SYNTHESIS AND MODIFICATION OF ZEOLITES FOR THE REMOVAL OF HEAVY METALS FROM WATER

Dissertation submitted to the Department of Chemistry, University of Zimbabwe in partial fulfilment of the requirements for the degree of

Master of Science in Chemistry

By

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Declaration

I declare that this research is my own, unaided work. It is being submitted for the Master of Science Degree in Chemistry at the University of Zimbabwe, Harare. It has never been submitted before for any degree or examination at any other University.

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Signature of candidate

Abstract

Zeolites were synthesised using the hydrothermal synthesis method. The synthesised zeolites were initially activated with sodium chloride and later functionalised using barium (barium sulphate) and copper (copper sulphate). The synthesised zeolites were characterised by FT-IR and X-ray fluorescence. The adsorption of the heavy metal ion was measured using the FAAS. The effect of the initial metal concentration, pH and contact time was studied. The zeolites used for this study had two different concentration with one made from 2M sodium hydroxide and the other was made using 3.5M sodium hydroxide. The heavy metals used for this study were zinc and nickel. The synthesised zeolites were activated with NaCI to discard contaminants from the zeolites matrices. From the FT-IR analysis of the synthesised zeolites it was noted that the O-H group (alcohol) stretch becomes broader. The peaks in the fingerprint region became sharper upon zeolites modification. From the XRF results it was concluded that the coal fly ash used in this study was class F and that from FAAS analysis it was observed that the optimum pH for Ni removal is 6 and that of Zn removal is 6. Removal of nickel ions reached equilibrium faster (within 30 minutes for 3.5M zeolites) compared with zinc ions (within 45 minutes for both 2M and 3.5M zeolites) using contact time.

Keywords: *zeolites, activation, functionalization, adsorption, initial metal concentration, contact time, pH, Nickel, Zinc, synthesis*

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I dedicate this work to my beautiful daughter Brianna N. Marova.

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CHAPTER 1

1.1. INTRODUCTION

Tavares and other researchers noted that heavy metals such as cadmium, chromium and lead are pollutants and industrial wastewater with low concentrations of these elements are an environmental problem because treatment processes like chemical precipitation, coagulation or membrane separation are expensive (Tavares *et al.* 2002). This has led to other cheap methods such as biosorption being investigated. It has been noted that biosorption performed by a supported biofilm can become attractive in terms of initial investment and maintenance costs. Biosorption is the accumulation of metals by biological materials without active uptake and is considered as a collective term for a number of passive accumulation steps which include ion exchange, coordination, complexation, chelation, adsorption and micro precipitation.

It has been noted that industrial activities have resulted in the contamination of wastewater with several heavy metals, including zinc and nickel. The use of nickel and zinc in industry means that large amounts of these metals can find their way into the aquatic environment. Nickel is used in several industrial activities, which include mineral processing, electroplating, production of paints and batteries, manufacturing of sulphate and porcelain enamelling. Zinc is released into the aquatic environment through a number of industrial activities, such as mining, metal coating, battery production and its use in paints, ceramics, wood, fabrics, drugs, sun blocks and deodorants. Human exposure to heavy metals such as zinc and nickel at significant levels is associated with serious health effects. Nickel is known to be associated with dermatitis, nausea, coughing, chronic bronchitis, gastrointestinal distress, reduced lung function and lung cancer. On the other hand zinc is associated with short-term “metal-fume fever”, nausea, diarrhoea, depression, lethargy, and neurological signs, such as seizures and ataxia. As a result, there is a need to effectively remove these metals from wastewater in order to ensure adequately treated effluent quality for various uses. A number of processes are available for the removal of heavy metals from water and wastewater which include chemical precipitation, adsorption, ion exchange, flotation, membrane filtration, electrochemical treatment and coagulation–flocculation. However, these processes have their own advantages and disadvantages (Malamisa and Katsoua, 2013).

Due to industrialisation, many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. Pb^{2+}, Cu^{2+},Fe^{3+}, and Cr^{3+} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorder. They are also common groundwater contaminants at industrial dump sites.

Heavy metals such as mercury and lead have also been linked to infertility and the good news is that if the levels of these toxic metals are reduced in the body, chances of conception can increase. Pure zeolite removes heavy metals and toxins from your body safely and effectively (Beckman-McNeil, 2014). It can also balance pH levels, bind to viral sub-particles, improve metabolic function and nutrient absorption, alleviate digestive complaints, boost the body's resistance to diseases, improve blood sugar regulation, and enhance immune functionality.

Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters. The day-by-day increment of stringent regulations on portable water demands new technologies for heavy metal removal from wastewater to attain today's toxicity-driven limits. It has been noted that in third world countries, 70 percent of industrial waste discharges are dumped untreated into water, polluting the usable water supply.

Natural zeolite can be used to filter and purify swimming pools, town water supplies, sewerage effluent, biological wetlands, industrial and mining wastewater and aquaculture ponds. Water filtration, apart from the removal of solids and colloids, increasingly demands the efficient removal of contaminants including heavy metals and other toxic substances, bacteria and other parasites. Conventional sand filter systems do not remove all contaminants and therefore alternative or additional systems are required so that the water quality meets compliance regulations.

Zeolite materials have been known allow an introduction of new functional groups through several processes of modification, improving substantially its activity and selectivity on the removal of several substances. Many researchers show the use of modified natural zeolite on environmental applications, which include cations and anions uptake from effluents by adsorption processes (Oliveira and Rubio, 2007)

A lot of parameters have been noted to influence the process of ion sorption/removal from water treatment. These parameters include conductivity, pH, temperature of treated water, ionic strength, initial concentration of cation and anion in solution, zeolite mass and particle size (Margeta et al, 2013).

1.2. AIM

The aim of the project was to synthesise and modify zeolites from coal fly ash for the removal of heavy cations from water.

1.3. OBJECTIVES

The objectives were:

1. To synthesise and modify zeolites from coal fly ash
2. To use the synthesised and modified zeolites to remove heavy cations ($Zn^{2+}$and Ni^{2+}) from water
3. To fully characterize the synthesised zeolites using X-ray Flourescence and FT-IR

4. To compare the performance of the modified and unmodified zeolites in heavy metal ion removal

1.4. JUSTIFICATION

Due to industrialisation and use of energy many toxic heavy metals have been known to be discharged into the environment as industrial waste which results in soil and water pollution. Cadmium, copper, nickel, lead and zinc are common metals that are usually accumulate in organisms, causing numerous diseases and disorders. There are a number of systems that exist for removing dissolved heavy metals, including sorption, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis. In recent research studies , researchers have been looking for other low-cost materials as potential sorbents for the removal of toxic heavy metals, and numerous treatment processes are available, among which sorption is considered to be cost-effective if low-cost sorbents such as zeolites are used due to the fact natural zeolites are abundant (Shaheen, 2012).

The removal of heavy metal ions such as Cd, Cu, Ni, Pb and Zn from industrial and municipal wastewaters is a matter of serious concern due to their toxic effect to various life forms (Pandey *et al.*, 2009). Zeolites are a good way of removing heavy metals from water because the heavy cations such as Rb, Cs, Ag, Cd, Pb, Zn, Ba, Sr, Cu, Hg, Co, and Cr have affinity towards zeolites. However, it has been noted that their selectivity by the zeolites for exchange depends on the hydrated molecular size of the cations (Jha and Singh, 2016).

Activated carbon adsorption is a competitive effective process for the removal of heavy metals at very small quantities. However, the use of activated carbon is not suitable in developing countries due to the fact that it is expensive as far as its production and regeneration is concerned. Other treatment processes are available, which include ion exchange which is considered to be cost-effective if low-cost ion exchangers such as zeolites are used (Erdem *et al.*, 2004).

A wide range of methods are noted to be available for the removal of toxic metal ions from aqueous solutions. The filtering abilities of Zeolites offer a versatile and environmentally friendly option to capture most contaminants found in water systems. Natural Zeolites can perform these functions due to their high ion exchange capacity, adsorption-desorption energies and ability for modification. Zeolites have an open, regular crystalline framework that generates an electric field that interacts, attracts and binds various cations and, after modification, anions.

In Zimbabwe, there is a shortage of clean water supplied to people due to high costs of chemicals involved in the water purification process. Therefore, there is need to use natural methods to purify water and waste water thereby utilising the natural resources. This research will benefit the community at large if the natural zeolites show excellence potential in bringing about clean water by eliminating heavy metals.

Natural exchangers such as zeolites are widely used in the treatment of industrial wastewaters for removing contaminants such as Cu^{2+}, Fe^{3+}, Cr^{3+}, Ni^{2+}, Cd^{2+}, Pb^{2+} and NH_4^+ amongst other metals. Natural zeolites are reported to remove sodium ions from solution by replacing them with calcium, thereby reducing Na^+. Natural zeolites have a high cation exchange capacity and selectivity due to their high porosity and sieving properties (Santiago et al, 2016).

CHAPTER 2

2.1. LITERATURE REVIEW

Some scholars have defined water pollution as the contamination of water bodies such as lakes, rivers, oceans, aquiefers, and groundwater. Water is a form of environmental degradation which occurs when pollutants are directly or indirectly discharged into water bodies without enough treatment to remove harmful compounds. Some scholars have suggested that water pollution is the leading worldwide cause of deaths, disease and that it has resulted in deaths of more than 14 000 people daily (Daniel, 2006)

In the industrially advanced world, regulations has been put in place to stop industry and agricultural operations from disposing of pollutants into water bodies. Technology has helped to come up with solutions in the form of expensive filtration and treatment plants that make our drinking water safe to drink. Some countries have even started to promote "green" infrastructure, which include green roofs and rain gardens, as a way of naturally removing pollutants. But in developing countries, things are different due to the fact that infrascture is not well developed due to political and economic instability, as well as other technical reasons. Developing countries fail to deal with the barrage of pollution threats facing freshwater and all of the species that rely on it. Hence, in developing countries, about 70 percent of industrial waste is dumped untreated into water, polluting the usable water supply.

Zeolites were discovered about 200 years ago. Zeolites occur naturally and they are an abundant, low cost resource. They have a crystalline hydrated aluminosilicate structure with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Hence, due to their high cation-exchange ability as well as their molecular sieving properties, natural zeolites have been widely used as adsorbents in separation and purification processes in the past years. Different natural zeolites show different ion-exchange capacities for cations such as ammonium and heavy metal ions. It has also been noted that some zeolites have shown adsorption of anions and organics from aqueous solution. Natural zeolites can be modified using different methods such as acid treatment, ion exchange, and surfactant functionalisation, making the modified zeolites attain higher adsorption capacities for organics and anions.

Recently, there has been fast economic development occurring in the world which means that energy supplies will have to be increased. Coal is a major source for energy production and accounts for 29.6% of global energy consumption. (Izidoro *et al.*, 2013).

In neighbouring South Africa, about 90% of electricity is derived from coal combustion. During coal mining and coal combustion operations, a lot of by-products are released which present environmental problems. These by-products include, waste materials such as mine water, produced during the process of the coal mining operation and fly ash, generated during the coal combustion process. Mine water and fly ash are considered to be an environmental liability and require expensive technologies to treat and dispose (Musyoka, *et al.*, 2013). As, fly ash disposal is a major issue in solid waste management, conversion to pure zeolites will provide an economic solution (Izidoro *et al.*, 2013).

In South Africa it has been noted that of the fly ash produced, out of the annual estimate of almost 36.2 million tonnes, only around 5% is recycled while the rest is disposed of in ash dumps (Eskom, 2011). In Poland, storage and disposal of wastes from the coal combustion process is a large problem to the power generation industry. The waste products of coal combustion, for example, ash-and-slag mixtures had the largest share of wastes and fly-ash from hard coal combustion constitutes the remaining part. However, only about 65 percent of furnace wastes is utilized. Instead of dumping the fly ash, it can be used as a significant resource for zeolite production. The use of the zeolites is in line with the regulations of balanced development which supports lithosphere protection (Adamczyk *et al*, 2005).

Many researchers have investigated different ways of recycling fly ash and it was noted that of the many properties and application of fly ash, was its ability to be converted into zeolites which have wide industrial use and that their sale can offset disposal cost as well as eradicate the environmental liability (Musyoka *et al*,2013). The properties and chemical composition of fly ashes vary depending on coal source and power-plant operation, which make these materials even more versatile (Izidoro *et al,* 2012).

The significant content of silica and alumina in fly ash makes it a suitable raw material for the synthesis of value-added zeolitic products used in various environmental applications, mostly in the field of industrial wastewater treatment (Shoumkova etal, 2012).

There have been a lot of proposed strategies in zeolite synthesis from fly ashes in order to obtain a pure zeolite other than a mixture of zeolitic materials. For example, a fusion step prior to a hydrothermal treatment can make alkali extraction of more silicates and aluminates from ashes, increasing the yield of pure zeolites. However, the formation of a particular zeolite strongly depends on the ratio of SiO_2/Al_2O_3 in the starting material for hydrothermal reaction (Izidoro etal, 2012).

The direct hydrothermal method can be used for the synthesis of zeolites because it is fast, economic and less involving than the fusion and the microwave methods(Chigondo *et al*. 2013). Microwave irradiation technique for utilization of fly ash has been developed for the synthesis of crystalline zeolite from fly ash by using microwave irradiation technique. The advantages of this method are time saving, very cheap, rapid heating, given a very high purity and yield (Patel and Srivastava).

Hydrothermal synthesis has been carried out at laboratory scale using fly ash with NaOH and KOH. However, the best results were obtained when using NaOH instead of KOH. This zeolite has unique ion-exchange properties for effluent treatment. Highly crystalline zeolites from coal fly ash have been successfully synthesised using the hydrothermal method for 48 hours at 140°C in 4-flat blade impeller at agitation for 200 rpm. Another method of synthesising zeolites from fly ash is alkali fusion followed by hydrothermal method. The process involves raising temperatures to 550 ^{o}C which results in the production of crystalline synthetic zeolite.

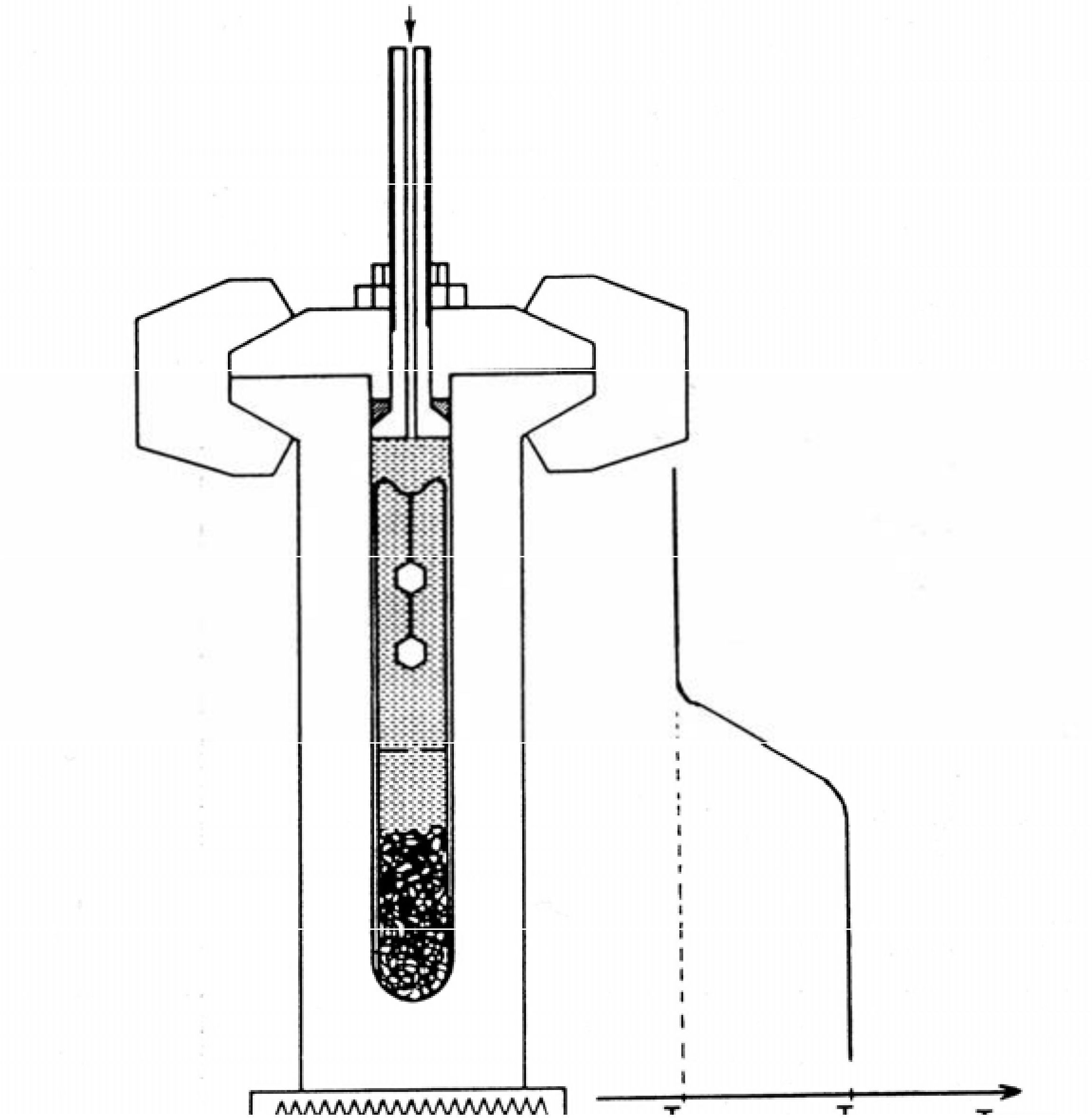

Figure 1: Autoclave used in hydrothermal synthesis

2.1.1. Chemical structure

Naturally occuring zeolites have been noted to hydrated aluminosilicates with an infinite three dimensional structure of tetrahedrons such as TO_4 (where T can be Si, Al, B, Ge, Fe, P, Co) which is joined by oxygen atoms. Zeolites have been noted that in its internal structure it has channels and cavities interconnected of molecular dimensions where compensation cations allow the ion exchange exist.

Zeolite materials can be modified by introducing a new functional group. Many researchers have shown the use of modified natural zeolite on environmental applications, mainly cation and anion uptake from effluents by adsorption processes (Rubio, 2007).

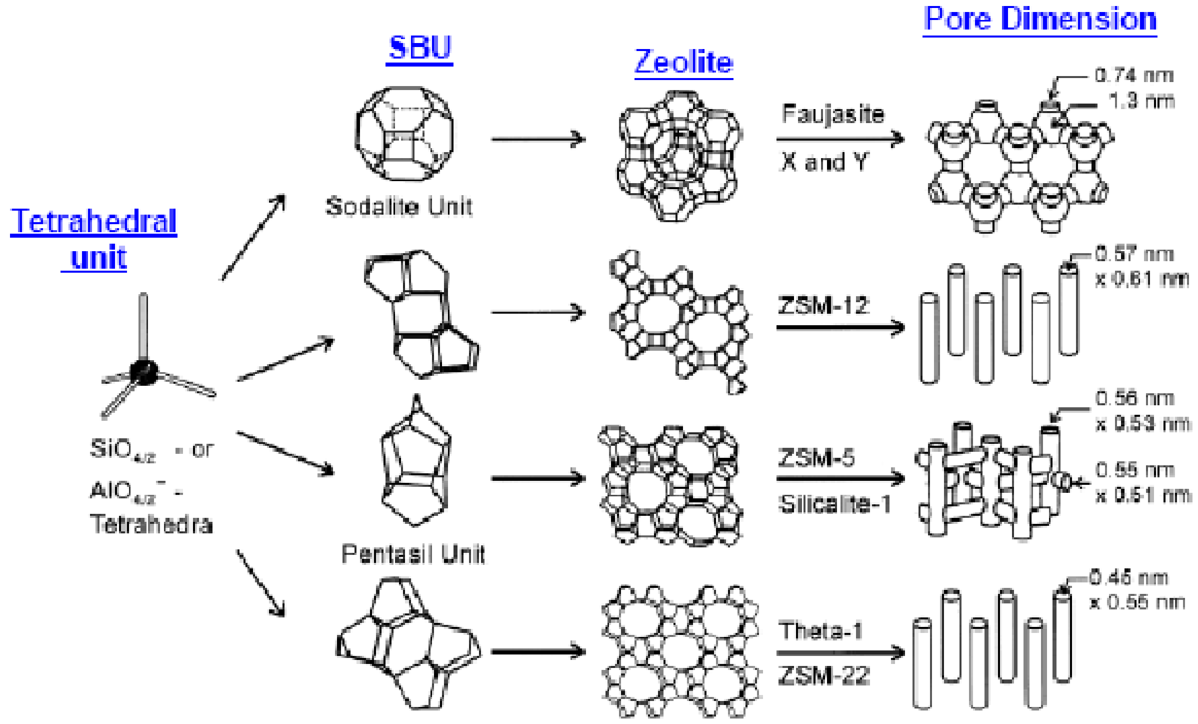

Figure 2: Building blocks of zeolites (Daramola *et al.* 2012)

Natural zeolites have been shown to be non-acidic crystalline microporous material which have special physical and chemical properties offering channels or cavities of molecular dimension, she results in them being called molecular sieves. Natural zeolites are also natural minerals that carry a negative charge which is balanced by freely moving cations which carry positive charges. This zeolitic enviroment provides an ideal trap for positive cations such as nitrogen rich ammonium and potash which are then released when required by plants. Zeolites have an open framework with a number of pores giving it a large surface area for trapping and exchanging valuable nutrients (Noori *et al.* 2005). Zeolites can also be explained as hydrated aluminosilicate minerals with a cage-like structure that offers large internal and external surface areas for ion exchange. The cages are filled with ions and water molecules with high freedom of movement. Zeolites possess a net negative structural charge due to isomorphic substitution of cations in the mineral lattice. Therefore zeolites have been noted to have a strong affinity for transition metal cations, but have a slightly low affinity for anions and non-polar organic molecules (Tavares *et al*. 2009).

Jha and Singh (2014) stated that zeolites are a group of more than 50 soft, white aluminosilicate minerals of tectosilicate type, i.e., a three dimensional framework of interconnected tetrahedra, comprising of aluminium, silicon and oxygen atoms. They reported that in the zeolitic structures, some of the Si^{4+} ions are replaced by Al^{3+} , giving rise to a deficiency of positive charge. The charge deficiency is then offset by the introduction of a cation such as Na^+, K^+, Ca^{2+} and Mg^{2+}.

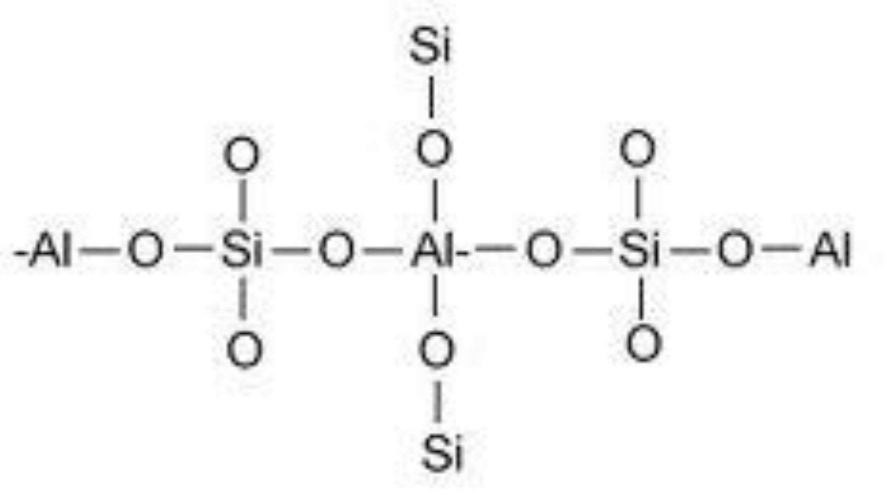

Figure 3: Chemical structure of zeolites

Zeolites have been known to be produced from produced from hydrogels aluminates and sodium silicates, but recently zeolites have been noted that they can be produced from alternative sources of silica and alumina such as ash, volcanic glasses, diatomites and clays. Investigations have been carried out with clays, investigating the preparation of zeolite from kaolin and have successful in the synthesis of zeolites, mainly NaA, mordenite, faujasites, and zeolite NaP (Hildebrandoa *et al.* 2013).

Natural zeolites such as clinoptilolite (i.e., popularly known as clino zeolites) and chabazite have applications in various diversified fields such as water treatment, fertilizer application for soil amendment and plant growth by establishing better retention of nutrients. The clinoptilolite has been broadly accepted for its usage in agriculture, soil amendment and feed additives because of its higher acid resistant silica content. However, such zeolites are contaminated by other minerals (e.g., Fe^{2+}, SO_4^{2-}, quartz, other zeolites, and amorphous glass) and hence they may not be suitable for several important commercial applications where uniformity and purity are essential.

Water molecules move freely in and out of pores but the zeolitic framework remains rigid. Another very important aspect of the zeolite structure is that the pore and channel sizes are almost uniform, allowing the crystal to act as a molecular siever.The porous zeolitic material is host to water molecules and ions of potassium and calcium, as well as other positively charged ions, but only those of appropriate molecular size to fit into the pores are admitted creating the "sieving" property. Because of their regular and reproducible structure, they behave in a predictable fashion.

2.1.2. Modifications of natural zeolite

Functionalization of the surface of a zeolite changes the material in ways determined by the functional group. Properties that can be varied include surface charge, hydrophobicity, molecular binding and reactivity. The advantage of nanocrystalline zeolites in this regard is the extremely high external surface area relative to micron-sized zeolites. Zeolite surfaces can be functionalized by multiple methods either one pot synthesis, or by post synthesis grafting.

Natural zeolites can be modified using different methods which include single or combined treatments such as heating or chemical modification using acids, bases or inorganic salts. The chemical treatment of water treatment zeolites results in cationic migration and thus affects the cation location and pore opening. Modification of zeolites results in some of the zeolite sorbent properties being used to our advantage. The process of ion exchange and that of adsorption in zeolite solution contact can occur concurrently.

2.1.2.1. Modification with solution of inorganic salts

Chemical modification of zeolites with inorganic salts such as sodium chloride, calcium chloride, barium chloride, ammonium chloride and iron chloride, or a cationic surfactant such as hexadecyltri-methylammonium (HDTMA) – bromide, gives rise to improved zeolite properties and increase efficiency in water treatment. For successful modification and improved zeolites, high-concentration solutions of inorganic salts on the surface of zeolite is significant. However, under normal conditions, large cavities and entries to the channels inside the zeolite framework are filled with water molecules forming hydration spheres around exchangeable cationic (Figure 4 -A). After the contact of zeolite with an inorganic salt solution such as sodium chloride, exchange of cations (H^+ or Na^+) from solution with exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) from the zeolite framework occurs (Figure 4-B). To remove anions from the water, zeolite surface has to be modified with a solution of inorganic salts (for example $FeCl_3$) whose adsorption on the zeolite surface leads to the formation of oxi-hydroxides, which then form stable complexes with anions in solution. This modification can result in the creation of an adsorption layer on zeolite surface and modification of surface charge on zeolite surface (from negative to positive) (Figure 4-C).

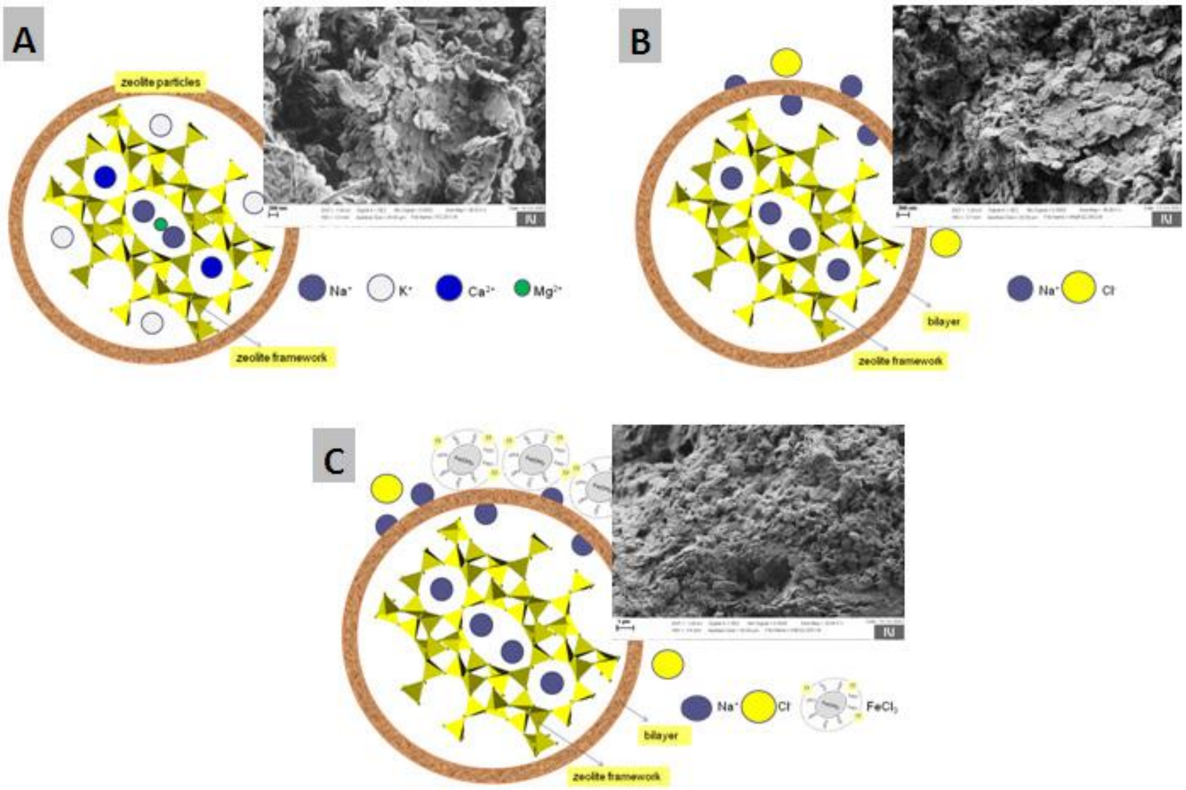

Figure 4: Showing modification of zeolites using inorganic salts (Margeta *et al.* 2013)

Zeolites modified with Na^+ ions have shown ver high selectivity for zinc ions when Zn^{2+} ions are mixed together with Fe^{3+} ions, and this has been reported to be highly dependent on the acidity of the solution and cation hydration enthalpy.

2.1.2.2. Modification with acid or basic

The zeolite structure, chemical and physical properties can also be modified with inorganic base solutions such as NaOH, or $Ca(OH)_2$ or acid solutions which include hydrochloric acid or nitric acid. Acid treatment has been observed to be among the most common and simple methods for zeolite modification. The effectiveness of acid treatment depends on the chemical composition, structure, mineral purity, and the working conditions. Dissolution of some amorphous materials that block the pores of natural zeolites is another consequence of acid modification (Margeta *et al.* 2013).

2.1.3. Types of zeolite

Zeolites are natural minerals that are mined in many parts of the world; most zeolites used commercially are produced synthetically. When making applications for zeolites, it is very essential to remember that not all of these minerals are the same.

There are over 50 different types of zeolites which include clinoptilolite, chabazite, phillipsite, and mordenite with varying physical and chemical properties. Zeolite crystal structure and chemical composition account for the primary differences. In zeolite particle density, cation selectivity, molecular pore size, and strength are only some of the properties that can differ depending on the zeolite in question.

There are numerous naturally occurring and synthetic zeolites, each with a unique structure. The pore sizes commercially available range from approximately 3 Å to approximately 8 Å. Some of the commercial materials are: A, beta, mordenite, Y, ZSM-5.

The biggest differences between natural and synthetic zeolites are: Synthetics are manufactured from energy consuming chemicals and naturals are processed from natural ore bodies. Synthetic zeolites have a silica to alumina ratio of 1 to 1 and clinoptotilite (clino) zeolites have a 5 to 1 ratio.

Clino natural zeolites do not break down in a mildly acid environment, where synthetic zeolites do. The natural zeolite structure has more acid resistant resistant silica to hold it’s structure together. The clino natural zeolite is broadly accepted for use in the agriculutral industry as a soil amendment and as a feed additive.

In 1948, Richard Barrer first produced a synthetic zeolite that did not have a natural counterpart. At approximately the same time, Milton made the first materials that had no natural counterpart such as zeolite A. New natural zeolites are still being discovered, and new synthetic zeolites are being invented in many laboratories around the world.

2.1.4. Applications of zeolites

Zeolites have a vast range of industrial uses due to their unique properties which enable them to act as catalysts, ion exchangers, adsorbents, and detergent builders.

Zeolites have been observed to be used as physical and chemical filters to enhance the sensitivity and selectivity of gas sensors. It has been noted that direct interaction of gas molecules with the extraframework cations in the nanoconfined space of zeolites has been explored as a basis to develop new impedance-type gas/vapour sensors (Zheng etal, 2012).

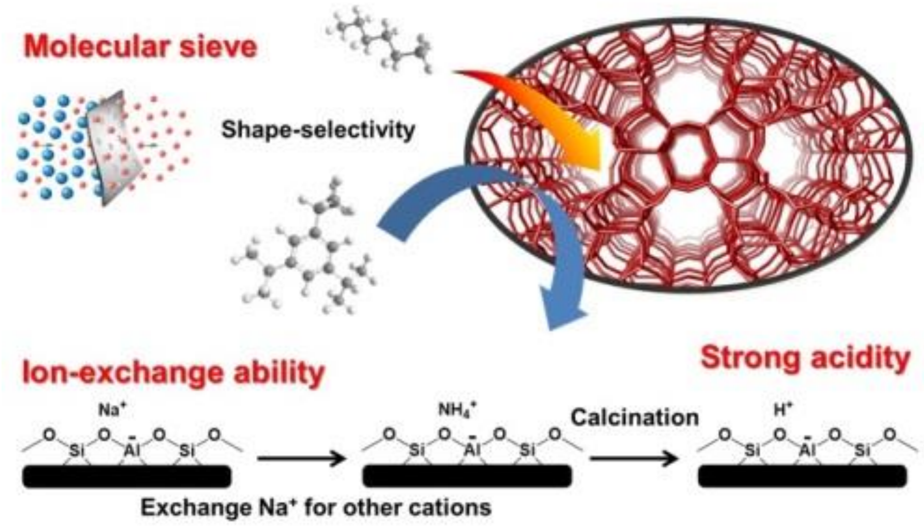

Figure 5: Ion exchange abilities of zeolites (Laboratory for chemistry and life science, 2017)

Zeolites have detoxing abilities and can be used to help improve our health. Zeolite have used for thousands of years to safely and effectively remove toxins and heavy metals from humans. The Centres for Disease Control (CDC), has reported that the average person now has approximately 212 environmental chemicals in their blood which include mercury, lead, cadmium and plastic by-products. However, nature provides protection against many of the toxic elements we encounter every day in the form of a natural mineral, zeolite. Clinoptilolite has been observed to work like a magnet, attracting positively-charged toxins, safely and gently carrying them out of the body within hours (Beckman-McNeil, 2014) . Other zeolites such as the activated liquid zeolite act by being absorbed into the blood and gut, these results in the decrease in the amount of heavy metals and toxins in the body. It has been reported that in some instances taking activated liquid zeolite results in an improvement in memory, energy levels, skin blemishes and libido. Some scientists have suggested that since activated liquid zeolite is safe and effective it means that it can be used to protect expecting mothers and their unborn babies from environmental toxins by taking during the gestational period. Other schools of thought have even suggested that all women of child bearing age should take activated liquid zeolites in order to reduce toxins before falling pregnant. The activated liquid zeolites will eliminate or help cut down the transfer of toxins from the mother to her unborn baby (Beckman-McNeil, 2014).

The natural zeolite clinoptiloptile has been observed to be of great help in helping the human body system by improving the immune system due to the fact that it possesses silicates and aluminosilicates such as AlO_4 and $SiO_{4.}$ Zeolites possess silicates and aluminosilicates in their structure; possess biological activity due to the fact that talc and silica have been used in skin care for many decades. Nontoxic clinoptilolite from Cuba which is both natural and biologically active has been observed to be a good glucose adsorbent, hence it has been suggested by some researchers that it is a potential medication for individuals with diabetes mellitus. Clinoptiloptile can be also be used as an antidiarrheal drug because it lowers the death and sickness produced by intestinal diseases in animals such as swine, rats and calves, due to its biological properties (Paveli, *et al*. 2000).

The removal of heavy elements (Zn, Cr, Pb, Cd, Cu, Mn, Fe,) from wastewater was the first area in which zeolites were used due to the environmental implications of wastewater. Researchers have shown an interest in looking at the properties of natural zeolites as purifiers of water and wastewater. The researchers have even looked at how they can modify the zeolites but it already has been noted that most natural zeolites have good very good ion-exchange capacities for cations such as ammonium and heavy metals. Natural zeolite’s performance can be improved by acid treatment, ion exchange, and surfactant functionalization. These improved zeolites have been noted to show high adsorption abilities for organic matter and anions (Margeta *et al*. 2013).

Results from research that has been carried out by some scientist have shown that natural zeolites can improve soil salinity this was noted when when natural zeolites where added to the soil and there was a noted improvement in the yield that resulted by using clinoptilolite which enhanced soil quality and increase quantification and quality of the crop. Clinoptilolite was applied to Raphanus sativus and it improved yield by retention of salts and their ability to pass through the roots to the plants. The zeolites also improve plant growth in the aerial section and help keep nutrients in the root area without affecting the soils ability to drain. Researchers have noted that natural zeolites can be used to improve soil fertility, develop slow release fertilizers enriched with ammonium and affect the buffer capacity of soils. Natural zeolites have been observed to be slightly alkaline and its use with fertilisers can help buffer soil pH levels therefore reducing the need for using lime (Noori *et al.* 2005).

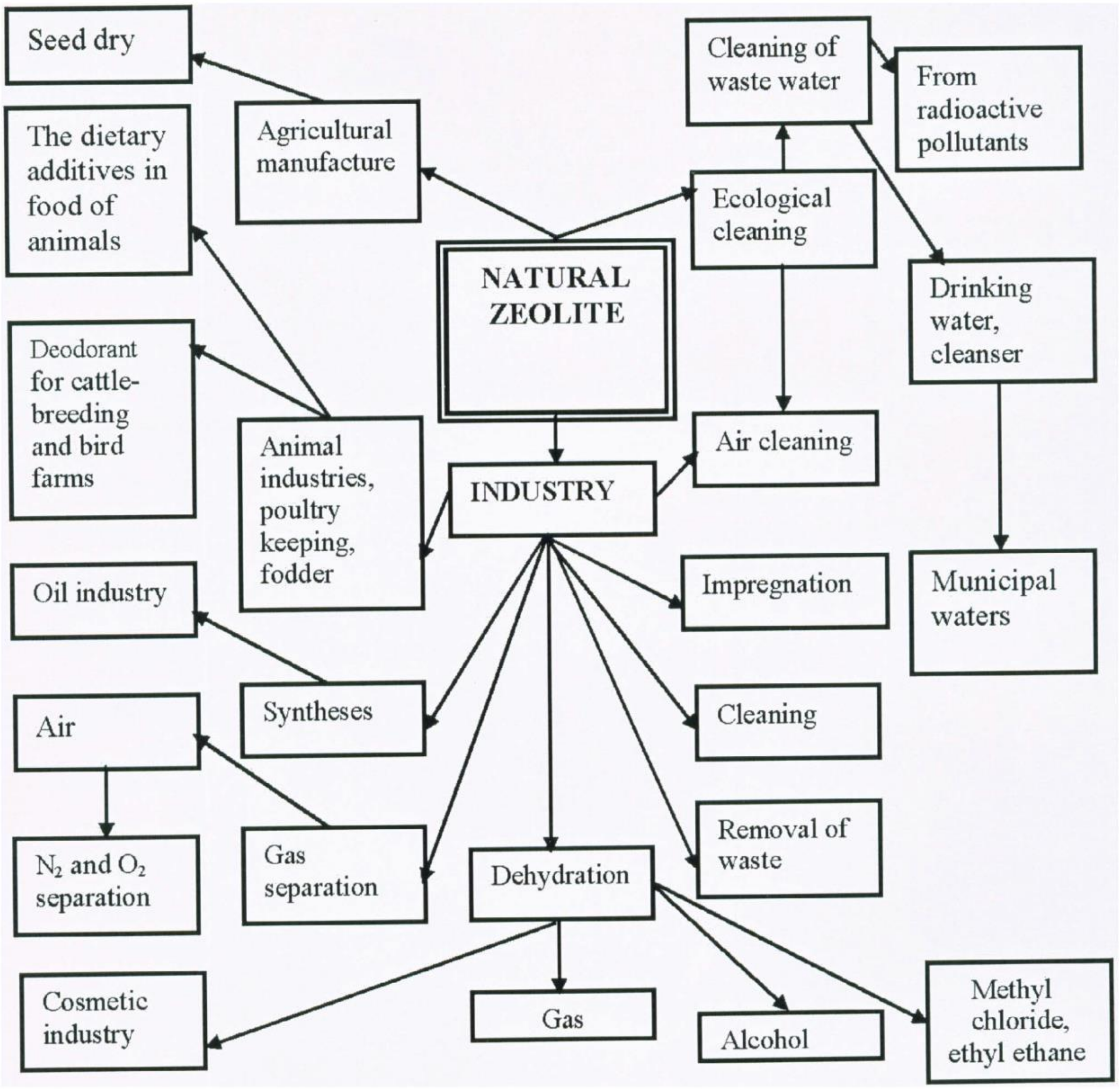

Figure 6: Schematic diagram for application of natural zeolite in public economy (Yeritsyan *et al*. 2013)

Zeolites can be charged with ‘antibiotic’ cations of Ag, Cu, Zn to provide antimicrobial properties. Zeolite filterbeds can remove contaminants to purify air (Ammonia NH_3, H_2S, CO_2, CO, SO_2). The hard, durable nature of Zeolites enables them to perform a range of filter functions to produce improved water quality more efficiently than both the conventional sand filter systems. Robust, insoluble zeolites have improved attrition qualities and are adaptable to re-use through regeneration and recycling

2.1.5 Characterization of zeolites

The properties of zeolites are mainly dependent on their structure, so it is absolutely necessary to characterize the structure of zeolites, as well as the changes in the structure during the synthesis, modification and use of zeolites. Vibrational spectroscopies such as IR and Raman are the most powerful techniques to supply detailed information on the structure of molecules. Hence, vibrational spectroscopies have been most frequently used to characterize the microporous materials (mainly zeolites) since the beginning of zeolite discovery and synthesis. Another advantage is that several vibrational spectroscopies can be applied under in situ conditions and they can be very successfully used for studies of highsurface-area porous materials like zeolites. IR and Raman spectroscopies have been successfully applied to the zeolite characterization in almost every aspect, such as

(a) framework and extraframework structure, e.g., lattice vibrations related to structure type, cation vibrations related to cation nature and location

(b) sites in zeolites, usually characterized by using probe molecules

(c) adsorption and catalytic reactions on zeolites

(d) the guest–host chemistry within zeolite channel and cavity.

IR spectrum gives information about the presence of the impurities, organic and inorganic materials in the zeolite structure. The fundamental vibrations of the framework of a zeolite have been studied in literature.

According to Breck, IR spectra can be divided into two classes. The first class of vibrations arises due to internal vibrations of the $T0_4$ tetrahedron, which is the primary unit of structure, and is not sensitive to other structural units. The second class of vibrations is related to the linkages between tetrahedra. The intense and adsorption characteristics of clinoptilolite are given in the table below.

Table 1: Clinoptile IR assignments (Brecks 1974)

Class	**Vibration**
Internal tetrahedra	• Asymmetry stretch 1250cm^{-1} – 950 cm^{-1} (O-Si(Al)-O stretching • Symmetry stretch 750cm^{-1} - 650cm^{-1} • T-O Double Ring 500cm^{-1} – 420 cm^{-1}
External linkages	• T-O Double ring 650cm^{-1} – 500cm^{-1} • Pore opening 420cm^{-1} – 300cm^{-1} • Symmetry Stretch 750cm^{-1} – 820cm^{-1} • Asymmetry Stretch 1150cm^{-1} – 1050 cm^{-1}
Additional	• H-bonded H_2O 3400cm^{-1} H-O stretching • Isolated OH 3700cm^{-1} stretching

Other methods used to characterise the zeolites include BET adsorption method, X-ray diffraction (XRD), scanning electron microscopy (SEM).

CHAPTER 3

3.1. METHODOLOGY

3.1.1. Sampling and Sample Pre-treatment

The coal fly ash samples were collected from Delta Beverages, a beverage company in Zimbabwe. The samples were transported in polythene bags and were dried in an oven at 65 ^{o}C for 24 h. Before use the coal fly ash was passed through 180 µm sieve followed by removal of magnetic materials mainly iron fillings using a magnet which interfere with zeolite formation.

3.1.2. Zeolite Synthesis

The direct hydrothermal method was used for the synthesis of zeolites. Two 10 g masses of fly ash were weighed and added each into 250 mL glass beakers containing 100 mL of sodium hydroxide of varying concentrations (2.0 and 3.5 moldm^{-3}) to produce double samples of two different groups of zeolite material coded ZM 2 and ZM 3.5 respectively. The resulting solutions were heated at 100°C for 24 h in an oven. The resulting zeolite cakes were recovered by filtration and washed several times with distilled water until the pH was between 10 and 11 because the pH of the reaction mixture should be maintained at a value of 10 or 11 to stabilise the zeolite precursors formed and avoid going to polymerisation. The resulting zeolite material was dried to constant mass at 100°C for 24 hours and cooled for the next stage.

3.1.2.1. Modification of zeolite

Modification of the zeolites was performed by two different stages which include activation with sodium ions and functionalisation with barium and copper ions.

3.1.2.2. Activation of the zeolite

Activation of the zeolite was done by mixing the powdered material with an aqueous solution of sodium chloride supplied by Merck. A known quantity of the adsorbent (5 g) was mixed with 50 mL of sodium chloride 1M solution for 24 h at room temperature, and the suspension was agitated for 10 min in glass conical flasks using a shaker. The resulting suspension was filtered using a vacuum pump and the material washed with 300 mL of deionised water. The activated material was dried in an oven at 100 °C for 24 ho and used in the functionalisation stage.

3.1.2.3. Functionalization of the zeolite

Functionalisation of the material with barium and copper ions of the activated zeolite was performed mixing the powdered material samples with aqueous solutions of barium sulphate supplied by Wako pure chemical industries and copper sulphate supplied by Glassworld, respectively. Thus, 5 g were added to 50 mL of the solutions (6.3 g of barium sulphate and 4.3 g of copper sulphate) for 24 h at room temperature and the suspension was agitated for 10 min, in glass flasks in the same shaker. The suspension was filtered, washed with 300 mL of deionised water, and dried in an oven at 100 °C for 24 h and later used in the adsorption studies

3.1.3. Characterisation of Coal Fly Ash and Zeolites

Raw and treated coal fly ash crystalline phases were characterised by X-ray Fluorescence (Zetium – Pan Analytical) and Fourier Transform Infrared (infra 3000A FTIR –Analytical Technologies Limited).

3.1.4. Preparation of stock solutions

The metal ions studied were Ni^{2+} and Zn^{2+}. Stock solutions of nickel and zinc were prepared using, nickel nitrate and zinc nitrate respectively. Preparation of stock solution of Zn^{2+} required 4.54 g of zinc nitrate hexahydrate dissolved in 1000 mL of deionised water 1000 ppm. Preparation of stock solution of Ni^{2+} required 4.94 g of nickel nitrate dissolved in 1000 mL of deionised to make 1000 ppm.

3.1.4.1. Preparation of standard solutions

A standard stock solution of 100 ppm of nickel was prepared by transfering 10 mL of 1000 ppm nickel stock solution into a 100 mL volumetric flask and making upto the mark with deionised water. The 100 ppm aliquots of the sample were transferred into 50 mL volumetric flasks, and working standards of 0.5, 1.0, 2.0, 4.0 and 6.0 ppm were prepared.

A standard stock solution of 100 ppm of zinc was prepared by transfering 10 mL of from zinc stock solution into a 100 mL volumetric flask and making up to the mark with deionised water. From the 100 ppm aliquots of the sample were transferred into 50 mL volumetric flasks, and working standards of 0.2, 0.4, 0.8, 1.6 and 2.0 ppm were prepared.

3.1.5. Batch adsorption studies

3.1.5.1. Effect of adsorbent concentration dose

The ion exchange of heavy metals on modified zeolite was carried out using the batch method. Batch adsorption experiments were conducted using 0.25 g of adsorbent with 20 mL of solutions containing heavy metal ions of desired concentrations at constant temperatures (25 ^oC) in 100 mL beaker. The beakers were shaken for 30 min and solutions containing heavy metals were filtered through a filter paper. The exact concentration of metal ions and filterable metal concentrations was determined by FAAS (AA-6701F).

The effects of initial pH, contact time, adsorbent concentration and initial metal concentration were investigated at 25 ^oC using 0.25 g of each adsorbent except for adsorbent loading experiments where various amounts were used.

The effect of initial solution pH on heavy metal removal was investigated on pH 2, 4, 6 and 8. The adsorbent material was agitated for 30 min with 100 mL of 0.25 g adsorbent and 50ppm of heavy metal solutions. The pH was adjusted using either 0.01 M sodium hydroxide or 0.01 M hydrochloric acid.

The effect of contact time on removal of heavy metals was studied using 0.25 g adsorbent and 100 mL of 50 ppm of heavy metal solution agitated with adsorbent for different contact times (0, 5, 15, 30, 45 and 60 min) at the optimum pH 6.

The effect of initial metal concentration was studied using three initial solution concentrations (5, 10 and 15 ppm) for each adsorbent at an optimum pH and sorbent dosage for each adsorbent.

CHAPTER 4

4.1.RESULTS AND DISCUSSION

4.1.1. Synthesis of the zeolites

The direct hydrothermal method was used for the synthesis of zeolites because it is fast, economic and less involving than the other methods such as the fusion and the microwave method (Chigondo *et al*, 2013). The coal fly ash was treated with sodium hydroxide of different concentration. The synthesised zeolites were subjected to thermal treatment at high temperature, in order to enlarge pore volume by removing water molecules and organics from pore channels. Water which was present in cages and channels of the zeolite framework contributes about 10 to 25 % of the total mass of zeolites. For zeolites to be used properly in water treatment, it is essential to know the properties of dehydration and structural stability of particular zeolite materials (Margeta *et al*, 2013).

4.1.1.1 Activation and functionalization of the zeolites

The zeolites used in this research were activated using sodium chloride because, besides containing the negative charge compensator such as alkali and alkaline earth cations, natural zeolites also contains the undesired component such as oxides of metals. The metal oxides are trapped in the frame of zeolite when it is formed naturally. The existence of these oxide contaminants have an effect of decreasing pore sizes and thereby decrease the ability of zeolite matrices as adsorbent. However, by activation, the contaminants would be discarded from the zeolite matrices. Another reason for activation is that zeolites are a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. The negative charge can be compensated by alkali and alkaline earth cations such as Na^+, K^+, Ca^{2+} or Mg^{2+}. Researchers have noted that natural zeolites have relatively low ion-exchange capacities, and should be activated by chemical or physical methods before being used. Ion-exchange with sodium chloride solution is widely employed, because sodium ions can readily remove other cations and therefore enhancing the adsorption capacity (Ola *et al*, 2013).

Functionalization of the zeolite was carried out using barium sulphate and copper sulphate. Copper was used in the functionalization stage because it is an inexpensive, earth-abundant, non-toxic metal.

4.1.2. Fourier Transform Infrared spectroscopy

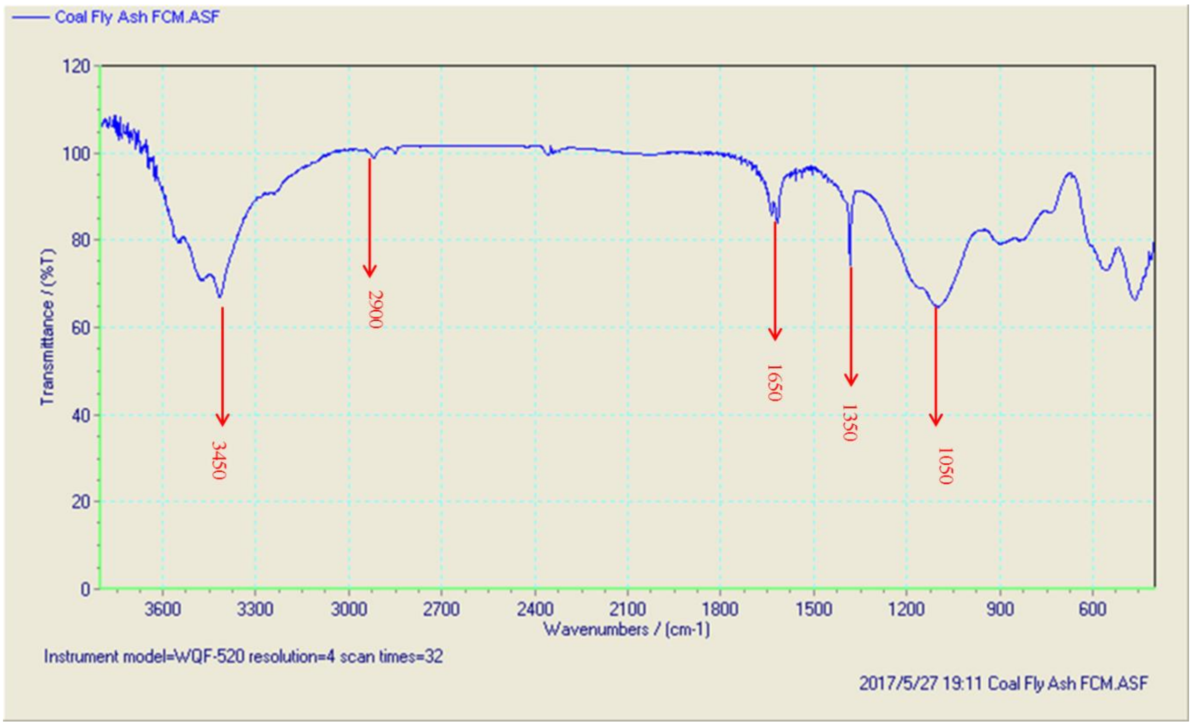

Figure 7: FT-IR spectrum of coal fly ash

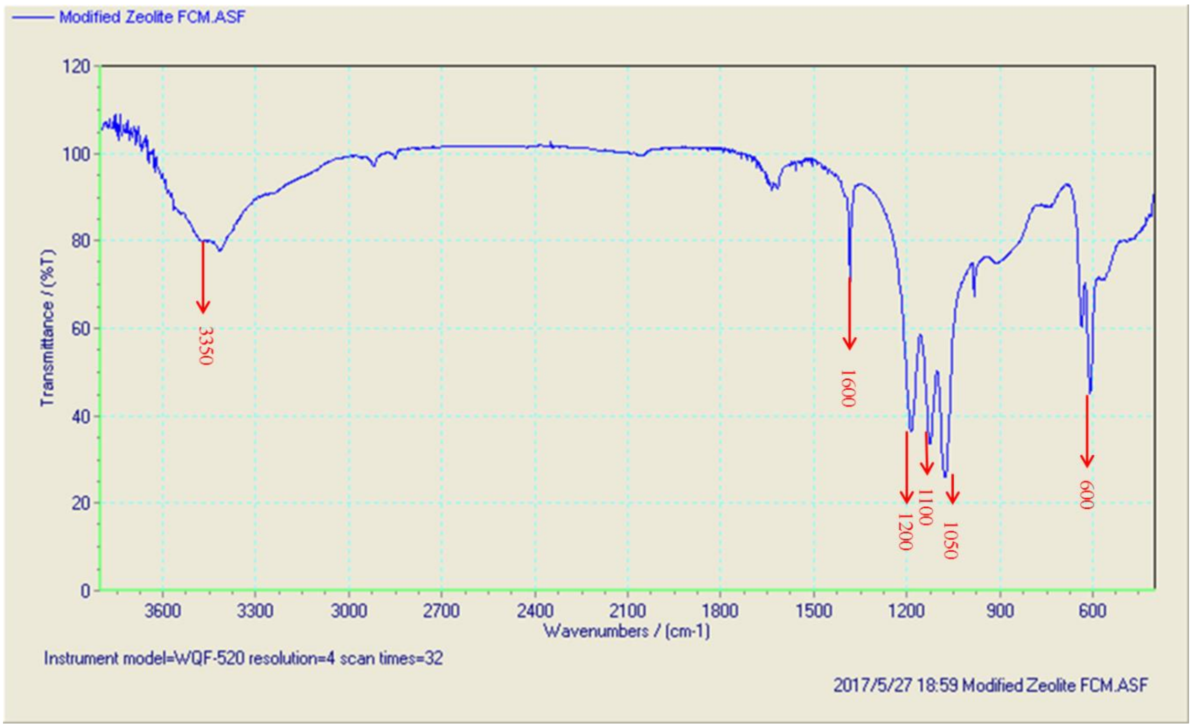

Figure 8: FT-IR spectrum of modified 2M zeolites before use

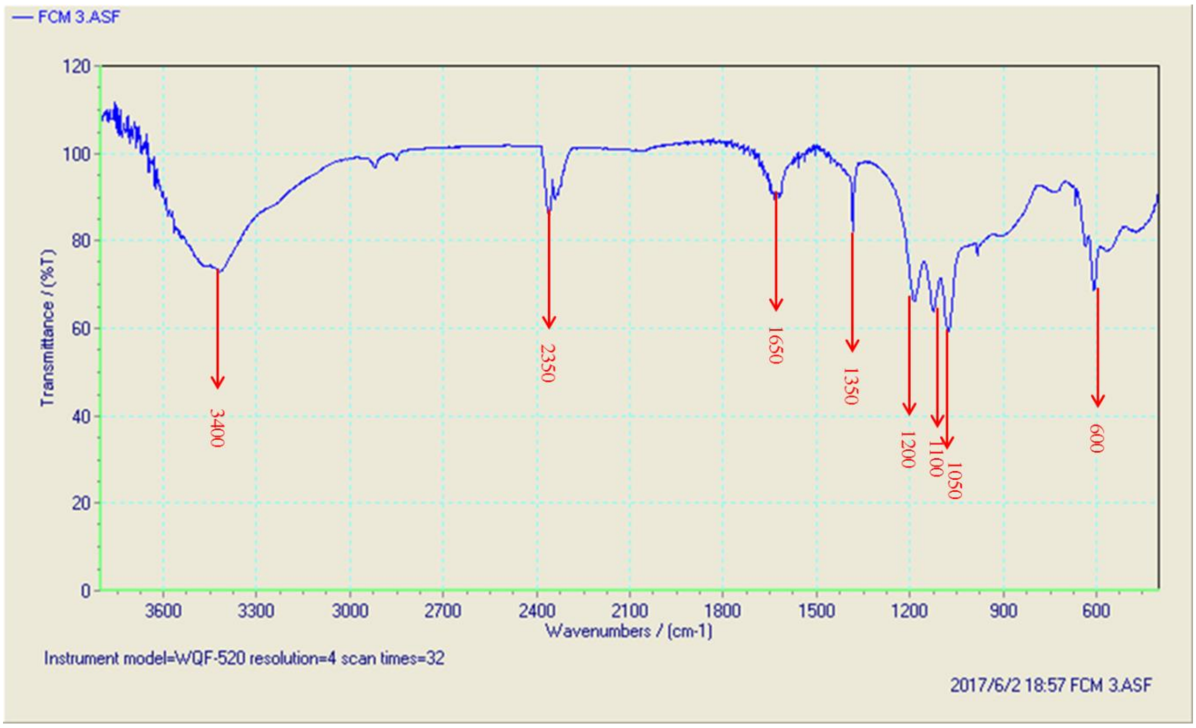

Figure 9: FT-IR spectrum of modified 3.5M zeolites before use

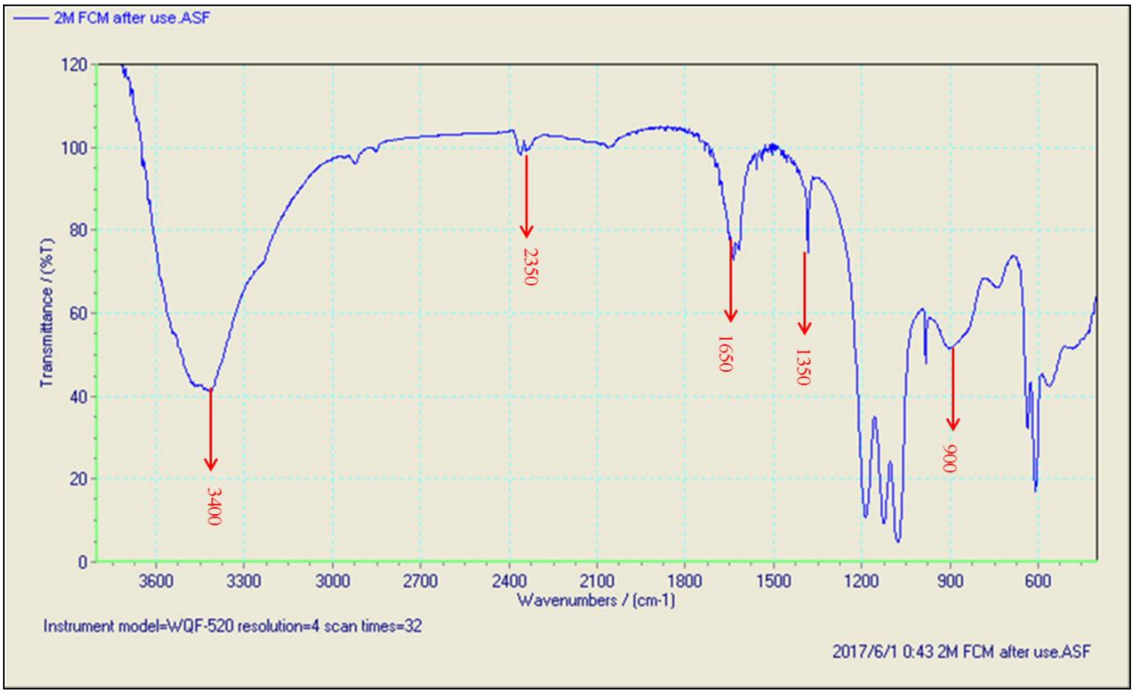

Figure 10: FT-IR spectrum of modified 2M zeolites after use

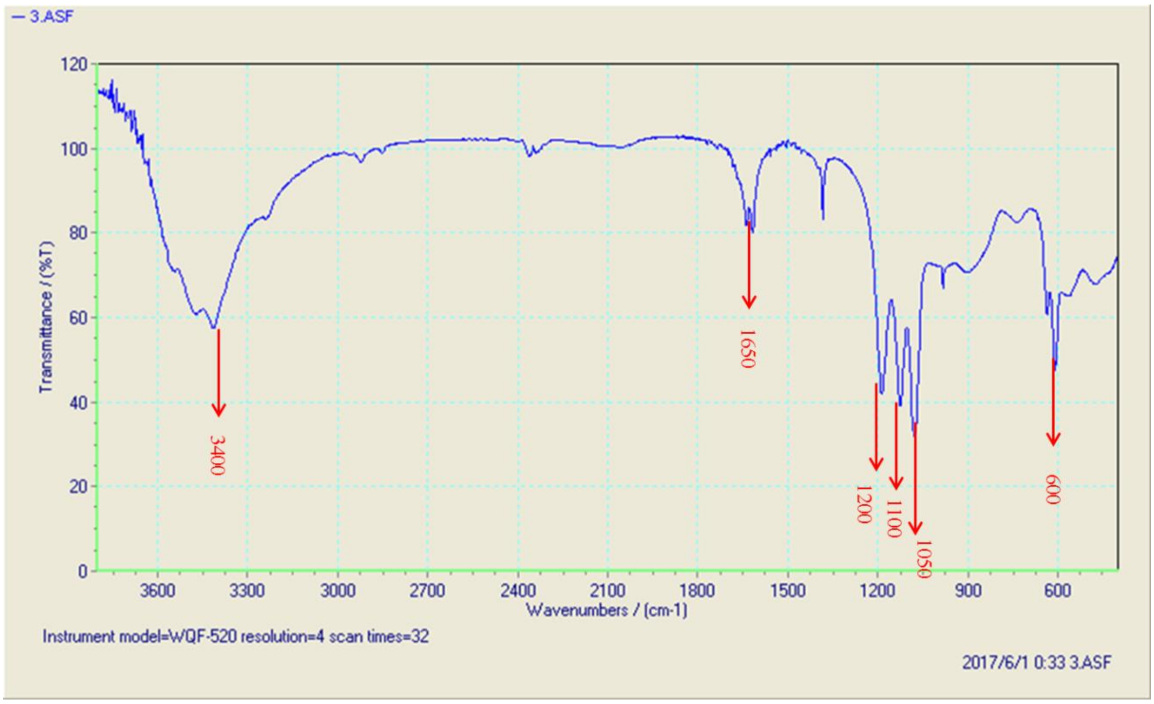

Figure 11: FT-IR spectrum of modified 3.5M zeolites after use

It can be noted from the FTIR spectra above that the alcohol (O-H) stretch is present because there is a broad and strong absorption between 3600 cm^{-1} and 3 300 cm^{-1}. The bends in the fingerprint region also became sharper upon zeolite formation and the bends that were below 600cm^{-1} shifted to above 600cm-1 and above. In the fingerprint region the C-O group can be noted it is very sharp and it lies between 1 500 cm^{-1} and 1 000 cm^{-1}. On the FTIR diagrams it can be noted that the bands between 1200 cm^{-1} and 900 cm^{-1} became sharper.

Another FT-IR run was carried out after the experimental work was done. It can be noted that from the FT-IR of the modified 2M zeolite that after use the transmittance of the O-H group was now very low to about 40% however the O-H group also became very broad and well defined. The functional group in the C=X stretch became more defined and its transmittance also reduced to 80%. The fingerprint region shows that the transmittance became very low almost close to zero, and a transmittance of zero means that the sample almost absorbed all of the radiation.

The bond stretch frequencies for O-H are in a high range because a H atom is involved, and broad because the actual frequency for each molecule is strongly determined by its exact environment. The H atom is so light that even for the simple bond it is involved in it will vibrate really fast. The change in the broadening of the OH can be attributed to the fact that the bond strength of the O-H is strongly dependent on hydrogen bonding and if hydrogen bond is formed, part of the electrons in the O-H bond are shared with the hydrogen bond acceptor. Therefore, this makes the O-H bond weaker and this lowers the vibration frequency. Another way to see this is that the "potential energy well" for the H between the donor O atom and the acceptor atom becomes broader. In the liquid, each O-H has a slightly different hydrogen bond geometry and thereby a different vibration frequency. In total, this broadens the peak (Merz etal, 2014).

However after use for the 3.5M zeolite the OH group had a transmittance of close to 60% and the OH group became broader.

4.1.1. X-ray Fluorescence Analysis

Table 4.1: XRF results of coal fly ash and modified zeolites

Components %	Coal fly ash	Modified zeolite
SiO_2	51.39	11.22
Al_2O_3	38.85	14.46
Fe_2O_3	3.4	0.14
CaO	2.26	1.31
MgO	0.36	0.10
SO_3	0.54	6.27
Na_2O	0.46	0.79
K_2O	1.02	0.13
Mn_2O_3	0.02	0.07
Ti_2O	1.56	0.42
P_20_5	0.21	0.01
Loss of ignition	2.17	1.14

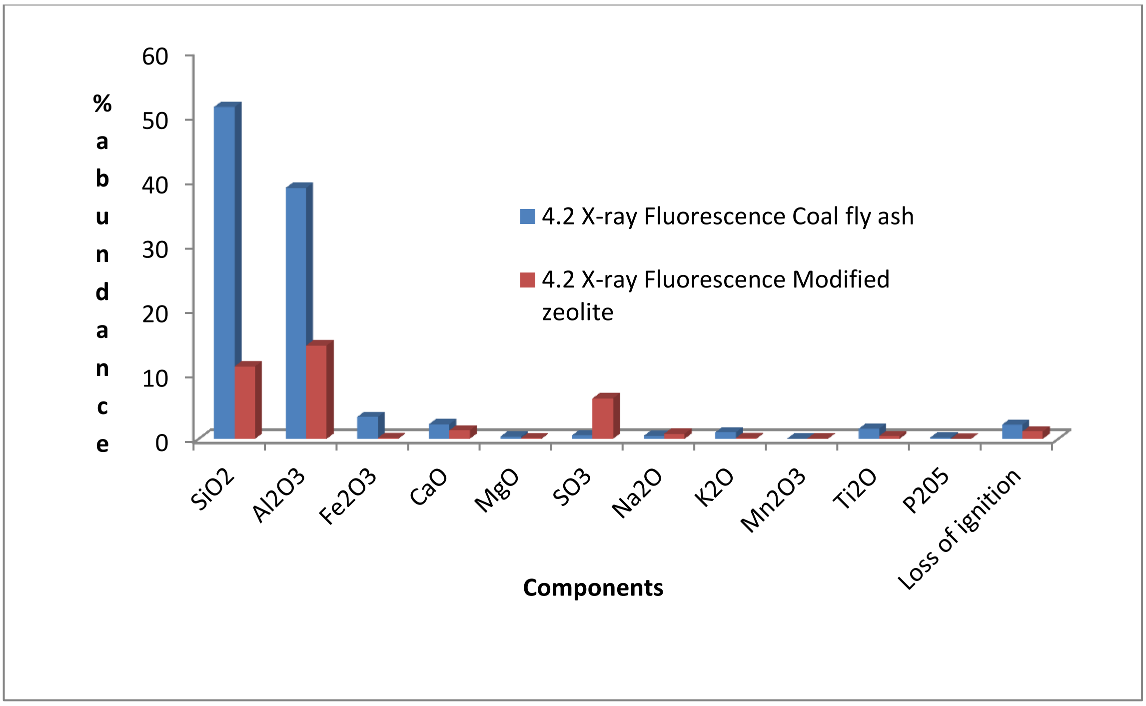

Figure 12: XRF analysis of coal fly ash and modified 2M zeolite

A chemical analysis of the treated zeolite by XRF shows that the synthesised zeolitic material contained sodium, potassium, and calcium ions. The zeolite contained high percentage of SiO_2, followed by Al_2O_3, and negligible percentage of Fe_2O_3, TiO_2, MgO, K_2O CaO and Na_2O (Shaheen *et al*, 2012).

The chemical compositions of coal fly ash and the synthesised zeolite from 2M of sodium hydroxide are shown in the table above. The type of coal fly ash used in this research is classified as class F because it contains a total percentage of SiO_2, Al_2O_3, and Fe_2O_3 which is above 70%. The coal fly ash mainly contains SiO_2 and Al_2O_3 with a ratio of 1.32 (Chigondo, 2013). The low loss on ignition can be attributed to the fact that they were very low percentage of moisture, carbonates and hydroxides (Merwe *et al*, 2011).

In can be noted from the x-ray fluorescence results that the percentage of SO_3 and Na_2O increased in the synthesised zeolites. The SO_3 increased from 0.54 to 6.27 due to the fact that barium sulphate and copper sulphate were used in the functionalization stage and the Na_2O increased from 0.46 to 0.79 due to the fact that sodium hydroxide was used in neutralising the negative charge of the aluminate in the zeolite during the hydrothermal treatment of the zeolite and also during the activation process of the zeolite with sodium chloride (Chigondo *et al.*, 2013).

4.1.2. Flame Atomic Absorption Spectroscopy

4.1.2.1. Results for Zinc

Table 4.2: Effect of pH on removal of Zn

pH	2M zeolite (ppm)	3.5M zeolite (ppm)
2	9.820	9.816
4	9.636	9.388
6	8.316	10.46
8	6.908	10.00

Table 4.3: Effect of contact time on removal of Zn

Time (minutes)	2M (ppm) zeolite	3.5M zeolite (ppm)
5	10.92	10.742
10	8.488	9.100
15	9.592	8.854
30	6.972	7.636
45	4.334	7.634
60	9.336	9.164

Table 4.4: Effect of initial metal concentration on removal of Zn

Metal concentration (ppm)	2M zeolite (ppm)	3.5M zeolite (ppm)
5	3.705425	4.096
10	5.47125	6.648
15	10.000	11.99

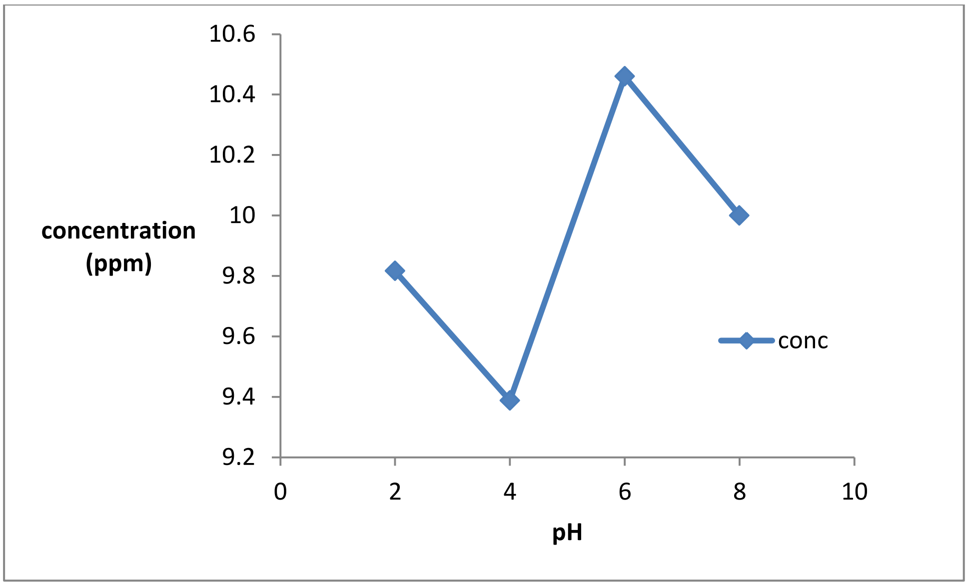

Figure 13: Effect of pH on removal of zinc using 3.5M zeolite

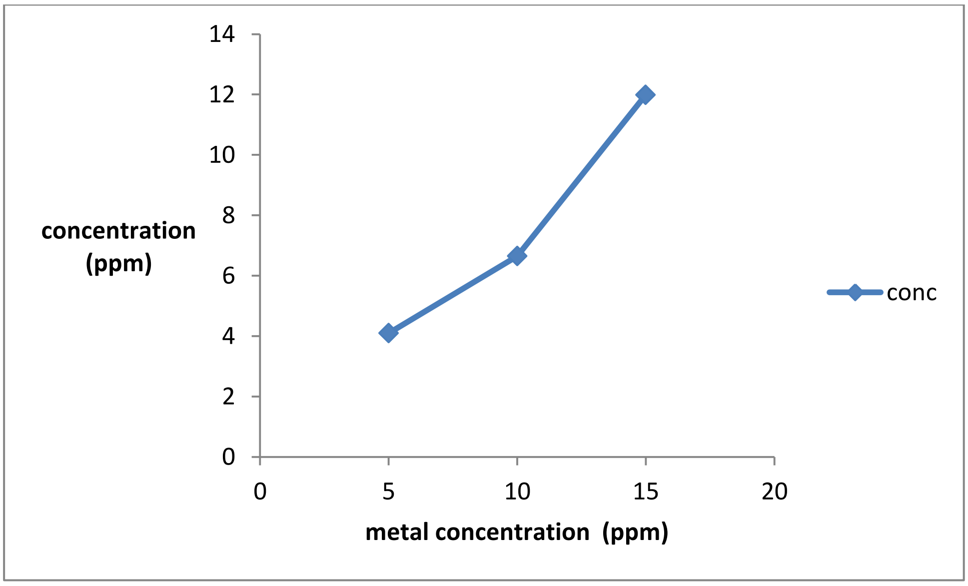

Figure 14: Effect of initial metal concentration on removal of zinc using 3.5M zeolite

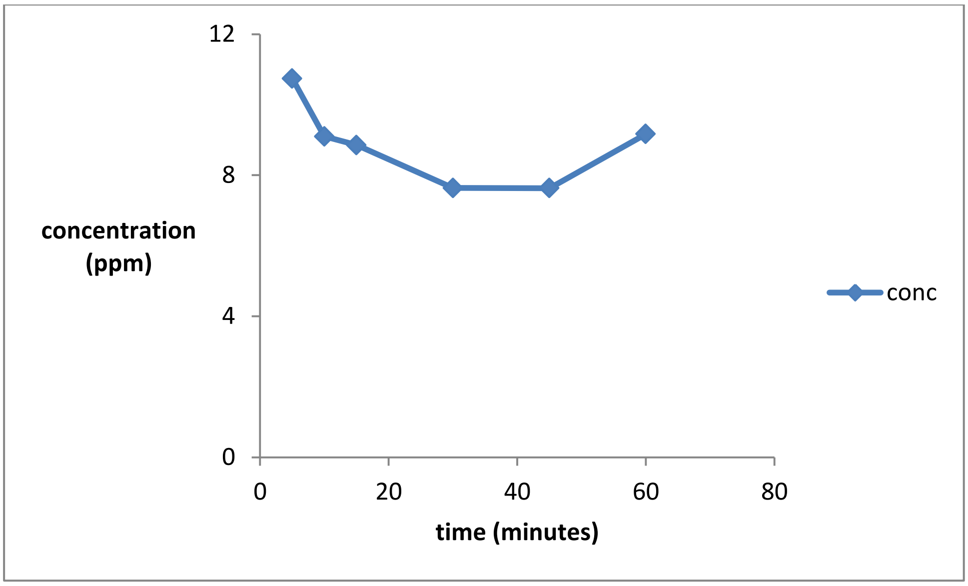

Figure 15: Effect of contact time on removal of zinc using 3.5M zeolite

Absorption of zinc using a 2M zeolite

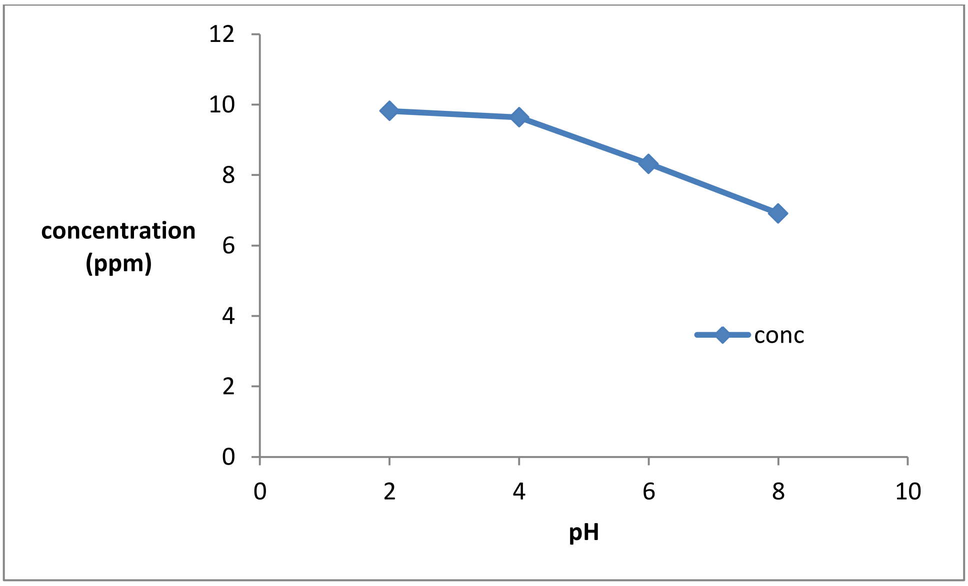

Figure 16: Effect of pH on removal of zinc using 2M zeolite

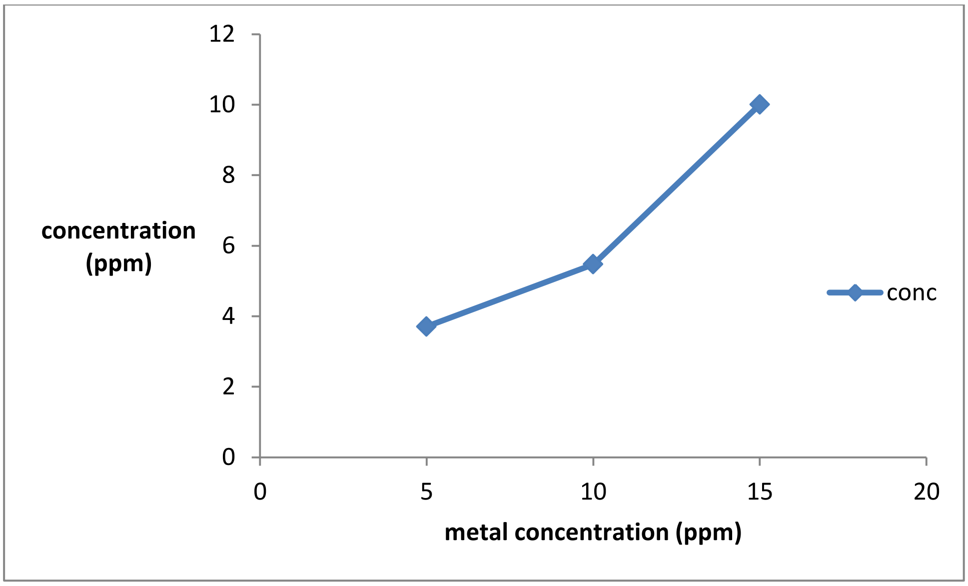

Figure 17: Effect of initial metal concentration on removal of zinc using 2M zeolite

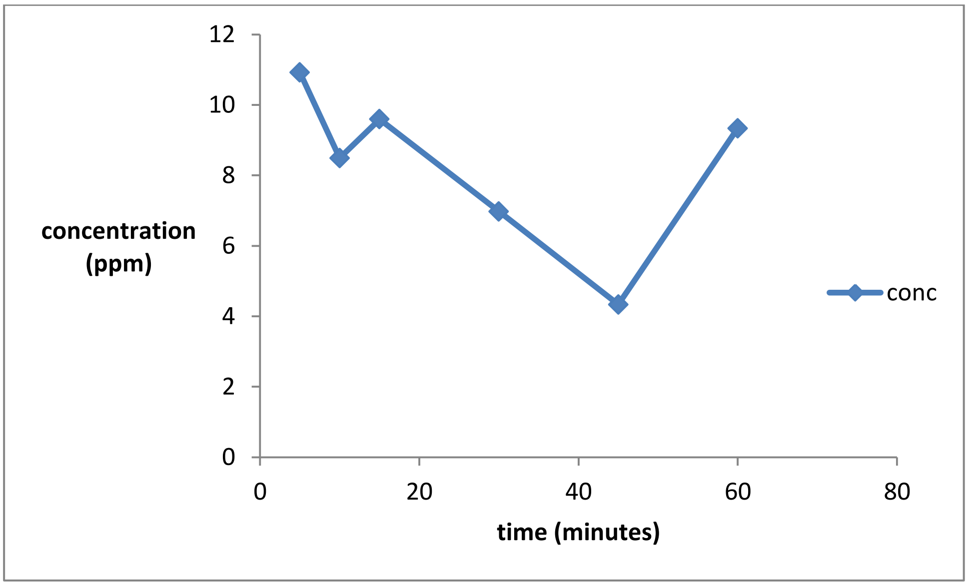

Figure 18: Effect of contact time on removal of zinc using 2M zeolite

4.1.2.2. Results for Nickel

Table 4.6: Effect of pH on removal of nickel

pH	2M zeolite (ppm)	3.5M zeolite (ppm)
2	9.0633	9.9452
4	8.2781	8.9471
6	6.3166	5.3065
8	2.8456	8.6075

Table 4.7: Effect of contact time on removal of nickel

Time (minutes)	2M zeolite (ppm)	3.5M zeolite (ppm)
5	9.9980	9.9918
10	7.8718	9.0661
15	7.5223	7.9801
30	8.2300	7.0874
45	8.4001	8.3990
60	6.6190	8.6973

Table 4.8: Effect of initial metal concentration on removal of nickel

Metal concentration	2M zeolite (ppm)	3.5M zeolite (ppm)
5	2.4632	4.7062
10	4.1016	9.2084
15	9.689	12.4063

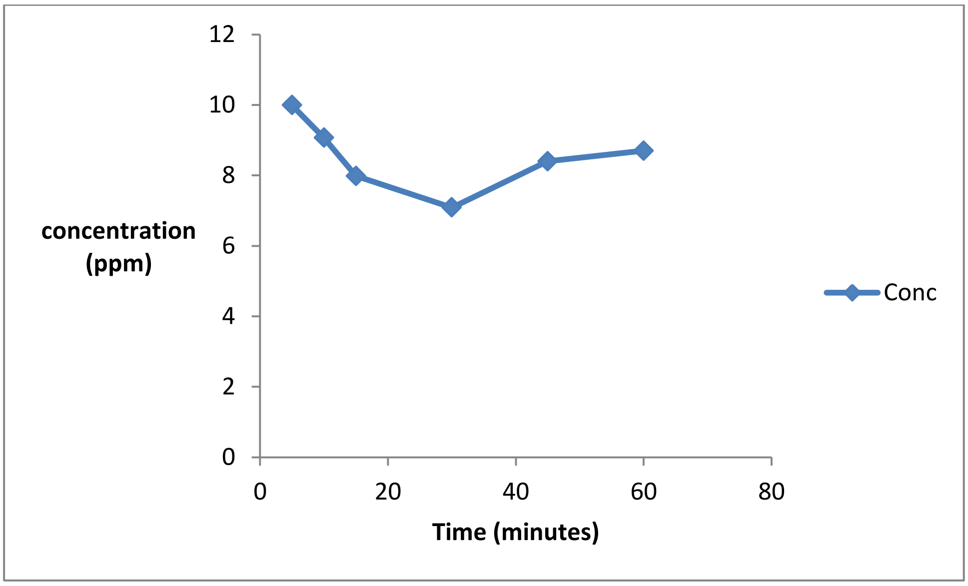

Figure 19: Effect of contact time on removal of nickel using 3.5M zeolite

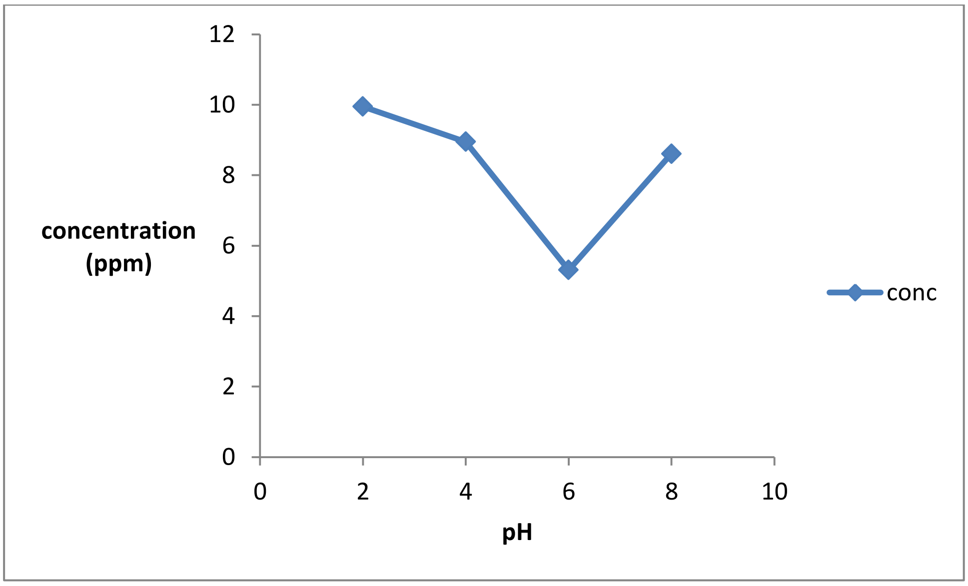

Figure 20: Effect of pH on removal of nickel using 3.5M zeolite

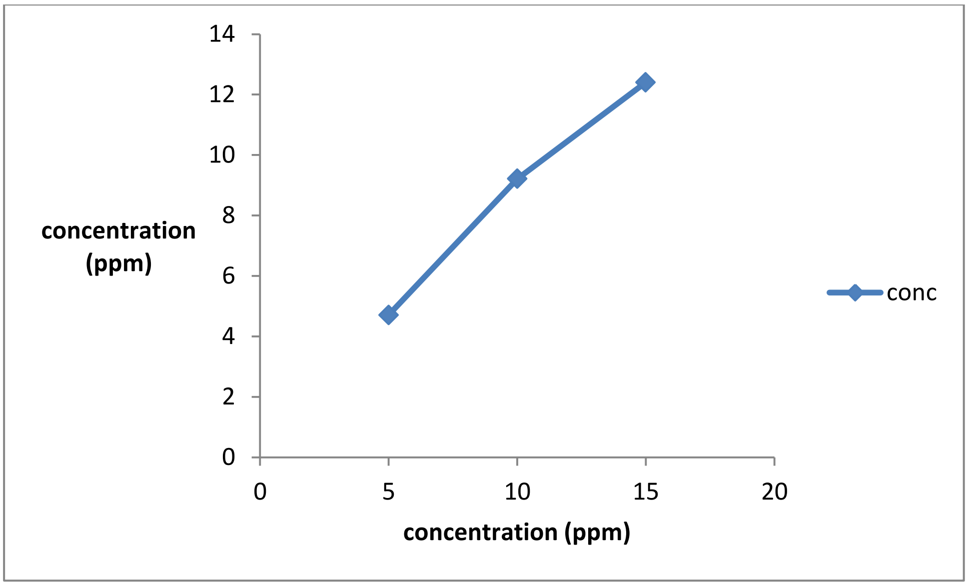

Figure 21: Effect of initial concentration on removal of nickel using 3.5M zeolite

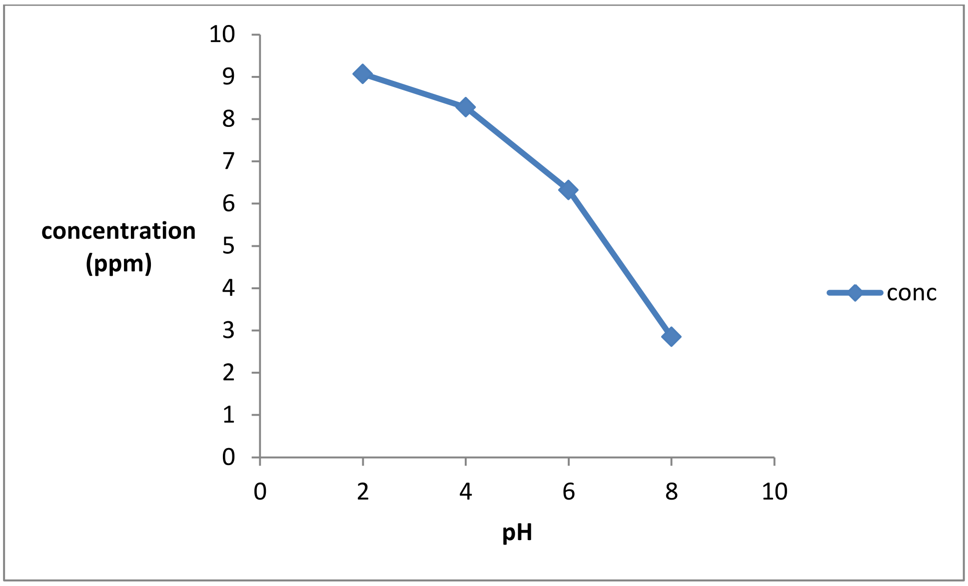

Figure 22: Effect of pH on removal of nickel using 2M zeolite

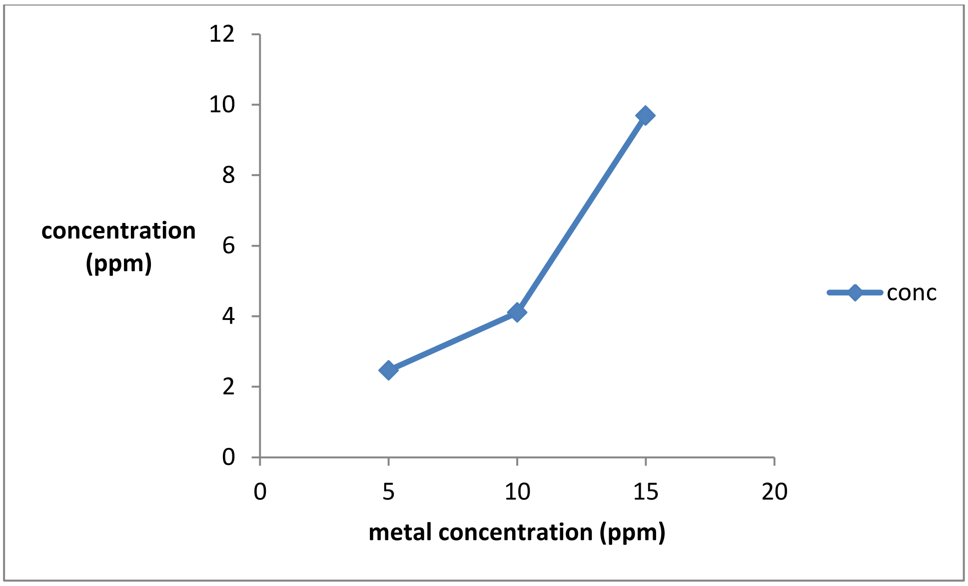

Figure 23: Effect of initial metal concentration on removal of nickel using 2M zeolite

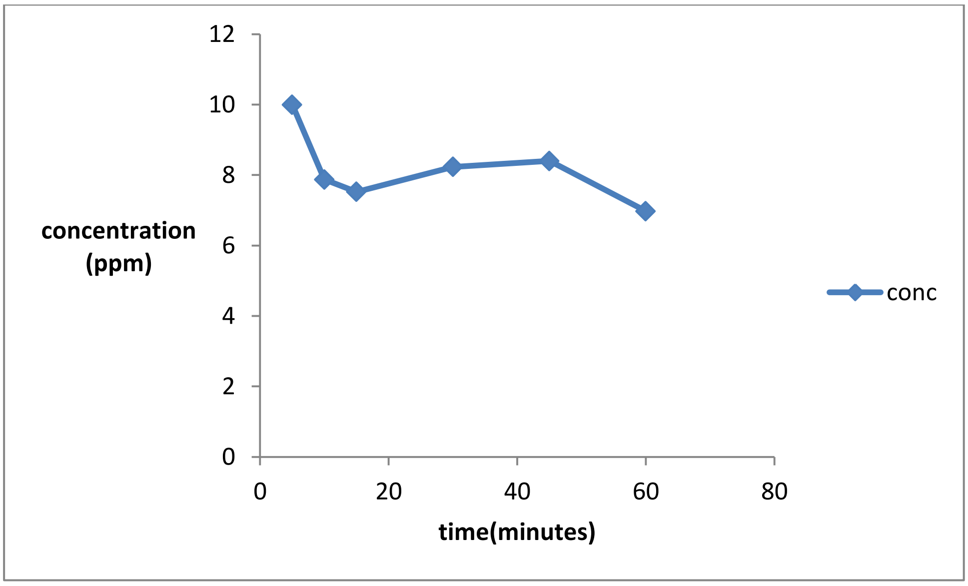

Figure 24: Effect of contact time on removal of nickel using 2M zeolite

From the results of both nickel and zinc it can clearly be observed that the optimum pH for nickel is 6 and that of zinc is 6. It is has been researched and found that pH is a very important parameter which has a strong impact on the adsorption processes. Nickel and zinc ion removal has been reported to be optimum at pH of 6 (Malamis and Katsou 2013).

Another observation that was made is as the pH was being altered to 2 and 8 there was also an increase in volume as more acid or base was need to reach those pH. Therefore metal uptake was not only affected by pH by also concentration due to the dilution by the acid or base.

From the results above, it was noted that the ideal metal concentration for Zinc is 10ppm and for Nickel it is 15ppm. However, some researchers have claimed that at very low initial metal concentrations, the ratio of metal cations to adsorbent mass is low and therefore adsorption does not depend on initial concentration (Malamis and Katsou 2013).

Contact time is the most important factor affecting the efficiency of removal of heavy metals. Predetermined optimal values of pH and intial metal concentration were used for analysing effects of contact time on removal of Ni^{2+} and Zn^{2+}. The results show the dependence of removal efficiency with contact time. The removal increases with time and attains equilibrium in 60 minutes for nickel removed in 2M of zeolites and 30 minutes for nickel removed in 3.5M zeolites, and in 45 minutes for zinc both for 2M and 3.5M zeolites with initial metal concentrations of 10ppm. It is clear that complete removal of nickel ions in 3.5 requires less residence time compared to zinc. The slow removal capacity with the subsequent time may be due to the diffusion of heavy metal ions into the surface of the zelites and fewer remaining binding sites.

CHAPTER 5

5.1.CONCLUSION

The spectra of the synthesised zeolites were studied and an assignment of the adsorption bands was made.

The zeolites were successfully synthesised, activated and functionalised for the removal of heavy metals such as nickel and zinc.

The zeolites showed that the zeolites favoured the removal of zinc more than that of nickel. The optimum pH was noted to be 6 and the contact time should be between 15 and 30 minutes. It can be concluded that the zeolites can be safely used to remove heavy metals.

The family of activated and modified zeolites that were used in this experiment showed that they are fully capable of efficiently adsorbing Zinc and Nickel.

The aim of this work was to investigate removal of nickel and zinc using synthesied zeolites. Optimal removal conditions for both metals were determined with batch experiments. Ion exchange process was pH-dependent and optimal removal efficiencies for both nickel and zinc were obtained at pH 6.

Removal of nickel ions reached equilibrium faster (within 30 minutes for 3.5M zeolites) comparing with zinc ions (within 45 minutes for both 2M and 3.5M zeolites).

CHAPTER 6

6.1.RECOMMENDATION

- It is recommended that barium chloride should be used for the activation of zeolites instead of barium sulphate as the sulphate in not soluble in water.
- The method of functionalisation should be extended to cover the removal of anions and organic materials.
- The study proved that coal fly ash use should be extended to the purification of of water and instead of the authorities producing this waste just dumping it. This use would culminate in reduced land pollution.

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