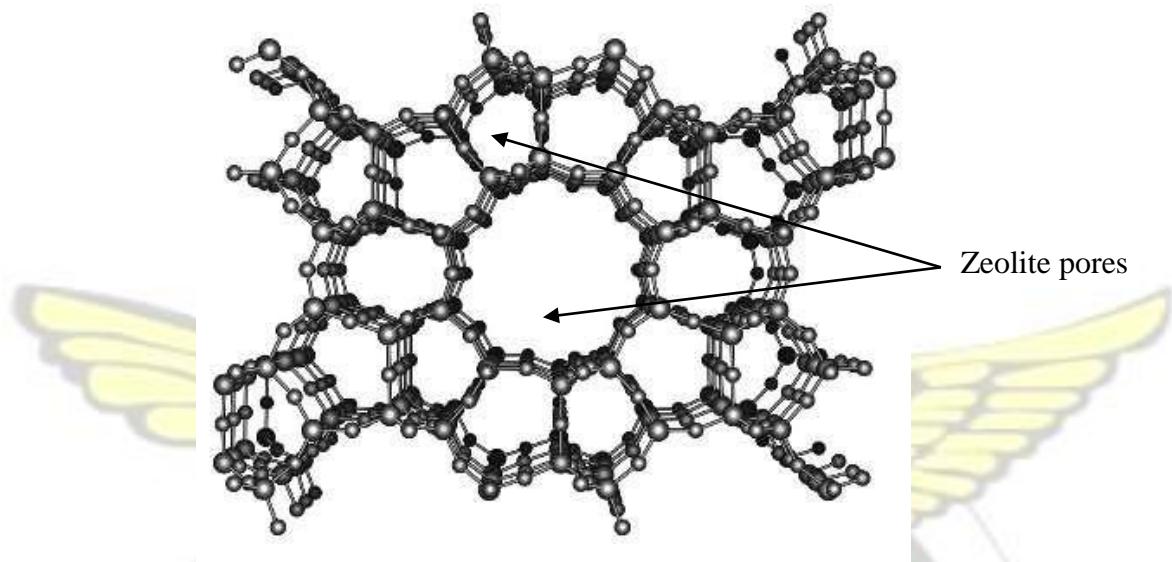
Figure 2–5: The framework structure of ZSM-5 MFI zeolite (Falcioni & Deem, 1999)

The very regular structure and pore sizes give zeolites a sponge-like appearance (as seen in Figure 2–5). 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 important role in the use of zeolites: permitting or prohibiting the entrance of the molecules to the system (Von-Kiti, 2012).

2.12.2 Sources and synthesis

Many zeolites occur naturally as minerals where they are extensively mined in many parts of the world. These zeolites are found in many applications in industry and medicine. However, most zeolites are produced synthetically from natural minerals (e.g. kaolin, bauxite, illite, smectite, bentonite etc.) and chemical reagents (e.g. sodium aluminate and sodium metasilicate). Waste materials such as coal fly ash, municipal incinerated ash and rice husk ash have also been used to synthesize zeolites (Shoumkova, 2011). These have found their use commercially while others are created by scientists to purposefully study their chemistry. According to Kulprathipanja (2010), the annual market for synthetic zeolites and molecular sieves had grown to 1.8×10^6 tons worldwide in 2008.

Zeolites are largely obtained by hydrothermal synthesis. The process involves the use of water as the solvent, a silicon source, an aluminum source, a mineralizing agent and a structure-directing agent in the presence of cations and basic environment (RoqueMalherbe, 2009). Crystallization usually occurs at high temperatures and at periods differing from few hours to a number of days. During the hydrothermal treatment, the purity, type and composition of zeolites produced are affected by several process conditions. Such conditions include the nature and pretreatments of the reactants, composition of the reaction mixture (Si/Al ratio, presence of seeds or templates, pH of the system), pre-reaction seeding, pressure, heating regime, hydrodynamic conditions, preliminary or post-heating ageing etc. (Shoumkova, 2011). A simplified synthesis route used in this researched is as shown in Figure 2–6.

```
┌─────────────────┐        ┌─────────────────┐
│  Alumina source │ ◄─────► │  Silica source  │
└─────────────────┘        └─────────────────┘
         │                          │
         ▼                          ▼
         ┌──────────────────────────┐
         │      Crystallization     │
         └──────────────────────────┘
                     │      │
                     ▼      ▼
         ┌──────────────────────────┐
         │        Quenching         │
         └──────────────────────────┘
                     │      │
                     ▼      ▼
         ┌──────────────────────────┐
         │        Filtration        │
         └──────────────────────────┘
                     │      │
                     ▼      ▼
         ┌──────────────────────────┐
         │          Drying          │
         └──────────────────────────┘
                     │      │
                     ▼      ▼
         ┌──────────────────────────┐
         │     Crushing/Grinding    │
         └──────────────────────────┘
                     │      │
                     ▼      ▼
         ┌──────────────────────────┐
         │      Zeolite powder      │
         └──────────────────────────┘
```
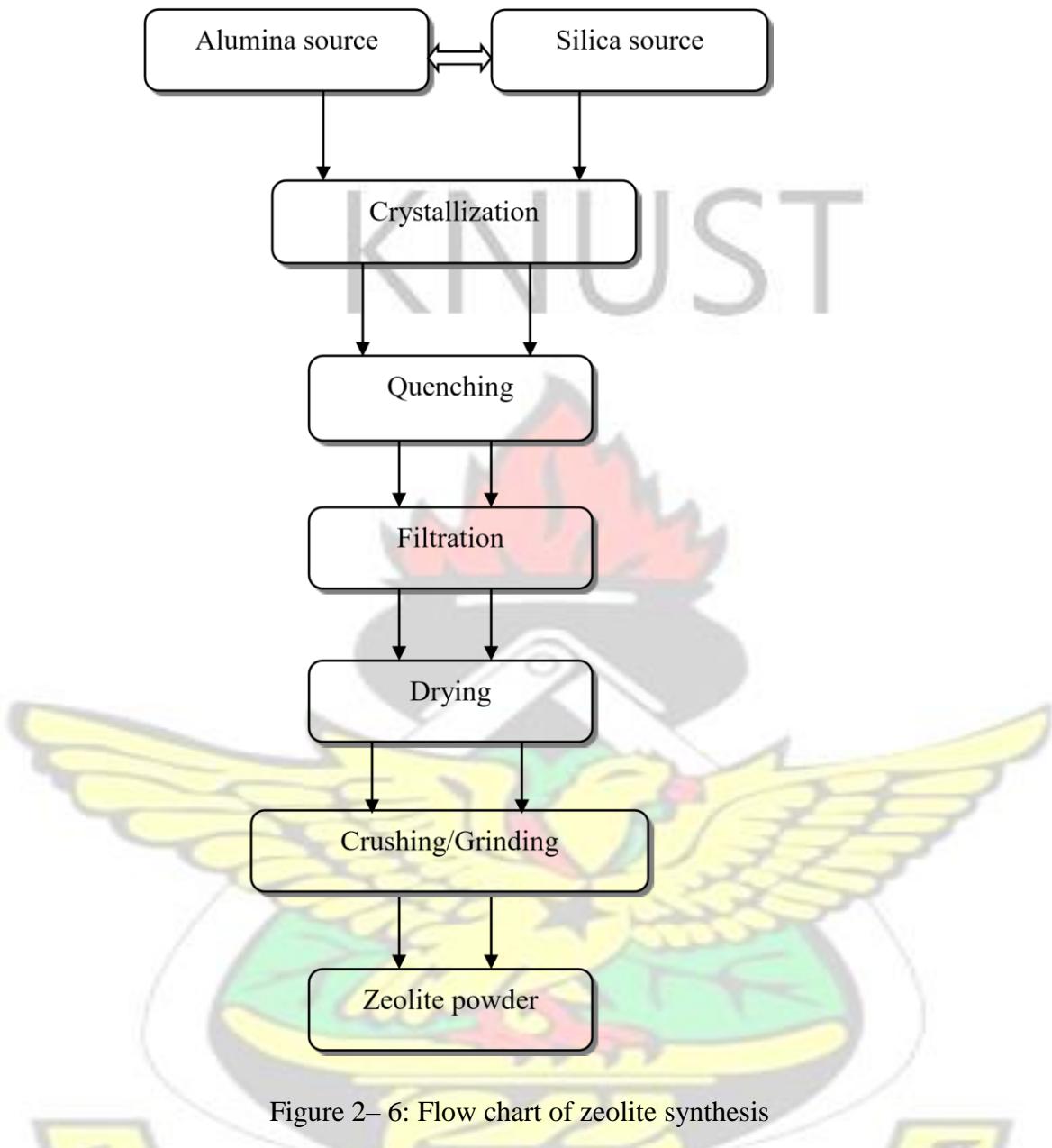
Figure 2– 6: Flow chart of zeolite synthesis

Presently, about 225 unique framework types of zeolites have been identified with over 60 naturally occurring zeolite frameworks. The most common synthetic zeolites used in industrial applications are zeolite X, A, Y, P and ZMS-5. Some naturally occurring zeolites are: analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumonite, mordenite, and phillipsite.

Zeolites could be synthetically produced in forms appropriate for industrial applications and hence are of great importance. The Swedish mineralogist, Cronstedt, first discovered the natural zeolite in 1756. However, the first synthesis was attempted by St. Claire-Deville in 86 . arrer's ground-breaking work in 1940s proved that a wide range of zeolites could be synthesized from aluminosilicate gels (Ríos *et al.,* 2007). Depending on the Si/Al ratio used, zeolites with different properties and structures could be synthesized to perform a needed function. Hence zeolites have found uses in applications such as petrochemical cracking, wastewater treatment, water softening and purification, and agriculture (Von-Kiti, 2012).

Synthetic zeolites have pure crystal products and uniform particle sizes. Due to this, synthetic zeolites are used commercially more often than natural zeolites (Georgiev *et al.* 2009). However, the hydrothermal synthesis of synthetic zeolites from reagent sources of silica and alumina is expensive. Cost limitations can therefore be overcome using low cost materials for zeolite synthesis, such as clay minerals (kaolin), natural clinker, volcanic glasses (perlite and pumice), rice husks, diatoms, fly or paper sludge ash as starting materials. Other zeolites has also been synthesized via the transformation of one zeolite type into other zeotypes (Ríos, 2008; Shoumkova, 2011)

2.12.3 Kaolin

Kaolin is the primary clay mineral material present in the kaolinite mineral group. More significantly kaolin is viewed industrially as a term that means clays which are composed chiefly of minerals called kaolinite and are amenable to property variation making them beneficial in the production of series of industrial products.

Impurities such as quartz, feldspar, and iron are usually found with clay minerals. Nonetheless, they do not exhibit plasticity and hence are non-clay or accessory minerals (Manning, 2007). This associated mineral requires removal or reduction because it generally reduces the commercial value of the clay mineral hence the need for purification before usage. Kaolinite is a dioctahedral 1:1 layered clay mineral with a general chemical composition of $Al_2Si_2O_5(OH)_4$ (Kovo, 2011).

Raw kaolin and reactive metakaolin have been reported to be the most frequent sources of alumina and silica for the synthesis of zeolite Linde Type Y, P, A, X, 4A, NaA, chabazite, faujasite and several other types of zeolites with modifications to its chemical composition, temperature variations and addition of extra silica. Kaolin contains high contents of aluminium and silicon which easily dissolve during the hydrothermal synthesis to form zeolite in high alkaline solutions (Kovo, 2011). The hydrothermal treatment methods employed in zeolite formation usually involves appropriate pretreatments processes such as grinding, acid washing, calcination and fusion with additives of the starting materials. These are rather high energy consuming processes (Shoumkova, 2011).

2.12.4 Zeolite characterization techniques

Generally the characterization of a zeolite provides information about the zeolite structure and morphology, the chemical composition, the ability to adsorb and retain molecules and the ability to chemically convert these molecules (Ríos, 2008). In order to derive a relationship between the chemical and physicochemical properties of zeolites on one side, and the adsorptive and catalytic properties on the other, information on the structural, chemical and catalytic characteristics of zeolites are essential. Such relations are of high

significance, since they allow the rational development of adsorbents, catalyst and advanced structural materials (Adzabe, 2011).

Several techniques have been employed to characterize the zeolite phases. The most commonly used techniques include: energy dispersive x-ray spectroscopy (EDX), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), the Fourier transform infrared spectroscopy (FTIR) and the thermogravimetric analysis (TGA). Other methods include: the Rietvield technique of structure refinement, neutron scattering, nuclear magnetic resonance (NMR), Raman, measurement of sorptive capacity, particle size and pore size distribution.

2.12.4.1 X-ray diffraction (XRD)

XRD is an important and definitive characterization tool widely utilized to elucidate the structure of synthesised zeolites and other crystalline samples. It is a test used to confirm the structural characteristics of a synthesised specimen. This gives a distinctive fingerprint of the samples under study (Kovo, 2011). The XRD technique also determines the symmetry, the unit cell dimensions as well as any crystalline impurities that may be present. In some cases, the full structure of crystalline powders can be determined. Information provided by XRD can be used for phase identification of known phases by comparing them to a database of previously indexed patterns maintained by the International Centre for Diffraction Data (ICDD).

XRD measurements use uKα radiations to determine zeolite crystallinity and also phase identification (Von-Kiti, 2012).

The X-ray diffraction technique is based on ragg's law which is given as:

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

Where: n is the order of reflection λ is the

wavelength of the incident X-rays d is

the lattice spacing and θ is the angle of

incidence

2.12.4.2 Energy dispersive x-ray spectroscopy (EDX)

EDX technique is used for local elemental identification of small objects or surfaces. Most EDX equipment is fitted to scanning electron microscopes (SEMs).

In its operation, an x-ray produced by a sample in an electric beam is detected. The electric beam excites the atoms in the sample to produce x-rays to discharge the excess energy. The energy of the x-ray is typical of the atoms that produced them, creating peaks in the spectrum and thus allowing the chemical composition of the sample to be established. Individual elements may have one or more peaks associated with them (VonKiti, 2012; Adzabe, 2011).

2.12.4.3 Fourier transform infrared spectroscopy (FTIR)

FTIR method can be useful in finding important information about the structure, channel size and cation exchange in the tetrahedral sites of the zeolite minerals   ansever rdo an . The FTIR measures vibrations caused by internal stretching of the framework tetrahedra and vibrations related to the external linkages between the tetrahedral (Von-Kiti, 2012).

The principle of FTIR used in this study is based on the principle of diffuse reflectance whereby an incident light from a source radiation is scattered in all directions. During the

process, a beam splitter splits the beam into two parts, one to the static mirror and the other to the moving mirror. Henceforth, an incident beams emits a spectra of both absorbance and reflectance features. The radiations passing through the sample are recorded by a detector.

The recorder is previously calibrated to be able to convert the radiation into energy. The energy is finally presented as a function of frequency (Bright Kwakye-Awuah, 2008; Labik, 2012)

2.12.4.4 Scanning electron microscopy (SEM)

SEM is a basic technique used to study the microstructural characteristics of solid materials including kaolin, zeolites and zeolite membranes. According to Kovo (2011) the use of SEM to image materials is principally due to its high resolution, with values in the order of 25 to 50 Å. It employs a beam of electrons instead of photons to provide higher magnifications.

The operating principle of the components of SEM is rather complex. A description of the major components and their functions are given. It 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 beam of electrons travels at high voltage from the filament. The electron lenses regulate the size of the beam leaving. Scan coils make the beam scan over the sample or target. The electrons hit the target and 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 comes out black (Ohrman, 2000; Von-Kiti, 2012).

2.12.5 Applications of zeolites

Zeolites are important materials widely used as adsorbents, catalysts (petrochemical cracking) and ion exchangers (water softening and wastewater treatment). Zeolites are depicted by their ability to lose and absorb water without destruction to their crystal structures (Gholikandi *et al.,* 2010). Their use in numerous environmental applications is becoming increasingly important due to their unique adsorption, ion exchange and porous properties. There is a growing interest for their use in water purification, mostly for the treatment of ammonia, heavy metals, radioactive species and organic substances. Other applications are in agriculture, animal husbandry and constructions (Apreutesei *et al.*, 2008).

2.12.5.1 Zeolites as ion exchangers

Zeolite frameworks provide substrates that support the mobility of the non-framework cations. This makes them good ion exchangers. Zeolites have been reported to be excellent materials for the removal of cationic pollutants such as NH_4^+, Cr^{6+} and As^{5+} Cu^{2+}, Pb^{2+} and Cd^{2+}, Fe^{3+} and Zn^{2+}, Sr^{2+} (Bogdanov *et al*., 2009).

Zeolite A (and recently type P) is predominantly used in detergent applications as ion exchangers. The detergency application constitutes the largest single market by volume (72%) for zeolites (Kulprathipanja, 2010). During detergency, zeolite A (LTA) acts as a water softener in laundry detergents preventing carbonate precipitation through the exchange of calcium and magnesium ions with the highly mobile sodium ion found in the zeolite framework. The increased application of zeolites in the detergent industry can be attributed to environmental concern. The use of phosphate builder has been banned in most

countries because it causes eutrophication and is difficult to degrade when placed in water bodies. However, zeolites (especially zeolites A and X) offer a good replacement because of their high ion exchanging capacities (Kovo, 2010).

In desalination processes, zeolites remove dissolved minerals from seawater, brackish water or treated waste water. A lot of recent experimental investigations have geared towards improving the capacity and potential of zeolites to desalinate seawater. This has been necessary due to the world's permanent growing need for fresh clean water. The desalination technique employs sodium zeolite softener whereby scale-forming calcium and magnesium ions are replaced with sodium ions (Von-Kiti, 2012).

2.12.5.2 Zeolite catalysis

Zeolites are exceptionally useful catalysts for several important organic molecular reactions.

Zeolite NaX and NaY have long been used in the petroleum industries as catalysts for cracking reactions of hydrocarbon conversion. They are involved in other organic reactions such as alkylation, isomerization, shape selective reforming, hydrogenation and dehydrogenation, methanol-to-gasoline conversion (MTG), etc. (Bogdanov, 2009).

Zeolites can stimulate a diverse range of catalytic reactions including acid-base and metal induced reactions (Win, 2012). During catalytic reactions zeolites molecules react in the inner pore volumes allowing for a greater degree of product control. Hence zeolites exhibit exceptional properties with respect to both activity and selectivity compared to other types of catalysts (Donk, 2002; Win, 2012).

2.12.5.3 Adsorption properties of zeolites

Zeolites have been used in gas purification and separation as redox catalysts and sorbents to remove atmospheric pollutants. Such pollutants include engine exhaust gases and ozone-depleting CFCs. Gas sweetening processes employ zeolites to purify the natural from the acid gases such as carbon dioxide and hydrogen sulfide. Besides their usage in upgrading natural gas, zeolites are used to separate oxygen and nitrogen in pressure swing adsorption columns (Shimekit & Mukhtar, 2012).

Zeolites have been used as solar thermal collectors and for adsorption refrigeration in heating and refrigeration applications. Their ability to withstand high temperatures coupled with the ability to hydrate and dehydrate while maintaining the structural stability is highly exploited in industrial applications. This hygroscopic property along with an inherent exothermic reaction, while transitioning from dehydrated to a hydrated form; make the natural zeolites effective in the storage of solar and the waste heat energy (Kreussler & Bolz, 1999).

In medicine, zeolite-based oxygen generation systems are used in producing medical grade oxygen. Zeolites have been used as molecular sieves for extracting oxygen from air in a process which involves adsorption of atmospheric nitrogen. Moreover, zeolite technology is also being explored to enhance quick clotting of severe bleeding (Virta, 2008)

Zeolites and zeolitic tufts have also been used to clean up low and intermediate-level liquid nuclear waste. As cited by Bowman (2003) clinoptilolites have been used to decontaminate cationic radioactive species (137Cs, 90Sr) from nuclear plant wastewaters and contaminated ground waters. Zeolites easily react with cement and glass systems thus allowing the radioactive waste to be captured and contained safely. Bowman (2003) also

posts that zeolites are less costly (compared to organic ion exchange resins), robust and resistant to nuclear degradation.

Clinoptilolite is a naturally occurring zeolite that can be applied in agriculture for soil treatment. It has been used to provide a source of slowly releasing potassium into soil. In a similar instance, previously loaded ammonium zeolites can also be used to slowly release nitrogen.

In closed aquacultural systems, a few ppm NH_4^+ can lead to gill damage and substantial reduction in growth rates of fishes. Zeolites technology has been employed in fish/prawn ponds and tanks to reduce ammonia levels and thus provide oxygen-enriched air for fish breeding. The use of low cost zeolites is highly tolerable to changing temperatures and chemical conditions compared to bio-filtration for removal of NH_4^+ in aquaculture (Mumpton & Fishman, 1977).

2.12.5.4 Other applications of zeolites

Natural zeolites have been reported useful in the manufacture of construction materials (Bekkum, 2005; Feng & Peng, 2005). According to Kulprathipanja (2010), world population of natural zeolites was estimated at about 3.0×10^6 tons in 2008. China and Cuba consume the largest quantity of natural zeolites, largely to enhance the strength of cement. They are particularly used as blended materials in most cement plants to solve the volume stability problem of hardened cement paste. When used as a mineral admixture for concrete production, it prevents bleeding, segregation and delamination of fresh concrete. This makes pumping process easier, decrease permeability of hardened concrete and enhances durability especially the resistance to alkali-aggregate reaction. Aside increasing

concrete strength, they further minimize cracks caused by self-shrinkage in high performance concrete (Feng & Peng, 2005)

2.12.6 Surfactant modified zeolites (SMZ)

There is an isomorphic substitution of silicon by aluminium atoms in the crystal zeolitic structure. This substitution is compensated by exchangeable cations (e.g., H^+, Na^+, K^+, Ca^{2+}) thus making the zeolitic materials possess a negatively charged surface Warchoł *et al.,* 2006). Hence, zeolites possess mainly cation exchange properties and little affinity for anions and organic compounds in aqueous solution (Hrenovic *et al*., 2010.; Wang & Peng, 2010; Shoumkova, 2011). Nonetheless, zeolites could be chemically treated and modified on their surface to provide them with an increased affinity for inorganic anions and non-polar organic species, while retaining much of their sorption capacity for metal cations. One of the methods to increase their selectivity for anionic components in solution is the use of surfactant modifiers.

During the last decade surfactant modified zeolites (SMZ) have been greatly researched on to be effective in removing BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), herbicides, phenols, humic acids, pesticides, dyes etc. from aqueous solutions. Apreutesei *et al*. (2008) and Shoumkova (2011) reviewed several researches that applied natural SMZ in removing organic matter from wastewaters. Batch and column tests have been conducted by Ranck *et al.* (2005) to assess the effectiveness of surfactant-modified zeolite (SMZ) to remove BTEX. The results revealed that SMZ totally removes BTEX from water up to a compound-specific capacity. Several experiments have shown SMZ to be effective adsorbents for removing both humic substances and dyes from waters.

According to Bowman (2003) and Shoumkova (2011), surfactant-modified zeolites possess sorption properties for both cations and anions. Thus they keep the cationic sorption ability typical for zeolites with the ability to sorb anionic species. Anionic species such as phosphates, arsenates, iodides, nitrates, chromates, perchlorates, antimonates etc. have been reported to be susceptible to SMZ sorption. Moreover, SMZs are effective in the removal of non-polar organics such as pesticides, herbicides, dyes, BTEX, phenols, etc. for which most raw zeolites have slight or no affinity. Modification of zeolites into SMZs are commonly employed using quaternary amines like hexadecyltrimethylammonium (HDTMA), octadecyldimethylbenzyl ammonium

(ODMBA), cetyltrimethylammonium bromide (CTMA), stearyldimethylbenzylammoniumchloride (SDBAC), N-cetylpyridinium (CPD), benzyltetradecyl ammonium (BDTDA) etc. Surfactants like HDTMA increase the surface area of the zeolite and accordingly increase the ability of the adsorption (Hussein *et al.,* 2014).
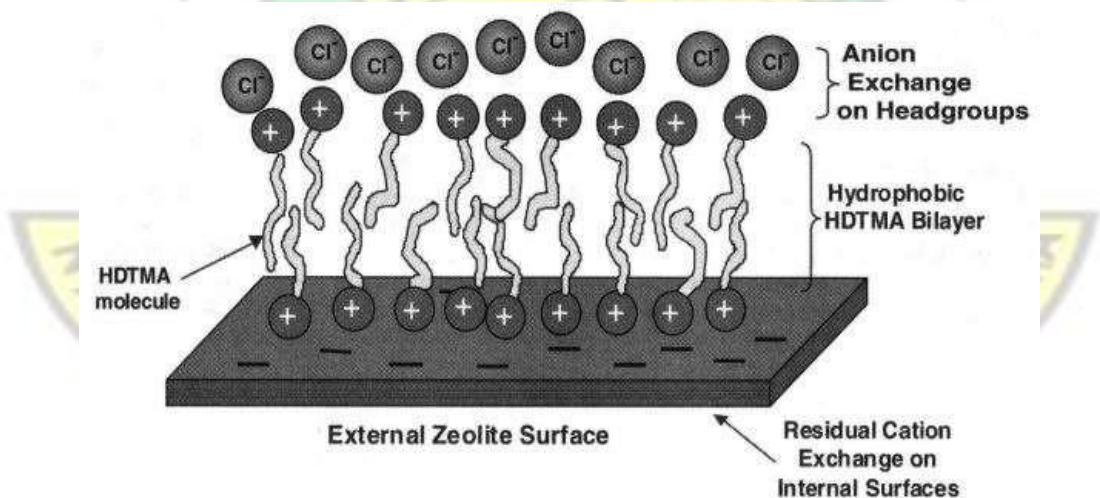
Figure 2–7: Anion exchange and organic partitioning on surfactant-modified zeolite (Schulze-Makuch *et al.*, 2002)

The attachment of a cationic surfactant molecule on the exterior surface of a natural zeolite can be mainly influenced by cationic exchange and hydrophobic interactions (Kazemian, 2012). Thus surfactant modification of zeolites is strongly influenced by the degree of surfactant adsorption on the solid surface. A bilayer or monolayer is formed when the surfactant concentration is higher or less, respectively, than its critical micelle concentration (CMC) (Kazemian, 2012; Ríos, 2008). At concentrations exceeding the critical micelle concentration (CMC), the external surface charge of the zeolite is converted from negative into positive and now displays anion exchange capability (Leyva-Ramos *et al.*, 2008). Thus, electrostatic force exist between the positively charged zeolite and the anions in solution (Masukume *et al.*, 2010).

Even though the surfactant modified zeolites possess sorption and anion exchange capabilities, they maintain the ability to adsorb inorganic cations. This is due to the fact that the relatively large surfactant molecules remain on the external surface of the zeolite crystal and do not enter the zeolite channels. Hence, the local surface charge remains negative (see Figure 2–7). Comparable anion sorption properties were displayed by polymer-modified zeolites and metal cation-modified zeolites (Shoumkova, 2011).

2.12.7 HDTMA-Br surfactant

Hexadecyltrimethylammonium bromide (HDTMA-Br) or Cetrimonium bromide, popularly called CTAB is a white powder cationic surfactant with a molecular formula $C_{19}H_{42}BrN$ and molecular mass of 364.45 g/mol.

Among its several uses, HDTMA-Br is used as a topical antiseptic for wounds and in buffer solutions for the extraction of DNA. They function as antistatic agents in fabric softeners

and hair rinse formulas. During textile manufacturing, they are used to prolong dye adsorption to help attain uniform coloration (Salager, 2002). More importantly, CTAB has been used in modifying zeolite nanoparticles to remove anionic and organic pollutants from water and wastewater effluents (Wikipedia.org).
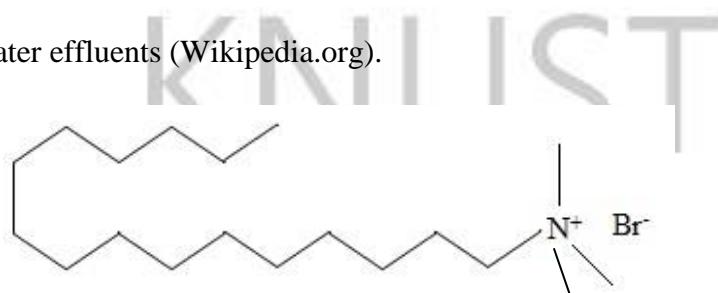
Figure 2–8: Molecular structure of HDTMA-Br ($C_{19}H_{42}BrN$)   ansever rdo an

The carbohydrate chain of hexadecyltrimethylammonium cation has a diameter of 4 A°, length of 23 A°, and the diameter of the polar head –N+(CH3)3 is 6.94 A°, which makes it too large to penetrate the largest channels of zeolites   ansever rdo an   . The molecular structure of HDTMA-Br and the general molecular structure of free cationic surfactant are as depicted in Figure 2–8 and Figure 2–9 respectively.
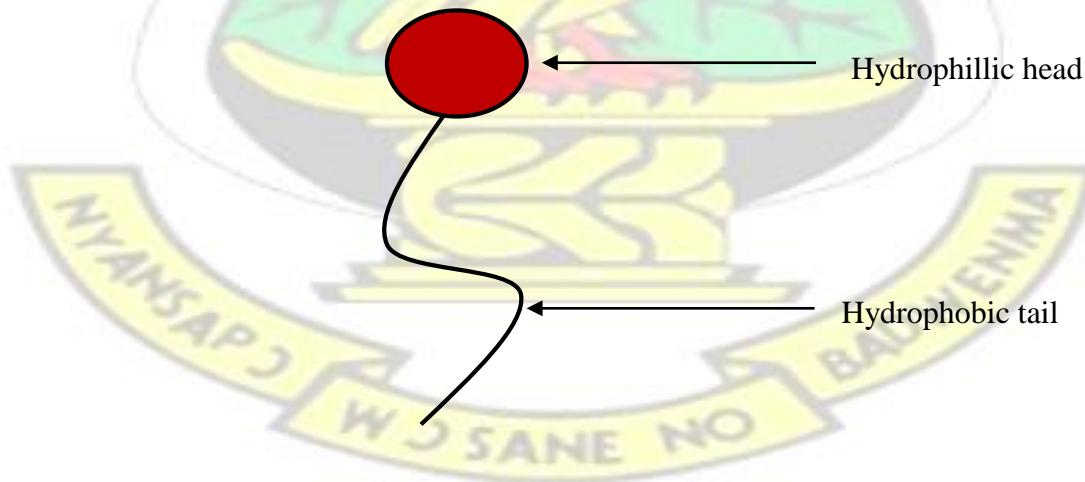
Figure 2–9: Molecular structure of a free cationic surfactant

When attached to zeolites, cationic surfactants form a bi-layer-like coating of positive and negative charges on the surface. Hrenovic *et al.* (2010) attributed the enhanced removal of phosphates by HDTMA-modified clinoptillolite zeolite to the change of zeta potential of the zeolite surface from negative to positive. The positive surface charge provides sites for sorption of anions (see Figure 2–7), whereas the organic-rich surface layer provides a partitioning medium for sorption of non-polar organic compounds (Apreutesei *et al*., 2008; Bowman, 2003).

2.12.8 Applications of surfactant modified zeolites to remove anions in water

Phosphates, nitrates, arsenates, and chromates are among the most familiar anionic water pollutants. Several successful investigations have been carried out to investigate the effectiveness of SMZs to decontaminate these anions in water.

Masukume *et al.,* (2010) reported surfactant modified zeolite as a potential material for nitrate removal from water. In their research, HDTMABr-modified clinoptillolite was used treat nitrate contaminated model water prepared in the laboratory. The results clearly revealed that unmodified zeolite had a very low NO_3^- removal capacity (<10%). Meanwhile, SMZ removed up to 92 % of the nitrate ions in solution using the same conditions.

Bansiwal *et al.*, (2006) investigated the feasibility of using surfactant-modified zeolite (SMZ) as a carrier for phosphate fertilizer and for slow release of phosphorus (P). It was reported that P loading on the SMZ increased by a factor of 4.9 as compared to the unmodified zeolite-A. The results indicated that SMZ is a good sorbent for PO_4^{3-} indicating that SMZ has a great potential as a phosphate fertilizer carrier for slow release of P.

Phosphate removal from wastewater by surfactant-modified clinoptillolite was studied by (Hrenovic *et al.,* 2010). It was observed that the phosphate adsorption capacity of the natural zeolite tuff was greatly enhanced by surface modification with HDTMA cations. The unmodified natural zeolite and its partially modified monolayer, monolayer, partial bilayer and bilayer modifications were used. Phosphate adsorption increased about 10 folds from using the unmodified zeolite through to its bilayer modification.

Haggerty & Bowman (1994) studied the adsorption of chromates using surfactant modified zeolite (SMZ) at varying pH ranges from an aqueous solution. They found that the SMZ was effective in adsorbing the three chromate oxyanions with CrO_4^- adsorbing at a highest extent. Moreover, desorption studies on these three oxyanions from the SMZ found that the adsorption process was irreversible. Leyva-Ramos *et al.* (2008) found that CrO_4^- was considerably removed from aqueous solution using surfactant (HDTMA) modified natural zeolite. The adsorption capacity (3.1 mg/g) was 22 times greater than its unmodified form (0.14 mg/g).

Several researchers including Chutia *et al.* (2009), Li *et al.* (2007) and Yusof & Malek (2009) etc. studied the uptake of arsenic from aqueous solution on modified synthetic zeolites. Similar observation from these individual researches was the significant improvement of arsenic/arsenate adsorption capacity by the modified zeolites.

Fluoride removal from aqueous solutions using HDTMA-modified zeolites has not been extensively investigated. Nonetheless, research by Kabuba & Mulaba-Bafubiandi (2013) and Rasuli *et al.*, (2014) demonstrated HDTMA-modified zeolites to be effective adsorbents for fluoride uptake. Rasuli *et al.* (2014) reported that the adsorption of fluoride

47

followed the pseudo-second-order kinetic model. Meanwhile the removal of fluoride was influenced by process variables such as the initial concentration of fluoride, pH of the solution, dosage of surfactant-modified zeolite (SMZ), modification contact time, effects of competing ions, temperature, and zeolite particle size.

2.12.9 Zeolites studied in this research

Several types of zeolites (both natural and synthetic) exist with a unique structure as well as composition controlling properties. According to the International Zeolites Association, there are 225 unique framework types for both synthetic and natural zeolites inclusive. In this study only synthetic zeolite sodium Linde Type A (Na-LTA) and sodium Low Silica X (Na-LSX) were synthesized and used in batch experiments to defluoridate water.

According to Kovo (2011), zeolite Na-LTA and Na-LSX belong to different zeolite groups. LTA belongs to an 8-member ring group with pore diameter of 4.2 Å whilst LSX belongs to a 12-member ring group with a pore diameter of 7.4 Å. Zeolite LTA has also been reported to be very hydrophilic than LSX. Thus, LTA is more reactive in aqueous solutions than LSX. These distinct properties determine their sorption and ion exchange capacities Shoumkova (2011).

2.12.9.1 Zeolite Na-LTA

The framework system of zeolite Linde Type A (LTA) comprises a combination of sodalite cages joined together via double 4-ring showing an α- cage at the epicenter of the unit cell. The framework structure of zeolite LTA is as depicted in Figure 2–10. The alternative silica and alumina tetrahedral has Si/Al ratio of 1 in the zeolite framework (Kovo, 2011). As cited by Kwakye-Awuah (2008), the pore diameter of 4.2 Å is defined by an 8 member

oxygen ring leading to a larger cavity of minimum free diameter of 11.4 Å. Furthermore, it contains a cavity volume fraction of 0.47 and it thermally decomposes above 700 °C. As depicted in the hydrated molecular formula, the high aluminium content in zeolite LTA makes it very hydrophilic (Kovo, 2011). Hence, their surface is extremely selective for water, polar and polarizable molecules which serves as the basis for many applications predominantly in drying and purification (Peskov, 2010). The hydrated molecular formula of zeolite LTA is given as: $Na_{96}(H2O)_{216}[Si_{96}Al_{96}O_{384}]$ (IZA,

2007).
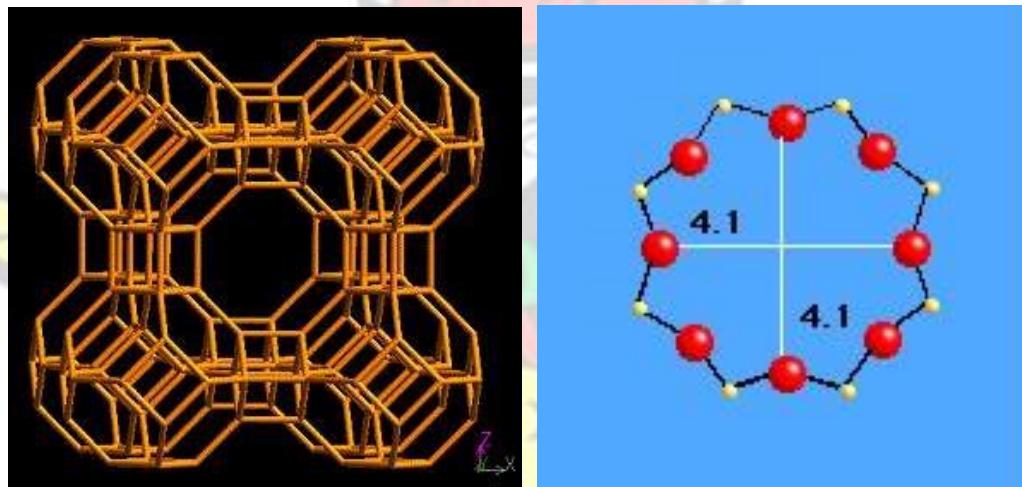
Figure 2–10: (a) Framework structure and (b) 8-ring structure of zeolite LTA showing pore diameter (IZA, 2008)

According to Kovo (2011), the framework of the zeolite LTA has the largest exchangeable cation making it a good material as an ion exchange agent. Labik (2012) reported very high arsenic and ammonia removal efficiencies of 71.87 – 96.00 % and 76.67 – 93.33 % respectively using zeolite LTA. The aluminium in the framework of zeolite LTA is unstable as it is susceptible to attack by acid and water vapour at high temperature. Due to this reason it is not widely used in catalysis (Kovo, 2011).

2.12.9.2 Zeolite Na-LSX

Sodium Low-Silica X (Na-LSX) zeolite is in the faujasite (FAU) family and similar to the LTA structure described earlier. However, the sodalite cage is interconnected with double six-ring resulting in a super cage with 12-ring pore opening. It is also called aluminium rich zeolite X and has a framework composition with a molar ratio of Si/Al of 1 – 1.5. LSX has a pore diameter of 7.4 Å with equidimensional channels running perpendicular to each other (as shown in Figure 2–11). It has very large microporous spaces which allow organic molecules to diffuse in and out (Von-Kiti, 2012).
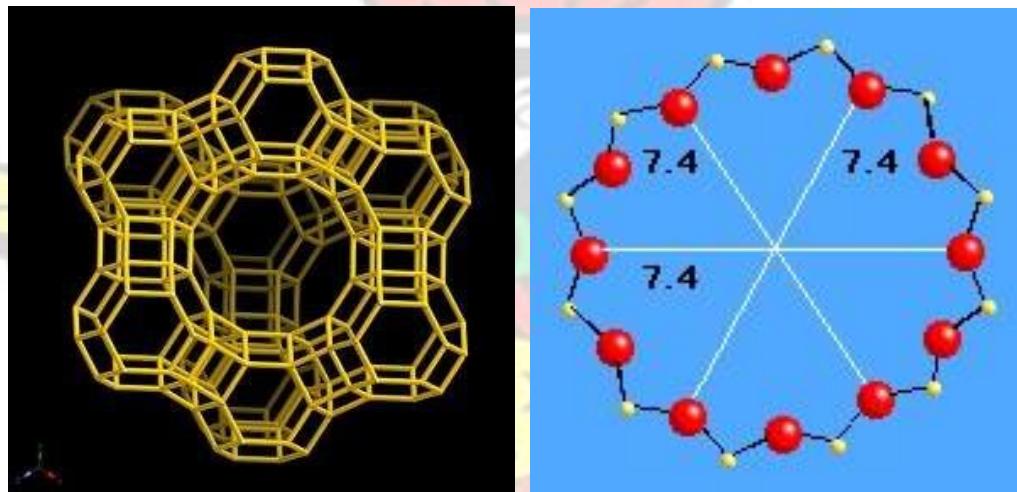
Figure 2–11: (a) Framework structure and (b) 12-ring structure of zeolite LSX showing the pore diameter (IZA, 2008)

Zeolite X has a broad range of industrial applications mainly due to the exceptional stability of the crystal structure, large pore volume and surface area (Kwakye-Awuah, 2008). Both zeolite Na-LSX and Na-LTA can be synthesized from several silica and alumina sources including natural clay such as kaolinite, oil shale ash, commercial silicates and aluminates, bauxite ore etc. (Shoumkova, 2011).

CHAPTER 3:

RESEARCH METHODOLOGY

3.1   Introduction

This chapter describes the methodologies and laboratory procedures employed to achieve the objectives of this study. They include: zeolite synthesis, modification and characterization of zeolite Na-LTA and Na-LSX. The batch adsorption experiments adopted to remove fluoride from water are also presented here.

3.2   Desk Study

Information and literature concerning the removal of contaminant anions in water, especially fluoride were collected and reviewed. Relevant methodologies found (on zeolite synthesis, modification and characterization) were modified and adopted in this work to help achieve the set objectives. Data obtained from this research were later analyzed and compared to reviewed literature to establish proper inferences, deductions and conclusions.

3.3   Zeolite Synthesis

Two protocols each were adopted to synthesize zeolites Na-LSX (Sodium Low Silica X) and zeolite LTA (Linde Type A) using different alumina and silica sources. Zeolite NaLSX was synthesized using a locally available kaolin mineral (Wassa kaolin) as the source of alumina and silica. Zeolite LTA (Linde Type A) was synthesized from locally available kaolin (Anfoega kaolin) and bauxite mineral as the source of silica and alumina respectively. Sodium metasilicate and sodium aluminate laboratory reagents were also used to synthesize another zeolite nicknamed zeolite ZR. Figure 3–1 and Figure 3–2 depict the synthesis routes for zeolite Na-LSX and Na-LTA respectively.

3.3.1   Zeolite Na-LSX synthesis from kaolin

Zeolite Na-LSX was synthesized using Wassa kaolin obtained from the Wassa community in Ghana. A slightly modified protocol devised by Donkor (n.d) was employed (see Figure 3–1).

0.25 mm pore sized sieve was used to sieve the Wassa kaolin and air dried at room temperature. A previously weighed quantity of the kaolin was calcined in a furnace at 600 °C for 2 hours and was allowed to cool. The calcined kaolin (now metakaolin) was fused with NaOH in the ratio of 1: 1.2 (kaolin: NaOH) in the furnace at 600 °C for an hour. The fused product was then allowed to cool and ground into a fine powder. Water was added to the fused product in a predetermined ratio of 1: 5 (fused kaolin: water) and mixed thoroughly for 30 minutes until homogenous. The slurry formed was transferred into tightly covered Teflon bottles and heated at 80 °C in an oven for 24 hours. The reaction was quenched immediately in cold water (to cease the reaction) and allowed to cool to room temperature. The zeolite product was filtered with Whatman No. 1 filter paper and rinsed with distilled water to a pH of 8.5 with the aid of a Buchner funnel connected to a vacuum pump. The molten zeolite was dried overnight at 100 °C and then ground in a mortar to obtain a smooth and evenly distributed powder.

3.3.2   Zeolite Na-LTA synthesis from kaolin

Anfoega kaolin and bauxite were used as silica-alumina source to synthesize zeolite NaLTA by adopting a method devised by Kwakye-Awuah *et al.* (2014) (see Figure 3–2).

The kaolin was sieved with a 0.25 mm pore sized sieve. A weighed amount of the kaolin was calcined at 600 °C for 2 hours to obtain the reactive metakaolin. The metakaolin was

mixed with 2 molar NaOH solution and heated at 110 °C for 2 hours. The resulting solution was filtered with Whatman No. 1 filter paper with the aid of a Buchner funnel connected to a vacuum pump. The filtrate was stored in plastic containers. Pre-weighed bauxite mineral was heated in a known volume of 2 molar caustic soda solution at 150 °C for 5 hours. The solution was allowed to settle and the clear solution (sodium aluminate) was decanted from the red mud. To obtain a molar ratio of $SiO_2/AlO_3 = 1 - 1.5$, amounts of the sodium aluminate from bauxite and sodium silicate from kaolin were calculated. For the reaction mixture, the sodium aluminate solution was added to the sodium silicate solution and the resulting gel was stirred for 20 minutes until homogenous. The resulting slurry was then aged at room temperature for 24 hours after which it was transferred into tightly covered Teflon bottles. Later, the solution was heated at 95 °C for 24 hours in an oven and the reaction was immediately quenched under cold water and allowed to cool at room temperature. The crystallized product was filtered and washed with distilled water until a pH of 8.5 was obtained. The molten zeolite was dried overnight at 100 °C and then ground in a mortar to obtain smooth and evenly distributed powder.
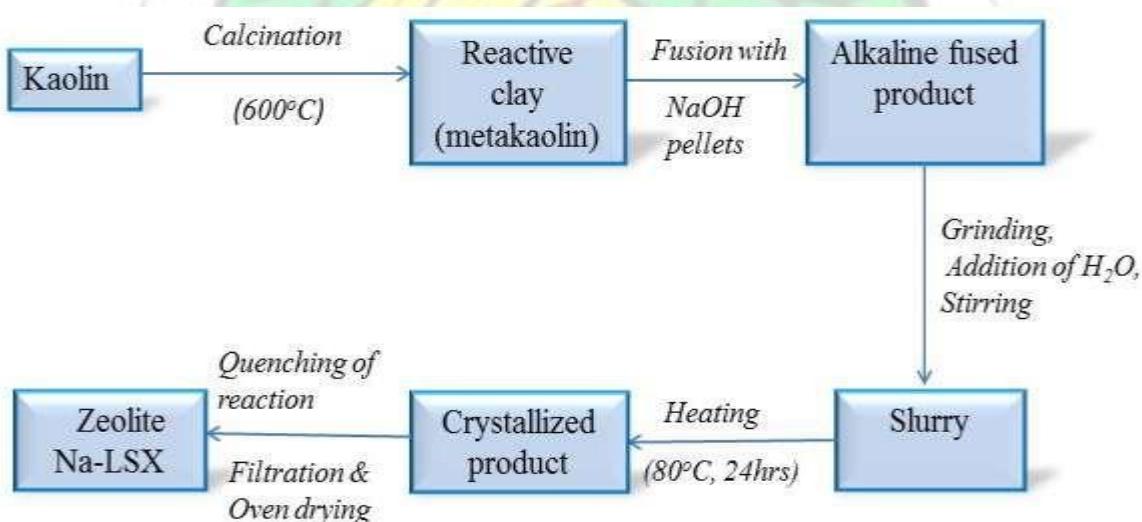
Figure 3–1: Flow chart for zeolite Na-LSX synthesis from kaolin
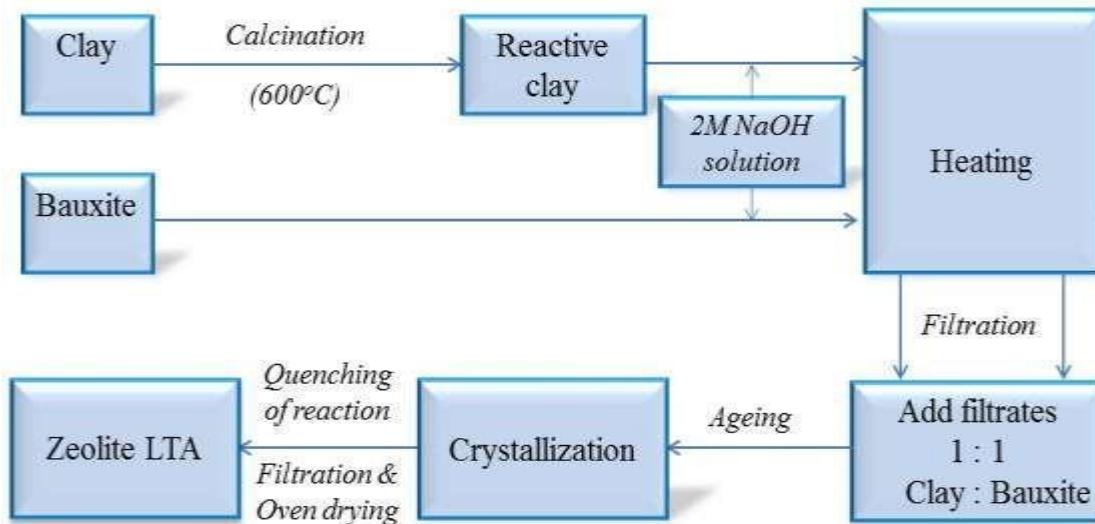
Figure 3– 2: Flow chart for zeolite Na-LTA synthesis from clay and bauxite

3.3.3 Zeolite synthesis from laboratory reagents

A third zeolite nicknamed zeolite ZR was synthesized following a method described by Thompson and Huber (1982) using only laboratory grade reagents (sodium aluminate and sodium metasilicate) as alumina and silica sources.

80 ml of 0.226 M sodium hydroxide solution (from Aldrich Chemicals, UK) was prepared and divided into two equal halves and each transferred into plastic beakers. 8.258 g of sodium aluminate (Sigma-Aldrich, UK) was added to the first halve with continuous stirring until homogenized. 15.48 g of sodium metasilicate (Aldrich, UK) was added to the other half and also mixed to homogenize. The two samples were mixed quickly and stirred continuously until homogeneous slurry was formed. The resulting slurry was transferred into Teflon bottles, tightly covered and heated in an electric oven at 100 °C for 4 hours. The reaction was quenched immediately in cold water and allowed to cool to room temperature. The crystallized product was filtered with the aid of a Buchner funnel connected to a vacuum pump and copiously washed with distilled water until a filtrate pH

of 8.5 was obtained. The molten zeolite was dried overnight at 105 °C and then ground in a mortar. The smooth and evenly distributed powder was finally stored in a Ziploc bag.

The apparatus used and the general processes used for the synthesis of zeolite Na-LSX, Na-LTA and ZR have been shown in Plate 1 below.
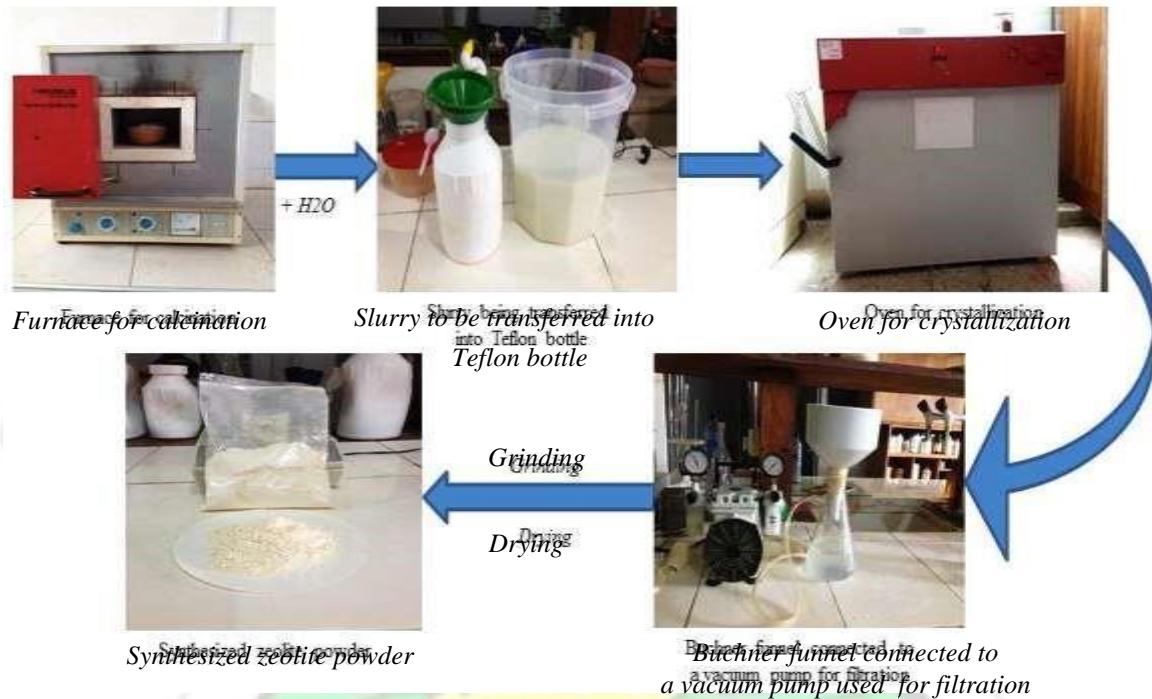
Plate 1: Flow diagram for zeolites synthesis and apparatus used

3.3.4 Modification of zeolites with surfactant

Two process conditions were varied during surface modification with surfactant: (a) surfactant dosage and (b) modification reaction time. Surfactant dosages of 0.5, 1, 2, 5, 10 and 15 g/L of Hexadecyltrimethylammonium-bromide (HDTMA-Br) also known as CTAB were prepared and used in the surface modification of the zeolites. 5 mg/L surfactant dosage was used to modify each zeolite by stirring in a flocculator at 150 rpm for an initial

24 hours. The modified zeolite that gave the best fluoride removal potential then was selected and varied at five other modification reaction times: 2, 6, 12, 18 and 36 hours.

In all instances, the modified zeolites were filtered, washed with distilled water and oven dried overnight at 105 °C. The dried modified zeolites were cooled to ambient temperature and evenly ground to fine powder with pistil and mortar. The powdered modified zeolite products were finally stored in Ziploc bags before their eventual use in the batch fluoride adsorption.

3.4 Characterization of Synthesized Zeolites and Modified Zeolites

Techniques used for zeolite characterization provide information about the structure, morphology, chemical composition as well as its catalytic and adsorptive abilities. Several techniques are employed to characterize the zeolite phases obtained. The most commonly used techniques include X-ray powder diffraction (XRD), Fourier Infrared Spectroscopy (FTIR), Scanning electron microscopy (SEM) and Energy dispersive x-ray spectroscopy (EDX), the Rietvield technique of structure refinement, Neutron scattering, nuclear magnetic resonance (NMR), Thermal, Laser Raman, measurement of sorptive capacity, particle size and pore size distribution, etc. The characterization of both synthesized and modified zeolites were conducted in the laboratories of the School of Applied Sciences, University of Wolverhampton, UK. The characterization techniques employed in this study have been described in this section.

3.4.1 X-ray diffraction pattern (XRD)

A detailed molecular understanding of zeolite structure is essential in explaining its catalytic, adsorption, and ion exchange properties. XRD was used to examine the

longrange atomic structure of the crystalline zeolite material. The technique measures and graphically presents the crystallinity, purity and amount of phases present in the sample.

XRD data of samples were collected using the Empyrean PANalytical X-ray powder diffractometer over 2θ within 5° to 80°. The diffractometer was equipped with a graphite monochromated $Cu\ K_\alpha$ radiation source. The voltage was 40 kV with a current of 40 mA and a wavelength, $\lambda = 1.54060$ Å. The XRD patterns were identified by comparing them with reference diffractograms.

3.4.2 Scanning electron mic. (SEM) & energy dispersive x-ray spec. (EDX)

The surface morphology of the zeolites as well as the elemental compostion were examined using a Zeiss EVO 50 equipped with energy dispersive X-ray spectrometer (EDX) (Zeiss, UK) shown in Plate 2.

Plate 2: ZEISS EVO50 SEM/EDX equipment

The sample was prepared by spraying dried zeolite powder onto aluminium stubs using double-sided adhesive carbon discs. The morphology of the solid phases was then

examined using the scanning electron microscope (ZEISS EVO50) under the following analytical conditions: I probe   nA   HT = .   kV beam current   μA Signal A = SE1, WD = 8.0 mm and 5mm. EDX analysis for the samples were prepared in a similar way to SEM. Instead of aluminium stud, a carbon sample holder was used to avoid errors in the aluminium content.

3.4.3   Fourier transform infrared spectroscopy (FTIR)

The vibrational properties were investigated by FTIR. The analysis was carried out on a Genesis 2000 Mateson FTIR spectrophotometer (shown in Plate 3) by taking readings from 400 cm^{-1} to 4000 cm^{-1}. In a transmission mode the spectrophotometer was used in conjunction with a diamond attenuated total reflectance (ATR) accessory. However, only the 1200 - 400 cm^{-1} region was investigated, taking into account that it is where the spectra showed remarkable changes (see Appendix Figure A1).

The powdered samples were sieved and particle sizes <5 $\square$m were collected and then placed onto the diamond ATR crystal surface. Finally, a force was applied to the sample for spectrum collection. The samples were then removed from the crystal surface in order to prepare the accessory to collect additional spectra.

Plate 3: Genesis 2000 Mateson FTIR spectrophotometer

3.5   Sorption Experiments

In this section, procedures adopted for the model fluoride water preparation, the batch adsorption process and fluoride measurements have been described.

3.5.1   Standardization

Fluoride measurements were taken using Accumet® Model 25 pH/Ion Meter and a Thermo Orion ionplus fluoride selective electrode (shown in Plate 4). In order to facilitate the monitoring and assaying of samples for fluoride concentrations, the meter was standardized and the fluoride selective electrode was also conditioned.

Plate 4: Accumet® Model 25 pH/Ion meter with fluoride selective electrodes

A series of standard solutions were prepared from a 1000 mg/L fluoride stock solution previously prepared from a powdered sodium fluoride (NaF) reagent. The pH/ion meter stores both the potential and the corresponding fluoride concentration of the standard solutions. The concentrations of the samples were directly computed using a linear regression model stored on the pH/ion meter along from the measured potential across the fluoride selective electrode.

3.5.2   Model fluoride water preparation

200 mL of 10 mg fluoride /L solutions were prepared from a 100 mg fluoride /L stock and used for the batch adsorption experiments. The dilution formula used is given as:

$$V_1 = C_2 V_2 / C_1$$

Where:

$$V_2 = 200 \text{ mL} \qquad = \qquad \text{Volume of initial solution used in a batch}$$

$$C_2 = 10 \text{ mg/L} \qquad = \qquad \text{Initial concentration fluoride}$$

$$C_1 = 100 \text{ mg/L} \qquad = \qquad \text{Concentration of stock solution}$$

$V_1 =>$ Volume of stock solution taken and topped with distilled water to 200 ml mark

3.5.3 Batch adsorption experiments

Batch adsorption experiments in this work (using zeolite Na-LSX and Na-LTA) were conducted to ascertain the fluoride removal performances of both unmodified and modified zeolites. Process conditions such as the HDTMA concentration or dosage and the contact time used in modifying the zeolites, as well as the pH of the fluoride contaminated water were varied in order to investigate their effect on fluoride uptake.

During the batch experiments, 500 mL beakers were filled with 200 mL fluoride contaminated aqueous solutions having an initial concentration of 10 mg fluoride / L. Two grams (2 g) each of the modified zeolites (Na-LSX, Na-LTA and ZR) were added into the beakers containing the fluoride contaminated solutions and stirred continuously at 90 revolutions per minute (rpm) with a Jar Test apparatus. An extra beaker in each batch served as a blank and was run under similar conditions without a zeolite. The setup (shown in Plate 5) was run for 4 hours and analyte samples were sampled into test tubes at pre-determined time intervals (i.e. 5, 10, 20, 30, 60, 90, 120, 150, 180 and 240th minute) by filtering through 0.45 µm polypropylene membrane filters. All solutions including the blank were adjusted to the required pH using 0.1 N NaOH, 10% and 20% HCl solutions. Finally, the concentration of fluoride and the corresponding potential of the analyte samples (collected in the test tubes) were measured with a Thermo Orion

Ionplus fluoride selective electrode connected to an Accumet® Model 25 pH/Ion meter (shown in Plate: 4). All batch adsorption experiments were conducted at room temperature.

Plate 5: Set-up for batch adsorption experiments

3.5.3.1 Batch fluoride adsorption using unmodified zeolites

The fluoride removal potentials by the three synthesized zeolites (i.e. Na-LSX, Na-LTA, ZR) were initially tested in their raw unmodified forms without any pH adjustments. The batch experiment was repeated as described in section 3.5.3 at a controlled pH of 6.5 ± 0.2.

3.5.3.2 Batch fluoride adsorption using modified zeolites

This batch adsorption follows the procedure as described under section 3.5.3. Each of the zeolite materials used (i.e. Na-LSX, Na-LTA, ZR) in this batch experiment had been previously modified with the following HDTMA concentrations or dosages: 0.5, 1, 2, 5, 10 and 15 g/L for 24 hours.

The best performing HDTMA dosage was then chosen and further tested to ascertain an optimal modification reaction time. Therefore, five other modification reaction times: 2, 6, 12, 18, and 36 hours each were used to modify the zeolite and applied in the batch fluoride removal process ascertain the optimal modification time.

3.5.3.3 Batch fluoride adsorption at different pH conditions

The experiment procedure at this sub-section was conducted to ascertain the effect of pH on fluoride removal of both modified and unmodified zeolite Na-LSX. Following the procedure described in sub-section 3.5.3, the pH conditions were adjusted and maintained at 5.5 ± 0.2, 6.5 ± 0.2 and 7.5 ± 0.2 before and during the batch process. The required pHs for the solutions, including the blank were achieved using 0.1 N NaOH, 0.5 N and 1 N HCl solutions.

The experiment was repeated with both the modified and unmodified zeolite Na-LSX without pH adjustments.

CHAPTER 4:

RESULTS AND DISCUSSIONS

4.1   Introduction

This chapter presents results obtained from all the conducted laboratory experiments in order to achieve the specific objectives of this study. The results found have been accordingly discussed and analyzed with inferences where appropriate. The discussions of the results encompass the characterization of both modified and unmodified zeolites using XRD, EDX, SEM and FTIR analysis. The application of the zeolites in batch adsorption processes to treat fluoride from water has also been discussed in this chapter.

4.2   Characterization of Synthesized Zeolites

The study focused on the synthesis and application of only zeolites Na-LSX and NaLTA. The following section elaborates on the nature of the synthesized zeolites. The significance of the characterization techniques was to provide a confirmation of the expected products by way of identification.

4.2.1   X-Ray Diffraction (XRD) analysis

XRD analysis was conducted using the Empyrean PANalytical X-ray powder diffractometer. The technique was used to interpret the crystallinity and phase purity of the synthesized zeolites. The results from the analysis are as presented in Figure 4–1. The analysis shows zeolite Na-LSX (90 %) as the major crystalline phase in the zeolite synthesized from Wassa clay (Figure 4–1[a]). The remaining 10 % is impure quartz. Meanwhile pure zeolite Na-LTA (100 %) was found in the zeolite that was hydrothermally synthesized from the Anfoega clay and bauxite filtrate (Figure 4–1[b]). The Na-LSX and Na-LTA gave sharp peaks at positions similar to findings reported by

Kwakye-Awuah *et al.* (2014) indicating high crystallinity.
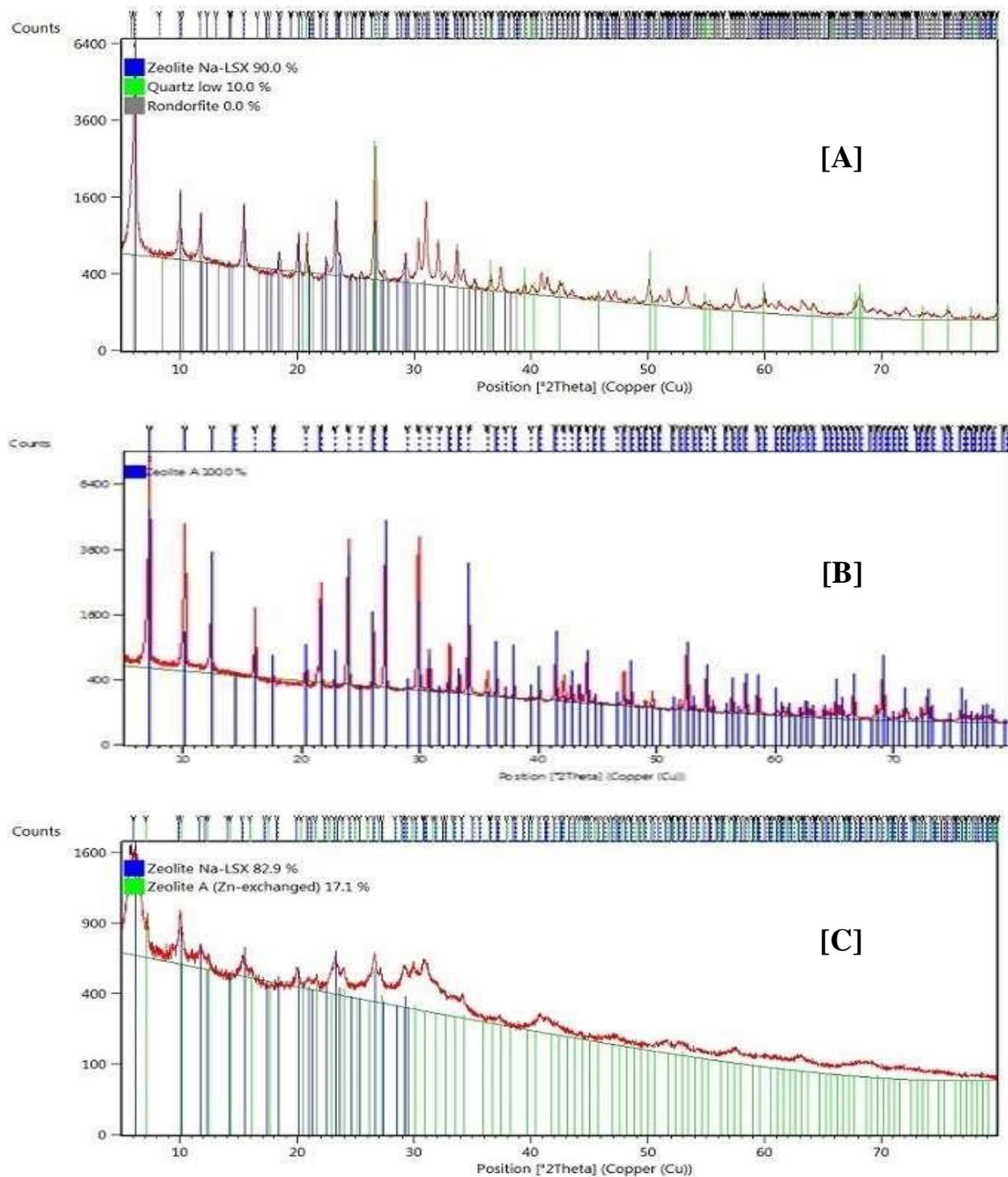
Figure 4–1: X-ray diffraction patterns of zeolite *(A)* Na-LSX *(B)* Na-LTA and *(B)* ZR

The initial intent of using only laboratory reagents was to synthesize zeolite Na-LTA. However it was realized after the synthesis that the product obtained had characteristics

more common to both Na-LSX (82.9 %) and Na-LTA (17.1 %) as shown in Figure 4– 1[c]. Nonetheless, the study proceeded to use this zeolite as part of the batch experiment.

The zeolite was thus nicknamed ‗ZR‗.

4.2.2   Energy Dispersive X-ray (EDX)

The elemental or chemical compositions of the synthesized zeolites were determined by an energy dispersive X-ray spectrometer fitted to a Zeiss EVO 50 scanning electron microscope. The elemental analysis presented in Figure 4–2 reveals O, Si, Al and Na to be the most predominant elements in the crystal structure of all the synthesized zeolites. Meanwhile S, K and Fe were also present as interlayer cations. The peaks corresponding to the relative abundances of the elements in the zeolites are also presented. The percent composition of Si and Al elements from the EDX analysis shown in Table 4–1 gives Si/Al ratios of 1.4, 1.0, 1.2 for zeolite Na-LSX, Na-LTA and ZR respectively. The Si/Al ratio of zeolite Na-LSX and Na-LTA is in consonant to what was found in literature (Flanigen *et al.*, 2010; Robson, 2001). However, the Si/Al ratio of 1.2 exhibited by zeolite ZR could be due to the presence of both zeolite Na-LSX and Na-LTA zeolitic phases.

Table 4–1: EDX analysis showing percent abundances of elements for unmodified zeolite *(A)* Na-LSX *(B)* Na-LTA and *(B)* ZR

[A]   **[B]**   **[C]**

Element	Weight (%)
O	68.49
Na	8.41
Al	9.19
Si	13.05
S	0.22
K	0.19
Fe	0.33
Cu	0.13
Total	100.00

Weight Element (%)
O 72.23
Na 8.85
Al 8.46
Si
S
Total 100.00

Weight (%)	Element	
66.65	O	
10.78	Na	
11.00	Al	
11.27	Si	10.14
0.31	S	0.32
100.00	Total	
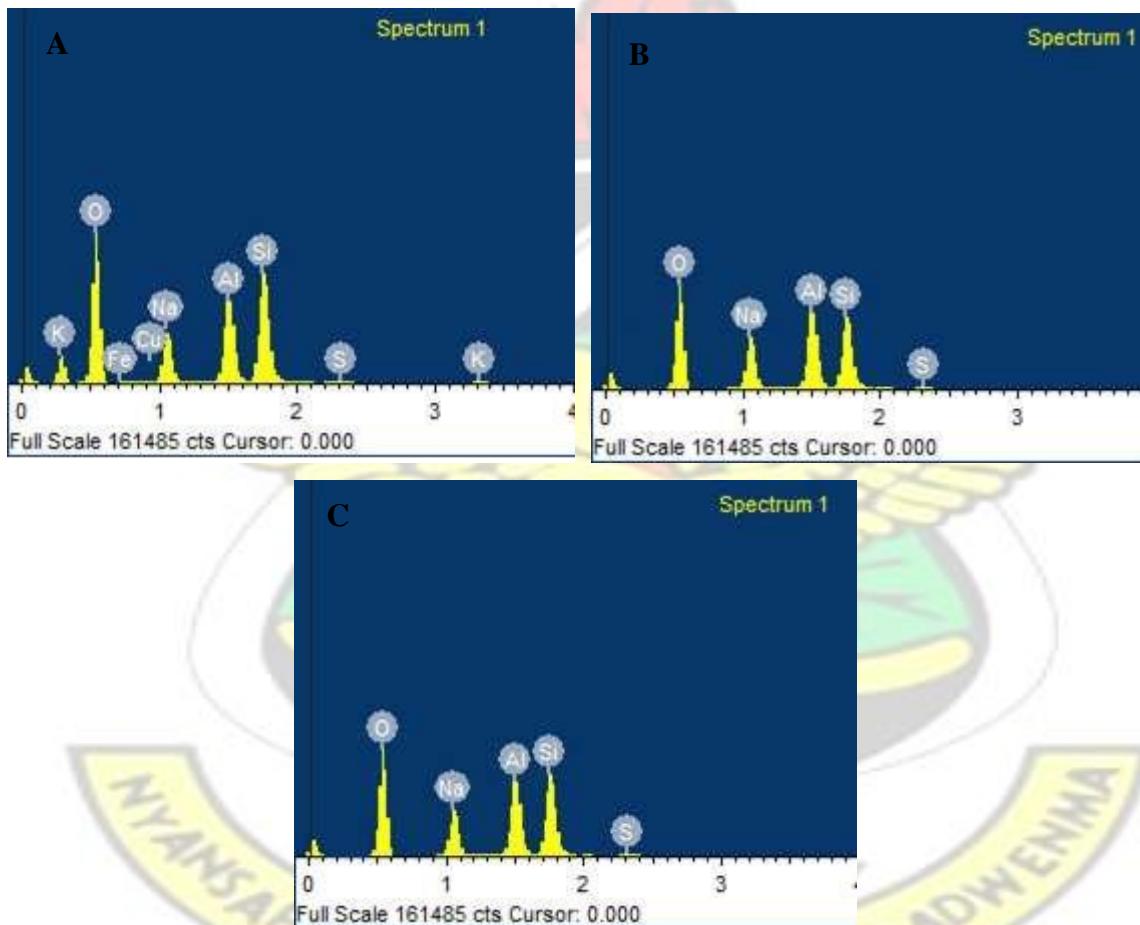
Figure 4–2: EDX spectra showing the elemental composition of unmodified zeolite *(A)* Na-LSX *(B)* Na-LTA and *(C)* ZR

4.2.3 Scanning Electron Microscopy (SEM)

Crystallite size and morphology of the synthesized zeolites were studied with the Zeiss EVO 50 SEM apparatus. Figure 4–3(A) depicts zeolite Na-LSX as an octahedral shape with an approximate particle size varying between   to   μm. Meanwhile, zeolite NaLTA (Figure 4–3(B)) shows cubic shaped crystals having an average particle diameter of   μm. Similar results were reported by Hui *et al.* (2013) and Kwakye-Awuah *et al.* (2014) for zeolite Na-LSX and Na-LTA respectively. The SEM of zeolite ZR (Figure 4–3(C)) shows various sizes of irregular and multi-faceted products probably due to the overlapping crystal phases of zeolite Na-LSX and Na-LTA.
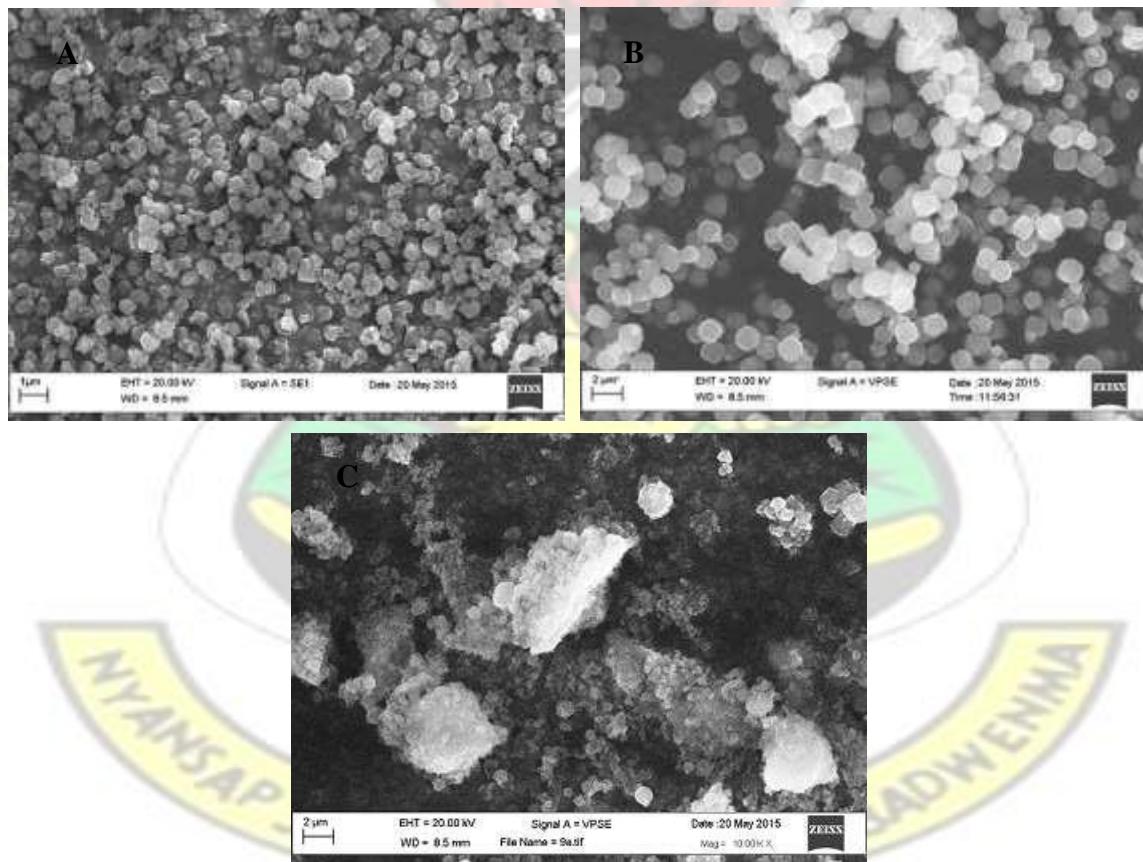
Figure 4–3: SEM micrographs showing the crystalline shape and size of zeolite *(A)* Na-LSX *(B)* Na-LTA and *(C)* ZR

4.2.4   Fourier Transform Infrared Spectroscopy (FTIR)

The synthesized zeolite Na-LSX was further characterized by the Genesis 2000 Mateson FTIR spectrophotometer (see Plate 3) to identify the functional groups in its structure. Figure 4–4 shows the characteristic peaks observed for zeolite Na-LSX. Vibrational spectrum of the zeolite shows strong IR absorption in the spectral region below 1200 cm^{-1}.

From Figure 4–4, the FTIR spectrum exhibits a large band at 963 cm^{-1}. This could be attributed to the overlapping of the asymmetric vibrations of Si–O (bridging) and Si–O− (non-bridging) bonds. The strongest peak at 450 cm^{-1} which shifts to a less strong band at 556 cm^{-1} is due to internal vibrations associated with T-O stretch and double ring vibrations respectively. Other peaks occur at 670, 740 and 1650 cm^{-1}. Khemthong *et al.* (2007) reported similar peaks for zeolite Na-LSX synthesized from rice husk ash. The general infrared assignments in zeolites as proposed by Flanigen *et al.*, (1978) and Mozgawa (2000) are presented in Table 4-2.
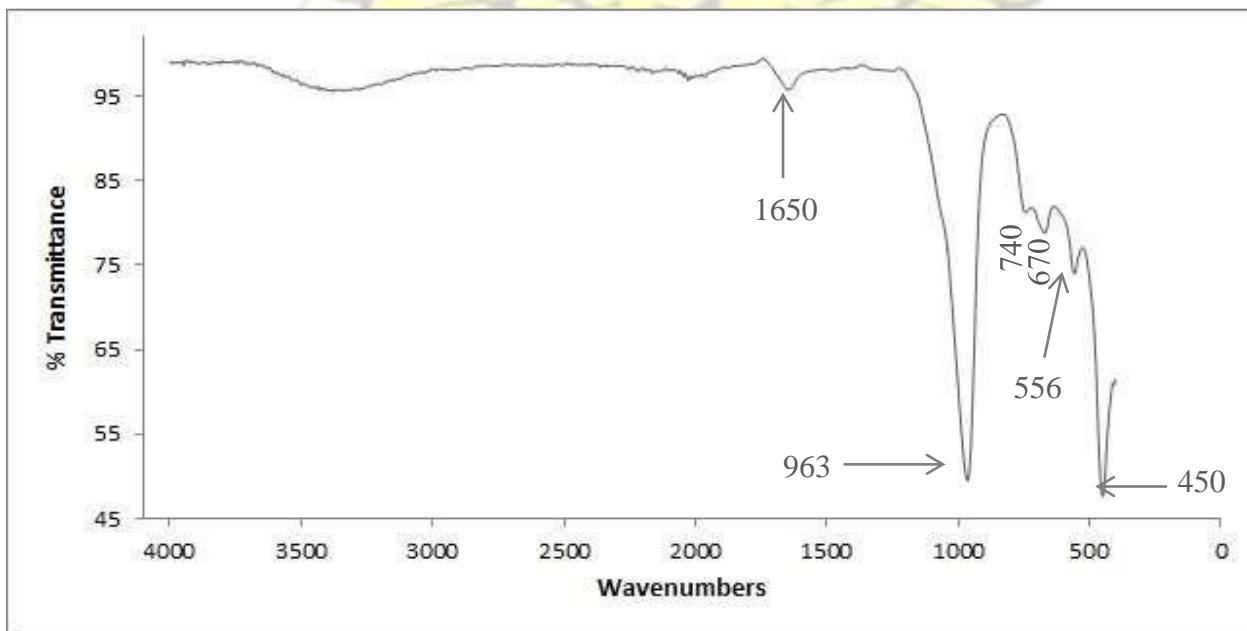
Figure 4–4: FTIR spectrum of zeolite **Na-LSX** showing various absorption peaks

Table 4–2: General infrared assignment (Flanigen *et al.*, 1978; Mozgawa, 2000)

Infrared Assignment	Theoretical band range wavenumber (cm^{-1})
Internal vibrations due to asymmetric stretching	1250 - 950
External T–O linkages due to asymmetric stretching	1150 - 1050
External T–O linkages due to symmetric stretching	820 - 750
Internal vibrations due to symmetric stretching	720 - 650
External T–O linkages due to double ring	650 - 500
Internal vibrations due to T – O bending	500 - 420
External T–O linkages due to pore openings	420 - 300

4.3 Characterization of HDTMA Modified Zeolites

In order to enhance or facilitate the anion adsorption performance, the synthesized zeolites were modified with HDTMA surfactant. In literature the HDTMA has been noted to promote anionic adsorption. Therefore, characterization of the modified zeolites gave insight into the change in properties that contributed to the increase in fluoride uptake.

4.3.1 X-Ray Diffraction (XRD) analysis

The phase purity and crystallinity of the surfactant (HDTMA) modified zeolites revealed that the major peaks of the zeolites were unchanged and only the intensities of these peaks decreased after modification. The closely matching 2θ and *d*-spacing values of the modified zeolites in Figure 4–5 indicates that the structural integrity of all the synthesized products is preserved after surfactant treatment. The retention of the structural integrity is an indication that the surfactant modification occurred only on the external surface of the zeolite structure. Similar observations were reported by Bansiwal *et al*. (2006), Kumar *et al.* (2007) and Mohammadi *et al.* (2012).
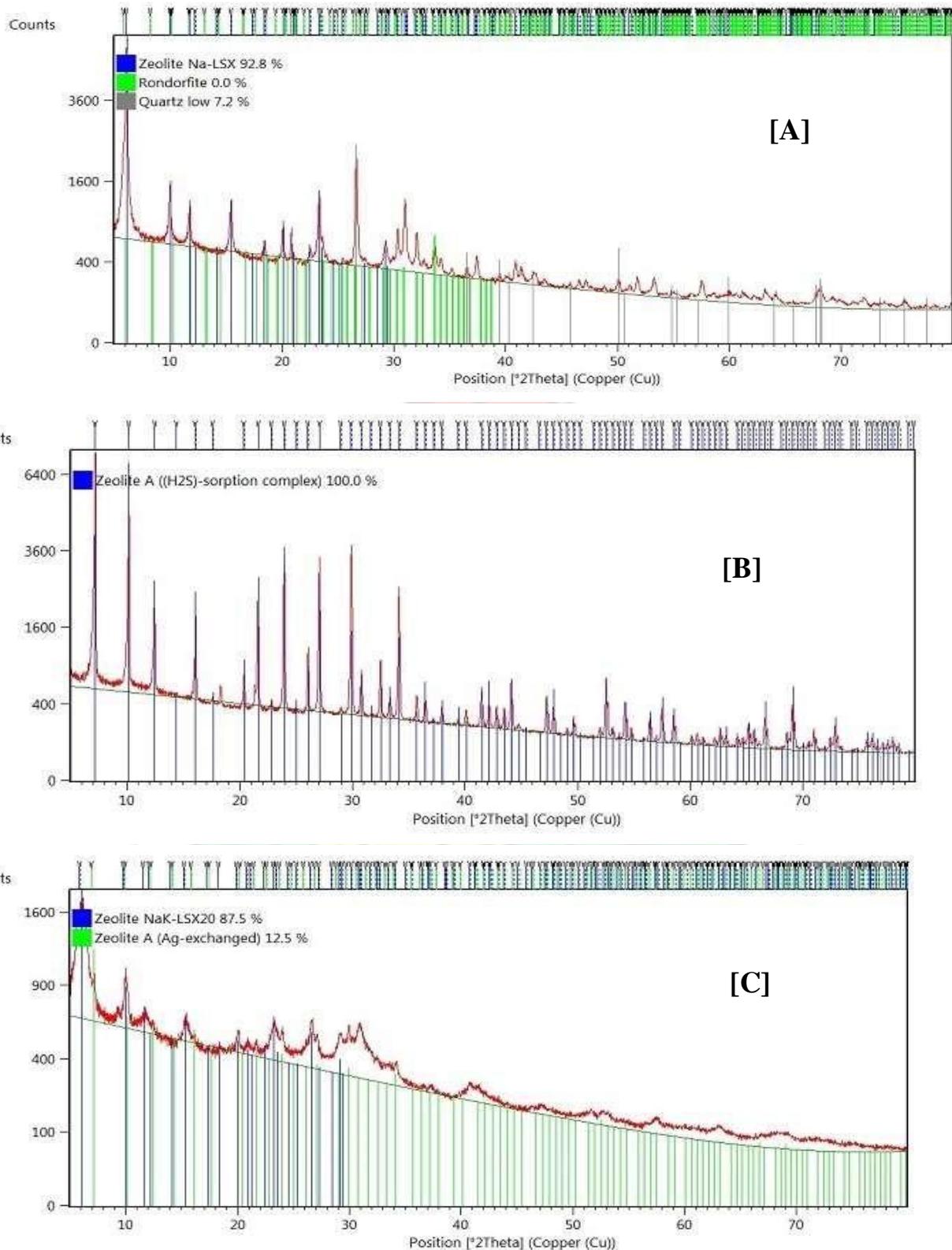
Figure 4–5: X-ray diffraction patterns of modified zeolite *(A)* Na-LSX *(B)* Na-LTA and *(C)*

ZR

4.3.2   Energy Dispersive X-ray (EDX)

The EDX analysis (Table 4–3) of the modified zeolites showed that weight percent values of exchangeable Na cations in the zeolite structure of raw unmodified Na-LSX, Na-LTA and ZR decreased whereas the introduction of elemental C after modification emanates from the organic carbon chain of the HDTMA molecules that might have exchanged the Na+ cations on the zeolitic surface (see Figure 4–6). This observation thus corroborates successful modification of the zeolite by the HDTMA surfactant. However it could not be established whether the extent of modification was proportional to the amount of HDTMA applied.

It would be recalled in the methodology chapter that the modification of the synthesized zeolites was conducted using five different protocols with different amounts of HDTMA. The EDX analysis showcased the Si/Al ratio of the modified zeolites to be constant indicating maintenance of structural integrity after the modification. These EDX observations further buttress the inference previously drawn from the XRD analysis, indicating successful HDTMA surfactant modification.
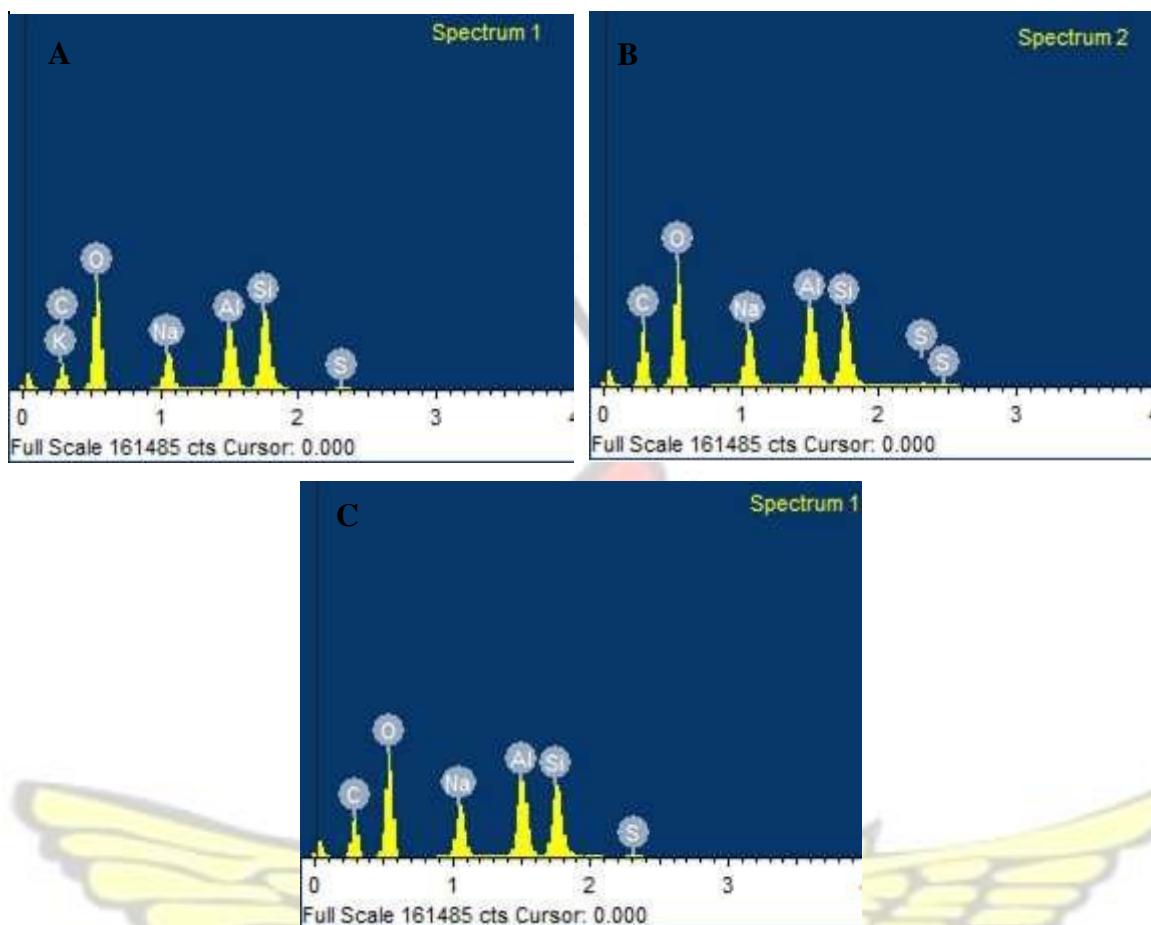
Figure 4–6: EDX spectra of modified zeolite *(A)* Na-LSX *(B)* Na-LTA and *(C)* ZR

Table 4–3: EDX analysis showing percent weight of elements for unmodified & modified zeolite *(A)* Na-LSX *(B)* Na-LTA and *(C)* ZR

[A]

*Unmodified——**Na-LSX***		*Modified*	
Element	Weight (%)	Element	Weight (%)
O	68.49	C	31.26
Na	8.41	O	48.05
Al	9.19	Na	5.61
Si	13.05	Al	6.09
S	0.22 0.19	Si	8.49
K	0.33	S	0.18
Fe	0.13	K	0.12
Cu		Fe	0.21
Total	**100**		

[B]

*Unmodified——**Na-LTA***		*Modified*	
Element	Weight (%)	Element	Weight (%)
O	66.65	C	35.64
Na	10.78	O	45.33
		Na	6.57
Al	11.00	Al	6.09
Si	11.27	Si	6.15
S	0.31	S	0.23

Total	100	Total	100	Total	100

[C]

Unmodified —— *ZR*		Modified	
Element	**Weight (%)**	**Element**	**Weight (%)**
O	72.23	C	28.57
Na	8.85	O	47.08
Al	8.46	Na	7.02
Si	10.14	Al	7.81
		Si	9.34
S	0.32	S	0.19
Total	**100**	**Total**	**100**

4.3.3 Scanning Electron Microscopy (SEM)

The SEM micrographs of modified zeolite Na-LSX and ZR in Figure 4-7 show a slightly reduced lustre appearance compared to their respective unmodified products (Figure 4-3). This could be attributed to the covering by the HDTMA molecules. The octahedral shape seen in the unmodified zeolites (Figure 4-3) has not changed much; probably, there are slight changes in the sharp edges and corners indicating successful modification. The SEM micrograph of modified Na-LTA however shows similar distinct cubic crystals as were observed in the raw unmodified Na-LTA. Thus, indicating HDTMA modification might not have been effective on zeolite Na-LTA.
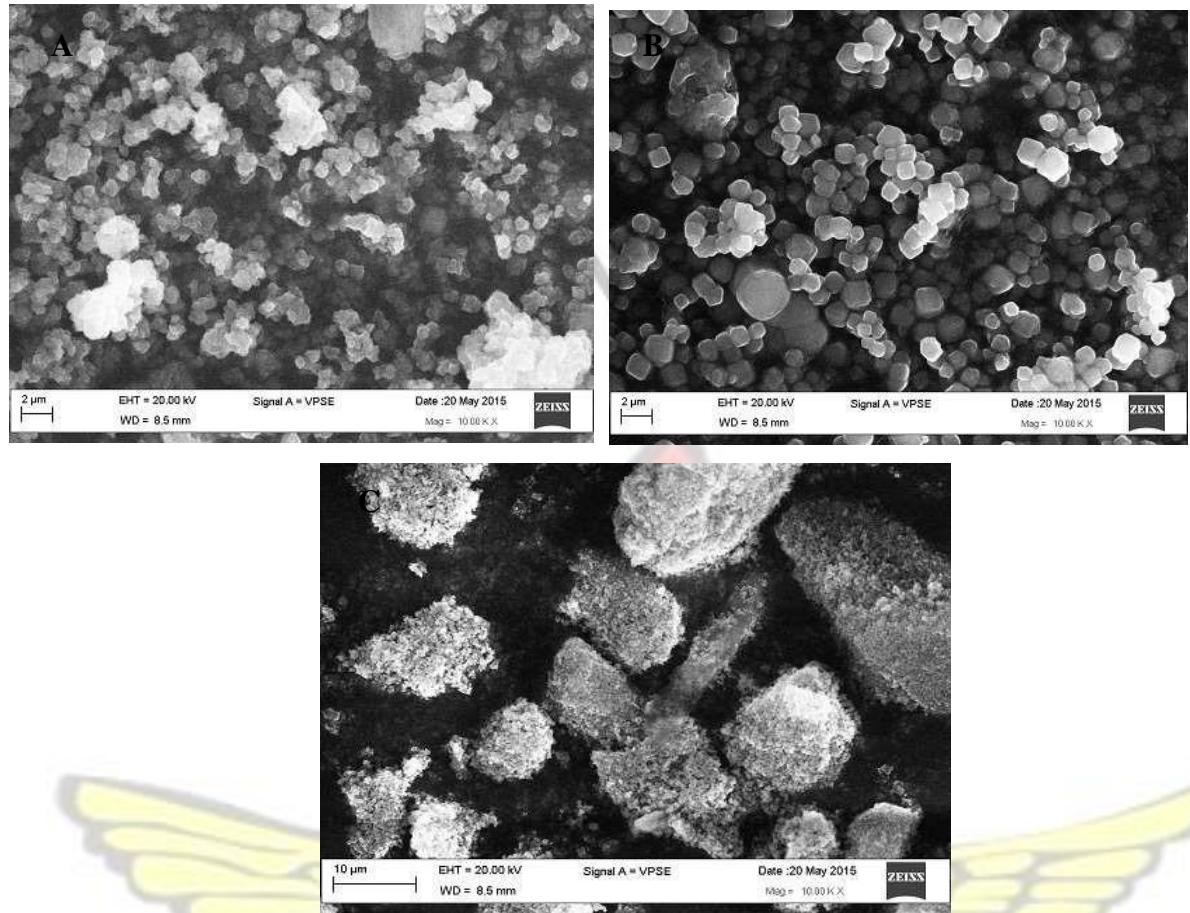
Figure 4–7: SEM micrographs of modified zeolite *(A)* Na-LSX *(B)* Na-LTA and *(C)* ZR

4.3.4   Fourier Transform Infrared Spectroscopy (FTIR)

Modified zeolite Na-LSX was characterized by FTIR to confirm successful HDTMA modification. The FTIR spectrum for the modified Na-LSX (Appendix: Figure A1) showed bands similar to its raw unmodified product at 955 cm^{-1} and 443 cm^{-1} in Figure 4–4. However, the spectrum reveals two new bands at 2923 and 2853 cm^{-1}. From the general infrared assignments table shown in Table 4-2, these bands are respectively attributed to the antisymmetric and symmetric C-H stretching of the methylene groups. rdo an (2011) recorded similar bands for HDTMA-modified clinoptillolite rich minerals. The added bands indicate the evidence of a successful modification by the cationic HDTMA surfactant. The shift in the characteristic bands of Na-LSX after the modification points

75

out the presence of adsorbed HDTMAs surfactant onto the zeolitic surface. Similar

observations were reported by Bansiwal *et al.* (2006), Khemthong *et al.*

(2007), and Kumar *et al.* (2007).

4.4   Batch adsorption experiments

The series of batch adsorption experiments in this work (using zeolite Na-LSX and

NaLTA) were conducted to determine the fluoride removal potentials of both unmodified

and modified zeolites. Process conditions such as the HDTMA concentration or dosage

and the contact time used in modifying the zeolites, as well as the pH of the fluoride

contaminated water were varied in order to investigate their effects on fluoride uptake.

The set-up for the experiment is shown in Plate 5.

4.4.1   Batch adsorption: Removal of fluoride using unmodified zeolites

This batch process was conducted to investigate the fluoride removal potential of the raw

or unmodified zeolites. Figure 4-8 depicts the fluoride removal performances by the three

unmodified zeolites (Na-LSX, Na-LTA, ZR) without any pH adjustment. The pH values

recorded for the experiment fell within 7.0 to 8.6.
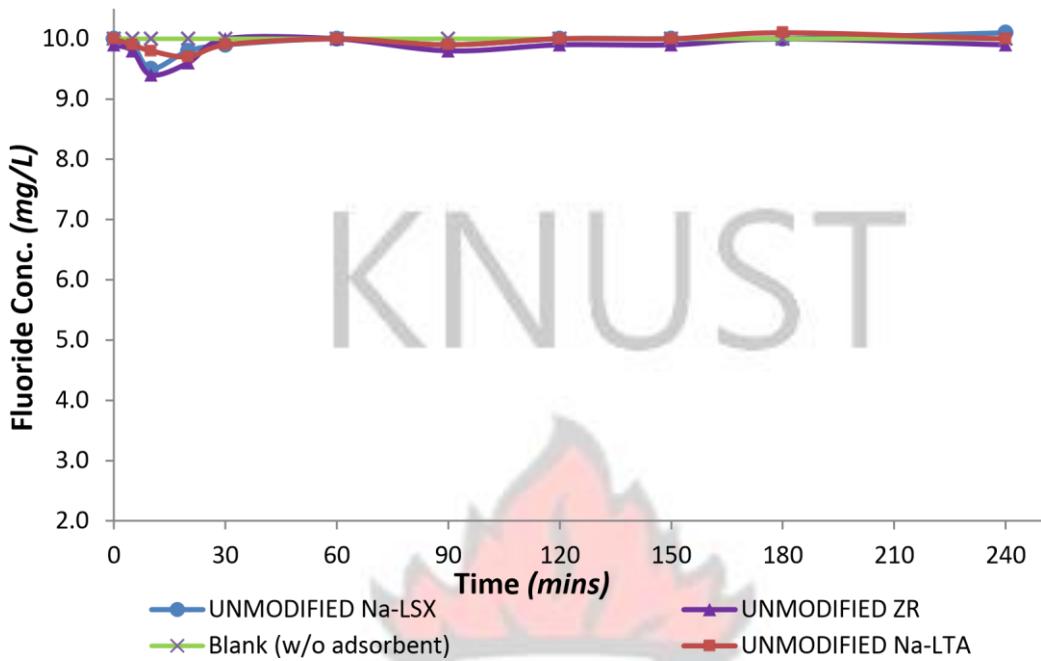
Figure 4–8: Fluoride removal using unmodified zeolites: Na-LSX, Na-LTA, ZR

(Model water composition: [F⁻]i = 10 mg/L, Blank = 10 mg F⁻/L without adsorbent)

From literature, the framework of raw zeolites is characterized by a net residual negative charge. Hence most zeolites exhibit little or no affinity for anionic constituents. As evident from Figure 4-8, the only slight fluoride removal by the unmodified zeolites occurred in the initial 20 minutes of the runtime. Beyond this, the fluoride concentration of the solution leached back into solution till the end. This poor fluoride uptake could be attributed to the repulsion between the negatively charged zeolite surface and the negatively charged fluoride ions.

The pH of the fluoride-contaminated solution plays an important role in the sorption of fluoride onto adsorbents. The pH values recorded for the test rose from an initial pH of 7.0 to

8.6. This increase in pH is probably responsible for the leach back of fluoride anions into solution.

Figure 4-9 depicts the fluoride removal performances by the three unmodified zeolites when the pH of the fluoride-contaminated solutions was maintained at 6.5 ± 0.2. From Figure 4-9, a remarkable fluoride uptake was observed within the initial 30 minutes of runtime for all the zeolites. The synthesized zeolite from only laboratory reagents (ZR) gave the highest fluoride removal (87 %) at the end of the 3 hours runtime. Zeolite NaLSX and Na-LTA followed with lesser fluoride removals of 66 and 55 % respectively. The result of the blank setup (without adsorbent) however indicates that there was no fluoride removal over the entire duration of the experiment. This suggests that the fluoride removal was only due to adsorption by the unmodified zeolites.

It can be observed from Figure 4-9 that when the pH of the solution was maintained at 6.5±0.2 the adsorption of fluoride significantly increased. Probably, the interference from the OH$^-$ anions was reduced, providing additional free adsorption sites for the fluoride ions. Due to this, there was a sharp decrease in fluoride concentrations within the initial 30 minutes of the test indicating rapid attachment onto the free sites. It was also observed during the experiment that the unmodified zeolites readily mixed in the aqueous media. This seemingly hydrophilic nature of the unmodified zeolites might have also enhanced the affinity and rapid uptake of fluoride anions.

Beyond the initial 30 minutes till the end of runtime, all the unmodified zeolites maintained maximum adsorption levels indicating a period of near equilibrium. At equilibrium, the rate of fluoride adsorption is equal to the rate of desorption in solution.
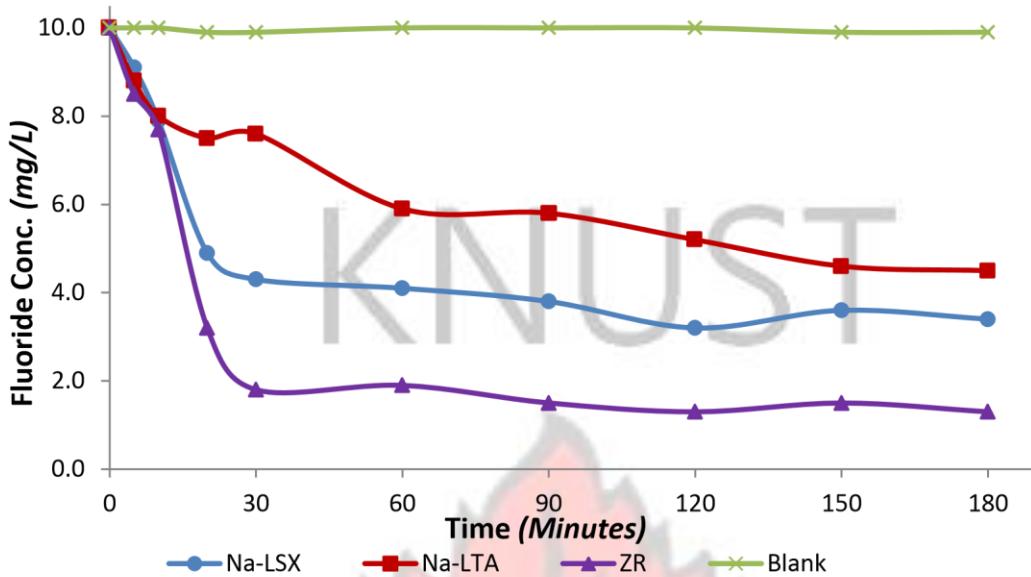
Figure 4–9: Fluoride removal using unmodified zeolites under controlled pH of 6.5 ± 0.2

(Model water composition: $[F^-]_i$ = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

The XRD analysis of zeolite ZR (Figure 4-1[c]) revealed that it is composed of zeolite Na-LSX (82.9%) and Na-LTA (17.1 %) phases. The high fluoride removal performance by zeolite ZR could be attributed to its inherent nature, that is the combined properties of zeolite Na-LSX and Na-LTA.

4.4.2   Batch adsorption: Effect of varying HDTMA dosage on fluoride uptake

The Figures, 4–10, 4–11 and 4–12 respectively depict the fluoride removal potentials of modified zeolites Na-LSX, Na-LTA and ZR with time. Each zeolite was modified with varying HDTMA dosages (or concentrations) of 0.5, 1, 2, 5, 10, and 15 g/L.

Evidently each modified zeolite exhibited significant fluoride removal till the end of the runtime for all the HDTMA modification dosages. As depicted in Figure 4–13, the 5 g/L HDTMA dosage recorded the highest fluoride removal potential at the end of the 3 hours runtime: Na-LSX (84.5 %), Na-LTA (50.3 %) and ZR (78.8 %).
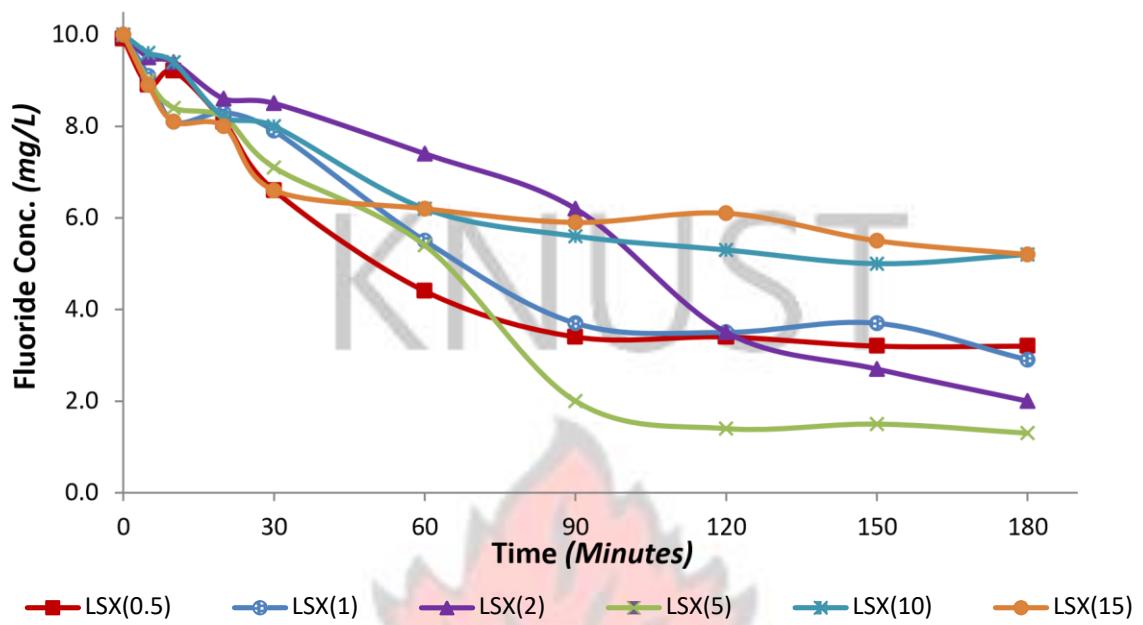
Figure 4–10: Fluoride removal using zeolite **Na-LSX** modified with different dosages of HDTMA

(Model water composition: $[F^-]_i$ = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)
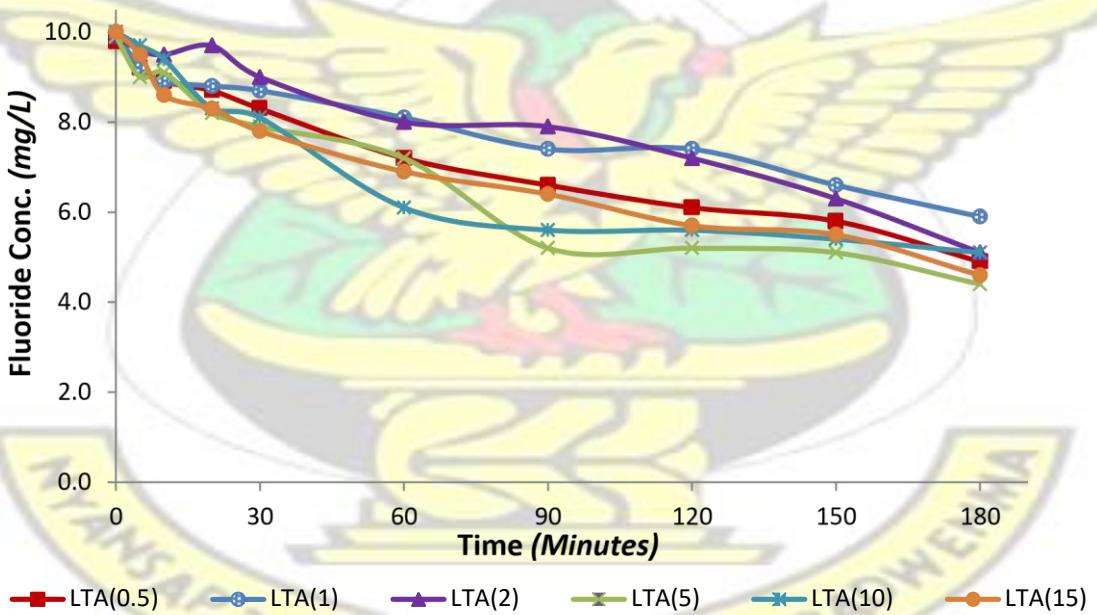
Figure 4–11: Fluoride removal using zeolite **Na-LTA** modified with different dosages of HDTMA

(Model water composition: $[F^-]_i$ = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)
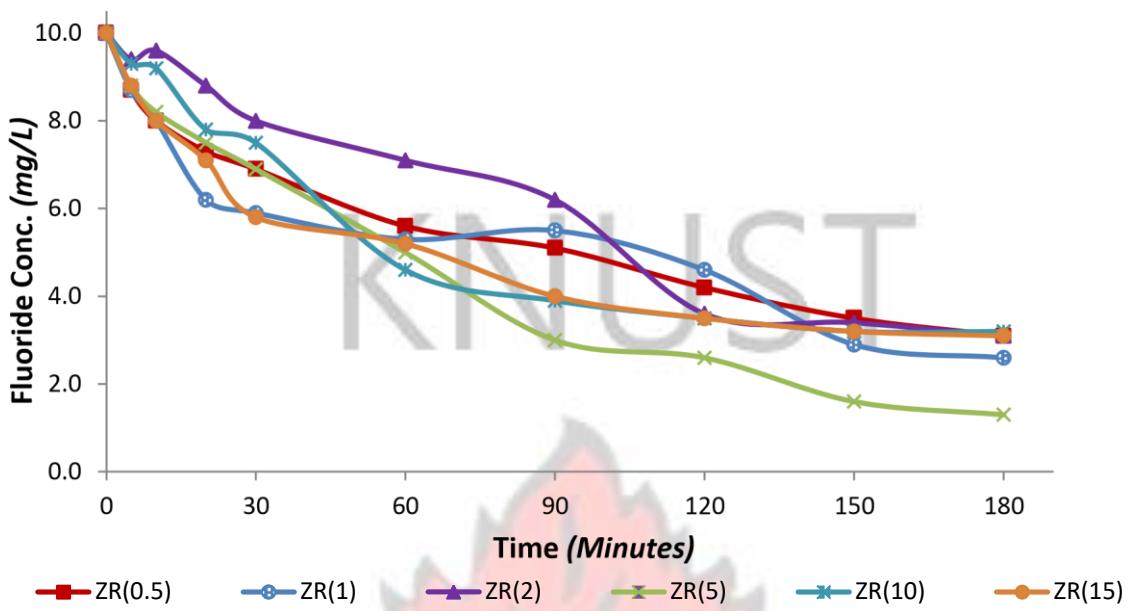
Figure 4–12: Fluoride removal using zeolite **ZR** modified with different dosages of HDTMA

(Model water composition: $[F^-]_i$ = 10 mg/L, Blank = 10 mg F$^-$/L without adsorbent)

Generally, the unmodified zeolites (Figure 4–9) recorded rapid fluoride removal in the initial 30 minutes of adsorption runtime compared to the modified zeolites (Figure 4-10, 4–11 and 4–12). The rather gradual fluoride uptake observed by the modified zeolites within 30 minutes of runtime could be due to increased hydrophobicity (or reduced hydrophilicity) from the hydrophobic organic tails of the HDTMA surfactants covering the zeolite surfaces Vujaković *et al.*, 2003). The modified zeolites therefore took longer time to mix in the aqueous solution and subsequently delayed interaction with the fluoride ions in solution. However, the observed downward trend at the end of the graphs indicates the presence of unexhausted adsorption sites on the modified zeolites. The trend also suggests that the HDTMA surfactant used in modification increased the adsorption and/or the ion exchange capacity of the raw or unmodified zeolites.

According to Wibowo *et al.* (2011), the critical micelle concentration (CMC) of HDTMA-Br surfactant is 0.9 mM. As explained by Apreutesei *et al.* (2008), the sorption of surfactants onto zeolite surface is governed by the initial concentration of surfactant in solution and the external cation exchange capacity (ECEC) of the zeolite. According to Rios (2008), a bilayer or monolayer is formed when the surfactant concentration is higher or less than its critical micelle concentration (CMC) respectively. At concentrations above the CMC, a bilayer is formed on the external surface of the zeolite. The external surface charge of the zeolite then changes from negative into positive and now displays increased anion exchange capacity (Leyva-Ramos *et al.*, 2008). Masukume *et al.,* (2010) reported that electrostatic forces now exist between the positively charged zeolite surface and the negative fluorine anions in solution resulting in increased attraction and adsorption. In this view, the highest fluoride removal exhibited by the 5 g/L HDTMA dosages could be due to the formation of a complete HDTMA bilayer coating on the

zeolitic surface.

The observed low fluoride removal performance by zeolites modified with 10 and 15 g/L surfactant dosages (far exceeding the CMC) could be due to interference from the release of excess, loosely bound HDTMA molecules on the bilayer surface into the aqueous solution. This subsequently resulted in competition between the fluoride and the HDTMA species in solution for the same adsorption sites. Haggerty & Bowman (1994) reported similar interferences when the natural zeolite clinoptilolite was treated with 200 % HDTMA above its ECEC to remove chromate anions in water. The excess HDTMA molecules also accounted for the high hydrophobic nature of the zeolites. This resulted in a decreased interaction between the zeolitic materials and the fluoride ions in solution.

Onyango *et al.* (2010) reported similar reduction in nitrate removal when the HDTMA dosage of zeolite Na-LSX was increased. Figure 4–13 depicts the fluoride removal performances after varying HDTMA dosages were used to modify zeolite Na-LSX, NaLTA and ZR.
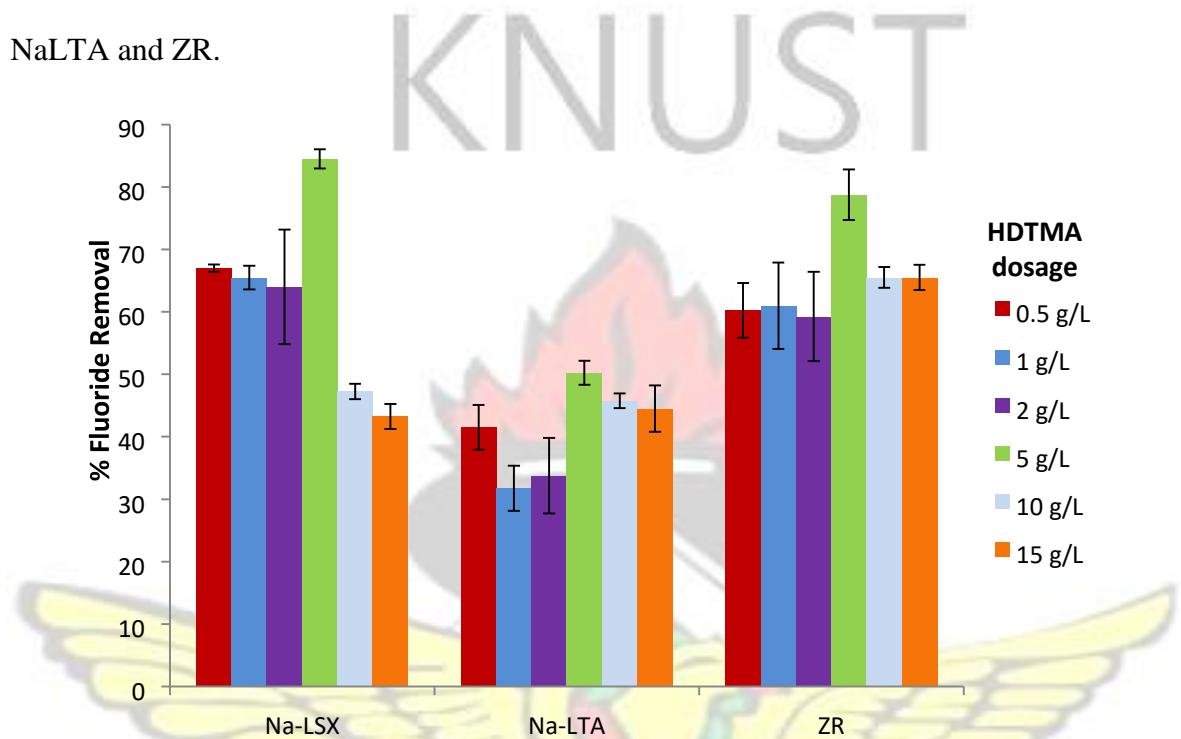
Figure 4–13: Effect of varying HDTMA surfactant dosage (conc.) on fluoride removal

4.4.3 Batch adsorption: Effect of modification reaction time on fluoride removal This batch adsorption experiment was carried out to determine the effect of modification reaction time on fluoride removal performance. Equal amounts of zeolite Na-LSX were modified by stirring in equal volumes of 5 g/L HDTMA with the aid of a flocculator. The modifications were varied for 2, 6, 12, 18, 24, and 36 hours.

From Figure 4–14 it is observed that fluoride removal is rapid for all the modification times within the first 120 minutes of runtime. Generally, fluoride removal performance increased with increasing modification time till 24 hours. Beyond the 24 hours to the 36 hours,

fluoride removal decreased slightly. Fluoride removal remains steady towards the end of the test indicating a period of near equilibrium.
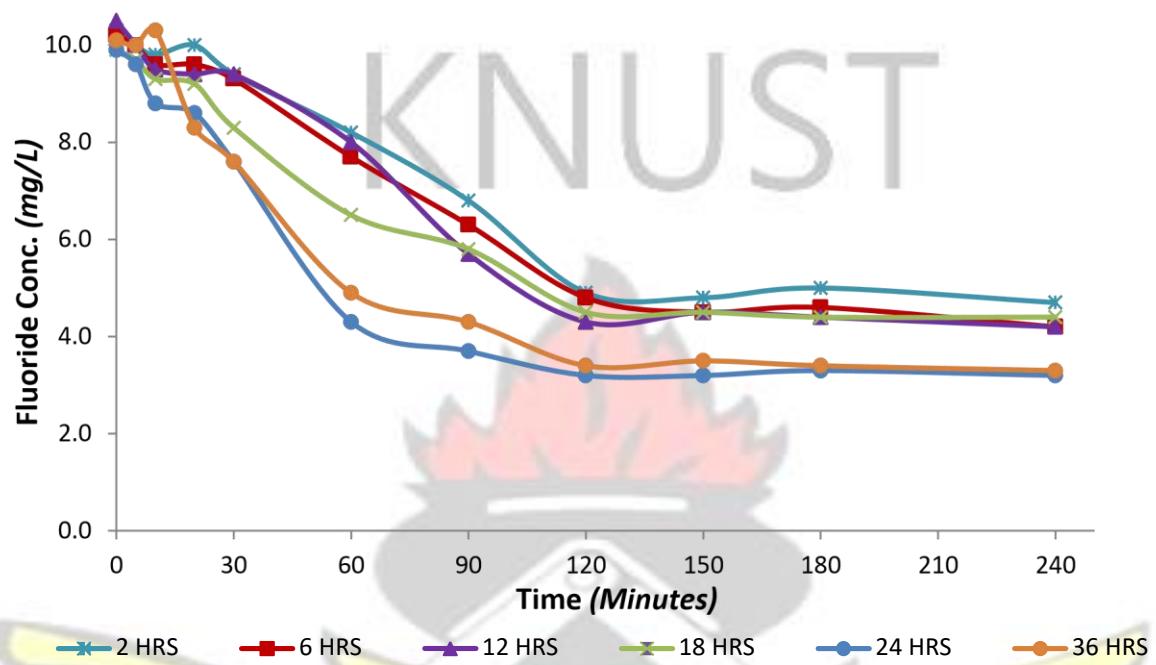
Figure 4–14: Fluoride removal by zeolite **Na-LSX** modified at different times (2, 6, 12, 18, 24, 36 hours) with HDTMA

(Model water composition: $[F^-]_i$ = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

According to Apreutesei *et al.* (2008), the amount of HDTMA sorbed onto the zeolite during modification is a function of the initial HDTMA concentration and the sorption time (i.e. reaction or contact time). Inferences from their work suggest that provided the concentration of HDTMA used in the modification of the zeolite is above the ECEC of the zeolite, HDTMA coating on the surface increases with increasing modification reaction time. Hence increasing the contact time for the HDTMA-zeolite modification favours its sorption equilibrium and the formation of bilayer coating on the zeolite surface. This effect was observed during the fluoride adsorption whereby the fluoride removal performance of zeolite Na-LSX increased with increasing modification reaction time. By increasing

84

modification or reaction time, the HDTMA molecules had ample time to rearrange themselves to form a bilayer coating on the zeolite surface. Thus, longer reaction times favored the coating of HDTMA on the zeolitic surface.

From Figure 4–14, fluoride removal performance increased from 53 to 68 % from 2 hours through to 24 hours modification times at the end of runtime. Probably the shorter modification reaction times resulted in the formation of patchy or partial surfactant bilayers on the zeolite surface. This resulted in decreased fluoride uptake. It is also observed that the 24 hours modification reaction time exhibited the highest fluoride removal potential (68 %) whilst the 36 hours resulted in a slightly lower performance (67 %). The slight discrepancy could be due to interference from the release of excess, loosely bound HDTMA molecules from the 36 hours modification reaction time. This subsequently resulted in competition between the fluoride and the HDTMA molecules in solution for the same adsorption sites (Haggerty & Bowman, 1994). In view of this, the formation of a complete bilayer HDTMA coating probably occurred at the 24 hours of modification reaction time. This translated into the increased fluoride removal during the batch adsorption process.

4.4.4 Batch adsorption: Effect of pH on fluoride removal

The effect of pH on fluoride uptake using modified zeolite Na-LSX was conducted considering the following pHs: 5.5 ± 0.2, 6.5 ± 0.2 and 7.5 ± 0.2. The solutions were maintained at their required pH using 0.1 N NaOH, 0.5 and 1 N HCl solutions. In addition, a batch setup was concurrently run without pH adjustments using modified Na-LSX. Figures 4–15 and 4–16 depict the results obtained.
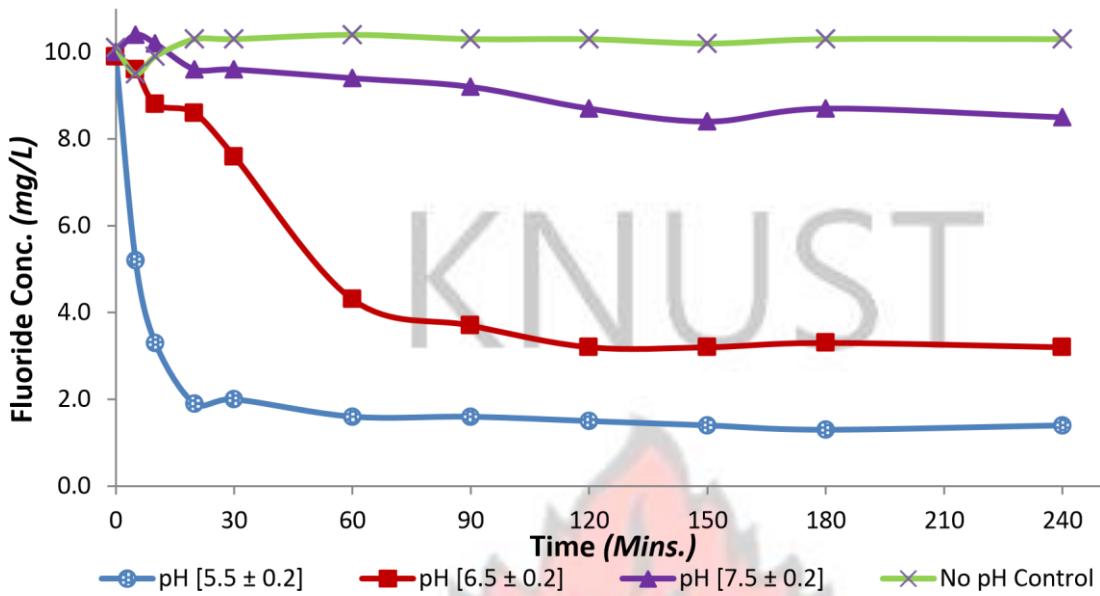
Figure 4–15: Fluoride removal with pH maintained at 5.5 ± 0.2, 6.5 ± 0.2 and 7.5 ± 0.2 using modified zeolite **Na-LSX**

(Model water composition: $[F^-]_i = 10$ mg/L, Blank = 10 mg F^-/L without adsorbent)
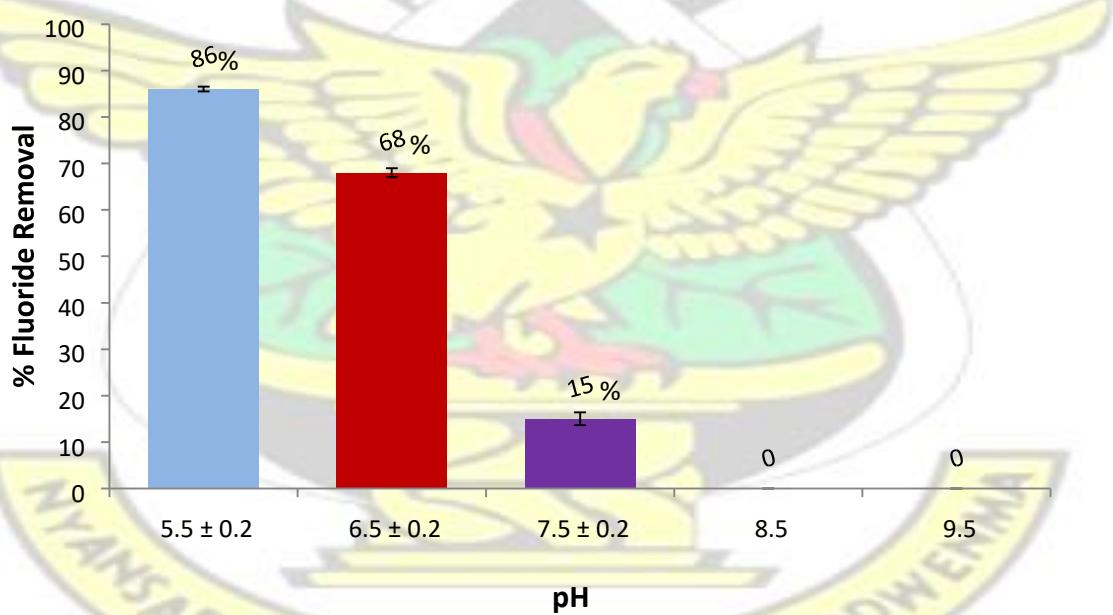
Figure 4–16: Fluoride removal performance under controlled pH (5.5 ± 0.2, 6.5 ± 0.2, 7.5 ± 0.2) and uncontrolled pH conditions using modified zeolite **Na-LSX** as adsorbent

As evident from Figure 4–15, the modified zeolite Na-LSX with no pH control recorded poor fluoride removal similar to its unmodified zeolite in Figure 4–8. The only slight

fluoride removal occurred within the first 5 to 10 minutes of runtime. This represents only 5 % fluoride removal from the initial 10 mg/L concentration. After this, the fluoride ions leached back into solution and thus increased the concentration of fluoride to about the initial concentration (10 mg/L). Contrary to this observation, the model waters with pH maintained at 5.5 and 6.5 recorded rapid fluoride removal (84 and 57 % respectively) within the first 60 minutes of runtime. After this, an almost steady fluoride concentration is recorded till the experiment was terminated. Meanwhile, the model water adjusted to a pH of 7.5 resulted in a gradual to steady decrease in fluoride removal performance over the entire duration of the batch removal process (i.e. 10 to 8.5 mg Fluoride/L). This represents 15 % fluoride removal from the aqueous solution.

Figure 4–16 clearly shows that changes in pH of the model water (solution) greatly influenced the fluoride removal performance of the modified zeolite Na-LSX. Fluoride removal significantly reduced when the pH of the model water was increased from 5.5 through to 9.5. Fluoride adsorption at the end of the 4 hour experiment recorded 86, 68 and 15 % respectively for pHs 5.5, 6.5 and 7.5. The pH readings for the test without pH adjustments increased from 7.0 through to 8.9 by the end of the batch process. No appreciable fluoride removal was recorded for this test.

During the fluoride removal process, the bromide ions bonded to the HDTMA layer is exchanged with the fluoride ions in solution. The free bromide ions that are released into solution perhaps interact with the sodium ions that were formerly bound to the fluoride and hydroxide entities. This later bromide reaction probably causes the release of more hitherto bound hydroxide molecules into solution thereby increasing the pH of the water as witnessed during the experimentation.

The surface complexation of aqueous ions in many cases depends on the development of the surface charge and the coulombic or electrostatic attraction between the surface binding sites and the aqueous ions (Sujana & Anand, 2011). The increasing pH of the aqueous solution increases the alkalinity and concentration of hydroxyl (OH^-) ions. The coulumbic attraction for the negatively charged OH^- ions therefore reduces the net positive charge on the zeolitic surface. For this reason, the affinity for other negatively charged species in solution such as fluoride is also reduced. During a similar pH increase,

Sajidu *et al.* (2008) attributed the decline in fluoride removal to both Le hatelier's principle and competition between the OH^- and F^- for the same adsorption sites. OH^- and F^- are isoelectronic with the same charge and ionic radii and thus the increase in concentration of OH^- reduces the activity of F^- to be adsorbed onto the zeolitic surface. Moreover, the observed rapid change in fluoride uptake with slight pH change could be ascribed to the point of zero charge (pzc) on the zeolitic surface. From Figure 4–16, the significant increase in fluoride removal performance from pH of 5.5 to pH of 7.5 could be due to how far below and above, respectively, the pHs are from the pzc of the zeolite surface. The pH of 5.5 is probably less than the pzc of the modified zeolite, rendering a positively charged surface to favour attraction of the negatively charged fluoride ions. Conversely, the pH of the aqueous solutions from 7.5 to 9.5 is likely to be above the pzc of the zeolite resulting in a negatively charged surface. The affinity for fluoride is therefore reduced and even repelled at a much greater pH (i.e. pH of 8.5 and 9.5). This observation is in consonance with what Leyva-Ramos *et al.* (2008) reported when activated alumina prepared from pseudo-boehmite was used as an adsorbent to remove fluoride from aqueous solution.

CHAPTER 5:

CONCLUSIONS AND RECOMMENDATIONS

5.1   Conclusions

From the study conducted, the following conclusions have been deduced:

⌘   The XRD of the synthesized zeolites confirmed the type of each zeolite produced. The zeolite synthesized from a combination of locally available clay and bauxite minerals produced 100 % pure zeolite Na-LTA. However, 10 % impure quartz was found in the zeolite Na-LSX synthesized from only clay. The zeolite, ZR, synthesized from chemical grade reagents had characteristics common to zeolite Na-LSX (82.9 %). Even though the initial intent was to produce pure zeolite Na-LTA, the final product had lesser extent of zeolite Na-LTA (17.1 %).

⌘   Comparing the EDX results of the modified zeolites to the unmodified zeolites, an increase in elemental C and a decrease in elemental Na was observed. These observed adjustments is as a result of the ion exchange between the organic HDTMA+ cations in solution and the Na+ ions on the surface of the zeolites. Hence the EDX analysis was able to confirm the surface modification of the zeolites.

⌘   Modification of the synthesized zeolites was successfully conducted using varying HDTMA dosages (0.5, 1, 2, 5, 10, 15 g/L). Using an initial 10 mg/L fluoride solution, the batch adsorption revealed that the fluoride removal potential of the modified zeolites generally increased with increase in HDTMA dosage (or concentration). The 5 g/L HDTMA dosage that was used to modify zeolite Na-LSX gave the best fluoride removal potential and hence was preferably chosen for further batch removal processes. ⌘ The

batch experiment further revealed that the fluoride removal potential of zeolite Na-LSX increased with increasing modification reaction time. The 24 hours modification reaction time that produced modified zeolite Na-LSX was found to be the best performing for fluoride removal. Beyond this 24 hours modification reaction time, the fluoride removal performance of the modified zeolite Na-LSX reduced slightly.

⌘ Fluoride removal was found to be significantly dependent on pH. Within the pH range of 5.5 to 9.5, fluoride removal increased with decreasing pH and vice versa for both unmodified and modified zeolite Na-LSX. Without pH control, the solution pH rose from 7.5 to 9.5 and no considerable fluoride removal was recorded in this basic region. Upon maintaining pH of fluoride solution at 6.5±0.2, both unmodified and modified zeolite NaLSX recorded considerable fluoride uptakes. Under the tested conditions (5 mg/L HDTMA dosage, 24 hours modification reaction time and a controlled pH of 5.5±0.2), maximum fluoride removal (86 %) was obtained using modified zeolite Na-LSX as adsorbent. This represents 71 and 18 % increase in fluoride removal from the controlled pH of 7.5 ± 0.2 and 6.5 ± 0.2 respectively.

5.2   Recommendations

⌘ Further works should be carried out to investigate the effects of temperature, size of modified zeolites and other competing anions in solutions on fluoride removal

⌘ Studies on the adsorption capacities of the modified zeolites should be   investigated using adsorption kinetics and isotherms

⌘ Further application of the HDTMA modified zeolites should be employed in column studies in order to understand how they behave in such applications

⌘ The treated water should be investigated for possible toxicity due to HDTMA-Br leachate into solution

⌘ Cost analysis should be conducted on the synthesis, modification and application of the HDTMA modified zeolite Na-LSX to determine their economic viability

REFERENCES

Adzabe, F. J. K. (2011). Synthesis of Linde-Type X Zeolite and its Application to Improve Soil Nutrients. MSc Thesis, Department of Physics, KNUST.

Aghaii, M. D., Pakizeh, M., & Ahmadpour, A. (2013). Synthesis and characterization of modified UZM-5 as adsorbent for nitrate removal from aqueous solution. *Separation and Purification Technology*, *113*, 24–32. http://doi.org/10.1016/j.seppur.2013.04.013

Apambire, W. B., Boyle, D. R., & Michel, F. A. (1997). Geochemistry, genesis, and health implications of fluoriferous groundwaters in the upper regions of Ghana. *Environmental Geology*, *33*(1), 13–24. http://doi.org/10.1007/s002540050221

Appropedia.org. (2013). Water defluoridation. Retrieved September 7, 2015, from http://www.appropedia.org/Water_defluoridation

Apreutesei, R. E., Catrinescu, C., & Teodosiu, C. (2008). Surfactant-modified natural zeolites for environmental applications in water purification. *Environmental Engineering and Management Journal*, *7*(2), 149–161.

Asare-Donkor, N. K., Wemegah, D. D., & Adimado, A. A. (2013). Chemical Analysis of Freshwater Bodies in the Kumasi Metropolis and Its Environs, Ghana. *Journal of Environment and Earth Science*. Retrieved from http://www.iiste.org/Journals/index.php/JEES/article/view/7325

Balkis, N. (Ed.). (2012). Water Pollution. InTech. http://doi.org/10.5772/1418

Bandewar, S., Mane, S. ., & Tirthakar, S. . (2015). Removal of fluoride from drinking water by using low cost adsorbent. *International Journal of Research in Engineering and Technology*, *04*(04), 349–351.

Bansiwal, A. K., Rayalu, S. S., Labhasetwar, N. K., Juwarkar, A. A., & Devotta, S. (2006). Surfactant-modified zeolite as a slow release fertilizer for phosphorus. *Journal of Agricultural and Food Chemistry*, *54*(13), 4773–4779.

Bedu-Addo, K., Akanwariwiak, W. G., & Mensa-Bonsu, I. F. (2013). Water Audit of reweries : A ase Study of a Modern rewery in Ghana. *Universal Journal of Environmental Research and Technology*, *3*(2), 311–317.

Bekkum, H. van. (2005). Zeolites and Ordered Mesoporous Materials: Progress and Prospects. Prague: Gulf Professional Publishing. Retrieved from https://books.google.com/books?id=XEfO7-41ZqsC&pgis=1

Bell, R. G. (2001). What are zeolites? Retrieved September 15, 2015, from http://www.bza.org/zeolites/

Bhatnagar, A., Kumar, E., & Sillanpää, M. (2011). Fluoride removal from water by adsorption-A review. *Chemical Engineering Journal*, *171*(3), 811–840. http://doi.org/10.1016/j.cej.2011.05.028

Bogdanov, B., Georgiev, D., Angelova, K., & Hristov, Y. (2009). Synthetic zeolites and their industrial and environmental applications -Review. In International Science conference ― conomics and Society development on the ase of Knowledge‖ (Vol. IV). Stara Zagora.

Bowman, R. S. (2003). Applications of surfactant-modified zeolites to environmental remediation. *Microporous and Mesoporous Materials*, *61*(1-3), 43–56. http://doi.org/10.1016/S1387-1811(03)00354-8

British Geological Survey.   . Groundwater Quality : Ghana   –4.

Brossok, G. E., McTigue, D. J., & Kuthy, R. A. (1987). The use of a colorimeter in analyzing the fluoride content of public well water. *Pediatric Dentistry*, *9*(3), 204–207.

Buamah, R., Mensah, R. A., & Salifu, A. (2013). Adsorption of fluoride from aqueous solution using low cost adsorbent. *Water Science & Technology: Water Supply*, *13*, 238–248. http://doi.org/10.2166/ws.2013.016 ansever rdo an   .   . Cr (VI) removal with natural, surfactant modified and bacteria loaded zeolites. İzmir Institute of Technology. Retrieved from http://openaccess.iyte.edu.tr:8080/xmlui/handle/11147/2888

Chutia, P., Kato, S., Kojima, T., & Satokawa, S. (2009). Adsorption of As(V) on surfactantmodified natural zeolites. *Journal of Hazardous Materials*, *162*(1), 204–211. http://doi.org/10.1016/j.jhazmat.2008.05.024

Davis, S., & Inoguchi, Y. (2013). Zeolites. Chemical Economics Handbook. SRI Consulting. Retrieved from https://www.ihs.com/products/zeolites-chemicaleconomics-handbook.html

Djaisi, K. K., & Bulley, R. (2015). Warning! Waste-water effluents account for high child mortality rates. B&FT Online Ghana. Retrieved from http://thebftonline.com/content/warning-waste-water-effluents-account-high-childmortality-rates

Donk, S. van. (2002). Adsorption, diffusion and reaction studies of hydrocarbons on zeolite catalysts. Utrecht University. Retrieved from http://dspace.library.uu.nl/bitstream/handle/1874/764/full.pdf

Edmunds, W. M., & Smedley, P. L. (1996). Groundwater geochemistry and health: an overview. *Geological Society, London, Special Publications*, *113*(1), 91-105

Electrodialysis.   (n.d.).   Retrieved   January   17,   2016,   from https://electrosynthesis.com/electrodialysis/

Falcioni, M., & Deem, M. W. (1999). A Biased Monte Carlo Scheme for Zeolite Structure Solution. *Journal of Chemical Physics*, *110*(3), 28. http://doi.org/10.1063/1.477812

Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L., & Magara, V. (2006). Fluoride in drinking-water. London: IWA Publishing, UK, p30. Retrieved from

https://books.google.com/books?hl=en&lr=&id=Hiet-EqiksQC&oi=fnd&pg=PR9&dq=fawell+Fluoride+in+drinking+water+(WHO+Drinking+%E2%80%93Water+Series)&ots=bT0TqDkap5&sig=UVhi3U8bffjHHhOt0o8aAmhLuY

Feng, N.-Q., & Peng, G.-F. (2005). Applications of natural zeolite to construction and building materials in China. *Construction and Building Materials*, *19*(8), 579–584.

Firempong, C., Nsiah, K., Awunyo-Vitor, D., & Dongsogo, J. (2013). Soluble fluoride levels in drinking water - a major risk factor of dental fluorosis among children in Bongo community of Ghana. *Ghana Medical Journal*, *47*(1), 16–23. Retrieved from http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=3645181&tool=pmcentrez&rendertype=abstract

Flanigen, E. M., Broach, R. W., & Wilson, S. T. (2010). Introduction. In S. Kulprathipanja (Ed.), Zeolites in Industrial Separation and Catalysis (pp. 1–26). Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA. http://doi.org/10.1002/9783527629565.ch1

Flanigen, E. M., Parton, R. L., & Katonah, W. P. (1978). Silica polymorph and process for preparing same. US.

Fordyce, F. M., Vrana, K., Zhovinsky, E., Povoroznuk, V., Toth, G., Hope, B. C., Baker, J. (2007). A health risk assessment for fluoride in Central Europe. *Environmental Geochemistry and Health*, *29*(2), 83–102. http://doi.org/10.1007/s10653-006-9076-7

Georgiev, D., Bogdanov, B., & Angelova, K. (2009). Synthetic zeolites–structure, classification, current trends in zeolite synthesis: Review. In International Science conference ― conomics and Society development on the ase of Knowledge‖ (Vol. VII). Retrieved from http://www.sustz.com/Proceeding09/Papers/Technical studies/D_GEORGIEV.pdf

Gholikandi, G. B., Baneshi, M. M., Dehghanifard, E., & Salehi, S. (2010). Natural Zeolites Application as Sustainable Adsorbent for Heavy Metals Removal from Drinking Water. *Iranian Institute of Toxicology*, *3*(3), 302–310. Retrieved from http://ijt.arakmu.ac.ir/files/site1/user_files_3a0bf3/godadmin-A-10-2-28-68f8de0.pdf

Gopal, R., & Ghosh, P. K. (1985). Fluoride in Drinking Water-Its Effects and Removal. *Defence Science Journal*, *35*(1), 71–88.

Gumbo, F. J., & Mkongo, G. (1995). Water Defluoridation for Rural Fluoride Affected Communities in Tanzania. In Proceedings of The 1st International Workshop on Fluorosis Prevention and Defluoridation of Water (pp. 109–114). Int. Soc. Fluoride Res.

Gyasi, S., Appiah-Effah, E., & Nkansah, A. (2014). Microbial Impacts of Brewery Effluent Discharge on Sissa River: A Case Study of Kaase in Kumasi, Ghana. *Research*

Journal of Microbiology, *9*(5), 239-245. Retrieved from http://scialert.net/qredirect.php?doi=jm.2014.239.245&linkid=pdf

Habuda-Stanić M. Ravančić M. . & Flanagan A. 4 . A Review on Adsorption of Heavy Metals from Aqueous Solution. *Materials*, *7*, 6317–6366. http://doi.org/10.3390/ma7096317

Haggerty, G. M., & Bowman, R. S. (1994). Sorption of chromate and other inorganic anions by organo-zeolite. *Environmental Science and Technology*, *28*(3), 452–458. http://doi.org/10.1021/es00052a017

Hrenovic, J., Ro, M., Tiblja, D., & Ivankovi, T. (2010). Phosphate Removal From Wastewater By Surfactant-Modified Clinoptilolite. In The 3rd Croatian-Slovenian Symposium on Zeolites (pp. 15–18).

Hui, H., Gao, J., Wang, G., Liu, P., & Zhang, K. (2013). Effects of Na and K ions on the Crystallization of Low-silica X Zeolite and its Catalytic Performance for Alkylation of Toluene with Methanol. *Journal of the Brazilian Chemical Society*, *25*(1), 65–74. http://doi.org/10.5935/0103-5053.20130269

Hussein, M. M., Khader, K. M., & Musleh, S. M. (2014). Characterization of raw zeolite and surfactant-modified zeolite and their use in removal of selected organic pollutants from water. *International Journal of Chemical Sciences*, *12*(3), 815–844.

IPCS & WHO. (2002). Environmental Health Criteria 227: Fluorides (pp. 1&2) . Geneva.

Kabuba, J., & Mulaba-Bafubiandi, A. (2013). Thermodynamics of Adsorption of Fluoride, Bromide and Iodide ions by an activated zeolite. In International Conference on Chemical, Mining and Metallurgical Engineering, 221–227. Johannesburg.

Kagya, A. W. (2011). Determination of effluent quality of two wastewater treatment systems: an activated sludge sewage treatment plant and waste stabilization ponds at Juapong. Kwame Nkrumah University of Science & Technology. Retrieved from http://ir.knust.edu.gh/bitstream/123456789/4095/1/KAGYA FINAL THESIS 2011.pdf

Kazemian, H. (2012). Handbook of Natural Zeolites. (V. J. Inglezakis & A. A. Zorpas, Eds.). Bentham Science Publishers, 214-237. Retrieved from https://books.google.com/books?id=p88zmymzTMUC&pgis=1

Khandare, H. W. (2013). Fluoride Contaminated Water and its Implications on Human Health- A Review. *International Journal of ChemTech Research*, *5*(1), 502–511. Retrieved from http://connection.ebscohost.com/c/articles/90515529/fluoridecontaminated-water-implications-human-health-review

Khemthong, P., Prayoonpokarach, S., & Wittayakun, J. (2007). Synthesis and Characterization of Zeolite Lsx From Rice Husk Silica. *Suranaree Journal of Science and Technology*, *14*(4), 367–379.

Kovo, S. A. (2011). Development of zeolites and zeolite membranes from Ahoko Nigerian Kaolin. PhD Thesis, School of Chemical Engineering and Analytical Science, The University of Manchester.

Kreussler, S., & Bolz, D. (1999). Experiments on solar adsorption refrigeration using zeolite and water. Laboratory for Solar Energy, University of Applied Sciences Lubeck. University of Applied Sciences, Stephensonstr, Germany. Retrieved from http://ptp.irb.hr/upload/mape/solari/26_Siegfried_Kreussler_EXPERIMENTS_ON_S OLAR_ADSORPTION_REFRIG.pdf

Kulprathipanja, S. (2010). Zeolites in Industrial Separation and Catalysis. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 6-7. Retrieved from https://books.google.com.gh/books/about/Zeolites_in_Industrial_Separation_and_Ca.h tml?id=_g6Ov87InikC&pgis=1

Kumar, P., Jadhav, P. D., Rayalu, S. S., & Devotta, S. (2007). Surface-modified zeolite-A for sequestration of arsenic and chromium anions. *Current Science*, *92*(4), 512–517.

Kupaza, R. (2013). Tanzania: Seminar On ―Roasted Teeth‖ In Arusha. The Arusha Times. Retrieved January 15, 2016, from http://fluoridealert.org/news/tanzania-seminar-onroasted-teeth-in-arusha/

Kwakye-Awuah, B. (2008). Production of silver-loaded zeolites and investigation of their antimicrobial activity. PhD Thesis, University of Wolverhampton.

Kwakye-Awuah, B., Labik, L., Nkrumah, I., & Williams, C. (2014). Removal of Arsenic in river water samples obtained from a minning community in Ghana using laboratory synthesized zeolites. *International Journal of Advanced Scientific and Technical Research*, *4*(4), 304–315.

Kwakye-Awuah, B., Von-Kiti, E., Buamah, R., Nkrumah, I., & Williams, C. (2014). Effect of Crystallization Time on the Hydrothermal Synthesis of Zeolites from Kaolin and Bauxite. *International Journal of Scientific & Engineering Research*, *5*(2).

Labik, K. L. (2012). Synthesis of zeolites and their applications to removal of arsenic and ammonia–nitrogen from samples of contaminated water. MSc Thesis, Department of Physics, KNUST.

Leyva-Ramos, R., Jacobo-Azuara, a., Diaz-Flores, P. E., Guerrero-Coronado, R. M., Mendoza-Barron, J., & Berber-Mendoza, M. S. (2008). Adsorption of chromium(VI) from an aqueous solution on a surfactant-modified zeolite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *330*(1), 35–41. http://doi.org/10.1016/j.colsurfa.2008.07.025

Leyva-Ramos, R., Medellin-Castillo, N. a, Jacobo-Azuara, A., Mendoza-Barrom, J., Landin-Rodriguez, L. E., Martinez-Rosales, J. M., & Aragon-Piña, A. (2008). Fluoride

removal from water solution by adsorption on activated alumina prepared from pseudo-boehmite. *J. Environ. Eng. Manage.*, *18*(5), 301–309.

Li, Z., Beachner, R., McManama, Z., & Hanlie, H. (2007). Sorption of arsenic by surfactant-modified zeolite and kaolinite. *Microporous and Mesoporous Materials*, *105*(3), 291–297.

Lyengar, L. (2002). Technologies for fluoride removal. Small Community Water Supplies (pp. 501–511). Retrieved from http://www.samsamwater.com/library/TP40_22_Technologies_for_fluoride_removal.p df

Manning, D. A. C. (2007). Handbook of Clay Science (Developments in Clay Science, 1) - Edited by F. Bergaya, B.K.G. Theng & G. Lagaly. *European Journal of Soil Science*, *58*(2), 518–519. http://doi.org/10.1111/j.1365-2389.2007.00898_4.x

Margeta K. Logar N. Z. Šiljeg M. & Farkaš A.   3 . Natural Zeolites in Water Treatment – How Effective is Their Use. In Water Treatment (pp. 81-112). InTech. Retrieved from http://cdn.intechopen.com/pdfs-wm/41947.pdf

Masukume, M., Onyango, M. S., Aoyi, O., & Otieno, F. (2010). Nitrate removal from groundwater using modified natural zeolite. Retrieved from http://www.ewisa.co.za/literature/files/144_97 Masukume.pdf

Meenakshi, & Maheshwari, R. C. (2006). Fluoride in drinking water and its removal. *Journal of Hazardous Materials*, *137*(1), 456–463. http://doi.org/10.1016/j.jhazmat.2006.02.024

Mehdizadeh, S., Sadjadi, S., Ahmadi, S. J., & Outokesh, M. (2014). Removal of heavy metals from aqueous solution using platinum nanopartcles/Zeolite-4A. *J Environ Health Sci Eng*, *12*, 7. http://doi.org/10.1186/2052-336X-12-7

Mohammadi, A., Bina, B., Ebrahimi, A., Hajizadeh, Y., Amin, M. M., & Pourzamani, H. (2012). Effectiveness of nanozeolite modified by cationic surfactant in the removal of disinfection by-product precursors from water solution. *International Journal of Environmental Health Engineering 1*(1), 14-19. Medknow Publications and Media Pvt. Ltd. http://doi.org/10.4103/2277-9183.94387

Mozgawa, W. (2000). The influence of some heavy metals cations on the FTIR spectra of zeolites. *Journal of Molecular Structure*, *555*(1), 299–304.

Mumpton, F. A., & Fishman, P. H. (1977). The application of natural zeolites in animal science and aquaculture. *Journal of Animal Science*, *45*(5), 1188–1203.

Murugan, M., & Subramanian, E. (2006). Studies on defluoridation of water by Tamarind seed, an unconventional biosorbent. *Journal of Water and Health*, *4*(4), 453–461. http://doi.org/10.2166/wh.2006.014

Ohrman, O. (2000). Synthesis and Characterization of Zeolite Coatings on Monoliths Support. MSc Thesis, Lulea University of Technology, Sweden.

Olajumoke, A., Oluwatosin, A., Olumuyiwa, O., & Abimbola, F. (2010). Impact Assesment of Brewery Effluent on Water Quality in Majawe , Ibadan , Southwestern Nigeria. *Researcher*, *2*(5), 21–28.

Onyango, M. S., Masukume, M., Ochieng, A., & Otieno, F. (2010). Functionalised natural zeolite and its potential for treating drinking water ontaining excess amount of nitrate. *Water SA*, *36*(5), 655–662. http://doi.org/10.4314/wsa.v36i5.61999

Pederson, T. L. (1997). Industrial Effluents as a Source of Drinking Water Contamination. Retrieved February 1, 2016, from http://extoxnet.orst.edu/faqs/safedrink/indust.htm

Peskov, M. (2010). Zeolites. Retrieved September 15, 2015, from http://www.asdn.net/asdn/chemistry/zeolites.shtml

Poudyal, M., & Babel, S. (2015). Removal of fluoride using granular activated carbon and domestic sewage sludge. 4th International Conference on Informatics, Environment, Energy and Applications, *82*(27).

Rafique, A., Awan, M. A., Wasti, A., Qazi, I. A., & Arshad, M. (2013). Removal of Fluoride from Drinking Water Using Modified Immobilized Activated Alumina. *Journal of Chemistry*, *2013*, 1–7. http://doi.org/10.1155/2013/386476

Ranck, J. M., Bowman, R. S., Weeber, J. L., Katz, L. E., & Sullivan, E. J. (2005). BTEX removal from produced water using surfactant-modified zeolite. *Journal of Environmental Engineering*, *131*(3), 434–442.

Rasuli, L., Emamjome, M. M., & Mahvi, A. H. (2014). Removal Of Fluoride From Water Solutions By Natural Zeolite Modified With Cationic Surfactant. *Fresenius Environmental Bulletin*, *23*(2), 2014. Retrieved from https://scholar.google.com/scholar?hl=en&q=REMOVAL+OF+FLUORIDE+FROM+WATER+SOLUTIONS+BYNATURAL+ZEOLITE+MODIFIED+WITH+CATIONIC+SURFACTANT&btnG=&as_sdt=1%2C5&as_sdtp=#0

Renuka, P., & Pushpanji, K. (2013). Review on Defluoridation Techniques of Water. *The International Journal of Engineering And Science (IJES)*, *2*(3), 86–94.

Ríos, C. A. (2008). Synthesis of zeolites from geological materials and industrial wastes for potential application in environmental problems. PhD Thesis, University of Wolverhampton. Retrieved from http://wlv.openrepository.com/wlv/bitstream/2436/39855/1/Reyes_PhD%2520thesis.doc

Ríos, C. A., Williams, C. D., & Maple, M. J. (2007). Synthesis of Zeolites and Zeotypes by HidrothermalTransformation of Kaolinite and Metakaolinite. *Bistua: Revista de La*

Facultad de Ciencias Básicas, *5*(1), 15–26. Retrieved from http://www.redalyc.org/articulo.oa?id=90350103

Robson, H. (2001). Verified Synthesis of Zeolitic Materials: Second Edition (2nd ed.). Amsterdam: Elsevier.

Roque-Malherbe, R. M. A. (2009). The Physical Chemistry of Materials: Energy and Environmental Applications. CRC Press. Retrieved from https://books.google.com/books?id=nAi1o4fAtiAC&pgis=1

Sajidu, S. M. I., Masamba, W. R. L., Thole, B., & Mwatseteza, J. F. (2008). Groundwater fluoride levels in villages of Southern Malawi and removal studies using bauxite. *International Journal of Physical Sciences*. Retrieved from http://ubrisa.ub.bw/jspui/bitstream/10311/1091/5/Sajidu_IJPS_2008.pdf

Salager, J.-L. (2002). Surfactants - Types and uses. Laboratorio FIRP, 2, 36. Retrieved from http://www.nanoparticles.org/pdf/Salager-E300A.pdf

Salifu, A., Petrusevski, B., Ghebremichael, K., Buamah, R., & Amy, G. (2012). Multivariate statistical analysis for fluoride occurrence in groundwater in the Northern region of Ghana. *Journal of Contaminant Hydrology*, *140-141*, 34–44. http://doi.org/10.1016/j.jconhyd.2012.08.002

Schulze-Makuch, D., Pillai, S. D., Guan, H., Bowman, R., Couroux, E., Hielscher, F., Kretzschmar, T. (2002). Surfactant-modified zeolite can protect drinking water wells from viruses and bacteria. *Eos, Transactions, American Geophysical Union*. http://doi.org/10.1029/2002EO000128

Shimekit, B., & Mukhtar, H. (2012). Natural gas purification technologies-major advances for CO_2 separation and future directions. InTech. Croatia, Europe.

Shoumkova, A. (2011). Zeolites for water and wastewater treatment: An overview. Australian Institute of High Energetic Materials. Retrieved from http://www.ausihem.org/web_documents/ISBN 978-0-9806811-1-6.pdf

Singh, R., & Maheshwari, R. C. (2001). Defluoridation of drinking water - a review. *Ind. J Environ. Protec.*, *21*(11), 983–991.

Smedley, P., Nkotagu, H., Pelig-Ba, K., MacDonald, A., Tyler-Whittle, R., Whitehead, E., & Kinniburgh, D. (2002). Fluoride in groundwater from high-fluoride areas in Ghana and Tanzania. ―Minimising fluoride in drinking water in problem aquifers.‖ Retrieved from http://resources.bgs.ac.uk/sadcreports/tanzania2002smedleyfluoridecr02316n.pdf

Smittakorn, S., Jirawongboonrod, N., Mongkolnchai-Arunya, S., & Durnford, D. (2010). Homemade bone charcoal adsorbent for defluoridation of groundwater in Thailand. *Journal of Water and Health*, *8*(4), 826–836. http://doi.org/10.2166/wh.2010.131

Srdjan, K., Dragoslav, S., Dragan, M., Slavisa, T., Slobodan, M., Slobodan, K., & Ljiljana, A. (2012). Effects of reactive filters based on modified zeolite in dairy industry

wastewater treatment process. *Chemical Industry and Chemical Engineering Quarterly*, *19*(4), 92–92. http://doi.org/10.2298/CICEQ120629092K

Sujana, M. G., & Anand, S. (2011). Fluoride removal studies from contaminated ground water by using bauxite. *Desalination*, *267*(2-3), 222–227. http://doi.org/10.1016/j.desal.2010.09.030

Suneetha, N., Rupa, K., Sabitha, V., Kumar, K., Mohanty, S., Kanagasabapathy, A., & Rao, P. (2008). Defluoridation of water by a one step modification of the Nalgonda technique. *Annals of Tropical Medicine and Public Health*, *1*(2), 56–58. http://doi.org/10.4103/1755-6783.50685

Thanos, A. G., Drakopoulos, V., Pavlatou, E. A., & Haralambous, K. J. (n.d.). Sorption of chromate anions by zeolite and vermiculite modified with organic and inorganic substances. School of Chemical Engineering, National Technical University of Athens, Zographou Campus, GR-15782 Athens, Greece, (Vi).

Umarani, P., & Ramu, A. (2014). Fluoride Contamination Status of Groundwater in East Coastal Area in Tamilnadu , India. *International Journal of Innovative Research in Science, Engineering and Technology*, *3*(3), 10045–10051.

UNEP-Nairobi K.   6 . hallenges to international waters : regional assessments in a global perspective. Nairobi, Kenya: UNEP, United Nations Environment Programme. Retrieved from http://www.unep.org/dewa/giwa/publications/finalreport/freshwater_shortage.pdf

USEPA.   (n.d.).   What   is   Nonpoint   Source?   Retrieved   from http://www.epa.gov/pollutedrunoff-nonpoint-source-pollution/what-nonpoint-source

USEPA. (1993). Fact Sheet: Office of Water. Retrieved January 1, 2016, from http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=20001P2M.txt

Vandas, S. J., Winter, T. C., & Battaglin, W. A. (2002). Water and the environment. Alexandria, Virginia: American Geological Institute. Retrieved from https://books.google.com.gh/books?id=sWXxAAAAMAAJ

Varadan, V. K. (2010). Nanoscience and Nanotechnology in Engineering. World Scientific. Retrieved from https://books.google.com/books?id=Trz3pLn0G68C&pgis=1

Virta, R. L. (2008). Natural and Synthetic Zeolites. U.S. Geological Survey. Retrieved from http://minerals.usgs.gov/mineralofthemonth/zeolites.pdf

Volterra, L., Boualam, M., Menesguen, A., Duguet, J. P., Duchemin, J., & Bonnefoy, X. (2002). Eutrophication and Health. WHO & European Commission, (pp. 1-32)

Von-Kiti, E. (2012). Synthesis of zeolites and their application to the desalination of seawater. MSc Thesis, Department of Physics, KNUST. Retrieved from

http://ir.knust.edu.gh/bitstream/123456789/4083/1/Final Thesis, 2012_ELIZABETH VON-KITI.pdf

Vujaković A. Daković A. Lemić J. Radosavljević-Mihajlović A. & TomasevicCanovic, M. (2003). Adsorption of inorganic anionic contaminants on surfactant modified minerals. *Journal of the Serbian Chemical Society*, *68*(11), 833–841. http://doi.org/10.2298/JSC0311833V

Wang, S., & Peng, Y. (2010). Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*. http://doi.org/10.1016/j.cej.2009.10.029

Warchoł J. Misaelides P. Petrus R. & Zamboulis D. 6 . Preparation and application of organo-modified zeolitic material in the removal of chromates and iodides. *Journal of Hazardous Materials*, *137*(3), 1410–1416. http://doi.org/10.1016/j.jhazmat.2006.04.028

Wibowo, W., Utari, T., & Yunarti, R. R. T. (2011). Anion exchange capacity of chromate on modified zeolite clinoptilolite with HDTMA-Br and its regeneration. *Makara, Sains*, *15*(1), 53–57. Retrieved from http://citation.itb.ac.id/pdf/JURNAL/JURNAL MAKARA SERI SAINS/VOL 15 No.1 APRIL 2011/837.pdf

Wikipedia.org. (2014). Cetrimonium bromide. In Wikipedia, The Free Encyclopedia. Retrieved from https://en.wikipedia.org/wiki/Cetrimonium_bromide Win,

D. T. (2012). Zeolites - earliest solid state acids. AUJT (pp. 36-41).

Worch, E. (2012). Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling. Walter de Gruyter. Retrieved from https://books.google.com/books?id=xUBhp6r6zwwC&pgis=1

World Health Organization (WHO). (2011). Nitrate and nitrite in drinking-water (Background document for development of WHO Guidelines for Drinking-water Quality). Retrieved from http://www.who.int/water_sanitation_health/dwq/chemicals/nitratenitrite2ndadd.pdf

Yusof, A. M., & Malek, N. A. N. N. (2009). Removal of Cr(VI) and As(V) from aqueous solutions by HDTMA-modified zeolite Y. *Journal of Hazardous Materials*, *162*, 1019–1024. http://doi.org/10.1016/j.jhazmat.2008.05.134

APPENDICES

Appendix 1: Selected Standard Curves Used for [F⁻] determination

y = -4.1886x + 69.756
R² = 0.956

y = -4.2892x - 24.62
R² = 0.9554
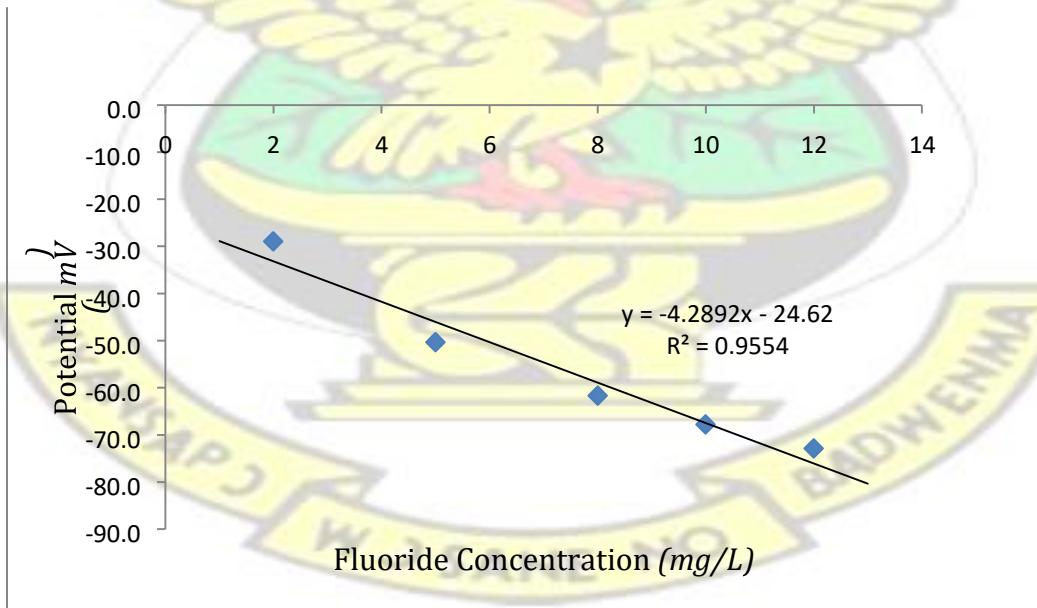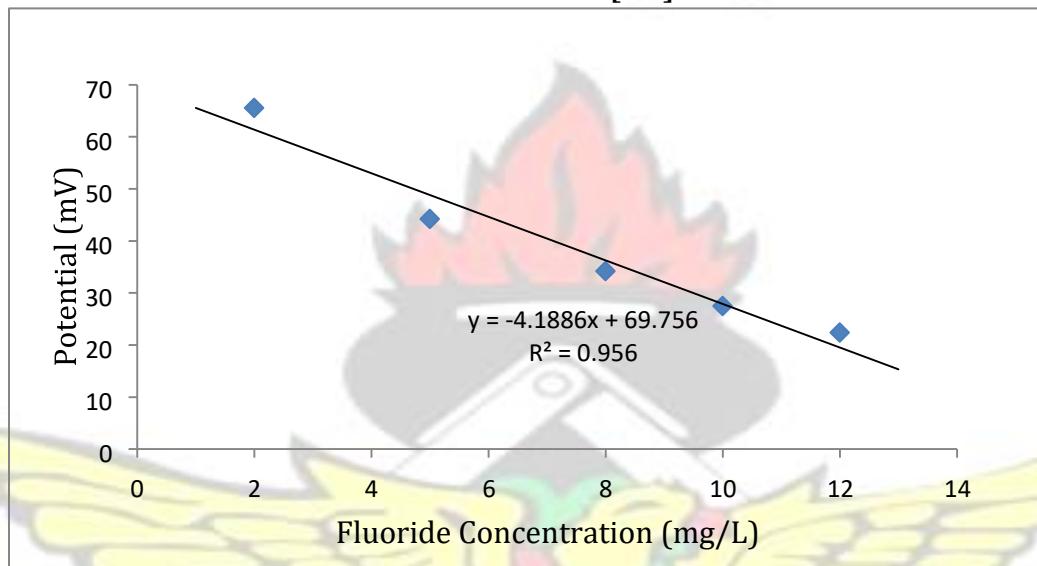
Appendix 2: Results of Batch Adsorption Studies Using Unmodified & Modified Zeolites

(a) Table showing measured potentials and corresponding F^- concentrations using unmodified zeolite **Na-LSX**, **Na-LTA** & **ZR**

Time (mins)	0	5	10	20	30	60	90	120	150	180
Blank										
Pot. (mV)	27.2	27.0	27.2	27.8	27.8	27.3	27.2	27.2	27.8	27.8
[F⁻] (mg/L)	10	10	10	9.9	9.9	10	10	10	9.9	9.9
Na-LSX										
Pot. (mV)	25.2	22.5	31.8	41.3	44.4	45.8	47.8	51.6	48.6	50.2
[F⁻] (mg/L)	10.0	9.1	7.9	4.9	4.3	4.1	3.8	3.2	3.6	3.4
Na-LTA										
Pot. (mV)	22.7	25.7	28.1	29.9	29.5	36.1	36.8	39.4	42.8	43.2
[F⁻] (mg/L)	10	8.8	8.0	7.5	7.6	5.9	5.8	5.2	4.6	4.5
ZR										
Pot. (mV)	25.3	27.2	32.2	51.5	65.3	65	70.0	73.7	70.8	73.0
[F⁻] (mg/L)	10	8.5	7.7	3.2	1.8	1.9	1.5	1.3	1.5	1.3

(b) Effect of varying HDTMA dosage on F^- removal: Table of results using zeolite **Na-LSX**

HDTMA dosage	Time (mins)	0	5	10	20	30	60	90	120	150	180
0.5 g/L	Pot. (mV)	21.7	24.7	23.8	27.2	32.2	41.9	48	48.1	49	49.8
	[F⁻] (mg/L)	9.9	8.9	.	.		4.4	3.4	3.4	3.2	3.2	.	.
							36.5	46.4	47.5	46.5	52.1
1 g/L	Pot. (mV)	20.8						5.5	3.7	3.5	3.7	2.9
	[F⁻] (mg/L)	10	9.1	.	.		·25.2	34.4	47.4	53.7	60.6	.	.	.
2 g/L	Pot. (mV)	21.4									
	[F⁻] (mg/L)	10	9.5	.	.	.			.	.	.

5 g/L	Pot. (mV)	21.4	.			7.4	6.2	3.5	2.7	2.0
						37.3	60.2	68.8	62.7	62.8
	[F⁻] (mg/L)	10				5.4	2.0	1.4	1.5	1.3
						34.8	37.4	39.3	40.6	39.5
10 g/L	Pot. (mV)	22.6	.	.	.					
	[F⁻] (mg/L)	10 9.6				6.2	5.6	5.3	5.0	5.2
			.	.	.	34.8	36.1	35.1	37.9	39.4
15 g/L	Pot. (mV)	22.7	.	.	.				. . .	
	[F⁻] (mg/L)	10 8.9 8.1 8.0 6.6 6.2							5.9 6.1 5.5 5.2	

(c) Effect of varying HDTMA dosage on F⁻ removal: Table of results using zeolite **Na-LTA**

HDTMA dosage	Time (mins)	0	5	10	20	30						60	90	120	150	180
0.5 g/L	Pot. (mV)	22.1	23.7	24.8	25.5	26.5						30.2	32.2	34.1	35.5	39.6
	[F⁻] (mg/L)	9.8														
1 g/L	Pot. (mV)															
	[F⁻] (mg/L)					8.3	7.2	6.6	6.1	5.8	4.9					
2 g/L	Pot. (mV)					23.6	25.6	28.2	28.2	31.5	34.5					
	[F⁻] (mg/L)	9.9				8.7	8.1	7.4	7.4	6.6	5.9					
5 g/L	Pot. (mV)					24.4	27.5	27.6	30.3	33.6	38.6					
	[F⁻] (mg/L)	9.9				9.0	8.0	7.9	7.2	6.3	5.1					
						27.9	30.1	38.0	38.0	38.5	41.2					
10 g/L	Pot. (mV)					7.9	7.2	5.2	5.2	5.1	4.4					
	[F⁻] (mg/L)					23.1	30.2	32.4	32.6	33.4	35.2					
15 g/L	Pot. (mV)					8.1	6.1	5.6	5.6	5.4	5.1					
						26.7	30.0	32.5	35.7	36.6	41.3					
	[F⁻] (mg/L)	10	9.5	8.6	8.3	7.8						6.9	6.4	5.7	5.5	4.6

(d) Effect of varying HDTMA dosage on F⁻ removal: Table of results using zeolite **ZR**

HDTMA dosage	Time (mins)	0	5	10	20	30	60	90	120	150	180

0.5 g/L	Pot. (mV)	21.5	25.5	27.5	29.8		31.1	36.4		38.6	43	47.3	50.4
	[F] (mg/L)	10	8.7					5.6 / 37.4	5.1 / 36.5	4.2 / 41.2	3.5 / 51.7		
1 g/L	Pot. (mV)	20.9											
	[F] (mg/L)	10	8.7	6.2 / 24.2	5.9 / 27.6	5.3 / 31.2					4.6 / 47	45.1 / :.9	2.6 / 50
2 g/L	Pot. (mV)	21.5	9.4					7.1 / 39.3	6.2 / 50.8	3.6 / 52.3	3.4 / 61.8		
	[F] (mg/L)	10											
5 g/L	Pot. (mV)	21.5											
	[F] (mg/L)	10	8.8					5.0 / 37.5	3.0 / 42.1	2.6 / 44.8	1.6 / 46.5		
10 g/L	Pot. (mV)	16.5											
	[F] (mg/L)	10	9.3	9.2	7.8					3.9 / 45.8	3.5 / 48.8	3.2 / 51.5	
15 g/L	Pot. (mV)	22.6	25.7	28									
	[F] (mg/L)	10	8.8	8.0	7.1		5.8	5.2		4.0	3.5	3.2	3.1

(e) Effect of varying HDTMA modification reaction time (**MRT**) (**2, 6, 12, 18, 24, 36 hrs**) on F^- removal using modified zeolite **Na-LSX**

MRT	Time (mins)	0	5	10	20	30	60	90	120	150	180	240
2 hrs	Pot. (mV)	16.5	17.9	18.4	17.9	19.6	23.0	27.6	35.7	36.2	35.0	36.8

Time								
[F] (mg/L)	10.3	8.2 6.8 4.9 4.8 5.0						
		24.7 29.2 35.8 37.3 36.8						
6 hrs Pot. (mV)	16.6							
[F] (mg/L)	10.2	9.6 9.3 7.7			4.8 4.5 4.6 4.2			
		19.5 19.6 23.9			39 38.5 39.			
		8.0 5.7 4.3 4.5 4.4						
Pot. (mV)	16.0	28.6 31.6 37.8 37.4 38.0						
12 hrs [F] (mg/L)	10.5							
18 hrs Pot. (mV)	17.6							
[F] (mg/L)	9.99.7	6.5 5.8 4.5 4.5 4.4						
		38.9 42.5 46.3 46.2 45.8						
24 hrs Pot. (mV)	18.4							
[F] (mg/L)	9.99.6							
36 hrs Pot. (mV)	17.8 10							
[F] (mg/L)	10.1	4.3 3.7 3.2 3.2 3.3						
		35.8 38.8 45.0 44.3 45.1						
	10.38.3	7.6 4.9			4.3 3.43.5 3.4		3.3	

(f) Effect of pH on F⁻ removal: Table of results using **modified** zeolite **Na-LSX** at pH **5.5**, **6.5**, **7.5**, **No pH Control** and **unmodified** zeolite **Na-LSX** at **No pH Control**

pH	Time (mins)	0	5	10	20	30	60	90	120	150	180	240
5.5±0.2	Pot. (mV)	12.2	39	45.8	53.7	53	58	58.2	58.3		61.2	61.5 61.3
	[F] (mg/L)	9.9	5.2	3.3 20.6	1.9	21.3	2.0 1.6 25		1.5	1.4	1.3 46.3 46.2 45.8	
6.5±0.2	Pot. (mV)	18.4	9.6 19.2									

106

	[F] (mg/L)	9.9		4.3 / 16.2	3.7 / 14.1	3.2 / 15.3	3.2 / 16.6	3.3 / 15.
7.5±0.2	Pot. (mV)	11.7						
	[F] (mg/L)	10		9.4 / 16.7	9.2 / 15.3	8.7 / 15.3	8.4 / 16.4	8.7 / 15.
No pH Cont.	Pot. (mV)	17.9						
	[F] (mg/L)	10 9.5 .1						
No pH Cont. (Unmodified Na-LSX)	Pot. (mV)	11.7 10.1	10. 1	10.4 / 11.2	10.3 / 11.8	10.3 / 12.2	10.2 / 12.3	10. / 12.
	[F] (mg/L)	10	9.8 10.4 10.3 10.2				10 9.9	9.9 9.8 10

Appendix 3: Fluoride Removal Efficiency

The efficiency of fluoride removal by the zeolites at a given sampling period was calculated using the equation:

$$R = \frac{C_i - C_t}{C_i} \times 100$$

R = removal efficiency at time, t (%)

C_t = fluoride concentration in solution at time, t (mg/L)

C_i = initial fluoride concentration (mg/L)

Table A1: Water quality of wells from Northern Ghana (Buamah *et al.*, 2013)

| pH	6.9 – 7.5	Mg^{2+} (mg/l)	5.6 – 17
Alkalinity (mg/l)	137 -171	Na^+ (mg/l)	22 – 28
SO_4^{2-} (mg/l)	28.6 – 34.7	K^+ (mg/l)	1.3 – 1.5
Cl^- (mg/l)	4.63 – 6.26	Fe^{2+} (mg/l)	0.001 – 0.004
NO_2^- (mg/l)	25	Mn^{2+} (mg/l)	0.003 – 0.004
NO_3^- (mg/l)	16.84 – 29.5	Al^{3+} (mg/l)	0.002 – 0.049
F^- (mg/l)	3.97 – 4.6	SiO_2 (mg/l)	49.2 – 74.87
Ca^{2+} (mg/l)	16 – 44	Sr (mg/l)	0.36 – 1.3
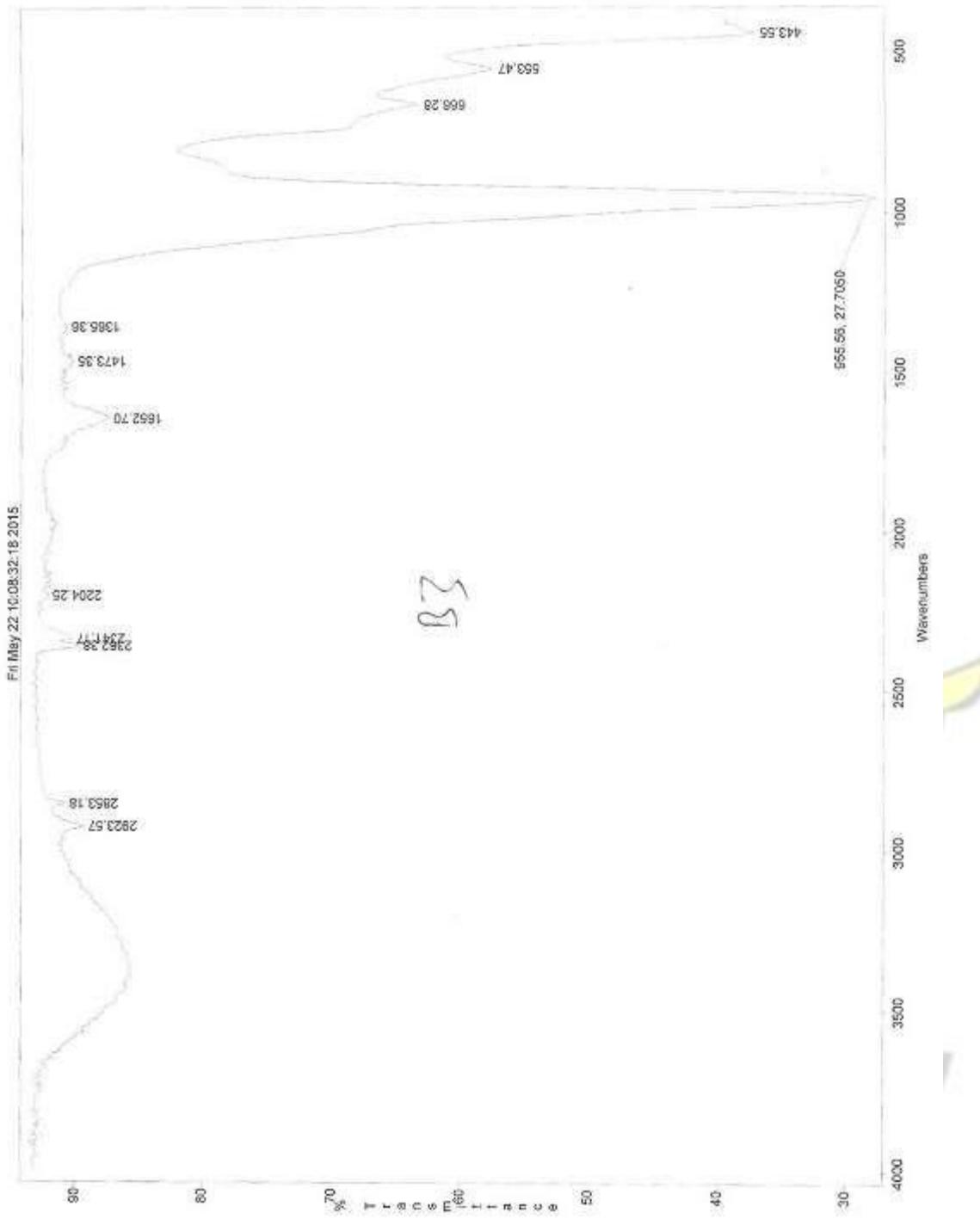
Figure A1: FTIR spectrum of modified zeolite Na-LSX