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# The removal of heavy metals from wastewater using South African clinoptilolite

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# THE REMOVAL OF HEAVY METALS FROM WASTEWATER USING SOUTH AFRICAN CLINOPTILOLITE.

Kutemba Kaina Kapanji

'A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Masters of Science in Engineering.'

Johannesburg, 2009.

## DECLARATION

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

_____

(Signature of candidate)

_____ day of _____ year _____

## ABSTRACT

This research concerns the further characterisation and establishment of adsorption behaviour of the South African clinoptilolite. Synthetic single- and multi-component wastewaters were used, and experiments conducted in both batch and column systems at 25$^{o}$C ± 2. Wastewaters containing heavy metals ions $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cr^{3+}$, were used at different feed concentrations (50 - 500 mg/L), and adsorbed onto natural and homoionic ($Na^{+}$, $K^{+}$, $Ca^{2+}$, $NH^{+}_{4}$) forms of the zeolite. The $Na^{+}$-form clinoptilolite had an improved cation exchange capacity over the natural one, and the selectivity series of metal ions by these two forms varied. Brunauer Emmett Teller surface area analysis carried out also confirms that preconditioning clinoptilolite with $Na^{+}$ ions results in an increase in pore diameter, allowing for easier diffusion of ions and more adsorption. An atomic adsorption spectrophotometer (AAS) was used to analyse metal ions in solution. Adsorption efficiencies with over 75% of metal ions adsorbed in the first hour of contact were recorded, and complete adsorption equilibrium being reached in 4 hrs. Regeneration of $Na^{+}$-form and natural clinoptilolite (using 0.5M NaCl stripping solution) initially showed an increase in loading capacities, then a decrease with the subsequent cycles. A comparison between two particle sizes revealed that smaller particle sized clinoptilolite have slightly higher adsorption capacities. The equilibrium data also fitted well with the linear form of the Langmuir and Freundlich isotherms at lower concentrations of 50 mg/L.

## DEDICATIONS

To my Abba Father in heaven

&

The entire Kapanji family

(Those gone before us, those with us and those not yet)

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# LIST OF SYMBOLS

| | |
|---|---|
| a | bonding strength used in Langmuir isotherm (L/mg). |
| b | Langmuir constant related to adsorption energy (L/mg). |
| $C_o$ | initial adsorbate concentration (mg/L). |
| $C_e$ | final aqueous phase concentration (mg/L). |
| $K_{ad}$ | adsorption rate constant for the adsorption equilibrium ($min^{-1}$). |
| $K_f$ | Freundlich constant for adsorption capacity (mg/g). |
| $K_L$ | Langmuir isotherm adsorption maximum (L/g). |
| m | mass of zeolite (g). |
| n | Freundlich constant for adsorption intensity (L/mg). |
| pH | negative log of hydrogen ions in solution. |
| $q_e$ | loading capacity at equilibrium (mg/g). |
| V | volume of solution (mL). |

# 1.0 CHAPTER ONE

## 1.1 Background and motivation

It has been stated that "Matter can neither be created nor destroyed, but if no one is looking, it may be thrown away" (Grimshaw and Harland, 1975, p.1). The introduction of hazardous wastes into the environment has become a worldwide concern including in developing countries. This has been accelerated in the last century by the many anthropogenic interferences (Dal Bosco et al., 2005; Pitcher et al., 2004), the establishment of many industries (Inglezakis et al., 2007; Argun, 2008), in Africa, and particularly the Republic of South Africa. For instance, acid mine drainage water from mine waste is the largest environmental problem facing the mining industry today (Mohamed et al., 1992), and at the same time, it also constitutes a major resource for the production of high quality drinking water through the process of precipitation and desalination (Healing, 2008). Acid mine drainage water is formed by the oxidation of sulphide minerals and reaction with water yielding sulphuric acid, which in turn increases the solubility of heavy metals and increases their mobility (Mohamed et al., 1992), and they easily find their way into 'receiving' waters.

Over a period of time, these accumulated pollutants become a potential hazard to human health, animals and ecological environments (Alvarez-Ayuso et al., 2003;

Kocaoba et al., 2007). To counteract such activities, there are international and national treaties, laws and regulations such as the 1998 International Kyoto protocol (United Nations Framework Convention on Climate Change, 2007), and the 1999 South African National Environmental Management Act (NEMA) (South African Government Information, 2004), all aimed at strictly finding ways of reducing, monitoring and controlling pollution, in its different forms and establishing sustainable wastewater treatment strategies (Gedik and Imamoglu, 2008).

It was only during the decade of the 1960s, that terms such as 'water' and 'air pollution', 'protection of environment' and 'ecology' became household words (Ramalho, 1997; Deunert et al., 2006). Therefore, over the years, many wastewater treatment processes have been developed such as chromatography, electrodialysis, adsorption, membrane technologies and ion exchange. Some of these processes are very cost effective, whilst others although necessary have high capital and operation costs and the problem of residual disposal. Due to the economic pressures experienced by many companies to reduce operating and maintenance costs, many industries opt for economically feasible processes.

The use of ion exchange and adsorption processes in water pollution control, with the potential use of the natural zeolite, clinoptilolite, has been the focus of intensive research over the last few years in different countries by researchers such as Gunay et al., (2007), Panayotova and Velikov (2003), Oztas et al. (2008), Argun (2008), Inglezakis et al. (2004), Polat et al. (2004). This work has identified the great

potential clinoptilolite has in removing different heavy metals from wastewaters because of their high ion exchange capacities, simplicity in operation, minimal waste generation, abundance and low costs (Gedik and Imamoglu, 2008; Peric et al., 2004; Misaelides et al., 1994; Erdem et al., 2004; Inglezakis et al., 2004). Some of the established uses of South African clinoptilolite are in its use as a food additive in poultry diets, building stones, fertilizers and mainly in ammonia gas adsorption due to its high capacity for this gas (Polat et al., 2004; Koon and Kaufman, 1975). It could also be applied on a much larger scale as an adsorbent of heavy metal ions from industrial wastewaters then regenerated and the metal ions initially adsorbed could be recovered and put back into process streams.

It is well established that the multiple uses of these zeolite materials are based on their physicochemical properties. These properties thus explain their wide range of applications in numerous agricultural and industrial areas (Rivera et al., 2000), and this is what makes them exhibit excellent metal ion adsorption capacities and selective properties. The sorption processes on zeolite particles on the whole however, are very varied and complex because of the unique porous structures, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds and other imperfections on the surface (Peric et al., 2004). Therefore, despite its promising results, the real applicability of these minerals to purify metal waste waters is still quite unknown (Leinonen and Lehto, 2001; Inglezakis et al., 2002). And as stated by Hamdaoui (2009), the sorption processes of ion exchange and adsorption are unit operations, which often share theory, although they have their

own special areas of concern. Therefore, more research on the South African clinoptilolite and its behaviour as an excellent metal ion adsorbent is of great interest in this dissertation.

Reducing metal ion levels in wastewaters to allowable limits can now be attained by use of effective and low cost, sustainable and environmentally friendly sorption processes. This makes adsorption and ion exchange very practical water pollution control methods, especially in developing countries.

## 1.2 Justification

The sorption process of adsorption and ion exchange is one technique that has received increasing interest over the years. There has also been a development of synthetic resins with excellent adsorption capacities and higher performances than natural zeolites, even after repeated regeneration cycles, but their drawback is that they are usually very expensive. Experiments have yielded good results and shown that zeolites have high adsorption capacities for pollutants and are able to reach adsorption equilibrium in very practical periods of time. It is also interesting to note that the clinoptilolite ores mined in different localities behave differently but successfully in their behaviour towards ion exchange and adsorption (Blanchard et al., 1984; Mercer et al., 1970; Erdem et al., 2004).

Thus, many researchers suggest the use of naturally occurring zeolites as discussed in section 1.1, for removing dissolved heavy metals from wastewaters (Blanchard et al., 1984). The South African natural zeolite clinoptilolite has also shown good adsorption capacities although, from the available literature, it has not been extensively researched and this work seeks to embark on this investigation.

## 1.3 Problem Statement

Heavy metal contamination of rivers and lakes and other water bodies has become a worldwide problem (Peng et al., 2009) in the 21$^{st}$ century. Modern society has therefore, become increasingly concerned by environmental issues related to industrial activity and so polluting industries have to conform to a more and more rigid environmental regulations (Hamdaoui, 2009).

In order to achieve this, techniques such as chemical precipitation, evaporation, adsorption, ion exchange and electrodialysis have been used to remove and recover heavy metals from wastewaters. Popuri et al. (2008) has emphasised that all other technologies apart from adsorption and ion exchange are ineffective and expensive. However, the latter two are cost effective, sustainable, environmentally friendly, and have abundant reserves such as the South African zeolite, clinoptilolite.

The added advantage of using clinoptilolite is that it exhibits improved adsorption capacities when chemically modified (Panayotova and Velikov, 2003).

## 1.4 Objectives of the research

This research will aim to further characterise the South African clinoptilolite and investigate some parameters that would favour clinoptilolite's adsorption abilities of heavy metals from industrial wastewaters.

a. In its natural form and state, does clinoptilolite have good selective properties to effectively adsorb heavy metals from wastewater effluents or would modification of the zeolite be necessary? How much can be gained by modifying the zeolite?
b. How long is its lifespan on repeated loading and regeneration?
c. What are some of the other limiting factors of the zeolite (i.e. the presence of impurities in the crystal lattice, initial sorbate concentrations) and how can they be used to improve the performance of the zeolite?

This will be achieved by:

a. determining whether pretreating the natural zeolite improves the selectivity properties or adsorption capacity of clinoptilolite.
b. analysing the zeolite capacity after regeneration.
c. determining whether the effluent's initial concentration or the other factors also have an impact on the performance of clinoptilolite.

d. determining the breakthrough points for a dynamic column before and after regeneration in order to evaluate its performance.
e. determining the applicability of Freundlinch and Langmuir isotherms and estimating the parameters characterizing the performance of the batch and column processes.

## 1.5 Layout of dissertation

In chapter two, the dissertation begins with a detailed literature review of the different wastewater technologies employed in the world today and also looks at the different adsorbents available. It also gives a brief explanation of the adsorption and ion exchange concepts and how these sorption processes play a major role in wastewater treatment. This chapter also covers the characteristics and properties of South African clinoptilolite and thoroughly discusses the different adsorbates being considered and their impact on human health, aquatic life and the environment.

Chapter three consists of a discussion on the experimental methods used for the adsorption of metal ions from synthesised wastewaters using South African clinoptilolite. Experiments included are for both batch and column systems, characterisation techniques of the zeolite and the sample preparation are also outlined in this chapter.

The results of the batch and the breakthrough curves for column adsorption of metal ions onto natural and modified clinoptilolite are discussed in chapter four. Characterisation studies of natural and modified clinoptilolite using an atomic adsorption spectrophotometer and x –ray diffractometer are considered and discussed. The effects of changing the adsorbate concentration and zeolite particle sizes on adsorption capacity are also included in this chapter. The regeneration and re-adsorption results are discussed, and the results look at the applicability of the Langmuir and Freundlich isotherms. The findings of BET surface area analysis together with the zeolites pore size distribution are recorded and discussed in great detail in this chapter too. Conclusions drawn from the results will be are summarised in chapter five of this dissertation.

# 2.0 CHAPTER TWO

## 2.1 Introduction

The United Nations Millennium Goal 7 was put forward to ensure environmental sustainability; to give every human being a right to gain access to safe drinking water and improved sanitation conditions. In the adoption of the Millennium Declaration in 2000, the international community pledged to “spare no effort to free our fellow men, women and children from abject and dehumanizing conditions of extreme poverty” (DESA, 2008, p. 3).

In the Republic of South Africa, Department of Water Affairs and Forestry (DWAF) deals directly with matters pertaining to wastewater and its treatment. This ministry is the custodian of South Africa's water and forestry resources. It is primarily responsible for the formulation and implementation of policy governing these two sectors and has the responsibility for water services provided by local government. DWAF regulates industries so that they treat their effluents and it funds many monitoring programmes and ecological impact studies to evaluate the environmental effects of their discharges (DWAF, 2008). In addition to the constitution, the government also has special environmental legislation like the National Environmental Management Act (NEMA) 1988, which follows principles of the constitution and gives details of the constitutional rights; it also guarantees basic human rights and provides guiding principles for society.

The necessity to maintain quality drinking water and pollutant-free waters has become a very important practice in order to prevent diseases and the destruction of the environment. The growth of industries worldwide and in South Africa has led to an increase in effluents (organic or inorganic) discharged from these industries. Nowadays, industries are required to practise environmentally safe activities in order that we do not live with the devastating consequences (Rostoll, 2008) of water pollution.

It is important to realise that with the exception of the synthetic elements and nuclides produced by nuclear installations (Pu, $^{60}$ Co) all pollutant metals are naturally present in aquatic environments (Harrison, 1993). The mere presence of a toxic metal in a water body is not sufficient to warrant pollution, it is when these metal ions are present in higher than usual concentrations, that biota are threatened. If no pollutants were discharged, waters would remain in pristine condition. However, early reduction of pollution discharge to zero is impractical; so industries are granted discharge permits; which are frequently reviewed and renewed, but at the same time companies are given the onus to make sure that the water discharged to receiving rivers, meets the required water quality criteria stipulated for the different industries, or the "polluter pays principle" is brought into effect. The limits on discharge have been set as a function of the type of pollutant, type of industry discharging it and desired water quality (Masters, 1998).

Below is a summary of the allowable limits in drinking water as tabulated by the World Health Organisation and South Africa (Kazi et al., 2009; Mamba et al., 2008).

Table 2.1: Allowable limits in drinking water

| Description | WHO maximum limit (µg/L) | S.A maximum limit (µg/L) |
|---|---|---|
| Chromium | 50 | 100 |
| Copper | 2 | 1 |
| Nickel | 20 | 150 |
| Cobalt | 40 | - |

It can be noted that environmental contamination by metals is mainly by the emission of liquid effluents with relatively low, although harmful, metal concentrations (up to hundreds of mg/L) (Rengaraj et al., 2007). Therefore, the removal of heavy metals from wasters is required prior to discharge into receiving waters. This dissertation will look at the reduction of metal ions from wastewaters to acceptable limits using adsorption techniques onto South African clinoptilolite.

## 2.2 Wastewater treatment stages

Wastewater treatment covers mechanisms and processes used to treat water that have been contaminated in some way by anthropogenic activities, prior to its release into

the environment or its reuse (Schroeder, 1977). Wastewater treatment is usually divided into four categories:

### *2.2.1 Preliminary*

The stage is intended to remove the larger floating and suspended debris. This is aimed to prevent blockages and damage to equipment. Generally, the preliminary stage does not reduce the pollution load but renders the wastewater amenable to treatment (Harrison, 1993).

### *2.2.2 Primary*

This is a screening stage which removes materials that can be easily collected and disposed off (suspended and settleable solids); materials that have passed through the preliminary stage such as sand, greases, grit and these are mechanically removed (Imhoff et al. 1971) (i.e. sedimentation) to prevent damage to pipe work and abrasion to pumps.

### *2.2.3 Secondary*

This treatment stage involves the removal of dissolved solids. The clear secondary effluent may then flow directly to receiving environments or to disinfection facilities prior to release to receiving waters (Masters, 1998), depending on the consumer using the water.

### *2.2.4 Tertiary*

The tertiary treatment stage is an advanced treatment stage to remove suspended and dissolved solids remaining after conventional secondary treatment. This can be accompanied by physical, chemical or biological treatment (Imhoff et al., 1971) to remove the targeted pollutants i.e. colour, odour, organic chemicals, metals or even nutrients (phosphorous).

## 2.3 Existing wastewater treatment technologies for heavy metal removal

Numerous processes have been developed for the removal of dissolved heavy metals from wastewaters. These technologies include ion exchange (Cavaco et al., 2007), precipitation (Hamdaoui, 2009), ultrafiltration (Richardson and Harker, 2002) reverse osmosis and electrodialysis (Peric et al., 2004; Rengaraj et al., 2007). Most of these methods are costly and require high levels of expertise, which restricts their application to the end-users. In most cases, the choice of method for wastewater treatment is based jointly on the concentration of heavy metals in solution and the cost of treatment (Richardson and Harker, 2002). Below is a brief description of the technologies.

### *2.3.1 Chromatography*

Chromatography is a sorptive separation process where a portion of a solute mixture (feed) is introduced at the inlet of a column containing a selective adsorbent

(stationary phase) and separated over the length of the column by the action of a carrier fluid (mobile phase) that is continually supplied to the column following introduction of the feed. (Wankat, 1986; Small, 1989). The stationary and mobile phases can be contacted with each other; in columns, as a thin layer on a plate, or as a paper strip suspended in a reservoir of solvent.

### *2.3.2 Membrane technologies*

The following four technologies use materials that selectively stop or slow the passage of particular types of molecules, such as stopping NaCl but not $H_2O$. Membranes have been made of materials such as solvent swollen gels, dry solids or immobilised liquids. In general these membranes have highly porous structures but pore sizes can be as small as 10 Å (Perry and Green, 1998). The pore shapes are generally irregular, although certain gel membranes have highly uniform diameters.

i. Osmosis

A membrane, which impedes the passage of a low molecular weight solute, is placed between a solute-solvent solution and pure solvent. The solvent then diffuses through the membrane onto the solution side by osmosis. In osmosis the potential of two solutions separated by a membrane is different because of the difference in the salt concentrations (Schroeder, 1977). There is therefore, an interaction between the pressure and chemical potentials, which results in equilibrium being attained by a combination of the two. The schematic diagrams below illustrate this process.

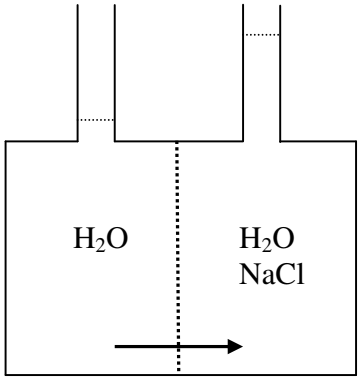


Fig. 2.1 Osmosis

ii. Reverse Osmosis (RO)

In reverse osmosis, a pressure difference is imposed in the reverse direction, which causes the flow of solvent to reverse. The process sometimes requires high pressures and is thus fairly costly in terms of energy (Hammer, 1986).

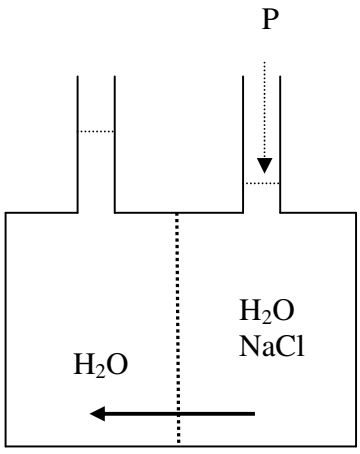


Fig. 2.2 Reverse Osmosis (RO)

iii. Electrodialysis

This is an ion exchange membrane separation technique, which has been widely used for the purification, separation, demineralisation and recovery of dissolved species from chemical, food, pharmaceutical and metallurgical industries (Basta, 1986). It involves the separation of ions by imposing an electromagnetic field (emf) difference across the membrane (Schroeder, 1977). Electrodialysis (ED) is widely used in removing salts from brackish water, but for high – quality water, ED can economically reduce salts in water when used as a hybrid process in conjunction with ion exchange systems (Perry and Green, 1998).

iv. Ultrafiltration (UF)

In this process, pressure is used to separate molecules by a semi-permeable polymeric membrane. The membrane discriminates on the basis of molecular size, shape or chemical structure and separates relatively high molecular weight solutes such as proteins, polymers, colloidal materials (Christensen and Plaumann, 1981) i.e. whey processing, and also in concentrating oil in water emulsions. The two most important characteristics of UF are its permeability and its retention characteristics, but fouling of the membrane is usually the major limiting factor in UF use.

### *2.3.3 Precipitation*

Precipitation is an initial purification process, particularly following centrifugation filtration and/or homogenization steps. Precipitation of solid products, impurities or

contaminants from a solution can be induced by adjusting the solution pH, increasing the solution temperature, or the addition of solvents, salts or polymers to the solution (Ayres et al., 1994). This operation is used often in the early stages of the separation sequences.

### *2.3.4 Oxidation processes*

Ozone is a powerful oxidant for water and waste water treatment. Once dissolved in water, ozone reacts with a great number of organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants like free radical species, in particular the hydroxyl radicals. Both ozone and hydroxyl radicals are strong oxidants and are capable of oxidizing a number of compounds (Bes–Pia et al., 2003) into insoluble metal oxides, which are removed by post-filtration.

### *2.3.5 Adsorption/ Ion exchange*

These two processes are discussed in detail in sections 2.4 and 2.5 below**.** Out of the many developed technologies, adsorption is one of the most attractive because its application is relatively simple and safe, as mild operating conditions are used, it is also widely available, abrasion resistant and cheap (Peric et al., 2004; Inglezakis et al., 2004) and can be very selective.

## 2.4 Adsorption

Adsorption is a separation process whereby the solute is preferentially removed from a solution by attachment to the surface of the solid, granular material called "adsorbent". The solute removed is called the "adsorbate".

Attachment of solutes to the solid surfaces happens by bond formation. According to the type of adsorbent – adsorbate bonds formed, there are two forms of adsorption:

- Physisorption (or physical adsorption), in which the adsorbate is joined to the adsorbent micropores by weak Van der Waal forces (Somorjai, 1993). This makes the physisorption process mostly reversible i.e. the adsorption bonds are easily formed and broken, due to the low energy of adsorption that characterises such systems.
- Chemisorption, is a result of chemical interaction between adsorbate molecules and adsorbent surface. During the chemisorption process, Somorjai, (1993, p. 54) "ionic and covalent bonds are normally formed and a high energy of adsorption is liberated". This process is usually irreversible as the bonds formed are semi-permanent; thus for desorption to occur, the adsorbate undergoes a chemical change.

Thermodynamically speaking, one explanation is that when an atom or molecule strikes a surface and forms a bond with it, heat is evolved, as heat of adsorption $\Delta H_{ads}$ (Somorjai, 1993).This heat evolved is usually measured by desorption – breaking the

adsorbate – surface bond. For each bond formed, there is an optimum temperature at which adsorbed material is removed at a maximum rate. This maximum rate at which desorption occurs is related to the activation energy, which in turn is closely related to the $\Delta H_{ads}$.

## 2.5 Ion exchange

Ion exchange is a chemisorption process, whereas adsorpsion may be physisorption or chemisorption. The ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase. The ion exchanger is usually insoluble in the medium in which the exchange is carried out (Grimshaw et al., 1975). All ion exchange processes are extremely rapid and they follow the general well known kinetic laws as shown in the equation below, however, the mathematical treatment of the reaction rates become quite cumbersome and difficult in heterogenous systems (Mumpton, 1999).

The following two reactions illustrate the basic interactions that take place between the solid phase and the ions in solution;

Cationic Exchanger; $M^-A^+_{(solid)} + B^+_{(solution)} <=> M^-B^+_{(solid)} + A^+_{(solution)}$.....(2.1)

Anionic Exchanger; $M^+A^-_{(solid)} + B^-_{(solution)} <=> M^+B^-_{(solid)} + A^-_{(solution)}$.....(2.2)

Ion exchange is a process that has become increasingly important in the field of water treatment because it is able to achieve complete demineralization (Ramalho, 1997), through simultaneous cation and anion exchange.

It is usually questioned whether adsorption and ion exchange are synonymous to each other. Hamdaoui (2009) has explained that the sorption processes of ion exchange and adsorption are unit operations, which often share theory, although they have their own special areas of concern. Schroeder (1977) also sums it up well in his book that strictly speaking, adsorption is the accumulation of materials at an interface, and this interface may be liquid – liquid, liquid – solid, gas – liquid or gas – solid. Ion exchange process becomes similar to an adsorption system in which a solid, usually porous particle with reactive sites on its surface comes into equilibrium with ions in solution. These reactive sites have exchangeable ions such as $Na^{+}$, $H^{+}$, $Cl^{-}$, $OH^{-}$ attached, and these ions exchange with ions in solution at equilibrium. Adsorption is mainly applicable in wastewater treatment whereas ion exchange is used in water treatment. In this dissertation, the terms “adsorption” or “exchange of ions” will be used interchangeably to encompass both processes.

In summary, the uptake of heavy metals in wastewater treatment is attributed to both mechanisms of ion exchange and the adsorption process (Curkovic et al., 1997). The authors Sprynskyy et al. (2006) describe the loading phenomenon of metal ions as comprising of three stages. The first stage involves a fast intake of metal ions as this is attributed to the ion exchange in the micropores on the microcrystal surfaces of the

clinoptilolite grains. The second stage involves an inversion of ion exchange for a period of time, due to the counter diffusion of exchangeable cations. This is common with $Ni^{2+}$ ions or solutions of higher metal concentrations. The third stage is described as adsorption of metal ions but at a much slower rate compared to the first stage.

## 2.6 Adsorbents used for tertiary wastewater treatment

These adsorbents range from natural to conditioned ones to those that are synthetically manufactured. Examples are discussed in the following sections.

### *2.6.1 Activated carbon*

Activated carbon is an excellent adsorbent, and it has been proven to very effective in the removal of both inorganic and organic compounds from wastewaters. It has a remarkably high specific surface area ranging between 500 and 1500 $m^2/g$ and widely different surface functional groups (Yin et al., 2007). Activated carbon is made from carbonaceous raw materials such as hard wood, rice husks, carbon black, bagasse ash, saw dust and lignin (Crittenden and Thomas, 1998). They are activated with steam or carbon dioxide at elevated temperature (700 – 1100$^oC$). Unfortunately, it is not suitable for use in developing countries due to the high costs associated with production and regeneration of the spent carbon (Panday et al., 1985).

### *2.6.2 Fuller earths*

These are natural clays that are mainly magnesium aluminium silicates. Their technical names are attapulgite or montmorillonite. The clays are heated and dried during which the structure develops a porous framework; it is then ground and screened. Fuller earths are widely used in industry to adsorb oil and grease, as a carrier of pesticides, in adhesives, paints and textiles. The advantage is that these fuller earth clays can be regenerated by washing and burning off the adsorbed organic matter accumulated on the clay. This however, poses a danger to the environment because the burned organics are freely released into the atmosphere (Masters, 1998).

### *2.6.3 Activated clays*

These clays have no adsorption ability unless activated by acid treatment. Activated clays are limited in use to the contact process and are not regenerated (Mantell, 1951). However, they are about four times as powerful as the natural clays. Activated clays are used for decolourising petroleum products.

### *2.6.4 Bauxite*

It is a naturally occurring hydrated alumina $Al_2O_3$ rock that is activated by heating to temperatures of 230 – 815 $^oC$. This process is a conceptually simple procedure but in actual fact, it is complex due to the heterogeneous nature of the bauxite. The bauxite rock undergoes phase changes in its purification stages over the whole process temperature range. Activated bauxite is used in the percolation treatment of

petroleum products and drying air (Miller, 1985; Mantell, 1951). It also finds many applications in metallurgical, abrasive, cement, chemical and refractory industries.

### *2.6.5 Silica gel*

Silica gel is the most widely used desiccant because of its hydrophilic nature, its large capacity for water and ease of regeneration and thus its use in dehydration of air and other gases (Yang, 2003).

### *2.6.6 Resins*

A broad range of synthetic, non–ionic polymers are available for use as adsorbents, ion exchangers and chromatographic column packing. This technology of designing and building porosity in polymers was accomplished in the late 1950s and early 1960s (Kunin et al., 1962). These polymeric resins can be further reacted to attach functional groups to the benzene rings to generate functionalities for ion exchange. The advantage of polymeric resins lies in their ease of regeneration and they can be tailored for special applications such as in the pharmaceutical and semiconductors industries (Yang, 2003).

### *2.6.7 Zeolites*

At least 40 different types of naturally occurring zeolites have been found. More than 150 types of zeolites have been synthesised and they are designated by a letter/ group

of letters (Type A, X, Y, ZSM-5) as adopted by the International Zeolite Association (IZA) (Yang, 2003). These naturally occurring and synthetic zeolitic minerals are used commercially because of their unique adsorption, ion exchange, molecular sieve and catalytic properties. The advantage of zeolites over resins, apart from their much lower cost, is their ion selectivity, generated by their rigid porous structures (Alvarez-Ayuso et al., 2003; Coruh, 2008), which gives good sieving characteristics. Zeolites are particularly suitable for the removal of heavy metals.

## 2.7 Theory of adsorption

Adsorption isotherms or models can be described as reference points for evaluating the characteristic performance of an adsorbent. The adsorption isotherms are plotted using the data obtained from experimental batch process. These models are used to predict the theoretical adsorption constants and the behaviour of different adsorbates for adsorbents. Despite their advantages, some of these isotherms have limiting and unrealistic assumption, which are discussed in detail in section 2.7.1 below.

### *2.7.1 Adsorption models in batch tests*

The Langmuir and Freundlich equations are the most used to describe sorption equilibrium for environmental studies (Erdem et al., 2004; Oren and Kaya, 2006; Kocaoba et al., 2007). The following expressions for a straight line were used, which are obtained by a mathematical transformation of isotherms:

For the Freundlich isotherm,

$$\log q_e = \log K_f + \mathbf{1/n} \log \boldsymbol{C_e} \quad (2.3)$$

This isotherm describes equilibrium on heterogeneous surfaces (Gunay et al., 2007) i.e. the energy of adsorption is not equivalent for all adsorption sites, which is a more realistic assumption than the Langmuir isotherm.

For the linear traditional Langmuir isotherm,

$$C_e/Q_e = (1/K_L) + (a/K_L)\, C_e \quad (2.4)$$

This model assumes that all adsorption sites are energetically identical and have equal energies of adsorption (i.e. adsorption is a monolayer) (Gunay et al., 2007).

The empirical constants $K_L$ and a for the Langmuir model are related to the heat of adsorption maximum (L/g) and bonding strength (L/mg) respectively (Yu et al., 2003; Oren and Kaya, 2006), whereas, $K_f$ (mg/g) and n (g/L) are the constants for the Freundlich model related to the adsorption capacity and intensity of adsorption (Yu et al., 2003).

Most industrial adsorption processes are carried out in column systems. Therefore, a laboratory batch adsorption test at equilibrium does not give sufficient data for the design of a clinoptilolite adsorption system. Batch adsorption kinetic studies give

concentration decay curves in terms of $C_t$ versus t. Column tests are required for design, with the kinetic adsorption information generated experimentally on a laboratory scale or pilot plant scale or theoretically by mathematical modelling. This is one advantage column systems have over the batch system approach.

### *2.7.2 Adsorption in columns*

In fixed bed columns, ion exchange is applied at low liquid flow rates and caution has been recommended by Hefferich (1995) and Milan et al. (1997) because of the possibility of relatively large unwanted maldistribution (i.e. channelling) and dispersion effects, in connection with ion exchange at low flow rates. The dynamic column used was 50 mm in diameter and the zeolite bed height was kept at 20 mm in all the experiments to avoid solution build-up in the column. An initial feed concentration of 50 mg/ L was used for both single and multi-component feeds. All the feeds were introduced at the top of the column and so the column operated under down flow conditions, pumped to try and improve the steadiness of the packed bed and maximise on the zeolite and influent's contact. The experiments were stopped when the column reached its exhaustion point (Inglezakis and Grigoropoulou, 2003); when the effluent concentration rose sharply and was nearly that of the influent concentration (Geankoplis, 1984). The breakthrough and exhaustion points used in this dissertation are 10% and 90% of influent and effluent concentrations, according to the work of Bhakat et al. (2007). Mathematically, the concentration – time curve is represented by a sigmoid shape and is called the breakthrough curve; expressed in terms of $C/C_o$ (the influent $C_o$ and effluent C metal ion concentrations) as a function

of time or bed volume of the eluate for a given bed height. This is a very important design feature of adsorption columns as it determines their operational time and capacity. Data obtained from the column tests was used with a software package called "Origins7.5", which is able to calculate the areas under the breakthrough curves between the two x-axis limits (breakthrough and exhaustion points).

Qualitative interpretation of breakthrough curves

What happens in a column is approximated by the presence of an adsorption active zone (MTZ - Mass Transfer Zone) across the column. Medvidovic et al. (2006) describes this zone as representing the layer between the equilibrium bed zone and the unused bed zone. A concentration wave, precedes the equilibrium bed zone; this wave zone that moves downwards (in the downward system), and the break point is assumed to occur when the active zone starts to move outside the column. Mathematically, working out the area under the breakthrough curve between the breakthrough and exhaustion points give the maximum exchange capacity, $q_e$.

## 2.8 Natural zeolite: clinoptilolite

The term 'zeolite' was created by Croestedt in 1756 from the two Greek words meaning "to boil" and "stone" for minerals which expel water when heated and seem to boil (Newsam, 1986; Gottardi and Galli, 1985; Polat et al., 2004).

### *2.8.1 Geographical distribution*

South African clinoptilolite mined by Pratley Perlite Ltd. has been found to have the formula:

$$(MgCaNa_2K_2)_{25}(AlO_2)_7(SiO_2)_{30}.21H_2O$$

This is based on the KwaZulu - Natal clinoptilolite's chemical composition. The chemical analysis yielded the above molecular formula, with the main exchange cations in this zeolite being $Mg^{2+}$, $Ca^{2+}$, $Na^{+}$ and $K^{+}$.

The idealised chemical formula of clinoptilolite is:

$$CaNa_4\ (AlO_3)_6(SiO_2)_{30}.\ 24H_2O$$

This generalised formula of clinoptilolite has two main dominating exchangeable cations namely $Ca^{2+}$ and $Na^{+}$.

Pratley Perlite. Ltd datasheet provides information on the elemental analysis in mass % of the natural zeolite clinoptilolite rock, using XRD analysis. The rock was found to contain 80 – 85% clinoptilolite. A breakdown of the elemental analysis is outlined in Table 2.2:

Table 2.2 Elemental Analysis of natural South African clinoptilolite

| **Element** | **%** | | |
|---|---|---|---|
| $SiO_2$ | 71.52 | MgO | 0.86 |
| $Al_2O_3$ | 12.10 | CaO | 1.53 |
| $Na_2O$ | 1.40 | Ni | trace |
| $K_2O$ | 3.85 | Cr | trace |
| $Fe_2O_3$ | 1.21 | Ba | trace |
| MnO | 0.07 | Sr | trace |
| Cu | trace | Co | nil |
| P | 0.009 | Total water | 7.30 |
| $TiO_3$ | 0.13 | (Free water 5.7%) | |

Other properties of clinoptilolite are outlined in tables A2 and A3 in Appendix A.

Clinoptilolite has been mined in many different countries. Work and publications have been carried out on clinoptilolite from Greece (Inglezakis et al., 2007), Turkey (Gedik and Imamoglu, 2008), Ukraine (Sprynskyy et al., 2006), Serbia and Montenegro (Medvidovic et al., 2006), Cuba (Rivera et al., 2000), California, U.S.A (Semmens and Martin, 1988), China (Du et al., 2005) and in South Africa (Semosa, 2005; Themistocleous, 1990). Clinoptilolite is common as a major constituent of submarine volcanic sediments of tuffites (Gottardi and Galli, 1985; Erdem et al., 2004) and it occurs principally as microcrystalline sedimentary masses (Gottardi and Galli, 1985).

In South Africa, up to 75% of pure zeolite beds (mainly consisting of heulandites and mordenite) are located in the Heildelberg – Riversdale area. It occurs in altered tuff beds overlying bentonite – rich horizons (Wipplinger and Horn, 1998).

Clinoptilolite has been found in two principle areas of South Africa namely:

i) Western Cape Province: in the Heildelberg Riversdale area.

ii) Northern KwaZulu - Natal: in the Nxwala Estate near the Mkuze Game Reserve of the Lebombo Mountains (Wipplinger and Horn, 1998). In this region, the clinoptilolite occurs in association with perlites. Other impurities found in clinoptilolites include quartz, k-feldspar, opal, cristobalite, montmorillonite, micas and calcite. Unfortunately, these impurities have densities very close to clinoptilolite, which makes the purification of this zeolite nearly impossible by conventional flotation methods (Themistocleous, 1990).

Polat et al. (2004), Koon and Kaufman (1975), Coruh (2008) and Mumpton (1999) list the following diverse applications of clinoptilolite and other natural zeolites:

i) Building stones

ii) Soil conditioner – in the retention of $NH^{+}_{4}$ and $K^{+}$, favourable for crops.

iii) Dietary supplement for pigs and roosters – percentages of about 6 and 7.5 respectively showed a weight increment in these livestock, with no effect on live mass.

iv) Wastewater purification – such as the recovery of carbons from radioactive wastewater and ammonia from municipal waste.

v) Dehydration for instance before a catalytic reaction, fill drying beds for gas, liquid dehydration.

vi) Gas separation and in catalysis.

vii) Chemical carrier – in agriculture, to carry herbicides and fertilizers.

Pratley's main application of South African clinoptilolite is for the manufacture of fertilisers and in gas adsorption [See Table A2 in Appendix 2].

### *2.8.2 Structure of clinoptilolite*

Clinoptilolite is a mineral zeolite of the heulandite group and crystallizes in the monoclinic system. Clinoptilolite and heulandite have similar aluminosilicate frameworks but the stability and dehydration behaviours are different. The table below summarises their differences as quoted by Sprynskyy et al. (2006) and Breck, (1974).

Table 2.3 Differences between clinoptilolite and heulandites

| CLINOPTILOLITE | HEULANDITE |
|---|---|
| Higher Si/Al ratio (4.0 – 5.3) | Lower Si/Al ratio ( 2.5 – 3.7) |
| Higher thermal stability (600 – 800 °C) | Lower thermal stability (350 – 450°C) |
| Mainly dominated by alkali monovalent cations ($Na^+$and $K^+$) | Mainly dominated by alkali earth divalent cations ($Ca^{2+}$, $Ba^{2+}$ and $Sr^{2+}$) |

In as much as these differences are noted, other researchers have forwarded the idea that clinoptilolite falls into the heulandites group because no clear and distinct difference occurs between the two minerals. Many zeolites of clinoptilolite structure have been found with intermediate Si/Al ratios (which determine their maximum exchange capacity (Covarrubias et al., 2006)) and the thermal stability of these two zeolites depends on the cations present on the mineral (Themistocleous, 1990). It has been demonstrated by authors such as Kitsopoulous (2001) and Breck (1974), that clinoptilolite in which the $Ca^{2+}$ is substituted for $Na^{+}$ and $K^{+}$ shows similar structural contraction to heulandites; $K^{+}$ substituted heulandites results in greater thermal stability.

Clinoptilolite finds many applications because of its framework that encloses cavities (pores or cage-like structures) occupied by cations and water molecules, both of which have considerable freedom of movement permitting the exchange of ions and reversible dehydration**.**

These crystals are characterised by three-dimensional pore systems, with pores of precisely defined diameters, which are interconnected to form long wide channels/ cage like structures. Zeolites have a basic tetrahedral arrangement of aluminium ($AlO_4$) and silicon ($SiO_4$) oxides as shown in Figure 2.3. This implies that the Si and Al are linked to each other by four oxygen bridges. Each silicon atom in the framework with a formal charge of 4+ balances the one negative charge on each the four oxygen atoms. The latter are formally charged -2 but at the same time shared

with two neighbouring Si or Al atoms. The isomorphous substitution of $Si^{4+}$ by $Al^{3+}$ creates an excess negative charge, which is balanced by innocuous extra framework ions such as $K^+$, $Ca^{2+}$ and $Na^+$ (Erdem et al., 2004). These extra framework ions are also exchangeable with larger metal ions in wastewaters such as $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cr^{3+}$ because the negatively charged ions are rigidly held in the zeolite lattice, whereas the harmless balancing ions are not.

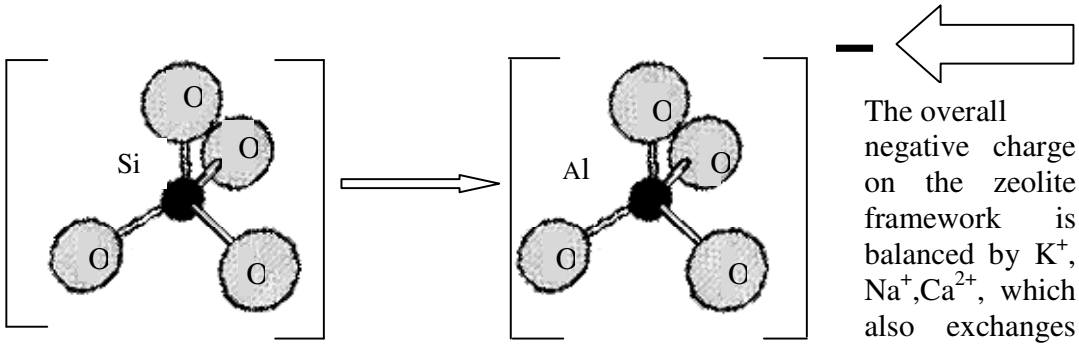



Fig. 2.3 Isomorphous substitution of $Si^{4+}$ by $Al^{3+}$

### *2.8.3 Properties of zeolites*

As described by Corma (1997), zeolites are characterised by;

i) high surface area properties. This is good for providing large adsorption capacities, but large internal surface area in a limited volume gives rise to a large number of small sized pores between adsorption surfaces.

ii) surface polarity. Surface polarity and molecular sieve distribution correspond to the zeolite's affinity for polar substances such as water. Polar substances like zeolite are hydrophilic, and non-polar carbonaceous adsorbents such as

activated carbon are hydrophobic, as they have an affinity for oil rather than water. This also serves as an advantage because this property can be controlled and varied.

iii) Large channel sizes in the range typical for the diameter of many species (5 – 12 Å). The large structural cavities and entry channels leading into the internal parts of the zeolites contain water molecules, which form hydration spheres around the exchangeable ions. On removal of the water by heating at 350°C – 400°C, smaller and large particles can pass through but larger molecules are excluded (Mumpton, 1999): this is called the molecular sieve effect of crystalline zeolites.

iv) Active sites, such as acid sites for instance, can be generated in the framework and their strength and concentration can be tailored for a particular application.

### *2.8.4 Regeneration*

The reversible nature of ion exchange makes the regeneration process of clinoptilolite an important step in ion exchange. It also makes the processes economical as the zeolite samples can be reused for a couple of cycles before the structures are exhausted. The adsorbed metal ions can be recovered and re-used.

Ion exchange in packed columns is inherently unsteady state or a batch type process. Due to the stationary nature of the sorbent (solid), it will saturate at the feed

concentration if the feed enters the column continuously (Wankat, 2007). Regeneration involves the removal of most sorbate (liquid) from the zeolite usually by washing or flushing with water, and then running an acidic or basic solution through the bed. Investigation into the regeneration of natural zeolites has already been conducted and it has been found that zeolite capacity decreases with each repeated regeneration cycle (Argun, 2008). This is caused by the difficulty of removing ions for which the zeolite framework has a high affinity. Some metal ions once exchanged onto the zeolite are rigidly fixed or become inaccessible to the incoming ions, thus ion exchange sites reduce with time. Another possible mechanism for the loss of capacity of the zeolite, is the removal of oxygen atoms from the lattice, when strongly held cationic species are removed during the regeneration step (Tsitsishvili et al., 1992). This would result in the destruction of the zeolite lattice and loss of adsorption/ ion exchange sites. More work is required on the regeneration of South African zeolite to improve its lifespan (Semosa, 2005).

### *2.8.5 Capacity and selectivity of natural and pretreated zeolites*

Most researchers in their work have observed that the pre-treatment of natural zeolites improves ion exchange capacity (Gunay et al., 2007; Inglezakis et al., 2004; Han et al., 2006). The selectivity of the zeolites for metal ions has also been studied by authors such as Semmens and Martin (1988), and Inglezakis et al. (2004).

The cation exchange capacity CEC of zeolites is basically the amount of $Al^{3+}$ ions that substitute the $Si^{4+}$ ions in the tetrahedral zeolite framework (Mumpton, 1999; Ouki and Kavannagh, 1999); the Si/Al ratio. The greater the aluminium content, the more incoming ions are needed to balance the charge, thus the higher the exchange capacity. Other factors that determine the adsorption capacity of zeolites by heavy metals are:

i. The hydration diameters; of ions sitting in the framework and those incoming into the zeolite.
ii. Hydration enthalpies
iii. Solubility of cations

The selectivity order of zeolites for metal ions is usually brought about by the various factors that influence adsorption and ion exchange behaviour in zeolites (Zamzow and Eichbaum, 1990). This brings about effects such as the sieving effect for metal ions or the availability of the specific exchange sites in the zeolite. Depending on the arrangement of the zeolite crystal lattice or pore volumes, the incoming ions will be affected, and may diffuse through the structure or fail to move through the pores. Most researchers have found different cation exchange capacities and interestingly, it was noted that clinoptilolite exhibits different selectivity series for different metal ions. A summary of these series are in table 2.4 below:

Table 2.4 Summary of selectivity series observed by different researchers.

| Authors | Selectivity series |
|---|---|
| Ouki and Kavannagh, 1997 | $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+}$ using natural clinoptilolite. |
| Semmens and Martin, 1998 | $Pb^{2+} > K^{+} > Ba^{2+} > NH_4^{+} > Ca^{2+} > Cd^{2+} > Cu^{2+} > Na^{+}$ using $Na^{+} -$ form clinoptilolite |
| Inglezakis et al., 2004 | $Pb^{2+} > Cr^{3+} > Fe^{2+} > Cu^{2+}$ using natural clinnoptilolite<br>$Pb^{2+} > Cr^{3+} \simeq Fe^{2+} > Cu^{2+}$ using $Na^{+}$ clinoptilolite |
| Kocaoba et al., 2007 | $Cd^{2+} > Ni^{2+} > Cu^{2+}$ using natural clinoptilolite. |
| Alvarez-Ayuso et al., 2003. | $Cu^{2+} > Cr^{3+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$ using natural clinoptilolite. |
| Zamzow et al., 1990 | $Pb^{2+} > Cd^{2+} > Cs^{+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$ using natural clinoptilolite. |

### *2.8.6 Effect of pH in adsorption*

pH is a very important controlling parameter in adsorption and ion exchange processes. Chemically, a change in solution pH influences metal speciation leading to the formation of complex inorganic species in solution. The exact speciation (the metal ion complex that predominates at a particular solution pH) of a metal has a significant impact on the removal efficiency of clinoptilolite and its selectivity (Hai et al., 2005). The presence of precipitates in solution, usually clog the zeolites and

hinder metal ion accessibility of sites (Alvarez-Ayuso et al., 2003; Dal Bosco et al., 2005; Inglezakis et al., 2004).

According to Ragnarsdottir et al. (1996), and Oren and Kaya (2006), adsorption dependency on lower pH values (< 4) is explained by the dissolution of the crystal structure and the zeolites may exchange some of their exchangeable cations with $H_3O^+$ ions. Between pH values of 4 and 6, the basic mechanism is the ion exchange process (Oren and Kaya, 2006. Then at higher pH values, precipitation process of metal ions takes effect (Alvarez – Ayuso et al., 2003; Dal Bosco et al., 2005). Generally, ion exchange increases with an increase in pH up to a maximum value, then slowly decreases thereafter (Argun, 2008, Yu et al., 2003; Oren and Kaya 2006: Alvarez – Ayuso et al., 2003). This increase in adsorption is because at higher pH values, fewer $H^+$ ions are present in the solution, and so there is reduced competition between the metal ions in solution and the $H^+$ for the active exchange sites on the zeolite (Alvarez-Ayuso et al., 2003).

### *2.8.7 Metal ions removed*

Process wastewaters containing heavy metals will be discussed in this section. Chromium, nickel, zinc, and copper are considered "priority metals" from the standpoint of potential hazards to human health, animals and ecological systems (Alvarez-Ayuso et al., 2003; Kocaoba et al., 2007). These priority metals are a list of 129 substances originally set forth in a consent decree between the Environmental

Protection Agency (EPA) of the U.S.A and several environmental organisations (Masters, 1998). General contaminants include organic materials and most heavy metals and their properties are listed based on risk assessment not on hazardous assessment only because toxicity is not absolute, but depends on concentration. Metals however, differ from other toxic substances in that they are totally non - degradable; they are virtually indestructible in the environment (Masters, 1998). The following four metal ions used in this research are discussed below: copper, cobalt nickel and chromium.

i. Copper

Copper is a very common element which occurs naturally in the environment. Human activities also aggravate the copper levels in the environment; examples include mining, metal and wood production and phosphate fertiliser production. It then settles and binds itself to water and soil sediments and livestock due to its non-biodegradable nature.

The most stable copper ion is $Cu^{2+}$, although it begins to hydrolyse at pH 4 to a small extent and precipitate with $OH^-$ or $O^{2-}$ soon afterwards (Baes Jr. and Mesmer., 1976). Short- and long-term exposure at high levels in humans leads to conditions such as metal fever, liver and kidney damage although its toxicity is considered moderate to humans and livestock (Alvarez- Ayuso et al., 2003). The allowable WHO limit of copper in water is 2 (µg/L) (Kazi et al., 2009).

ii. Cobalt

Pure cobalt is not found in nature but is found in various metallic- lustred ores such as cobaltite (CoAsS). Cobalt is essential to the body in minute amounts for vitamin $B_{12}$ formation. It is also produced as a copper and nickel by-product in mining processes.

Cobalt (II) is the most stable valency in water, and cobalt (III) is a powerful oxidising agent, which decomposes water (Miller, 1985), whereas, cobalt–60 is radioactive and used in radiotherapy. However, at higher doses it has mutagenic and carcinogenic effects similar to those of nickel exposure. Cobalt also causes poisoning but this is less than lead poisoning because it is excreted by the body. The allowable WHO limit of cobalt in water is 40 (µg/L) (Kazi et al., 2009).

iii. Nickel

Most of the Nickel on earth is inaccessible because it is locked away in the planet's iron–nickel molten core. It therefore, occurs in the environment at very low levels.

The +2 oxidation state of nickel is the most important one, particularly in its aqueous chemistry (Baes Jr. and Mesmer, 1976). Nickel exposure at high levels varies from dermatitis to damage to lungs, nervous system and mucous membranes. It is also a known carcinogen (Argun, 2008); therefore, its removal from wastewater is essential. The allowable WHO limit of nickel in water is 20 (µg/L) (Kazi et al., 2009).

iv. Chromium

Chromium exists naturally in mineral chromite $FeCr_2O_4$. Two- fifths of the world reserves of this mineral deposit are found in Southern Africa. Therefore, its natural abundance implies that it can be found in soils, water, fauna and flora, volcanic dust and gases, in doses that are not harmful to man (Gomez and Callao, 2006). The higher valency chromium (III) is an essential micronutrient in the body and combines with various body enzymes to transform sugars, proteins and fat, it is also used in a number of commercial products. Due to human activities such as in dyestuff industries, metallurgy, electroplating and tanning, chromium species have found their way into receiving waters and environments.

Chromium (VI) is a powerful oxidant and easily penetrates biological membranes. Chromium (VI) is hundred times more toxic than Chromium (III), and has been found to be carcinogenic and mutagenic. It is also known to induce dermatitis, when in solution and not just inhaled (Rengaraj et al., 2007; Gomez and Callao, 2006; Olad and Nabavi, 2007; Porter et al., 1999). The allowable WHO limit of chromium in water is 50 (µg/L) (Kazi et al., 2009).

Due to the heavy metals' mobility, toxicity and non-biodegradable natures (dependent on its chemical form/oxidation), it is very important that we control them and dispose of them using acceptable methods.

## 2.9 Concluding statement

Various wastewater technologies have been successfully used to remove metal ions from wastewater, but unfortunately, some technologies are very expensive to operate and others generate more waste in the process, which sometimes poses a threat to the environment.

Much research work has been done on the selectivity sequences and adsorption capacities of natural clinoptilolite for a range of metals, and different results have been observed (Erdem et al., 2004), but most researchers agree that generally clinoptilolite has good adsorption capacities for heavy metals. In addition, the pre-treatment of natural zeolites either by acids, bases or surfactants enhances ion exchange and adsorption capacity (Gunay et al., 2007; Malliou et al., 1994; Wark et al., 1994; Oztas et al., 2008).

It is well established that the multiple uses of these zeolite materials are based on their physicochemical properties. The adsorption of metal ions onto clinoptilolite has more advantages than most technologies, as has been alluded to in section 2.3. Many authors have investigated the use of clinoptilolite and found it to have high cation exchange capacities (CEC) (Kocaoba et al., 2007) and thus they are suitable for use as adsorbents of metal contaminants in solution up to hundreds of mg/L (Rengaraj, et al., 2007). The cationic exchange capacity of zeolites is a function of the amount of aluminium that substitutes for silicon in the framework. The greater the aluminium

content, the more extra framework cations are needed to balance the charge (Mumpton, 1999). The sorption processes on zeolite particles on the whole however, are very varied and complex because of the unique porous structures, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds and other imperfections on the surface (Peric et al., 2004).

# 3.0 CHAPTER THREE

## 3.1 Experimental

The experiments carried out in this dissertation were conducted using South African clinoptilolite. The methodology of this dissertation was of two types;

i) Comparative: looking at the similarities between the research results in this dissertation and those already established in literature concerning adsorption of metal ions onto clinoptilolite.

ii) Manipulative: varying set point conditions and then carefully noting the results obtained and establishing their effect of adsorption efficiencies.

### *3.1.1 Clinoptilolite and reagent samples.*

The natural clinoptilolite (also referred to as CLINO) mined in KwaZulu - Natal and supplied by Pratley Perlite Ltd. plc, was used in the following forms: untreated (as received), sodium, potassium, calcium and ammonium. These samples were conditioned according to the method of Gunay et al. (2007) and Spryskyy et al. (2006), which is outlined in section 3.1.2 below. The two particle sizes provided were 1.0mm - 4.0mm (bigger particle size) and 0.4mm – 0.8mm (smaller particle size).

### *3.1.2 Sample preparation*

i. Zeolite preparation

The natural zeolite used 'as received' was first washed in ample distilled water to remove fines and impurities as explained by Medvidovic et al. (2006), Gunay et al. (2007) and Du et al. (2005) and dried at room temperature for 24 hours.

Some of the natural zeolite was modified/ converted/ homoionised into different forms prior to their use by washing it in distilled water and soaking it in 2M chloride salts (NaCl, KCl, $CaCl_2$ and $NH_4Cl$) for 24 hours, after which the sample was rinsed with distilled water and then finally dried at room temperature for a further 24 hours. The aim of the pre-treatment is to increase the content in a single ion (homoionic form) so that certain ions from the zeolite structure are removed, whilst the more easily removable ones are well located (Inglezakis et al., 2001).

ii. Feed preparation

The synthetic feed solutions in concentrations ranging from 50 - 500 mg/ L were prepared using distilled water and Merck Ltd. high grade salts of $Cu(NO_3)_2.3H_2O$, $Co(NO_3)_2.6H_2O$, $NiSO_4.7H_2O$ and $Cr(NO_3)_3.9H_2O$. The solutions were well mixed prior to use.

## 3.2 Experimental methods

### *3.2.1 Batch studies*

For the batch tests, 2g, 4g and 10g zeolite samples were contacted in conical flasks with 100 mL of single-and multi - component synthetic feed solutions. They were agitated at 300 rpm in a shaking incubator (Labex) at room temperature, in the aim of reducing the film boundary layer surrounding the clinoptilolite particles, thus increasing the external film transfer coefficient and hence the rate of metal ions uptake (Kesraoui - Ouki et al., 1993) and eliminate mass transfer control by diffusion (Kocaoba et al., 2007; Inglezakis et al., 2007). Every hour, 2 mL supernatant samples were taken for metal ion concentration analysis using the atomic adsorption spectrophotometer, AAS (Spectro AA, 55B Varian) and pH measurement using a pH meter (labX Direct - Seven Multi Mettler Toledo). The pH values were just monitored and not adjusted. Contact was continued usually for 24 hours, until adsorption equilibrium was attained (determined using AAS as the stage at which the supernatant concentration becomes constant with time).

Data obtained from the batch adsorption tests was used to determining the loading capacity, $q_e$ (mg/g) of the different adsorbents, using the following mass balance:

$$q_e = (C_o - C_t) \times V/m \quad (3.1)$$

The percentage removal of metal ions from solution was also determined using the relationship below:

$$\%\, removal\ q_e = \{(C_o - C_t)100\}/C_o \quad (3.2)$$

where, $C_o$ and $C_t$ are the initial and final metal ion concentrations in solution (mg/L) respectively, V is the solution volume (L) and *m* is the weight of the zeolite used (g).

Regeneration in batch studies

Regeneration of the natural and $Na^+$- form zeolite was performed using 0.5M NaCl as eluant. After each run, the zeolite sample was shaken in the stripping solution at 300 rpm for 45 mins, rinsed twice in ample distilled water for a total period of 15 mins and dried in open air. It was then re-used for the next service run and the regeneration was repeated 4 to 5 times in order to observe the adsorption efficiencies with time. The adsorption/ desorption cycle was carried out to determine the reversibility of the reactions and reusability of clinoptilolite (Oztas et al., 2008; Han et al., 2006).

For the batch processes conducted, repeat tests were carried out with varying conditions as follows:

i) Initial feed concentrations ($C_o$) between 50 mg/L (initially used on South African clinoptilolite by Semosa (2005) and 500 mg/ L (the chosen upper limit).
ii) Clinoptilolite particle sizes (1.0mm - 4.0mm and 0.4mm – 0.8mm)
iii) Forms of the clinoptilolite (natural and conditioned/ pretreated samples)

iv) Regenerated clinoptilolite samples (up to 4 or 5 regeneration cycles).

All experiments in the batch and continuous processes were conducted at room temperature and pressure.

### *3.2.2 Column studies*

Most industrial adsorption processes are carried out in column systems. The dynamic adsorption tests were carried out at isothermal conditions (T = 25 ± 2$^{o}$C) using an AKTAprime set of equipment as shown below.




Fig.3.1 AKTAprime dynamic column apparatus

The equipment consists of a vertical tightly sealed column packed with zeolite, through which the feed solution (and later, the elution solution) is continuously pumped so that the packed zeolite bed meets fresh feed each time as the feed trickles down the column. The AKTAprime equipment automatically collects effluent samples in the fraction collector at set intervals of time and the remaining solution is discarded through the outlet tubing just before the fraction collector. The collected samples are then analysed for metal ion concentrations using the AAS.

Regeneration in column studies

After every run, the column was regenerated using 0.5M NaCl as stripping solution, which was being feed to the column at the top at 2mL/min until the effluent was exhausted of most of the metal ions it adsorbed. The elution stage was left to run for 85 mins, and by this time, most of the ions would have been desorbed. After the stripping stage, the column was washed with water that was also feed from the top at 4 mL/min for10 mins. After this the column was ready for use again. About 2 to 3 regeneration cycles were carried out for each experiment and the adsorption efficiencies determined.

All experimental analyses were carried out in duplicate and mean values are presented in all the results.

## 3.3 Characterisation techniques/ experimental procedures

### *3.3.1 B.E.T Surface Area Analysis*

The Brunauer Emmett and Teller (BET) method was employed to measure natural, $Ca^{2+}$, $K^{+}$, $NH^{+}_{4}$, $Na^{+}$ - form clinoptilolite for their specific surface areas. The zeolite samples were dried in flowing helium for 2 hours at room temperature. Thereafter, they were cooled by submerging the reactor in liquid nitrogen, over which a stream where 30% nitrogen in helium flowed. The zeolite samples were then heated to room temperature and desorption isotherms for $N_2$ were measured. To calibrate the equipment, samples of known surface area were used.

### *3.3.2 Atomic Adsorption Spectrophotometer (AAS)*

Metal ions concentrations in solution were determined by atomic adsorption spectrophotometry (Spectro AA, 55B Varian). Adsorbate was aspirated into the spectrophotometer, where metal ions present in solution were ionised in an air and acetylene flame environment until a corresponding concentration was recorded on the screen. The wavelengths and slit widths were varied to suit the optimum working range required for the particular metal ion. Before every run, the equipment was calibrated using known high grade standard solutions and the appropriate lamp until a curve was obtained, which was in agreement with the calibration curves in the AAS working manual.

### *3.3.3 Scanning Electron Microspectrometer (SEM)*

The surface morphology of the different zeolite samples was determined using the Scanning Electron Microscopy (SEM) model Jeol JSM840 at varying magnifications. The SEM was operated at an accelerated voltage of 20 keV. The zeolite samples were coated with carbon to make their surfaces conductive.

### *3.3.4 X-Ray diffraction*

XRD was used to identify the bulk phases of the natural zeolite. The sample was ground to a fine powder and pressed firmly into the sampler holder before analysis using the Philips PW 1830 diffractometer. The x - ray diffractometer was operated at 40kV and 40mA for 45 minutes, over a range of °2θ from 0° to 80º, and a step size of 0.04. The patterns were collected and phase identification was done using X'Pert HighScore software containing ICDD (International Centre for Diffraction Data) files for comparison.

# 4.0 CHAPTER FOUR

## 4.1 Results and discussion

Batch and column experiments were carried out to investigate the adsorption capacities of natural and modified zeolites for nickel, cobalt, copper and chromium. The chromium metal ion was introduced to try and observe the effect of a higher valency metal ion in adsorption by the zeolites. The adsorption capacities were determined using theoretical techniques, making use of the Langmuir and Freundlich isotherms for the batch tests. Desorption of metal ions from clinoptilolite was also determined. The aim of this work is to establish the reversibility and reusability of the South African clinoptilolite.

## 4.2 Characterisation results

### *4.2.1 X-ray diffraction*

X ray – diffraction was carried out on the natural, $Na^+$, $K^+$, $Ca^{2+}$ and $NH^+_4$ - form clinoptilolite. The results are presented in figures 4.1 to 4.5.

Natural form

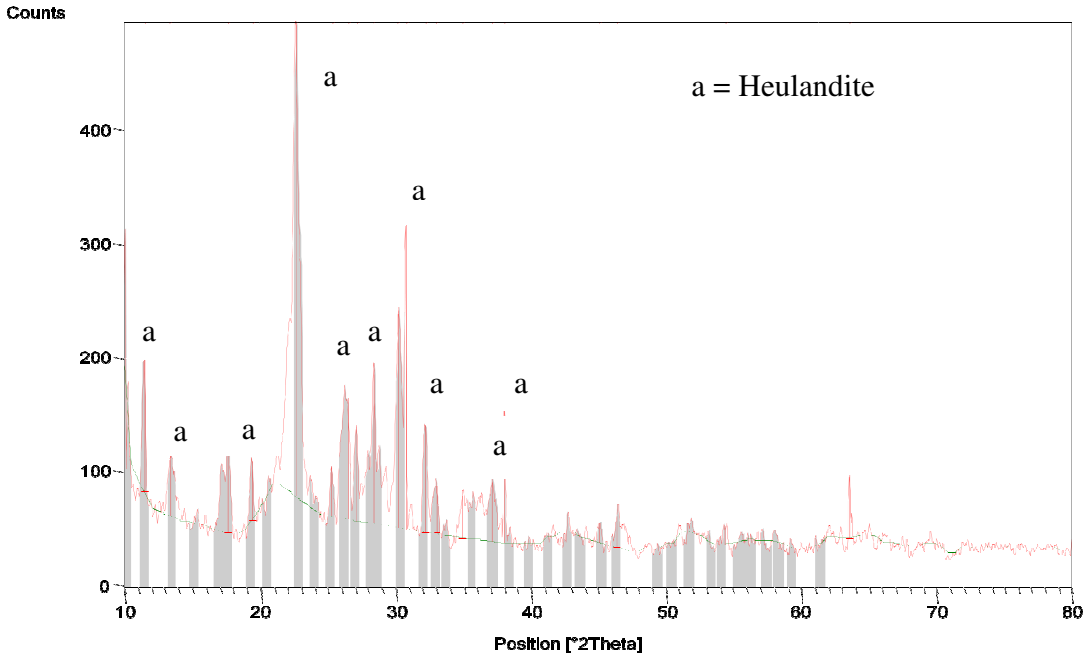



Fig. 4.1 XRD analysis of natural clinoptilolite.

The natural zeolite was found to be crystalline, monoclinic, and mainly consisting of heulandite, ($CaAl_2Si_7O_{18}$. 16 $H_2O$), with the highest peak occurring at a °2θ value of 22 and most of the peaks lying between 2θ values of 10 – 40. The dominant exchange ion on this natural sample is $Ca^{2+}$.

$Na^+$ -form

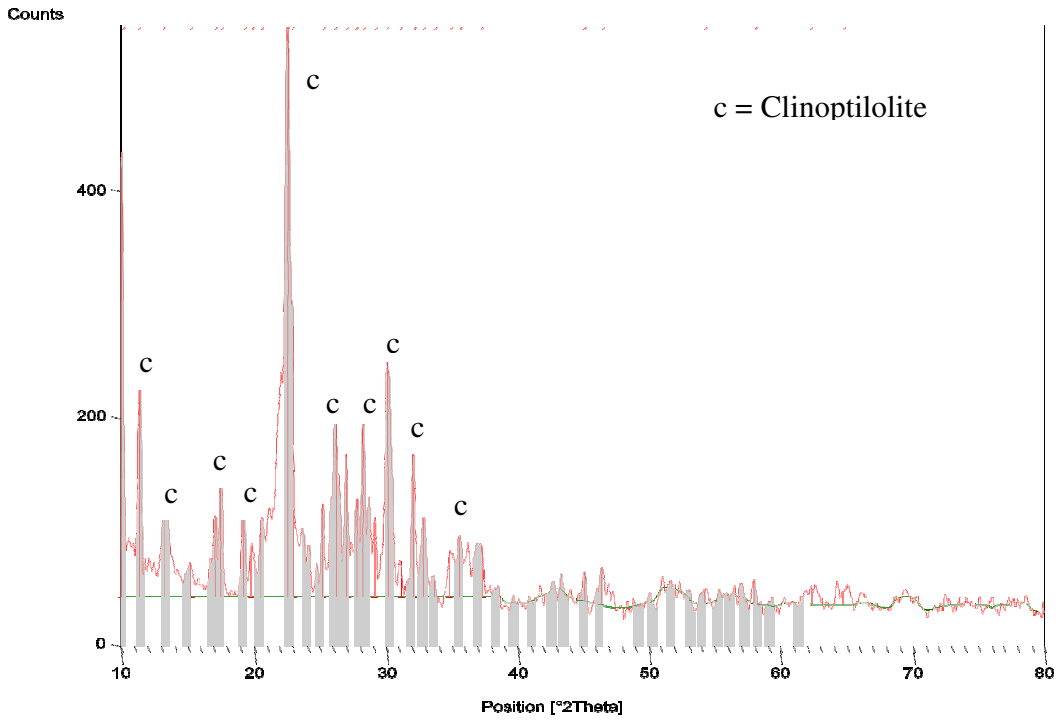



Fig. 4.2 XRD analysis of $Na^+$ modified clinoptilolite

The sharp peaks in the diffraction pattern for the $Na^+$ -form clinoptilolite indicate the crystalline and monoclinic nature of this zeolite. The highest peak also occurs at a °2θ position of 22 and the peaks are mostly concentrated between 2θ values of 10 - 40. The sample consists of clinoptilolite, $(NaKCa)_6(SiAl)_{36}O_{72}.120H_2O$ indicating that the zeolite is predominantly in the $Na^+$ -form. The ions calcium and potassium are still present in the zeolite because $Na^+$ ions are not able to totally displace all of these ions from the framework; they are rigidly bound to the framework or occluded in the zeolite. Semmens and Martin, (1988) and Inglezakis et al. (2004) observed the same.

This also confirms that complete homoionic conversion of natural clinoptilolite is difficult to achieve.

$K^+$ -form

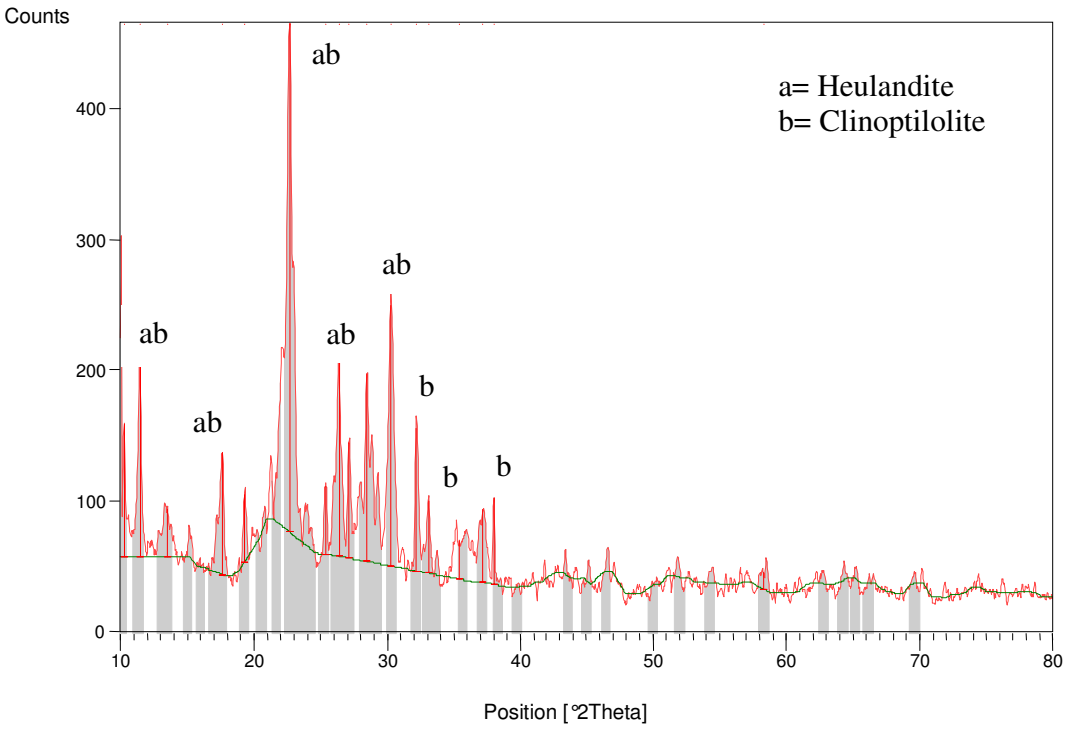



Fig.4.3 XRD analysis of $K^+$ modified clinoptilolite

The crystallography of $K^+$-form clinoptilolite was monoclinic and the highest peak was also at °2θ value of 22, and the range of the sharp peaks was 10 – 40. The $K^+$–modified zeolite sample mainly constituted of clinoptilolite, $(NaK)_4CaAl_6Si_{30}O_{72}.124H_2O$ and heulandite, $CaAl_2Si_7O_{18}.16H_2O$. This suggests that

$K^+$ is not as good at displacing $Ca^{2+}$ as $Na^+$ is, and it is also not able to displace $Na^+$ from the zeolite framework.

<u>$Ca^{2+}$ - form</u>

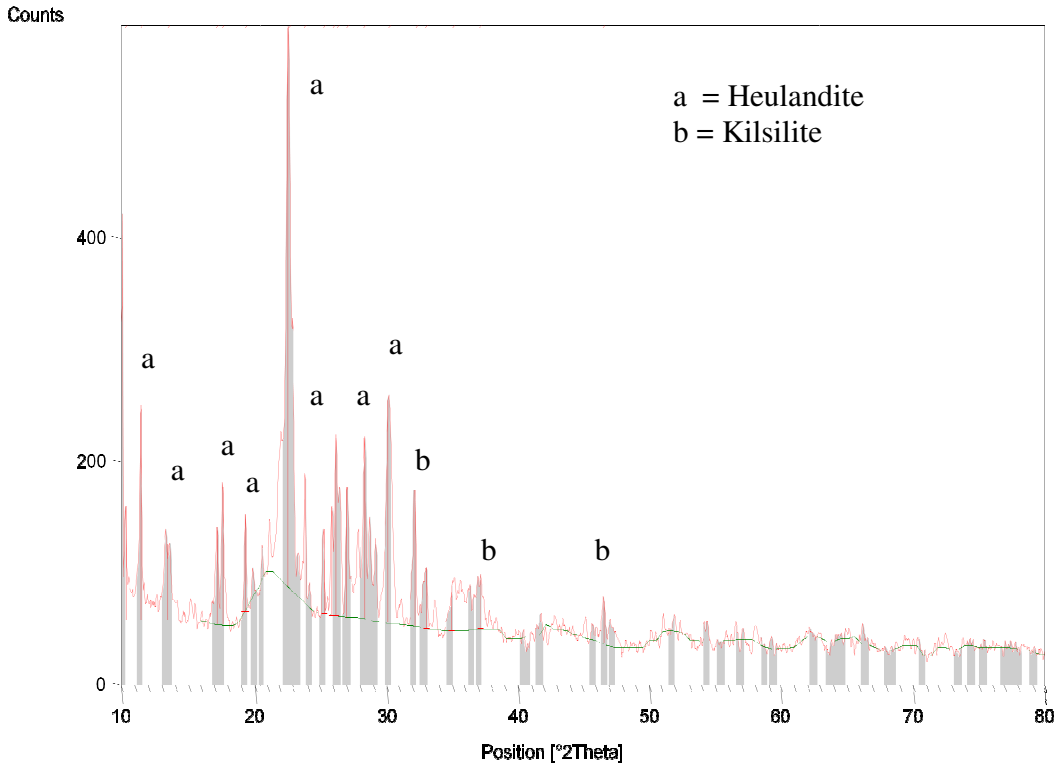



Fig. 4.4 XRD analysis of $Ca^{2+}$ modified clinoptilolite

The $Ca^{2+}$-form of clinoptilolite was also crystalline and monoclinic in nature, with the highest peak similar to the natural, $Na^+$ and $K^+$ forms; occurring at °2θ value of 22. The 2θ range was 10 – 40 as well, and the main component was heulandite ($CaAl_2Si_7O_{18}.16H_2O$) occurring in conjunction with hexagonal kilsilite ($KAlSiO_4$), as

the main impurity. As expected $Ca^{2+}$ ions are the predominant ions, although it cannot completely displace $K^+$ ions in kilsilite.

<u>$NH^+_4$-form</u>

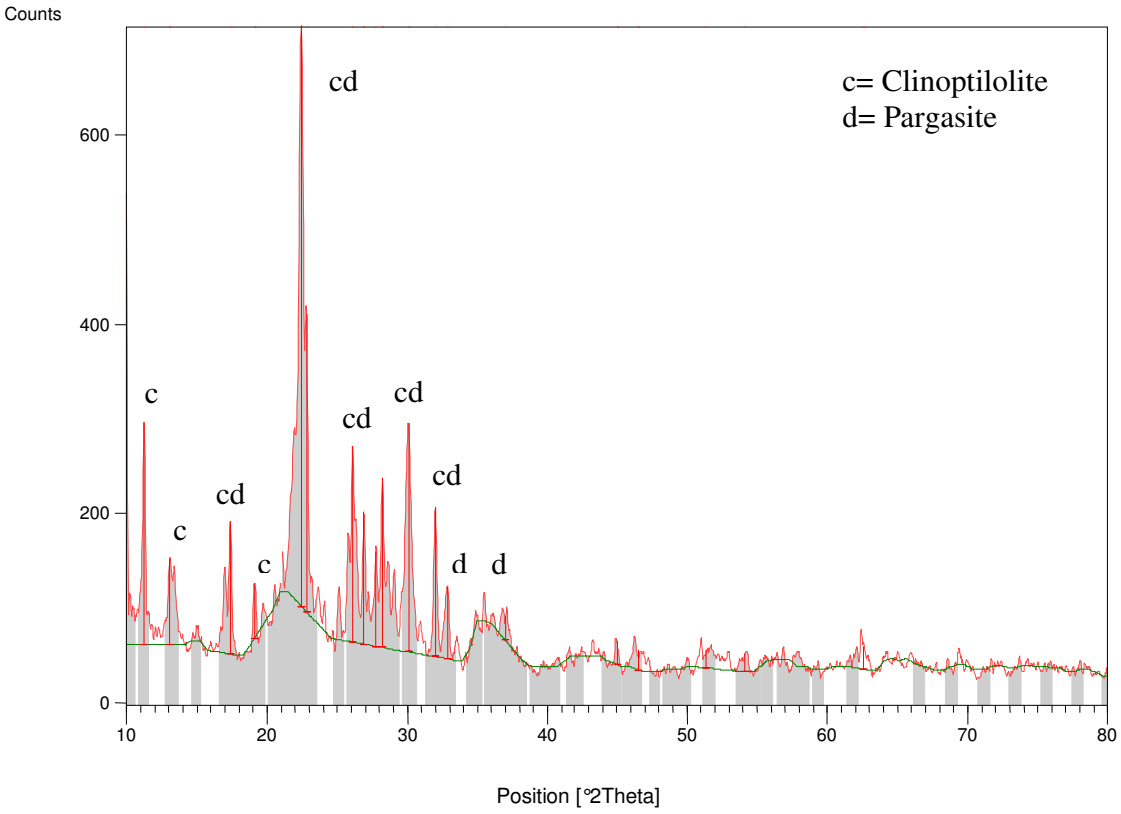



Fig. 4.5 XRD analysis of $NH_4^+$ modified clinoptilolite

The $NH^+_4$-form of zeolite has a monoclinic crystallography too, with the highest crystalline peak appearing at a °2θ position of 22, and most of the peaks occurring between 2θ values of 10 – 40. The $NH^+_4$–modified samples consisted of clinoptilolite

$(NaKCa)_6(SiAl)_{36}O_{72}.120H_2O$, with the predominant ions being $Na^+$ ions. This modified sample also consists of an aluminium silicate hydroxide mineral identified as pargasite ($NaCa_2Mg_4Al(Si_6Al_2)O_{22}(OH)_2$). This compound has been identified as calcic clinoamphiboles (Brodie and Rutter, 1985). The main component in the $NH^+_4$– form zeolite was clinoptilolite, which suggests that $NH^+_4$ ions are not good at displacing $Na^+$, $K^+$ and $Ca^{2+}$ ions from the zeolite structure .

In summary, the XRD diffraction patterns of all the zeolite samples had monoclinic crystollographies (glassy) with an average density of 2.2 g/cm$^3$. Most of the sharp peaks were assigned to clinoptilolite and heulandite. The main impurities observed were with kilsilite (found in the $Ca^{2+}$ - form clinoptilolite) and pargasite (found in the $NH_4^+$-form clinoptilolite). In all the XRD patterns, the highest crystalline peak was situated at 2θ value of 22, agreeing with the work of Themistocleous (1990). The $Na^+$ form clinoptilolite was found to be closest to homoionic form. The $NH_4^+$-form clinoptilolite was not able to displace any of the other metal ions ($Na^+$ ,$Ca^{2+}$ and $K^+$) from solution, and the $Ca^{2+}$ does not displace $K^+$ from the zeolite framework and vice versa. This could suggest that separate exchange site exist for particular ions on the zeolite framework, and these sites are independent of the incoming metal ion. Sprynskyy et al. (2006) has stated that "apparently all metal ions except nickel are sorbed on their own sorption positions."

*4.2.2 Scanning Electron microscopic*

The following surface morphologies were found when the zeolite samples were analysed. The figures 4.6 and 4.7 below represent the images obtained when natural clinoptilolite samples were analysed using SEM at different magnifications.

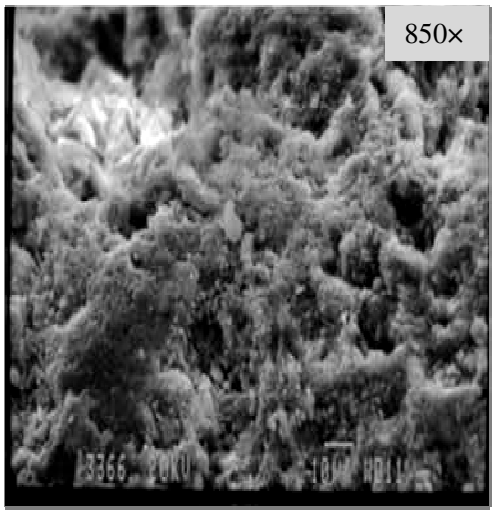



Fig. 4.6 SEM at 850×

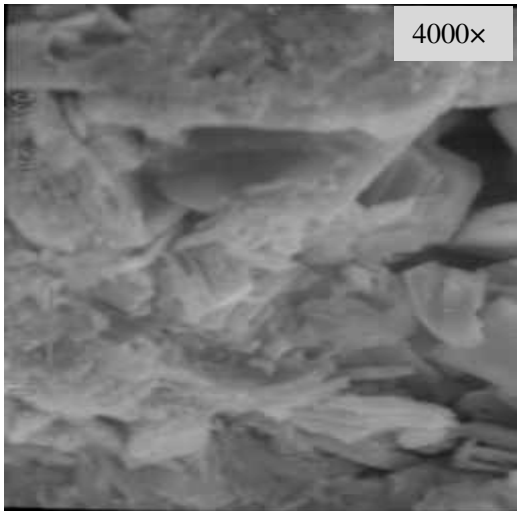



Fig. 4.7 SEM at 4000×

Figures 4.6 and 4.7 above show the randomly oriented crystallites and figure 4.7 particularly indicates the crystalline nature of the zeolite.

*4.2.3 BET surface area analysis*

Below is a table of the surface areas and pore volumes of the natural and homoionised zeolites (based on B.E.T analysis that was carried out in this research). The table (Table 4.1) also has data of the exchange cations atomic radii and hydrated radii as summarized by Nightingale, Jr. (1959):

Table 4.1 BET analyses of natural and homoionised zeolites before loading

| SAMPLE | SURFACE AREA $m^2/g$ | PORE VOLUME $cm^3/g$ | Crystal ionic radius at 25°C (Å) | Hydrated radius at 25°C (Å) |
|---|---|---|---|---|
| Natural | 14.9 | 0.054 | - | - |
| $Na^+form$ | 16.5 | 0.054 | 0.95 | 3.58 |
| $K^+$ form | 15.6 | 0.049 | 1.33 | 3.31 |
| $Ca^+$ form | 10.2 | 0.043 | 0.99 | 4.12 |
| $NH_4^+$ form | 16.1 | 0.051 | 1.48 | 3.31 |

When the natural zeolite was converted to the $Na^+$ -form, the surface area increased from 14.9 $m^2/g$ to 16.5 $m^2/g$ but the pore volume remained constant at 0.054 $cm^3/g$. This supports the results on the preconditioning of zeolites; that $Na^+$ -form clinoptilolite exhibits slightly higher adsorption capacities than natural clinoptilolite. Converting the natural clinoptilolite to $Na^+$ displaces other cations sitting in the zeolite and opens up more sites in this almost homoionic form, thus the increase in the surface areas. It was found that after conditioning, the pore volume remained constant implying that the presence of the $Na^+$ ions does not affect the pore volumes.

When the natural zeolite was conditioned to the $K^+$ form, it was noticed that the surface area increased to 15.6 $m^2/g$ and the pore volume decreased from 0.054 to 0.049 $cm^3/g$. From the XRD analysis, the $K^+$ form clinoptilolite contained

clinoptilolite, with $Na^+$ as the dominant ion, and $K^+$ is not able to completely displace $Na^+$ and $Ca^{2+}$ ions from the framework. The surface area was measured to be more than that of the natural clinoptilolite, but adsorption capacities at 50 mg/L were still lower than that of the natural clinoptilolite (see Table 4.1 in section 4.2.3 above). The decreased pore volume might have restricted the accessibility of exchange sites in the $K^+$ form zeolite.

$Ca^{2+}$ pretreated zeolites exhibited the smallest surface area (10.2 $m^2/g$) and pore volume (0.043 $cm^3/g$), which coincides with its lower percentage adsorption of all metal ions at lower concentrations as also shown in figures 4.27, 4.28 and 4.29. The $Ca^{2+}$ ions also have the largest hydrated radius as stated by Nightingale, Jr. (1959). So once these ions sit in the zeolite framework, the ions bound with water molecules close up the zeolite pores, reduce interaction with the adsorbent and restrict ion movement in and out of the structure

The $NH^+_4$ -form clinoptilolite exhibited a higher surface area than the natural zeolite, namely 16.1 $m^2/g$ as compared to the 14.9 $m^2/g$ of the natural zeolite. However, the natural zeolite had a pore volume of 0.054 and the $NH^+_4$ 0.051 $cm^3/g$. This slight difference in the pore volume may have had an effect on the loading capacity (Figures 4.27, 4.28 and 4.29). The other exchange ions ($Na^+$ and $Ca^{2+}$) sitting in the $NH^+_4$ -form clinoptilolite, which $NH^+_4$ is not able to displace may have contributed to the closing up of the pores and reducing loading capacities as compared to the natural or $Na^+$ clinoptilolites.

In summary, it was interesting to observe that the $Na^+$-form clinoptilolite with the larger surface area (16.5 $m^2/g$) adsorbed more metal ions from solution as compared to that natural, $K^+$ and $NH^+_4$-form zeolites, with a smaller surface areas. Despite the natural zeolite having a smaller surface area than $K^+$ and $NH^+_4$-form zeolites, it seems to exhibit a higher cation exchange capacity than those two homoionised zeolites possibly due to its slightly larger pore volume, which makes it more accessible for metal ions to move in and out of the zeolite framework and exchange ions at the different sites.

## 4.3 Batch processes

### *4.3.1 Particle size effect*

A big particle size (4.0 mm – 1.0mm) and a small zeolite particle size (0.8 mm – 0.4mm) were used at a feed concentration of 50 mg/L and zeolite weights of 2 and 4g, and the amounts of adsorbate remaining in solution with respect to the two particle sizes were observed. This experiment was initially done for $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$ and the results obtained are presented in figure 4.8 below.

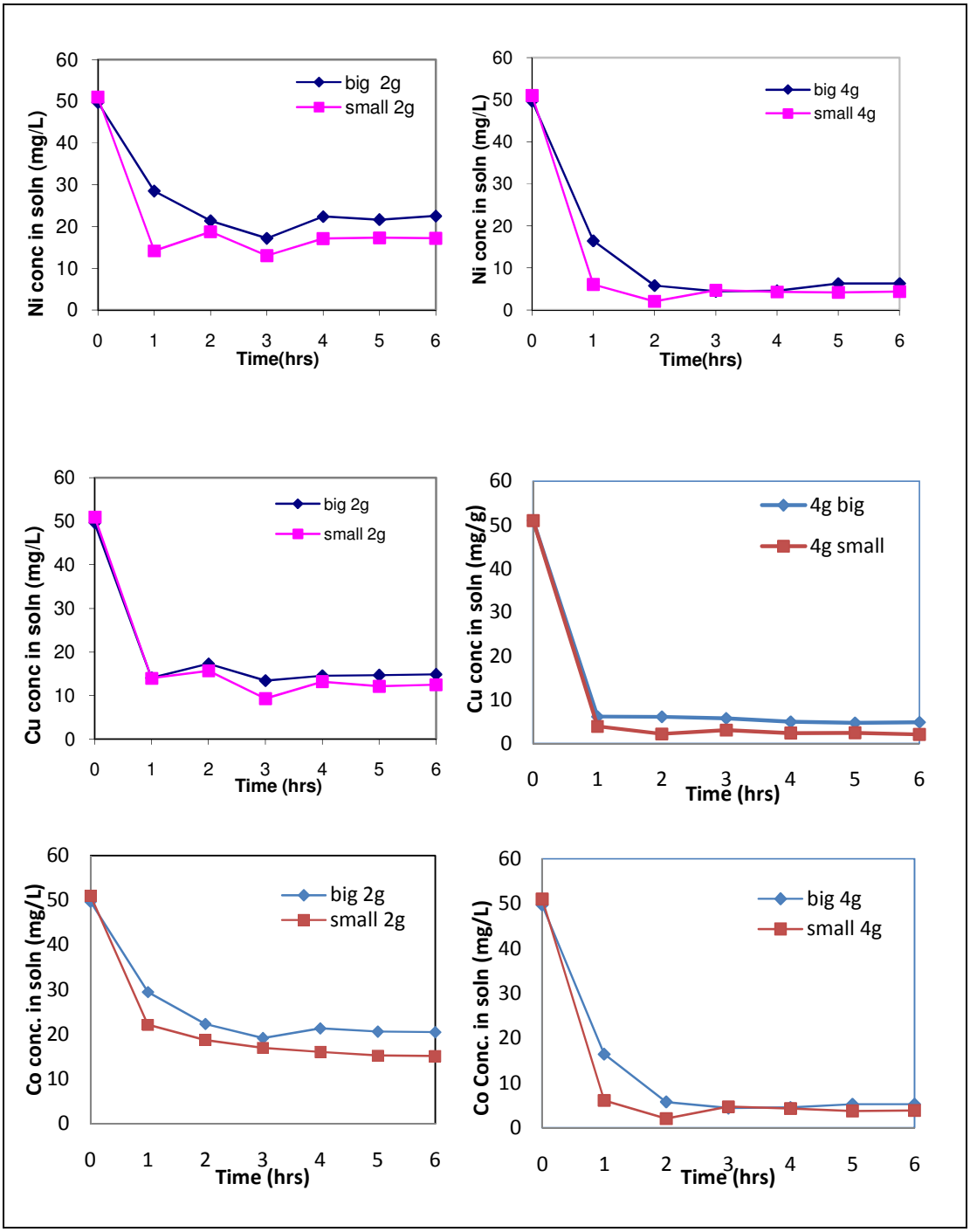



Fig. 4.8 Adsorption of metal ions on big and small sized natural zeolite

It was observed that the smaller particle sized samples adsorbed slightly more metal ions of $Ni^{2+}$, $Cu^{2+}$ and $Co^{2+}$, and so less metal ions remained in the supernatant solution at equilibrium for the smaller particle sizes than the bigger particle sized zeolite. For instance, adsorption of nickel ions using 2g clinoptilolite samples showed final supernatant concentrations of 19 and 23 mg/L for the smaller and bigger particle sizes respectively. For $Cu^{2+}$ ions, the final ions in solution were 12 and 14 mg/L, and for $Co^{2+}$ ions, the remaining ions in solution were 14 and 19 mg/L, with the smaller particle sized natural clinoptilolite adsorbing the most ions The lower final concentration (with the smaller particle sized particles) implies a greater loading for metal ions onto the zeolite. This increase in loading capacity can be attributed to the exposure of more internal pores in the particles, which in turn makes adsorption centres more exposed and accessible in relation to the incoming ions, and so adsorption and ion exchange capacities are increased. Authors such as Sprynskyy et al. (2006) and Inglezakis et al. (2007) observed the same behaviour using clinoptilolite and bentonite clay. The bigger particle sized clinoptilolite had lower adsorption capacities than the smaller particle sizes possibly because the exchangeable sites were occluded within the bulk of the zeolite structure, and breaking it up into smaller sizes makes the sites more available to the incoming ions and thus increases the adsorption capacity.

The availability of sites relates to the equilibrium behavior of the ion exchange system whereas the accessibility relates to the kinetic behavior of the ion exchange

system; the ease of movement of the specific ions within the pores leading to the sites.

On the whole, as seen in figure 4.8, adsorption capacity slightly increases with a decrease in zeolite particle size for the three metal ions discussed. From this experiment, it was therefore decided to use the smaller particle sized clinoptilolite samples in the rest of the experiments because of their slightly higher adsorption capacities and less variability, which is expected in adsorption studies.

### *4.3.2 Adsorption Equilibrium*

The adsorption equilibrium was observed for $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$ using 50 and 500 mg/L single feed stocks. Figure 4.9 and 4.10 show the results obtained at 50 and 500 mg/L, after the results of the metal ions were superimposed onto one graph. Adsorption equilibrium was completely attained by the $4^{th}$ hour (240 mins) of running at lower and higher feed concentrations of 50 mg/L and 500 mg/L. However, at 50 mg/L feed concentrations, about 99%, 99%, 98% and 89% of $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cr^{3+}$ were adsorbed in the first hour of contact using 10g of clinoptilolite; a very fast intake of metal ions was observed. Therefore, at lower concentrations, the adsorption equilibrium is said to be completely reached by the $4^{th}$ hour, although the process can be stopped after the $1^{st}$ hour. It was observed that at 500 mg/L feed concentration, only 75%, 43%, 51% and 26% of $Cu^{2+}$,$Co^{2+}$, $Ni^{2+}$ and $Cr^{3+}$ were adsorbed respectively, at equilibrium ($4^{th}$ hour) using 10g zeolite samples. Beyond this time,

the amount of adsorbate removed from solution with increase in time is negligible. This behaviour was observed in single and multi-component feeds and at all concentrations.

During the removal of metal ions from the supernatant solutions, a bumpy trend was observed for the nickel lines at both 50 and 500 mg/L feed concentrations. The nickel ions adsorbed initially and then desorbed with time. Sprynskyy et al. (2006) also observed this behaviour with $Ni^{2+}$ ions or when conducting experiments at higher metal concentrations. This inversion phenomenon was attributed to the counter diffusion of exchangeable cations. Figures 4.9 and 4.10 indicate the time at which adsorption equilibrium was attained and the adsorption and desorption behaviour of nickel ions.

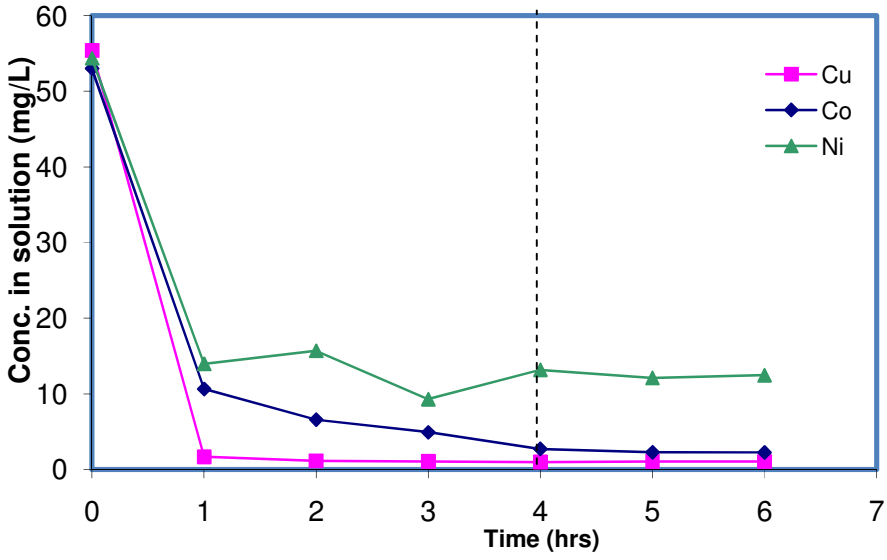



Fig. 4.9 Adsorption equilibrium on 2g natural clinoptilolite using 50 mg/L feed.

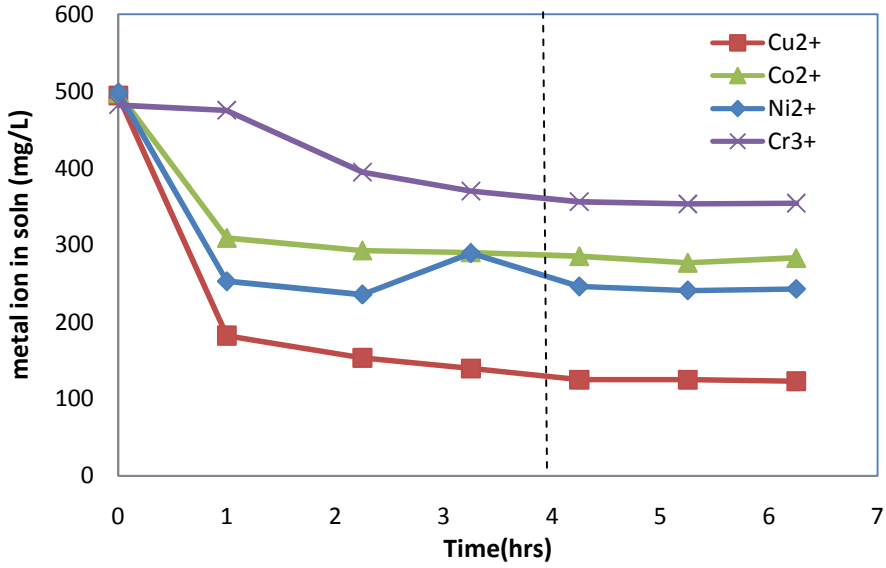



Fig. 4.10 Adsorption equilibrium on 10g natural clinoptilolite using 500 mg/L feed.

### *4.3.3 Natural zeolite loading*

Using the mass balance equation (3.1) from chapter 3, the loading capacity,

, was determined. The loading capacity of the natural zeolite, and later on, the modified zeolites were determined, giving the maximum exchange capacities reached after at equilibrium (4 hours). The loading capacities are given figures 4.11 and 4.12 below.

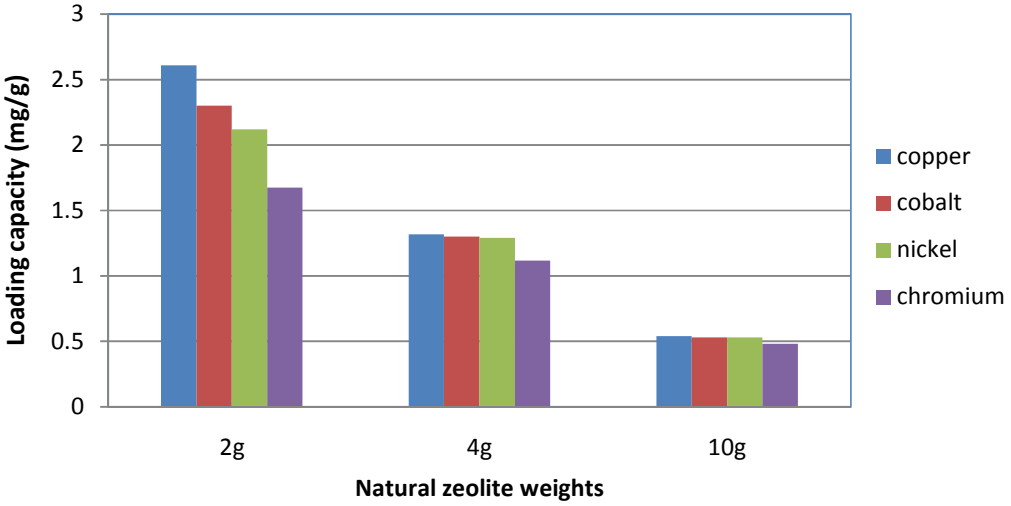



Fig. 4.11 Equilibrium loading capacities of natural clinoptilolite at 50mg/L feed.

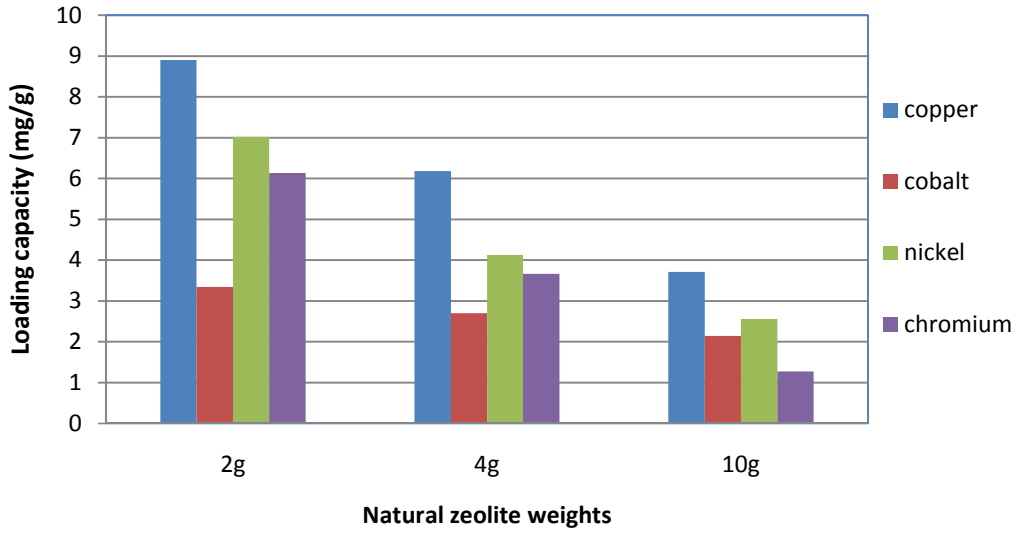



Fig. 4.12 Equilibrium loading capacities of natural clinoptilolite at 500 mg/L feed.

The experimental maximum equilibrium sorption capacity was found to be obtained at lower masses of the zeolite; at 2g, regardless of metal ion concentration used (Also

see table B1 in Appendix B). The natural South African clinoptilolite maximum adsorption capacities for copper, cobalt, nickel and chromium (Figure 4.11) was found to be 2.6, 2.3, 2.1 and 1.7 mg/g respectively at 50 mg/L feed. Almost 100% removal was achieved for these experiments at 50mg/L. This however, was not conclusive because the loading capacity was limited by insufficient initial metal ions in solution. For the 500 mg/L feed, the loading capacity onto 2g natural clinoptilolite was 8.9, 3.3, 7.0, and 6.1 mg/g, respectively (Figure 4.12). Copper metal ions were adsorbed the most in the single-component feeds at both 50 mg/L and 500 mg/L. Clearly, it can be seen that the loading capacity is dependent on the amount of zeolite added to a fixed volume; the larger the amount of zeolite used in a fixed volume, the lower the loading capacity and vice versa.

Many researchers have tested the sorption capacity of clinoptilolite samples, but results are often difficult to compare. For instance in this experiment, copper seemed to be exchanged most with the 2g clinoptilolite samples and 500 mg/L feed concentration, giving 8.9 mg/g as the loading capacity. Erdem et al. (2004) estimated this value to be 9.10 mg/g for 400 mg/L copper feed concentration, whereas, Alvarez-Ayuso et al. (2003) studied metal uptake from solutions with metal concentrations ranging from 10 to 200 mg/L and found copper loading to be about 5.91 mg/g. Then again, according to Sprynskyy et al. (2006), from the Langmuir isotherm investigations, the maximum sorption capacity for copper was 6.74 mg/g. The noted discrepancies of the published data can be attributed to the mineralogy and chemical features of the used sorbents as well as by experimental parameters such as sorbent–

solution ratio, duration of experiments and equilibrium concentration values (Sprynskyy et al., 2006; Erdem et al., 2004).

### *4.3.4 Batch adsorption isotherm models*

Adsorption isotherms or models can be used as reference points for evaluating the characteristic performance of an adsorbent.

Langmuir isotherm

Different equilibrium feed concentrations (50 and 500 mg/L) using 2g, 4g and 10g zeolite weights were used at 25°C ± 2 to yield the following results shown in figures 4.13 and 4.14,when $C_e/Q_e$ was plotted against $C_e$ values at equilibrium. The three metal ions are superimposed onto one graph for comparative purposes.

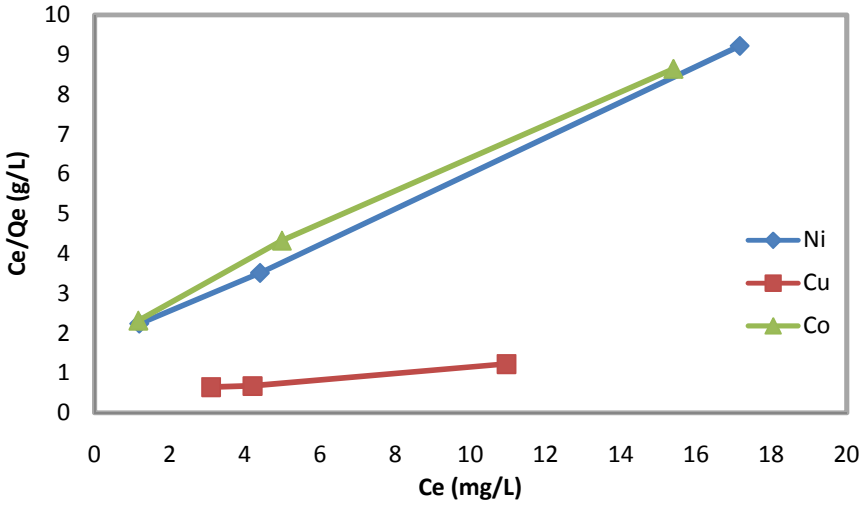



Fig. 4.13 Langmuir isotherm of natural clinoptilolite in 50 mg/L feed.

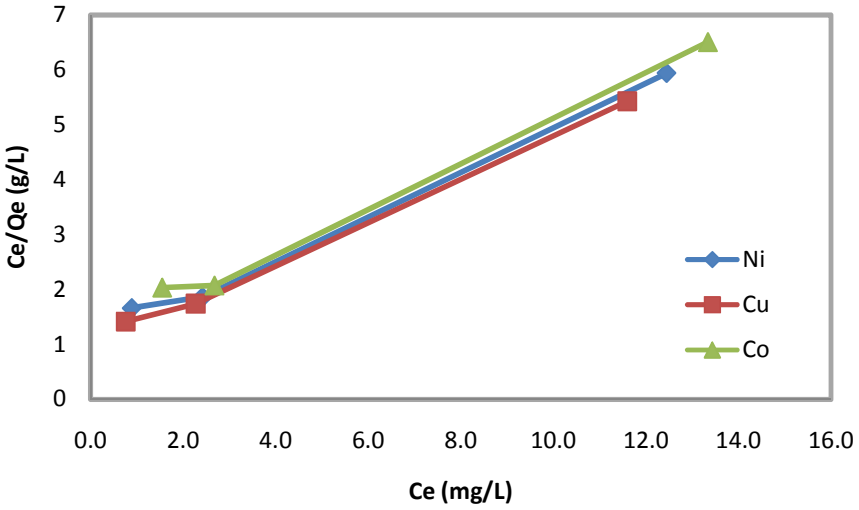



Fig. 4.14 Langmuir isotherm of $Na^+$ form clinoptilolite in 50 mg/L feed.

As seen from figures 4.13 and 4.14, the experimental data for both natural and $Na^+$ form zeolite at a lower initial feed concentrations of 50 mg/L fitted reasonably well with the Langmuir isotherm. This is under the assumptions that all adsorption sites are identical and the adsorption sites have equal energies of adsorption (i.e. adsorption is a monolayer) (Gunay et al., 2007). The correlation coefficients, $R^2$, were all above 0.99 for all the metal ions. The values of $K_L$ and *a,* relating to the adsorption maximum (l/ g) and bonding strength (l/mg) respectively are presented in Table 4.2 below.

Table 4.2 Parameters for Langmuir isotherms at 50 mg/ L

| | *Natural zeolite* | | | *Na+ form zeolite* | | |
|---|---|---|---|---|---|---|
| | $Cu^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ |
| $K_L$ *(l/g)* | 2.6 | 0.51 | 0.60 | 0.98 | 0.81 | 0.87 |
| *a (l/mg)* | 0.20 | 0.22 | 0.27 | 0.37 | 0.32 | 0.34 |
| $K_L/a$ **(mg/g)** | 13.0 | 2.3 | 2.2 | 2.6 | 2.5 | 2.6 |
| $R^2$ | 0.9929 | 0.9971 | 0.9996 | 0.999 | 0.9937 | 0.9935 |

The experimental equilibrium loading capacity at the 50 mg/L feed concentration was found to be in the range of 1.6 – 2.6 mg/g for all the metal ions. The theoretical maximum monolayer adsorption capacity, $\mathbf{q_m}$ from the Langmuir model was found using the relationship $\mathbf{K_L/a}$ (mg/ g) (Gunay et al., 2007), and the range obtained was 2.27 – 2.64 mg/g (which is relatively close to the experimental values) although one theoretical adsorption capacity value for $Cu^{2+}$ loading onto natural zeolite was as high as 13.0 mg/g (see first column in table 4.2).

A plot of the Langmuir isotherms was done using 2g, 4g and 10g zeolite samples, and equilibrium data using initial feeds of 50 and 500 mg/L. The following results were obtained;

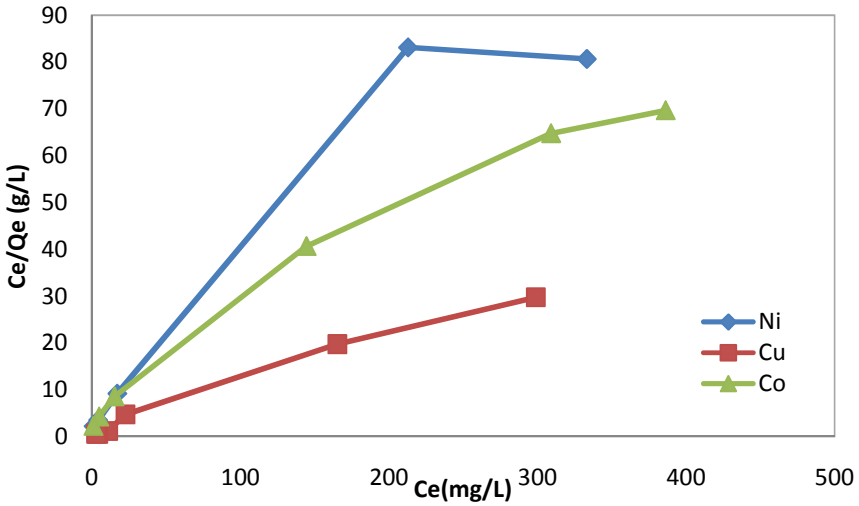



Fig. 4.15 Langmuir isotherm of natural clinoptilolite in 50 and 500mg/L feed.

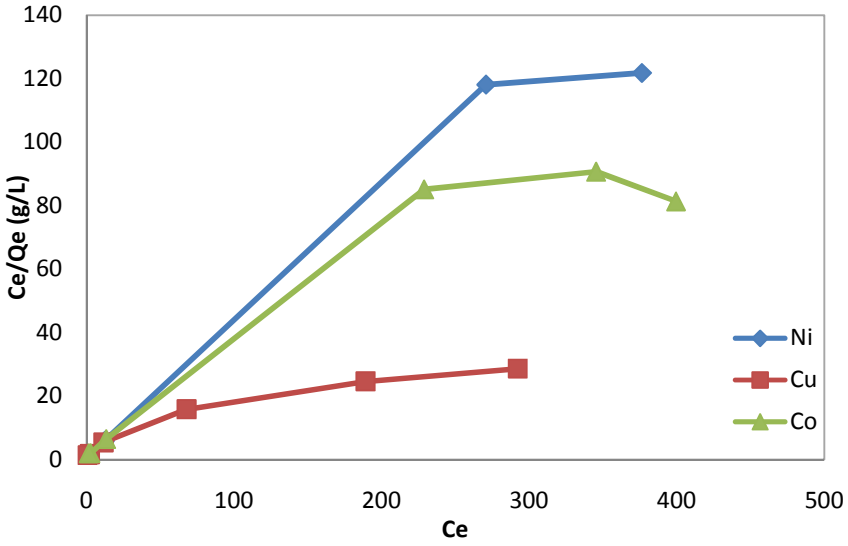



Fig. 4.16 Langmuir isotherm of $Na^{+}$ clinoptilolite in 50 and 500 mg/L feed.

It was seen that at higher concentrations (figures 4.15 and 4.16); the data did not fit the linear form of the Langmuir isotherm. The curves at higher concentration were beginning to invert and decrease with an increase in concentration except for $Cu^{2+}$

line, which increases with increasing concentration but with different gradients (Also see figures E5 and E6 in Appendix E). Thus, the Langmuir isotherm model applies well to lower concentrations but not at higher concentrations. This may indicate that the Langmuir isotherms assumptions do not hold at higher concentrations such as 500 mg/L.

Freundlich isotherm

This was conducted at different equilibrium feed concentrations (50 and 500 mg/ L) using 2g, 4g and 10g zeolite samples, and at 25$^{o}$C ± 2. The following results (Table 4.3) were obtained:

Table 4.3 Parameters for Freundlich isotherms at 50 mg/ L

| | ***Natural zeolite*** | | | ***Na+ form zeolite*** | | |
|---|---|---|---|---|---|---|
| | $Cu^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ |
| $K_f$ ***(mg/g)*** | 3.0 | 0.5 | 0.5 | 0.7 | 0.7 | 0.7 |
| ***n(g/ L)*** | 2.1 | 2.0 | 2.1 | 2.0 | 2.4 | 2.0 |
| $R^2$ | 0.9631 | 0.989 | 0.9523 | 0.9261 | 0.9037 | 0.9071 |

At 50 mg/L, the data only fitted moderately well with the linear form of the Freundlich isotherm with the correlation coefficients $R^2$, ranging from 0.9037 – 0.989. The values of $K_f$ and *n,* relating to the adsorption capacity (mg/g) and adsorption intensity (g/L) respectively were also calculated. The theoretical

maximum loading capacity range was found to be in the range 0.5 – 3.0 mg/g, which is closely related to the experimental values obtained (1.6 – 2.6 mg/g). It has been observed that for values of n between 2 and 10, the zeolite shows good adsorption (Erdem et al., 2004). At higher feed concentrations (500 mg/L), the data did not fit the Freundlich isotherm, implying that the isotherm does not hold, even when it assumes that the energies of adsorption are not identical.

### *4.3.5 Zeolite modification/homoionisation and their performance*

Adsorption data for $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$ onto natural clinoptilolite and zeolites which had been modified with $Na^{+}$, $K^{+}$, $Ca^{2+}$ and $NH^{+}_{4}$ are shown below in figures 4.17, 4.18 and 4.19. The graphs were superimposed, to compare their performances as shown below:

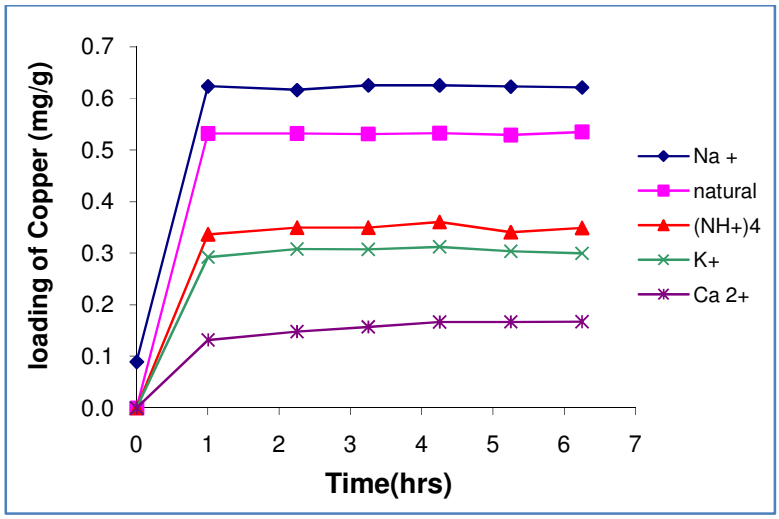



Fig. 4.17 $Cu^{2+}$ loading onto 10g natural and homoionised clinoptilolite using 50mg/L feed.

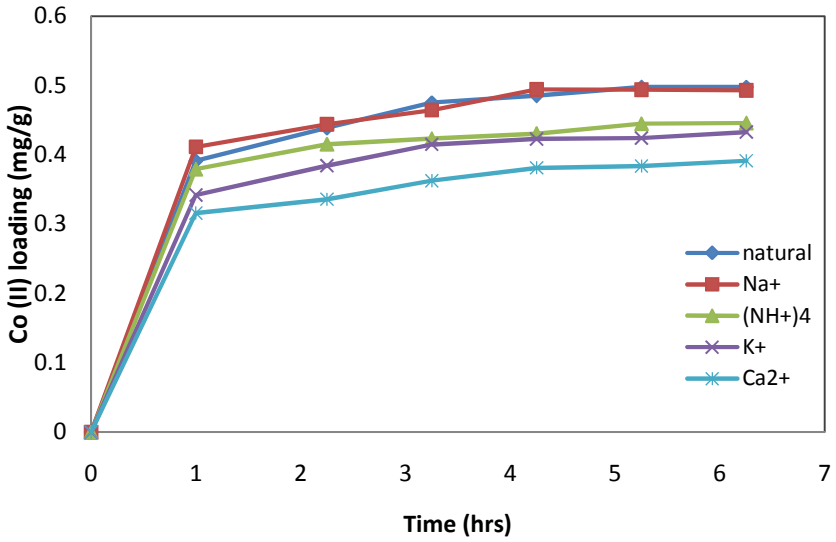



Fig. 4.18 $Co^{2+}$ loading on 10g of natural and homoionised clinoptilolite using 50 mg/L feed.

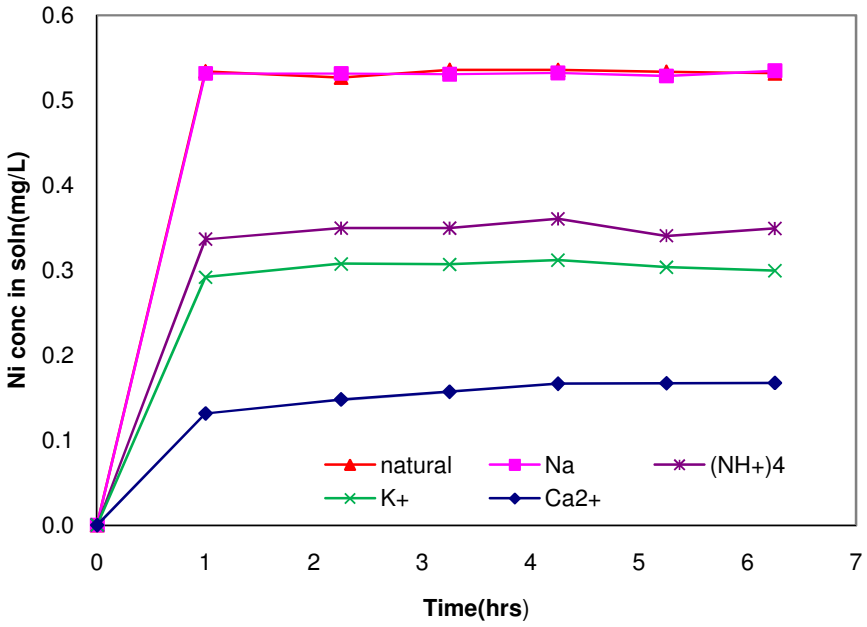



Fig. 4.19 $Ni^{2+}$ loading onto 10g of natural and homoionised clinoptilolite using 50 mg/L feed.

i) At 50 ppm

When the three metal ions were loaded onto natural and modified zeolites, a similar order was observed, regardless of the mass of zeolite used (Also see Figures C7, C8 and C9 in Appendix C). For $Cu^{2+}$ and $Ni^{2+}$ ions, The loading capacities for the $Na^{+}$ form and natural clinoptilolite were closer to each other, followed by the $NH^{+}_{4}$ and $K^{+}$ -forms, which were also close together, then lastly $Ca^{2+}$ -form clinoptilolite, which recorded the lowest adsorption capacities at 50 mg/L. This trend was observed for single component feed solutions of $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$ using 2g, 4g and 10g zeolite weights. This trend shows that natural and $Na^{+}$ form clinoptilolite have similar adsorption capacities, although $Na^{+}$ form has a slightly higher adsorption capacity that the natural zeolite. This adsorption capacity was followed by $K^{+}$ and $NH^{+}_{4}$, and lastly $Ca^{2+}$. Panayotova and Velikov (2003), as stated in section 1.3, also observed a higher adsorption capacity of $Na^{+}$ pretreated clinoptilolite compared to the natural one (improved loading capacities when the zeolite is modified). This coincides with $Na^{+}$ - form zeolite's higher BET surface areas and pore volumes than that of $K^{+}$,$Ca^{2+}$ and $NH^{+}_{4}$- form zeolites, as was observed during BET analysis in Table 4.1 of section 4.2.3.

$NH^{+}_{4}$ and $K^{+}$ -form clinoptilolites have surfaces areas larger than $Ca^{2+}$ but lower than $Na^{+}$ -form zeolite. Their ionic radii and hydrated radii are the same (Table 4.1), which

accounts for the small difference in their adsorption capacities values of the three metal ions.

$Ca^{2+}$ form zeolite adsorbs the smallest amount of metal ions. One explanation is attributed to the pore sizes of the zeolite crystallites, which are usually affected by the size of the exchange cations sitting in the zeolite framework. $Ca^{2+}$ has the largest hydrated radius (Table 4.1), and when it exchanges its ions with the ions in the zeolite, the hydrated ion occupies the exchange sites but restricts the pore size openings and thus creates a sieving effect on the metal ions in solution. Therefore, most of the ions have restricted access into the framework to exchange with the $Ca^{2+}$ ions. The performance of the natural and pretreated zeolites showed the following adsorption capacity order for the metal ions;

$$Na^{+} \geq \text{natural} > NH^{+}_{4} > K^{+} > Ca^{2+}$$

This order was very pronounced for $Ni^{2+}$ and $Cu^{2+}$ adsorption. For $Co^{2+}$ the same trend was followed although the difference in the adsorption capacities by the natural and modified zeolites was very small

Also, at low concentrations of 50 mg/L, it was noticed that the loading capacities were ranging between 0.6 mg/g to 2.13 mg/g (using 10g natural zeolite). From this, it can be concluded that at equilibrium, almost all the $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$ ions have been loaded onto the zeolite (very negligible amounts are present in the supernatant solutions). Theoretically, the amount of $Na^{+}$, $NH^{+}_{4}$, $K^{+}$ and $Ca^{2+}$ ions that are displaced from the zeolite equals the number of moles of metal ions adsorbed

(depending on the metal ions charge balance and valency). Therefore, the amount of $Na^+$ ions displaced from the zeolite is very minimal in comparison with the bulk of $Na^+$ ions still in the zeolite. This implies that the natural and $Na^+$ form zeolites take up $Ni^{2+}$ metal ions (Figure 4.19) for instance, but it is essentially still in the $Na^+$ form, which is characterized by high surface area and pore volumes as shown in BET surface area results in table 4.1. This explains the consistent trends obtained for $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$, where the loading depends on the initial form of the zeolite.

ii) At 500 ppm

At higher feed concentrations of 500 mg/L, no consistent order was observed in the adsorption of the metal ions, regardless of the mass of zeolite used; see figures 4.20 to 4.22 below:

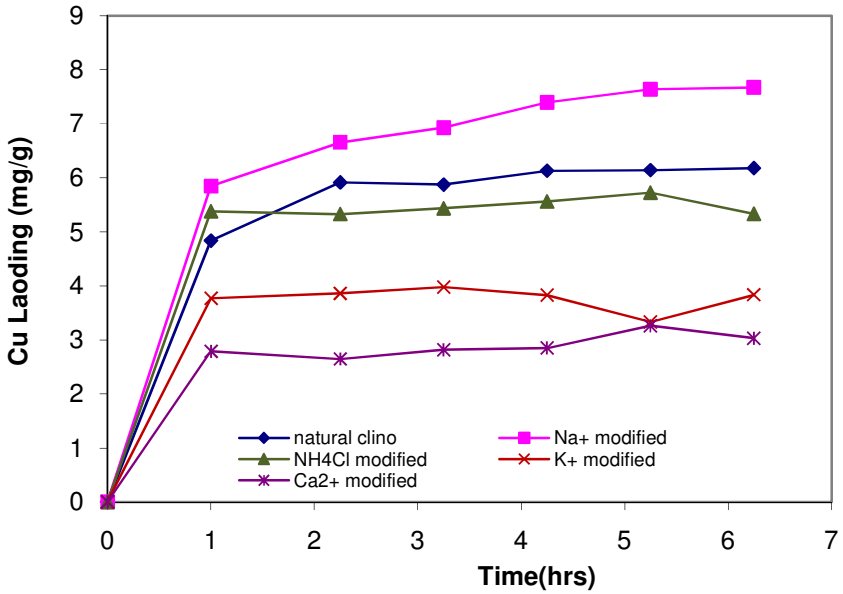



Fig. 4.20 $Cu^{2+}$ loading on 2g natural and homoionised clinoptilolite using 500 mg/L feed.

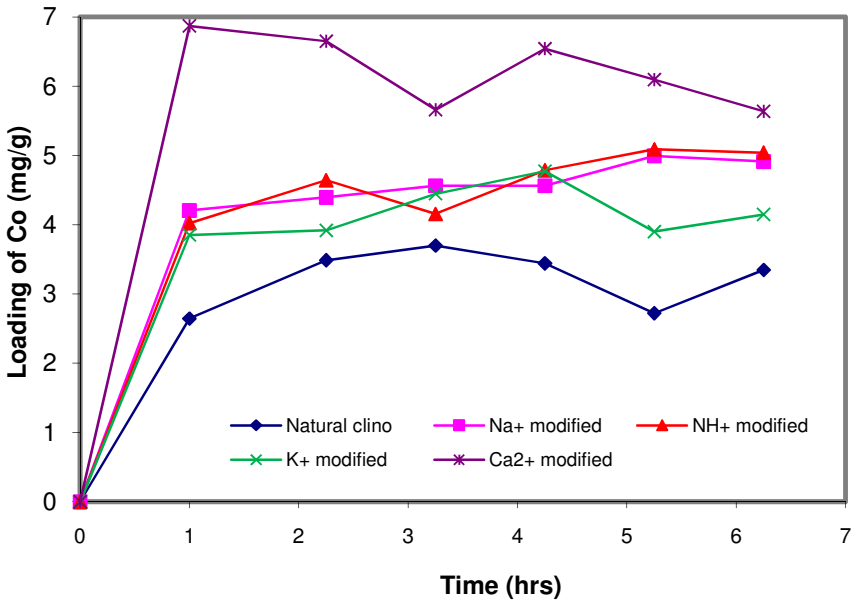



Fig. 4.21 $Co^{2+}$ loading on 2g natural and homoionised clinoptilolite using 500 mg/L feed.

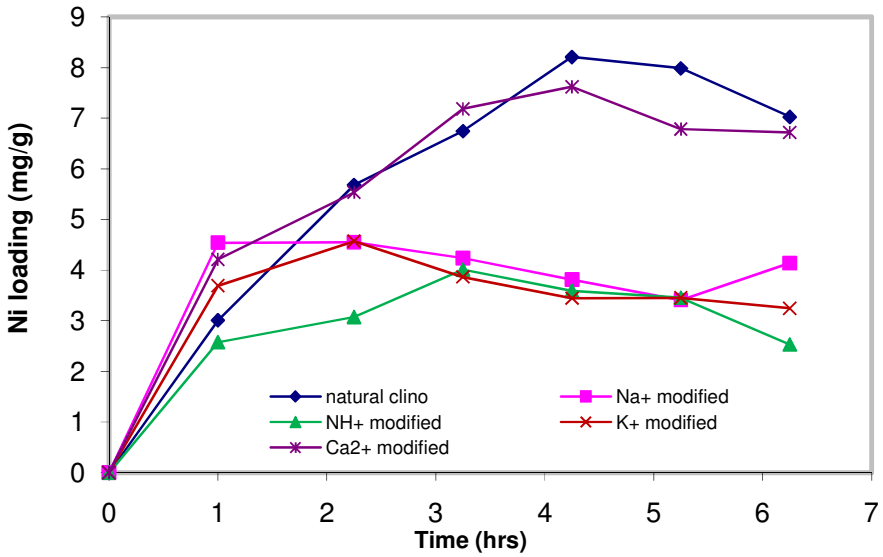



Fig. 4.22 $Ni^{2+}$ loading on 2g natural and homoionised clinoptilolite using 500 mg/L feed.

It was noted that there was a reversal of capacity (and selectivity) at higher concentrations. The following order of the 2g zeolites' performance for the metal ions was as given below:

$Cu^{2+}$ adsorption: $Na^{+} > \text{natural} > NH^{+}_{4} > K^{+} > Ca^{2+}$

$Co^{2+}$ adsorption: $Ca^{2+} > NH^{+}_{4} \simeq Na^{+} > K^{+} > \text{natural}$

$Ni^{2+}$ adsorption: $\text{natural} > Ca^{2+} > Na^{+} > K^{+} > NH^{+}_{4}$

No consistent order was observed at higher concentrations of 500 mg/L like it was when 50 mg/L feed concentration was used. Interestingly, $Ca^{2+}$-form zeolite loading capacity of $Co^{2+}$ and $Ni^{2+}$ metal ions improved at higher concentrations, even higher than the $Na^{+}$ form clinoptilolite, despite the $Ca^{2+}$ -form clinoptilolite having narrow pores. This is possibly because the increased concentration gradient between the metal ions in solution and the exchange ions in the zeolite framework may have triggered the exchange of ions due to the created concentration potential, causing the weak Van der Waals forces to easily break off (Somorjai, 1993), and release $Ca^{2+}$ ions into solution. At equilibrium, the high residual metal ions in solution are able to displace $Ca^{2+}$ ions and so modify the $Ca^{2+}$ zeolite to a $Ni^{2+}$ or $Co^{2+}$ zeolite for example. Therefore the zeolite takes on pore volumes that correspond to $Ni^{2+}$ and $Co^{2+}$ ions. That is probably why the zeolite performance does not follow the same trend followed at lower concentrations.

The above results demonstrate that metal selectivity (and capacity) can be controlled, at low loadings and feed concentrations using natural and homoionic forms, where the surface areas and pore volumes can be altered. It was therefore, decided to use the natural and $Na^+$ form zeolites for the remainder of the experiments because they generally exhibited better and consistent metal ion adsorption than the other homoionised zeolites.

### *4.3.5 Regeneration of natural and $Na^+$ form zeolites*

The regeneration process of clinoptilolite is an important step in ion exchange, in order to make the process economical, as it is able to recover adsorbed metal ions from the zeolites, which can then be put back into the process stream. Regeneration employs the adsorption and desorption mechanisms, which in turn determine the reversibility and reusability of the zeolite material (Argun, 2008; Oztas et al., 2008; Han et al., 2006).

Regeneration of the natural zeolite

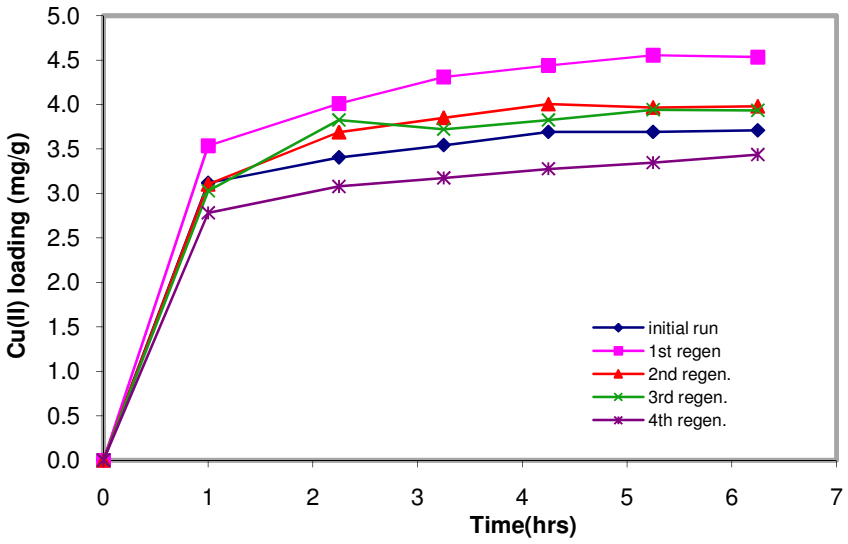



Fig. 4.23 Loading of $Cu^{2+}$ using 10g regenerated natural clinoptilolite and 500 mg/L.

Figure 4.23 above showed that when the natural clinoptilolite was initially used at 500 mg/L, the loading capacity for $Cu^{2+}$ ions was 3.6 mg/L, and after the first regeneration with 0.5M NaCl stripping solution, the loading capacity increased by 25%. The third and forth loading capacities after regeneration were around 3.8 mg/L (lower than the first regeneration run but still higher than the initial run) and the forth run had a loading capacity with was slightly lower than the initial run (Figure 4.23).

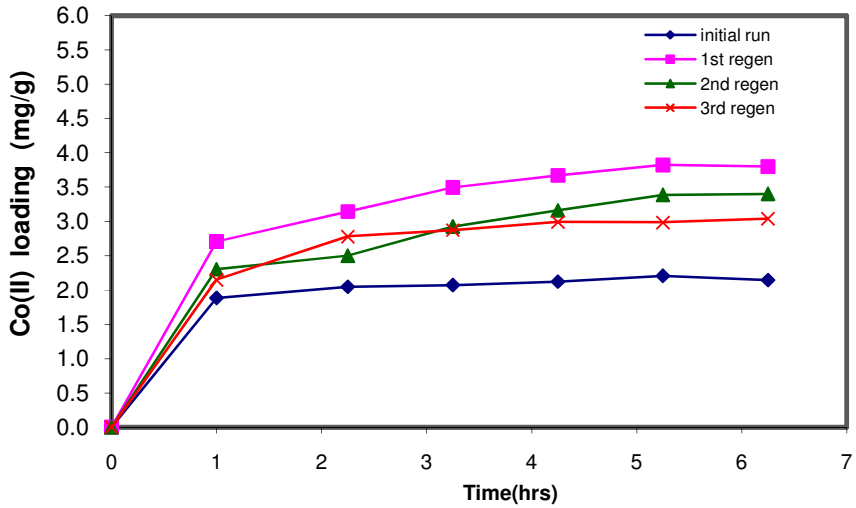



Fig. 4.24 Loading of $Co^{2+}$ using 10g regenerated natural clinoptilolite and 500 mg/L.

The initial loading capacity of $Co^{2+}$ ions at 500 mg/L was 2.1 mg/g. and after the first regeneration cycle, the loading capacity increased by about 75%. The second and third regeneration cycles also recorded loading capacities higher than the initial run but lower than the first regeneration cycle (Figure 4.24).

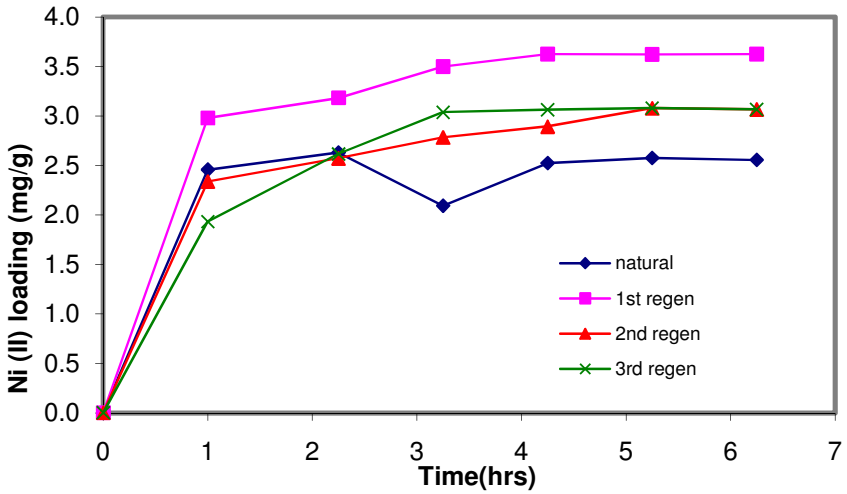



Fig. 4.25 Loading of $Ni^{2+}$ using 10g regenerated natural clinoptilolite and 500 mg/L.

The initial $Ni^{2+}$ ions loading capacity recorded when using 500 mg/L was 2.4 mg/g. The inversion phenomenon of nickel (also discussed in 4.3.2) was also observed at higher concentrations; the adsorption and desorption phenomenon of nickel ions due to counter diffusion of ions. After the first regeneration cycle, the loading capacity increased by 50%. The second and third regeneration cycles loading capacities were almost the same, at 3 mg/g (which was higher than the initial run but lower than the first regeneration cycles).

In summary, it was observed that the subsequent regeneration runs had higher adsorption capacities than the first initial service run (Figures 4.23, 4.24 and 4.25) when natural clinoptilolite and feed concentrations of 500 mg/L were used. This shows that the natural zeolite, after regeneration is converted to $Na^{+}$ form zeolites (Du et al., 2005) (with increased surface area and pore volume), which opens up more vacant exchangeable sites and easily exchanges with incoming ions. This then explain why after the initial run, the regenerated runs adsorb more metal ions. This was applicable to the three metal ions $Co^{2+}$, $Cu^{2+}$ and $Ni^{2+}$. The natural clinoptilolite exhibited good adsorption capacities using 0.5M NaCl as the stripping solution and the first three regeneration cycles were able to achieve loading capacities that were higher than the initial run.

Regeneration of $Na^+$ form zeolite

$Na^+$ form clinoptilolite and 500 mg/L of feed concentration were used to observe the regeneration behaviour. Figures 4.26, 4.27 and 4.28 illustrate the loading capacities obtained:

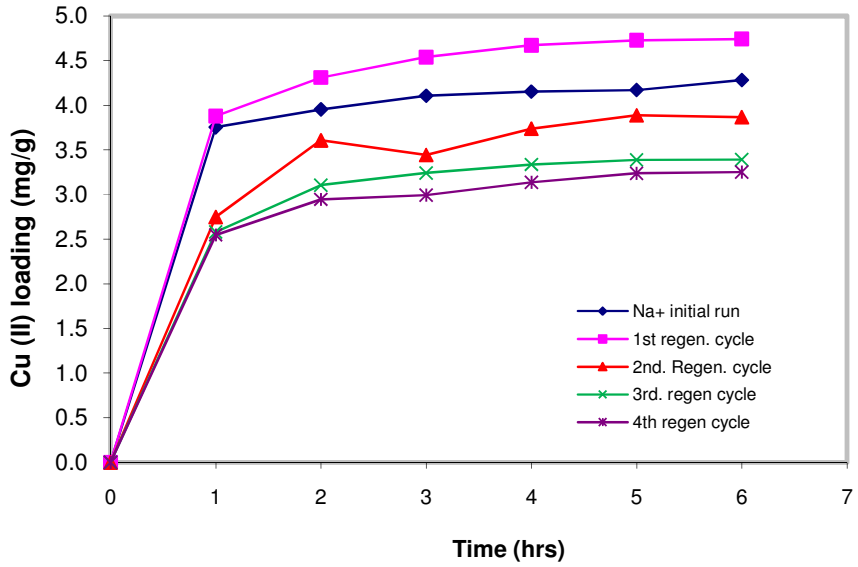



Fig. 4.26 Loading of $Cu^{2+}$ using 10g regenerated $Na^+$-form clinoptilolite and 500 mg/L.

It was observed that when $Na^+$ clinoptilolite was first regenerated with 0.5M NaCl, the loading capacity increased by about 12% (Figure 4.26). The second regeneration run was 14% lower than the initial run. Then the subsequent third and forth regeneration runs were also lower than the initial run.

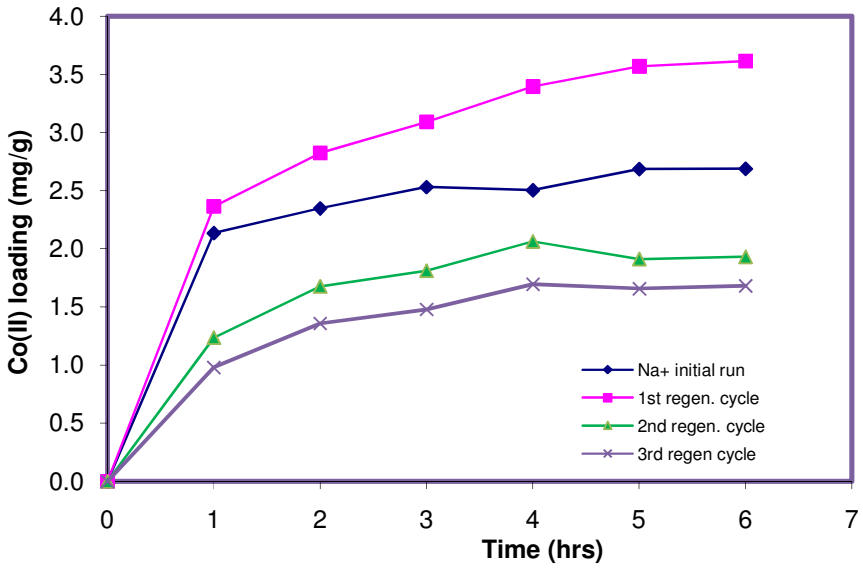



Fig. 4.27 Loading of $Co^{2+}$ using 10g regenerated $Na^{+}$-form clinoptilolite and 500 mg/L.

With an initial loading capacity of $Co^{2+}$ ions of 2.7 mg/g (Figure 4.27), it was observed that the first regeneration loading capacity increased to 3.6 mg/g. The subsequent second and third regeneration cycles recorded loading capacities lower than the initial run.

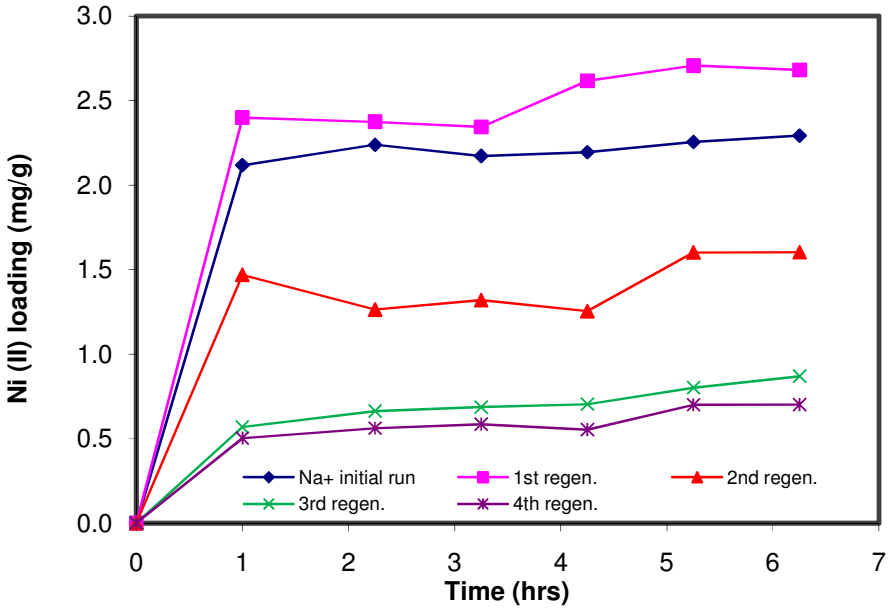



Fig. 4.28 Loading of $Ni^{2+}$ using 10g regenerated $Na^{+}$-form clinoptilolite and 500 mg/L.

The initial $Na^{+}$-form clinoptilolite loading capacity for $Ni^{2+}$ ions was calculated to be 2.3 mg/g. After the first regeneration cycle, the loading capacity slightly increased to 2.6 mg/g. The second, third and forth regeneration cycles also recorded loading capacities lower than the initial run (Figure 4.28).

In summary, even though $Na^{+}$ -form clinoptilolite has higher loading capacities than the natural clinoptilolite, it was observed that after the first regeneration, the adsorption capacity increased slightly more over the first service run but the subsequent $2^{nd}$ and $3^{rd}$ regenerations had adsorption capacities lower than the initial run. This may be due to the fact that the $Na^{+}$ -form zeolite has almost all of its

exchangeable sites saturated or 0.5M NaCl could not effectively regenerate the zeolites. Therefore, regenerating the $Na^+$ form clinoptilolite may have only opened up a few sites that for further exchange of ions (Giles et al., 1974). This relationship was observed for all the three metal ions at 500 mg/L, regardless of the amount of zeolite used.

$Na^+$ -form zeolite shows better adsorption capacity than natural clinoptilolite. However, when regenerated, the $Na^+$-form clinoptilolite exhibited lower regeneration adsorption capacities compared to the natural clinoptilolite. Inglezakis et al. (2004) also observed a similar pattern. With the $Na^+$-form clinoptilolite, only the first regeneration cycle was able to achieve loading capacities higher than the initial run but with the natural clinoptilolite, the first three regeneration cycles achieved loading capacities higher than the initial run, using 0.5M NaCl as the stripping solution and feed concentrations of 500 mg/L.

### *4.3.6 Adsorption in multi-component feed*

A mixed feed at 50 mg/L and then 500 mg/L was used to observe the percentage removal of metal ions from solution during competitive adsorption at equilibrium using natural clinoptilolite.

i. Using 50 mg/L.

Table 4.4 Percentage metal ions removal at 50 mg/L.

| Time | 2g natural clino. | | | | 4g natural clino. | | | | 10g natural clino. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (hr) | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Cr^{3+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Cr^{3+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Cr^{3+}$ |
| 0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 74.0 | 93.1 | 72.9 | 63.8 | 88.8 | 98.6 | 93.4 | 80.2 | 98.2 | 98.9 | 99.3 | 88.6 |
| 2 | 65.6 | 93.1 | 79.2 | 65.1 | 96.2 | 97.9 | 95.3 | 85.7 | 96.9 | 98.3 | 99.2 | 92.4 |
| 3 | 76.1 | 94.0 | 81.9 | 67.1 | 91.3 | 98.1 | 96.5 | 86.5 | 98.6 | 98.0 | 99.5 | 94.1 |
| 4 | 68.6 | 95.5 | 84.5 | 64.3 | 92.0 | 98.2 | 97.1 | 85.6 | 98.5 | 97.3 | 99.1 | 93.7 |
| 5 | 68.2 | 96.9 | 87.8 | 64.3 | 92.3 | 98.4 | 97.0 | 85.8 | 98.1 | 98.5 | 99.1 | 96.8 |
| 6 | 68.4 | 97.0 | 87.8 | 64.4 | 91.9 | 98.3 | 97.2 | 85.9 | 97.8 | 98.5 | 98.8 | 96.9 |

At 50 mg/L, the percentage removal of metal ions increased with an increase in the amount of natural zeolite used (Table 4.4). For nickel removal, the percentage removal range was from 68% - 98% at equilibrium (using the $4^{th}$ hour values). All the metal ions were removed from solution using 10g of zeolite. For copper removal, the average percentage range observed, using 2g - 10g weights of zeolite was 96% - 97%. The range obtained for cobalt removal was 84% - 97% and for chromium 64% - 94%.

The percentage adsorption of the metal ions $Cu^{2+}$, $Co^{2+}$, $Cr^{3+}$ and $Ni^{2+}$ was also very good in mixed feeds of 50 mg/L. The amount of metal ions removed increased with an increase in the amount of adsorbent used. All the metal ions were removed when 10g zeolite amounts were used but when 2 and 4g samples were used, the zeolite removed the copper and cobalt preferentially, followed by nickel and then chromium.

In the case of low concentrations, the ratio of the initial number of moles of metal ions to the available surface area is larger and consequently the fractional adsorption becomes independent of initial concentrations. That is why all the metal ions were removed at initial feeds of 50 mg/L. Copper was mostly removed from solution followed by cobalt possibly because the $Cu^{2+}$ and $Co^{2+}$ ions are adsorbed more strongly, thus bringing in an aspect of competition of the ions in solution for the available sites. Another explanation is that more of the copper is adsorbed than the other metal ions because each metal ion, despite having similar properties to each other interacts only with specific sorption centres of the clinoptilolite and in different sorption forms (Sprynskyy et al., 2006).

Thermodynamically, the ionic radius of an ion plays a role in determining the size of the hydrated radius. The smaller this ionic radius, the more water molecules it draws to itself thus the larger the hydrated radius, which then does not easily diffuse through the zeolite framework. Nightingale Jr. (1959) gives the ionic radii of $Ni^{2+}$, $Cu^{2+}$, $Co^{2+}$ and $Cr^{3+}$ as 0.69, 0.71, 0.78 and 0.91 Å respectively. Chromium (III) has the smallest ionic radius and thus the highest hydrated radius of any known heavy metal and its exchange in zeolitic materials requires a favourable pore opening (Covarrubias et al., 2006). This may explain why chromium when introduced into the experiments in multi-component and single–feed solutions was least adsorbed. Dal Bosco et al. (2005) concluded that highly charged ions, such as chromium (III), tend to have a higher affinity with cation–exchange sites on the zeolite surface than divalent cations. However, this was not observed in the experiments in this dissertation.

Effect of initial metal ion concentration

ii. Using 500 mg/L feed

The following metal removal percentages at higher feed concentration of 500 mg/L, using 2g, 4g and 10g natural zeolite weights, were obtained (Table 4.5) and are presented below:

Table 4.5 Percentage metal ions removal at 500 mg/L.

| Time | 2g natural clino. | | | | 4g natural clino. | | | | 10g natural clino. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (hr) | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Cr^{3+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Cr^{3+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Cr^{3+}$ |
| 0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 12.1 | 27.0 | 10.6 | 4.4 | 33.2 | 39.2 | 18.9 | 3.7 | 49.3 | 63.2 | 37.9 | 1.4 |
| 2 | 22.8 | 32.0 | 14.0 | 3.8 | 44.2 | 47.9 | 21.0 | 4.5 | 52.8 | 69.0 | 41.2 | 18.1 |
| 3 | 27.1 | 36.5 | 14.9 | 17.6 | 32.5 | 47.6 | 19.8 | 27.8 | 42.0 | 71.8 | 41.7 | 23.2 |
| 4 | 32.9 | 35.4 | 13.8 | 26.2 | 39.9 | 49.6 | 24.1 | 30.4 | 50.6 | 74.8 | 42.6 | 26.1 |
| 5 | 32.0 | 34.8 | 10.9 | 26.0 | 41.3 | 49.7 | 20.5 | 31.6 | 51.7 | 74.8 | 44.4 | 26.7 |
| 6 | 28.2 | 36.0 | 13.4 | 25.5 | 33.2 | 50.0 | 21.7 | 30.4 | 51.3 | 75.1 | 43.1 | 26.5 |

From table 4.5 above, it can be seen that generally, the amount of metal ions removed also increased with an increase in the amount of adsorbent used. At higher metal ion concentrations, the percentage metal ion removal drastically dropped compared to the values obtained at 50 mg/L. The following ranges were obtained at equilibrium, using the $4^{th}$ hour values. For nickel removal, the range obtained was 33% - 51% and for copper removal, it was 35% - 75%. Cobalt removal was in the range 14% - 43% and chromium, 26% - 30%.

At higher concentrations, the available sites of adsorption become fewer in relation to the adsorbates and hence the percentage removal of metal ions is also dependent on initial concentration (Yu et al., 2003). The following metal ion selectivity was observed at 500 mg/L:

i. 2g zeolite : $Cu^{2+} > Ni^{2+} > Cr^{3+} > Co^{2+}$

ii. 4g zeolite: $Cu^{2+} > Ni^{2+} > Cr^{3+} > Co^{2+}$

iii. 10g zeolite: $Cu^{2+} > Ni^{2+} > Co^{2+} > Cr^{3+}$.

The zeolite selectivity for the metal ions at higher feed concentrations of 500 mg/L was seen to vary, with 2g and 4g giving the same series, and $Co^{2+}$ and $Cr^{3+}$ reversing in order for 10g. This shows that clinoptilolite's selectivity for metal ions is affected by other factors too, not only on metal ions concentrations in solution or pore volumes or hydrated radii of ions sitting in the framework but it can also be altered by equilibrium parameters and several physicochemical causes (Inglezakis et al., 2004).

### *4.3.7 Hydrolysis of metal ions*

Hydrolysis of metal ions from solution also contributes to the removal of metal ions from solution. The pH values in most the experiments were monitored, to observe to what extent hydrolysis had an influence on the metal ions in solution. Hydrolysis is a chemical reaction involving the decomposition of an ion by water (Baes Jr. et al., 1976). In inorganic chemistry, this leads to the formation of precipitates, oxides, hydroxides or basic salts. Baes Jr. et al. (1976, p1) have stated that "the determination of the identity and stability of dissolved hydrolysis products has proved to be a difficult and a challenging task" because hydrolysis of a cation often appears to run

its course to precipitation, within a narrow range of pH, typically 1–2 units, so this makes it hard to determine.

Although the exact hydrolysis species were not qualified and fully studied in this dissertation, the precipitation of metallic species and the formation of complexes are acknowledged as parameters that affect the separation of metal ions using zeolites. Only the pH values were observed, but not controlled in these experiments. The possibility of precipitation taking place explains to an extent the reason why the selectivity series and efficiencies kept varying in the experiments carried out in this dissertation; many different factors are at play, including external ones.

Self- regulated pH

The pH measurements were taken without adjustments, just to observe the natural path followed. The range observed for the metal ions is as follows:

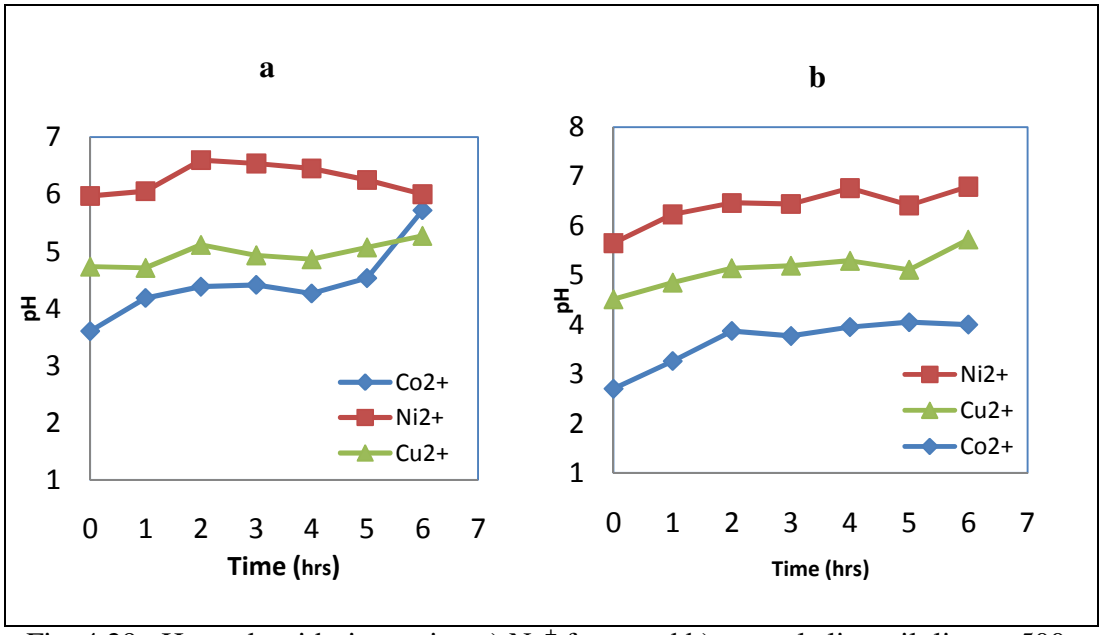



Fig. 4.29 pH trends with time using a) $Na^+$ form and b) natural clinoptilolite, at 500 mg/L.

There was a general rise in the pH with time compared to the initial pH value recorded in the natural and $Na^+$ zeolites at higher feed concentrations. The pH values at lower concentration i.e. 50 mg/L rose slightly (Figures D3 in Appendix D), with an average value of 6.8.

At higher feed concentrations of 500 mg/L, the pH was seen to increase with increase in time for both natural and $Na^+$ - form clinoptilolite (Figure 4.29b and D4 in Appendix D). For instance, during nickel adsorption, the pH of the supernatant solution ranged between 6.0 – 6.8 and 5.8 – 6.7, for both $Na^+$ -form and natural clinoptilolites respectively.

It cannot be ignored that with these small changes in pH values, hydrolysis of metal ions was taking place, and regardless of what specific basic mechanism was taking place at that pH, the inorganic complexes in solution had an effect on the sorption processes.

## 4.4 Column processes

### *4.4.1 Breakthrough curves*

The successful design of a column adsorption process requires the prediction of the concentration – time profile or the breakthrough curve for the effluent (Han et al., 2006). An estimation of the area under the breakthrough curves in the continuous process between the breakthrough and exhaustion points, gives the maximum column capacity, $q_e$ (mg/g).

The characteristic S-like shaped sigmoidal graphs were obtained (though not well defined) in these experiments and the breakthrough and exhaustion points were defined as the points when effluent concentrations were about 10% and 90% of the initial feed concentration respectively (Han et al., 2006, Kundu and Gupta, 2005). The influent was a synthetic mixed (competitive) feed of $Cu^{2+}$, $Co^{2+}$, $Cr^{3+}$ and $Ni^{2+}$ ions.

This dissertation will aim to look at the adsorption and desorption behaviour of clinoptilolite in column studies and its performance following regeneration.

### *4.4.2 Column performance with mixed feed*

Figure 4.30 below shows the breakthrough curves obtained with a mixed feed containing $Cu^{2+}$,$Co^{2+}$, $Ni^{2+}$ and $Cr^{3+}$ ions at 50 mg/L and feed rate of 2mL/min (an

average flow rate used in many studies as observed in literature). The effluent samples were collected and concentrations analysed. The $C/C_o$ ratio was plotted against time to observe the behaviour of natural clinoptilolite in column studies.

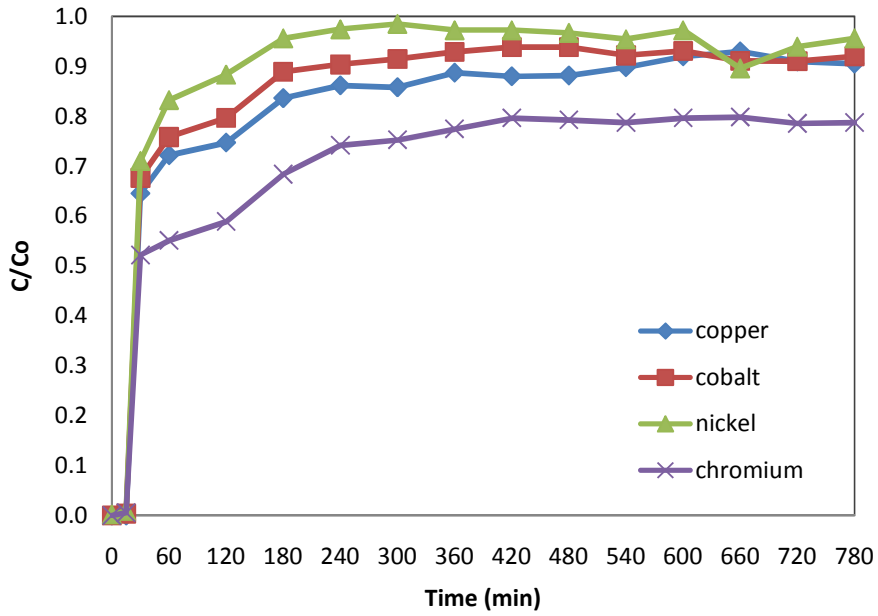



Fig. 4.30 Breakthrough curves for a mixed feed in 50mg/L at 2mL/min.

The initial breakthrough point (10% of 50mg/L $\simeq$ 0.1 as a $C/C_o$ ratio) was obtained at almost the same time (20 minutes) for all the four metal ions in solution. This implies that the zeolite exchange sites were readily available and easily accessed (almost at the same time) by all the four metal ions. The exhaustion points however were different for all the metal ions (the point at which the final effluent concentration was 90% of the initial feed). The exhaustion point for nickel was attained at 120mins (2h) and 200mins ($3\frac{1}{2}$ h) for cobalt. This exhaustion point for copper was attained at

360mins (6h) and interestingly for chromium ions, the exhaustion point could not be reached, with the final value below 90% of the initial feed. For the first three metal ions, the saturation points of the zeolite for nickel, cobalt and copper was reached at 2h, $3\frac{1}{2}$ h and 6h respectively; this implies that nickel was taken up into the exchange sites at a faster rate than the other ions. Its specific exchange centres were more readily available so that the nickel diffused more quickly through the zeolite than for $Co^{2+}$ and $Cu^{2+}$ ions. For the chromium ions, it can be said that the effluent concentration could not reach 90% of the feed concentration of 50mg/L because the rate, at which chromium was adsorbed from the surface film into the micropores, may have been slowed down by the large hydrated radius of chromium. The metal ions where preferred in the following order by the natural zeolite (based on the metal ion that reached exhaustion point quickly):

$$Ni^{2+} > Co^{2+} > Cu^{2+} > Cr^{3+}$$

The selectivity series again was different from those in the batch tests at 50 mg/L, indicating that many factors/ experimental conditions affect the selectivity series of clinoptilolite for different metal ions.

The inversion phenomenon of nickel was still observed in column studies, as the nickel adsorbed and desorbed during the experiments giving fluctuating effluent concentrations. This is attributed to the ease of counter diffusion of nickel ions with those in the sites.

### *4.4.3 Performance of regenerated zeolites*

This was conducted on the multi–component feed of $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$ and $Cr^{3+}$ metal ions. The regeneration solution used was 0.5M NaCl fed at 2 mL/min. However, for easier comparison, the discussion makes an analysis of each metal ion with every repeated/regenerated cycle as shown in figures 4.31, 4.32, 4.33 and 4.34 below:

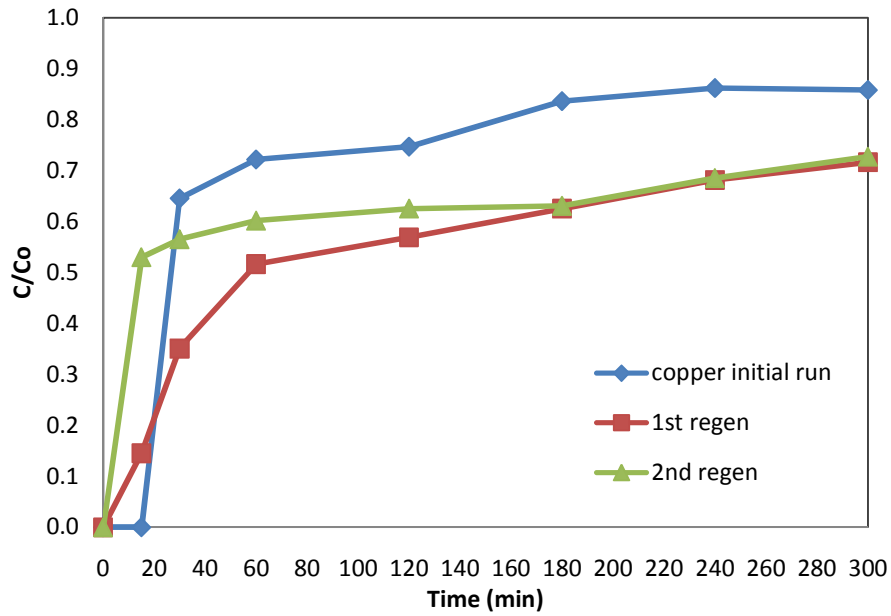



Fig. 4.31 Initial and regenerated cycles of $Cu^{2+}$ ions in 50mg/L feed.

From figure 4.31, it was observed the C/Co ratio of the first and second regeneration cycles were the same (no change in regeneration efficiency), with their final equilibrium value being 11% lower than the initial run (See table H1 in Appendix H). The breakthrough points for the regenerated cycles shifted to the left. From an initial value being attained at the $20^{th}$ minute, the value shifted to 10mins for the first

regeneration cycle and 3mins for the second. Only the initial run for copper was able to achieve 90% exhaustion value. The first and second regeneration runs had values below this exhaustion point value.

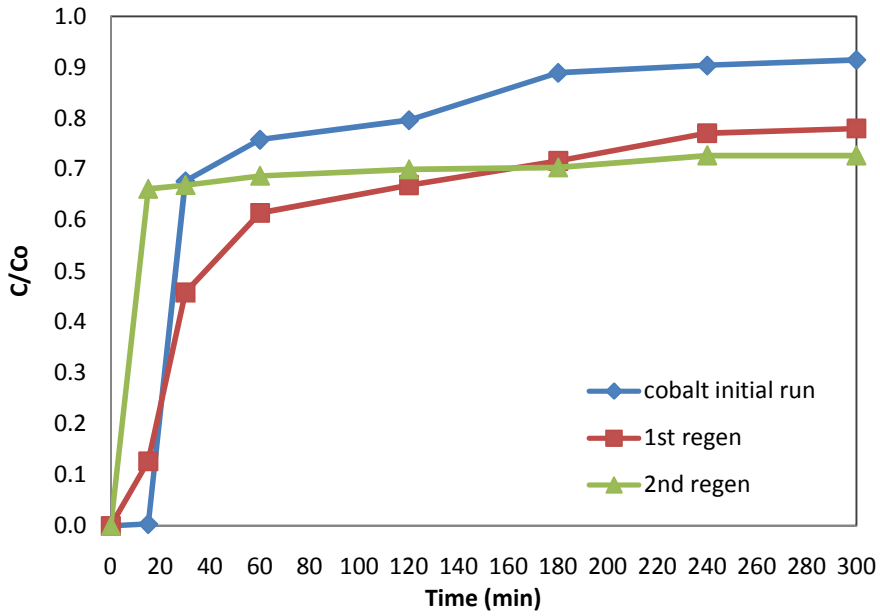



Fig. 4.32 Initial and regenerated cycles of $Co^{2+}$ ions in 50mg/L feed.

Figure 4.32 showed that the breakthrough points also shifted to the left with every new regeneration cycle. From an initial value at 20mins, it reduced to 18mins for the first regeneration run and 4mins for the second regeneration cycle. The zeolite was losing its loading capacity for cobalt with every new regeneration cycle, or its sites became inaccessible due to metal ions competing for sites and so the metal ions did not adsorb onto the zeolite. This explains why the breakthrough points were reached much earlier. The loading capacities reduced with every new regeneration cycle; the

first regeneration cycle reduced by 11% and the second, by 19% in comparison to the initial run (Table H2 of Appendix H). The two regenerated cycles could not reach the value of the exhaustion point (90% of the influent feed).

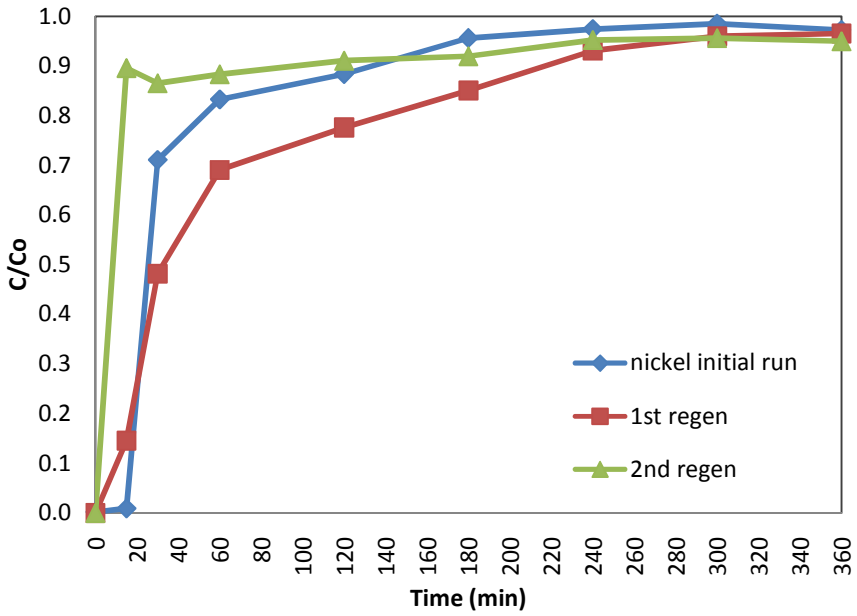



Fig. 4.33 Initial and regenerated cycles of $Ni^{2+}$ ions in 50mg/L feed.

The breakthrough points for $Ni^{2+}$ column adsorption also shifted to the left with every repeated regeneration cycle (Figure 4.33); from an initial value at 20mins, to about 12mins for the first regeneration cycle. The second regeneration cycles had a breakthrough point attained at 2mins. The regeneration cycles had a slightly lower loading of 1%, compared to the initial run (Table H3 in Appendix H). In nickel adsorption with the regeneration cycles, all the runs were able to achieve the

exhaustion point values; the initial run attained this point at 150mins, the first regeneration cycle at 250mins and the second at 120mins.

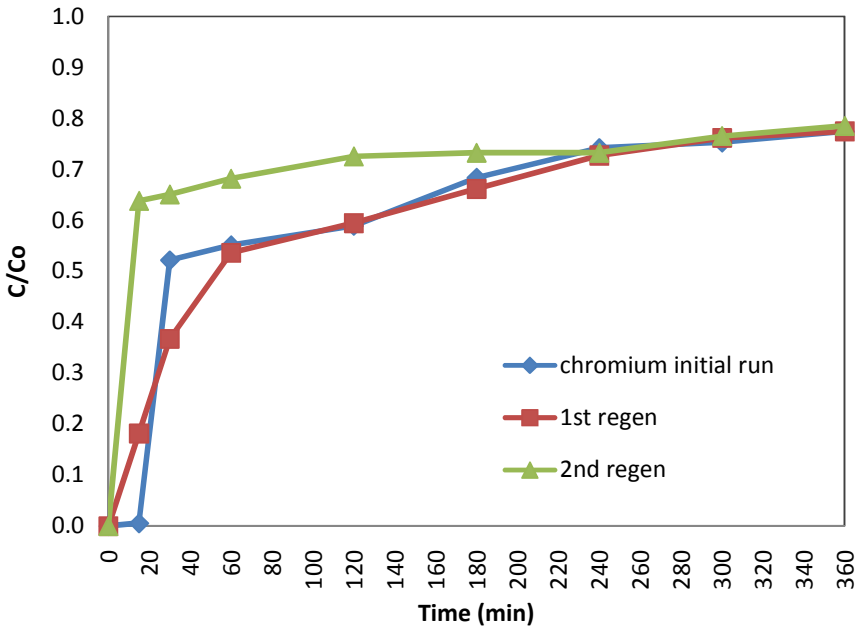



Fig. 4.34 Initial and regenerated cycles of $Cr^{3+}$ ions in 50mg/L feed.

The column adsorption of $Cr^{3+}$ ions (Figure 4.34) showed the breakthrough points also shifted to the left, giving values at 20mins for the initial run, 10mins for the first regeneration and 4mins for the second. After regenerating the zeolite with 0.5M NaCl as stripping solution at 2mL/min, the loading seemed to remain constant and almost equal to the initial run (Also see table H4 in Appendix H). The column adsorption for chromium ions did not reach the exhaustion point of 90% of the initial feed concentration.

Following the first and second regenerations of the natural clinoptilolite in the column studies, a summary of the results is given below:

i. The breakthrough point shifted to the left hand side with every repeated regeneration cycle, as compared to the initial run. The more the zeolite was regenerated, the shorter the time to reach the breakthrough point. It is likely that at this stage the zeolite structure had reduced loading capacities or non available sites due to metal ions initially competing for exchange sites. This therefore, led to the breakthrough point being quickly reached.

ii. Only the regeneration cycles for nickel removal were able to reach the exhaustion point of 90% of 50 mg/L feed. After the first regeneration for nickel ions, it took a longer time to reach the exhaustion point and a much shorter time during the second regeneration. This suggests that for nickel column adsorption a longer time was recorded for the column to reach exhaustion point because of the effect $Na^+$ ions have on the pore volume of the zeolite; this may have slowed down diffusion of nickel into the zeolite, thus the longer the time needed to reach this point or more adsorption sites became readily available after regeneration due to the zeolite conversion to $Na^+$ form. During the second regeneration, the exhaustion point was reached much earlier possible because the loading capacity reduced.

The ions cobalt, copper and chromium could not reach the 90% exhaustion point possibly because the sites were readily available but the

exchange rate of these ions with those in the zeolite framework was greatly reduced due to the alteration in pore volume caused by the conversion to natural clinoptilolite to $Na^{+}$ -form after regeneration.

iii. The selectivity series for the first and second regeneration cycles also kept varying.

$1^{st}$ regeneration: $Ni^{2+} > Co^{2+} > Cr^{3+} > Cu^{2+}$

$2^{nd}$ regeneration: $Ni^{2+} > Cr^{3+} > Co^{2+} > Cu^{2+}$

This further consolidates the explanation given earlier that metal ion selectivity is affected by different internal and external factors.

### *4.4.4 Elution curves and desorption studies*

Once the column reached exhaustion (the effluent concentration 90% of the influent concentration), the zeolite was regenerated using 0.5M NaCl as the stripping solution. The column was finally washed with distilled water at 4mL/min for 10 minutes. The following trend was observed on a mixed feed that was run at 2mL/min;

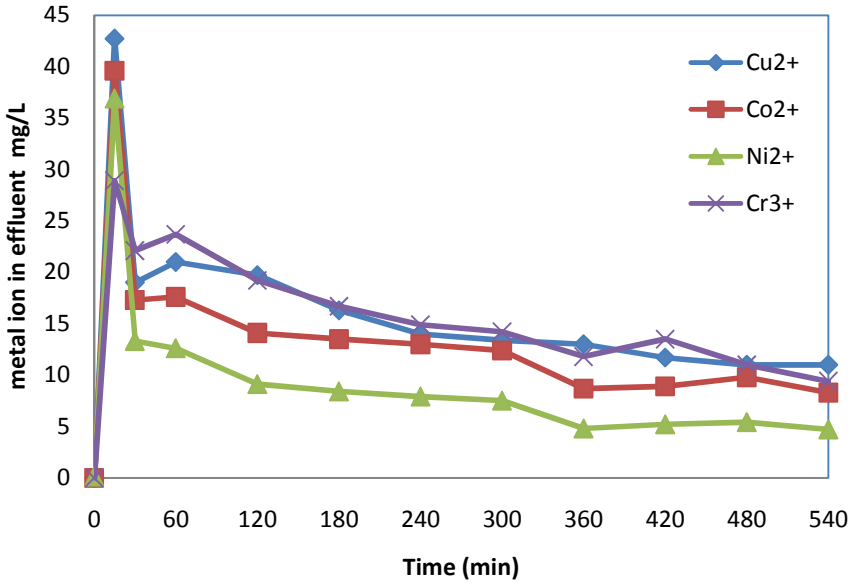



Fig. 4.35 Elution of metal ions during 1st cycle of regeneration.

The above elution curve (Figure 4.35) was obtained for all regeneration cycles (1st and 2nd). All the curves showed a rapid/sharp increase in metal ion concentration in the exit solution, which was followed by a decrease in effluent values with time (also see figures F2, F3 and F4 in Appendix F). The same elution trends were observed by Medvidovic et al. (2006) and Du et al. (2005), when they conducted experiments on lead and ammonium column studies. The initial high concentrations in effluent solution suggested that the solution not only contained metal ions from within the zeolite lattice but also metal ions in the column between the particles, because values in the second elution stage where as high as the initial feed of 50 mg/L (100% elution) and some even more than 50 mg/L (Figures F2 and F4 in Appendix F). This type of desorption trend is useful in determining in how much time/ volume the majority of the metal ions

had been eluted in these experiments. Extrapolating the graphs to metal ion concentration values of zero (complete elution) would indicate the time needed for complete elution of the zeolite bed, if this were possible. For instance, it would take approximately 690mins to completely expel $Ni^{2+}$ ions from the South African clinoptilolite, if the stripping solution is 0.5M NaCl (fed to the column at 2mL/min). The South African clinoptilolite exhibited good elution efficiencies after first regeneration cycles with elution efficiency values of 76%, 84%, 86% and 92% for copper, chromium, cobalt and nickel ions respectively. Gedik et al. (2008) also recorded high elution efficiencies for cadmium removal using clinoptilolite.

The elution efficiencies, after the 2$^{nd}$ regeneration were also high and close to the first regeneration values (Figures F2, F3, F4 and F5 in Appendix F). This corresponds to the good adsorption capacities and high $C/C_o$ values of clinoptilolite after the first and second regeneration cycles (See Tables H1, H2 and H3 in Appendix H).

*4.4.5 Theoretical estimation of the loading capacity in column adsorption*

The area under the curve for copper, cobalt and nickel metal ions was calculated between the breakthrough and exhaustion points. A summary is given below:

Table 4.6 Theoretical estimation of loading capacities in column studies

| Metal ion | Area under the curve ≃ theoretical loading capacity (mg/g) |
|---|---|
| $Cu^{2+}$ | 7.20 |
| $Co^{2+}$ | 2.97 |
| $Ni^{2+}$ | 2.25 |

Most of the calculated values were close to those obtained in the batch tests. For the nickel breakthrough curve between the breakthrough and exhaustion points, the area under the curve corresponding to the $q_e$ value was 2.25 mg/g (Table 4.6). In the batch tests conducted, it was calculated as 2.12 mg/g. The value of the maximum equilibrium loading capacity for copper was calculated to be as high as 7.19 mg/g compared to a value of 2.61 mg/g from batch experiments. The calculated value for $Co^{2+}$ was 2.96 mg/g and 2.30 mg/g from batch tests. Figures G1, G2 and G3 in Appendix G, show the breakthrough curves with their calculated areas under the curves/loading capacities, using "Origins 7.5" software.

The values obtained above were approximates, but the accuracy of this procedure would be improved if the frequency at which the samples were collected was increased. However this could not be done as the volume of the samples would be insufficient for metal ion analysis.

## 4.5 Summary of results and discussion

Natural South African clinoptilolite has the ability to remove metal ion contaminants from solution in both batch and column studies. The pre-treatment of the natural clinoptilolite and a decrease in the zeolite particle size increases the surface area of available sites and enhances the cation exchange capacity (CEC) of the zeolite, thus improving its metal uptake. The good fit of adsorption isotherms at lower concentration (50 mg/L) and the calculated adsorption capacities also indicate the large adsorption capacities of clinoptilolite.

The advantage of the natural South African clinoptilolite also lies in its reversibility as was seen that it is able to be regenerated and re-used before it begins to lose capacity and the efficiencies of the regenerated zeolites are very good. In batch tests, the loading capacities for regenerated samples increased slightly compared to the original runs before it started decreasing. However, in the column tests, the loading capacities after regeneration either remained constant or slightly reduced in comparison to the initial runs.

Clinoptilolite's selectivity of metal ions is not only affected by factors such as the metal ions concentration in solution, the opening and closing of pores depending on what hydrated radii of ions are sitting in the framework but it can also be altered by equilibrium parameters and several physicochemical causes. This conclusion explains why different researchers as well as work done in this dissertation have stated

different selectivity series/inconsistencies of clinoptilolite for metal ions. Therefore, the determination of selectivity series of clinoptilolite for metal ions is very complex, but again, this is one of the zeolite's strength because the zeolite can be specifically conditioned for a desired adsorption operation/selectivity.

# 5.0 CHAPTER FIVE

## 5.1 Conclusions

The ability of South African clinoptilolite to adsorb metal ions was researched in this dissertation. All the metal solutions used as feed were prepared in the laboratory.

The following conclusions can be drawn from this research work:

i) Like other clinoptilolites mined from other countries, natural South African clinoptilolite exhibits good adsorption capacities for metal ions $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cr^{3+}$ in both batch and column studies.

ii) The experimental data was slightly better suited to the Langmuir isotherm than Freundlinch isotherm especially at lower feeds of 50 mg/L, but this did not hold at higher feed concentrations of 500 mg/L.

iii) Pre-treatment of the natural zeolite into $Na^+$ form showed an improved cation exchange capacity at lower (50 mg/L) feed concentrations. The order of performance of the modified zeolites was:

$$Na^+ \geq \text{natural} > NH^+_4 > K^+ > Ca^{2+}$$

However, at higher concentrations of 500 mg/L, $K^+$, $NH^+_4$ and $Ca^{2+}$ modified zeolite samples showed higher adsorption capacities than the natural zeolite, although the order of performance changed due to the

alteration in pore diameters caused by the type of zeolite sitting in the framework. The selectivity series of metal ions by natural and $Na^+$ form zeolite was found to be different. This inconsistency of the selectivity series of metal ions is dependent on the pore diameters of metal ions initially sitting in the zeolite structure, equilibrium parameters, physicochemical causes as well as external factors such as metal ion complexes/ precipitates affecting zeolite pores.

iv) Natural zeolite has the ability to be regenerated and re-used for subsequent runs (in batch and column processes) before it begins to lose capacity. This makes it very economical especially for developing countries like South Africa. The elution of natural clinotilolite in batch and column processes using 0.5M NaCl was very efficient. This corresponds to high adsorption capacities of clinoptilolite after regeneration.

# 6.0 RECOMMENDATIONS

p.115 “Some of the parameters that affect adsorption of metal ions where researched in this dissertation, and their effects observed. To fully consolidate the findings on the behaviour of metal ions during adsorption onto clinoptilolite, it is recommended that the kinetics of the adsorption process and how this may vary for different metal ions be researched. Factors such as the potential effect of hydrolysis of metal ions and adsorption onto clinoptilolite (i.e. $Cr^{3+}$, being trivalent, undergoes hydrolysis reactions at neutral pHs) should be studied. Also the possible effect of complexation during regeneration of clinoptilolite with 0.5M NaCl should be investigated, as some of the metals form stronger chloride complexes than others, notably $Ni^{2+}$, and some metal ions like $Cr^{3+}$ have slow kinetics during complexation reactions.”

# 7.0 REFERENCES

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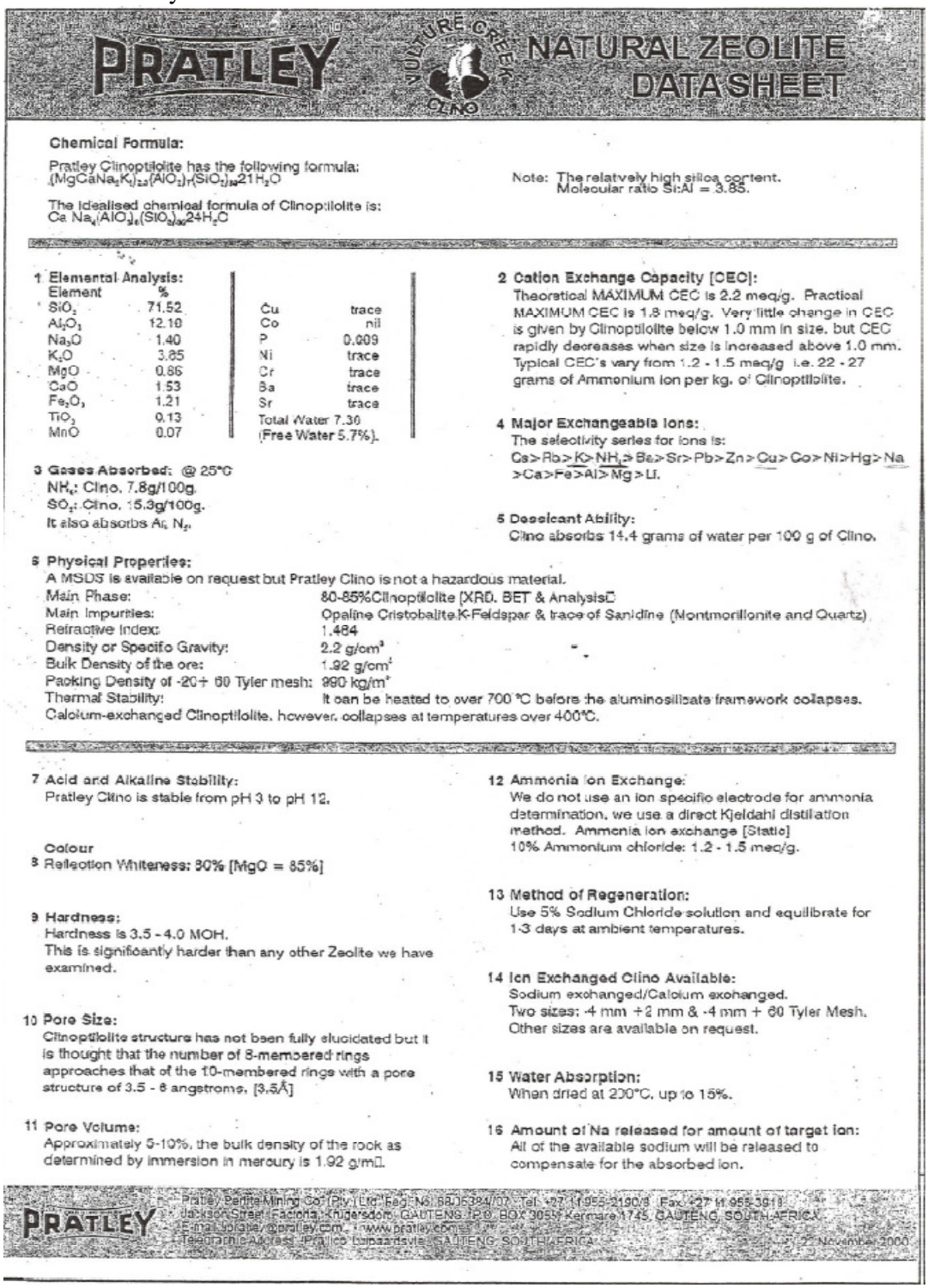
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# APPENDIX A: Data Sheets

Table A2 Pratley data sheet



PRATLEY — VULTURE CREEK CLINO

# NATURAL ZEOLITE DATASHEET

**Chemical Formula:**

Pratley Clinoptilolite has the following formula:
$(MgCaNa_2K_2)_{12}(AlO_2)_6(SiO_2)_{30}21H_2O$

The idealised chemical formula of Clinoptilolite is:
$Ca\ Na_4(AlO_2)_6(SiO_2)_{30}24H_2O$

Note: The relatvely high silica content.
Molecular ratio Si:Al = 3.85.

**1 Elemental Analysis:**

| Element | % |
|---|---|
| $SiO_2$ | 71.52 |
| $Al_2O_3$ | 12.10 |
| $Na_2O$ | 1.40 |
| $K_2O$ | 3.85 |
| MgO | 0.86 |
| CaO | 1.53 |
| $Fe_2O_3$ | 1.21 |
| $TiO_2$ | 0.13 |
| MnO | 0.07 |

| | |
|---|---|
| Cu | trace |
| Co | nil |
| P | 0.009 |
| Ni | trace |
| Cr | trace |
| Ba | trace |
| Sr | trace |
| Total Water | 7.30 |
| (Free Water | 5.7%). |

**2 Cation Exchange Capacity [CEC]:**
Theoretical MAXIMUM CEC is 2.2 meq/g. Practical MAXIMUM CEC is 1.8 meq/g. Very little change in CEC is given by Clinoptilolite below 1.0 mm in size, but CEC rapidly decreases when size is increased above 1.0 mm. Typical CEC's vary from 1.2 - 1.5 meq/g i.e. 22 - 27 grams of Ammonium ion per kg. of Clinoptilolite.

**3 Gases Absorbed:** @ 25°C
$NH_4$: Clino. 7.8g/100g.
$SO_2$: Clino. 15.3g/100g.
It also absorbs Ar, $N_2$.

**4 Major Exchangeable Ions:**
The selectivity series for ions is:
Cs>Rb>K>$NH_4$>Ba>Sr>Pb>Zn>Cu>Co>Ni>Hg>Na >Ca>Fe>Al>Mg>Li.

**5 Dessicant Ability:**
Clino absorbs 14.4 grams of water per 100 g of Clino.

**6 Physical Properties:**
A MSDS is available on request but Pratley Clino is not a hazardous material.

| | |
|---|---|
| Main Phase: | 80-85%Clinoptilolite (XRD, BET & Analysis□ |
| Main Impurities: | Opaline Cristobalite,K-Feldspar & trace of Sanidine (Montmorillonite and Quartz) |
| Refractive Index: | 1.484 |
| Density or Specific Gravity: | 2.2 g/cm³ |
| Bulk Density of the ore: | 1.92 g/cm³ |
| Packing Density of -20+ 60 Tyler mesh: | 990 kg/m³ |
| Thermal Stability: | It can be heated to over 700 °C before the aluminosilicate framework collapses. Calcium-exchanged Clinoptilolite, however, collapses at temperatures over 400°C. |

**7 Acid and Alkaline Stability:**
Pratley Clino is stable from pH 3 to pH 12.

**Colour**
**8 Reflection Whiteness: 90% [MgO = 85%]**

**9 Hardness:**
Hardness is 3.5 - 4.0 MOH.
This is significantly harder than any other Zeolite we have examined.

**10 Pore Size:**
Clinoptilolite structure has not been fully elucidated but it is thought that the number of 8-membered rings approaches that of the 10-membered rings with a pore structure of 3.5 - 8 angstroms. [3,5Å]

**11 Pore Volume:**
Approximately 5-10%, the bulk density of the rock as determined by immersion in mercury is 1.92 g/m□.

**12 Ammonia Ion Exchange:**
We do not use an ion specific electrode for ammonia determination, we use a direct Kjeldahl distillation method. Ammonia ion exchange [Static]
10% Ammonium chloride: 1.2 - 1.5 meq/g.

**13 Method of Regeneration:**
Use 5% Sodium Chloride solution and equilibrate for 1-3 days at ambient temperatures.

**14 Ion Exchanged Clino Available:**
Sodium exchanged/Calcium exchanged.
Two sizes: -4 mm +2 mm & -4 mm + 60 Tyler Mesh.
Other sizes are available on request.

**15 Water Absorption:**
When dried at 200°C, up to 15%.

**16 Amount of Na released for amount of target ion:**
All of the available sodium will be released to compensate for the absorbed ion.

PRATLEY
Pratley Perlite Mining Co (Pty) Ltd. Reg. No. 88/05394/07. Tel: +27 11 955-2190/8 Fax: +27 11 955-3918
Jackson Street, Factoria, Krugersdorp, GAUTENG. P.O. BOX 3055 Kermare 1745, GAUTENG, SOUTH AFRICA
E-mail: pratley@pratley.com http://www.pratley.com
Telegraphic Address: Pratley Randfontein, GAUTENG, SOUTH AFRICA

2nd November 2000

Table A3 Material Safety Data Sheet

## ANNEXURE 1

| MATERIAL SAFETY DATA SHEET | No: 1 |
|---|---|
| | Date Issued: 10 April 2006 |
| | Page 1 of 6 |

| COMPANY DETAILS | | | |
|---|---|---|---|
| Supplier Name: | Pratley Perlite Mining (Pty) Ltd | Emergency Tel Nr: | +27-11-9552190 |
| Address: | Jackson St, Factoria, Krugersdorp 1740 | Telex: | N/A |
| Tel: | +27-11-9552190 | Fax: | +27-119553918 |

1 Product and Company Identification:
(Page 1 may be used as an emergency safety sheet)

| | | | |
|---|---|---|---|
| Trade name: | Pratliperl / Slag Ag / Pretreated PratliPerl | Chemical abstract No: | 93763-70-3 130885-09-5 (SlagAg) |
| Chemical family: | Amorphous glassy volcanic rock | NIOSH no: | 0491 |
| Chemical name: | Perlite | Hazchem code: | Non combustable solid |
| Synonyms: | NA | UN no: | None |

2. Composition:

| | |
|---|---|
| Hazardous components: | Perlite is considered a nuisance dust & is not hazardous |
| EEC Classification: | Not regulated |
| R Phrases: | None |

3. Hazards Identification:

| | | |
|---|---|---|
| Main Hazard: | Nuisance dust | |
| Flammability: | Not flammable | |
| Chemical Hazard: | None | |
| Biological Hazard: | None | |
| Reproduction Hazard: | None | |
| Eye effect: | Eyes: | None |
| Health effects: | Skin: | None |
| Health effects: | Ingestion: | None |
| Health effects: | Inhalation: | None |
| Carcinogenicity: | Not listed by OSHA / NTP / IARC | |
| Mutagenicity: | ND | |
| Neurotoxicity: | NO | |

The information provided on this MSDS is correct to the best of our knowledge. The information is designed only as a guidance for safe handling, use, storage & transportation and is not considered as a warranty or quality specification. We do not accept any liability arising out of the use of the information provided here.
Attention is drawn to hazards from improper use of the product. The user must assume all risk from the use thereof.

## ANNEXURE 1

| MATERIAL SAFETY DATA SHEET | No: 1 |
|---|---|
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4 First Aid Measures:

| | |
|---|---|
| Product in Eye: | Wash out with copious amounts of water |
| Product on Skin: | N/A |
| Product Ingested: | N/A |
| Product Inhaled: | Remove affected individual from dusty area to an area with clean air |

5. Fire Fighting Measures:

| | |
|---|---|
| Extinguishing Media: | None |
| Special Hazards: | None |
| Protective Clothing: | NIOSH approved masks suitable for nuisance dust |

6. Accidental Release Measures:

| | |
|---|---|
| Personal Precautions: | Wear eye protection & dust mask |
| Environmental Precautions: | None |
| Small Spills: | Vacuum clean or sweep material |
| Large Spills: | Vacuum clean or sweep material |

7. Handling and Storage:

| | |
|---|---|
| Suitable Material: | N/A |
| Handling/Storage Precautions: | None |

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| 8 Exposure Controls/Personal Protection: | |
|---|---|
| Occupational Exposure Limits: | ACGIH TLV: 10 mg/M$^3$ OSHA PEL: 15 mg/M$^3$ |
| Engineering Control Measures: | None considered as a nuisance dust |
| Personal Protection Respiratory: | NIOSH approved masks suitable for nuisance dust |
| Personal Protection Hands: | None |
| Personal Protection Eyes: | Protective Goggles |
| Personal Protection Skin: | None |
| Other Protection: | Use good housekeeping to avoid dust |

| 9 Physical and Chemical Properties: | |
|---|---|
| Appearance: | Pratliperl- white Slag Ag- Black particles |
| Odour: | None |
| pH (1%): | N/A |
| Boiling point: | N/A |
| Melting point: | 1100 °C |
| Flash point: | None |
| Flammability: | Not Flammable |
| Auto Flammability: | N/A |
| Explosive Properties: | Not explosive |
| Oxidizing Properties: | N/A |
| Vapour Pressure: | N/A |
| Density: | Slag Ag 2.2 Kg / Litre<br>Pratliperl: 0.3 Kg / litre |
| Solubility Water: | Slight |
| Solubility Solvent: | None |
| Solubility Coefficient: | N/A |
| Neurotoxicity: | ND |

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| 10 Stability and Reactivity: | |
|---|---|
| Conditions to avoid: | Any environment which will generate nuisance dust |
| Incompatible material: | None |
| Hazardous decomposition products: | N/A |

| 11. Toxicological Information: | |
|---|---|
| Acute Toxicity: | Not toxic |
| Skin and Eye Contact: | Not toxic |
| Chronic Toxicity: | Not toxic |
| Carcinogenicity: | Not listed by NTP / IARC /OSHA |
| Mutagenicity: | Not reported to produce mutagenic effects in humans |
| Reproductive hazards: | Not reported to produce reproductive effects in humans. |

| 12. Ecological Information: | | |
|---|---|---|
| Aquatic Toxicity: | Fish: | No information but will act as any particulate material |
| Aquatic Toxicity: | Daphnia: | No information but will act as any particulate material |
| Aquatic Toxicity: | Algae: | No information but will act as any particulate material |
| Biodegradability: | Will not degrade | |
| Bio-accumulation | Natural mineral product will not degrade | |
| Mobility: | Only mobile as a windborne dust | |
| German wgk: | ND | |

| 13 Disposal Considerations: | |
|---|---|
| Disposal Methods | Vacuum sweep or sweep and dispose according to local regulations |
| Disposal Packaging: | Dispose in bulk containers or bags |

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14 Transport Information:

| | |
|---|---|
| UN no: | None |
| Substance identity No: | N/A |
| ADR/RID class:<br>DOT: / UPS: / Transport Canada: / | Not classified, not a hazardous material. |
| ADR/RID item no: | N/A |
| ADR/RID hazard identity no: | N/A |
| IMDG – Class: | Not classified, not a hazardous material. |
| IMDG – Packing Group: | N/A |
| IMDG – Marine Pollutant: | No |
| IMDG – EMS no: | N/A |
| IMDG – MFAG table no: | N/A |
| IMDG – Shipping name: | |
| IATA – Shipping name: | Not classified, not a hazardous material. |
| IATA – Class: | N/A |
| IATA – Subsidiary risk(s): | N/A |
| ADG – | Not classified, not a hazardous material. |
| UK – Description: | Not classified, not a hazardous material. |
| UK – Emergency action class: | Not classified, not a hazardous material. |
| UK – Classification: | Not classified, not a hazardous material. |

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| 15 Regulatory Information: | |
|---|---|
| EEC hazard classification: | Not classified, not a hazardous material |
| USA hazard classification: | Not subject to SARA reporting. N/A to CERCLA. Listed on TSCA |
| Australian Hazard Classification | Not classified as hazardous according to Worksafe Australia |
| Risk Phases: | N/A |
| Safety Phases: | N/A |
| National Legislation: | Not listed as a hazard in SANS 10228, Annex B2. (March 2003) |

| 16. Other Information: | |
|---|---|
| Harmonized Tariff Code : | 2530.10 (9) |

| | |
|---|---|
| LD50 | Lethal dose kill 50% |
| MEL | Maximum Exposure Limits (UK) |
| PEL | Permissable Exposure Limit |
| TLV | Threshold limit Value |
| TWA | Time weighted average airborne concentration over an 8 hour day, for 5 day week, over an entire working life |
| STEL | Short term exposurelimit – average airborne concentration over a 15 min period which should not be exceeded at any time during a normal 8 hour working day |
| MAK | Maximale Arbeitsplatzkonzentrationen (Germany) |
| TRK | technische Richtkonzentrationen (Germany) |
| MAC | Maximale aanvaarde concentratie (Netherlands) |
| VME | Valeurs limites de Moyenne d'Exposition (France) |
| VLE | Valeurs limites d'Exposition à court terme (France) |
| EC | Indicative occupational exposure limit values ( Directive 2000 /39 / EC) |
| ACGIH | American Conference of Governmental Hygienists |
| CERCLA | Comprehensive Environmental Response,Compensations & Liability Act (USA) |
| CFR | Code of Federal Regulations (USA) |
| CWA | Clean Water Act (USA) |
| DOT | Department of transportation (USA) |
| HMIS | Hazardous Communication System (USA) |
| NFPA | National Fire Prevention Association (USA) |
| NIOSH | National Institute for Occupational Safety & Health (USA) |
| RCRA | Resource Conservation & Recovery Act |
| SARA | Superfund Amendments & Reorganisation Act (USA) |
| TSCA | Toxic Substances Control Act (USA) |
| DSL | Dangerous Substances List (Canada) |
| CEPA | Canadian Environmental Protection Act. |
| ADR | Agreement on dangerous Goods (EU) |
| DSCL | Dangerous Substances Classification & Labelling (EU) |
| OES | Occupational Exposure Standards (UK) |
| EINECS | European Inventory of Existing Commercial Chemical Substances. |
| IARC | International Agency for Research on Cancer |
| OSHA | Occupational Safety & Health Administration |
| WHMIS | Workplace Hazardous Material Information |
| NOHSC | Australian National Occupational Health & Safety Commission. |

| | |
|---|---|
| N/A | Not Applicable |
| N/D | Not Determined |

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# APPENDIX B: Maximum loading capacities using 500mg/L feed

Table B1 Maximum loading capacities of natural clinoptilolite at 2g and 500 mg/L feed

| Time (hrs) | NATURAL CLINOPTILOLITE | | | | |
|---|---|---|---|---|---|
| | Copper (mg/g) | Cobalt (mg/g) | Nickel (mg/g) | Chromium (mg/g) | |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | |
| 1.0 | 3.0 | 6.7 | 2.6 | 1.4 | |
| 2.0 | 5.7 | 7.9 | 3.5 | 2.9 | |
| 3.0 | 6.7 | 9.0 | 3.7 | 5.0 | |
| 4.0 | 8.2 | 8.8 | 3.4 | 6.8 | equilibrium |
| 5.0 | 8.0 | 8.6 | 2.7 | 6.9 | |
| 6.0 | 7.0 | 8.9 | 3.3 | 6.9 | |

Table B2 Maximum loading capacities of $Na^+$ clinoptilolite at 2g and 500 mg/L

| Time (hrs) | Na- FORM CLINOPTILOLITE | | | | |
|---|---|---|---|---|---|
| | Copper (mg/g) | Cobalt (mg/g) | Nickel (mg/g) | Chromium (mg/g) | |
| 0 | 0.0 | 0.0 | 0.0 | 0.0 | |
| 1 | 8.0 | 4.2 | 4.5 | 0.6 | |
| 2 | 9.8 | 4.4 | 4.6 | 2.3 | |
| 3 | 10.7 | 4.6 | 4.2 | 4.6 | |
| 4 | 10.7 | 4.6 | 3.8 | 5.8 | equilibrium |
| 5 | 10.1 | 5.0 | 3.4 | 6.4 | |
| 6 | 10.2 | 4.9 | 3.1 | 6.7 | |

# APPENDIX C: Metal ions loading onto natural and modified clinoptilolite at 50mg/L

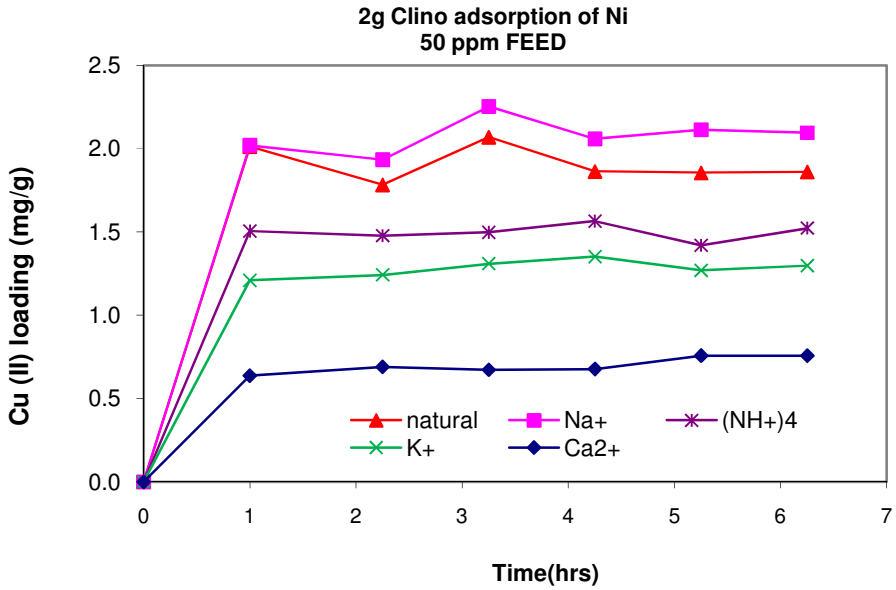



Fig. C7 $Cu^{2+}$ loading on 2g of natural and homoionised clinoptilolite using 50 mg/L feed.

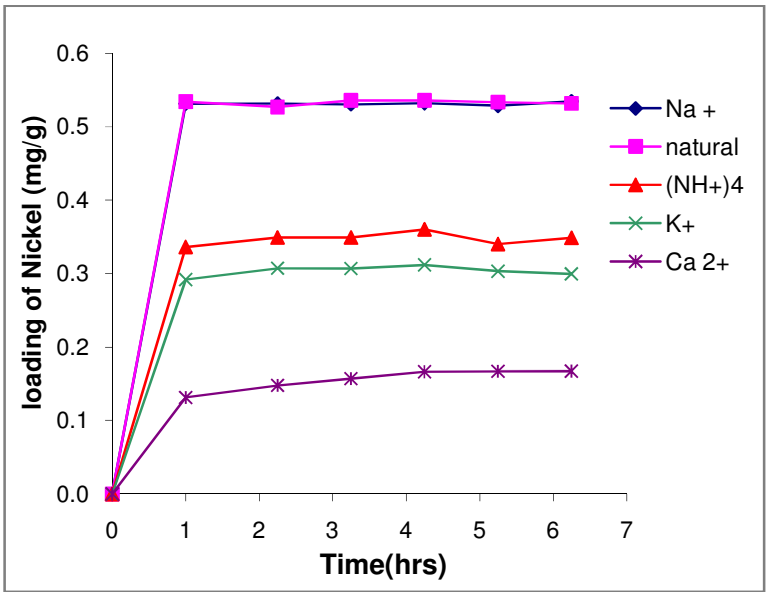



Fig. C8 $Ni^{2+}$ loading on 4g of natural and homoionised clinoptilolite using 50 mg/L feed.

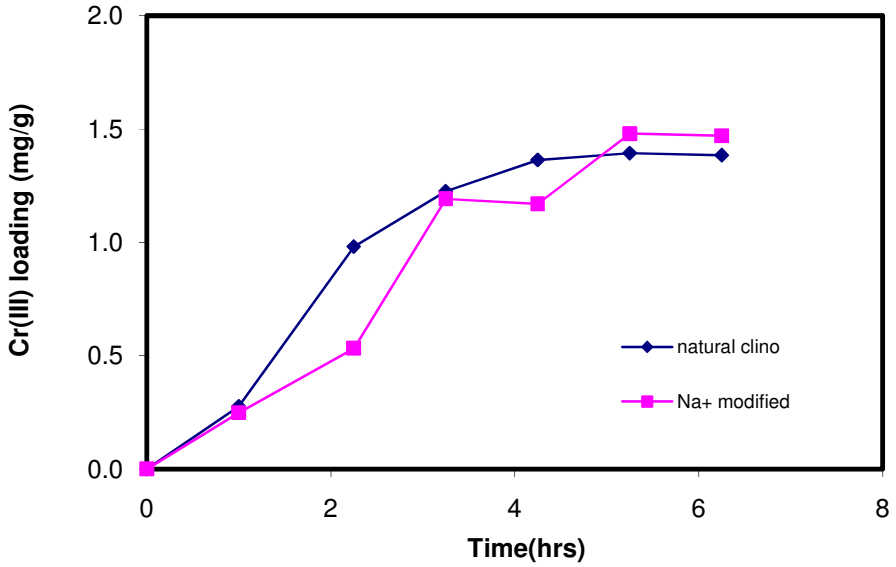



Fig. C9 $Cr^{3+}$ loading on 10g of natural and homoionised clinoptilolite using 50 mg/L feed.

# APPENDIX D: pH trends with time

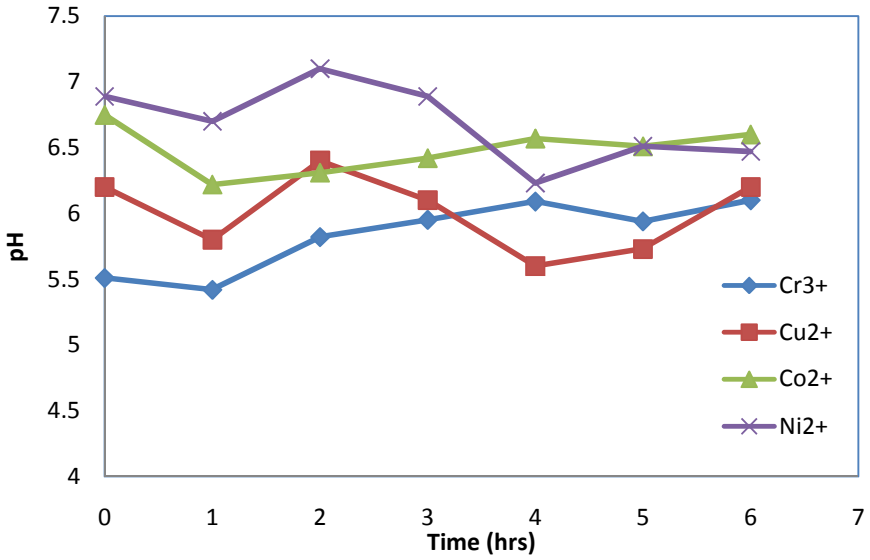



Figure D3 pH values vs time at 50 mg/L feed concentration onto Natural clinoptilolite.

| | |
|---|---|
| $Cu^{2+}$ pH range: | 5.6 – 6.4 |
| $Co^{2+}$ pH range: | 6.2 – 6.6 |
| $Ni^{2+}$ pH range: | 6.2 – 7.1 |
| $Cr^{3+}$ pH range: | 5.4 – 6.1 |

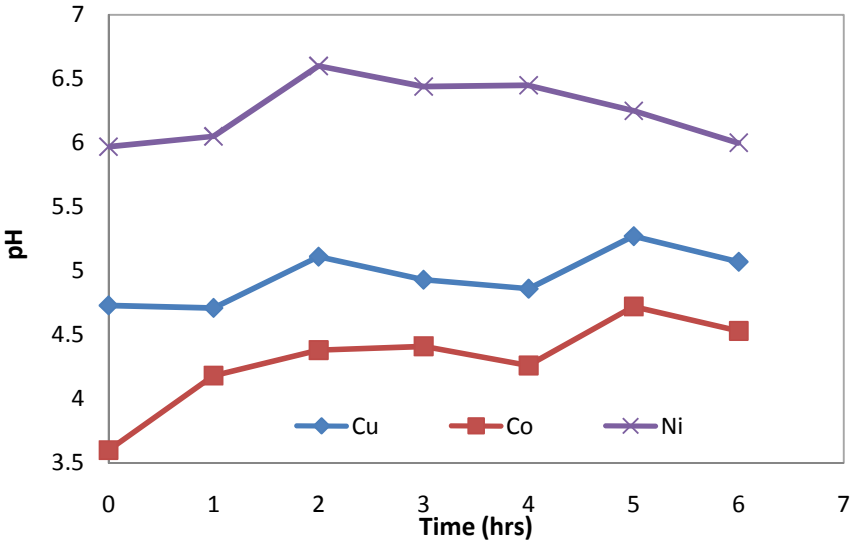



Figure D4 pH values vs time at 500 mg/L feed concentration onto $Na^{+}$-form clinoptilolite.

| | |
|---|---|
| $Cu^{2+}$ pH range: | 4.7 – 5.3 |
| $Co^{2+}$ pH range: | 3.6 – 4.72 |
| $Ni^{2+}$ pH range: | 6.0 – 6.6 |

# APPENDIX E: Langmuir isotherms andchanges in slopes with changes in zeolite form.

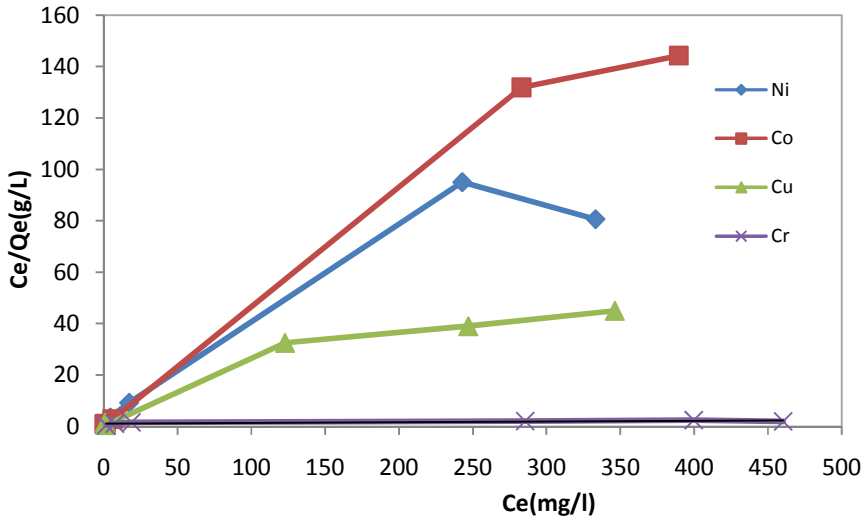



Figure E5 Superimposed Langmuir isotherms for metal ions using 50 and 500 mg/L feeds on natural clinoptilolite

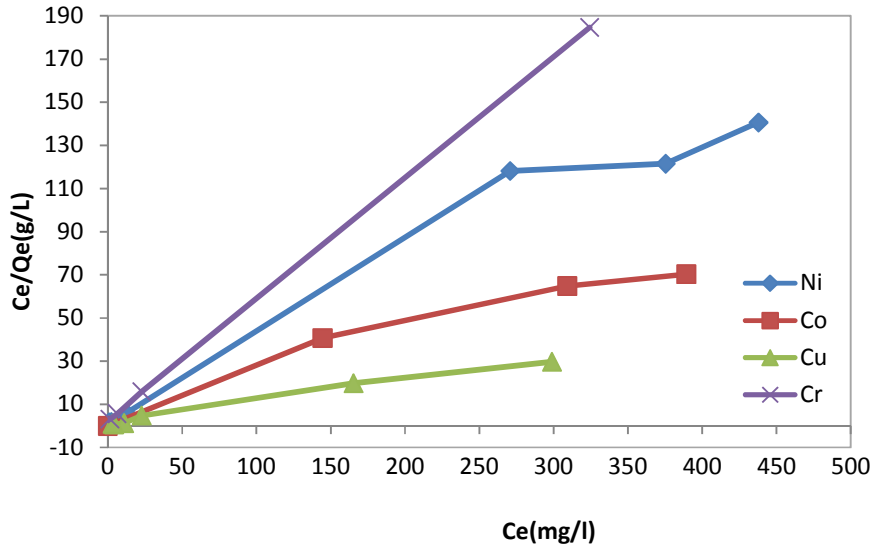



Figure E6 Superimposed Langmuir isotherms for metal ions using 50 and 500 mg/L feeds on $Na^{+}$ clinoptilolite

# APPENDIX F: Elution of metal ions in column systems

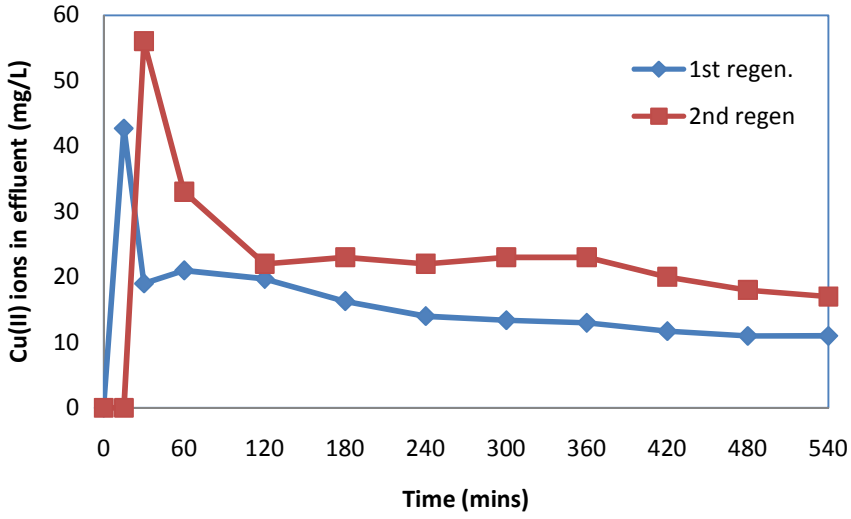



Figure F2 Cu (II) elution during 1st and 2nd regeneration

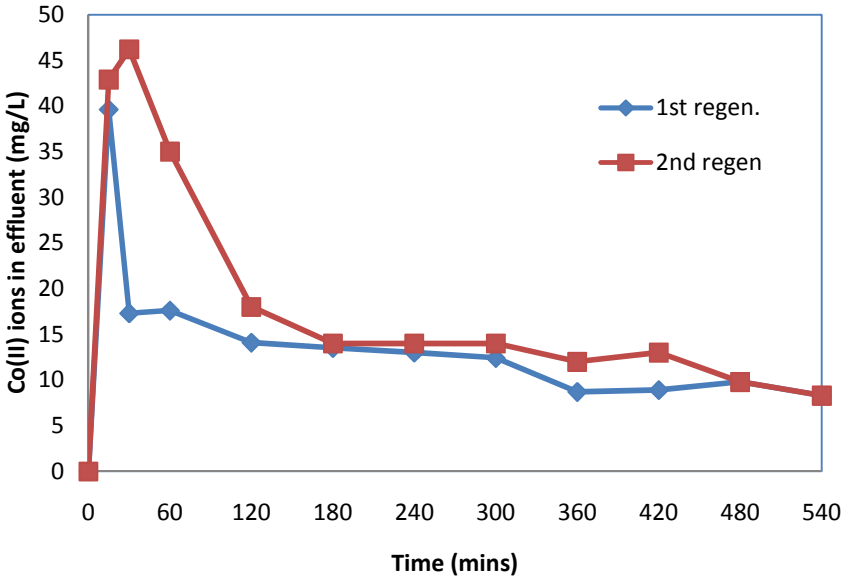



Figure F3 Co (II) elution during 1st and 2nd regeneration.

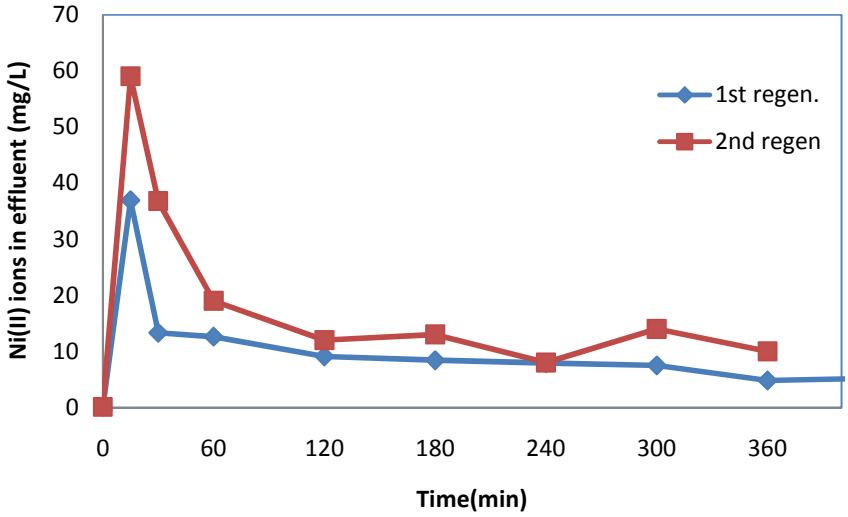



Figure F4 Ni (II) elution during 1st and 2nd regeneration

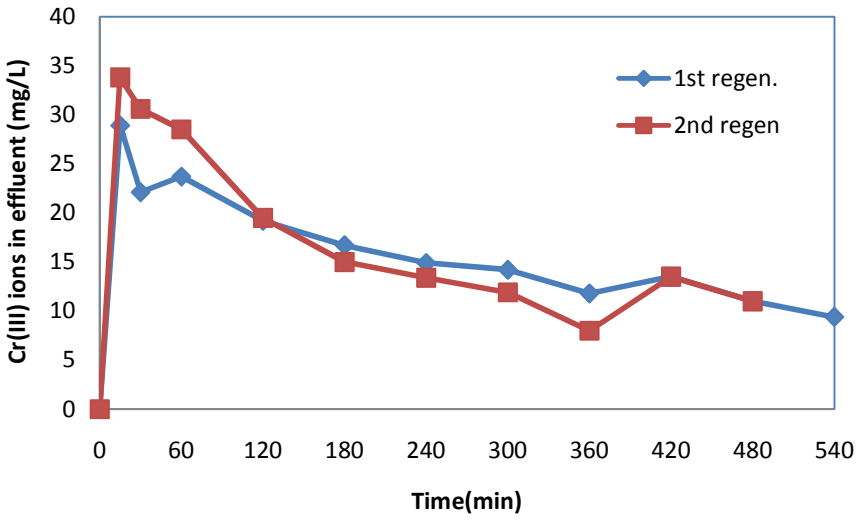



Figure F5 Cr (III) elution during 1st and 2nd regeneration

# APPENDIX G: Area under breakthrough curves

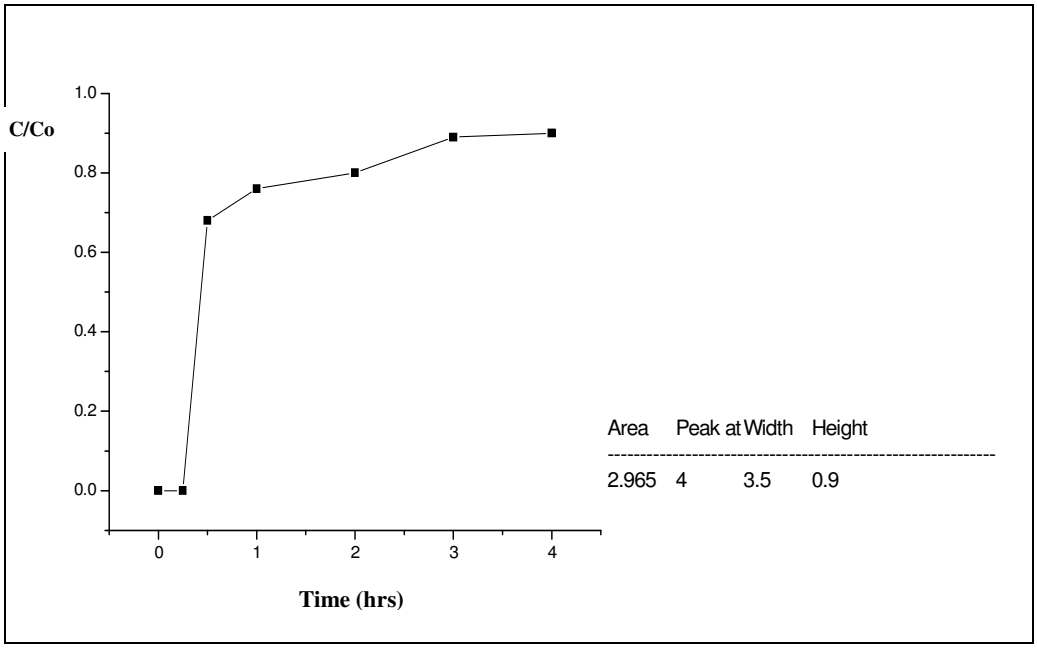



Fig. G1 Area under the breakthrough curve for Co(II)

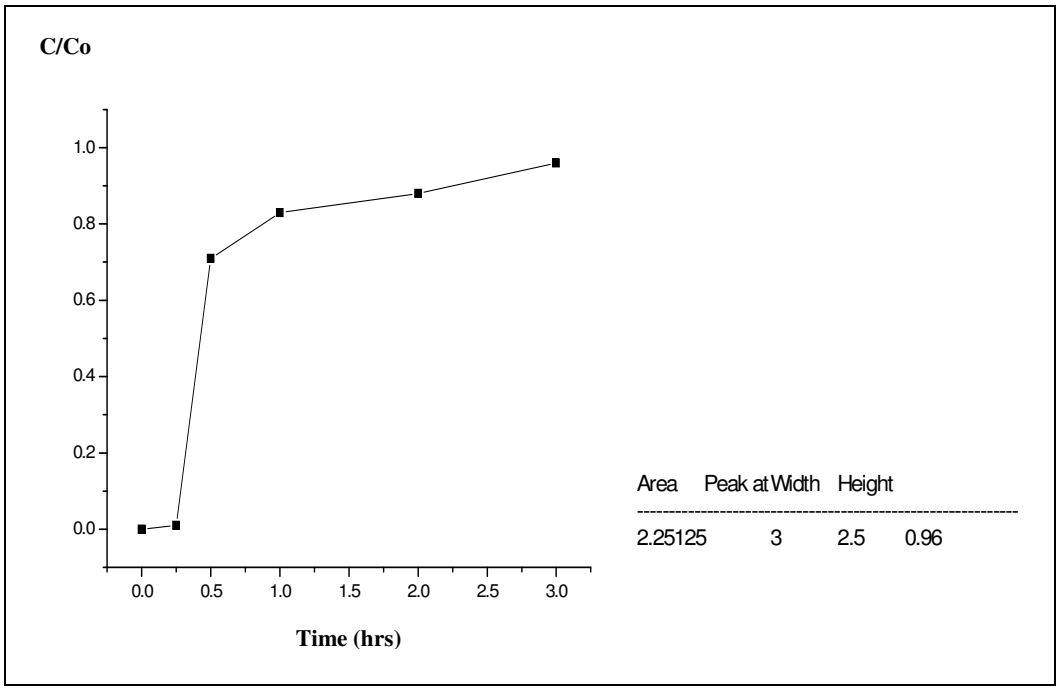



Fig G2 Area under the breakthrough curve for Ni(II)

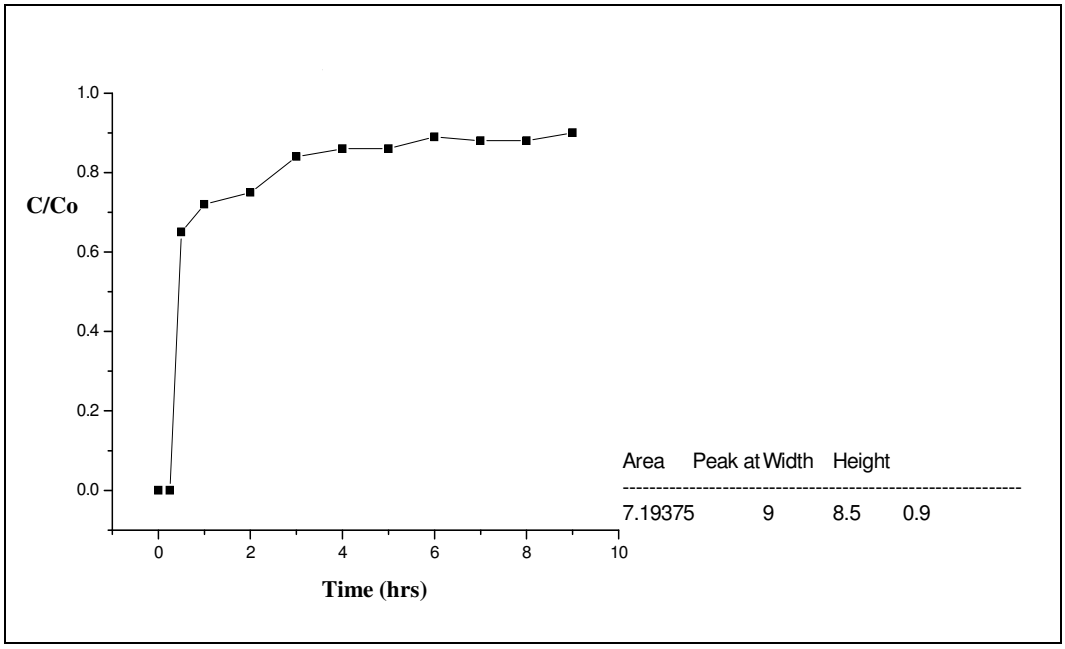



Fig. G3 Area under the breakthrough curve for Cu (II)

# APPENDIX H: Performance of column adsorption after regeneration

Table H1 1st and 2nd regeneration natural zeolite in column with 50 mg/L Cu (II) feed

| Time (min) | Initial C/Co | 1st regen C/Co | 2nd regen C/Co |
|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 |
| 15 | 0.00 | 0.15 | 0.53 |
| 30 | 0.65 | 0.35 | 0.57 |
| 60 | 0.72 | 0.52 | 0.60 |
| 120 | 0.75 | 0.57 | 0.63 |
| 180 | 0.84 | 0.63 | 0.63 |
| 240 | 0.86 | 0.68 | 0.69 |
| 300 | 0.86 | 0.72 | 0.73 |
| 360 | 0.89 | 0.76 | 0.74 |
| 420 | 0.88 | 0.77 | 0.75 |
| 480 | 0.88 | 0.77 | 0.76 |
| 540 | 0.90 | 0.78 | 0.78 |
| 600 | 0.92 | 0.81 | 0.79 |
| 660 | 0.93 | 0.81 | 0.80 |
| 720 | 0.91 | 0.80 | 0.81 |
| 780 | 0.91 | | |

Table H2 1st and 2nd regeneration of natural clinoptilolite in columns with 50 mg/L Co (II) feed.

| time (min) | Initial C/Co | 1st regen C/Co | 2nd regen C/Co |
|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 |
| 15 | 0.00 | 0.13 | 0.66 |
| 30 | 0.68 | 0.46 | 0.67 |
| 60 | 0.76 | 0.61 | 0.69 |
| 120 | 0.80 | 0.67 | 0.70 |
| 180 | 0.89 | 0.72 | 0.70 |
| 240 | 0.90 | 0.77 | 0.73 |
| 300 | 0.91 | 0.78 | 0.73 |
| 360 | 0.93 | 0.79 | 0.74 |
| 420 | 0.94 | 0.80 | |
| 480 | 0.94 | 0.82 | |
| 540 | 0.92 | 0.81 | |
| 600 | 0.93 | | |
| 660 | 0.91 | | |
| 720 | 0.91 | | |
| 780 | 0.92 | | |

Table H3 1st and 2nd regeneration of natural clinoptilolite in columns with 50 mg/L Ni (II) feed.

| time (min) | Initial C/Co | 1st regen C/Co | 2nd regen C/Co |
|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 |
| 15 | 0.01 | 0.15 | 0.90 |
| 30 | 0.71 | 0.48 | 0.87 |
| 60 | 0.83 | 0.69 | 0.88 |
| 120 | 0.88 | 0.78 | 0.91 |
| 180 | 0.96 | 0.85 | 0.92 |
| 240 | 0.97 | 0.93 | 0.95 |
| 300 | 0.99 | 0.96 | 0.96 |
| 360 | 0.97 | 0.97 | 0.95 |
| 420 | 0.97 | 0.98 | 0.95 |
| 480 | 0.97 | 0.98 | |
| 540 | 0.95 | 0.98 | |
| 600 | 0.97 | | |
| 660 | 0.90 | | |
| 720 | 0.94 | | |
| 780 | 0.96 | | |

Table H4 1st and 2nd regeneration of natural clinoptilolite in columns with 50 mg/L Cr(III) feed

| Time (min) | Initial C/Co | 1st regen C/Co | 2nd regen C/Co |
|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 |
| 15 | 0.01 | 0.18 | 0.64 |
| 30 | 0.52 | 0.37 | 0.65 |
| 60 | 0.55 | 0.54 | 0.68 |
| 120 | 0.59 | 0.59 | 0.73 |
| 180 | 0.68 | 0.66 | 0.73 |
| 240 | 0.74 | 0.73 | 0.73 |
| 300 | 0.75 | 0.76 | 0.77 |
| 360 | 0.77 | 0.77 | 0.79 |
| 420 | 0.80 | 0.79 | |
| 480 | 0.79 | 0.80 | |
| 540 | 0.79 | 0.83 | |
| 600 | 0.80 | | |
| 660 | 0.80 | | |
| 720 | 0.80 | | |
| 780 | 0.80 | | |