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**2012-07-06**
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# EFFECT OF THE HOMOIONIC FORM OF CLINOPTILOLITE ON $Ni^{2+}$ ADSORPTION ISOTHERMS: A THERMODYNAMIC STUDY

**Joshua Gorimbo**

**A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering.**

**Johannesburg, 2011**

# DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

……

(Signature of Candidate)

…….day of …….year……..

# ABSTRACT

This study investigates the effect of zeolite modification on $Ni^{2+}$ removal from synthetic wastewaters. In this study sorptive removal of nickel ions from solutions containing 1-100mg/L using natural and pretreated clinoptilolite ($Na^{+}$, $K^{+}$, and $Ca^{2+}$ homoionic forms) was investigated. The natural clinoptilolite (from Kwa-Zulu Natal, South Africa) was pretreated with 2M metal chlorides for 24 hrs to yield near homoionic Na, K, and Ca-forms. Experiments were carried out as a function of solute concentration and different zeolite masses. The equilibrium distribution was determined by contacting tared amounts of clinoptilolite (2g batches to 100mL of solution) with a known concentration of $Ni^{2+}$ until equilibrium was reached. The natural and pretreated clinoptilolite samples were structurally studied using X-ray fluorescence (XRF), X-ray diffraction (XRD), BET, FTIR and scanning electron microscopy (FIB/SEM). The cation exchange capacity of this zeolite was determined to be 2.45×10-3 eq/g from XRF major elemental analysis. The equilibrium concentration of the solution was analysed for $Ni^{2+}$ using Atomic Absorption Spectroscopy and results presented by plotting ion exchange isotherms. A comparison of the isotherms for the $Na^{+}$-$Ni^{2+}$, $K^{+}$-$Ni^{2+}$, $Ca^{2+}$-$Ni^{2+}$ and natural-$Ni^{2+}$ systems gave us insight into how the displaced ion affects the selectivity of the clinoptilolite for $Ni^{2+}$.The Na, K and natural forms presented highly selective convex isotherms whereas the Ca-form has a concave graph suggesting that the selectivity series is $Ca^{2+}$> $Ni^{2+}$> ($Na^{+}$, $K^{+}$,

Natural). Fitting of the Langmuir and Freundlich isotherms to experimental data gave good fits, $R^2$ values ranging from 0.9 – 0.99. Thermodynamic parameters revealed that the $Ni^{2+}$ sorption capacity increases as the values of $K_{eq}$ and $\Delta G°$ increase with increasing temperature from 25 to 75°C. The $\Delta G°$ values were all negative except for calcium exchanged clinoptilolite at 25 and 35°C, where the $\Delta G°$ values were positive 3.098kJ/mol and 0.527kJ/mol respectively. $\Delta H°$ was positive for all forms of clinoptilolite and ranged from 18.72 to 42.05 kJ/mol, this provides an indication that the sorption reaction is endothermic for Ni(II). The values of $\Delta S°$ for $Ni^{2+}$ sorption were positive and ranged from 0.08 to 0.14 kJ/mol.K. These positive values indicate increased randomness at the solid-solution interface during the adsorption of $Ni^{2+}$ on clinoptilolite. As expected from theory, the enthalpy obtained from the Van't Hoff plot is dependent not only on the metal ion being adsorbed, but also on the ion being displaced.

To My Mother

## ACKNOWLEDGEMENTS

Thanks are due to my supervisor, Professor Linda L Jewell for her help, inspiration and useful criticisms during the process of writing this dissertation. Her unending energetic, open and light spirit has truly been a stronghold for me during this process. My family, Christopher, Trust, Washington and Rudo Gorimbo who have all been a consistent support, I thank them for their patience, time and space given to me. I extend a special thanks to NRF for the financial support. I acknowledge the fruitful discussions I had with Dr Sanyasi Sitha, Mr Blessing Taenzana and Miss Sthembile Dlamini.

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## LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| AAS | Atomic absorption spectrometry |
| B | Sorption equilibrium constant (L/mg). |
| $C_e$ | Equilibrium concentration in the fluid (mg/L), |
| CEC | Cation exchange capacity of the zeolite (in eq/g) |
| $C_i$ | Initial heavy metal concentration in the aqueous phase, mg/L |
| D-R | Langmuir, Dubinin-Radushkevitch |
| FTIR | Fourier transform infrared spectroscopy |
| $\Delta G$ | Standard Gibbs free energy of exchange |
| $\Delta H$ | Enthalpy changes |
| $K_{eq}$ | Thermodynamic equilibrium constant |
| $K_f$ | Freundlich constant related to the adsorption capacity |
| m | Mass of clinoptilolite (g) |
| $m_s^A$ | Molarities of the ions A |
| $M_{A,f}$ | Final concentration of the exchanging ion (moles per litre) |
| $M_{A,i}$ | Initial concentration of the exchanging ion (moles per litre) |
| $m_s^B$ | Molarities of the ion B |
| NLLS | Nonlinear least-squares analysis |
| $Q_e$ | Adsorbate loading (mg/g) at equilibrium |
| $Q_m$ | Adsorption capacity (mg/g) |

| | |
|---|---|
| R | Universal gas constant, (8.314 $Jmol^{-1}K^{-1}$ ) |
| SEM | Scanning Electron Microscopy |
| T | Absolute temperature (K). |
| V | Solution volume used in liters |
| *W* | Zeolite masses in grams |
| wt% | Weight Percent |
| XRF | X-ray diffraction |
| XRF | X-ray fluorescence |
| $X_{sol}$ | Equivalent fraction ($X_{sol}$) of the ingoing cation in solution |
| $X_{zeo}$ | Equivalent fraction in the zeolite |
| *α* | Separation factor |
| a | Activity of the aqueous species |
| ā | Represents activities of the species adsorbed in the zeolite |
| 1/n | Freundlich constant related to the adsorption intensity |

# 1 INTRODUCTION

Preventing pollution of natural waters and soil by toxic heavy metals is a serious environmental concern. It has been found that heavy metals are cumulative toxins which in even small quantities are detrimental to most forms of life. Heavy metals are elements that have atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 at 4°C (Srivastava and Majumder, 2008).

Heavy metals enter the environment dissolved in wastewaters from different branches of industry, in particular: mining, smelting, metallurgy, leather tanning, pesticides, animal feed manufacturing, electroplating, batteries, spinning baths from chemical fibre plants, used dye solutions, chemical plant wastes and electroplating shops in machine-building factories (Wang, 2011). These industries however discharge wastewaters contaminated with high concentrations of pollutants, especially Ni(II), Cd(II), Hg(II), Pb(II) and Cu(II), and current technologies for treating such wastewaters are expensive. Hence adsorption onto zeolites can be a low-cost procedure of choice in wastewater treatment.

The increasing levels of heavy metals in the environment pose a serious threat to human health, living resources and ecological systems. Soluble and mobile heavy metals species are non-biodegradable and tend to

bioaccumulate in living organisms causing various diseases and disorders. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (Mufula, 2010).

Soluble and mobile heavy metals species are non-biodegradable and tend to bioaccumulate in living organisms causing various diseases and disorders. Nickel (II) ion is one such heavy metal frequently encountered in raw wastewater streams from industries, such as the manufacturing of magnetic tape, electroplating, jewellery, welding rods, dental procedures, pigments and it is also used as a catalyst in oil hydrogenation (Wang et al. 2007). It enters the human body through inhalation and ingestion, causing coughing, dyspenea, tachycardia, pneumonia, cerebral hemorrhage, asthma, insomnia and carcinoma of the lungs, nasal cavities, kidneys, stomach, and prostate (Sprynskyy et al., 2006).

## 1.1 Background

During the last 55 years, increasing amounts of nickel have found their way into the soil, especially by deposition of ash residues from coal combustion and disposal of municipal sewage sludge (Gupta, 2006).The higher nickel load on soils may increase its uptake by plants and lead to adverse effects on humans and aquatic ecosystems. Gupta's studies indicate that changes in faunal composition and soil fertility due to nickel pollution are observed in many places and humans suffer from allergies due to nickel containing diets and also due to exposure to nickel containing materials. Therefore removal of nickel and other heavy metals from wastewaters prior to discharging them into receiving waters is of paramount importance.

Nickel enters the human body through inhalation, ingestion and by skin contact with soil, water and metals containing nickel as well as with metals plated with nickel. Nickel is recognized as a human carcinogen. Those who get exposed to nickel dust or nickel steam will have respiratory inflammation, dermatitis, leukocytosis, nasal cancer, lung cancer and other illnesses. According to a field investigation, that Shi Biqing et al., (2008) conducted the high incidence of cancer is correlated with nickel sulfide, nickel oxide and nickel carbonyl content.

Conventional physicochemical treatment methods such as ion exchange, ultrafiltration, electrodialysis, solvent extraction, reverse osmosis, precipitation

and adsorption have been proposed for the treatment of wastewater contaminated with heavy metals (Erdem, Karapinar & Donat 2004). However, these processes have significant disadvantages such as incomplete metal removal, particularly at low concentrations and high operational cost (Cochrane et al. 2006)**,** hence cost effective treatment methods are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration.

Cost is an important parameter for comparing the sorbent materials; the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, a sorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from other industry. Some of the reportedly low-cost sorbents include lignin, chitosan, chitin, algae, zeolite, clay, fly ash, peat moss, modified cotton and dead biomass. Among several chemical and physical methods, the adsorption of heavy metals onto zeolites has been found to be superior to other techniques because of the zeolite properties, chemical stability, simplicity, safety of operation and capability of the zeolite to remove several cations simultaneously from aqueous solution by utilizing ion exchange, as well as the recovery potential of both the adsorbent and heavy metals (Al-Haj Ali, El-Bishtawi 1997),(Baker, Massadeh & Younes 2009).

Natural and synthetic zeolites have been studied for heavy metal removal. A study by Argun (2008) reported that zeolites, clinoptilolite in particular, demonstrate a strong affinity for nickel and other heavy metals. Zeolites are naturally occurring silicate minerals, which can also be produced synthetically. Clinoptilolite is probably the most abundant of more than 40 natural zeolites species (Breck, 1974). Deposits of this mineral occur in abundance in South Africa and the western United States among other parts of the world, making it readily available and inexpensive.

Zeolites have found uses in animal feeds, nuclear waste cleanup, pollution control, ion exchange, catalysis, molecular sieving, fish farming, swimming pool filtration, odor control, concrete production and in the petrochemical industry. What a zeolite does, and how it does it, depends upon the exact shape, size, and charge distribution of the lattice structure of the zeolite. Activated carbon is considered to be a particularly competitive alternative for the removal of heavy metals. However, activated carbon may not be suitable due to the high costs associated with production and regeneration of spent carbon (Srivastava, 2008). For instance the cost of zeolite ranges from US$240- 260/Ton as compared to US$950- 2000/Ton of activated carbon as of May 2011 (Alabala, 2011). Chemical precipitation is also used on wide scale to clean wastewaters. However, the production of significant amounts of sludge that is difficult to filter and requires careful, frequently expensive, disposal techniques, is the major disadvantage of this process (Wang, 2011).

In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents such as zeolites in industries for wastewater treatment applications today are strongly recommended. In addition, the use of zeolites may not only benefit the industries, but the living organisms and the surrounding environment will also benefit from the decrease or elimination of potential toxicity due to the heavy metal.

Selecting the right technology depends on the economic aspects and scaling up. Scaling up refers to the migration of a process from the lab-scale to the pilot plant-scale or commercial scale. The capital costs of setting up the treatment plants and the costs of chemicals or other operating costs can also determine which technology will be adopted by an industry. Finally environmental constraints can also make their presence felt, especially where the industries are very close to large cities or residential areas or even environmentally fragile surroundings.

## 1.2 Motivation and Research Problem

Industries play a vital role in the development of a country. Mining and manufacturing industries are among the key sectors that contribute to the gross domestic product and keep the economic engine of a country running so instead of complaining about ill-effects of industrial water pollution, methods of treating this should be developed. One such method is ion

exchange using zeolites. It is one of the most simple and efficient methods of industrial wastewater treatment, and hence drawing attention from many researchers.

Although major breakthroughs have been made in removing several heavy metals (such as $Ni^{2+}$, $Cd^{2+}$,$Pb^{2+}$, $Cu^{2+}$, $Zn^{2+}$ etc) from wastewater using zeolites, clinoptilolite (and several other natural zeolites) has been shown to exhibit a very low affinity towards $Ni^{2+}$ (Breck, 1974). Therefore, improvements in $Ni^{2+}$ selectivity are important for industrial applications. Although several authors have reported that converting the zeolite to a homoionic form improves selectivity, we are still not aware of any studies which compare different homoionic forms for the removal of $Ni^{2+}$ aqueous solution. In this study physical (pore diameter and volume) and thermodynamic differences between these forms will be investigated with reference to $Ni^{2+}$ selectivity.

Despite the excitement with which many researchers have reported the effective use of zeolites in environmental remediation, it should be noted that the chemical composition of the zeolites differs from region to region and as a result their ion - exchange behavior is also different, thus justifying the study of zeolites from different sources. For instance, clinoptilolite from one source will not necessarily have the same properties as clinoptilolite from another distinct source. Crystal structure and chemical composition account for the primary differences. Particle density, cation selectivity, molecular pore size,

and strength are only some of the properties that can differ depending on the zeolite in question. Exchange sites on a particular zeolite may contain nearly all K, nearly all Na, some Ca or Mg, or a combination of these. Source plays a large role in these variations. Environmental conditions during and following the geologic genesis of each source are rarely the same, causing these variations. Hence this study will look at the removal efficiency of $Ni^{2+}$ from aqueous solution using local clinoptilolite.

### 1.2.1 Research Questions

In solving the research problem mentioned above the following questions must be answered;

- What is the effect of clinoptilolite pretreatment with NaCl, KCl and $CaCl_2$ solutions on the removal efficiency of $Ni^{2+}$ from aqueous solution?
- What effect does the nature of the exchangeable ions ($Na^{+}$, $K^{+}$, $Ca^{2+}$) have on the enthalpy of adsorption of $Ni^{2+}$ ?
- Is the selectivity for $Ni^{2+}$ dependent on the exchangeable ion being displaced?
- Is the cation exchange capacity of the clinoptilolite changed by pretreatment?
- What effect do temperature and initial concentration have on the shape of ion-exchange isotherms?

## 1.3 Aims

To establish the most favorable pretreatment agent that corresponds to the highest selectivity for $Ni^{2+}$ removal from aqueous solution using clinoptilolite mined in KZN.

### 1.3.1 Objectives

This aim would be achieved via the outlined objectives:

i. To investigate the optimum operational parameters for removal of $Ni^{2+}$ from aqueous solutions.
ii. To investigate the maximum removal capacities of as-received and modified forms of clinoptilolite for $Ni^{2+}$ by means of equilibrium studies,
iii. To compare different homoionic forms on the removal of $Ni^{2+}$ from aqueous solution.

### 1.3.2 Hypothesis

Pretreatment of the zeolite will result in more nickel (meq/g) being loaded onto the zeolite, and may alter the selectivity, isotherm and adsorption energy from one homoionic form to another.

## 1.4 Scope of Research

The scope of the research encompasses the pretreatment of zeolites, preparation of synthetic water, characterization of pretreated zeolites and optimization of exchange conditions for maximum performance.

## 1.5 Dissertation Outline

This dissertation is divided into a number of chapters, each explaining different aspects of the investigation. A summary of each chapter is given below.

Chapter 1: Introduction

A brief background of nickel heavy metal pollution is given together with the different solutions to the problem. An outline of the motivation of the research, research problem, aims and objectives, hypothesis and the scope of the research is also briefly discussed.

Chapter 2: Literature Review

An in-depth explanation into the source, ecological effects of heavy metals and different treatment technologies available is given. The treatment of wastewater using natural zeolite is also explained, that is, the treatment mechanism. Natural zeolites are also described in greater detail with their general characteristics. A review of previous research involving the use of

different adsorbents including natural zeolite is also presented on theoretical basis.

Chapter 3: Materials and Methods

This chapter describes the research methodology and experimental procedures for the research work. The experimental techniques used in order to determine the potential of natural zeolite as a low cost adsorbent in treating wastewater are also described in detail. Different methods of characterizing the properties of natural zeolite are described and these include the X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

Chapter 4: Results and discussion

This chapter dwells on the results and discussion associated with the equilibrium experiments for the removal of nickel from synthetic wastewater under different conditions. The experimental data were analysed using adsorption isotherms. From these studies the selectivity of natural zeolite for the heavy metals under investigation was determined

Chapter 5: Conclusions and Recommendations

This chapter presents a summary of the findings and conclusions of the work performed in this project and recommendations are given for further study. Lastly the list of referenced material and appendices are given.

# 2 LITERATURE REVIEW

The Literature review looks at firstly the sources of heavy metals and the technologies used to remove them from wastewater. It is then followed by a brief survey of commonly used adsorbents with a bias towards natural zeolites. Finally the review of the adsoption processes, ion exchange isotherms, regeneration and disposal of zeolites concludes the chapter.

## 2.1 Heavy Metals

Heavy metal pollution is an environmental problem of concern worldwide and industry is required to diminish contamination down to acceptable levels. Metals of particular interest in acid mine drainage and industrial wastewaters include copper, zinc, cadmium, arsenic, manganese, aluminium, lead, nickel, silver, mercury, chromium and iron, in concentrations that can range from 6 to 102 g/L (Huisman, Schouten & Schultz 2006a).The composition of such wastewater reflects the particular combination of heavy metals originating from a metallurgical operation. This toxic leachate can cause severe aquatic habitat degradation downstream of the mine when discharged untreated. Slag from metallurgical processes poses a similar problem. Even though it often contains high concentrations of potentially valuable heavy metals, it is

dumped in landfills or tailings ponds. Depending on the composition of the slag, these metals can be released as a result of weathering of the slag. Increasing levels of such heavy metals in the environment represent a serious threat to human health, living resources and ecological systems (Çoruh and Ergun 2009). In order to meet water quality standards, concentration of heavy metals in wastewater must be controlled.

## 2.2 Technologies Used for the Removal of Heavy Metals from Wastewater.

Several physico-chemical methods have been widely used for removal of heavy metals from industrial wastewater, such as ion exchange, solvent extraction, membrane filtration, coagulation and flocculation, electrochemical treatment, chemical precipitation (hydroxide precipitation and sulpfide precipitation) and adsorption (Papadopoulos et al. 2004); (Lalhruaitluanga, Prasad & Radha 2011); (Fu, Wang 2011). The conventional methods used for the treatment of heavy metals from industrial wastewater present some limitations. There are still some common problems associated with these methods such as, high capital and operational costs and the process may be associated with the generation of secondary waste which presents treatment problems.

Chemical precipitation is effective and by far the mostly widely used process in industry because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. These precipitates can be separated from the water by sedimentation or filtration, and the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation (Huisman, Schouten & Schultz 2006b). However, the major disadvantage of this process is the production of significant amounts of sludge that are difficult to filter and require careful frequently expensive disposal techniques.

Activated carbon has been recognized as a highly effective adsorbent for the removal of heavy metal-ion from concentrated and dilute metal-bearing effluents (McBride, 2000). But the process has not been used by small and medium scale industries for the treatment of effluents, because of its high manufacturing cost.

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultrafiltration, reverse osmosis, nanofiltration and electrodialysis.

## 2.3 Use of Natural Materials to Remove Heavy Metals from Wastewater

It is clear from the previous section that there has been a growing interest in decontaminating wastewater of heavy metals and hence the need for an economically viable process capable of achieving the desired results. Adsorption has been convincingly demonstrated to be a method with great potential for the removal and recovery of heavy metals from wastewater.

Searching for low-cost and easily available adsorbents to remove heavy metal ions has become a focus of much research. To date, hundreds of studies on the use of low-cost adsorbents have been published. Agricultural wastes, industrial byproducts and natural substances have been studied as adsorbents for heavy metal removal from wastewater. Various low-cost materials have been investigated for the treatment of wastewater. Lalhruaitluanga et al. (2011) studied the adsorption of Ni (II) and Zn (II) on chemically activated and raw charcoals of melocanna baccifera. Gupta and Bhattacharyya (2006) reviewed the adsorption of Ni (II) on clays (kaolinite, montmorillonite and poly(oxo zirconium) and tetrabutylammonium derivatives in aqueous media**.** Sud et al (2008) reviewed agricultural waste material as a potential adsorbent for sequestering heavy metal ions from aqueous solutions. Ji et al. (2011) studied the treatment efficiency of a multi-media biological aerated filter (MBAF) containing clinoptilolite and bioceramsite in a brick-wall embedded design.

The parameters which have been investigated for optimizing the use of adsorbent in wastewater treatment include the nature of the adsorbent and the adsorbate metal concentration, the temperature and pH of the aqueous solution, kinetics of adsorption, adsorption isotherm and the type of contacting system and the contact time. Different adsorbents from agricultural waste, industrial by-products and natural materials have been employed in the removal of nickel (II) from aqueous solution.

The adsorption of heavy metals onto zeolites has been found to be superior to other techniques because of the capability of the zeolite to remove several cations simultaneously from aqueous solution by utilizing ion exchange (Colella 1996, Dubinin, Isirikyan & Regent 1974, Faghihian, Ghannadi Marageh & Kazemian 1999, Genç-Fuhrman, Mikkelsen & Ledin 2007). One of the important properties of zeolites is that, in general they show some selective adsorption, i.e. they possess different affinities for different ions (Oter, Akcay 2007). The idea of using natural zeolites for the removal of heavy metal from solution has been investigated by a number of authors. Loizidou, and Townsend (1987) studied the ion-exchange properties of natural clinoptilolite, ferrierite and mordenite for the removal of lead and ammonium. Karadag et al. (2006) studied the removal of ammonium ions from aqueous solution using natural Turkish clinoptilolite, Abd El-Rahman et al. (2006) investigated the removal of $Cs^{2+}$, $Sr^{2+}$, $Ca^{2+}$ and $Mg^{2+}$ ions from aqueous waste solutions using Zeolite A. Çoruh and Ergun (2009) studied

$Ni^{2+}$ removal from aqueous solutions using conditioned clinoptilolite, García-Mendieta et al. (2009) evaluated the sorption properties of a Mexican clinoptilolite-rich tuff for iron, manganese and iron-manganese systems and more recently Cortés-Martínez et al (2010) studied cesium sorption by clinoptilolite-rich tuffs.

Rajic et al. (2010) studied Ni(II) adsorption from a simulated wastewater solution using natural clinoptilolite. These authors found an adsorption capacity of 1.9 mg/g at pH 6.0. Monolayer adsorption might occur on the adsorbent surface, as indicated by the applicability of the Langmuir isotherm for the equilibrium sorption. This result is in agreement with an earlier study undertaken by Argun (2008) who used Turkish Clinoptilolite for Ni(II) uptake and reported an adsorption capacity of 1.56 mg/g at pH 7. Although all are zeolites of the same type, i.e. Clinoptilolite, the Ni(II) adsorption capacity of Transcarpathian Clinoptilolite (13.03 mg/g) was almost seven times higher than that of Serbian clinoptilolite (1.9 mg/g) at the same pH of 6 (Sprynskyy et al. 2006). This may be due to the fact that the chemical composition of the zeolite differs from region to region and consequently the ion exchange behavior is also different. Hence it is important to study the South African clinoptilolite for $Ni^{2+}$ removal.

## 2.4 Adsorption Process

The term ‘’sorption” is used to describe every type of capture of a substance from the external surface of a solids or a liquid as well as from the internal surface of porous solids or liquids (Dyer, 1988). Sorption covers adsorption, chemisorption and ion exchange as three different phenomena. Depending on the type of bonding involved adsorption can be classified as physical, chemical and electrostatic sorption (ion exchange).

### 2.4.1 Physisorption and Chemisorption

In physical sorption (physisorption), no exchange of electrons is observed; rather intermolecular attractions between favorable energy sites takes place and are therefore independent of the electronic properties of the molecules involved. The adsorbates are held onto the solid’s surface by relatively weak intermolecular van der Waals forces. In chemical adsorption, a chemical reaction occurs at the solid’s surface, and the adsorbate is held on the surface by relatively strong chemical bonds. Physical adsorption is nonspecific, for instance during wastewater treatment using zeolites heavy metals will be physically adsorbed on any site of the zeolite provided the temperature is low enough. Chemisorption is similar to an ordinary chemical reaction in that it is highly specific.

The enthalpy changes for chemisorption are usually substantially greater in magnitude than those for physical adsorption. Typically $\Delta H$ for chemisorption lies in the range 40 to 800 kJ/mol (10 to 200 kcal/mol), whereas $\Delta H$ for physical adsorption is usually from 4 to 40 kJ/mol (1 to 10kcal/mol) (Levine, 2003).

For chemisorption, once a monolayer of adsorbed species covers the solid's surface, no further chemical reaction between the adsorbate and the solid can occur. For physical adsorption, once a monolayer has formed intermolecular interactions between adsorbed species in the monolayer and the same species in the solution can lead to the formation of a second layer of adsorbed species. The enthalpy change for formation of the first layer of physically adsorbed species is determined by the solid-adsorbate intermolecular forces, whereas the enthalpy change for the formation of a second, or third physically adsorbed layer is determined by adsorbate-adsorbate intermolecular forces. Although only one layer can be chemically adsorbed, physical adsorption of further layers on top of a chemisorbed monolayer sometimes occurs. Substantial physical adsorption usually occurs only at low temperatures (Levine, 2003).

### 2.4.2 Ion Exchange Theory

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineral 'ion exchangers'. Ion exchangers are insoluble solid materials which carry exchangeable cations or anions. When the ion exchanger is in contact with an electrolyte solution, the loosely held exchangeable ions enable the exchanger to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers) stoichiometrically without any physical alteration to the ion exchanger. As a rule, an ion-exchanger consists of the inert carrier of a microporous structure and the ion-active pore wall component carrying fixed positive or negative charges (Helfferich, 1995). Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. Typical ion exchangers are ion exchange resins, zeolites, montmorillonite, clay and soil humus. Although ion exchange is similar to sorption since a dissolved species is captured by a solid in both processes, the characteristic difference between the two phenomena is that ion exchange, in contrast to sorption, is a stoichiometric process. Every ion which is removed from the solution is replaced by an equivalent amount of another ionic species of the same sign

to maintain a lattice that is charge balanced. In sorption, on the other hand, a solute is taken up without being replaced by another species. However, it is sometimes difficult to apply it in practice since nearly every ion exchange process is accompanied by solute sorption or desorption, and most of the common sorbents such as zeolite and activated carbon can act as ion exchangers (helfferrich, 1995). Ion removal by solids could involve more phenomena as for example in inorganic natural materials where ion uptake is attributed ion exchange and adsorption processes or even an internal precipitation mechanism.

Several types of ion exchangers are available based on the type of the functional groups attached to the matrix and their layout and distribution in the matrix. Carriers of exchangeable cations are called cation exchangers, and carriers of exchangeable anions, anion exchangers. Certain materials are capable of both cation and anion exchange. These are called amphoteric ion exchangers.

Heavy metal cations can be immobilized by zeolites by two mechanisms: ion exchange and chemisorption (Jenne 1998). Ion exchange involves substitution of ions present in zeolite crystalline lattice by metal ions from the solution (Inglezakis, Loizidou & Grigoropoulou 2002). The type of cation (the position of the cation in the selectivity series) as well as the cation concentration in the solution will determine the ion-exchange efficiency. In

contrast, the second mechanism of metal ions immobilization, i.e. chemisorption, results in the formation of stable inner-sphere complexes (Godelitsas, 1999). This is due to the fact that functional groups (mainly $OH^-$) form strong chemical bonds with metal ions outside the hydration envelope (Jenne 1998). In zeolites, ion-exchange processes generally dominate chemisorption. Several authors have reported ion exchange as the principal process in the removal of several cations from aqueous solution by means of zeolites (Barrer, Klinowski 1974a, de Barros et al. 1997, Inglezakis, Loizidou & Grigoropoulou 2004). In order to construct the isotherm for an ion exchange couple on a zeolite a basic assumption has to be made to ensure that cations in the liquid phase are exchanged only with one type of solid state cations (Pabalan 1994).

## 2.5 Commonly Used Adsorbents

There are a number of microporous adsorbents in use for adsorption purposes in industry; these include activated carbon, activated clay, inorganic gels such as silica gel and activated alumina and crystalline aluminosilicate zeolites. Most adsorbents are manufactured, such as activated carbons, but some zeolites occur naturally. Each material has its own characteristics such

as porosity, pore structure and the nature of its adsorbing surfaces. Pore sizes in adsorbents may be distributed throughout the solid. Pore sizes are classified generally into 3 ranges: macropores have diamaters in excess of 500 Å, mesopores have diameters in the range 20 – 500 Å, and micropores have diameters which are smaller than 20 Å. Activated carbons, activated alumina and silica gel do not possess an ordered crystal structure and consequently the pores are nonuniform. The distribution of the pore diameters within the adsorbent particles may be narrow 20 to 50 Å. Zeolite molecular sieves have pores of uniform size from 3 to 10 Å, these pores will completely exclude molecules which are larger than their diameter (Breck, 1974).

Most coal is not porous and hence the need to activate it in order to generate a system of fine pores. This is achieved by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperatures (700 – 1100 ºC). Activation is simply the removal of tarry carbonisation products formed during pyrolysis, thereby creating pores. Activated carbon is made of randomly stacked micro – crystallites of graphite, it is the spaces between these crystals that form the micropores. Activated carbon is usually used for adsorbing organic material since it tends to be organophilic (Ruthven, 1984).

Activated alumina is a porous high surface area form of aluminium oxide, prepared either directly from bauxite ($Al_2O_3.3H_2O$) or from the monohydrate by dehydration and re –crystallization at elevated temperatures. The surface

of activated alumina exhibits both acidic and basic characteristics, thus reflecting the amphoteric nature of aluminium metal. These also show a high affinity for water. Activated alumina is usually used for adsorption at elevated temperatures in preference to silica gel, which loses its adsorptive capacity at high temperatures.

Silica gel is a partially dehydrated form of polymeric colloidal sicilic acid. It is formed when a silicate like sodium silicate is acidified, producing an agglomerate of micro – particles, subsequent heating expels water leaving a hard, glassy porous structure. The surface of silica gel is hydrophilic and hence its use in drying gases.

## 2.6 Natural Zeolites

Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon, and oxygen in their regular framework, cations and water are located in the pores. The structure consists of a three dimensional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. The aluminium ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms and the isomorphous replacement of $Al^{3+}$

for $Si^{4+}$ raises a negative charge in the lattice. The net negative charge is balanced by the exchangeable cations which are mainly alkali or alkali- earth metals such as sodium, potassium, calcium ions etc (Johnson et al. 2003). The cations are quite mobile and may usually be exchanged to varying degrees with heavy metals during wastewater treatment (Breck, 1974). The fact that the exchangeable ions of natural zeolites are relatively harmless makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. Changing the exchangeable cation by ion exchange provides a useful and widely exploited means of modifying the adsorptive properties.

In considering zeolite frameworks it is convenient to regard the structures as built up from assemblages of secondary building units, which are themselves polyhedral made up of several $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. The secondary building units and some of the commonly occurring polyhedral are shown in Figure 1. In these diagrams each vertex represents the location of a Si or Al atom while the lines represents the diameter of the oxygen atoms or ions which are very much larger than the tetrahedral Si or Al atoms.

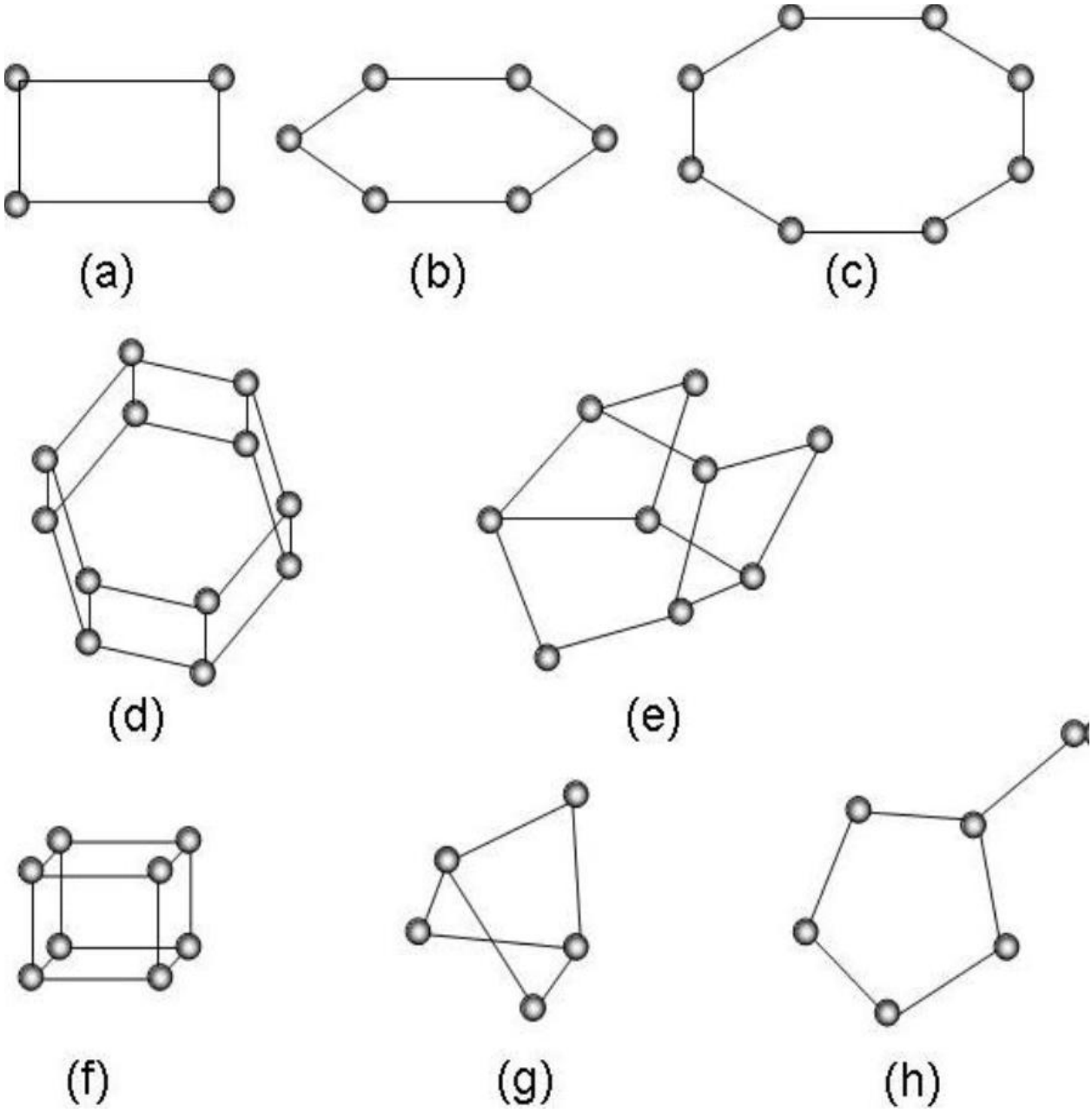



**Figure 2.1**: Secondary building units in zeolite frameworks; (a) single four ring (S4R),(b) single six ring (S6R), (c) single eight ring (S8R), (d) double six ring (D6R), (e) complex 4-4-1 (f) double four ring (D4R), (g) complex 4-1 and (h) complex 5-1 (Ruthven, 1984: Dyer, 1988).

The structural formula of a zeolite is best expressed for the crystallographic unit cell as $M_{x/n}[(AlO_2)_x (SiO_2)_y].wH_2O$ where M is the cation of valence n, w is the number of water molecules and the ratio y/x usually has values of 1-5 depending upon the structure. The sum (x + y) is the total number of tetrahedra in the unit cell. The portion with square brackets represents the framework composition.

About 40 natural zeolites have been identified during the past 200 years, only a few have practical significance at the present time. The most common are analcime, chabazite, clinoptilolite (used in this study), erionite, ferrierite, heulandite, laumontite, mordenite and phillipsite (Breck, 1990).

Clinoptilolite hails from the heulandite family of zeolites, which shares the same topology of eight- and 10-membered ring channels running parallel to the *c*-axis and an intersecting eight-membered ring channel parallel to the *a*-axis. The defining difference between heulandite and clinoptilolite is the Si/Al ratio, clinoptilolite being assigned if the Si/Al ratio is greater than 4.0.

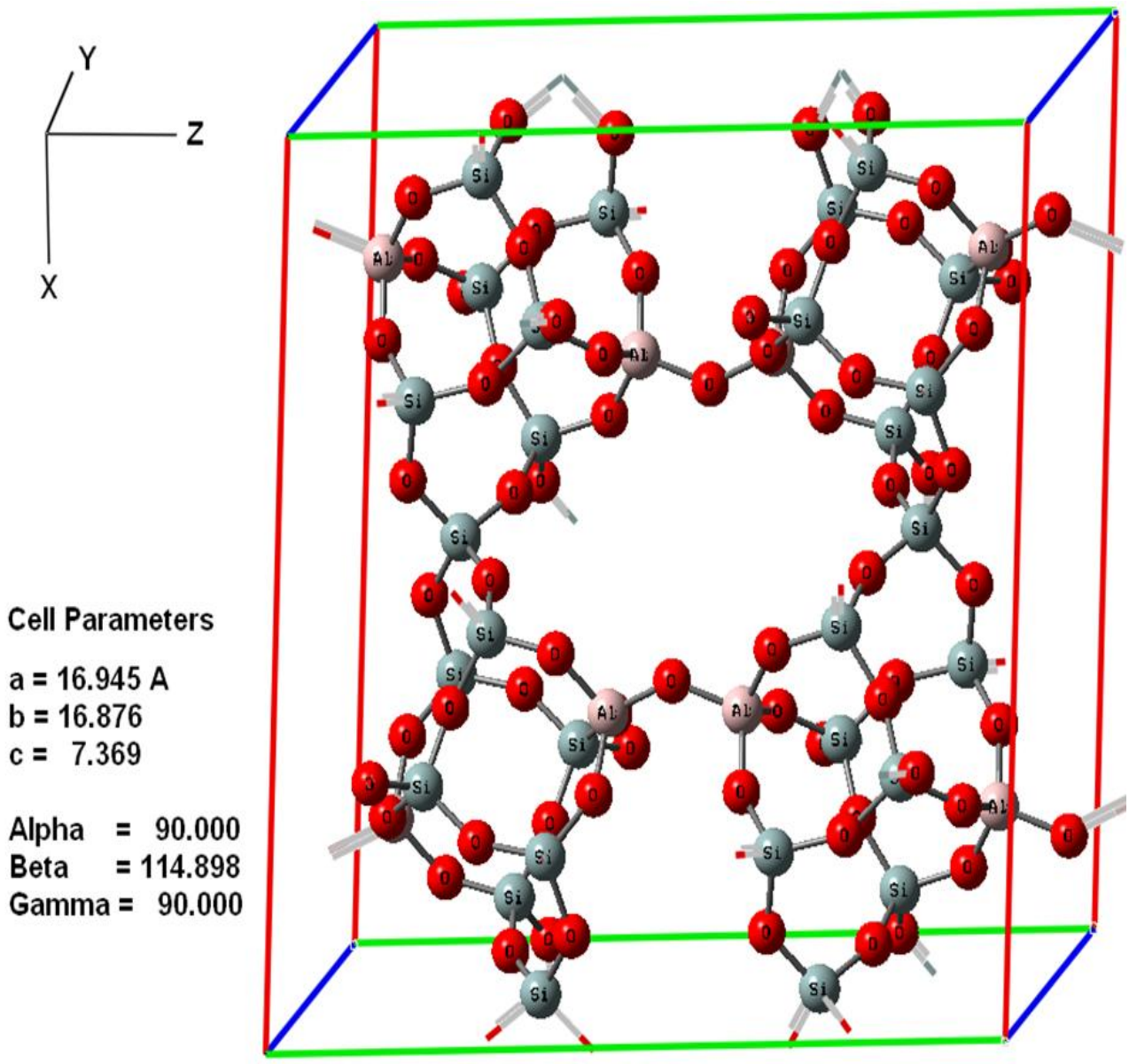



**Figure 2. 2**: The crystallographic unit cell of clinoptilolite, Na [SiAlO] structure generated by Gauss View 1998.

Zeolite mined in South Africa is limited in type and only clinoptilolite is excavated. The main uses of natural zeolites as an adsorbent are as drying

agents, deodorants, adsorbents for air separation, ion exchangers for water purification especially for removing ammonium ions and heavy metal ions and for water softening, soil upgrading and so on. Zeolites exhibit high selectivities for various heavy metals and are considered suitable for the removal of precious and semi-precious metals as well as the removal of heavy metals from industrial and processing waste waters. Because of their abundant availability locally, natural zeolites have been investigated for the removal of cadmium, copper, lead and zinc from wastewater (Kapanji, 2009). Clinoptilolite has the capability of removing small quantities of various heavy metal cations from aqueous solutions by utilizing ion-exchange and adsorption.

### 2.6.1 Selectivity of Clinoptilolite for Different Metal Cations

The selectivity of ion exchangers, i.e. defined as the selection by the ion exchanger of one counter ion in preference to the other. This may have various physical causes as outlined below.

The ion exchangers tend to prefer:

- the counter ion with the smaller solvated equivalent volume
- the size of the ion relative to the size of the pores in the zeolite.
- counter ions of high valence
- the counter ion that is more polarisable

- counter ions which interact more strongly with fixed ionic groups or with the matrix
- counter ions which participate least in complex formation with the co-ion

The first two of these effects are steric effects, while the remainder are charge and bonding effects. Table 2.1 reveals that each clinoptilolite sample has a unique selectivity series. The reason for this difference may be attributed not only to the different experimental conditions but also to the chemical composition of the clinoptilolite (Inglezakis et al., 2003).

**Table 2. 1**: Some examples for selectivity series obtained in different studies for clinoptilolite

| Study | Selectivity series | Reference |
|---|---|---|
| 1 | $Pb^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Cs^{2+} > Ni^{2+}$ | Faghihian et al. (1999) |
| 2 | $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+}$ | Ouki and Kavannagh (1999) |
| 3 | $Pb^{2+} > Cd^{2+} > Cs^{2+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+}$ | (Zamzow et al. 1990) |
| 4 | $Pb^{2+} > K^{+} > Ba^{2+} > NH^{4+} > Ca^{2+} > Cd^{2+} > Cu^{2+} > Na^{+}$ | Semmens and Martin (1988) |
| 6 | $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > Ag^{+} > Cs^{+} > Rb^{+} > K^{+} > NH_4^{+} > Na^{+}$ | Helfferich,(1995) |

Despite the observation of a different selectivity series in every single research report (Table 2.1) it is common for almost all studies that clinoptilolite has the highest affinity towards $Pb^{2+}$ among the heavy metal cations that have been studied. As mentioned earlier, this is attributed to the fact that, heavy metal cations with low hydration energies are sorbed preferentially compared to cations with high hydration energies (Langella et al., 2000; Wingenfelder et al., 2005). Some examples of Gibbs free energies of hydration are -1425 kJ/mol for $Pb^{2+}$, -1755 kJ/mol for $Cd^{2+}$, 2105 kJ/mol for $Ni^{2+}$ and -2100 kJ/mol for $Cu^{2+}$ (Cotton, 1999). In addition to hydration energy, physicochemical and stereochemical factors such as the hydrated radii, space requirements in the micropores of clinoptilolite and the type, number and location of exchangeable cations (Abusafa and Yücel 2002) also affect both selectivity order and dependence of total uptake (Inglezakis and Grigoropoulou 2003).

### 2.6.2 Zeolite Pretreatment

The effect of converting the zeolite initially to a homoionic form for the removal of some heavy metal ions from wastewater has been studied by many authors (Inglezakis et al. 2001) (Panayotova, Velikov 2003) (Günay, Arslankaya & Tosun 2007).These authors pointed out that zeolite in homoionic forms exhibits significantly increased ability to remove heavy

metals from wastewaters. Sodium chloride is most often used as the pretreatment agent. Prior to any ion exchange application, most exchangeable ions from the structure of the material are removed by pretreatment and replaced by more easily removable ones. Pretreatment of natural zeolites with acids, bases and surfactants, etc. is also used to improve their ion exchange capacity. Practically, any pretreatment operation increases the content of a single cation, called a homoionic form. Kesraoul-Ouki et al. (1993) demonstrated that the as-received zeolites contained a complement of exchangeable K, Ca and Na ions but exposing them to a concentrated NaCl solution converts them to a homoionic state in the Na-form, which significantly improves their exchange capacity. The exchangeable cations can be exchanged to fine-tune the pore size or the adsorption characteristics. The sodium form of a particular zeolite has a comparatively larger pore opening than the potassium form.

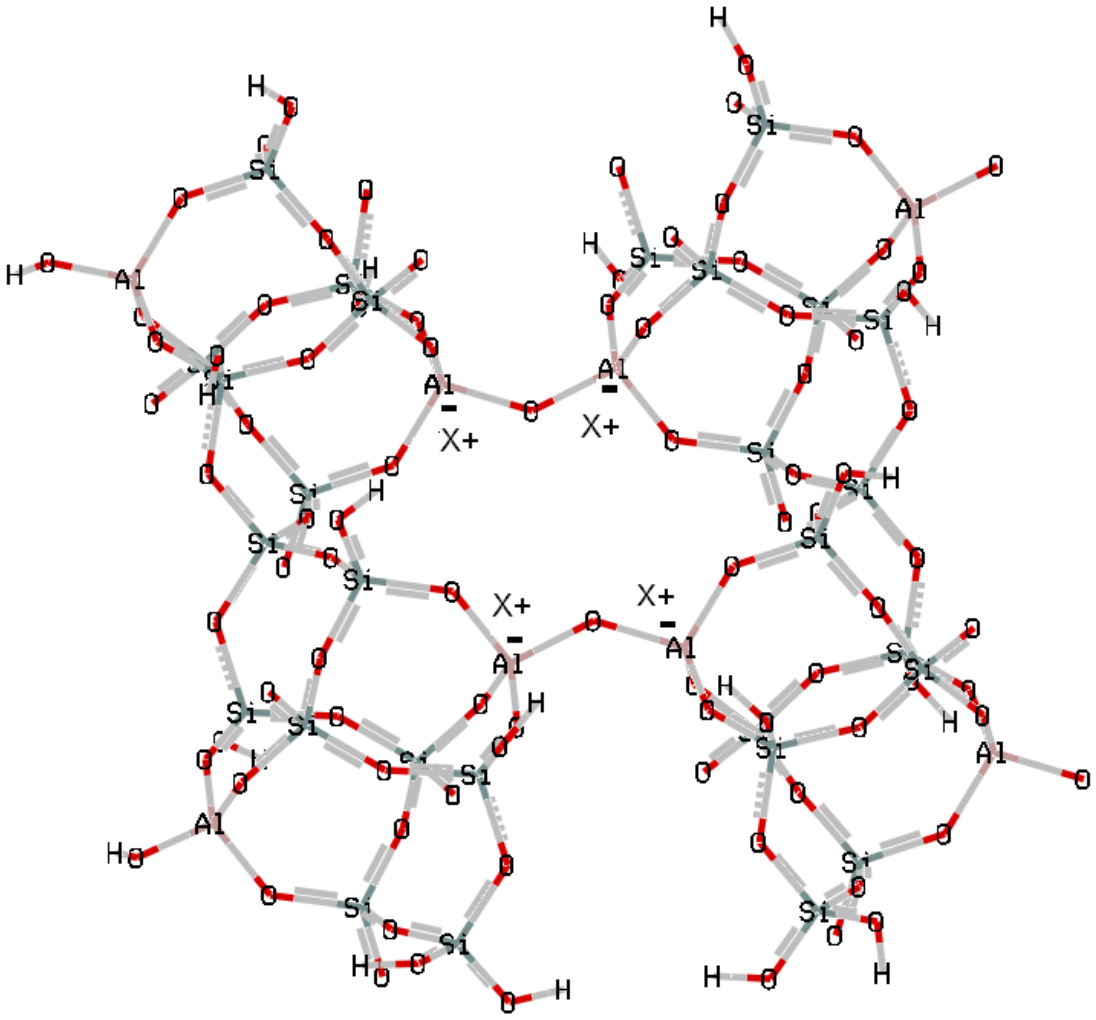



**Figure 2. 3**: Zeolite in homoionic X-form. (X represents any alkaline metal, for alkaline earth metals each divalent ion neutralizes two negative sites thus reducing the cation population in the pore openings.

The theoretical ion exchange capacity is independent of any pretreatment applied. The effective ion exchange capacity exhibits to the amount of cations, which can be exchanged that are contained in a specific quantity of the material under specific experimental conditions.

Semmens and Martin (1988) reported that clinoptilolite is highly selective for barium and lead but showed a considerably lower selectivity toward copper, cadmium, and zinc. They suggested that clinoptilolite exchange capacity depends significantly on the zeolite treatment method and they recommended that the zeolite should be conditioned with NaCl solutions for at least two exhaustion-regeneration cycles before equilibrium capacities are measured.

The pretreatment solution concentrations used was varied between 1 and 2 mol/L (Semmens, Martin 1988); (Wang et al. 2007);(Papadopoulos et al. 2004). The effect of the concentration of the pretreatment solution is examined with controversial results: Semmens and Martin (1988) concluded that although total exchange capacity remained unaltered, the sodium content of the pretreated samples was increased with concentration increasing from 1 to 2 mol/L. Comparison of as received, conditioned and treated zeolites for the removal of Pb and Cd showed that conditioning and pretreatment improved both the exchange capacity and the removal efficiency when operating at metal concentrations greater than 250mg/L (Kesraoul-Ouki, Cheeseman & Perry 1993). Hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity, are used extensively in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis as Hammett acids.

In agreement with Eisenman's theory, namely that natural zeolites pre-exchanged in sodium form, are fairly selective for monovalent heavy metal cations, provided these are characterized by low charge densities (Eisenman, 1962). As regards divalent cations, selectivity is predominantly determined by their hydration energies more than by the cation-lattice interaction. Accordingly, natural zeolites tend to prefer cations with lower hydration energies, e.g. lead over cadmium. The affinity of a cation exchanger, and therefore of a zeolite, for an uni-univalent cation depends on the anionic field strength exhibited by the solid. In the case of low field strength, presented by the most siliceous zeolites, cations with lower charge density, such as Cs, are preferred, so that the selectivity essentially depends on the difference in the free energy of hydration of the two cations in competition, more than on the difference in electrostatic interaction of the cations with the framework. On the contrary, it is predictable that the aluminous zeolites, characterized by high field strengths and low Si: Al ratios, tend to prefer cations with higher charge density, such as Li and Na. In this case selectivity is controlled more by zeolite (cation-framework interaction) than by solution (cation-water interaction) (Colella 1996).

### 2.6.3 Ion Exchange in Zeolites

Ion-exchange properties of zeolites are due to the presence of non-compensated negative charges, which originate from heterovalence substitution ($Si^{4+}$ by $Al^{3+}$ in tetrahedral positions) as well as the presence of surface functional groups (mainly $OH^-$ and $H_2O$) in crystalline lattice discontinuity points. As the result of lattice negative charge compensation by metal exchange cation, outer-sphere or inner-sphere complexes are formed. Stability of the outer-sphere complexes is very low because the binding of the zeolite with the metal ion complexed is in such a way that intermolecular forces dominate (McBride, 2000).

The following theoretical approach assumes that:

a) the system is in a true state of equilibrium
b) the exchange process is fully reversible. If the system is not reversible then there

   will be two different reactions (one representing the forward exchange and another the reverse exchange) that need to be examined separately. These processes must have different standard Gibbs energies also, in the reversible case, the forward and reverse reactions have different Gibbs energies although the difference is only in sign.

The ion exchange behavior of various inorganic exchangers and other types of crystalline silicates such as clay minerals and zeolites has been

extensively studied. Because of their three dimensional framework structure, most zeolites and feldspathoids do not undergo any appreciable dimensional structure with ion exchange. Clay minerals, because of their two dimensional structure may undergo swelling or shrinkage with cation exchange (Breck, 1974).

Equilibrium studies generally involve the determination of the adsorption capacity of a given material, this is important in accessing the potential of the material as an economic and commercially viable adsorber. The material is contacted with the solute until equilibrium is achieved. The adsorption equilibrium is a dynamic concept achieved when the rate at which molecules are adsorbed onto a surface is equal to the rate at which they are desorbed (Richardson et al., 2002).

### 2.6.4 The Binary Ion Exchange Process

The equilibrium relations for an ion-exchanger in contact with a solution of a mixture of ions have been discussed by several writers. In general, the ion exchange reaction between a solution containing the cation $A^{zA^+}$ and the $B^{zB^-}$ form of clinoptilolite (B being a cation of valence $z_B$) may be written as:

$$z_B A^{zA+}_{(aq)} + z_A(BL_{Z_B}) \rightleftharpoons z_A B^{zB+}_{(aq)} + z_B(AL_{Z_A}) \qquad (2.1)$$

in which L is the portion of the clinoptilolite framework holding a unit negative charge and the subscript (*aq*) denotes the solution phase. For simplicity, consideration is confined to the exchange of a pair of positive ions, *A* and *B,* with valencies *ZA* and *ZB.* The solid is assumed to be of constant exchange capacity and to be incapable of adsorbing negative ions.

If the zeolite is contacted with a series of isonormal solutions, constituted from differing proportions of the ingoing and counter cations, an ion exchange isotherm can be constructed at a standard condition of temperature and pressure, to yield the distribution of cations between zeolite and solution phases when equilibrium has been reached (checked by prior kinetic tests). It is also imperative that the ratio of the volume of solution (mL) in contact with a known mass of zeolite (g) is at least 20, and larger if experimentally feasible. The correct experimental methodology has been fully described by (Dyer, Townsend & Enamy 1981) and reinforced by(Pabalan 1994), who emphasises the importance of carrying out complete analyses of both solid and liquid phases. This may be difficult at both ends of the isotherm.

This enables an isotherm to be plotted recording the equivalent fraction ($X_{sol}$) of the ingoing cation in solution against its equivalent fraction in the zeolite ($X_{zeo}$). These quantities can be defined as:

$$\boldsymbol{x_{sol}} = \frac{\boldsymbol{Z_A m_s^A}}{\boldsymbol{Z_A m^A + Z_B m_s^B}} \qquad (2.\ 1\ )$$

Where $m_S^A$ and $m_S^B$ are the molarities of the ions A and B in solution respectively. The equivalent cation fraction in the clinoptilolite is given by:

$$\boldsymbol{x_{zeo}} = \frac{\boldsymbol{z_A(M_{A,i} - M_{A,f})V}}{\boldsymbol{W.CEC}} \qquad (2.\ 2\ )$$

Where *W* is the zeolite masses in grams, V is the solution volume used in liters, $M_{A,i}$ and $M_{A,f}$ are the initial and final concentration of the exchanging ion (in moles per litre) and CEC is the cation exchange capacity of the zeolite (in eq/g) determined by elemental analysis. $Fe^{3+}$ and $Al^{3+}$ are taken as lattice cations (Pabalan, Bertetti 1999).

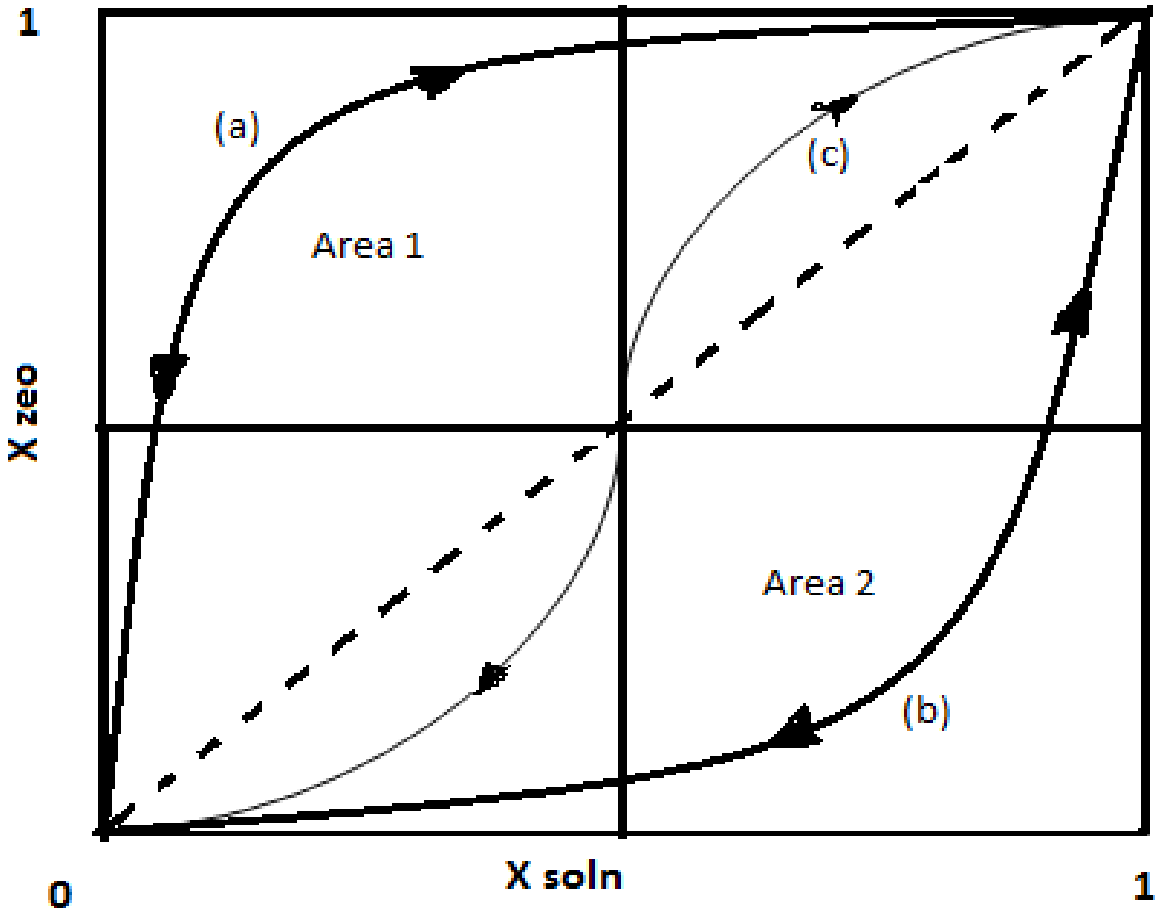



**Figure 2. 4** : Idealised cation exchange isotherms.

Idealised isotherm shapes are shown in Figure 2.4 for A in solution and B in the solid, initially. They give a pictorial indication of the relative preferences of the cations for the solid and solution phases. When the zeolite phase has equal affinity for both cations the isotherm is a straight line (the dotted line in Figure 2.4). Isotherm (b) is the shape adopted when A remains in solution, i.e it does not readily displace B from the zeolite phase, at the conditions of temperature and concentration of the experiment. Isotherm (a) occurs when A

replaces B from the zeolite. The sigmoidal shape of (c) arises when a change in selectivity occurs, in the concentration range being studied, and may be indicative of more than one type of exchange site being available in the zeolite for the competing cations (Colella 1996). By convention, the isotherm reports the equivalent fraction of the incoming cation, $X_{sol}$, present at equilibrium in the liquid phase, against the equivalent fraction $X_{zeo}$ of the same cation in the zeolite. In addition, by definition $X_{(A\ in\ sol)} + X_{(A\ in\ zeo)} = 1$ and $X_{(B\ in\ sol)} + B_{(B\ in\ Zeo)} = 1$

Barrer and Klinowski (1974) studied the effect of electrolyte concentration on selectivity. They concluded that when competing cations have different valencies, selectivity increases for the cation with the higher valence as dilution increases. Changes in isotherm shape can occur, with both the loss and gain of sigmoidal shape being possible, so that the absence of inflexions in an isotherm may not be taken as evidence that there is only one possible exchange site in the zeolite. When ions have the same valence, changes in isotherms with dilution are very small. When the isotherm exhibits a convex profile, e.g. curve (a) in Fig. 2.3 the uptake of the incoming cation A by zeolite from solution usually follows a Langmuir-type isotherm (Colella 1996). The analysis of the equilibrium data according to the Langmuir-type equation is possible when the cations A and B have equal or unequal charges and are in competition with each other, i.e. zeolite exhibits comparable affinities for both of them (Boyd, Schubert & Adamson 1947).

The selectivity of a zeolite for the entering ion $A^{zA+}$ may be expressed quantitatively as a separation coefficient $\alpha$ (sometimes referred to as a separation factor) which is defined as:

$$\alpha = (X_{(A \text{ in zeo})}X_{(B \text{ in sol})}) / (X_{(A \text{ in sol})}X_{(B \text{ in zeo})}) \quad (2.3)$$

In Figure 2.3, α can be estimated for isotherm (c) from the ratio of area (1) to area (2). Often isotherms representing incomplete exchange are observed. The separation factor cannot be considered as a measure of the selectivity, because it varies as a function of the composition of both the solid and liquid phase at the equilibrium. A comprehensive estimation of selectivity can result from the knowledge of either the thermodynamic equilibrium constant, $K_{eq}$ or the standard Gibbs free energy of exchange, $\Delta G$.

### 2.6.5 Thermodynamics of Ion Exchange Processes

The evaluation of the ion exchange properties of zeolites is based on equilibrium data for a particular exchange reaction. On the basis of these data, the main thermodynamic parameters, such as the equilibrium constant ($K_{eq}$) and Gibbs free energy $\Delta G^{\circ}$ can be computed from first principles. The use of the correct set of equations to describe the exchange process is

particularly important when one needs to predict the ion exchange behavior of the zeolites for different compositions of the aqueous phase based on experimental data. Many works have dealt with evaluating the equilibrium constant of ion exchange in zeolites.

The value of $K_{eq}$ can be calculated from the equilibrium cation exchange data using an integration procedure derived by (Dyer, Townsend & Enamy 1981)) provided the activity coefficients of the cations in the liquid phase can be estimated accurately. A commonly used activity coefficient expression for dilute electrolytes is given by Glueckauf (1949), although other expressions exist for more concentrated solutions. A comprehensive description of the procedure for obtaining the thermodynamic quantities connected with cation exchange reactions involving zeolites may be found in several papers (Dyer, Townsend & Enamy 1981); (Pabalan 1994); (Caputo, Pepe 2007). Studying a certain number of cation exchange equilibria in a given zeolite type allows us to learn the specific selectivity sequences, which are very useful in predicting the zeolite behaviour in any practical application. In order to obtain the parameter capable of describing the selectivity of a given form of the zeolite, the thermodynamic equilibrium constant ($K_{eq}$) is evaluated using the following procedure :

$$K_{eq} = [\ (\bar{a}_A)^{zB}(a_B)^{zA}] / [(a_A)^{zB}(\bar{a}_B)^{zA}\ ] \qquad (2.\ 4)$$

Where a denotes the activity of the aqueous species and ā represents activities of the species adsorbed in the zeolite. The adsorption standard free energy change (∆G°) is given by the following equations:

$$\Delta G^\circ = -RT \ln K_{eq} \qquad (2.5)$$

where R is the universal gas constant, 8.314 $Jmol^{-1}K^{-1}$ and T is the absolute temperature, K. It should be noted that ∆G° is calculated for a particular pair of ions, both in-going and out-going. The temperature dependence of equilibria in general is related to the standard enthalpy change which accompanies the reaction. The free energy change indicates the degree of spontaneity of the adsorption process, a more negative value reflects a more energetically favourable adsorption. High temperature discourages the reaction which occurs with evolution of heat. The temperature dependence of ion-exchange equilibria is given by the thermodynamic relation:

$$\frac{d\ln Keq}{dT} = \frac{-\Delta H^\circ}{RT^2} \qquad (2.6)$$

According to Eq. 2.7**,** the effect of temperature on the equilibrium constant $K_{eq}$ is determined by the sign of ∆*H* °. Thus when ∆*H* ° is positive, i.e., when the adsorption is endothermic, an increase in T results in an increase in *a* $K_{eq}$. Conversely, when ∆*H* ° is negative, i.e., when the adsorption is exothermic,

an increase in T causes a decrease in $K_{eq}$. This implies a shift of the adsorption equilibrium to the left. The integrated form of Eq. 2.7 becomes

$$\ln k_{eq} = \frac{-\Delta H^\circ}{RT} + Y \qquad (2.7)$$

Eq 2.8 can be rearranged to obtain

$$RT \ln k_{eq} = -\Delta H^\circ + TRY \qquad (2.8)$$

where $\Delta S^\circ$ is RY . The change with temperature of the free energy change and the equilibrium constant can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (2.9)$$

$$\ln k_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (2.10)$$

Eq 2.11 shows clearly that there are two contributions to the the adsorption process, namely enthalpy and entropy, which characterize whether the reaction is spontaneous. Ion exchange is not a chemical reaction and occurs, as a rule, with little evolution or uptake of heat. Standard enthalpy changes are usually smaller than 8.37 KJ/mol, though values of up to 41.86 kJ/mol have been observed in exceptional cases. Accordingly, the temperature dependence of ion exchange equilibria is usually minor. However, ion exchange may be followed by other processes, for example precipitation, with considerable enthalpy changes (Helfferich, 1995).

## 2.7 Adsorption Isotherms

Fitting of adsorption isotherm equations to experimental data is often an important aspect of data analysis. The Langmuir and Freundlich models are widely used since they are simple and have an ability to describe experimental results in wide ranges of concentrations. Both isotherm models can be easily transformed into linear forms to obtain adjustable parameters by graphical means or by linear regression analysis. The Langmuir isotherm is used for homogeneous surfaces, and to handle nonhomogeneous surfaces new isotherms were derived using the Langmuir isotherm as a basis. The models, having more than two adjustable parameters, are not easily fitted to the experimental data by linear regression or graphical means. In this case, it is necessary to apply nonlinear least-squares (NLLS) analysis.

In most of the literature, nickel ion adsorption with clinoptilolite was generally examined with the Langmuir, Dubinin-Radushkevitch (D-R) and Freundlich isotherms (Rajic et al. 2010). Argun (2008) studied nickel ion removal using Turkish clinoptilolite and suggested that the capacity of clinoptilolite to exchange certain metals can be calculated using the Langmuir, D-R and Freundlich isotherms. Several researchers have reported the applicability of the Langmuir and Freundlich isotherms to the removal of heavy metals from wastewater by natural zeolites and applied linearised forms to experimental data with results showing conformity over a wide concentration range (Erdem,

Karapinar & Donat 2004); (Wang, Hu & Sun 2007); (Álvarez-Ayuso, García-Sánchez & Querol 2003).

The Langmuir isotherm is based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites all have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules. By applying these assumptions and the kinetic principles (i.e. the rate of adsorption and desorption from the surface are equal), the Langmuir isotherm can be expressed as:

$$\frac{Ce}{Qe} = \frac{1}{Qmb} + \frac{Ce}{Qm} \qquad (2.\ 11)$$

where $Q_e$ is the adsorbate loading (mg/g) at equilibrium, $C_e$ the equilibrium concentration in the fluid (mg/L), $Q_m$ the adsorption capacity (mg/g) and b the sorption equilibrium constant (L/mg). $Q_m$ represents the practical limiting adsorption capacity when the surface is fully covered with heavy metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation. A plot of $C_e/Q_e$ versus $C_e$ should indicate a straight line of slope $1/Q_m$ and an intercept of $1/Q_mb$.

The Freundlich isotherm is originally of an empirical nature, but has since been used as a model for the interpretation of adsorption onto heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation. According to this model, the adsorption capacity can be expressed by a power law function of the solute concentration as follows

$$Q_e = K_f \boldsymbol{Ce^{1/n}} \qquad (2.\ 12)$$

Which can be linearised to:

$$\log Q_e = \log K_f + \frac{\mathbf{1}}{\boldsymbol{n}} \log C_e \qquad (2.\ 13)$$

where,

$Q_e$= the amount adsorbed (mg/g)

$C_e$ = the equilibrium concentration of the adsorbate (mg/L)

$K_f$ = the Freundlich constant related to the adsorption capacity

1/n = the Freundlich constant related to the adsorption intensity (n is the dimensionless heterogeneity coeffient)

The Freundlich equation is one of the most widely used mathematical models, which usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface

heterogeneity and the exponential distribution of active sites and their energies (Erdem, 2004).

## 2.8 Disposal and Regeneration of Metal Saturated Zeolites

Disposal of zeolites loaded with heavy metal cations is a significant issue in zeolite science. Utilization of zeolites in removal of heavy metals is nothing but transforming the phase of contamination from aqueous phase to solid phase. Therefore, management of heavy metal loaded zeolites must also be taken into account for the further fate of heavy metals at the site they are disposed of. In addition to disposal, metal loaded zeolites can also be made use of in various technological areas. Many researchers studied regeneration of metal saturated zeolites and concluded that regeneration of metal saturated zeolites works well and effective capacity does not decrease significantly even after several exhaustion-regeneration cycles (Zamzow et al., 1990, Kim and Keane, 2002, Petruzzelli et al., 1999). Apart from reuse in removal of heavy metals via regeneration, it has been known that heavy metals possess antibacterial properties and the exchange with these metals imparts antibacterial activity to the zeolites (Rivera et al., 2000, Mumpton, 1999, Top and Ülkü, 2004). Top and Ülkü (2004), studied the antibacterial activities of $Ag^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ exchanged Gördes clinoptilolite with different exchange levels and the authors reported that a considerable suppression in

the growth of P.aeruginosa and E.coli was achieved. Heavy metal saturated zeolites can also be converted to glass which has an extremely low leach-rate (Ouki et al., 1994). Additionally, sorption and desorption characteristics of micronutrients ($Fe^{2+}$, $Zn^{2+}$, $Mn^{2+}$ and $Cu^{2+}$) by zeolites make addition of them attractive in soils either directly or as a component of other fertilizers (Sheta et al., 2003).

# 3 EXPERIMENTAL APPARATUS AND METHODS

## 3.1 Characterisation

Various characterization techniques have been employed to obtain information about the structural and chemical characteristics of the zeolite material. Characterisation is critical to elucidate the critical properties of zeolites which include chemical composition, surface area , pore volume and morphology amongst others. These properties are in turn responsible for the benefits realized in environmental remediation especially wastewater treatment, hence characterisation becomes vital. For example, powder X-Ray diffraction (XRD) was used to assess the crystallinity and verify the identity of zeolites. Electron microscopy was used to determine particle morphology and crystallite size. $N_2$ adsorption isotherms were used to measure surface area and Fourier transform infrared spectroscopy (FT-IR) to identify functionalities present in the natural and pretreated clinoptilolite.

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### 3.1.1 X-Ray Diffraction and X-Ray Fluorescence

Mineralogical analysis of the natural and pretreated zeolite samples was carried out using an X-Ray Diffraction on a Siemens D500 Diffractometer. Chemical analysis to determine the chemical composition of the samples was

obtained by X-Ray Fluorescence (XRF) using a PanAnalytical PW2404 model.

### 3.1.2 BET Surface Area Analysis and Porosity Analysis

Surface area measurements for the natural zeolite and pretreated zeolite were determined by nitrogen adsorption and multipoint analysis in triplicate fitted to the BET equation (Brunauer, 1943) using a TRISTAR 3000 analyzer. Fourier Transformed Infrared (FTIR) Spectroscopy.

### 3.1.3 Fourier Transformed Infrared (FTIR) Spectroscopy

Changes in zeolite functionalities after treatment with different metal chlorides were determined by FTIR as reported by Mamba et al. (2009). In this study a Fourier transform infrared spectroscopy Bruker Tenser model 27 (FT-IR) was used for qualitative analysis.

### 3.1.4 Morphology of Natural and Pretreated Clinoptilolite

Morphological structures of natural and pretreated clinoptilolite were obtained on a FEI Nova FIB/SEM using its unique low vacuum capabilities. Grains of 0.60 -0.80mm size range were mounted on to 10 mm aluminium stubs with carbon tape, followed by coating with gold palladium for 9 minutes to make the zeolite surface conductive and reduce charging. The coated samples were finally examined under the microscope for morphological imaging.

## 3.2 Zeolite

The raw zeolite sample used in this study was obtained from the Pratley Perlite Manufacturing and Engineering (Pty) Ltd in KwaZulu Natal Province South Africa. All chemicals and reagents used for experiments and analyses were analytical grade reagents.

### 3.2.1 Zeolite Preparation

Small grains of zeolite were obtained by first using a hammer to break the as received samples into small pieces. These small pieces were then ground using a pestle and mortar and sieved to yield different fractions of diameter

0.60 to 0.85mm. Sieving was repeated several times to minimize the retention of smaller grains in a sample with a larger size range. Prior to the batch adsorption experiments, the crushed zeolite was washed with distilled water three times to remove the surface dust, and then dried in an oven at 70$^{o}$C for 24h until a constant weight was attained.

### 3.2.2 Preparation of Homoionic Forms

Near homoionic forms of Na, K and Ca- clinoptilolite were generated by treating 30g batches of the purified clinoptilolite with 300mL of 2M chloride salts (NaCl, KCl and $CaCl_2$ respectively). The mixtures were then placed in a labex shaking incubator at 25˚C for 24hrs at a speed of 200rpm. A labex Shaking incubator shown in Figure 3.2 is used in the batch experiments to get good mixing between the solution and the zeolite granules, which tend to lie at the bottom of the flask. The shaking incubator is set at a constant speed and temperature so that all the results are comparable.




**Figure 3. 1:** Labex Shaking Incubator

The solutions of the chloride salts were replaced with fresh ones for a further 24hrs. The clinoptilolite grains thus treated were washed several times with distilled water to eliminate excess metal-chlorides, and dried in an oven at 70˚C for 24hrs. In preliminary experiments 24hrs shaking of suspensions was found to be sufficient to attain equilibrium and for stabilization of pH (Cerjan-Stefanovic et al., 1996). Treated zeolite fractions were used as adsorbents for nickel ion removal. Metal chloride treatment was conducted based on the findings that alkali and alkaline earth metals are cheap, commonly available and are the most effective exchangeable ions for heavy metal removal .

### 3.2.3 Equilibrium Studies

Equilibrium studies were done as follows. A stock solution (1000mg/L) of $Ni^{2+}$ was prepared by dissolving 2.04g of $NiCl_2 \cdot 6H_2O$ in 1L of distilled water. The composition of the synthetic aqueous solution used in this study was based on those used previously and the concentrations were within the range of typical industrial wastewaters of 0.1mg/L to 100mg/L (Argun, 2008).

Synthetic samples were prepared to give Ni (II) concentrations of 20, 40, 60, 80 and 100 mg/L by adding an appropriate amount of $NiCl_2 \cdot 6H_2O$ stock solution to distilled water. The masses of clinoptilolite used in the experiments ranged from 0.2 to 1.5g and the solution volume ranged from 10 to 100 mL. Before adding the adsorbents, the pH of the solution was adjusted to 7 (where the $H^+$ competition with the $Ni^{2+}$ is at minimal) following the method of Gaus and Lutze (1976) using either 0.1 M NaOH or 0.1 M $HNO_3$ solution. The zeolite-mass to solution volume ratios and the aqueous mixture compositions used in the experiments were designed to yield a relatively evenly spaced distribution of points along the ion exchange isotherm and significant differences in the initial and final concentrations of the cation in solution. Furthermore a background electrolyte has not been added during the ion exchange experiments.

The clinoptilolite zeolite samples were put in 250 mL Erlenmeyer flasks that were agitated in a labex shaker at 25, 35, 50, 60 or 75°C for 24 hrs (Kapanji, 2008). After equilibrium was established, the clinoptilolite was separated from

the solution by centrifugation and the pH of the supernatant was adjusted to 7.

### 3.2.4 Sample Analysis

The equilibrium concentration of the exchangeable ions ($Na^+$, $K^+$, $Ca^{2+}$) and $Ni^{2+}$ in the samples was determined by atomic absorption spectrometry (AAS, Varian 55B). A SpectrAA 55B Atomic Absorption Spectrometer as shown in Figure 3.1 was used to analyse metal ion solution. Instrument parameters such as lamp current, fuel, support gas and wavelength used for analysis of the metal ion of interest were as recommended in the SpectrAA 55B working manual. The AAS uses an air – acetylene flame and single element hollow cathode lamps.




**Figure 3. 2** SpectrAA 50/55 Atomic Absorption Spectroscopy (AAS)

The AAS is generally used to analyse relatively low metal concentrations and hence dilution of some of the samples was necessary. The AAS was calibrated using standard solutions of the respective metals in the range 0.1 – 20mg/L. Distilled water was used for all dilution purposes. The standards

were analysed and were found to be in agreement with the calibration curves in the atomic absorption spectrometry-working manual. The metal concentration in the liquid phase was determined at the beginning ($C_o$) and at the end ($C_e$) of the adsorption. The following equation was used to compute the percentage uptake of the metal by the clinoptilolite:

$$\text{Sorption \%} = \frac{(Co - Ce)100}{Co} \qquad (3.1)$$

# 4 Results and Discussion

## 4.1 Chemical Composition of Natural and Pretreated Clinoptilolite.

The chemical analysis of the natural and homoionic clinoptilolite samples is given in table A-1 in appendix A. The samples contained sodium, potassium, calcium and magnesium as exchangeable cations. Manganese and titanium occur in trace amounts (Argun 2008).

The elemental analysis of the natural and pretreated clinoptilolite revealed that it is mainly composed of Si, Al, Fe with very low amounts of Mn and Ti in the framework. The extra-framework ions Na, K, Mg and Ca show considerable variation depending on the pretreatment agent used and this change was mainly at the expense of sodium and calcium content. The silica ranges from 76.13% to 77.37%, with an average value around 69% per unit cell; aluminium tetrahedra ranges from 12.93% to 13.30% per unit cell.

In the natural sample about 50% of the exchangeable ions are potassium. Complete exchange of cations was impossible to achieve especially for sodium and calcium treated clinoptilolite as it is assumed that potassium present in the clinoptilolite does not exchange significantly with other cations. This behavior is attributed to the location occupied by potassium. Jama and Yucel (1989) proposed that the potassium is located in inaccessible

exchange sites which are situated in an eight membered ring and has the highest coordination among all the cation sites in the unit cell. From the chemical analysis results given in Table A-1 in Appendix A, about 2.65% of potassium ions occupied these positions.

Based on the chemical composition of the natural clinoptilolite used in this study, the molecular formula for the natural zeolite was:

$(Na_{1.25}K_{1.6})(Ca_{0.49}Mg_{0.43})(Al_{5.14}Fe_{0.31})(Si_{25.67}Ti_{0.04})O_{62}$

The pretreatment process led to the production of different forms of zeolite depending on the treatment agent used, and the molecular formulae of the pretreated samples were modified as follows:

Na- Clinoptilolite

$(Na_{2.45}K_{1.24})(Ca_{0.27}Mg_{0.35})(Al_{5.13}Fe_{0.31})(Si_{25.5}Ti_{0.04})O_{62}$

K- Clinoptilolite

$(Na_{0.15}K_{3.36})(Ca_{0.31}Mg_{0.34})(Al_{5.21}Fe_{0.35})(Si_{25.7}Ti_{0.04})O_{62}$

Ca-clinoptilolite

$(Na_{0.88}K_{1.53})(Ca_{1.14}Mg_{0.38})(Al_{4.84}Fe_{0.29})(Si_{24.35}Ti_{0.033})O_{59}$

The cation exchange capacity (CEC milliequivalents (meq) per gram) of the zeolite samples was derived from the analysis given in Table A-1 in Appendix A. The calculation of CEC was based on the assumption that (1) $Al^{3+}$ and

$Fe^{3+}$ substitute for $Si^{4+}$ in the tetrahedral sites and result in a negatively charged structure, (2) this negative charge is balanced by the alkali and alkaline earth ions in the intracrystalline cation exchange sites, (3) that any other exchangeable ions present in a homoionic form of clinoptilolite are assumed to occupy inaccessible sites for instance, the $K^{+}$, $Ca^{2+}$ and $Mg^{2+}$ present in the Na-clinoptilolite are in inaccessible exchange sites and do not participate in the ion exchange process. An additional assumption is that negligible mineral impurities are present in the sample (Pabalan 1994).

Experimental cation exchange capacities (CEC) of clinoptilolite were determined and were found to range from 1.38meq/g to 2.29meq/g for all forms of clinoptilolite (for natural and pretreated clinoptilolite).

**Table 4. 1**: The calculated CECs based on simplified formulae

| Zeolite form | Formulae | CEC |
|---|---|---|
| Natural-form | $(NaK_2)(Al_5Si_{26}O_{62}) \cdot 12H_2O$ | [1.38 meq/g] |
| Na-form | $(Na_3K)(Al_5Si_{26}O_{62}) \cdot 12H_2O$ | [1.83 meq/g] |
| K-form | $(K_3)(Al_5Si_{26}O_{62}) \cdot 9H_2O$ | [1.40 meq/g] |
| Ca- form | $(NaCaK_2)(Al_5Si_{24}O_{59}) \cdot 16H_2O$ | [2.29 meq/g] |

It is often convenient to express cation-exchange capacity in terms of weight percent (the number of grams of nickel ion ($Ni^{2+}$) that could be exchanged onto 1 gram of natural or pretreated clinoptilolite.

The following table lists the theoretical number of grams of nickel atoms that could be taken up by one gram of clinoptilolite (untreated or pretreated) having the indicated CEC. wt. % (g/100 g).

**Table 4. 2:** Cation-exchange capacity expressed in terms of weight percent.

| Zeolite form | CEC | weight removed |
|---|---|---|
| Natural-form | [1.38 meq/g] | 4.05 wt. % (g/100 g) |
| Na-form | [1.83 meq/g] | 5.37 wt. % (g/100 g) |
| K-form | [1.40 meq/g] | 4.11 wt. % (g/100 g) |
| Ca- form | [2.29 meq/g] | 6.72 wt. % (g/100 g) |

Hence, a clinoptilolite material having a measured CEC of 1.38, 1.83, 1.40 and 2.29 would theoretically be able to take up 4.05, 5.37, 4.11 and 6.72 of $Ni^{2+}$ from solution per gram of material respectively. Inspection of Table 4.1 and 4.2 indicates that Ca- clinoptilolite is the best form to use in removing nickel.

From the XRF results the Si/Al ratio was calculated to be 5.14 and a Si/Al ratio ranging from 4- 5.5 is typical for clinoptilolite in general (Watling, Rees 1994)**.** Low silica members are enriched with calcium, whereas high-silica clinoptilolites are enriched with potassium, sodium, and magnesium (Erdem, Karapinar & Donat 2004) .

## 4.2 BET Analysis of Natural and Pretreated Clinoptilolite.

Surface area measurements were determined by nitrogen adsorption fitted to the BET equation (Brunauer, 1943). Divalent ion exchange opens the aperture to full diameter whereas exchange with a larger univalent ion diminishes the aperture size, as shown in Table 4.3. Sodium ion exchange into the zeolite reduces the effective adsorption pore diameter. The selectivity of a zeolite depends on the ionic size, charge and hydration radii of the exchanging ions in the solution.

The $Ca^{2+}$ with the smallest ionic radii has the highest hydration radii in comparison to the two ions with larger ionic radii ($K^{+}$ and $Na^{+}$). These ions irregardless of charge are able to loose their hydration water to fit through the zeolite pores. The smallest ion (Calcium) binds more strongly to the zeolite negative sites and they are not able to detach from them easily, hence Ni ionic radii 0.60 Å tend to displace Na and K easily.

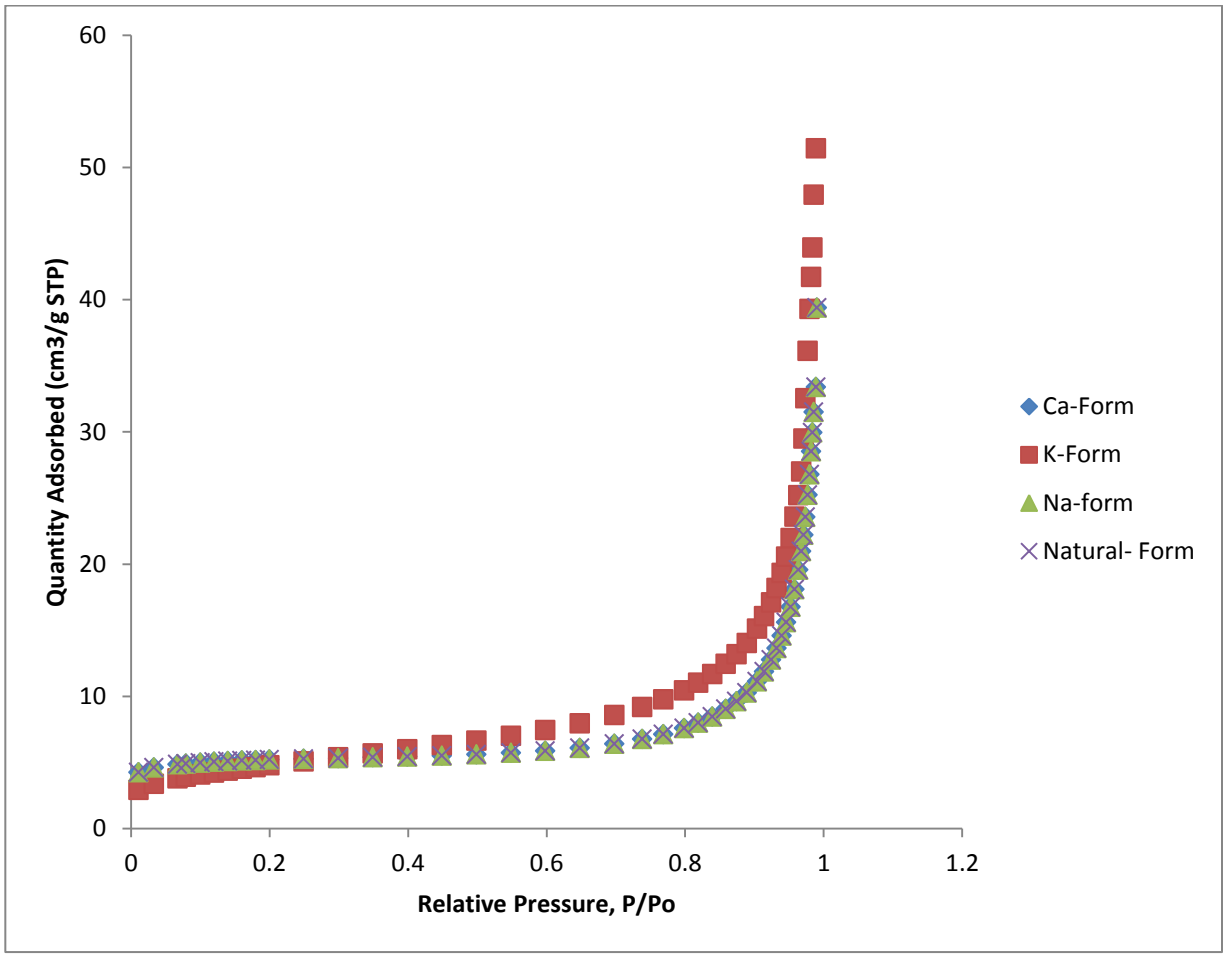



Figure 4.1. Adsorption isotherms of nitrogen on different forms of clinoptilolite.

**Table 4. 3**: Strucutral characteristics of different homoionic forms of Clinoptilolite.

| Adsorbent | Surface Area $S_{BET}$ ($m^2/g$) | Pore Volume $V_t$ ($cm^3/g$) | ionic radii (Å) radii(Å) | Hydration |
|---|---|---|---|---|
| Ca-form | 14.31 | 3.28 | $Ca^{2+}$ (1.14) | $Ca^{2+}$ (2.53) |
| K-form | 16.49 | 3.79 | $K^+$ (1.52) | $K^+$ (2.01) |
| Na-form | 13.54 | 3.11 | $Na^+$ (1.16) | $Na^+$ (1.83) |

Cotton,1999; Michael, 2002

## 4.3 Characterization of Natural and Pretreated Clinoptilolite using FT-Infrared Spectroscopy.

Infrared spectroscopy has been extensively used for characterizing functionalities present in zeolites (Mamba, 2009). In this study Infrared spectra were measured on a Bruker Tenser 27 spectrometer, and spectra were collected in the region of 500- 4000 $cm^{-1}$. In the FTIR spectra of natural and pretreated clinoptilolite three groups of bands are present and common according to Mozgawa (2000).

The bands connected with the internal Si–O(Si) and Si–O(Al) vibrations in tetrahedra or alumino and silico-oxygen bridges (the range of 400 $cm^{-}1$-1200). The bands due to the presence of zeolite water (the range of 1600–3700 $cm^{-1}$). The bands due to pseudo-lattice vibrations of structural units (the range of 500–700 $cm^{-1}$).

The introduction of non-tetrahedral cations into alumino-silicate frameworks can change their IR spectra in the range of pseudo-lattice vibrations located at about 500– 700$cm^{-1}$ and lattice vibrations below 400 $cm^{-1}$ according to Mozgawa (2000). A comparative analysis of the FTIR spectra does not show essential changes after pretreatment with metal (in comparison with the natural clinoptilolite spectrum). The unchanged position of the main band at 1016.42 $cm^{-1}$ (in individual spectra), due to stretching Si–O(Si) and Si–O(Al) vibrations, indicates that framework dealumination does not occur. The loss of $Al^{3+}$ cations should cause shifting of this band to higher wavenumbers (Handke, Mozgawa 1993).

The essential changes connected with the presence of non-tetrahedral cations can be observed in the region of 520– 800$cm^{-1}$ (see Figs 4.2 – 4.5). This is clearly visible in the expanded spectra in Figure 4.6. The change of cations does not result in the distinct shift of these band positions but causes a change in their intensity. A comparison of the band at 584$cm^{-1}$ shows a particular trend in intensity. The intensity of the band increases in the following order Ca- form > K- form > Na-form. The cationic masses also

follows the same trend. The exact positions of these bands depend on the nature of the cation, that is, on the Coulomb potential q/r (q: electric charge; r: radius of the respective cation) (Handke, Sitarz & Mozgawa 1998).

All the spectra studied yielded indistinguishable vibrational bands in the region studied 520 – 800 $cm^{-1}$ (see Fig 4.6), as vibrations of cations against the framework occur in the far infrared region 50– 200 $cm^{-1}$ according to Mozgawa (2000).

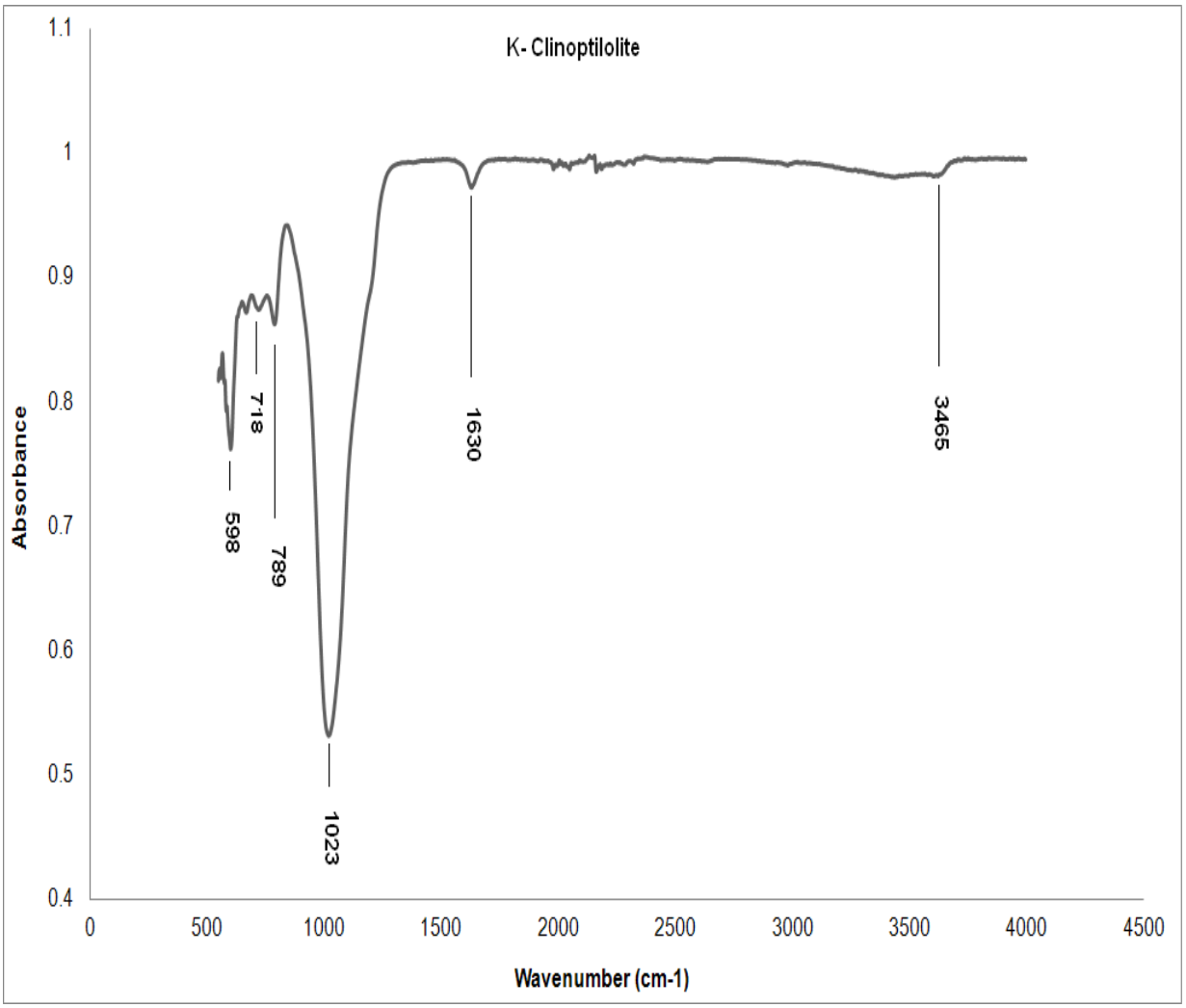



**Figure 4. 2**: The FTIR spectrum for K- Clinoptilolite.

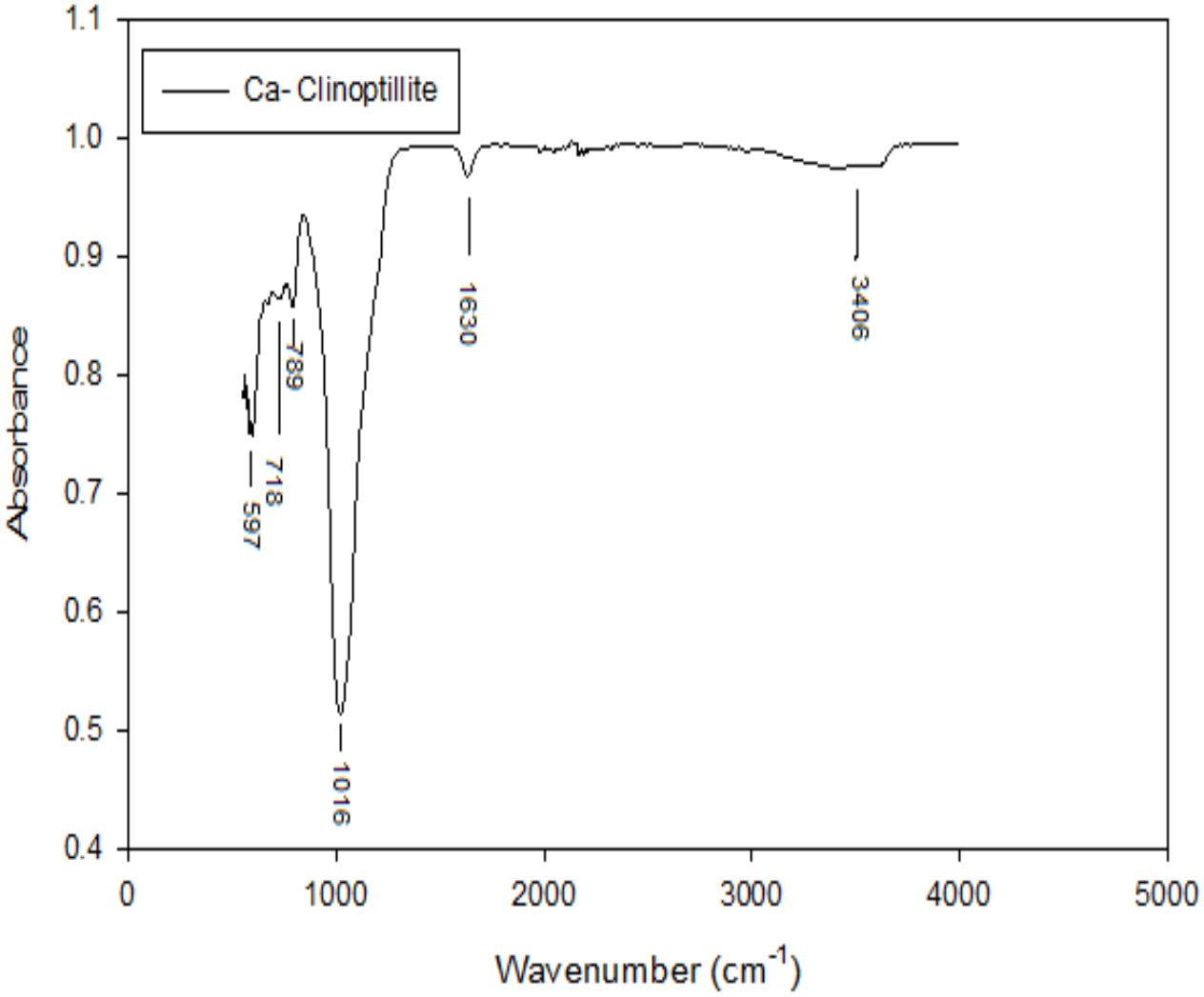



**Figure 4. 3**: The FTIR spectrum for Ca- Clinoptilolite.

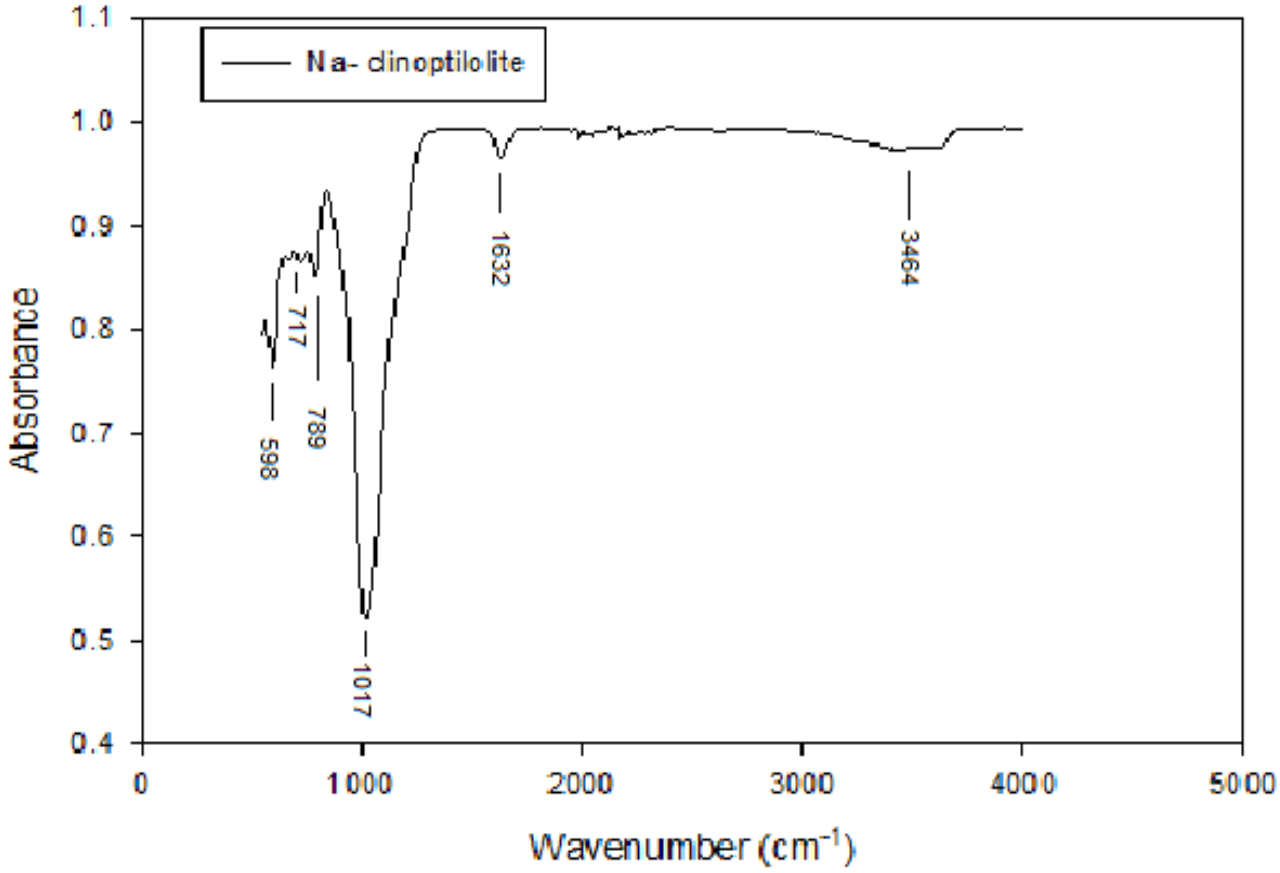



**Figure 4. 4**: The FTIR spectrum for Na- Clinoptilolite.

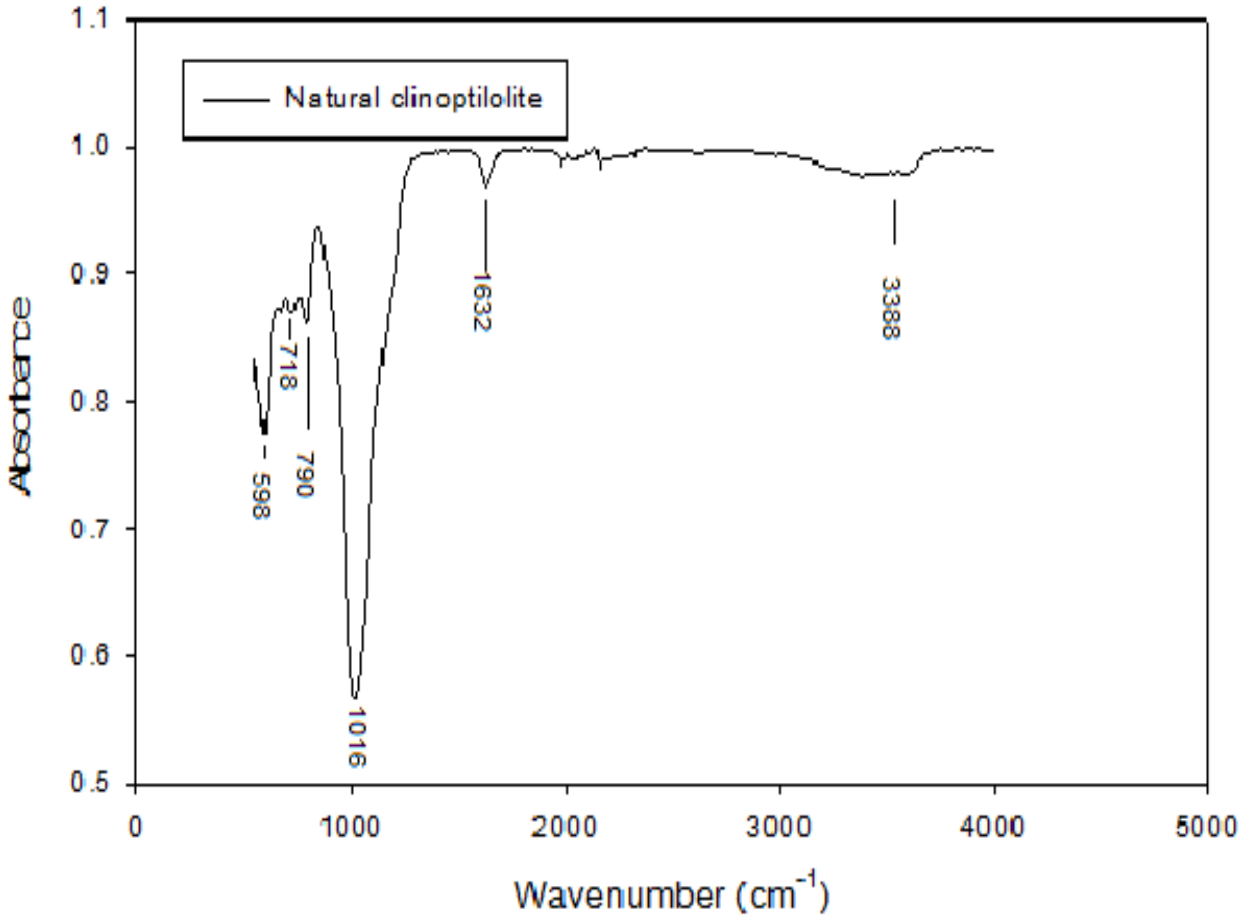



**Figure 4. 5:** The FTIR spectrum for Natural Clinoptilolite.

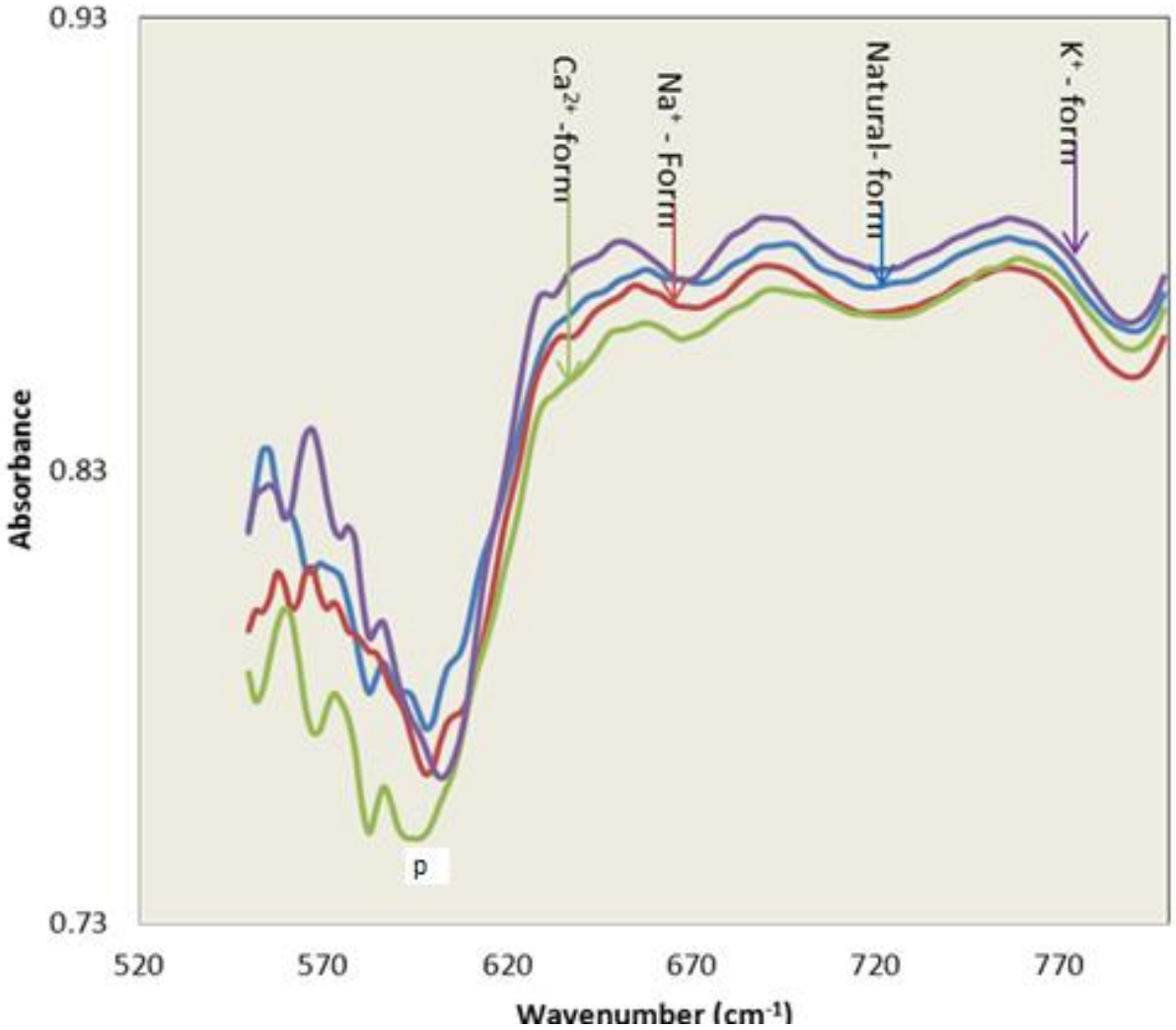



**Figure 4. 6**: The FTIR spectra for natural and pretreated clinoptilolite. A comparison of the band at 584cm$^{-1}$ (point marked P) shows a particular trend in intensity for different forms of clinoptilolite.

The results of FTIR led to a conclusion that the pretreatment of clinoptilolite does not lead to significant structural changes.

### 4.4 X-ray Diffraction Analysis of Natural and Pretreated Clinoptilolite.

A comparative analysis of the XRD spectra of Natural, Na, K and Ca-form of clinoptilolite showed no significant changes in the position of the most intense peaks. The results are presented in Figure 4.7. These results suggest that pretreatment with 2.0 M metal chloride solution has no effect on the crystal structure of the clinoptilolite. An examination of X- ray patterns of natural and pretreated clinoptilolite shows a slight change in peak intensities at $2\Theta$ = 28.34° and 30.1°.

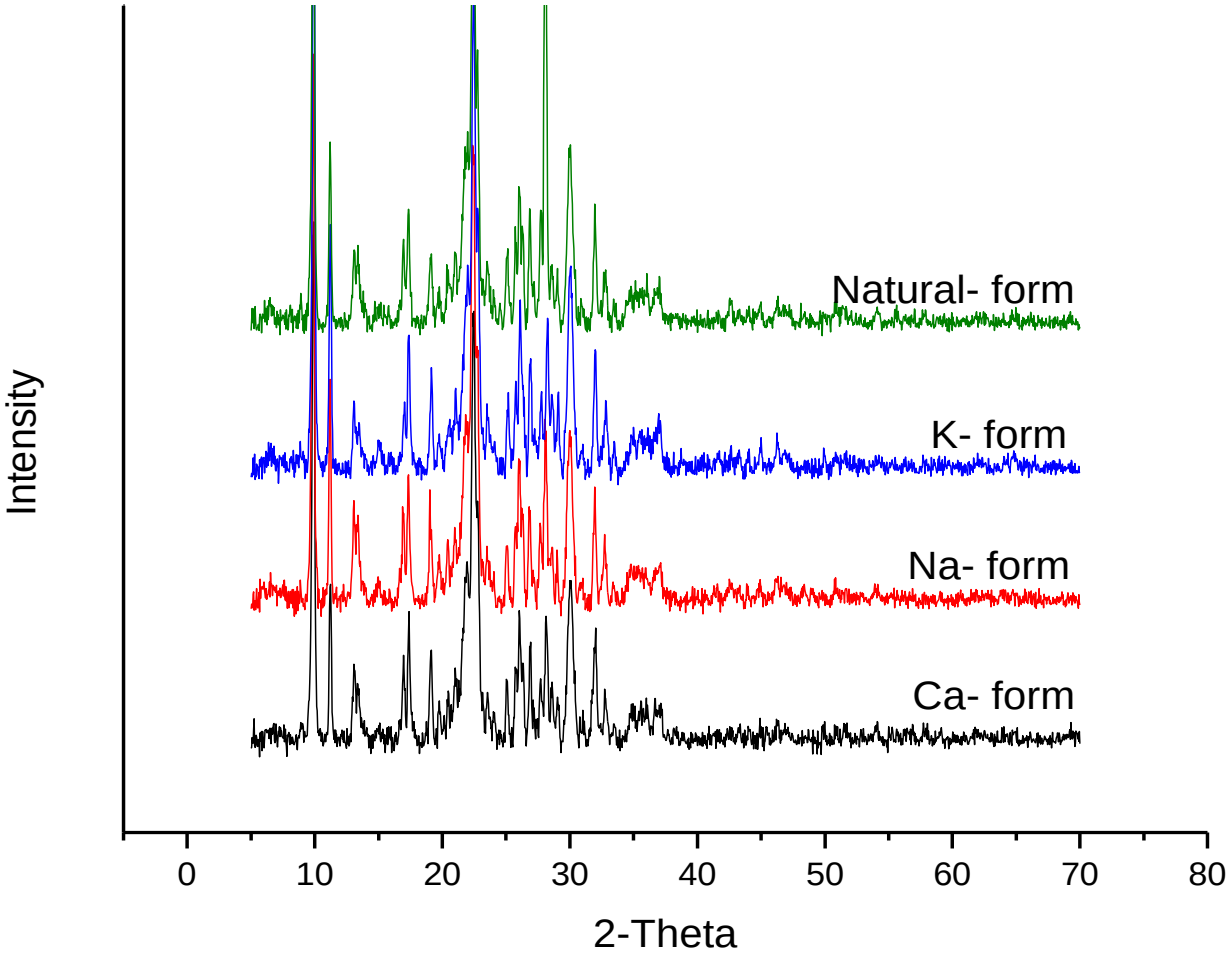



**Figure 4. 7**: X-ray diffraction (XRD) pattern of natural and pretreated forms of clinoptilolite. The patterns were determined with a Siemens D500 x-ray diffractometer.

## 4.5 Physical Characterisation of the Natural and Pretreated Clinoptilolite.

SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials (Kesraoul-Ouki, Cheeseman & Perry 1993). Visual examination of natural and pretreated clinoptilolite specimens by an FEI Nova FIB/SEM reveals important information about the surface structure. Figs 4.9- 4.11 are SEM photomicrographs of Ca, Na, K form of clinoptilolite clearly showing a more open structure at ×10000 magnification and no significant structural changes were observed compared to natural clinoptilolite (Fig 4.8). The natural form is found to be largely covered with foreign materials on the surface which could be impurities or very fine zeolite particles. Higher magnification micrographs for calcium and natural-form of clinoptilolite could not be taken as charging was more pronounced at magnification greater than 10000 times. Comparison of the structure of natural and pretreated clinoptilolite demostrated the benefit of pretreatment as it enhances the crystal structure and cleans up the zeolite surface.

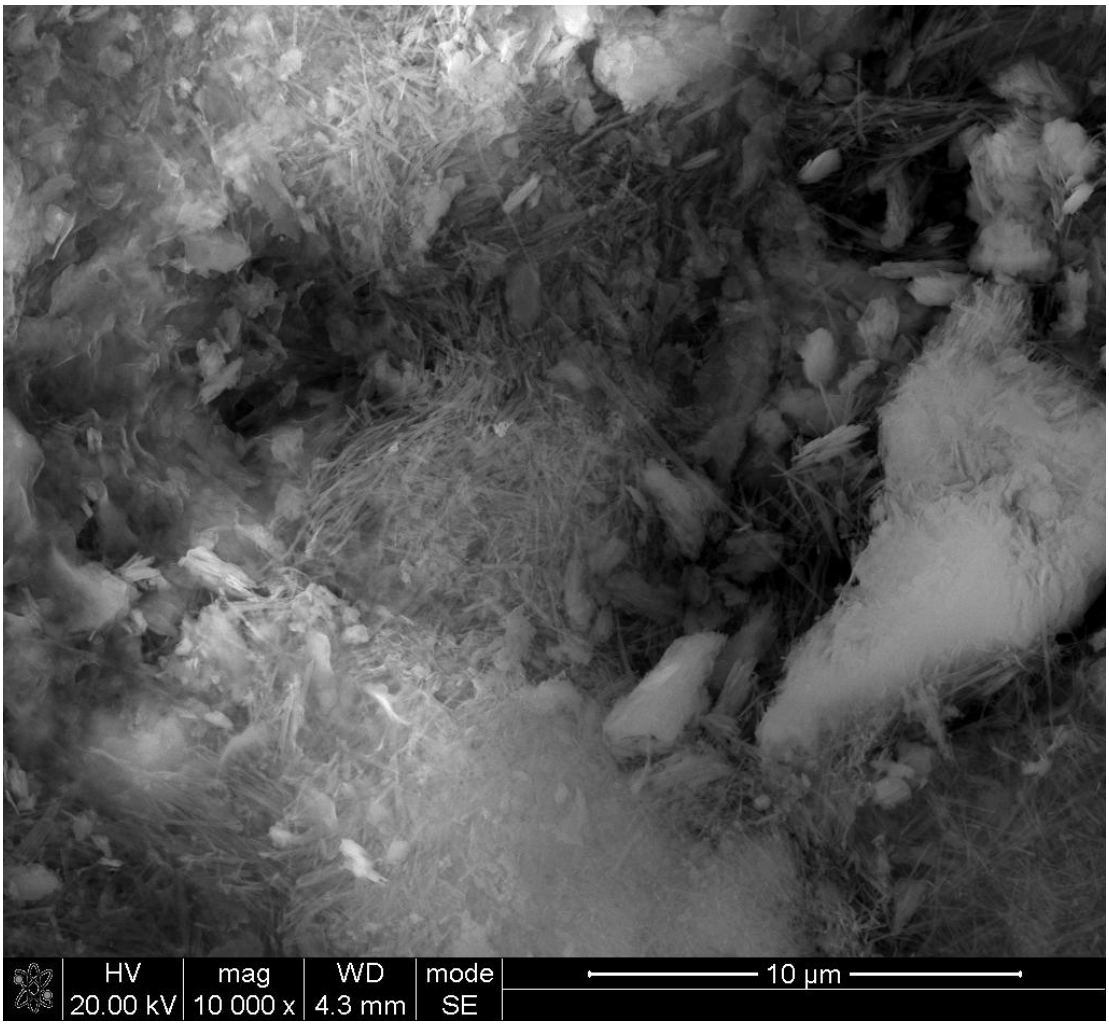



**Figure 4.8**: Micrograph of natural clinoptilolite showing surface and pores covered by extraneous material.

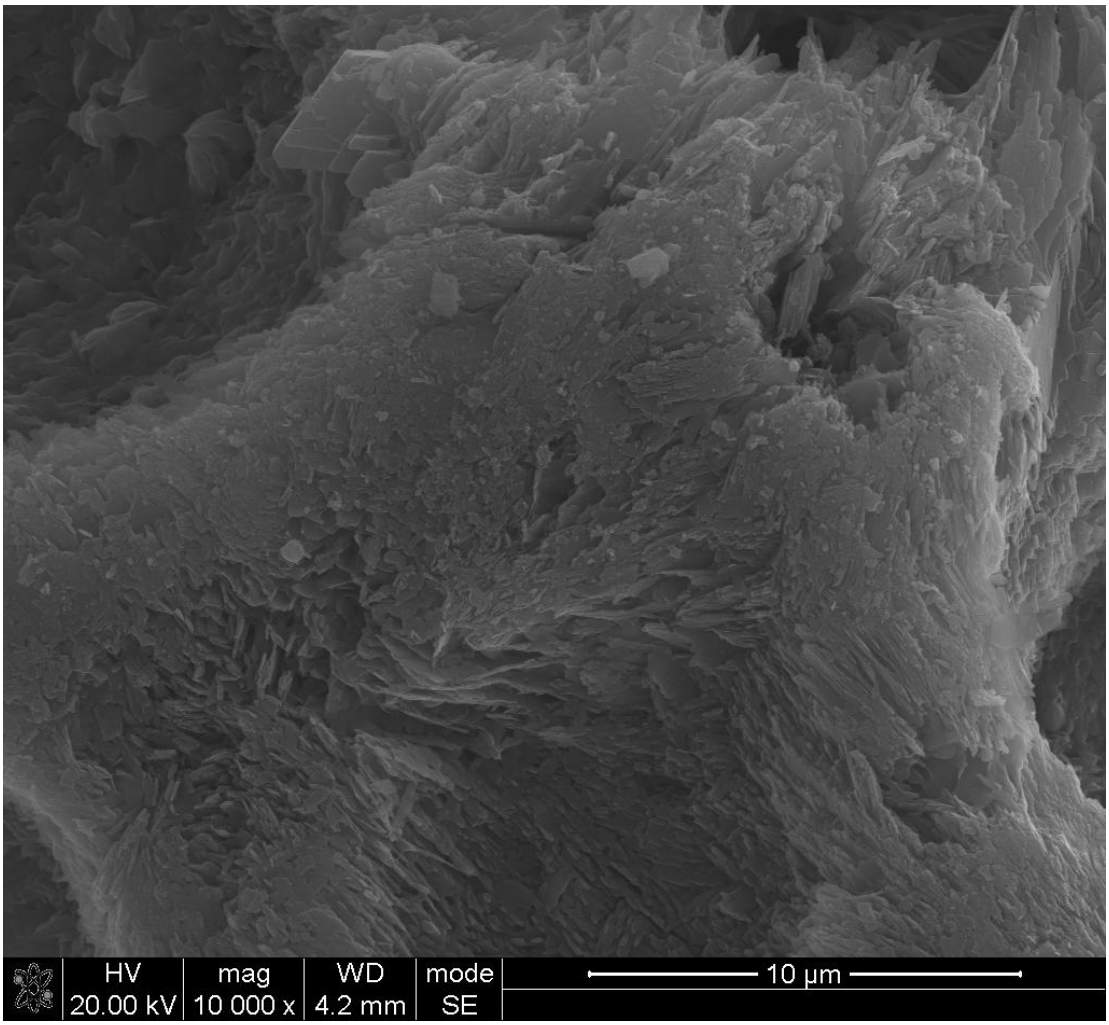



**Figure 4.9**: Electron micrograph of Na- form of clinoptilolite.

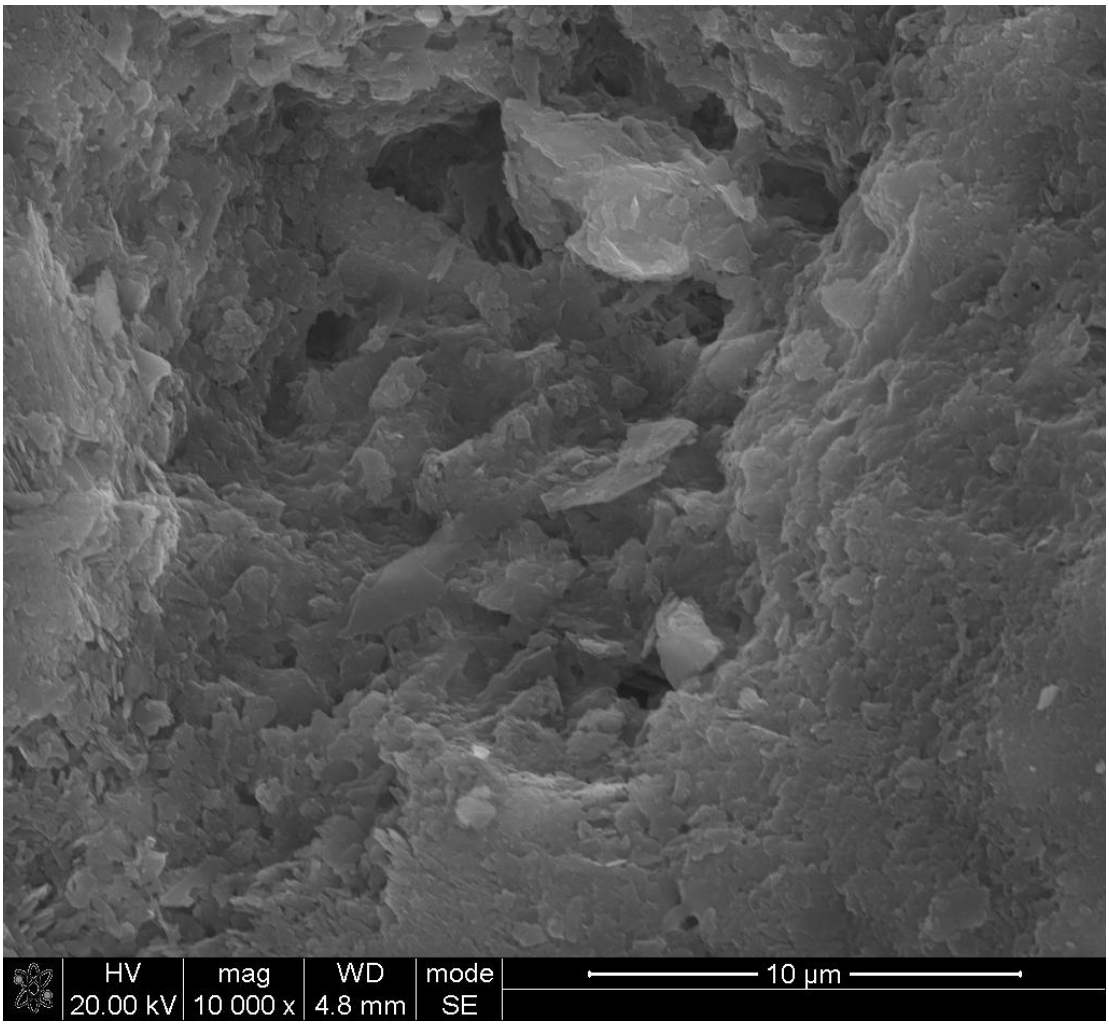



**Figure 4.10**: Electron micrograph of K- form of clinoptilolite.

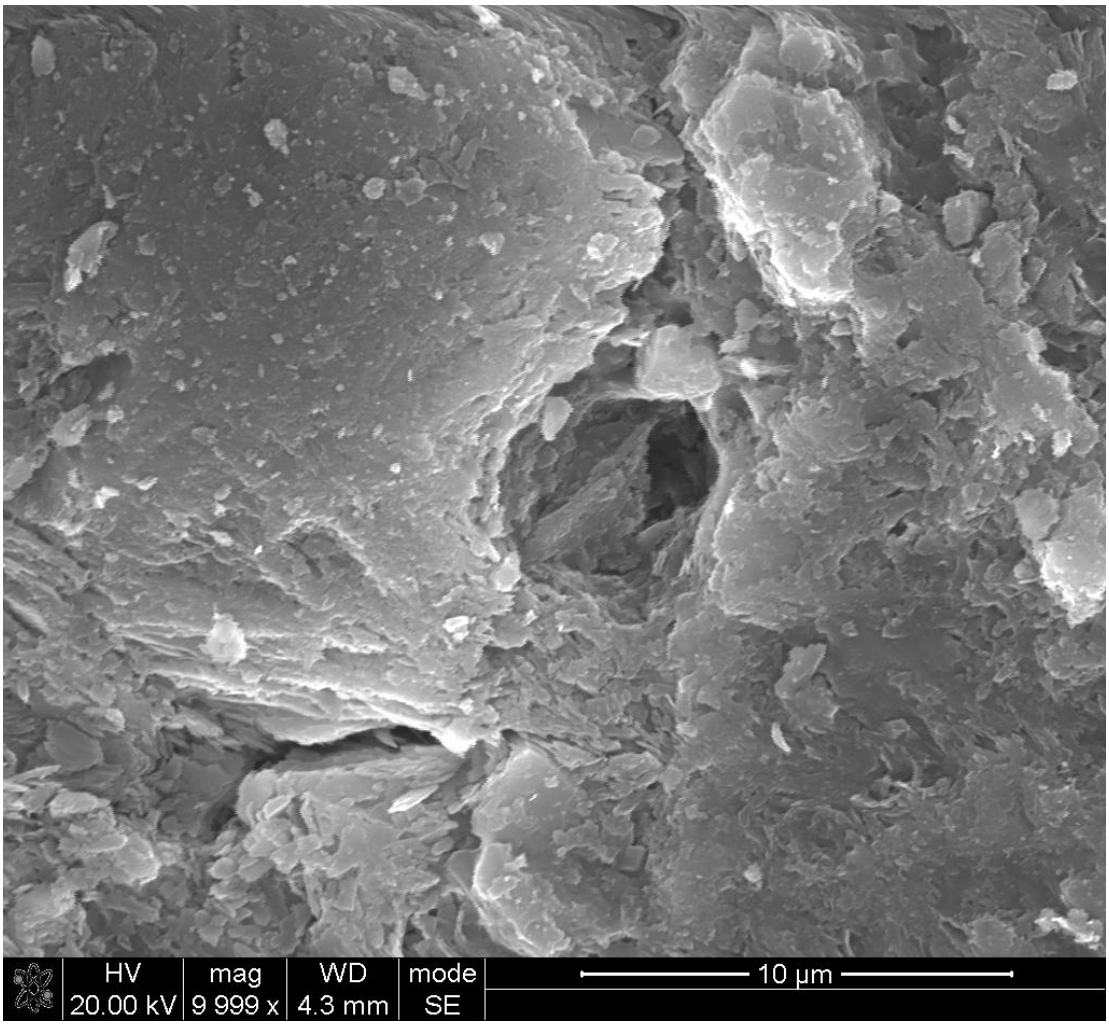



**Figure 4.11**: Electron micrograph of Ca- form of clinoptilolite.

## 4.6 Ion Exchange Isotherms

experimental solutions are given in Tables B1 to The measured initial and final concentration of $Ni^{2+}$ of the B8 in Appendix B. Also tabulated are the zeolite masses and solution volumes used in these experiments. In this study ion exchange results are presented by plotting ion exchange isotherms. Ion exchange isotherms are plots of the equilibrium fraction of an exchanging ion in solution against the equilibrium fraction of the same ion in the zeolite at the same temperature (Dyer, Townsend & Enamy 1981). The following graphs (Figs 4.12 to 4.15) were used to present the experimental ion exchange results. The isotherms were plotted in terms of equivalent cation fraction of the ion in the solution (Xsol) against that in the solid (Xzeo) as described elsewhere (Pabalan 1994).The equivalent cation fraction in solution and on the clinoptilolite was calculated by using equations (2.2) and (2.3) respectively. The initial and final concentration of $Ni^{2+}$ was measured as well as the concentration of displaced ions $Na^{+}$ for Na-form, $K^{+}$ for K-form and $Ca^{2+}$ for Ca- form of clinoptilolite. These measured concentrations, zeolite masses and the volumes of solutions used, were used in the construction of ion exchange isotherms.

The ion exchange isotherms were plotted in terms of the equivalent cationic fraction of the nickel ion in solution (Eqn 2.2) against that in the zeolite (Eqn 2.3). The values of $X_{Ni^{2+}\ in\ zeolite}$ and $X_{Ni^{2+}\ in\ solution}$ were calculated from the

zeolite mass (W, grams), the solution volume (V, liters), cation exchange capacity (CEC, meq/g) and the initial (i) and final (f) molar concentrations of $Ni^{2+}$ as given in Table B1 to B4 in Appendix B. The theoretical exchange capacity of 2.29 meq/g was employed as the experimental cation exchange capacity depended on the nature of exchanging cations. The $Na^{+}$- $Ni^{2+}$, $K^{+}$-$Ni^{2+}$, Natural-$Ni^{2+}$ and $Ca^{2+}$- $Ni^{2+}$ exchange isotherms are shown in Figures 4.12, 4.13, 4.14 and 4.15 respectively.

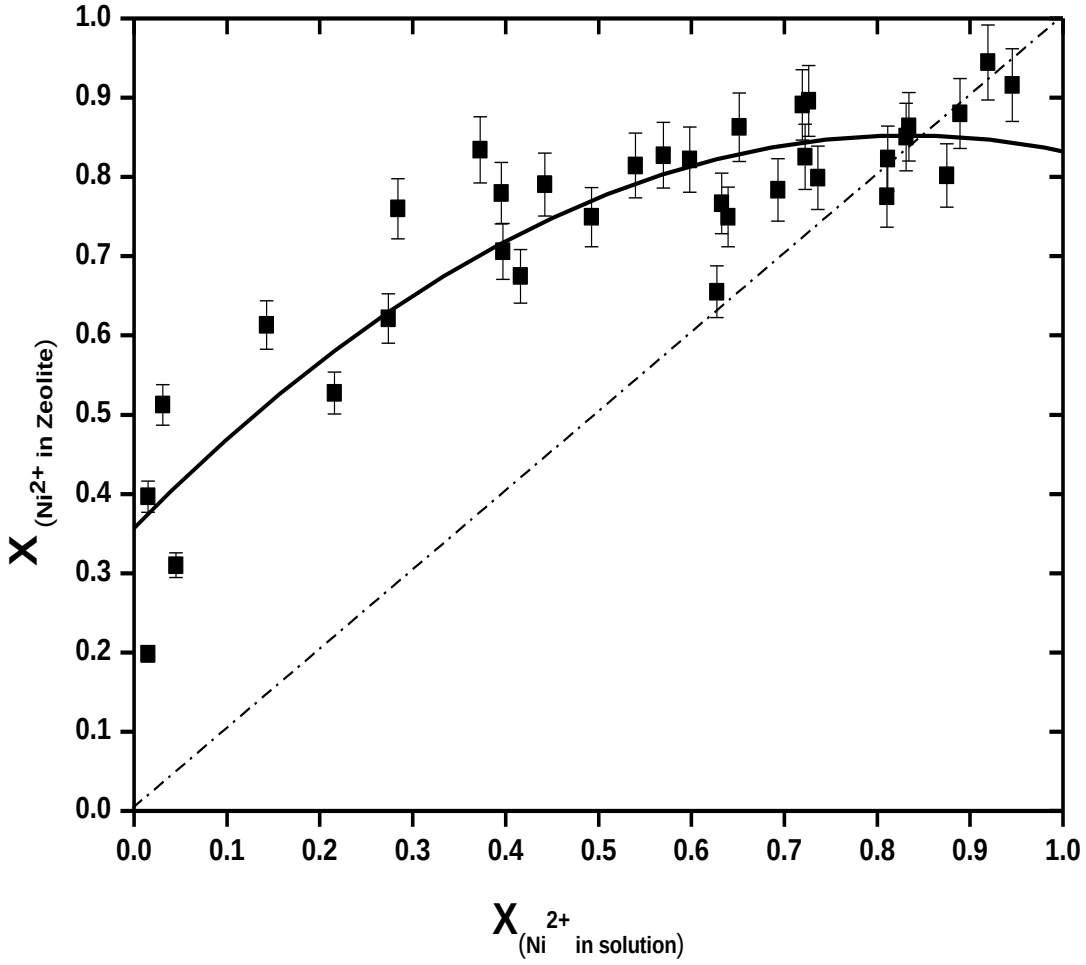



**Figure 4.12**: The $Na^{+}$-$Ni^{2+}$ isotherm at 25°C. $X_{(Ni^{2+}\ in\ soln)}$: equivalent fraction of ingoing nickel in the liquid phase; $X_{(Ni^{2+}\ in\ Zeo)}$: equivalent fraction of nickel cation in the solid phase. Error bars for all points are indicated.

The $Ni^{2+}$-$Na^{+}$ exchange isotherm rose steeply and attained a plateau above the diagonal line, this convex shape reveals that $Ni^{2+}$ was preferred over $Na^{+}$

over the whole concentration range of $Ni^{2+}$. The isotherm however lay below the diagonal line in the range $X_{(Ni^{2+} \text{ in Solution})} > 0.85$ which indicates that the cation exchange is incomplete and the actual CEC is in fact lower than that used to calculate the isotherm.

$$2Na^{+}Zeo^{-} + Ni^{2+}(Cl^{-})_2 \rightleftharpoons Ni^{2+}(Zeo^{-})_2 + 2Na^{+}Cl^{-} \qquad (4.\ 1)$$

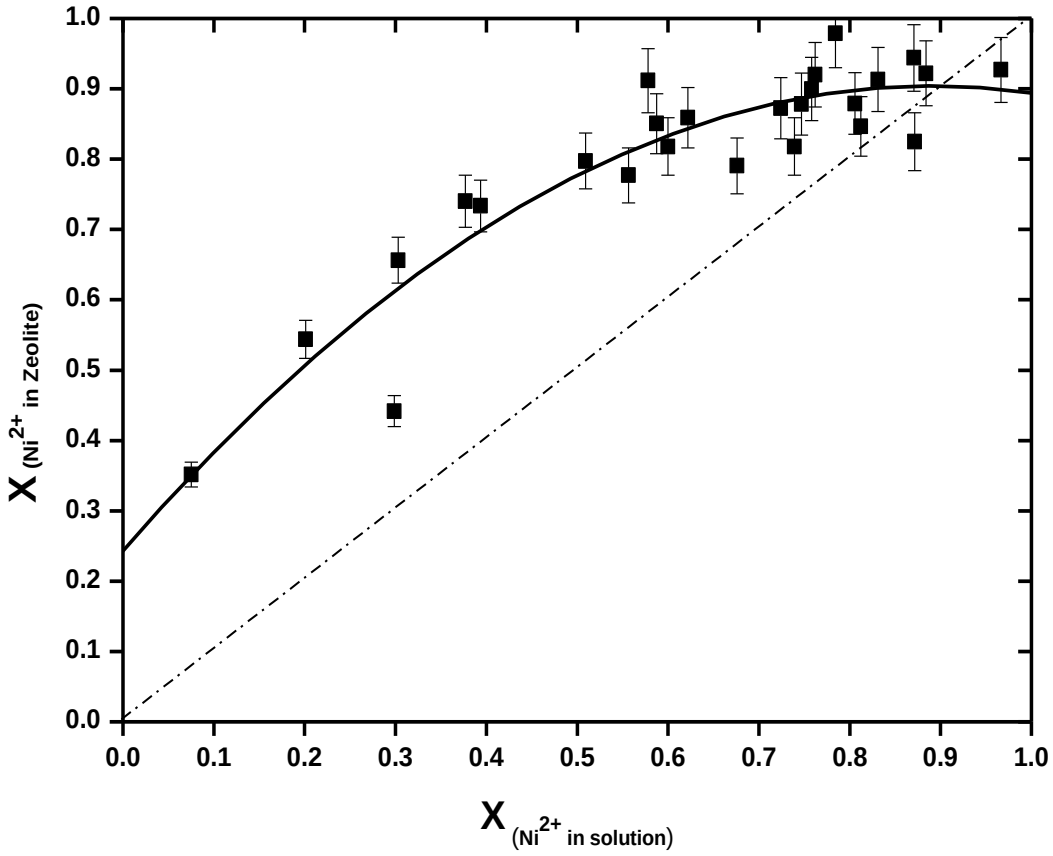



**Figure 4.13**: The $K^+$-$Ni^{2+}$ isotherm at 25°C. $X_{(Ni^{2+}\ in\ soln)}$: equivalent fraction of ingoing nickel in the liquid phase. $X_{(Ni^{2+}\ in\ Zeo)}$: equivalent fraction of nickel cation in the solid phase. Error bars for all points are indicated.

$$2K^{+}Zeo^{-} + Ni^{2+}(Cl^{-})_2 \rightleftharpoons Ni^{2+}(Zeo^{-})_2 + 2K^{+}Cl^{-} \qquad (4.2)$$

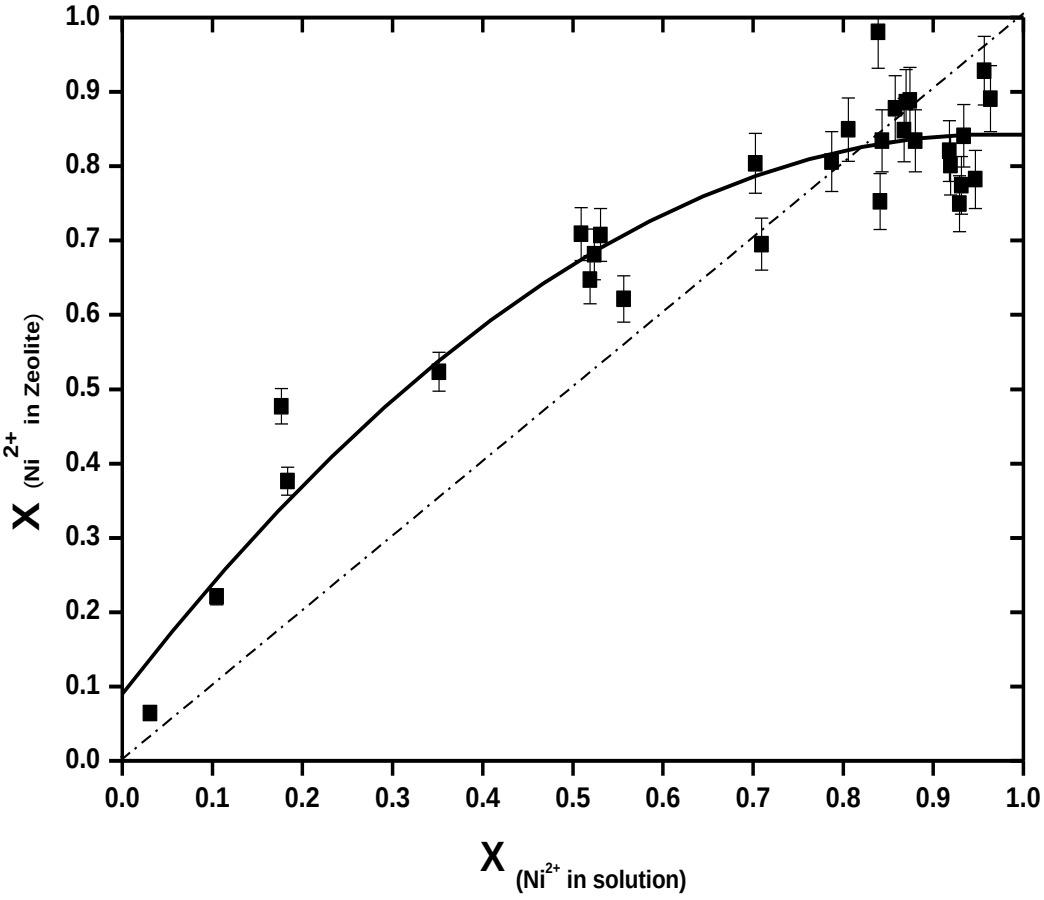



**Figure 4.14**: The Natural-$Ni^{2+}$ isotherm at 25°C. $X_{(Ni^{2+}\ in\ soln)}$: equivalent fraction of ingoing nickel in the liquid phase. $X_{(Ni^{2+}\ in\ Zeo)}$: equivalent fraction of nickel cation in the solid phase. Error bars for all points are indicated.

The $K^+$ - $Ni^{2+}$ and Natural- $Ni^{2+}$systems also increased steeply above the diagonal line and presented highly selective convex isotherms when $Ni^{2+}$ was

adsorbed. High selectivity for $Ni^{2+}$ is confirmed by the high values of exchange constant ~$K_{eq}$>16. Both isotherms lay below the diagonal line the range $X_{(Ni^{2+} \text{ in Solution})} > 0.89$ for $K^+$ - $Ni^{2+}$ and $X_{(Ni^{2+} \text{ in Solution})} > 0.83$ for Natural-$Ni^{2+}$system, which revealed that the effective CEC is probably lower than that used to calculate the isotherm.

The enthalpies of exchange for both of these systems are positive and are almost of the same magnitude (18.75 for $K^+$ - $Ni^{2+}$ system and 22.38 KJ/mol for Natural- $Ni^{2+}$system. This confirms the fact that the $K^+$ are common in both systems as an exchangeable ion (see Table A-1 in Appendix A).

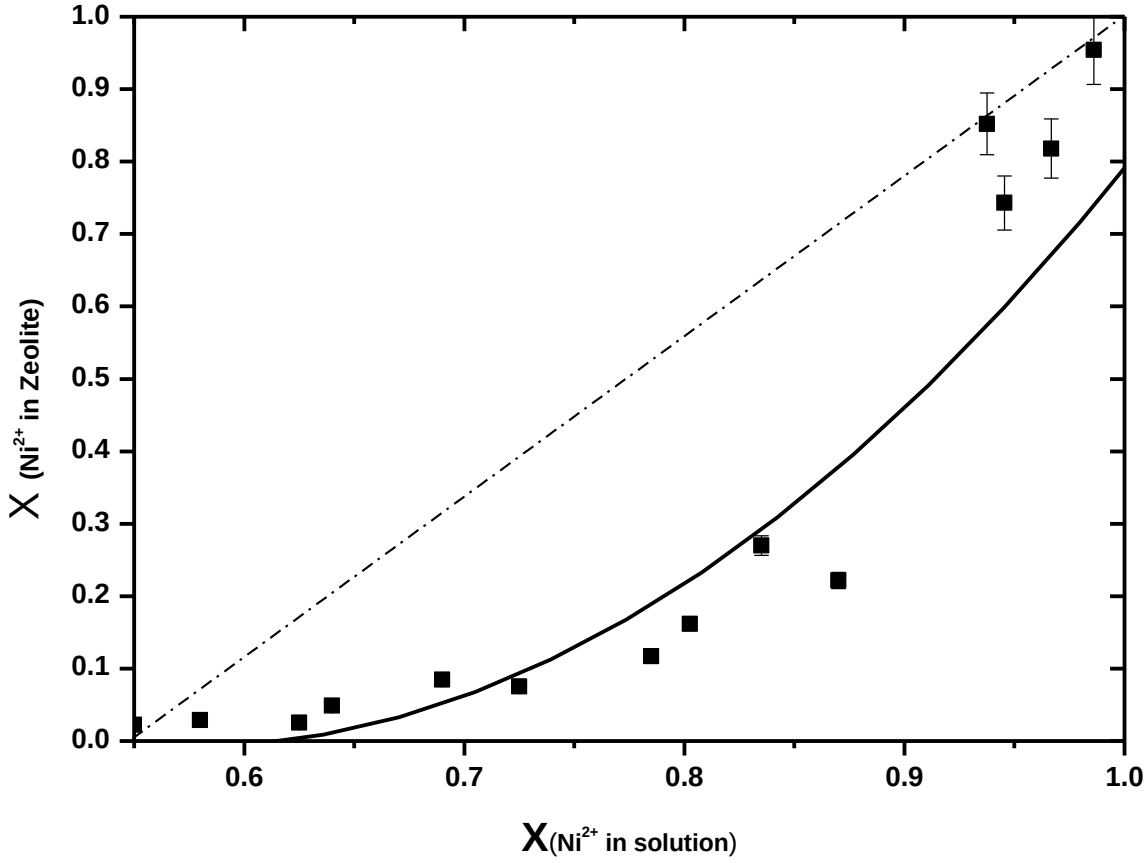



**Figure 4.15:** The $Ca^{2+}$-$Ni^{2+}$ isotherm at 25°C. $X_{(Ni^{2+}\ in\ soln)}$: equivalent fraction of ingoing nickel in the liquid phase. $X_{(Ni^{2+}\ in\ Zeo)}$: equivalent fraction of nickel cation in the solid phase. Error bars for some points are indicated.

$$Ca^{2+}(Zeo^{-})_{2\,(s)} + Ni^{2+}(Cl^{-})_{2\ (aq)} \rightleftharpoons Ni^{2+}(Zeo^{-})_{2\,(s)} + Ca^{2+}(Cl^{-})_{2\ (aq)} \qquad (4.3)$$

Analysis of the above isotherms ($Na^{+}$-$Ni^{2+}$, $K^{+}$-$Ni^{2+}$, natural-$Ni^{2+}$ and $Ca^{2+}$-$Ni^{2+}$) gives us insight into how the displaced ion affects the selectivity of the clinoptilolite for $Ni^{2+}$. It is observed that all of the isotherms reported in Figs 4.11- 4.14 do not proceed to completion (do not attain $X_{Ni^{2+}\text{ in solution}} = 1$ for $X_{Ni^{2+}\text{ in zeolite}} = 1$) this is attributed to the fact that in these systems only a fraction of the whole cation exchange capacity is available to the incoming cation but nonetheless, gets close i.e. 0.9 ±0.1. The same observation was reported by Breck (1974)**.** When the isotherm exhibits a convex profile e.g. for $Na^{+}$-$Ni^{2+}$, $K^{+}$-$Ni^{2+}$ and natural-$Ni^{2+}$ systems the uptake if $Ni^{2+}$ from the solution is known to follow a Langmuir- type isotherm (Colella, 1996).The Na, K and natural forms presented highly selective convex graphs whereas the Ca-form has a concave graph suggesting the selectivity series to be $Ca^{2+}$> $Ni^{2+}$> ($Na^{+}$, $K^{+}$, Natural).This selectivity series is in concordance with the investigation done by Colella (1996) on Italian clinoptilolite. Fig 4.15 demonstrates that the clinoptilolite has a higher affinity for calcium ions than nickel ions. This observation is consistent with the expectation that the $Ca^{2+}$ ion has a relatively lower desorption ratio than $Na^{+}$ and $K^{+}$ due to the strong interaction (ionic in nature) between clinoptilolite and $Ca^{2+}$ (It is difficult to destroy the $Ca^{2+}$ - O – Al bonds). A similar observation was made by Ćurković, Cerjan-Stefanović & Filipan (1997) for Serbian clinoptilolite**.** A remarkably high selectivity of natural, K and Na-exchanged clinoptilolite for $Ni^{2+}$ is observed.

In order to obtain the parameter capable of describing the relative selectivity of a given form of zeolite, the thermodynamic equilibrium constant ($K_{eq}$) was evaluated using the following procedure as outlined by Khan and Singh (1987).

$$K_{eq} = a_z / a_s = f_z C_z / f_s C_s \qquad (4.4)$$

Where $a_Z$ denotes the activity of adsorbed Ni(II), $a_S$ is the activity of Ni(II) in solution at equilibrium. $C_z$ is the milligrams of Ni(II) adsorbed per litre of solution in contact with the clinoptilolite surface, $C_s$ denotes the milligrams per litre of Ni(II) in solution at equilibrium. $f_z$ is the activity coefficient of the adsorbed Ni(II) and $f_s$ is the activity coefficient of the Ni(II) in solution . The method used to calculate ion activities is the one proposed by Debye and Huckel in 1923 in which the ionic strength of the solution is calculated first and then the activity coefficient. Since at very low concentrations the activity coefficient approaches unity, equation (4.4) can be written as

$$\lim_{Cz \to 0} \frac{Cz}{Cs} = a_z / a_s = K_{eq} \quad \text{which reduces to} \qquad (4.5)$$

$$K_{eq} = \frac{Cz}{Cs} \qquad (4.6)$$

The values of $K_{eq}$ were obtained by plotting ln(Cz/Cs) v.s. Cz and extrapolate the results to Cz=0, these plots did not yield very good straight lines.

The adsorption standard free energy change ($\Delta G°$) was calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_{eq} \qquad (4.7)$$

Several researchers have reported $\Delta G^\circ$ values for adsorption in zeolites (Inglezakis, Loizidou & Grigoropoulou 2002) ; (Fridriksson et al. 2004). In their calculations they only reported $\Delta G^\circ_{ads}$, and did not mention the $\Delta G^\circ_{des}$ of the ion being displaced. By considering these two parameters a true Gibbs free energy of exchange ($\Delta G^\circ_{exc}$) can be computed which is representative of the whole system. Therefore equation (4.7) is used to calculate the standard free energy of reaction.

$$\Delta G^\circ_{exc} = \Delta G^\circ_{ads} - \Delta G^\circ_{des} \qquad (4.8)$$

Where: $\Delta G^\circ_{exc}$ denotes the Gibbs free energy of ion exchange reaction

$\Delta G^\circ_{ads}$ is the Gibbs free energy of adsorption of nickel onto clinoptilolite and

$\Delta G^\circ_{des}$ is the Gibbs free energy of desorption of exchangeable ions in the clinoptilolite (Na, K, and Ca).

R is the universal gas constant (8.314 J/mol.K) and T is the temperature in Kelvin.

The $\Delta S^\circ$ and $\Delta H^\circ$ values were obtained from the slope and intercept of the Van't Hoff plots (which are plots of the natural logarithm of equilibrium constant of the reaction vs. the reciprocal of temperature in Kelvin as shown if Figures C-1 to C-4 in Appendix C)

$$\ln K_{eq} = \Delta S^\circ/R - (\Delta H^\circ/R)1/T \qquad (4.9)$$

The Van't Hoff plot is widely used to analyze the effect of temperature on the reaction (Varshney, Gupta & Singhal 1995, Khan, Singh 1987). The change in enthalpy of reaction can be found from the gradient of the plot, which equals $-\Delta H^{\circ}/R$ and the change in entropy can be evaluated from the intercept, $\Delta S^{\circ}/R$. Evaluation of thermodynamic parameters viz. $K_{eq}$, $\Delta G^{\circ}$, $\Delta H^{\circ}$ and $\Delta S^{\circ}$ provides an insight into the mechanism of $Ni^{2+}$ sorption in clinoptilolite. Table 4.4 reports thermodynamic values at different temperatures.

**Table 4. 4:** Values of various thermodynamic parameters for the adsorption of Ni (II) in solution onto natural and pretreated clinoptilolite.

| Form of zeolite | Thermodynamic parameters | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Keq | | | | | ΔG°rxn (KJ/mol) | | | | | ΔH° (KJ/mol) | ΔS° (KJ/mol.K) |
| | 25°C | 35°C | 50°C | 60°C | 75°C | 25°C | 35°C | 50°C | 60°C | 75°C | | |
| Na-form | 29.60 | 44.21 | 53.85 | 83.75 | 144.48 | -9.12 | -10.54 | -11.63 | -13.49 | -15.90 | 26.00 | 0.12 |
| K-form | 8.73 | 11.26 | 16.45 | 21.73 | 24.47 | -5.58 | -6.46 | -7.82 | -8.90 | -9.82 | 18.72 | 0.08 |
| Ca-form | 0.35 | 0.989 | 1.34 | 2.2 | 9.01 | 3.10 | 0.53 | -0.34 | -3.94 | -6.11 | 42.05 | 0.14 |
| Natural-form | 23.69 | 24.53 | 39.87 | 60.45 | 76.73 | -8.50 | -9.70 | -10.69 | -12.20 | -13.50 | 22.38 | 0.10 |

The ion exchange isotherms shown in Fig. 4.12 show the extreme selectivity of $Na^{+}$-clinoptilolite for the incoming $Ni^{2+}$ cations, which is confirmed by the high values of the equilibrium constant~$K_{eq}$> 1, cited in the Table 4.4 and the corresponding negative values of the free energies of exchange. The data also indicates that the value of $K_{eq}$ increases with increasing temperature from 25°C to 75°C in all forms of the zeolite.

The enthalpy of exchange is positive for $Ni^{2+}$–Na-clinoptilolite. This is explained on the one hand by the substitution of $Na^{+}$ cations by $Ni^{2+}$ cations, which have a greater heat of hydration (-406 for $Na^{+}$ and -2105 kJ/mol for $Ni^{2+}$), in the aqueous phase, and on the other hand by the greater interaction energy of the $Ni^{2+}$ cations with the exchange centers of clinoptilolite as a result of their similarity in size.

Equilibrium constants $K_{eq}$ derived from this study were quite high compared to those reported by Argun (2008) despite using the same type of zeolite. This author reported very low $k_{eq}$ values of 3.28, 2.97 and 2.65 at 20, 40 and 60°C respectively using Turkish natural clinoptilolite, and in this study we found $K_{eq}$ to be 23.69 for the natural form at 25°C which increased as temperature was increased (see Table 4.4).The differences are largely due to the time given for equilibrium to be reached and different methods being used to calculate equilibrium parameters. A reevaluation of Argun's isotherm data (after 3hrs contact time) at 20°C and at 25mg/L initial concentration of Ni(II) for 1g of clinoptilolite using equations 4.5 to 4.9 yields a $K_{eq}$ of 18 for natural-$Ni^{2+}$

system, which is very close to the values obtained in this study. The recalculated $\Delta G°$ value at 20°C is -7.04kJ/mol (from -2.89kJ/mol).This analysis demonstrates that the reliance on linearized Langmuir equations potentially limits the ability to model sorption data accurately.

The thermodynamic quantities reported in Table 4.4 are in agreement with the selectivity series obtained from the isotherm plots. The Gibbs free energies of the natural and pretreated clinoptilolite have been evaluated, and the spontaneity of adsorption is seen to follow the series Na-form > natural-form > K-form > Ca-form. The symbol ">" between two clinoptilolite forms in the sequence above indicates that adsorption onto the former form is more spontaneous than the latter.

In all cases, the free energy ($\Delta G°$) of the Ni(II) sorption was negative except for Ca- form at 25 and 35˚C, suggesting that the spontaneity of the process increased with increasing temperature. The values of the $\Delta G°$ also confirm that the maximum adsorption is obtained with the $Na^{+}$-exchanged clinoptilolite followed by the natural, $K^{+}$ and lastly the $Ca^{2+}$- form.

The $\Delta H°$ were positive for all forms of clinoptilolite and ranged from 18.72 to 42.05KJ/mol (Table 4.4), this provides an indication that the sorption reaction is endothermic for Ni(II). These values were calculated from plots of ln $K_{eq}$ versus 1/T. The linear nature of the plot indicates that the mechanism of adsorption is not changed as temperature is changed. If the values of $\Delta H°$ for

$Ni^{2+}$ adsorption had been within the range of 8.4 to 12.6 KJ/mol this would be an indication that the adsorption process was ionic in nature (Günay, Arslankaya & Tosun 2007). The values obtained in this study were greater than 12.6 kJ/mol which indicates that the mechanism for the adsorption of these ions in zeolites occurs via a mechanism besides ion exchange.

The $Ca^{2+}$- $Ni^{2+}$system*.*

In distinction from the latter systems, the $Ni^{2+}$-$Ca^{2+}$ system yielded a concave isotherm (the exchange isotherm lay below the diagonal line), so that $Ca^{2+}$ > $Ni^{2+}$ and the equilibrium constants ($K_{eq}$) are less than 1 at 25 and 35°C (see Table 4.4). The Gibbs free energy of exchange is positive at these temperatures, but a further increase in temperature results in the reaction becoming spontaneous. The $\Delta G°$ values were positive at 25 and 35°C (3.098KJ/mol and 0.527KJ/mol respectively), and negative at temperatures greater than 50°C. Pabalan (1994) also reported a positive $\Delta G°$ value of 4.19 KJ/mol at 25°C for a system involving $Ca^{2+}$ - $Na^{+}$ using American clinoptilolite (Inglezakis, Loizidou & Grigoropoulou 2002).

The substitution of the doubly charged $Ca^{2+}$ cations with another doubly charged $Ni^{2+}$ ions, proved to be accompanied by an endothermic exchange effect (positive enthalpy). The entropy for the $Ca^{2+}$ - $Ni^{2+}$ exchange system is

positive since the strongly hydrated double charged cations ($Ca^{2+}$) in the aqueous phase are substituted by the similarly hydrated $Ni^{2+}$cations.

## 4.7 Isotherm Models

The experimental data was also fitted to the linear forms of the Langmuir and Freundlich isotherms. The Langmuir plots for nickel adsorption onto various homoionic forms of clinoptilolite and at 25°C are shown in Figures 4.16 to 4.19.

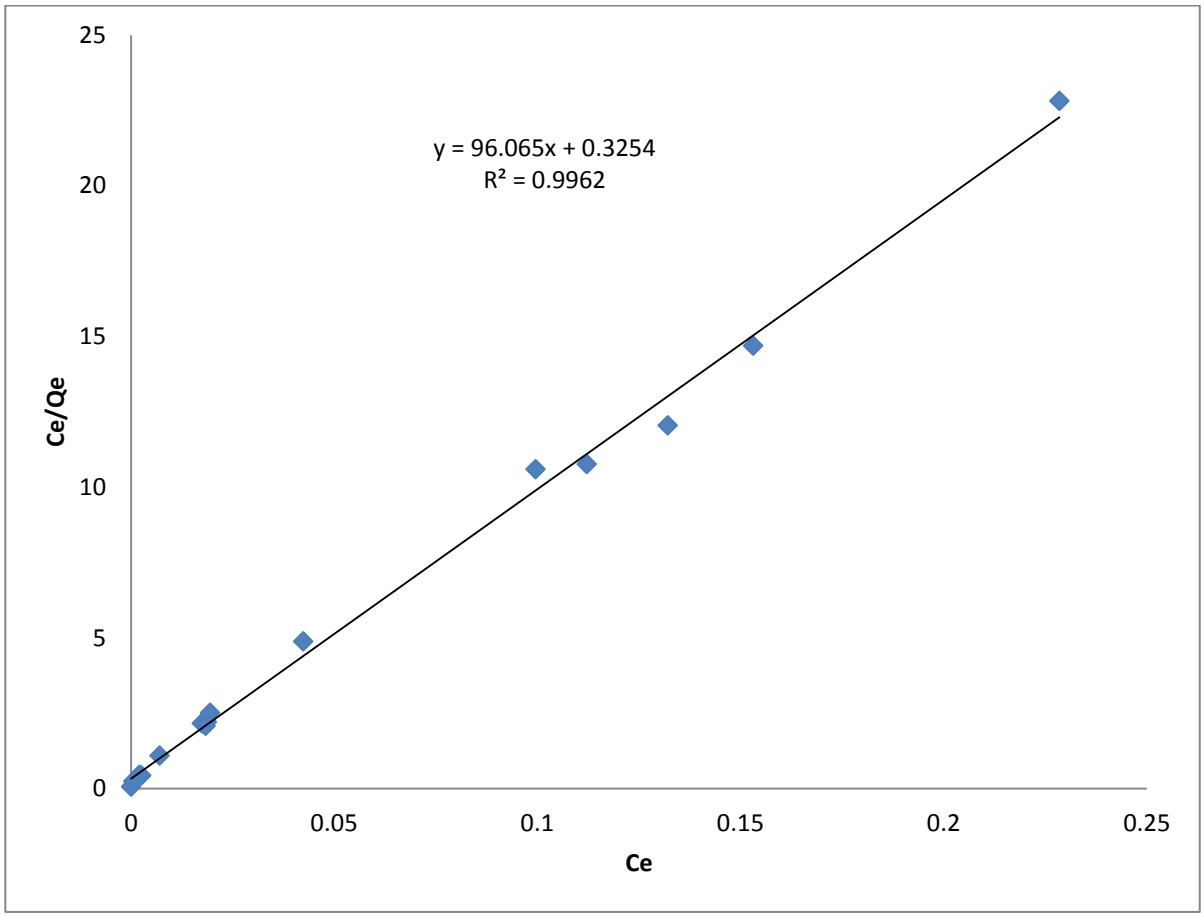



**Figure 4.16**: Langmuir isotherm the adsorption of nickel onto natural zeolite at 25°C

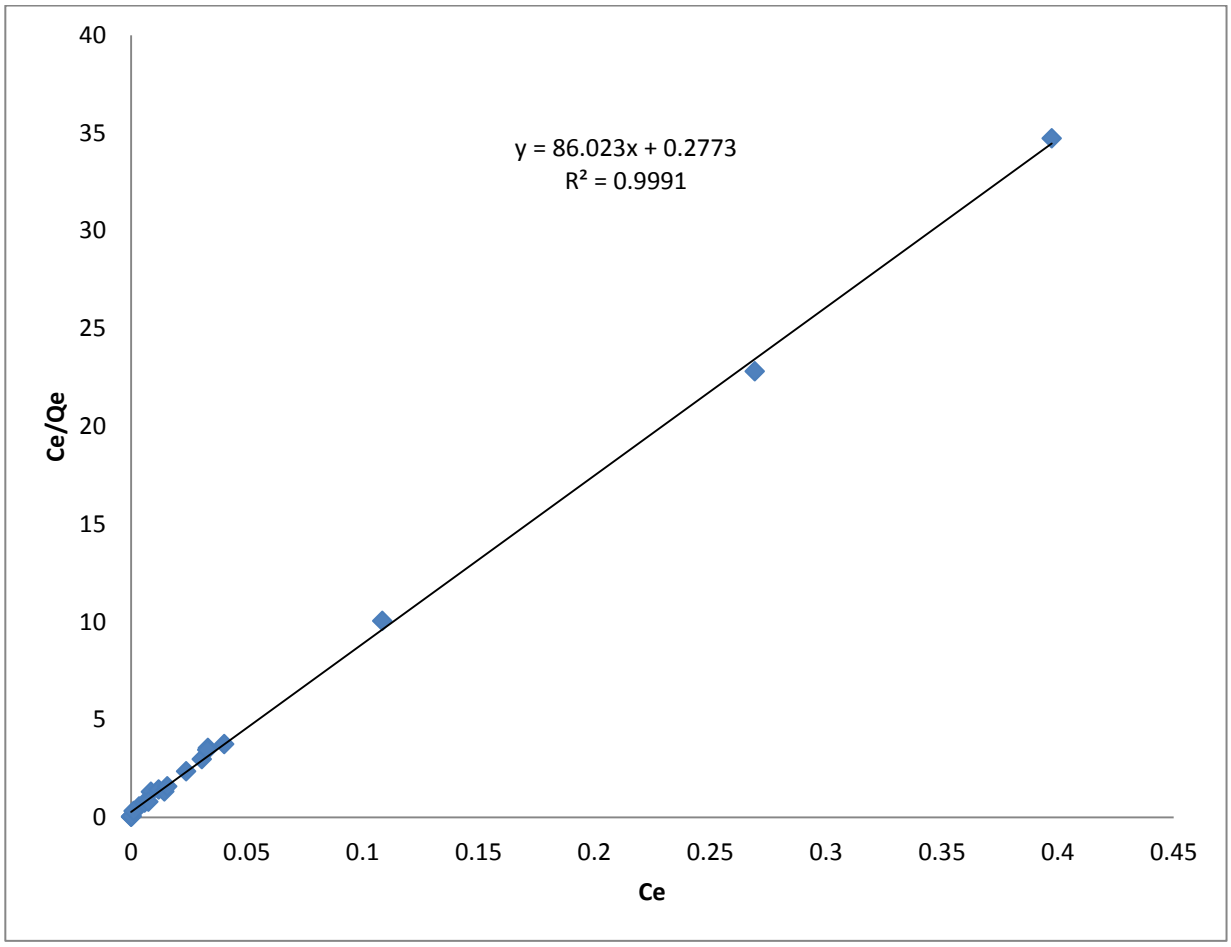



**Figure 4.17**: Langmuir isotherm the adsorption of nickel onto Na-form of zeolite at 25°C

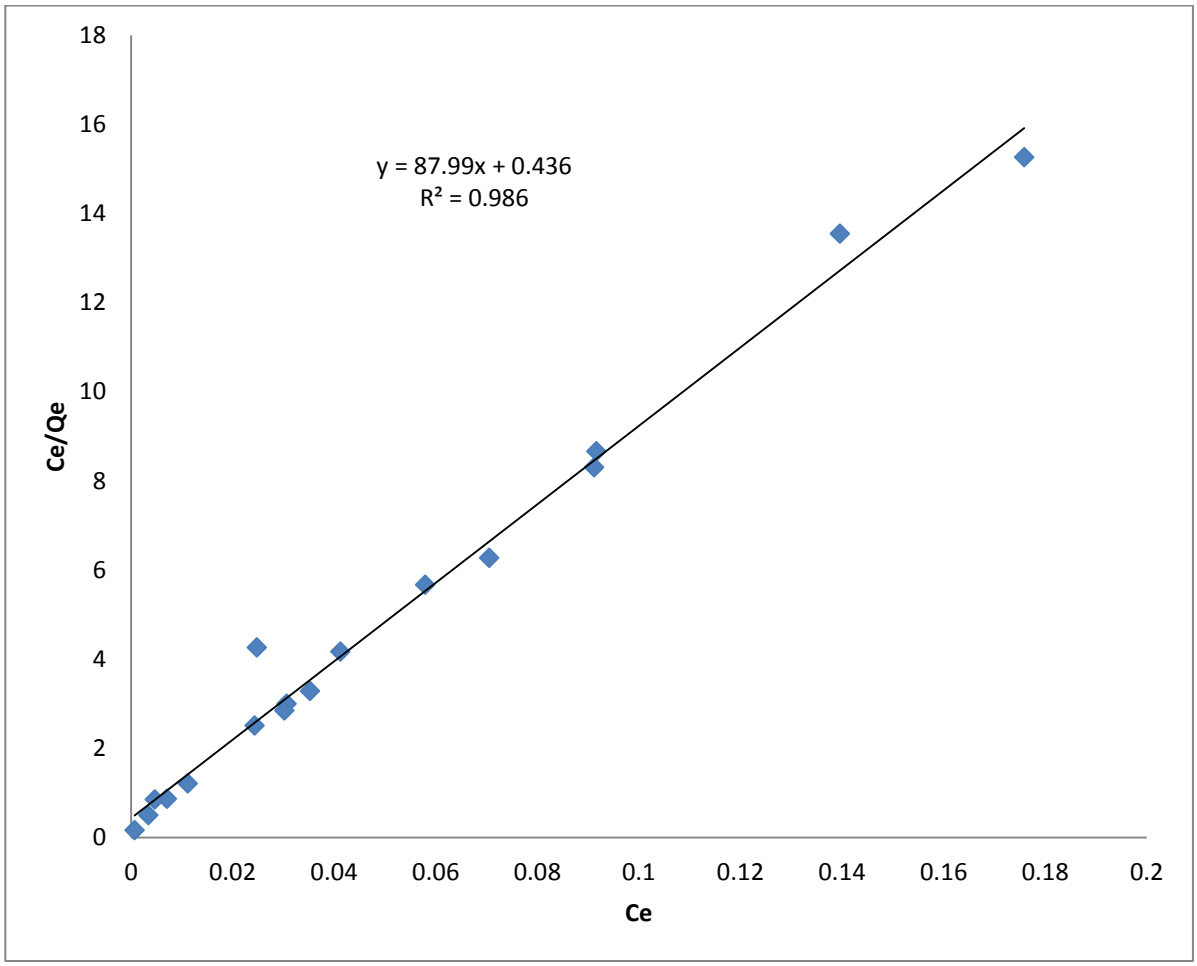



**Figure 4.18**: Langmuir isotherm the adsorption of nickel onto K-form of zeolite at 25°C

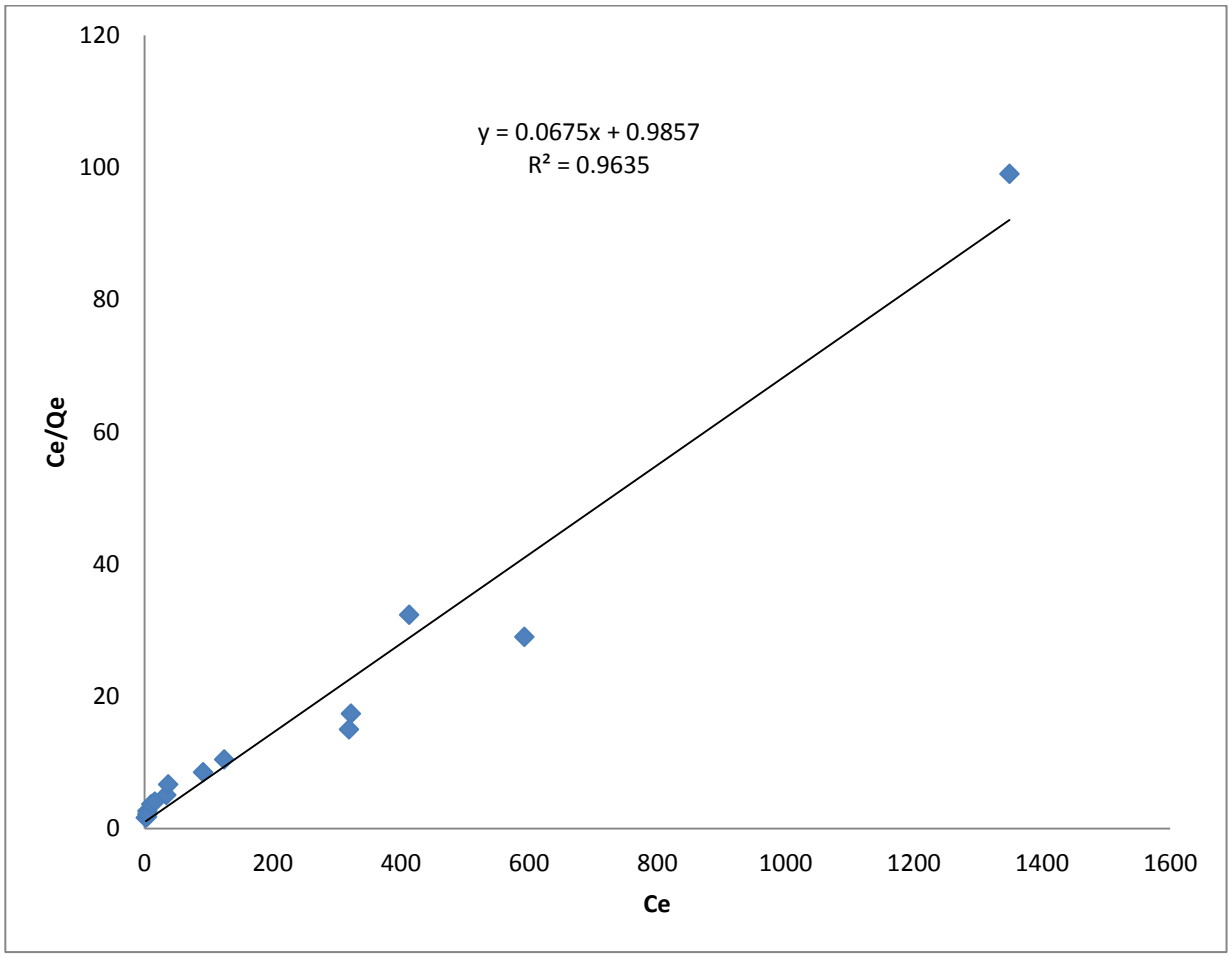



**Figure 4.19**: Langmuir isotherm the adsorption of nickel onto Ca-form of zeolite at 25°C

The linear plots of $C_e/Q_e$ versus $C_e$ suggest the applicability of the Langmuir isotherms. Values of $Q_m$ and b were obtained from the gradient and intercepts of the plots and presented in Table 4.5. It is observed from this table that the values of $Q_m$ and b are determined by the nature of the exchangeable ion. The maximum amount of exchanged $Ni^{2+}$ according to the Langmuir parameters was given by Ca-form of clinoptilolite (14.81 mg/g), and this can

be attributed to the fact that divalent ions ($Ca^{2+}$ ) opens the aperture of the zeolite to full diameter hence more area of physisorption, whereas exchange with a with a large univalent ion diminishes the aperture size. The ionic radii of $Na^{+}$, $K^{+}$, and $Ca^{2+}$ are 1.16 ,1.33 and 1.14Å (Cotton, 1999). For isoelectronic $K^{+}$ and $Ca^{2+}$ the charge effect is more pronounced.

The Langmuir model effectively described the adsorption data of $Ni^{2+}$ onto natural and pretereated clinoptilolite with $R^2$ values > 0.95. According to the b pamameter (L/mg) the adsorption sequence is given by Natural form > Na-form > K-form > Ca- form.

**Figure 4.5**: Langmuir isotherm results.

| Metal ion | Zeolite form | $R^2$ | $Q_m$ | b |
|---|---|---|---|---|
| Nickel ion | Na-form | 0.999 | 0.0116 | 310.22 |
| adsorption | K-form | 0.986 | 0.0113 | 201.77 |
| | Ca-form | 0.964 | 14.81 | 0.0684 |
| | Natural form | 0.979 | 0.01 | 295.8 |

The ion exchange data were also modelled using the Freundlich model in logarithmic form (See equation 2.14). The Freundlich plots for nickel adsorption onto various forms of clinoptilolite at 25°C are shown in Figures 4.20 to 4.23.

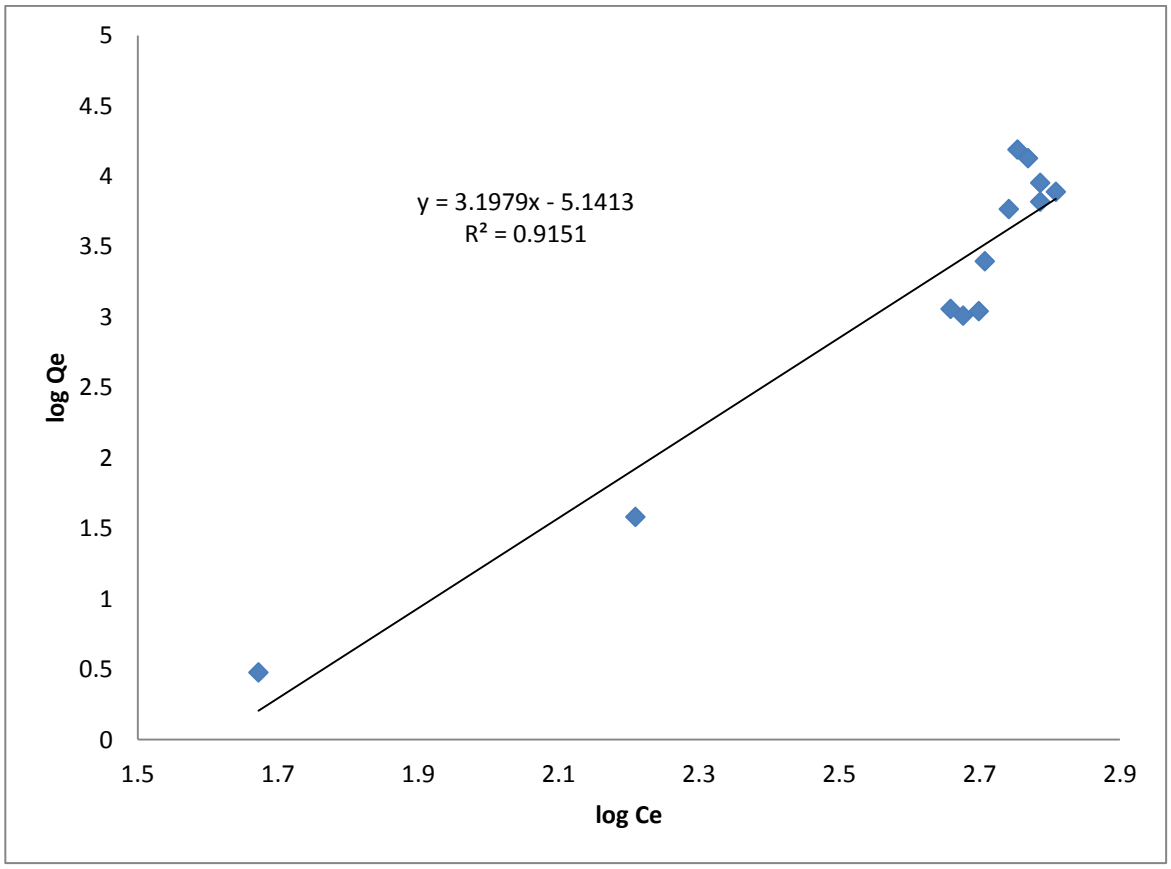



**Figure 4.20**: Freundlich isotherm the adsorption of nickel onto natural zeolite at 25°C.

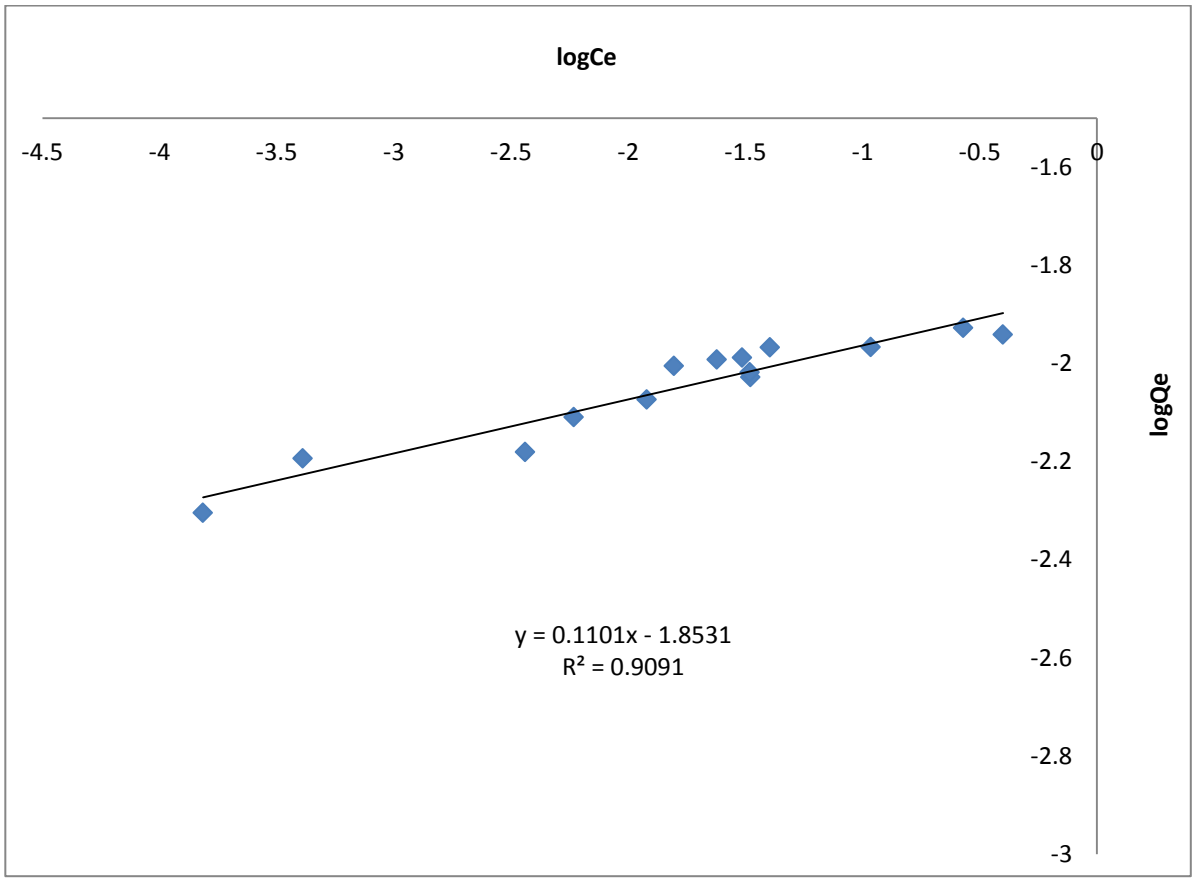



**Figure 4.21:** Freundlich isotherm the adsorption of nickel onto Na- form of zeolite at 25°C.

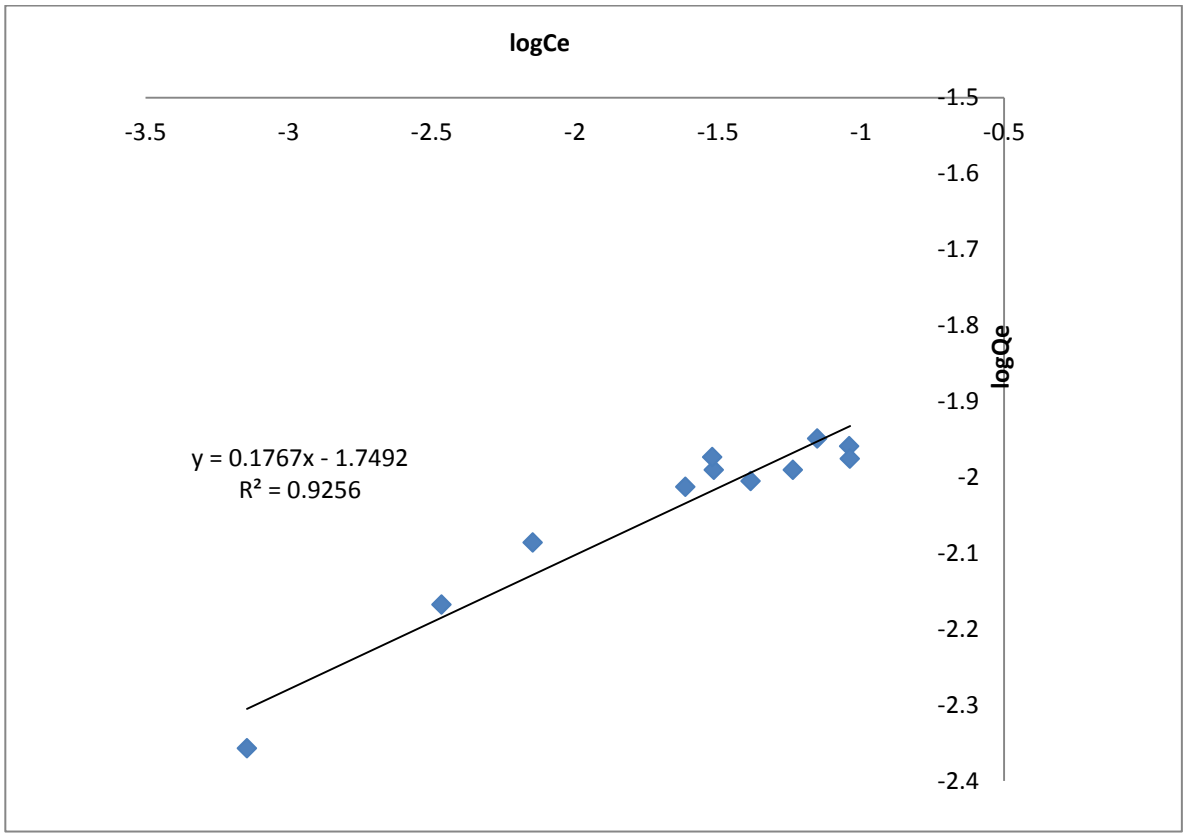



**Figure 4.22**: Freundlich isotherm the adsorption of nickel onto K- form of zeolite at 25°C.

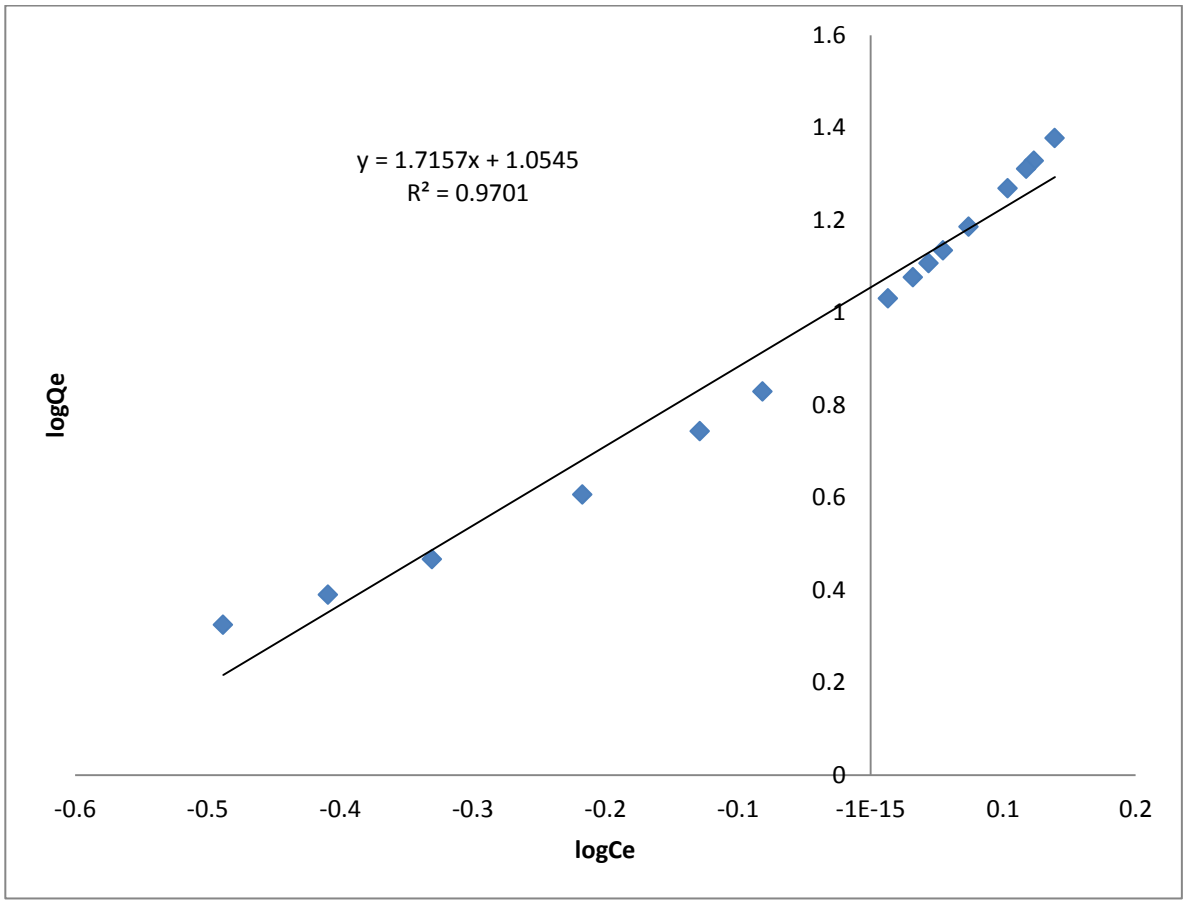



**Figure 4.23**: Freundlich isotherm the adsorption of nickel onto Ca-form of zeolite at 25°C.

Freundlich model clearly fails to represent the data. The Freundlich isotherm is originally of an empirical nature, but has since been used as a model for the interpretation of adsorption onto heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation.

The Freundlich equation, one of the most widely used mathematical models, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies (Erdem 2004).

**Table 4. 6:** Freundlich isotherm results.

| Metal ion | Zeolite form | $R^2$ | Kf | n |
|---|---|---|---|---|
| Nickel ion | Na-form | 0.909 | 0.156 | 9.08 |
| adsorption | K-form | 0.925 | 0.173 | 5.65 |
| | Ca-form | 0.970 | 2.87 | 0.583 |
| | Natural form | 0.915 | 0.0058 | 0.313 |

The constants $K_f$ and n were calculated for each form of zeolite and the results have been presented in table 4.6**.** $K_f$ is a parameter related to the temperature and n is a characteristic constant for the adsorption system under study. Values of n between 2 and 10 shows good adsorption. A larger value of n (smaller value of 1/n) implies a strong interaction between the adsorbate and the adsorbent (Arámbula-Villazana, Solache-Ríos & Olguín,

2006). The numerical value of 1/n less than one indicates that adsorption capacity is slightly suppressed at lower equilibrium concentrations (Erdem,2004).

Table 4.6 provides results on Freundlich isotherm parameters for the removal of Ni(ll) by clinoptilolite in different forms; the Na and K-forms of clinoptilolite have n values between 2 to 10 suggesting a good adsorption capacity whereas for Ca and natural form suggest a suppressed adsorption capacity. This can be attributed to the ease with which the $K^+$ and $Na^+$ can be exchanged by the $Ni^{2+}$ in solution.

## 4.8 Limitations of Langmuir and Freundlich isotherms

Fitting of adsorption isotherm equations to experimental data is often an important aspect of data analysis. ln most of the literature studies, nickel ion adsorption with clinoptilolite was generally examined with the Langmuir, Dubinin-Radushkevitch(D-R) and Freundlich isotherms (Rajic et al. 2010). Argun (2008) studied nickel ion removal using Turkish clinoptilolite and suggested that the capacity of clinoptilolite to exchange certain metals can be calculated using Langmuir, D-R and Freundlich isotherms (Altin, 1998).

The Langmuir Equation assumes that the adsorbed species forms a monolayer. But, monolayer formation is possible only for dilute solutions. Under high concentration conditions the assumption breaks down as

adsorbates accumulate to form multiple layers. The Langmuir equation also assumes that adsorbed molecules do not interact with each other laterally. This is impossible as weak forces of attraction exist even between molecules of the same type.  Another assumption is that all the sites on the solid surface are equivalent in size and shape and have equal affinity for the adsorbate molecules i.e. the surface of the solid is homogeneous. But real solid surfaces are heterogeneous. Since, clinoptilolite minerals have high surface irregularities, the adsorption models (Langmuir and Freundlich) should not be used to explain the adsorption equilibrium phenomenon. Hence these adsorption isotherms must be modified on thermodynamic grounds to model ion exchange and adsorption on zeolites.

# 5 CONCLUDING REMARKS

The study revealed that clinoptilolite in its natural form is rich in sodium and potassium content. Characterisation studies showed that pretreatment of clinoptilolite did not affect its structure. The natural, K, and Na-forms of clinoptilolite exhibited exceptional selectivity for the removal of $Ni^{2+}$ from aqueous solution compared to the Ca-form suggesting the selectivity series to be $Ca^{2+}$> $Ni^{2+}$> ($Na^{+}$, $K^{+}$, natural). Thermodynamic parameters are important in providing a quantitative understanding of ion exchange interactions between zeolites and ions in aqueous solution.

# 6 CONCLUSION AND RECOMMENDATIONS

Evaluation of the thermodynamic parameters viz. $K_{eq}$, $\Delta G°$, $\Delta H°$, $\Delta S°$ provides insight into the mechanism of Ni(II) sorption in the zeolite. The results of this research showed that clinoptilolite is an effective low cost adsorbent for the removal of $Ni^{2+}$ from aqueous solution. Pretreatment of zeolites enhances the removal efficiency if mono-valent ions are used, and selectivity depends on the type of the exchangeable ions on the zeolite. Treating the zeolite with $CaCl_2$ decreased the zeolite's ability to remove $Ni^{2+}$ from aqueous solution. Calcium ions bind comparatively strongly to the zeolite compared to sodium

and potassium. The thermodynamic parameters revealed that $Ni^{2+}$ sorption in clinoptilolite was spontaneous and endothermic. The values of $\Delta H°$ for $Ni^{2+}$ adsorption onto natural and pretreated clinoptilolite are within the range of 4 to 42 KJ/mol suggesting that the adsorption process to be physisorption in nature.

Nickel removal results using natural and pretreated clinoptilolite showed that the treatment improved both the exchange capacity and the removal efficiency when operating at metal concentrations of 10 to 100 mg/L. The Na-form of clinoptilolite demonstrated to perform the best with 98% removal efficiency at 20 mg/L nickel initial concentration. Metal precipitation during the ion exchange mechanism was virtually negligible as the pH of the solution was maintained at 7. Overall, metal removal exceeding 98% was achieved hence, clinoptilolite in its natural or Na- modified form can be used for treating effluent contaminated with high levels of nickel.

The use of zeolites in heavy metal removal from water is still in its infancy and research efforts have focussed on fundamental aspects of cation exchange reactions involving heavy metals, but not much has been done as far as actual applications are concerned. In other words, most of the literature on this subject concerns exchange isotherms and related equilibrium and thermodynamic data, while not many investigations concern the removal of

heavy metals from real wastewaters, or even from model solutions simulating real wastewaters. Future work could focus on these aspects of industrial application.

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# APPENDICES

## Appendix A

**Table A-1**: Chemical Composition (Wt %) of treated clinoptilolite sample determined by XRF.

| Component | Weight percent (%) | | | |
|---|---|---|---|---|
| | **Natural form** | **Na-form** | **K- form** | **Ca-** |
| $SiO_2$ | 77.24 | 77.37 | 76.13 | 76.50 |
| $Al_2O_3$ | 13.30 | 13.18 | 13 09 | 12.93 |
| $Fe_2O_3$ | 0.14 | 0.13 | 0.14 | 0.12 |
| FeO | 1.09 | 1.01 | 1.14 | 0.12 |
| MnO | 0.04 | 0.01 | 0.02 | 0.02 |
| MgO | 0.86 | 0.71 | 0.67 | 0.80 |
| CaO | 1.40 | 0.77 | 0.87 | 3.35 |
| $Na_2O$ | 1.94 | 3.84 | 0.23 | 1.43 |
| $K_2O$ | 3.78 | 2.94 | 7.78 | 3.77 |
| $TiO_2$ | 0.14 | 0.14 | 0.14 | 0.14 |
| **Total** | **100.44** | **100.01** | **100.00** | **99.97** |

To calculate the cation exchange capacity (CEC) the formula hereunder was used.

CEC = number of equivalents/ weight of a formula unit.

Eg calculations for CEC

For natural form $(NaK_2)(Al_5Si_{26}O_{62}) \cdot 12H_2O$

Number of equivalents = 3

Weight of formula unit = (22.99 + 39.098*2) + (26.982 + 28.086*26 + 16*62) + (12*18) = 2173.913g/mol

This particular zeolite form would have a cation exchange capacity of 3 equivalents per 2173.913 grams or recalculating 0.00138 equivalents per gram, or 216milliequivalents per gram.

## Appendix B

**Tablel B-1**. Experimental data for ion exchange between $Ni^{2+}$ and $Na^{+}$-form of clinoptilolite at 25˚C.

| Sample number | Initial concentration ($\times 10^{-3}$ molar) | Final concentration ($\times 10^{-3}$ molar) | Mass used (g) | Volume used ( L) |
|---|---|---|---|---|
| 1 | 2.556 | 0.076 | 1.00 | 0.10 |
| 2 | 3.408 | 0.153 | 0.42 | 0.05 |
| 3 | 4.089 | 2.330 | 0.17 | 0.10 |
| 4 | 5.111 | 0.153 | 1.00 | 0.10 |
| 5 | 5.111 | 1.278 | 1.00 | 0.10 |
| 6 | 6.815 | 4.276 | 0.31 | 0.10 |
| 7 | 6.815 | 2.539 | 0.82 | 0.20 |
| 8 | 6.815 | 0.408 | 1.00 | 0.10 |
| 9 | 8.178 | 5.908 | 0.11 | 0.05 |
| 10 | 8.859 | 4.363 | 0.96 | 0.20 |
| 11 | 10.222 | 3.629 | 1.00 | 0.10 |
| 12 | 10.223 | 7.423 | 0.25 | 0.10 |
| 13 | 11.926 | 10.606 | 0.12 | 0.10 |
| 14 | 13.630 | 11.926 | 0.17 | 0.10 |
| 15 | 13.630 | 5.861 | 1.00 | 0.10 |
| 16 | 15.333 | 11.028 | 0.58 | 0.15 |
| 17 | 15.334 | 10.632 | 0.96 | 0.20 |
| 18 | 15.334 | 8.689 | 1.00 | 0.10 |
| 19 | 16.356 | 13.269 | 0.60 | 0.20 |
| 20 | 17.038 | 7.539 | 1.00 | 0.10 |
| 21 | 20.445 | 15.053 | 1.08 | 0.20 |
| 22 | 20.445 | 16.567 | 0.40 | 0.10 |
| 23 | 20.445 | 16.990 | 0.65 | 0.20 |
| 24 | 20.445 | 12.012 | 1.00 | 0.10 |
| 25 | 25.556 | 14.524 | 1.00 | 0.10 |
| 26 | 25.556 | 15.675 | 1.00 | 0.10 |
| 27 | 34.075 | 23.895 | 1.00 | 0.10 |
| 28 | 40.891 | 30.616 | 1.00 | 0.10 |
| 29 | 42.594 | 33.223 | 1.00 | 0.10 |
| 30 | 42.594 | 33.010 | 1.00 | 0.10 |
| 31 | 51.113 | 40.328 | 1.00 | 0.10 |
| 32 | 119.264 | 108.47 | 1.00 | 0.10 |
| 33 | 281.124 | 269.317 | 1.00 | 0.10 |
| 34 | 408.907 | 397.458 | 1.00 | 0.10 |

**Table B-2**. Experimental data for ion exchange between $Ni^{2+}$ and $K^{+}$-form of clinoptilolite at 25˚C.

| Number of samples | Initial concentration ($\times 10^{-3}$M) | Final concentration ($\times 10^{-3}$ M) | Mass used (g) | Volume used (L) |
|---|---|---|---|---|
| 1 | 5.111342 | 0.715588 | 1 | 0.1 |
| 2 | 10.22268 | 3.424599 | 1 | 0.1 |
| 3 | 10.22268 | 8.587055 | 0.15 | 0.1 |
| 4 | 10.22268 | 6.900312 | 0.5 | 0.15 |
| 5 | 10.22268 | 5.775817 | 0.97 | 0.2 |
| 6 | 10.22268 | 4.702435 | 1 | 0.1 |
| 7 | 15.33403 | 7.130322 | 1 | 0.1 |
| 8 | 20.44537 | 11.19384 | 1 | 0.1 |
| 9 | 20.44537 | 19.02953 | 0.12 | 0.1 |
| 10 | 20.44537 | 17.68524 | 0.48 | 0.2 |
| 11 | 20.44537 | 14.97623 | 0.96 | 0.2 |
| 12 | 30.66805 | 24.84112 | 1 | 0.1 |
| 13 | 34.07561 | 24.36406 | 1 | 0.1 |
| 14 | 40.89074 | 30.25915 | 1 | 0.1 |
| 15 | 40.89074 | 30.66805 | 1 | 0.1 |
| 16 | 40.89074 | 37.12368 | 0.33 | 0.1 |
| 17 | 40.89074 | 34.96158 | 0.81 | 0.15 |
| 18 | 40.89074 | 35.94807 | 1.01 | 0.25 |
| 19 | 46.00208 | 35.26826 | 1 | 0.1 |
| 20 | 51.11342 | 41.23149 | 1 | 0.1 |
| 21 | 68.15123 | 57.92854 | 1 | 0.1 |
| 22 | 81.78147 | 70.53652 | 1 | 0.1 |
| 23 | 102.2268 | 91.23746 | 1 | 0.1 |
| 24 | 102.2268 | 91.64636 | 1 | 0.1 |
| 25 | 149.9327 | 139.6248 | 1 | 0.1 |
| 26 | 187.4159 | 175.8898 | 1 | 0.1 |
| 27 | 681.5123 | 669.9266 | 1 | 0.1 |
| 28 | 1703.781 | 1691.854 | 1 | 0.1 |

**Tablel B-3:** Experimental data for ion exchange between $Ni^{2+}$ and Natural-form of clinoptilolite at 25˚C.

| sample number | Initial concentration ($10^{-3}$ M) | Final concentration ($10^{-3}$ M) | Mass used (g) | Volume used (L) |
|---|---|---|---|---|
| 1 | 0.851890345 | 0.051113 | 1 | 0.1 |
| 2 | 3.407561379 | 0.647437 | 1 | 0.1 |
| 3 | 6.815122757 | 2.112688 | 1 | 0.1 |
| 4 | 8.518903447 | 2.555671 | 1 | 0.1 |
| 5 | 10.64862931 | 5.652292 | 1.13 | 0.2 |
| 6 | 10.64862931 | 7.483857 | 0.63 | 0.2 |
| 7 | 10.64862931 | 8.93207 | 0.14 | 0.1 |
| 8 | 13.63024551 | 7.087728 | 1 | 0.1 |
| 9 | 13.63024551 | 11.85831 | 0.16 | 0.1 |
| 10 | 20.44536827 | 17.74045 | 0.51 | 0.2 |
| 11 | 25.55671034 | 17.46375 | 1 | 0.1 |
| 12 | 25.55671034 | 22.33656 | 0.58 | 0.2 |
| 13 | 25.55671034 | 23.45424 | 0.41 | 0.2 |
| 14 | 27.26049103 | 19.49125 | 1 | 0.1 |
| 15 | 27.26049103 | 18.40083 | 1 | 0.1 |
| 16 | 27.26049103 | 18.74159 | 1 | 0.1 |
| 17 | 31.94588793 | 30.55305 | 0.12 | 0.1 |
| 18 | 31.94588793 | 25.14354 | 1.35 | 0.2 |
| 19 | 42.59451723 | 41.03556 | 0.28 | 0.2 |
| 20 | 42.59451723 | 34.31414 | 1.56 | 0.2 |
| 21 | 51.11342068 | 42.42414 | 1 | 0.1 |
| 22 | 85.18903447 | 79.56656 | 1.07 | 0.2 |
| 23 | 109.0419641 | 99.63709 | 1 | 0.1 |
| 24 | 122.6722096 | 112.2451 | 1 | 0.1 |
| 25 | 143.1175779 | 132.1452 | 1 | 0.1 |
| 26 | 163.5629462 | 153.1358 | 1 | 0.1 |
| 27 | 238.5292965 | 228.5111 | 1 | 0.1 |
| 28 | 255.5671034 | 246.1963 | 1 | 0.1 |
| 29 | 272.6049103 | 262.9274 | 1 | 0.1 |
| 30 | 272.6049103 | 264.972 | 1 | 0.1 |
| 31 | 357.7939448 | 348.0142 | 1 | 0.1 |

**Tablel B-4** : Experimental data for ion exchange between $Ni^{2+}$ and $Ca^{2+}$-form of clinoptilolite at 25˚C.

| initial concentration ($10^{-3}$ M) | Final concentration ($10^{-3}$ M) | Mass used (g) | Volume used (L) |
|---|---|---|---|
| 3.407561 | 2.129726 | 1 | 0.1 |
| 6.815123 | 4.940964 | 1 | 0.1 |
| 6.815123 | 4.361679 | 1 | 0.1 |
| 6.815123 | 4.702435 | 1 | 0.1 |
| 13.63025 | 10.69974 | 1 | 0.1 |
| 20.44537 | 16.40741 | 1 | 0.1 |
| 40.89074 | 34.14377 | 1 | 0.1 |
| 42.59452 | 37.05723 | 1 | 0.1 |
| 102.2268 | 91.49302 | 1 | 0.1 |
| 136.3025 | 124.376 | 1 | 0.1 |
| 340.7561 | 322.1849 | 1 | 0.1 |
| 340.7561 | 319.4589 | 1 | 0.1 |
| 425.9452 | 413.1668 | 1 | 0.1 |
| 613.361 | 592.9157 | 1 | 0.1 |
| 1363.025 | 1349.394 | 1 | 0.1 |
| 1703.781 | 1679.928 | 1 | 0.1 |
| 2555.671 | 2540.337 | 1 | 0.1 |

**Tablel B-5:** Experimental data for ion exchange between $Ni^{2+}$ and $Na^{+}$-form of clinoptilolite at different temperatures

| Sample number | Initial Concentration ($\times 10^{-3}$ molar) | Final concentration at different temperatures ($\times 10^{-3}$ molar) | | | | Mass Used (g) | Volume Used (L) |
|---|---|---|---|---|---|---|---|
| | | 35˚C | 50˚C | 60˚C | 75˚C | | |
| 1 | 0.340756 | 0.017038 | 0.017038 | 0.017038 | 0.017038 | 1.00 | 0.10 |
| 2 | 0.340756 | 0.025557 | 0.017038 | 0.017038 | 0.017038 | 1.00 | 0.10 |
| 3 | 0.681512 | 0.127784 | 0.07667 | 0.051113 | 0.020445 | 1.00 | 0.10 |
| 4 | 0.681512 | 0.136302 | 0.074966 | 0.054521 | 0.020445 | 1.00 | 0.10 |
| 5 | 1.022268 | 0.29305 | 0.267494 | 0.119265 | 0.073263 | 1.00 | 0.10 |
| 6 | 1.022268 | 0.289643 | 0.289643 | 0.132895 | 0.073263 | 1.00 | 0.10 |
| 7 | 1.363025 | 0.630399 | 0.567359 | 0.255567 | 0.182305 | 1.00 | 0.10 |
| 8 | 1.363025 | 0.63551 | 0.562248 | 0.277716 | 0.185712 | 1.00 | 0.10 |
| 9 | 1.703781 | 0.937079 | 0.853594 | 0.473651 | 0.357794 | 1.00 | 0.10 |
| 10 | 1.703781 | 0.971155 | 0.843371 | 0.494096 | 0.39187 | 1.00 | 0.10 |

**Tablel B-6:** Experimental data for ion exchange between $Ni^{2+}$ and $K^{+}$-form of clinoptilolite at different temperatures

| Sample number | Initial Concentration ($\times 10^{-3}$ molar) | Final concentration at different temperatures ($\times 10^{-3}$ molar) | | | | Mass Used (g) | Volume Used (L) |
|---|---|---|---|---|---|---|---|
| | | 35˚C | 50˚C | 60˚C | 75˚C | | |
| 1 | 0.340756 | 0.13971 | 0.093708 | 0.068151 | 0.051113 | 1.00 | 0.10 |
| 2 | 0.340756 | 0.136302 | 0.102227 | 0.073263 | 0.068151 | 1.00 | 0.10 |
| 3 | 0.681512 | 0.361202 | 0.349275 | 0.221491 | 0.166971 | 1.00 | 0.10 |
| 4 | 0.681512 | 0.408907 | 0.364609 | 0.231714 | 0.172082 | 1.00 | 0.10 |
| 5 | 1.022268 | 0.800777 | 0.816111 | 0.764998 | 0.732626 | 1.00 | 0.10 |
| 6 | 1.022268 | 0.800777 | 0.799073 | 0.771813 | 0.732626 | 1.00 | 0.10 |
| 7 | 1.363025 | 1.073382 | 1.080197 | 0.971155 | 0.88767 | 1.00 | 0.10 |
| 8 | 1.363025 | 1.083605 | 1.09042 | 0.971155 | 0.903004 | 1.00 | 0.10 |
| 9 | 1.703781 | 1.380062 | 1.345987 | 1.274428 | 1.192646 | 1.00 | 0.10 |
| 10 | 1.703781 | 1.38347 | 1.368136 | 1.27102 | 1.213092 | 1.00 | 0.10 |

**Tablel B-7**: Experimental data for ion exchange between $Ni^{2+}$ and Natural - form of clinoptilolite at different temperatures.

| Sample number | Initial Concentration ($\times 10^{-3}$ molar) | Final concentration at different temperatures ($\times 10^{-3}$ molar) | | | | Mass Used (g) | Volume Used (L) |
|---|---|---|---|---|---|---|---|
| | | 35˚C | 50˚C | 60˚C | 75˚C | | |
| 1 | 0.340756 | 0.221491 | 0.221491 | 0.187416 | 0.187416 | 1.00 | 0.10 |
| 2 | 0.340756 | 0.228307 | 0.238529 | 0.170378 | 0.170378 | 1.00 | 0.10 |
| 3 | 0.681512 | 0.460021 | 0.533283 | 0.420834 | 0.43276 | 1.00 | 0.10 |
| 4 | 0.681512 | 0.477059 | 0.517949 | 0.43276 | 0.420834 | 1.00 | 0.10 |
| 5 | 1.022268 | 0.903004 | 0.933672 | 0.931968 | 1.008638 | 1.00 | 0.10 |
| 6 | 1.022268 | 0.923449 | 0.931968 | 0.933672 | 1.008638 | 1.00 | 0.10 |
| 7 | 1.363025 | 1.126199 | 1.165386 | 1.063159 | 1.073382 | 1.00 | 0.10 |
| 8 | 1.363025 | 1.139829 | 1.170497 | 1.069974 | 1.078493 | 1.00 | 0.10 |
| 9 | 1.703781 | 1.260798 | 1.466955 | 1.078493 | 1.069974 | 1.00 | 0.10 |
| 10 | 1.703781 | 1.311911 | 1.463548 | 1.114273 | 1.063159 | 1.00 | 0.10 |

**Tablel B-8:** Experimental data for ion exchange between $Ni^{2+}$ and $Ca^{+}$-form of clinoptilolite at different temperatures.

| Sample number | Initial Concentration ($\times 10^{-3}$ molar) | Final concentration at different temperatures ($\times 10^{-3}$ molar) | | | | Mass Used (g) | Volume Used (L) |
|---|---|---|---|---|---|---|---|
| | | 35˚C | 50˚C | 60˚C | 75˚C | | |
| 1 | 0.340756 | 0.221491 | 0.221491 | 0.187416 | 0.187416 | 1.00 | 0.10 |
| 2 | 0.340756 | 0.228307 | 0.238529 | 0.170378 | 0.170378 | 1.00 | 0.10 |
| 3 | 0.681512 | 0.460021 | 0.533283 | 0.420834 | 0.43276 | 1.00 | 0.10 |
| 4 | 0.681512 | 0.477059 | 0.517949 | 0.43276 | 0.420834 | 1.00 | 0.10 |
| 5 | 1.022268 | 0.903004 | 0.933672 | 0.931968 | 1.008638 | 1.00 | 0.10 |
| 6 | 1.022268 | 0.923449 | 0.931968 | 0.933672 | 1.008638 | 1.00 | 0.10 |
| 7 | 1.363025 | 1.126199 | 1.165386 | 1.063159 | 1.073382 | 1.00 | 0.10 |
| 8 | 1.363025 | 1.139829 | 1.170497 | 1.069974 | 1.078493 | 1.00 | 0.10 |
| 9 | 1.703781 | 1.260798 | 1.466955 | 1.078493 | 1.069974 | 1.00 | 0.10 |
| 10 | 1.703781 | 1.311911 | 1.463548 | 1.114273 | 1.063159 | 1.00 | 0.10 |

## Appendix C

Plots of a linear relationship between lnK and the reciprocal of the temperature

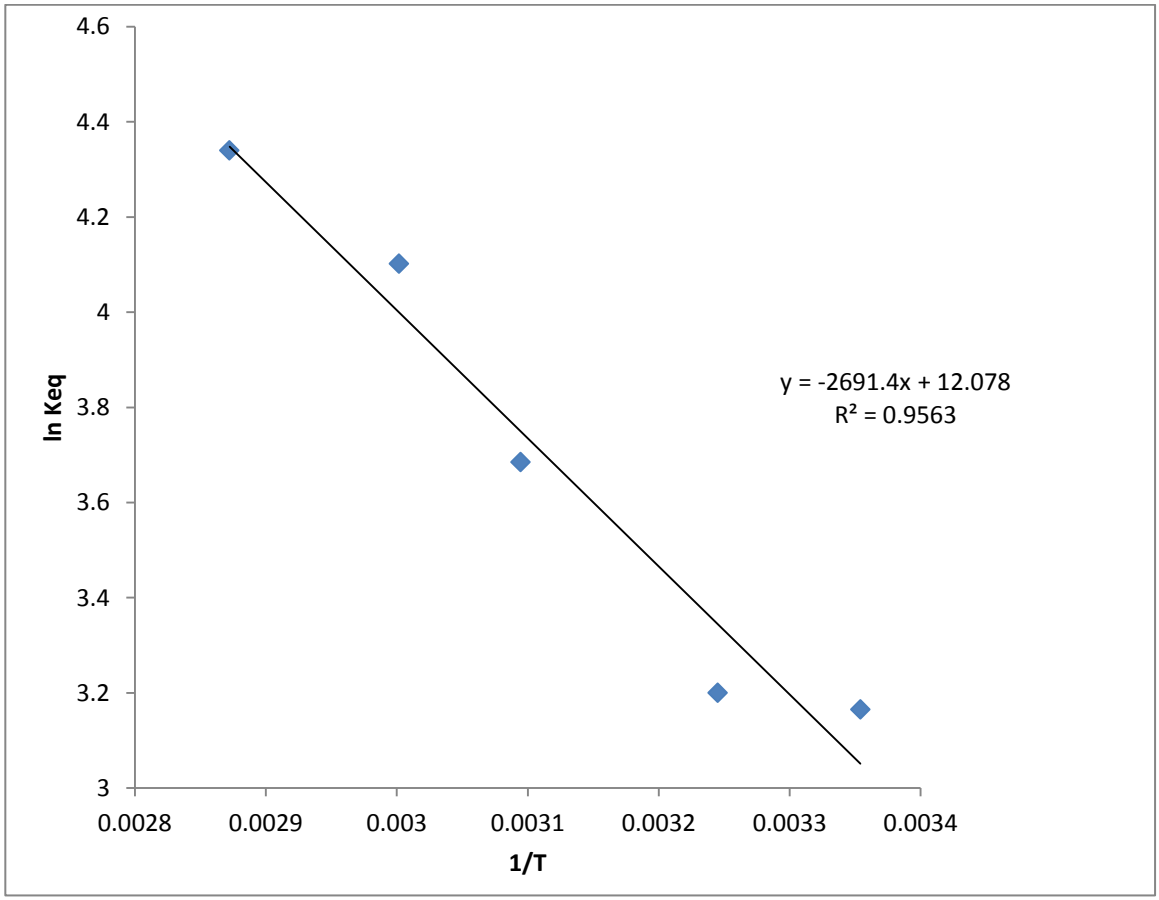



**Figure C- 1**: Plot of lnKeq versus 1/T (For Natural clinoptilolite).

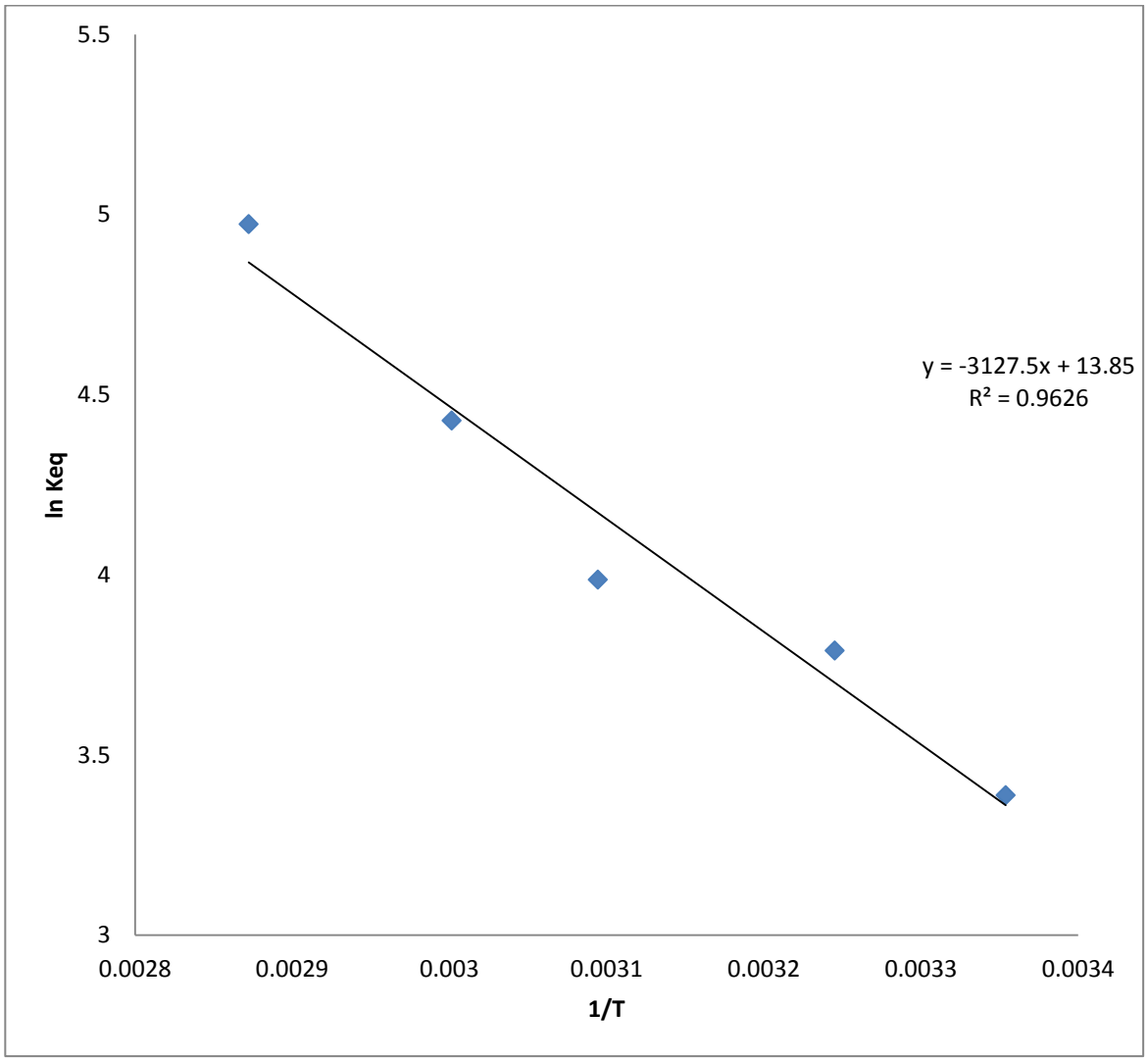



**Figure C- 2**: Plot of lnKeq versus 1/T (For Na-form of clinoptilolite).

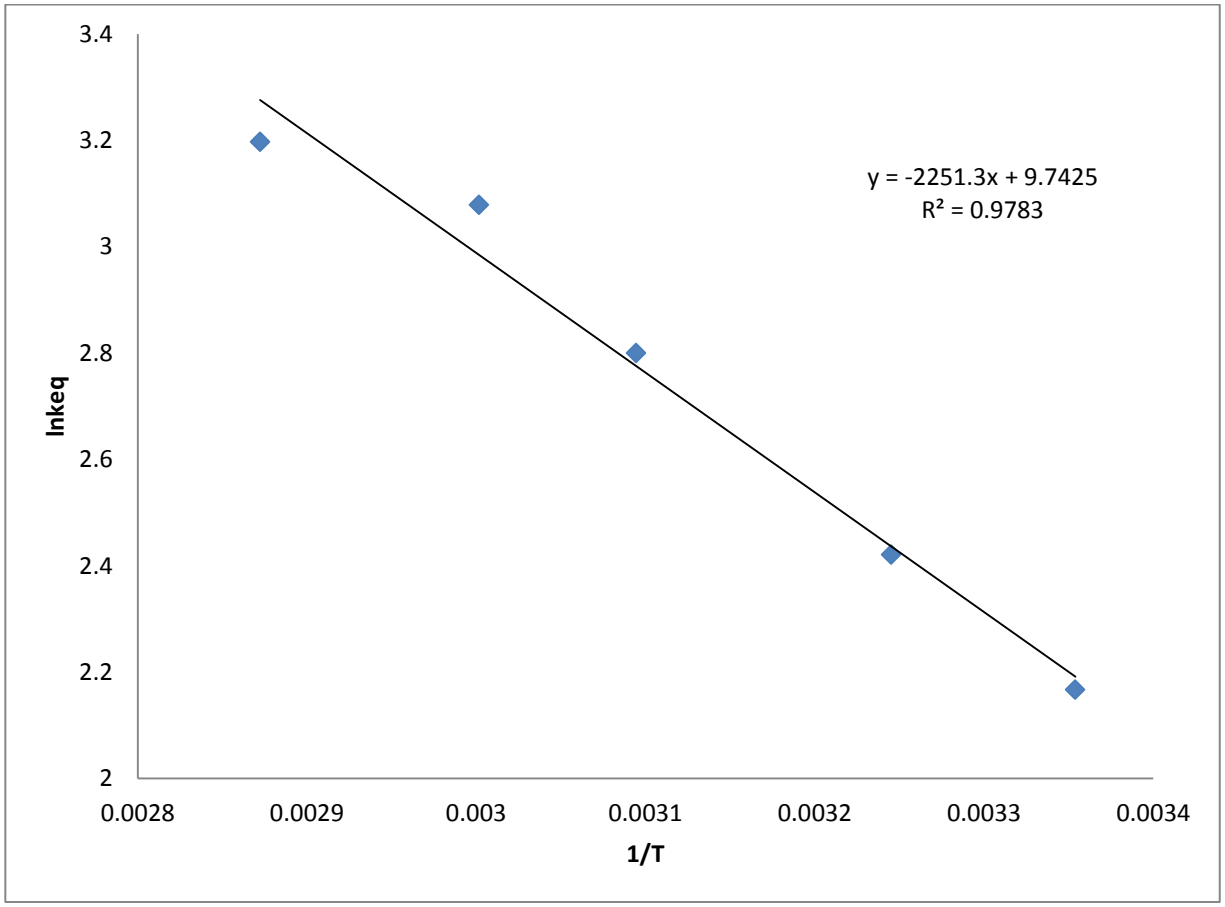



**Figure C- 3**: Plot of lnKeq versus 1/T (For K-form of clinoptilolite).

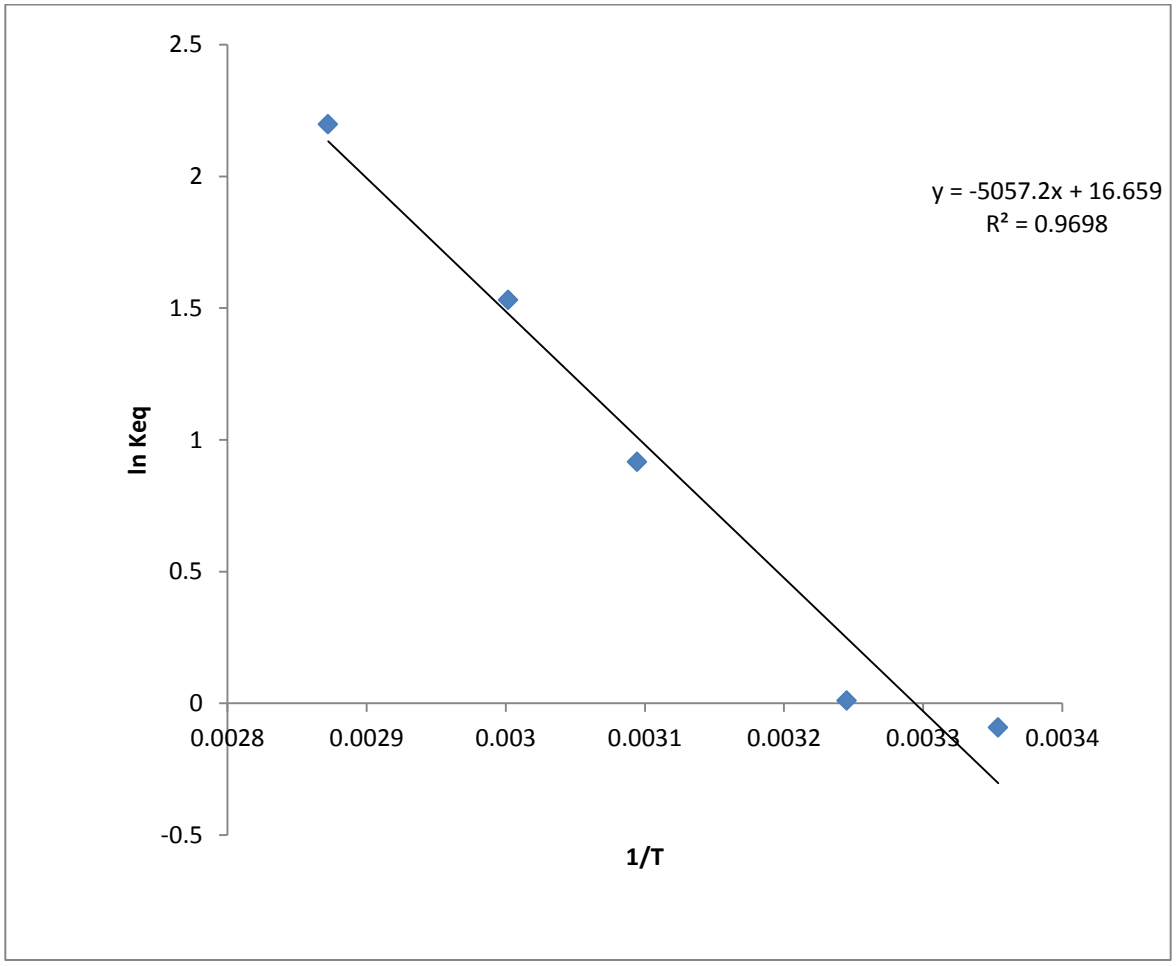



**Figure C- 4**: Plot of lnKeq versus 1/T (For Ca-form of clinoptilolite).

## Appendix D

The values of Keq were obtained by ploting ln(Cz/Cs) against Cz.

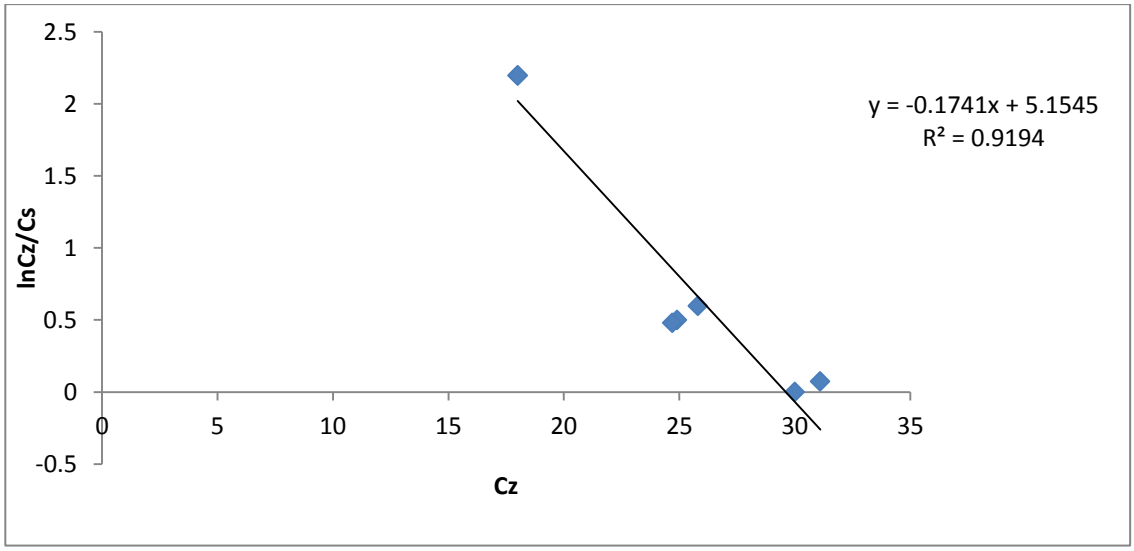



**Figure D-1**: Plot of ln(Cz/Cs) versus Cz (For Na-form at 25˚C).

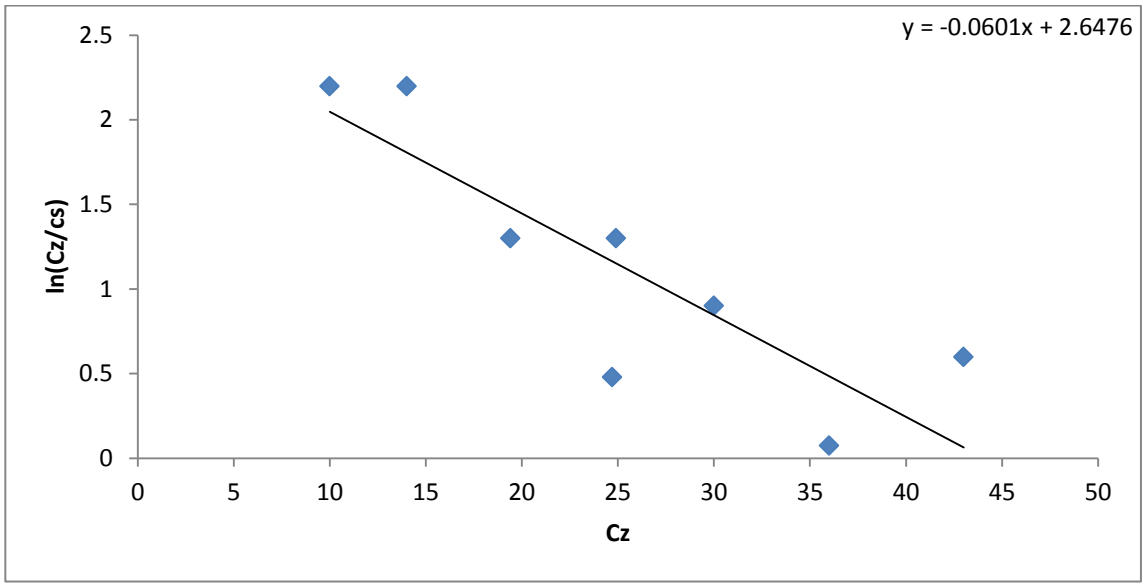



**Figure D-2**: Plot of ln(Cz/Cs) versus Cz (For Na-form at 35˚C).

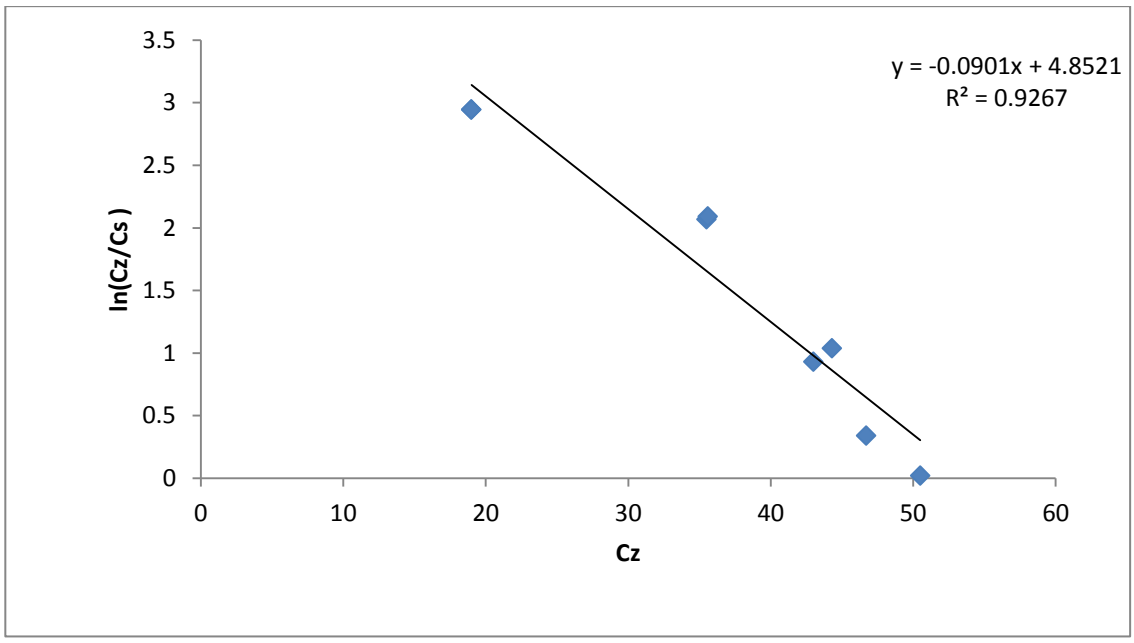



**Figure D-3**: Plot of ln(Cz/Cs) versus Cz (For Na-form at 50˚C).

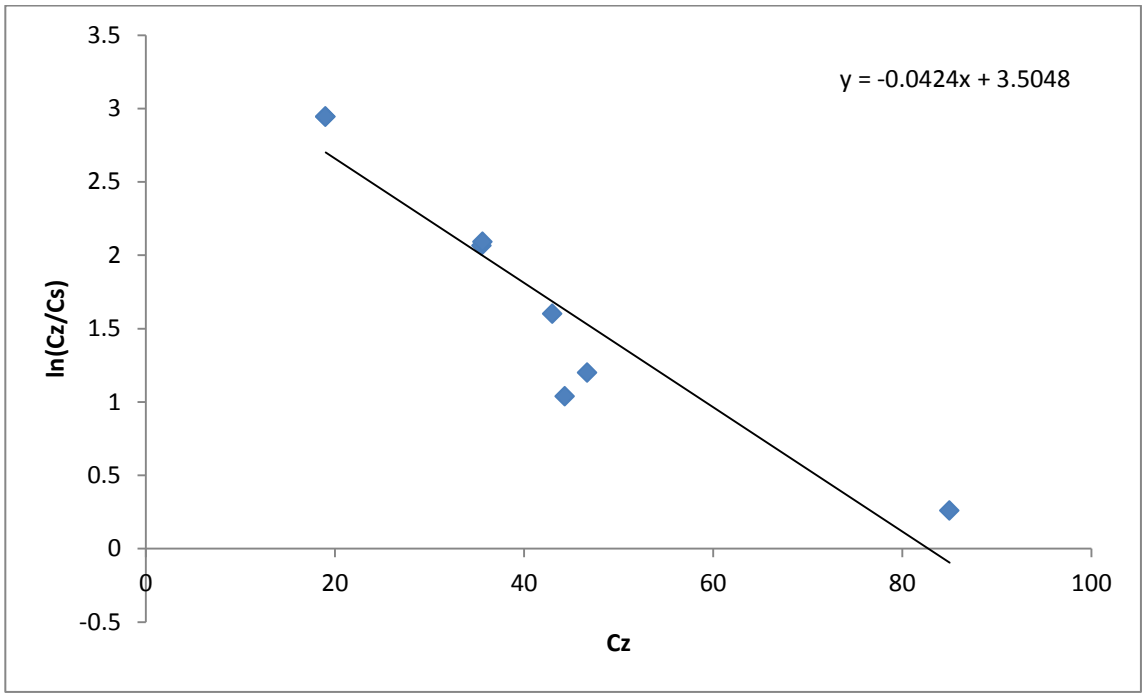



**Figure D-4**: Plot of ln(Cz/Cs) versus Cz (For Na-form at 60˚C).

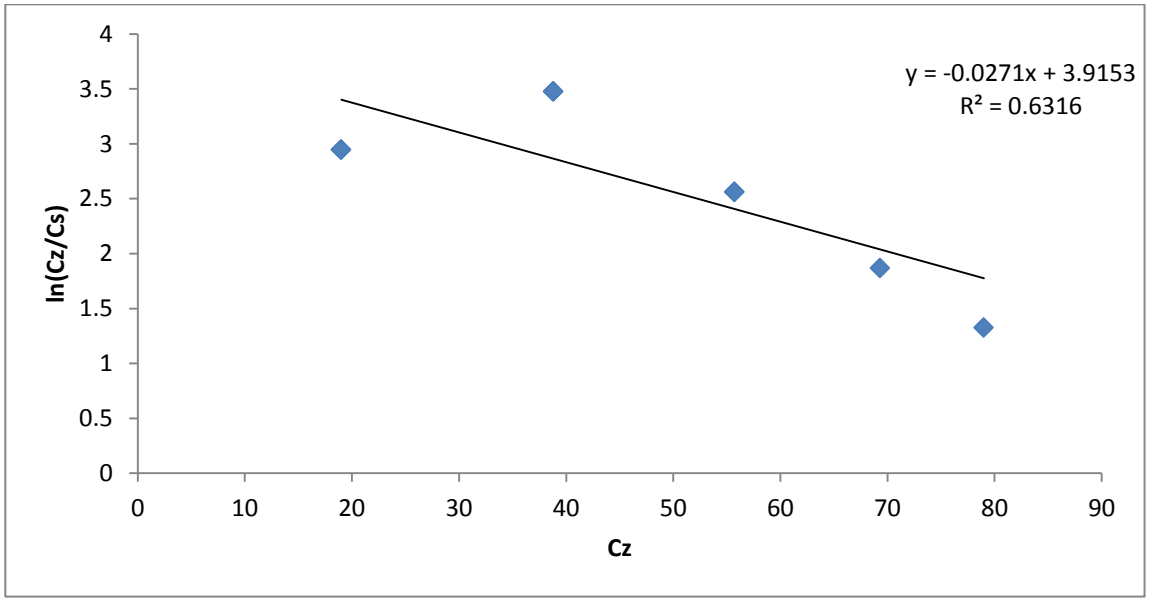



**Figure D-5**: Plot of ln(Cz/Cs) versus Cz (For Na-form at 75˚C).

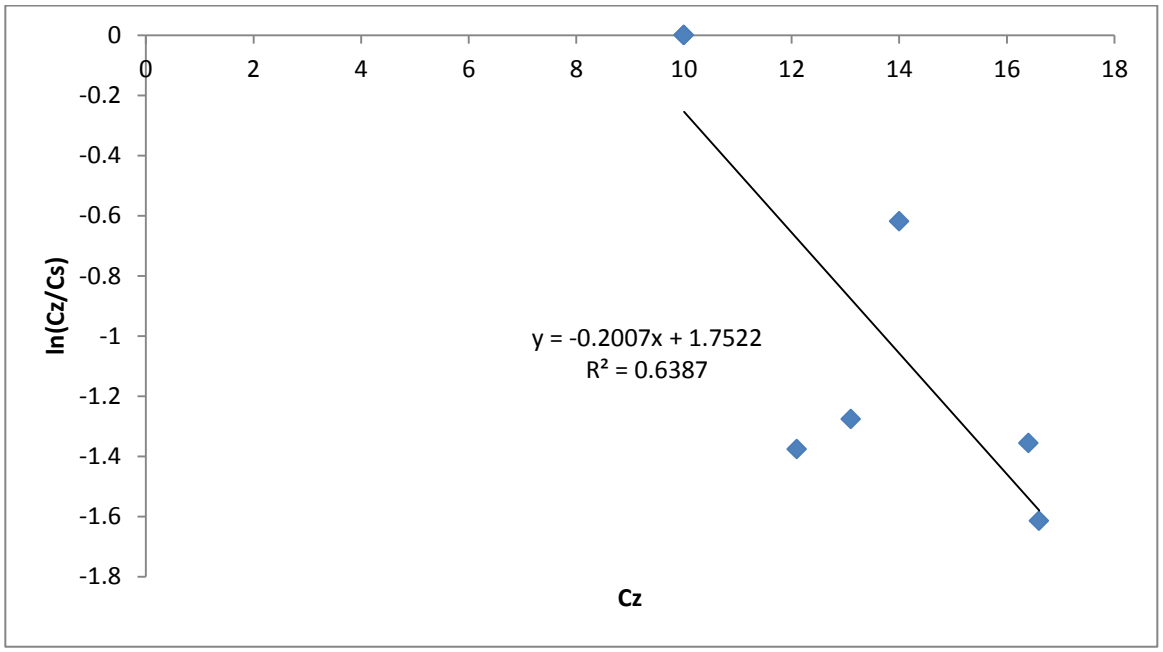



**Figure D-6**: Plot of ln(Cz/Cs) versus Cz (For K-form at 25˚C).

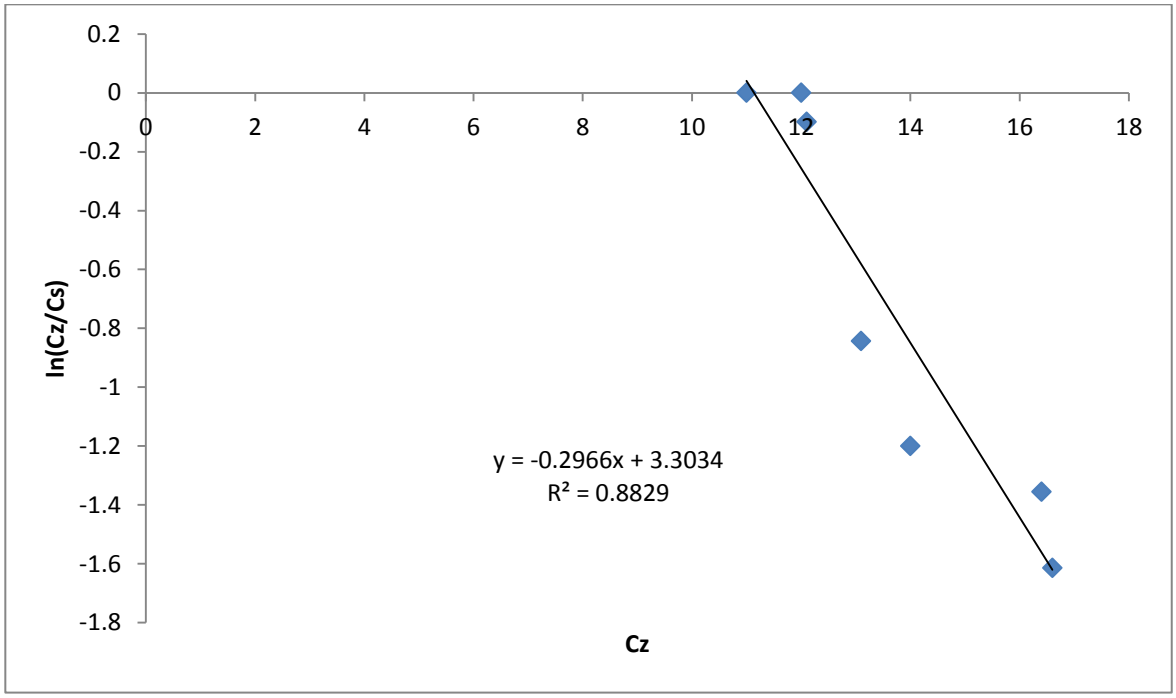



**Figure D-7**: Plot of ln(Cz/Cs) versus Cz (For K-form at 35˚C).

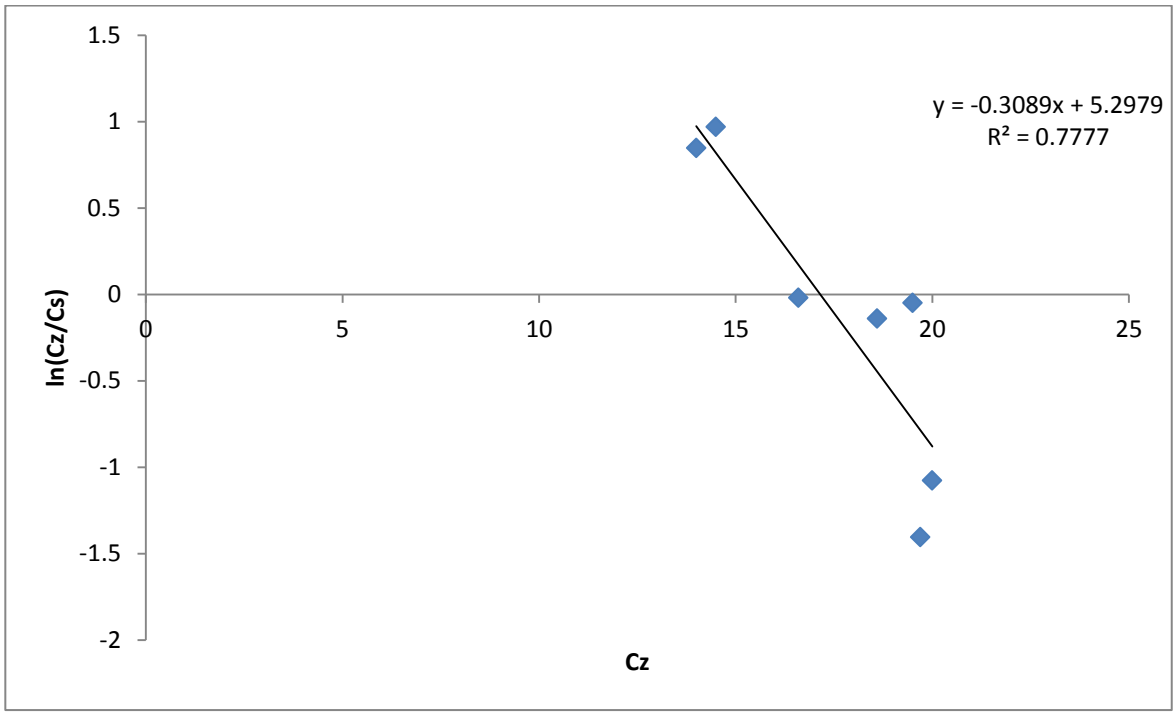



**Figure D-8**: Plot of ln(Cz/Cs) versus Cz (For K-form at 50˚C).

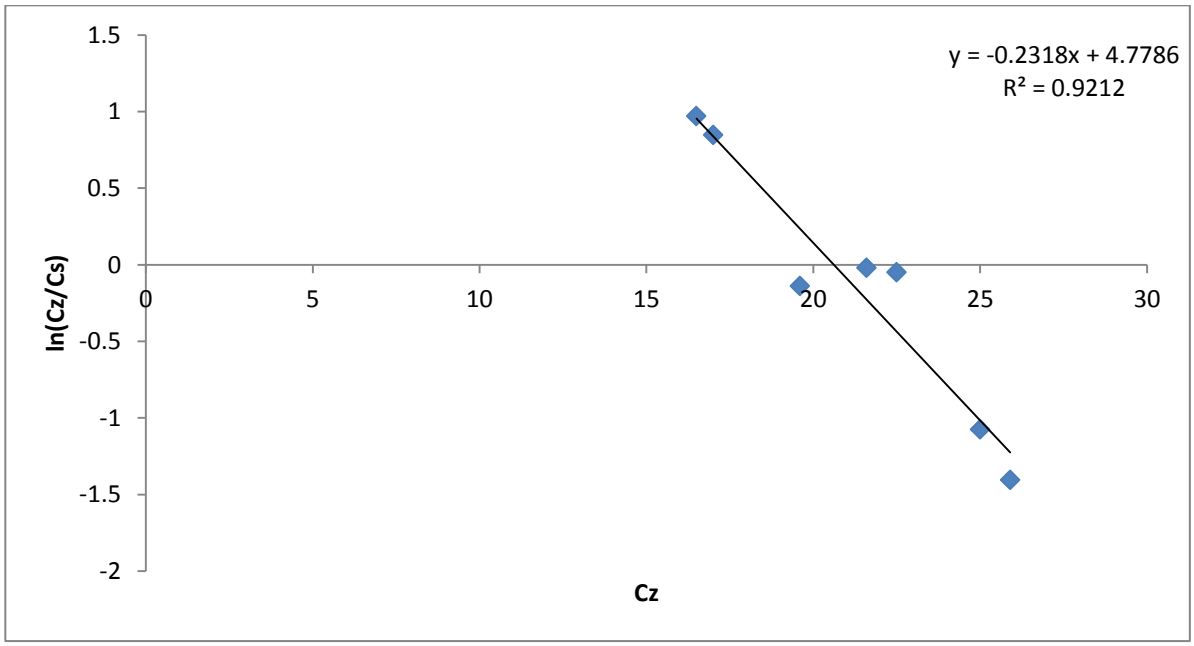



**Figure D-9**: Plot of ln(Cz/Cs) versus Cz (For K-form at 60˚C).

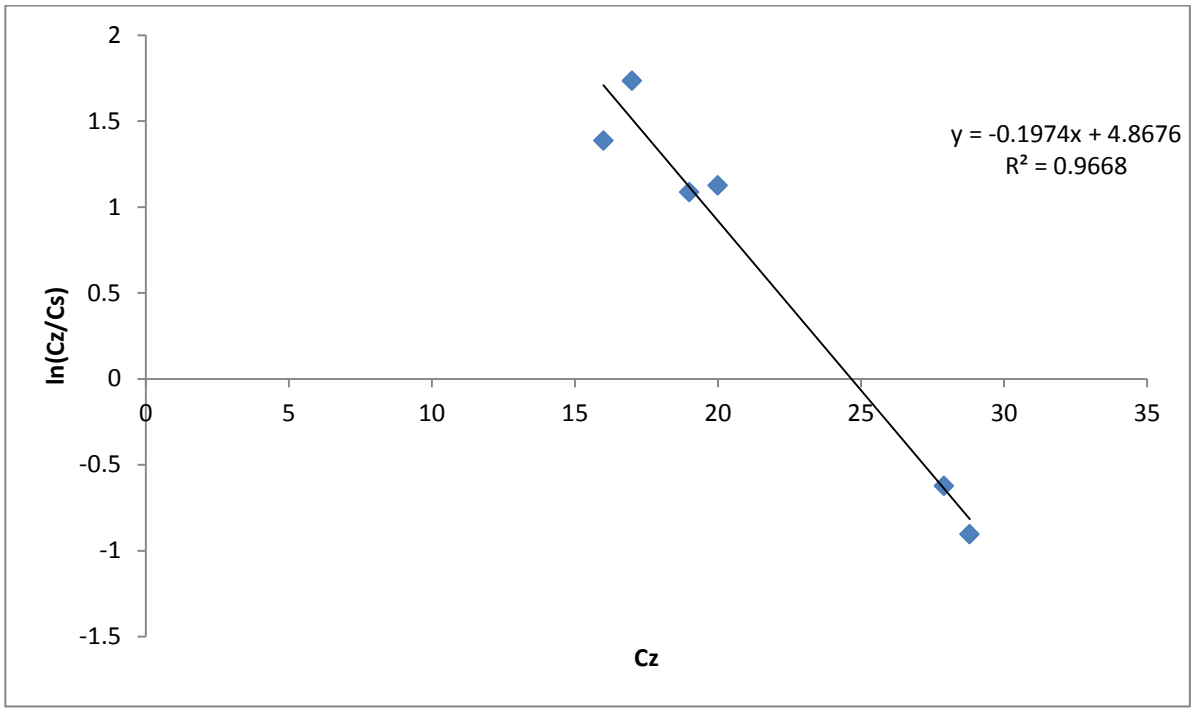



**Figure D-10**: Plot of ln(Cz/Cs) versus Cz (For K-form at 75˚C).

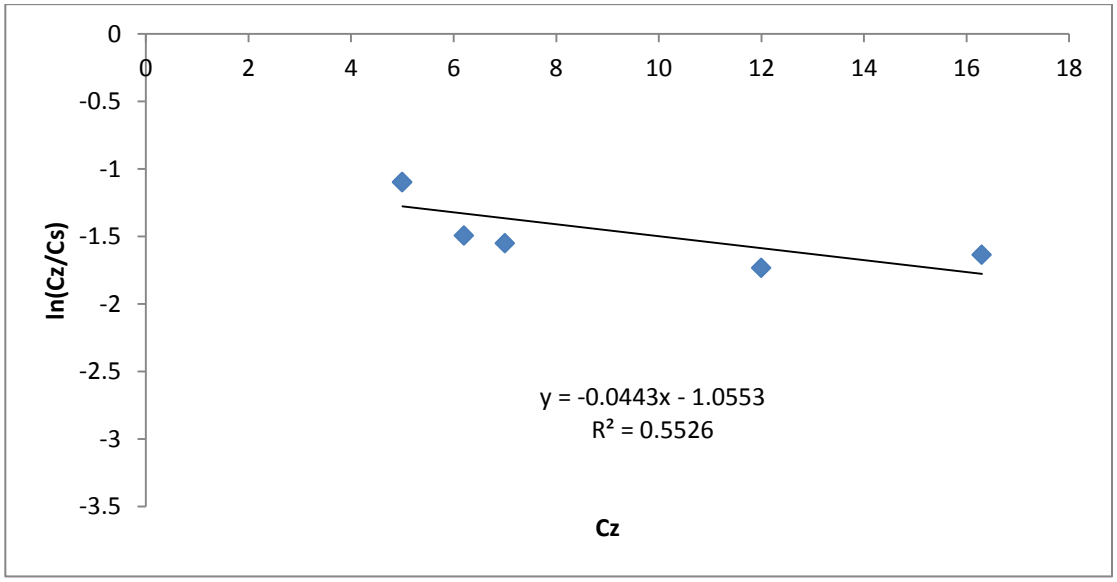



**Figure D-11**: Plot of ln(Cz/Cs) versus Cz (For Ca-form at 25˚C)

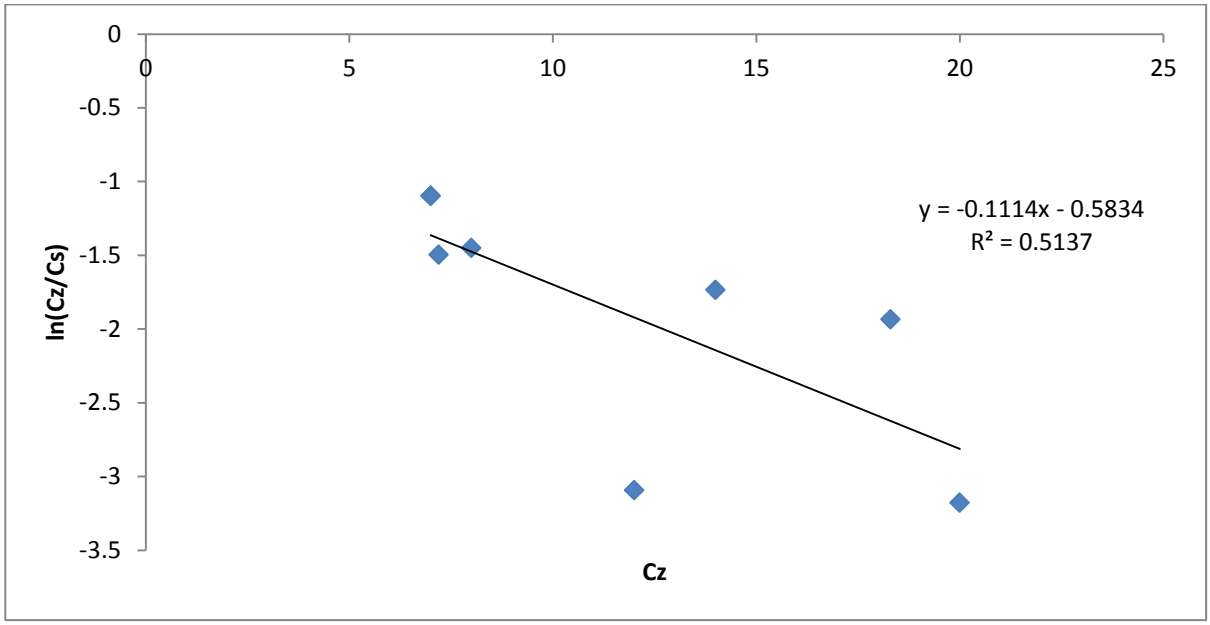



**Figure D-12**: Plot of ln(Cz/Cs) versus Cz (For Ca-form at 35˚C).

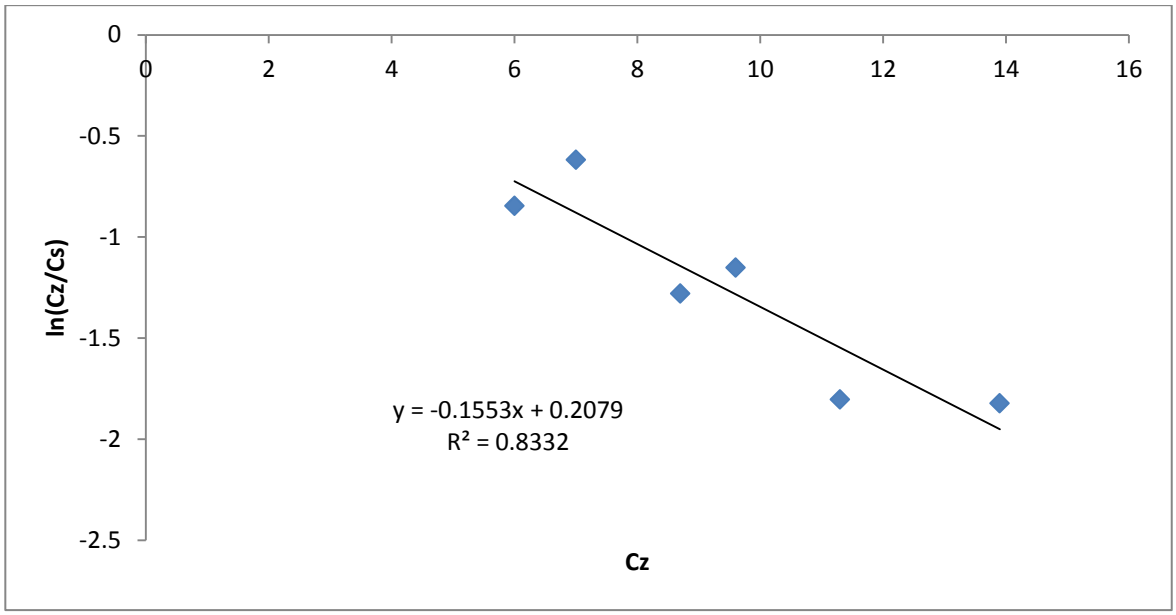



**Figure D-13**: Plot of ln(Cz/Cs) versus Cz (For Ca-form at 50˚C)

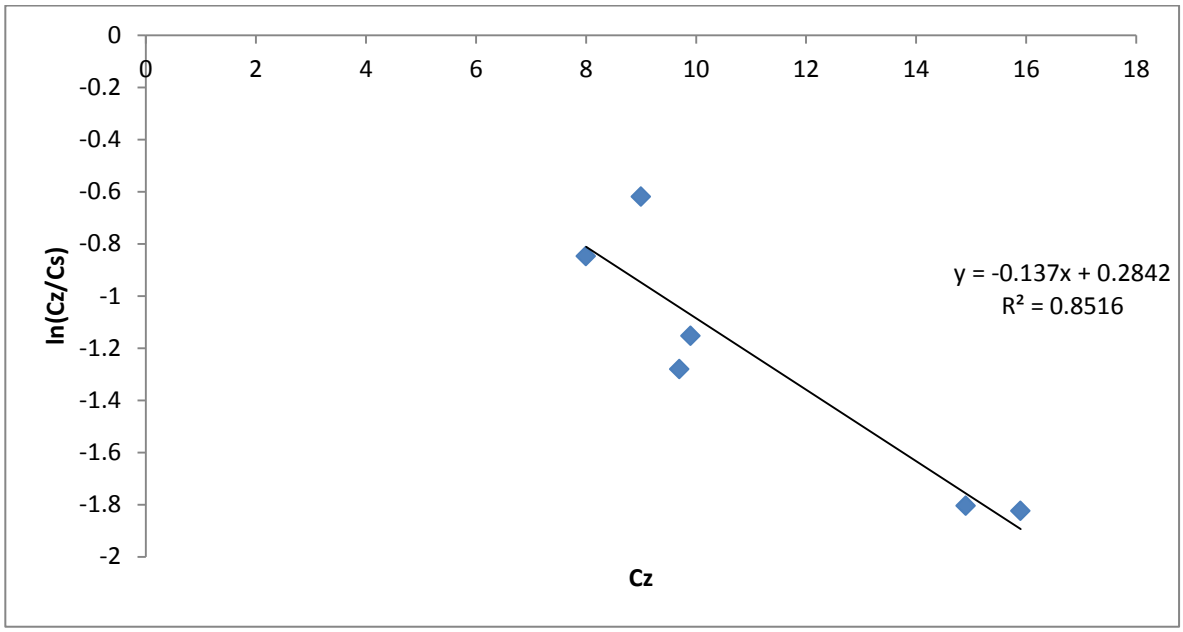



**Figure D-14**: Plot of ln(Cz/Cs) versus Cz (For Ca-form at 60˚C).

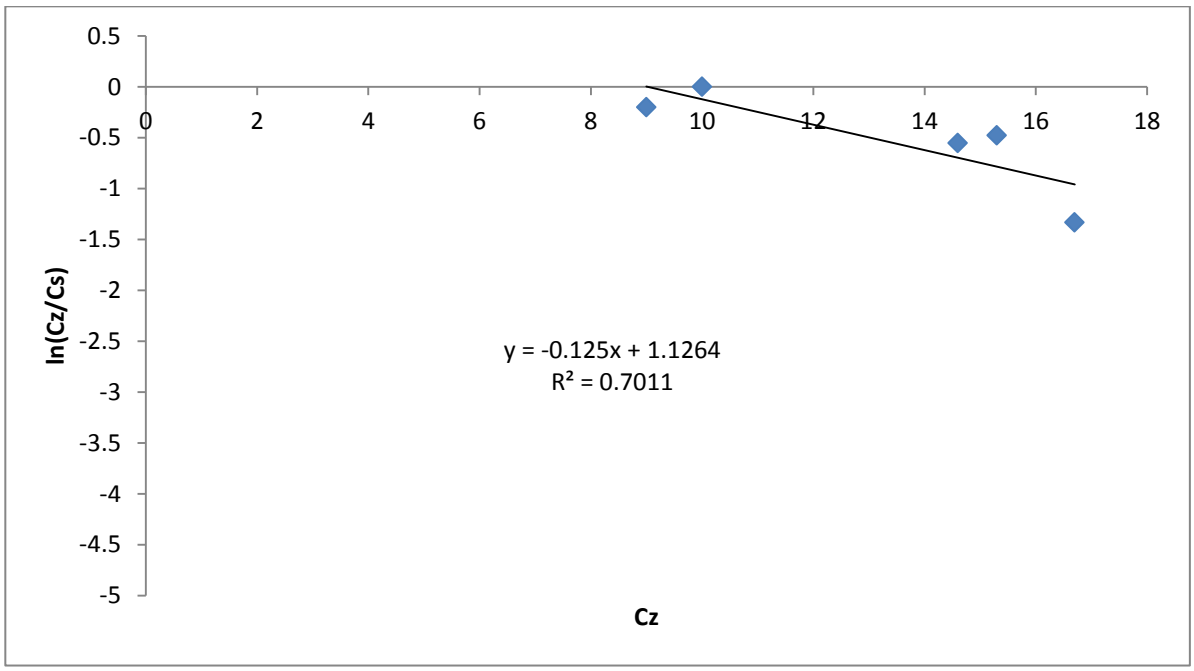



**Figure D-15**: Plot of ln(Cz/Cs) versus Cz (For Ca-form at 75˚C).

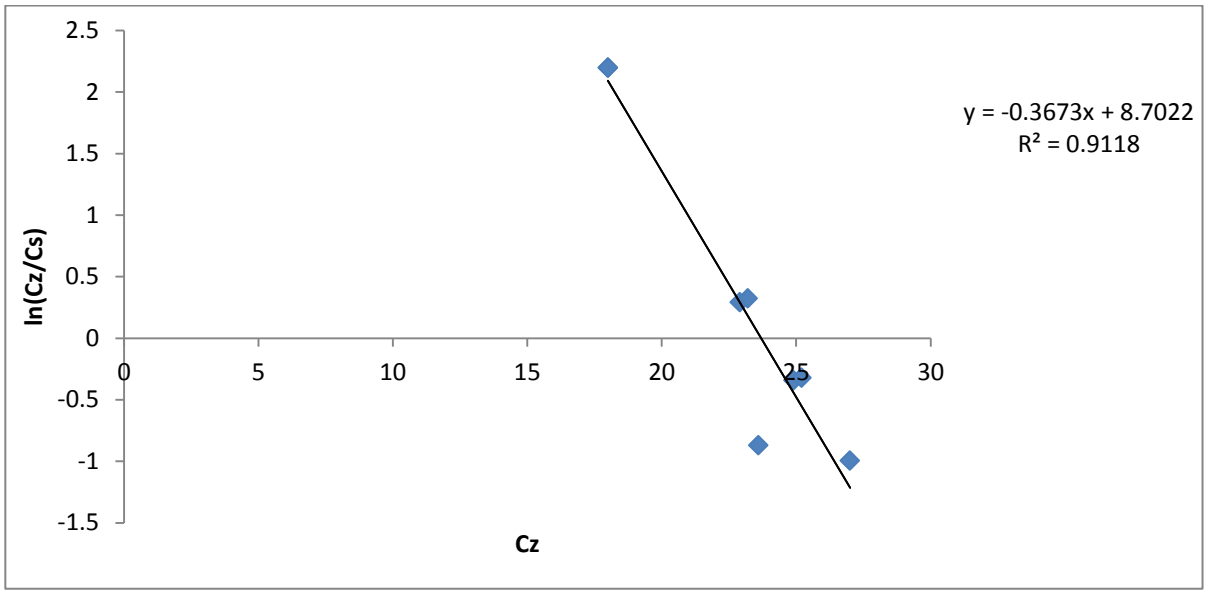



**Figure D-16**: Plot of ln(Cz/Cs) versus Cz (For Natural-form at 25˚C).

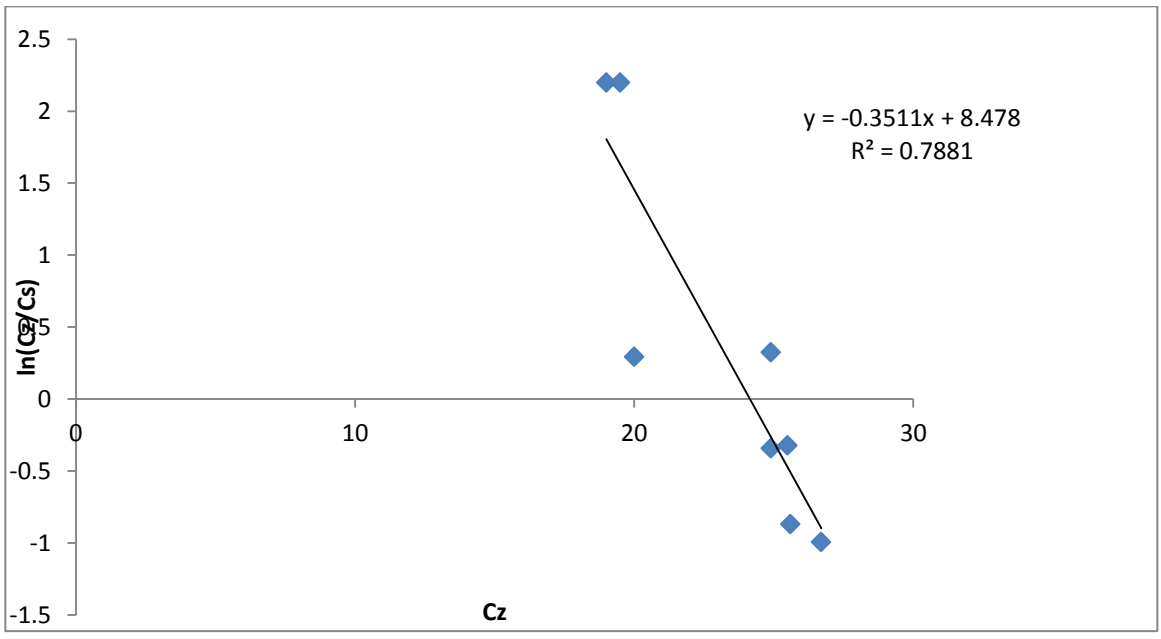



**Figure D-17**: Plot of ln(Cz/Cs) versus Cz (For Natural-form at 35˚C).

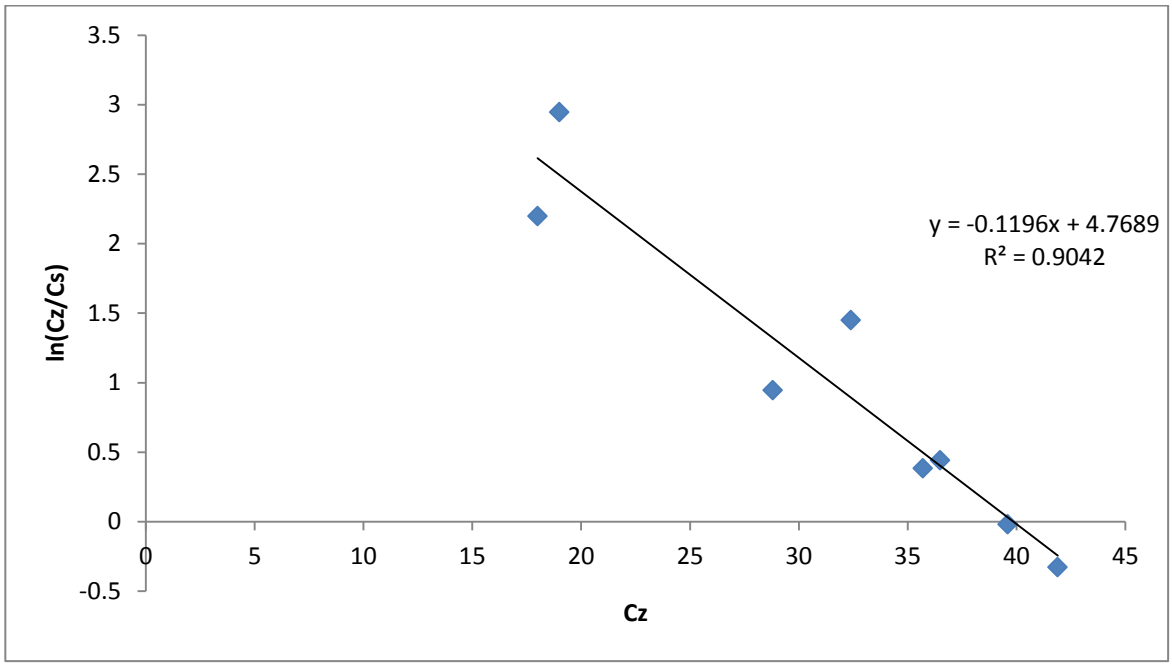



**Figure D-18**: Plot of ln(Cz/Cs) versus Cz (For Natural-form at 50˚C).

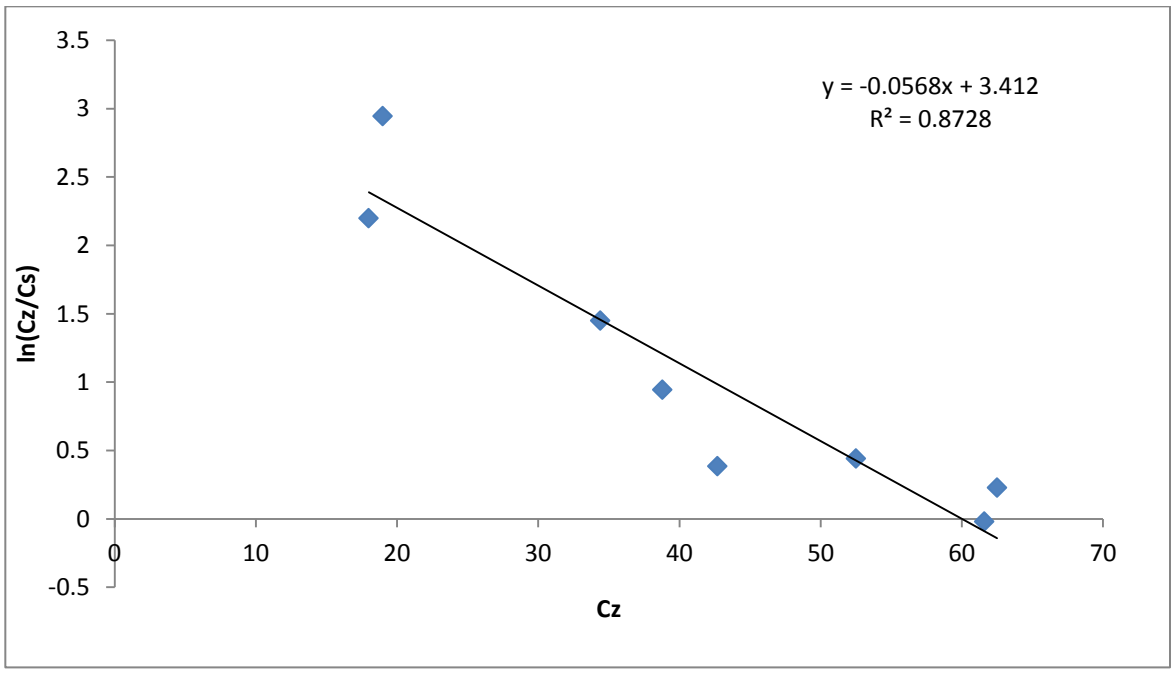



**Figure D-19**: Plot of ln(Cz/Cs) versus Cz (For Natural-form at 60˚C).

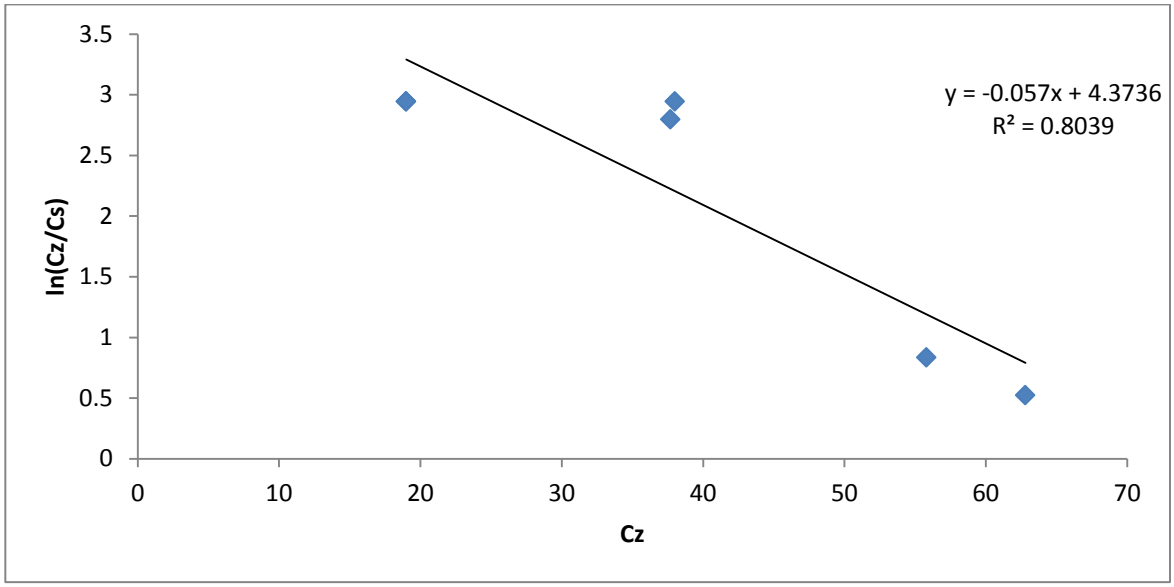



**Figure D-20**: Plot of ln(Cz/Cs) versus Cz (For Natural-form at 75˚C).