ADSORPTION OF CADMIUM, NICKEL AND LEAD ON MODIFIED NATURAL ZEOLITE

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering.

University of the Witwatersrand, 2011

DECLARATION

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

Blessing Taenzana

____th day of ______ 2011

DEDICATION

In memory of my late mother. Surely you will be missed. May your soul rest in peace. One day we shall meet again. My entire family members, brothers and sisters and to my beloved wife Nomatter this is all for you.

ABSTRACT

Environmentally friendly treatment methods for heavy metals prior to discharge are considered favourable so as to protect ecosystems. The performance of modified zeolite from two different sources (South African and the USA) for the adsorption of Ni²⁺, Cd²⁺ and Pb²⁺ from synthetic industrial effluent contaminated with metal concentration levels at 50, 150 and 500mg/L was assessed. The selectivity of the zeolite for the adsorption of Ni²⁺, Cd²⁺ and Pb²⁺ was investigated at mixed feed solutions containing all three ions in equal concentrations and single component concentrations containing only one of the ions. The homoionic forms of the zeolite were made Na⁺, K⁺ and Ca²⁺. Batch experiments were then conducted to measure the uptake of metals by the zeolites. The zeolites were characterised using XRD and BET. The South Africa clinoptilolite has a higher surface area and pore volume $(17.52 \text{ m}^2/\text{g} \text{ and } 0.047 \text{ cm}^3/\text{g} \text{ respectively})$ than the USA zeolite $(12.26m^2/g \text{ and } 0.028cm^3/g \text{ respectively})$ for the Na⁺ homoionic form. According to the equilibrium studies, the selectivity sequence can be given as $Pb^{2+} > Cd^2$ >Ni²⁺, with good fits being obtained using Langmuir and Freundlich adsorption isotherms for low metal concentrations as compared to higher concentrations. The adsorption was found to depend on the homoionic form of the zeolite and to a lesser extent the source of the zeolite. The selectivity of a particular zeolite for a particular heavy metal can be altered by the homoionic form of the zeolite. Generally, the adsorption capacity of the USA clinoptilolite is higher than the capacity of the RSA clinoptilolite revealing the potential of clinoptilolite in industrial effluent treatment.

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LIST OF SYMBOLS

Å	Angstrom
AA	Atomic Absorption Spectroscopy
As	Specific surface area
β_i	Regression coefficient
G	Grams
ppm	Parts per million
С	BET constant
Co	initial adsorbate concentration (mg/L)
Ce	final aqueous phase concentration (mg/L)
C_{t}	Liquid-phase solute concentration at time, t
i	=0,1,2k
K_{f}	Freundlich constant for adsorption capacity (mg/g)
K _L	Langmuir isotherm adsorption maximum (L/g)
m	Mass of dry adsorbent
N_a	Avogadro number
nm	Nanometre
p	equilibrium pressure
p_o	saturation pressure
q_e	Equilibrium adsorption capacity (mg/g)
q_{max}	Maximum adsorption capacity (mg/g)
R^2	Correlation coefficient
R_L	Equilibrium constant
σ_x	Area covered by one nitrogen molecule
S	surface area
$S_{\rm BET}$	BET surface area
t	Time
V	volume of solution (mL)
V _{ads}	volume adsorbed
V_{m}	monolayer volume
Ν	Nitrogen

LIST OF ABBRIVIATIONS

AAS	Atomic Absorption Spectrometer
BET	Brunauer-Emmett-Teller
DEAT	Department of Environmental Affairs and Tourism
DWAF	Department of Water Affairs and Forestry
IUPAC	International Union of Pure and Applied Chemistry
PSD	Pore Size Distribution
RSA	Republic of South Africa
SEM	Scanning Electron Microscope
USA	United States of America
XRD	X-ray Diffraction

1.0 CHAPTER ONE

1.1 Introduction

The accumulation of heavy metals in the environment is a threat to the health and wellbeing of humans and the global ecosystem (Alloway and Ayres, 1997). The discharge of these heavy metals has a direct impact on the receiving waterbodies and has an indirect effect on human beings and ecological systems. Notably, anthropogenic sources of nickel, cadmium and lead are from mining and metallurgical engineering, electroplating, nuclear power plants, aerospace industries, battery manufacturing industries, production of glass, paints and pigments, and occur in municipal waste (Argun, 2008).

Nickel, cadmium and lead are some of the toxic heavy metals that are considered nonbiogradable and they bio-accumulate in living organisms causing diseases and disorders. The effects of nickel on human beings include renal, cardiovascular, reproductive and immunological effects. Human intake of cadmium causes endocrine disrupting effects (Alloway and Ayres, 1997). Lead has been found to be responsible for quite a number of aliments in human beings such as chronic neurological disorders especially in foetuses and infants (Rafiu et al., 2007). Removal of excessively high concentrations of heavy metals is essential to protect human health and the environment. Therefore it is important to treat wastewater and industrial effluent to regulated levels prior to discharge into the environment. Several methods have been used for the treatment of industrial waste to achieve permissible ambient levels for wastewater discharge. Most of them are physicochemical processes and these include precipitation, ion exchange, solvent extraction, adsorption, reverse osmosis, ultrafiltration and electrodialysis. In general, these processes have been found to be only partially and not economically feasible for the removal of heavy metals to the required discharge levels (Çoruh, 2008). However due to limitations of the aforementioned methods, zeolite use for heavy metal removal has been found to economically viable, in abundance in nature and highly effective for heavy metal removal (Argun, 2008).

The ion exchange property of zeolites has been attributed to its aluminosilicate structure. Isomorphous replacement of Al with Si in the structure results in an excess negative charge. This negative charge is balanced by alkali and alkaline earth cations of Na⁺, K⁺, Ca²⁺ or Mg²⁺ in the channels of the zeolite (Erdem et al., 2004; Perić et al., 2004). The exact composition of the counter ions in the natural zeolite varies from one geographical location to another. This appears to affect the performance of the zeolite for heavy metals removal. Zeolites have been used extensively in many processes because of their isormophic substitution property. Notably, they have been used in agricultural applications, wastewater treatment (Argun, 2008; Álvarez-Ayuso et al., 2003), radioactive waste treatment (Faghihian et al., 1999) and to treat mine waters (Wingenfelder et al., 2005; Motsi et al., 2009).

Modification of natural zeolites to form a homionic state which will improve the ion exchange capacity has been studied by several researchers (Semmens and Martin 1988;

Curkovic et al., 1997; Faghihian et al., 1999). Due to the range of ions found in a natural zeolite and the effect that this has on adsorption, for the purpose of this study the zeolite was first converted to homoionic form. Moreover, zeolites from two different geographical locations, namely South African and United State of America were used for the removal of nickel, cadmium and lead from synthetic wastewater solutions.

1.2 Justification

Natural zeolites have been reported to be abundant and highly selective for heavy metal removal (Argun, 2008) in wastewater treatment. The ions adsorbed on the zeolite initially (Sprynskyy at al., 2006) affect the order of the selectivity sequence for the heavy metal being adsorbed. There are two explanations for selectivity series for adsorption on zeolites: hydrated (or ionic radius) of the ion being adsorbed and the enthalpy of hydration (Ören and Kaya, 1999; Helfferich, 1995; Erdem et al., 2004) where the lower the enthalpy of hydration of a series of ions with a particular valence, the more selective the zeolite is for that ion (Panayatova and Velikov, 2003). The homoionic form, i.e. the ion being displaced, affects the selectivity series of the zeolite (Jewell and Kapanji, 2009).

Homoionic states of Na⁺, K⁺ and Ca²⁺ have been chosen for comparison of adsorption and selectivity on both the South African and United States of American zeolites. Divalent cations (Ni²⁺, Cd²⁺ and Pb²⁺) that are most common in industrial effluent have been chosen for adsorption under static conditions from single- and multi-component aqueous solutions on modified clinoptilolite (Na⁺, K⁺ and Ca²⁺). In this work we have investigated the effect of homoionic form on pore diameter and the uptake of heavy metals in solution.

1.3 Problem Statement

Modification of South African and United States of America zeolites improve the selectivity series and capacity of adsorption for Ni²⁺, Cd²⁺ and Pb²⁺ removal in industrial effluent treatment.

1.4 Research Objectives

The use of South African and American zeolites in wastewater treatment has not yet been fully exploited. Several researchers have studied the clinoptilolite effect on wastewater around the world and the adsorption potential and comparison of the two zeolites from different countries needs more exploration. Thus the aims of this study are to:

- investigate the effects of zeolite modification on the removal of Ni²⁺, Cd²⁺ and Pb²⁺ from single- and multi-component contaminated with heavy metal solutions at concentration of 50, 150 and 500mg/L.
- assess the selectivity and capacity of modified zeolite on Ni²⁺, Cd²⁺ and Pb²⁺ from wastewater

1.5 Research Report Overview

The dissertation will be structured as follows:

Chapter 1: Introduction. This introductory chapter outlines the research problem and sets out the objectives of the research work.

Chapter 2: Literature Review. This chapter reviews adsorption processes that are used in wastewater treatment. Economically viable adsorbents other than zeolites have been compared to zeolites. Zeolites have been elucidated in terms of structural, physical and chemical properties. This chapter further discusses the modification methods that have been used on zeolites and the findings that have been made.

Chapter 3: Methodology. This chapter outlines and justifies the researcher's selected methodological design and experiments. Experiments mentioned for comparison of adsorption capacity and selectivity for RSA and USA zeolites were mainly simple batch experiments and the characterisation techniques used were BET, XRD, and SEM.

Chapter 4: Results and discussion. This chapter reports in detail the research findings of the adsorption capacity and selectivity and the results of characterisation with BET, XRD, and SEM techniques. The chapter also provides a possible interpretation of the data and it further discusses the data in the context of the literature.

Chapter 5: The chapter summarises the major points of the study and draws conclusions reached from the study. The chapter provides recommendations of possible zeolites modification methods for further studies in order to improve the knowledge base.

2.0 CHAPTER TWO

2.1 Introduction

South African legislation, such as the National Water Act (Act No. 36 of 1998) (DWAF, 1998) the National Environmental Management Act (Act No. 107 of 1998) (DEAT, 1998) and the Water Services Act (Act No. 108 of 1997) (DWAF, 1997), gives rights to every human being to safe drinking water and proper sanitation and to live in an environment that is conducive for living. It is therefore the prerogative of local authorities to ensure the provision of safe and sufficient water to all their people. In most cases clean water is subject to contamination from industrial wastewater that is normally discharged in water ways before being properly treated for contaminants like heavy metals. Effluent can harm the environment if improper treatment technologies are implemented.

Heavy metal contamination occurs in several industries like metal, fishing, mining and mineral processing, oil refining and tanneries (Teutli-Sequeira et al., 2009). Heavy metals in wastewater are collected along the sewer system from not only industries and mines, but also homes and businesses. Wastewater is then delivered to treatment plants for treatment prior to discharge into streams or other receiving waters, or for reuse. There are several wastewater treatment methods that are currently in use worldwide and South Africa has a vast array of such plants. These treatment plants clean wastewater thereby reducing levels of heavy metals found in wastewater. Thus, the basic function of wastewater treatment is to speed up the natural processes by which water is purified. In general there are two basic stages in wastewater treatment that are primary and

secondary. In the primary stage, solids are allowed to settle and are removed from the wastewater (Imhoff et al., 1971). The secondary stage uses biological processes to further purify the wastewater. Effluent from the sedimentation tank is usually disinfected with chlorine before being discharged into receiving waters. Sometimes, these stages are combined into one operation.

The expansion of industries worldwide poses new challenges for wastewater treatment processes. Pollutants in wastewater such as heavy metals, chemical compounds and toxic substances have proved to be difficult to remove from water. Rising demands on the water supply and the rising capital and operational costs associated with the conventional advanced wastewater treatment technologies such as ion exchange, membrane separation and electrolysis aggravate this problem. Additionally, shortages of water have increased the need to reuse water and calls for better wastewater treatment. These challenges can be met through better methods of removing pollutants at treatment plants, or through prevention of pollution at the source. Pre-treatment of industrial waste, for example, removes many heavy metal pollutants at the beginning, not the end, of the pipeline. To return more usable water to receiving lakes and streams, new methods for removing pollutants are being developed. Advanced waste treatment techniques in use or under development range from biological treatment to physicalchemical separation techniques such filtration, adsorption, distillation, and reverse osmosis. These wastewater treatment processes, alone or in combination, can achieve almost any degree of pollution control desired. Waste effluents purified by such treatment, can be used for industrial, agricultural, or recreational purposes, or even drinking water supplies.

2.2 Toxicity of heavy metals

Nickel, cadmium and lead are some of the heavy metals found in wastewater and mostly come from industries. Practically, these metals concentrations in drinking water are regulated by South African legislation. As such, the allowable concentrations of cadmium, nickel and lead in water are $150\mu g/L$, $5\mu g/L$ and $20\mu g/L$ respectively (DWAF, 2005). If these concentrations are exceeded then drinking the water will cause acute and chronic effects in the human body. Some of the potential human effects that may be caused by high level of cadmium, nickel and lead are elaborated below.

2.2.1 Nickel

On contact with skins, high toxic levels of nickel contact with the skin result in disease, nickel inflation, which can be followed by sudden death (Madhava et al., 2009). Acute nickel exposure causes chest pain, tightness of the chest and shortness of breath. While long-term nickel exposure increases the risk for nasopharyngeal and lung cancer.

2.2.2 Cadmium

Cadmium is one of the most toxic metals which slowly accumulates in the bodies of living creatures in food chain. Symptoms of acute cadmium exposure are nausea, vomiting, abdominal pain, and breathing difficulty. Chronic exposure to cadmium can result in chronic obstructive lung disease, renal disease, and fragile bones. Symptoms of chronic exposure could include alopecia, anemia, arthritis, learning disorders, migraines, growth impairment, emphysema, osteoporosis, loss of taste and smell, poor appetite, and cardiovascular disease (Ferner, 2001). Cadmium and several cadmium-containing compounds are known carcinogens and can induce many types of cancers.

Lead has been found to be responsible for quite a number of ailments in human beings such as chronic neurological disorders especially in infants (Rafiu et al., 2007). Chronic exposure to lead may result in birth defects, mental retardation, autism, psychosis, allergies, dyslexia, hyperactivity, weight loss, shaky hands, muscular weakness, and paralysis beginning in the forearms. In addition to the symptoms found in acute lead exposure, symptoms of chronic lead exposure could be allergies, arthritis, autism, colic, hyperactivity, mood swings, nausea, numbness, lack of concentration, seizures, and weight loss (Woolf et al., 2007).

2.3 Heavy metal removal processes

Several processes are available for heavy metal removal from wastewater. Many such processes are uneconomical hence it is important to find a treatment strategy that would be simple and that uses local resources (Ouki and Kavannagh, 1999). According to Kamarowski and Yu (1997), rapid population increase and greater public awareness of environmental issues worldwide means that the wastewater industry has been faced with the difficult tasks of keeping up with population growth while meeting increasingly stringent nutrient discharge standards.

2.4 Adsorption

Adsorption is a popular method for the removal of heavy metals from wastewater (Ahmaruzzaman and Sharma, 2005). Adsorption is effective when natural materials that are available in large quantities or certain waste products from industrial or agricultural activities are used as inexpensive sorbents (Bailey et al., 1999). The application of clinoptilolite as a means of separating heavy metals has been well studied by many authors (Motsi et al., 2009). The use of natural zeolite as an adsorbent has gained interest among researchers; mainly because of its sorption properties that provide a combination of ion exchange and molecular sieve properties which can also be easily modified (Cincotti et al., 2006). Effective adsorption processes involve the use of an adsorbent that has an affinity for heavy metals. However, an adsorption process to be developed on a commercial scale requires the availability of suitable adsorbents in tonnage quantities at an economic cost (Ruthven, 1984).

There are two types of adsorption namely: physisorption and chemisorption. Physisorption, also called physical adsorption, is a process in which the adsorbate is joined to the adsorbant by Van der Waals forces. Chemisorption is a classification of adsorption characterised by a strong interaction between an adsorbate and a substrate surface. Chemisorption is characterised by ionic and covalent forces as opposed to physisorption which is characterised by a weak Van der Waals force (Somorjai, 1993).

2.5 Adsorbents

Different adsorbents have been found through extensive research. There are several adsorbents that are available in the market and some of them include the following:

2.5.1 Silica gel

Silica gel is one of the best inorganic materials that can be used for adsorption of heavy metals since its surface is both thermally and chemically stable during the reaction process, and it is also an abundant and inexpensive material. Silica gel is non-toxic, inert and is prepared by the reaction between sodium silicate and acetic acid. Structurally, silica gel is rigid with a continuous network of spherical colloidal particles and the bulk structure has a random packing of SiO₄ tetrahedrons. These silicon tetrahedrons give the silica gel in a number of reactive sites which will enhance good sorption capacity for heavy metals (Rangsayatorn et al., 2004).

2.5.2 Activated alumina

Activated alumina is the most widely used adsorbent because it possesses amphoteric properties allowing it to act as either an acid or a base. The ability to alter its pore or particle size provides it with a spectrum of unique properties that can allow the adsorption of micropore, mesopore and macropore adsobates. Furthermore, activated alumina can be efficiently regenerated, which significantly reduces treatment costs. Activated alumina is described as porous and granular and is produced by the dehydration of aluminium hydroxide at high temperatures. Activated alumina is a filter medium made by treating aluminium ore so that it becomes porous and highly

adsorptive. Activated alumina removes a variety of contaminants including excessive fluoride, arsenic, and selenium (Farooqi et al., 2007). The medium requires periodic cleaning with an appropriate regenerant such as alum or acid in order to remain effective. The main disadvantage of activated alumina is that the adsorption efficiency is highest only at low pH and contaminants like arsenites must be preoxidized to arsenates before adsorption (Johnson, 2005).

2.5.3 Activated carbon

Activated carbon has unquestionably been the most popular and widely used adsorbent in wastewater treatment processes (Ho, 2004). Activated carbon is a well-known commercial material that is effectively used as an adsorbent for the removal of a wide variety of organic and inorganic pollutants in sugar refining, the chemical and pharmaceutical industries, water and wastewater treatment. It has been one of the most effective solutions for water purification issues. Activated carbon is well suited to this task because of its exceptionally high surface area and well-developed internal microporous structure resulting high surface area (Satyawali and Balakrishnan, 2008). Its structure consists of a distorted three dimensional array of aromatic sheets and strips of primary hexagonal graphic crystallites (Stoeckli, 1990).

It is prepared from a variety of carbonaceous materials, including wood, peat, coal, oil products and coconut shells which are carbonized (Davidson et al., 1968). These materials are then activated by oxidation with either steam or carbon dioxide at high temperature. While the effectiveness of activated carbon to act as an adsorbent for a variety of contaminants is well known, activated carbon remains a costly material,

especially in developing countries, since the higher the quality of activated carbon, the greater the cost of production (Babel and Kurniawan, 2003).

2.5.4 Zeolites

Zeolites are naturally occurring alumino-silicates with a three dimensional framework structure bearing AlO₄ and SiO₄ tetrahedra. These are linked to each other by sharing all of the oxygen atoms to form interconnected cages and channels (Englert and Rubio, 2005) where exchangeable cations are present which counterbalance the negative charge. The physical structure is porous, enclosing interconnected cavities in which the metal ions and water molecules are contained. Zeolites have high ion exchange and size selective adsorption capacities as well as thermal and mechanical stabilities (Wang et al., 2009). Also, zeolites can be either synthetic (Hui et al., 2005) or natural. They have been used as water softeners (Ali and El-Bishtawi, 1997), chemical sieves and adsorbents (Hui et al., 2005) for a long time. Zeolites are well known materials for the removal of heavy metals such as cadmium, lead, cobalt and nickel (Blanchard et al., 1984).

There is however a fundamental difference between silica, gel, activated alumina, activated carbon and zeolites. For silica, gel, activated alumina and activated carbon the distribution of micropore diameter and the width of the distribution about the mean are controlled by the manufacturing process. By contrast, the micro pore size of a zeolite adsorbent is controlled by the crystalline structure and there is virtually no distribution of pore size. This leads to significant differences in the adsorption properties, and it is therefore convenient to consider zeolite (Ruthven, 1984) in adsorption processes.

Furthermore zeolite is a natural adsorbent which is industrially viable, cost effective and environmentally compatible adsorbent unlike activated carbon, activated alumina and silica gel.

2.5.5 Ion exchange resins

Ion exchange resins are polymers that are capable of exchanging ions with the ions in the solution that is passed through the resins beads without any physical alteration to the ion exchange resin material. There are two types of ion exchange resins namely the natural and the synthetic ones. Natural resins substances include proteins, cellulose and living. Synthetic ion exchange resins include phenolic polymers and polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchanger. The synthetic resins are used primarily for water treatment, but also for various other applications like catalysis. The advantage of ion exchange resins is that they are easily regenerated and offer low operational costs (Yang, 2003). The limitation of the synthetic ion exchange resins lies in the design stage of the resins.

2.6 Adsorption isotherms

Adsorption is influenced by the nature of the solution in which the contaminant is dispersed, molecular size and polarity of the adsorbate and the type of adsorbent. Hence, it is important to be able to relate the amount of contaminant adsorbed from the wastewater stream to the amount of adsorbent needed to reduce the contaminant to acceptable levels (Rowe and Abdel-Magid, 1995). The presentation of the amount of solute adsorbed per unit mass of adsorbent as a function of the equilibrium

concentration in the bulk solution at constant temperature is termed the adsorption isotherm. Adsorption isotherm models can be regarded as a benchmark for evaluating the characteristic performance of an adsorbent. Analysis of the isotherms is important in order to develop an equation that accurately represents the results and which could be used for design purpose (Ahmarruzzaman and Sharma, 2005).

2.6.1 Freundlich isotherm

The Freundlich isotherm describes adsorption in which the number of adsorption sites is large relative to the number of contaminant molecules. It was originally of an empirical nature, but was later interpreted as sorption on heterogeneous surfaces or surfaces supporting sites of varied affinities. It assumes equilibrium on heterogeneous surfaces (Gunay et al., 2007). This means that the energy of adsorption is not the same for all adsorption sites. According to this model the adsorbed mass per mass of adsorbent can be expressed by a power law function of the solute concentration, C_e , as (Freundlich, 1906):

$$q_e = k_F C_e^{\frac{1}{n}} \tag{4.1}$$

where K_F is the Freundlich constant related to adsorption capacity, q_e (mg/g), 1/n is a measure of the surface heterogeneity, ranging between 0 and 1. For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log q_e = \log k_F + \left(\frac{1}{n}\right) \log C_e \tag{4.2}$$

2.6.2 Langmuir adsorption isotherm

This is often used for the adsorption of a solute from a liquid solution. In the Langmuir model adsorption increases linearly with increasing solute concentration at low concentration values and approaches a constant at higher concentration values because there are a limited number of adsorption sites per mass of adsorbent. The Langmuir isotherm is also called the ideal localized monolayer model and was developed to represent chemisorption (Wang *et al.*, 2009). Langmuir (1918) theoretically examined the adsorption of gases on solid surfaces, and considered sorption as a chemical phenomenon. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent (Pérez et al., 2007), that is, all the adsorption sites are equivalent and the ability of a molecule to be adsorbed on a given site is independent of its neighbouring sites occupancy (Febrianto et al., 2009; Sarkar and Acharya, 2006). For linearization of the data, the Langmuir equation can be expressed as:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\max}}\right) \frac{1}{C_e} + \frac{1}{q_{\max}}$$
(4.3)

where q_e is the adsorption capacity at equilibrium (mg/g), q_{max} is the theoretical maximum adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir affinity constant (L/mg) and C_e is the supernatant equilibrium concentration of the system (mg/L). This isotherm equation has been most frequently applied in the study of adsorption equilibrium, however, it should be realized that the Langmuir isotherm offers no insights into the adsorption mechanism (Liu and Liu, 2008).

The essential characteristic of the Langmuir isotherm can be described by a separation factor which is called the equilibrium constant, R_L . The equilibrium factor is thus defined as:

$$R_{L} = \frac{1}{1+K_{L}} \cdot \frac{1}{C_{o}}$$
(4.4)

where K_L is the affinity constant (l/mg), C_o is the initial concentration of the adsorbate (mg/L). An R_L value that is between 0 and 1 indicates a favourable adsorption process.

2.7 Ion exchange

Zeolites are widely used as low-cost ion exchangers. They exchange cations from their structure with dissolved ones. Ion exchange is one of the methods used for the removal of several toxic substances, including heavy metals and adsorption by zeolite is considered to be one of the main adsorbents for the removal of toxic metals from solutions (Inglezakis et al., 2001). Theoretically, exchange capacity refers to the maximum exchange level, expressed as the total amount of the exchangeable cations in a specific quantity of the material. It is a constant value, independent of any pre-treatment. Of practical interest is the effective capacity, which refers to the real amount of the exchangeable cations contained in a specific quantity of the material, under specific experimental conditions (Helfferich, 1995). The ions that represent the difference between these two different capacity values cannot be removed easily, because of low mobility and strong bonding forces within the material (Gradev et al., 1988). The total exchange capacity is usually determined by chemical analysis (Pabalan,

1994). Ion exchange by clinoptilolite is used to remove several cations, such as lead, cadmium and nickel from aqueous solutions and its order of selectivity is $Pb^{2+} > NH^{4+} > Ba^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$ (Blanchad et al., 1984).

2.8 Natural and synthetic zeolites

The unique physical and chemical properties of zeolites have attracted many researchers from the 18th century onwards (Gottardi and Galli, 1985). According to Gottardi and Galli (1985) "zeolite" was created by Cronstedt (1756) from the Greek "Z€0" meaning "to boil" and " λ θos" meaning "stone" and this means minerals that expel water when heated and hence are seen to boil. Zeolites have the ability to loose water at high temperatures from the atmosphere. According to Gottardi and Galli (1985) clinoptilolite was named by Schaller around 1932.

A survey of the literature has indicated that natural zeolites provide an economic and effective mechanism to remove heavy metals dissolved in a wastewater. Zeolites have been intensively studied in the last half century with the emphasis on synthetic zeolites, and it is only in recent years that natural zeolites have started gaining interest. Zeolites are natural minerals, thermally stable and resistant to radiation (Faghihian et al., 1999); they have been mined in many parts of the world including South Africa. The characteristics of a zeolite deposit are decided in its genesis. Small natural differences such as temperature, geographic location and ash/water properties impart a slightly different composition and therefore some unique properties to each deposit. These small

differences present during the formation of a zeolite deposit are the reason that natural zeolite from a particular location has distinct and unique properties.

There are about 50 different natural zeolite structures that have been identified. These different zeolite types differ in the crystal structure and chemical composition of the elements present. Some of the examples of natural zeolite structures include chabazite, clinoptilolite, analcime, phillipsite, ferrierite, heulandite and mordenite. Among these naturally occurring zeolites, clinoptilolite is one of the most abundant. It is found in large deposits and mined all over the world, including South Africa and the United States of America. Synthetic zeolites have also been developed and these constitute about 150 different zeolite structures (Tihmillioglu and Ulku, 1996). Both natural and synthetic zeolites have been used in adsorption and ionic exchange of heavy metals. According to Pitcher et al. (2004), the synthetic MAP zeolite showed greater than 95% removal of heavy metals from motorway storm water than the natural zeolite. However the use of synthetic zeolites has been limited due to the environmental implications of the synthesis process and cost effectiveness. Natural and synthetic zeolites are different in many ways including the following:

- Natural zeolites are generated through geological processes while synthetics are chemically manufactured from chemicals with a carbon footprint
- Natural zeolites have a higher silica to alumina ratio than the synthetic zeolites
- Natural zeolites are resistant to acidic conditions while synthetic zeolites rupture in mildly acidic environments

2.8.1 Clinoptilolite

Clinoptilolite is one of the most abundant forms of zeolite that is found naturally on earth. It is very stable towards dehydration and its thermal stability, 700 °C in air, is considerably greater than the stability of other natural zeolites with a similar structure (Çulfaz and Yağız, 2004). Breck (1974) gave the typical formula for the clinoptilolite as M_{2/n}O.Al₂O₃.xSi₂.yH₂O. The atomic structure of clinoptilolite is based on threedimensional frameworks of silica and alumina tetrahedra. The Si/Al ratio changes between 4 and 5.5 and low-silica members are enriched with calcium, whereas highsilica clinoptilolites are enriched with potassium, sodium, and magnesium. Each oxygen atom in the tetrahedron is bonded to two adjacent silicon or aluminum ions, linking them together. This gives clinoptilolite a negative charge and a high cation exchange capacity that will adsorb and freely exchange positively charged ions (Kamarowski and Yu, 1997). Such sorptive properties have been utilized in a variety of applications such as adsorption of ammonia (Jorgensen, 1976; Nijoroge and Mwamachi, 2004) and removal of heavy metals.



Figure 2.1 A typical structural model of clinoptilolite (Natural and Synthetic Zeolites, 1987)

2.9 Selectivity of zeolite for heavy metals

Zeolites have large surface areas and high cation exchange capacities (CEC) that provide an ion exchange medium that can absorb variable-sized ions (Babel and Kurniawan, 2003). During the 1970s, natural zeolite was shown to preferentially remove heavy metals such as Sr and Cs from wastewater (Babel and Kurniawan, 2003), and this property made zeolite a preferred adsorbent for wastewater treatment systems. The selectivity of clinoptilolite for heavy metals based on the ionic radius and dissociation constant was in the order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+}$ $> Ni^{2+}$ (Ouki and Kavannagh, 1997). Langella et al. (2000) reported that the ion selectivity of clinoptilolite was in the order: $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} = Zn^{2+}$.

The high selectivity for toxic metals such as Ni, Cd and Pb makes clinoptilolite a good adsorbent for the treatment of mine wastewater (Erdem et al., 2004). Faghihian et al. (1999) have studied Ni²⁺, Cd²⁺ and Pb²⁺ removal for wastewater and they have found that the selectivity of the clinoptilolite to heavy metals in both the natural and Na⁺ - modified clinoptilolite did not differ with the literature. However, the capacity of clinoptilolite is influenced significantly by the source from which clinoptilolite originates and both the chemical and physical treatment (Klieve and Semmens, 1979).

2.10 Modification of zeolite

Zeolite can be modified by introduction of functional groups in order to improve its activity and selectivity for the removal of several substances (Ćurkovic et al., 1997). A

significant number of studies have suggested that a pretreatment or modification of zeolitic rocks enhances their ion exchange abilities. Modification is recommended in order to reach a homoionic or near homoionic state of the zeolite that will improve their effective exchange capacities and their performance in ion exchange applications. Different researchers have used different modification or pretreatment methods to make the zeolite homoionic. Modification of the natural clinoptilolite by alteration of temperature, pH, and addition of sodium counter ions to enhance the effectiveness of its adsorption capacity has been studied ((Pabalan, 1994; Çoruh, 2008).

2.10.1 Effect of temperature

Temperature has a small effect on Pb^{2+} removal and a slight effect on Ni^{2+} (Malliou et al., 1994; Ali and El-Bishtawi, 1997). For nickel the temperature effect can be attributed to enhancement of ion diffusivity (Ali and El-Bishtawi, 1996). The author is not aware of any cases in which the effect of temperature on Cd^{2+} removal has been studied.

2.10.2 Effect of pH

Natural zeolites have a higher resistance to acidic conditions (Wingenfelder, et al., 2005) than synthetic zeolites. The effect of pH on the zeolite has been studied by Inglezakis et al. (2001) and Faghihian et al. (1999) who have found that the zeolites work best in a limited pH range. The pH affects the character of the zeolite itself and the metal speciation in solution (Ouki and Kavannagh, 1997). As the pH is below 2, the adsorption effect of the zeolite is reduced. At high pH, above 10, it is necessary to avoid chemical precipitation of metal ions and the hydroxides which will be formed during the

adsorption process which block the pores. Zeolites become unstable at high pH (Basu, et al., 2006) while very low pH, below 2, tends to affect the chemical structure of the zeolite (Blanchard, et al., 1984) and for this reason; chemicals are added to adjust the pH, which is an additional operating cost (Ouki and Kavannagh, 1997).

2.10.3 Particle size effect

According to Ali and El-Bishtawi (1997) metal uptake by zeolite takes place on the exterior surface of the particle as well as sites within the particles. However, only a fraction of the internal sites is accessible to metal ions due to the occlusion of crystallites. Thus decreasing the particle size increases the external sites for adsorption.

2.10.4 Homoionic forms

Several modifications of zeolite in wastewater treatement have been reported (Semmens and Martin, 1988; Ćurkovic et al., 1997; Faghihian et al., 1999) in order to improve heavy metal adsorption Modification with salt solutions to produce homoionic forms has been studied particularly for sodium chloride (Semmens and Martin, 1988; Ćurkovic et al., 1997; Faghihian et al., 1999). Na⁺ ions in NaCl can readily displace other cations and since Na⁺ ions are easily removable the adsorption capacity is enhanced once all of the counter-ions have been replaced with Na⁺ (Kesraoui-Ouki et al., 1993).

 K^+ modified clinoptilolite and Ca^{2+} modified clinoptilolite have not been fully researched however Ca^{2+} modified clinoptilolite is reported as unsuitable adsorbent
because Ca^{2+} is difficult to displace (Panayotova and Velikov, 2003). Ca^{2+} has been found to adsorb strongly to clinoptilolite which a high selectivity for Ca^{2+} and this may be due to low hydration enthalpy of Ca^{2+} , which is -1577 kJ/mol (Panayotova and Velikov, 2003).

2.11 BET surface area

This method for determining the surface area of a porous solid was developed by Brunauer, Emmett, and Teller and is a widely used tool for determining the monolayer volume (V_m) and the specific surface area (A_s). The BET method is based on gas sorption (both adsorption and desorption) on the surface of dry solid powders. Nitrogen, N₂, adsorption at 77 K and at sub-atmospheric pressures represents the most widely used technique to determine catalyst surface area and to characterize its porous texture (Leofanti et al., 1998). N₂ is applied over a wide range of relative pressures (p=p_o) and produces adsorption isotherms that provide information on size distributions in the micro-, meso- and macroporosity ranges approximately 0.5–200 nm (Groen, 2003). The amounts of gas molecules adsorbed or desorbed are determined by the pressure variations due to the adsorption or desorption of the gas molecules by the material (the adsorbent). The total surface area of the adsorbent is calculated using the adsorption model and the total area that will be occupied by the nitrogen. The surface area, *S* equation is in the form (Gregg and Sing, 1982):

$$S_{BET} = \frac{V_m N_a \sigma_X}{V}$$
(4.5)

where V_m is the volume of gas for an adsorbed monolayer, V is the molar volume of the adsorbed gas, N_a is the Avogadro number and σ_x is the area covered by one nitrogen molecule.

2.11.1 BET Theory

According to Gregg and Sing (1982), BET theory suggests that the surface of the adsorbent is uniform thus the heat of adsorption of the first monolayer is constant. It further assumes that there is no lateral interaction of adsorbed particles, adsorbed molecules can act as a new adsorption surface for subsequent layers and this is a repetitive process. Finally the heat of adsorption of all monolayers but the first is equal to the heat of condensation. From this BET theory, the derived BET equation is (Leofanti et al., 1998):

$$V_{ads} = V_m \frac{cp/p_o}{(1-p/p_o)(1+(c-1)p/p_o)}$$
(4.6)

where p and p_o are the equilibrium and saturation pressures of the adsorbates at the temperature of adsorption, V_{ads} is the adsorbed gas volume, V_m is the monolayer adsorbed gas volume and c is the BET constant, which is related to the heats of adsorption and liquefaction.

2.12 Pore size distribution analysis

Pore size distribution (PSD), a very important property of adsorbents, determines the fraction of the total pore volume accessible to molecules of a given size and shape (Zhu, 2007). Pores can have a regular and/or irregular shape. In most cases these pores are of different sizes (Leofanti et al., 1998). According to the IUPAC definitions the pore sizes of activated carbon can roughly be classified as micropores (< 2 nm), mesopores (2 - 50 nm) and macropores (> 50 nm) (Gregg and Sing, 1982; Roquerol et al., 1994; Stoeckli et al., 2002). The macropores act as transport pathways, through which the adsorptive molecules travel to the mesopores, from where they finally enter the micropores. Thus, macro- and mesopores can generally be regarded as the highways into the zeolite particle, and are crucial for kinetics. The micropores usually constitute the largest proportion of the internal surface of the zeolite and contribute most to the total pore volume (Rodriguez-Reinoso and Linares-Solano, 1989).



Figure 2.2 Four types of adsorption isotherms found by nitrogen adsorption (Leofanti et al., 1998).

Figure 2.2 shows the four types of adsorption isotherms found by nitrogen adsorption (Leofanti et al., 1998). Though they are six types of adsorption isotherms, only four are usually found in characterisation and these are type II, IV, I and VI. This is so because Types III and V have weak interactions between gas and adsorbent. This adsorption indicates that type VI is for the uniform ultramicroscopic solids, type I is for the

microporous solids, type IV is for mesoporous solids and finally type II is for macroscopic solids.

2.12 Concluding remarks

It is a human right to have safe drinking water to avoid chronic and acute diseases due to heavy metals exposure. However, water sources are under threat due to untreated industrial wastewater being disposed into the environment. It is thus of paramount importance and a legal obligation to treat industrial effluent before discharge into the environment.

Different wastewater treatment methods are used worldwide. However most of these methods are uneconomical and this has lead to research on locally available resources (Ouki and Kavannagh, 1999). Several commercially available adsorbents are available and some of them are: silica gel, activated alumina, activated carbon and zeolite. Zeolite is naturally occurring and differs from other adsorbents which are synthetic in terms of its physico-chemical properties. Actually, zeolites have a large surface area and high cation exchange capacity that provide an exchange complex that adsorbs ions of variable size effectively (Babel and Kurniawan, 2003).

Zeolites have been modified to increase the content of a single cation to homoinic form (Semmens and Martin, 1988). This removes ions that are more easily displaced. Literature has documented that homoinic and near homoionic zeolite performs better in heavy metal removal (Semmens and Martin, 1988; Kesraoui-Ouki et al., 1993). In particular zeolite modified with NaCl (Panayotova and Velikov, 2003; Faghihian et al., 1999) has been found to give higher adsorption capacity than raw clinoptilolite. Particle size, temperature, pH and pore size distribution affect adsorption capacity of zeolite with small particle size yielding a higher heavy metal adsorption (Ali and El-Bishtawi, 1997). Pore size distribution determines the fraction of the total pore volume accessible to chemical species of a given size and shape (Zhu et al., 2007).

3.0 CHAPTER THREE

3.1 Experimental methods

A batch technique was used as a quick way to assess the ability of clinoptilolite samples to remove heavy metals from synthetic wastewater solutions, both in terms of capacity and selectivity. The samples tested originated from South Africa and the United States of American clinoptilolite.

3.2 Clinoptilolite samples

The clinoptilolite samples used in the experiments that were from the United States of America, are referred to as USA clinoptilolite, and those from South Africa, referred to as RSA clinoptilolite. The USA clinoptilolite was supplied in the Na⁺ homoionic form and was supplied by Zeox Mineral Material Corporation (trade name Cabsorb®). The RSA clinoptilolite was mined in KwaZulu-Natal and it was supplied by Pratley Mining Company (trade name Pratliperl). The RSA clinoptilolite which was supplied was not modified. These two clinoptilolites were crushed separately and sieved to 0.4 to 0.8mm size fraction.

3.2.1 Clinoptilolite modification procedure

Both clinoptilolites were washed with distilled water to remove fine dust particles prior to modification (Medvidovic et al., (2006), Gunay et al., (2007) and capacity adsorption measurements. Both RSA and USA clinoptilolites were modified by contacting them to 2M NaCl, KCl or CaCl₂ for 24 hours to allow conversion of the clinoptilolites to a homoinic form. The clinoptilolite samples were mixed at a ratio of 40g to 100mL of the modification solution at room temperature without stirring. However, since the USA clinoptilolite was received in Na⁺ form it was not modified for Na⁺ form experiments. Then, the suspension was filtered and the clinoptilolite was washed with distilled water and dried at 55°C for 24 hours, and used in the adsorption studies.

3.3 Batch experimental method

3.3.1 Synthetic wastewater preparation

Standard solutions containing the three heavy metal cations, namely: Ni²⁺, Cd²⁺ and Pb²⁺ were prepared from the chlorides salts: NiCl₂.6 H₂O, CdCl₂.2 $\frac{1}{2}$ H₂O and PbCl₂ respectively. Stock solutions of 1 000ppm were prepared in 1L flask and the mass of used for NiCl₂.6 H₂O, CdCl₂.2 $\frac{1}{2}$ H₂O and PbCl₂ were 4.05g, 2.03g and 1.67g respectively. A feed synthetic solution was prepared by mixing the required volumes of the solutions above to obtain synthetic wastewater solutions of 50, 150 and 500ppm of each of the three cations mentioned above. All solutions were prepared with distilled water and Merck Ltd. high grade chloride salts.

Batch adsorption experiments were conducted on both clinoptilolites: RSA clinoptilolite and USA clinoptilolite. Three different masses of each clinoptilolite that is 2g, 4g and 10g were contacted in conical flasks with 110mL solution that contained either all three cations or only a single cation. The conical flasks were then stoppered. Batch experiments were performed in a shaking incubator (Labex) at 150 rpm and the temperature was maintained at 25°C. Every hour for a 6 hour period, 6mL of the suspension was filtered from the mixture and tested for metal ion concentration using the atomic adsorption spectrophotometer, AAS (Spectro AA, 55B Varian). The experiments were then left to run for a period of 24 hours to determine the equilibrium concentrations.

The performance of the clinoptilolite at removing heavy metals in both the feed and the single-component wastewater solutions was assessed by calculating the percentage removal. The following equation was used for each of the heavy metals tested:

% metal removal
$$q_e = [(C_i - C_x)/C_i] \ge 100$$
 (3.1)

where C_i is the initial metal concentration and C_x is the metal concentration after contact with the clinoptilolite.

3.4 Clinoptilolite mineralogy and characterization

3.4.1 X-Ray diffraction analysis of clinoptilolite

The as-received clinoptilolite form of each of the USA and RSA samples were ground using mortar and pestle and the fine powdered diffractograms of the clinoptilolite were obtained using a Philips PW 1830 diffractometer. Conventional diffractograms were obtained at 40kV and 40mA for 45 minutes, over a range of 20 from 0° to 80°, and a step size of 0.04. These conventional diffractograms were then used to verify crystallinity and composition.

3.4.2 Specific surface area and pore volume analysis

The specific surface area of the Na⁺, K⁺ and Ca²⁺ forms of both RSA and US clinoptilolite were determined by the Brunauer Emmet Teller (BET) technique. The nitrogen adsorption isotherms were measured at 77K and the BET surface areas were determined by standard multipoint techniques of nitrogen using Micromeritics ASAP 2000 instrument. Clinoptilolite samples of 3g were heated to 150°C under flowing N₂ to remove H₂O.

3.4.3 Scanning Electron Microscopy (SEM)

Clinoptilolite of both RSA and USA samples were mounted directly onto the Scanning Electron Microscope model Joel JSM840 holders and then observed at a voltage of 20keV. Visual information of the surface structure, shape and distribution of the crystal size on each clinoptilolite was examined.

4.0 CHAPTER FOUR

4.1 Results and discussion

Zeolites from two different geographical locations were converted into Na⁺, K⁺ and Ca²⁺ homoionic forms. These homoinic forms were characterised using XRD and SEM. Pore size distribution, zeolite surface area and pore volume were determined by the BET method. Simple batch experiments were conducted on the different homoionic forms from both RSA and USA to test the adsorption capacity and selectivity for Ni²⁺, Cd²⁺ and Pb²⁺. Isotherm models were fitted to the data and parameters were obtained.

The results presented in this research report have been selected from a wide range of obtained results that came out from the experimental work. Mixed feed concentrations of Ni²⁺, Cd²⁺ and Pb²⁺ were used on heavy metal removal percentages since in real situation heavy metal are in a mixture. Removal percentages of single metal ions have been attached in Appendix B. The equilibrium adsorption capacities for 2g data was used for illustration in this research report and the data for 4g and 10g is shown on the Appendix C. On modelling description, the Na⁺ form clinoptilolite was selected since Na⁺ form clioptilolite performed better than the K⁺ and Ca²⁺ forms on both RSA and USA and the results of the USA Na⁺ linear regression analysis are attached in Appendix D.

4.2 X-ray diffraction data

From the XRD results (Figures 4.1 to 4.6), it can be seen that the Na⁺, K⁺ and Ca²⁺ zeolites are crystallographically different from each other. The highest peak was almost at α °2 θ position of 22° and the peaks are mostly concentrated between 2 θ values of 10° to 40°. The best fit from the data library for the natural zeolite is heulandite (CaAl₂Si₈O₁₈·16H₂O), for Na⁺ form it is clinoptilolite ((NaKCa)₆(SiAl)36O₇₂·120H₂O) and for Ca²⁺ form it is a mixture heulandite and kilsilite (KAlSiO₄) (Kapanji, 2009). The library matches are not conclusive evidence for the nature of the counter ions, but this shows that the different homoionic forms are distinct from each other. All the peaks of the modified zeolites showed sharp peaks in the diffraction pattern and this is indicative of the crystalline and monoclinic nature of the zeolite.

4.2.1 Na⁺ modified clinoptilolite

As it can be seen from Figures 4.1 and 4.2, both RSA and USA modified Na⁺ form zeolite predominantly consist of clinoptilolite, $(NaKCa)_6(SiAl)_{36}O_{72}$ ·120H₂. The ions calcium and potassium are still present in the zeolite because Na⁺ ions are not able to displace all these ions from the framework; K⁺ and Ca²⁺ 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 clinoptilolite is difficult to achieve. The analysis of the X-ray diffraction pattern indicated that the zeolite sample was somewhat richer in clinoptilolite.



Figure 4.1 X-ray diffraction pattern of RSA clinoptilolite modified with Na⁺



Figure 4.2 X-ray diffraction pattern of the USA clinoptilolite modified with Na⁺

4.2.2 K⁺ modified clinoptilolite

It is evident from Figure 4.3 that the RSA K⁺ modified zeolite sample mainly consists of clinoptilolite, $(NaK)_4CaAl_6Si_{30}O_{72}\cdot124H_2O$ and heulandite, $CaAl_2Si_7O_{18}.16H_2O$ and from Figure 4.4 the USA K⁺ consists clinoptilolite, $(NaK)_4CaAl_6Si_{30}O_{72}\cdot124H_2O$, heulandite, $CaAl_2Si_7O_{18}.16H_2O$ and kilsilite (KAlSiO₄). This suggests that K⁺ is not as

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



Figure 4.3 X-ray diffraction pattern of RSA clinoptilolite modified with K⁺



Figure 4.4 X-ray diffraction pattern of the USA clinoptilolite modified with K⁺

4.2.3 Ca²⁺ modified clinoptilolite

Figures 4.5 and 4.6 indicate that the main component of the Ca^{2+} modified clinoptilolite (USA and RSA) form was heulandite ($CaAl_2Si_7O_{18}\cdot 16H_2O$ occurring with kilsilite (KAlSiO₄), as the main impurity. As expected Ca^{2+} ions are the predominant ions, although it cannot completely displace K⁺ ions in kilsilite.



Figure 4.5 X-ray diffraction pattern of RSA clinoptilolite modified with Ca²⁺



Figure 4.6 X-ray diffraction pattern of the USA clinoptilolite modified with Ca²⁺

In summary, most of the sharp peaks are assigned to clinoptilolite and heulandites. The main impurities observed were with kilsilite that was found in Ca^{2+} .

4.3 Scanning Electron Microscopy

Figure 4.7 shows the SEM photographs of Na⁺ modified clinoptilolite of USA and RSA clinoptilolites at the same magnification. The SEM images of the Na⁺ treated zeolite showed a typical morphology of sedimentary, clinoptilolite rich tuffs for both the RSA and USA. Cavities of different sizes and different shapes could be observed. It can be seen from the micrographs that the external surface of Na⁺ modified clinoptilolite is full of cavities that will facilitate adsorption of heavy metals.



Figure 4.7 SEM images of Na⁺ modified clinoptilolite for (a) USA clinoptilolite and (b) RSA clinoptilolite

4.3 BET nitrogen adsorption

The pore size distribution (PSDs) data of the studied modified clinoptiololites was deduced from the BET nitrogen adsorption data obtained. The adsorption isotherms for clinoptilolite are shown in Figures 4.8 and 4.9. Based on the conventional classification of adsorption isotherms, all measured isotherms can be considered as isotherms of type IV (Korkuna et al., 2006). The hysteresis loops are typical of mesoporous materials with flat slits between crystalline planes. At high relative pressures the adsorption in mesopores leads to multilayer formation until, at a pressure dependent on Kelvin-type rules (larger mesopore=higher pressure), condensation takes place, giving a sharp adsorption volume increase. As mesopores are filled, adsorption continues on the low external surface. Additionally, the entire treated zeolite exhibits a type IV isotherm with well-developed mesoporous structure (Zhu et al., 2007).

As observed in Figures 4.8 and 4.9, the boundary ascending curves of the Na⁺-, K⁺- and Ca²⁺-clinoptilolites isotherms with a narrow, high hysteresis loop is akin to a standard nitrogen isotherm on a non-porous substrate. This might be due to ions (e.g. Na, K, Ca) located in narrow channels forming barriers to nitrogen diffusion. Much less is adsorbed is observed for RSA and USA Ca²⁺-forms implying that the pore diameters of these micropores are much smaller. Therefore the contribution of narrow pores to BET isotherms is insignificant. At low relative pressures formation of a monolayer of adsorbed molecules is the prevailing processes (Leofanti et al., 1998).



Figure 4.8 Adsorption-desorption isotherms of nitrogen on the RSA clinoptilolite modified with Na⁺, K⁺ and Ca²⁺



Figure 4.9 Adsorption-desorption isotherms of nitrogen on the USA clinoptilolite modified with Na⁺, K⁺ and Ca²⁺

4.4 BET pore size distribution

Pore size distribution (PSD), a very important property of an adsorbent, determines the fraction of the total volume of a particle that is accessible to molecules of a given size and shape (Zhu et al., 2007). According to the classification adopted by the IUPAC, pores are classified as micropores, mesopores and macrospores. The pore size of the zeolites showed that the vast majority of the pores fall into the range of mesopore (between 10 and 15nm) (Figures 4.10 and 4.11). In Figure 4.10, Ca²⁺ clinoptilolite form for RSA shows a pore size distribution below 5nm which indicate that there are fewer zeolite channels available for heavy metal adsorption. Figure 4.11 showed Ca²⁺ form clinoptilolite for USA with no pore volume at a 5nm pore diameter which suggest that the zeolite channels were completely closed. Therefore, this supports the low adsorption of Ni²⁺, Cd²⁺ and Pb²⁺ by Ca²⁺ clinoptilolite.



Figure 4.10 BJH pore size distribution (PSD) derived from the adsorption branch of the isotherm of RSA clinoptilolite modified with Na^+ , K^+ and Ca^{2+}



Figure 4.11 BJH pore size distribution (PSD) derived from the adsorption branch of the isotherm of the USA clinoptilolite modified with Na^+ , K^+ and Ca^{2+}

A summary of the BET surface area, S_{BET} , pore volume, Vp, and pore size is presented in Table 4.1. The BET surface areas obtained for RSA zeolite modified with Na⁺, K⁺ and Ca²⁺ were 17.5m²/g, 18.8 m²/g and 16.6 m²/g respectively. The BET surface areas for USA zeolite modified with Na⁺, K⁺ and Ca²⁺ were 12.2m²/g, 10.8 m²/g and 10.7 m²/g respectively. The specific surface areas for the RSA modified clinoptilolite follows the sequence RSA-K > RSA-Na > RSA-Ca. The USA modified clinoptilolite had the sequence of USA-Na > USA-Ca \geq USA-K. A comparison of the two zeolites shows that the RSA zeolite has a slightly higher BET surface area than that of the USA clinoptilolite. This can be explained by the fact that these zeolites are from different sources and the modification specifications for the USA (Na⁺- form) received were not provided by the supplier. The total sorption pore volume V*p* (estimated at *p*/*p*₀ =0.98, where *p* and *p*₀ denote the equilibrium and saturation pressures of nitrogen respectively) and the mean pore radium (R_{*p*}=2V_{*p*}/ S_{BET}) assuming a cylindrical shape for the pores. The values of these parameters are given in Table 4.1 below:

Table 4.1

	Surface Area	Pore Volume	Pore size	$R_{\rm p}({\rm nm})$
Adsorbent	$S_{\rm BET}$ (m ² /g)	$V_{\rm t}~({\rm cm}^3/{\rm g})$	(nm)	
RSA-Na	17.5	0.0629	15.5	0.00531
RSA-K	18.8	0.0640	13.60	0.00680
RSA-Ca	16.5	0.0465	10.62	0.00759
USA-Na	12.2	0.0278	9.04	0.00453
USA-K	10.8	0.0256	9.47	0.00473
USA-Ca	10.7	0.00151	5.64	0.00281

Structural characteristics of the studied adsorbents

4.5 Heavy metal removal

The performance of the clinoptilolite in adsorbing heavy metals levels from synthetic industrial effluent was assessed by calculating the percentage of metal removed. The following equation was used for each metal tested:

% metal removal
$$q_e = [(C_i - C_x)/Ci] \ge 100$$
 (4.1)

where C_i is the initial metal concentration and C_x is the metal concentration after the contact time with the zeolite. Comparing the removal efficiencies (%) obtained from the different modified zeolites in Figures 12 to 14 reveals that the Na⁺ modified zeolite performs considerably better that the K⁺ and Ca⁺ and the order of performance is: Na⁺ > K⁺ > Ca²⁺ for the both RSA and USA clinoptilolite. The results appeared to show some interference in the adsorption of heavy metals in a mixed synthetic solution. This could

be due to a change in the metal species or competition from other cations for the same sites (Pitcher et al., 2004).

The results of the analysis of metal removal are shown in Figures 4.12 to 4.14 for the USA clinoptilolite which is much more efficient than the RSA clinoptilolite. It can remove an excess of 95% of Ni²⁺, Cd²⁺ and Pb²⁺ present in the mixed metals solution and single component solution. This is mainly attributed to the different sources and the modification specifications for the USA (Na⁺- form) received which were not provided by the supplier. The initial adsorption in the first hour was high and this is attributed to adsorption on the surface of the zeolite material and in the microprores. The subsequent adsorption as shown in Figures 4.12 to 4.14 may occur inside the zeolite cavities or channels of the zeolite structure.

The result again revealed that the USA clinoptilolite has high potential in achieving the best removal performance than the RSA clinoptilolite. The clinoptilolite selectivity sequence is as follows: $Pb^{2+} > Cd^{2+} > Ni^{2+}$. The time required to reach equilibrium was assumed to be 24hrs; however, the results demonstrated that more than 90% removal was achieved in the first 1 hour when using both the RSA and USA clinoptilolite.

4.5.1 Heavy metal removal from 50ppm wastewater



Figure 4.12 Removal of Ni^{2+} , Cd^{2+} , and Pb^{2+} from mixed solution (50 mg/L of each cation) using 2g RSA (1a to c) and 2g USA (2a to c) zeolite modified with Na^+ , K^+ and Ca^{2+}

i. Nickel

The percentage removal of Ni²⁺ ions from 50 mg/L mixed feeds of Ni²⁺,Cd²⁺, and Pb²⁺ using Na⁺, K⁺ and Ca²⁺ form clinoptilolite is presented in Figure 4.12. The USA Na⁺ form had a higher percentage adsorption values than the RSA Na⁺ clinoptilolites in the mixed feeds (90 and 85% respectively). The Na⁺ modified clinoptilolite has a higher removal percentage of Ni²⁺ than K⁺ clinoptilolite as observed by Panayotova and Velikov (2003). Interestingly is the fact that the K⁺ clinoptilolite and Ca²⁺ clinoptilolite showed a similar percentage removal of between 76% and 80%, with USA Ca²⁺ having

the latter percentage. Oztas et al. (2008) and Giles et al. (1974) attribute these higher values in NaCl modified clinoptilolite to the opening up of more adsorption sites for further ion adsorption.

The percentages of adsorption of nickel ions on Na⁺ and K⁺ clinoptilolite in single components showed the same trend as in the mixed feeds. However, the metal removal in single feeds by the zeolites (of the same form) were higher than those in mixed feeds due to the competition between ions for exchange sites in mixed feeds (Motsi et al., 2009). The sequence observed, in terms of percentage nickel uptake was the same for both single and mixed feeds and both RSA and USA clinoptilolite, which also confirms the advantage of modification with NaCl: Na⁺ > K⁺ \geq Ca²⁺.

ii. Cadmium

The cadmium curves show that the sorption rate is rapid at beginning of the processes and then becomes slower as equilibrium is approached, the equilibrium is reached in about 24 hr and no desorption was observed and the same trend was observed by Teutli-Sequeira et al. (2009). The percentage removals of Cd^{2+} using Na⁺, K⁺ and Ca²⁺ clinoptilolite, in mixed feed at 50 mg/L are shown in Figure 4.12. Na⁺ form clinoptilolite had slightly higher percentage metal uptakes for cadmium than the K⁺ and Ca^{2+} clinoptilolites (higher by 5 and 12 % respectively for both RSA and USA clinoptilolite) in the mixed feeds (i.e. in the presence of nickel and lead). The same was observed for the cadmium only feed. The general trend was that the single feeds had higher metal uptakes than the mixed feeds. However, the percentage adsorption for the Na⁺ form was higher than that for the K⁺ and Ca²⁺ forms in the single feed. This shows that the modification of clinoptilolite with NaCl improves cadmium ions uptake by the clinoptilolite and to less extent that which is modified by $CaCl_2$ showed a lower adsoprtion. The Ca^{2+} ions once anchored in the zeolite framework seem to be difficult to displace with incoming metals in solution. This might be due to its low enthalpy of hydration -1577kJ/mol (Panayotova and Velikov, 2003).

In both the single and mixed feeds, the K⁺ and Ca⁺ forms had values close to each other for both RSA and USA clinoptilolite. The percentage removal of cadmium ions in mixed feed onto K⁺ and Ca²⁺ clinoptilolite was about 93% to 96%. The trend observed, in terms of percentage cadmium removal was the same for both single and mixed feeds: Na⁺ > K⁺ \ge Ca²⁺. The same order as for Ni²⁺.

iii. Lead

The percentage removal data for Pb^{2+} ions by natural, Na^+ , K^+ and Ca^{2+} form clinoptilolite from 50 mg/L mixed feed solutions has been plotted in Figure 4.12. Lead uptake was higher than that of both cadmium and nickel in both single and mixed feeds, with values as high as 99%, 98% and 97% for Na^+ , K^+ and Ca^{2+} clinoptilolite respectively. For, the Ca^{2+} clinoptilolite in the lead only solution, the lead percentage adsorption was higher than that of the nickel and cadmium.

In the mixed feed, the Na⁺ still exhibited a higher percentage adsorption for lead than cadmium and nickel and the percentage removal is high for both RSA and USA clinoptilolite. This indicated that clinoptilolite from the USA and RSA has a higher affinity for lead ions, regardless of the competing ions in solution or the form of the zeolite at 50 mg/L. The effect of the competing ions in solution was also observed; the percentage lead uptake was higher in single feeds than in mixed feeds for the same zeolite forms. The trend observed, in terms of percentage lead uptake was the same for both single and mixed feeds: $Na^+ \approx K^+ \approx Ca^{2+}$.

4.5.2 Heavy metal removal from 150ppm wastewater



Figure 4.13 Removal of Ni⁺, Cd²⁺ and Pb²⁺ from mixed solution (150 mg/L) using 2g RSA (1a to c) and 2g USA (2a to c) zeolites modified with Na⁺, K⁺ and Ca²⁺

i. Nickel

The percentage removal data of Ni^{2+} ions from 150 mg/L mixed feeds by Na^+ , K^+ and Ca^{2+} form clinoptilolite is presented in Figure 4.13. The USA Na^+ form and the USA K^+ form clinoptilolites had similar percentage adsorption values in the mixed feed 60% and

these values were higher than their similar forms in the RSA (40% in Na⁺ form and 20% in K⁺ form. The percentages of adsorption of nickel ions on Ca^{2+} clinoptilolite in mixed feeds were close to each other at around 20% in both the RSA and USA clinoptilolite.

It was also observed that the metal uptake in single feeds by the zeolites (of the same form) were higher than those in mixed feeds due to the competition between ions for exchange sites in mixed feeds. The sequence observed, in terms of percentage nickel uptake was the same for both single and mixed feeds, which also confirms the advantage of modification with NaCl.

ii. Cadmium

The percentage removal data of Cd^{2+} using Na⁺, K⁺ and Ca²⁺ clinoptilolite, in mixed feed at 150 mg/L are given in Figure 4.13. Na⁺ form clinoptilolite had slightly higher percentage metal uptakes for cadmium than K⁺ and Ca²⁺ clinoptilolite (RSA and USA); it was higher by between 20% and 30% in the mixed feed. The same was observed for mixed feeds (i.e. in the presence of nickel and lead).

The general trend was that, the single feeds in Appendix B had higher metal uptakes than the mixed feeds of the same form. However, the percentage adsorption for the Na⁺ mixed feed experiments was higher than that for the Ca²⁺ and K⁺ form in the single feed. Again this shows that the modification of clinoptilolite with NaCl improves cadmium ion uptake by the zeolites and not that of the zeolites pretreated with CaCl₂. The Ca²⁺-form Cd²⁺ removal was around 65% and this is by far less than that of the Na⁺ form (97%) and K⁺ form (70-80%). This also explains that Ca^{2+} ions once anchored in the zeolite framework seem to be difficult to exchange with incoming ones. The orders observed, in terms of percentage metal uptake was the same for both single and mixed feeds: $Na^+ > K^+ > Ca^{2+}$.

iii. Lead

The percentage removal data for Pb^{2+} ions by Na^+ , K^+ and Ca^{2+} form clinoptilolite from 150 mg/L mixed feed solutions has been plotted in Figure 4.13. The percentage removal of lead uptake was higher than that of both cadmium and nickel in single and mixed feeds, with values as high as 98% and 93% for Na^+ and for K^+ and Ca^{2+} RSA clinoptilolite respectively. For, the Ca^{2+} clinoptilolite in the mixed feed, lead percentage adsorption was higher than the nickel and cadmium percentage removal with a difference of between 60% and 70%.

In the mixed feed, the Ca^{2+} still exhibited higher percentage adsorption for lead than cadmium and nickel, despite the percentage values being lower than those for Na⁺ clinoptilolite but the percentage removal were quite similar to the K⁺ form. This implies that clinoptilolite has a higher affinity for lead ions, regardless of the competing ions in solution or the form of the zeolite at 150 mg/L and the modification status of the clinoptilolite. The effect of the competing ions in solution was also observed; the percentage lead uptake was higher in single feeds than in mixed feeds for the same zeolite forms. The trend observed, in terms of percentage lead uptake was the same for both single and mixed feeds: Na+ > K⁺ \geq Ca²⁺.

4.5.3 Heavy metal removal from 500ppm wastewater



Figure 4.14 Removal of Cd^{2+} , Ni^{2+} and Pb^{2+} from mixed solution (500 mg/L) using 2g RSA (1a to c) and 2g USA (2a to c) zeolites modified with Na^+ , K^+ and Ca^{2+}

i. Nickel

The percentage removal data of Ni^{2+} ions from 500 mg/L single and mixed feeds by Na^+ , K^+ and Ca^{2+} form clinoptilolite for both RSA and USA is presented in Figure 4.14.

There was a reduced performance of the Na⁺ clinoptilolite for nickel ions in the single and mixed feeds. The Na⁺ clinoptilolite percentage uptake of nickel was higher than that on the K⁺ and Ca²⁺ (in fact the Ca²⁺ nickel uptake almost similar to that of K⁺ in mixed feed). Again in the mixed feed, the Na⁺ clinoptilolite's nickel uptake was also higher than the K⁺ and Ca²⁺ with the K⁺ and Ca²⁺ having almost the same value. The percentage nickel uptake dropped drastically for the Na⁺ form clinoptilolite at 500 mg/L mixed and single feeds compared to that at 50 mg/L (from about 96 % to 35%) for both RSA and USA clinoptilolite. The Ca²⁺ clinoptilolite has a lower affinity for Ni²⁺ ions than for Cd²⁺ or Pb²⁺. The order of nickel uptake at 500 mg/L was: Na⁺ > Ca²⁺ > K⁺ for the single feeds and Na⁺ > K⁺ \approx Ca²⁺ for the mixed feeds.

ii. Cadmium

The percentage removal of Cd^{2+} ions from 500 mg/L mixed feeds by Na⁺, K⁺ and Ca²⁺ form for RSA and USA clinoptilolite is presented in Figure 4.14. At 500 mg/L, the percentage metal adsorption dropped at higher feed concentrations especially for the K⁺ and Ca⁺ clinoptilolite in both single and mixed feeds. The Na⁺ clinoptilolite still exhibited higher cadmium uptake than the K⁺ and Ca²⁺ in the single cadmium feed, whereas in the mixed feed, the K⁺ and Ca²⁺ had similar percentage cadmium uptake. The effect of competing ions was also observed at 500 mg/L, where the single feeds had higher percentage removals than the mixed feeds, apart from the Ca²⁺ form, where the reverse was observed; the mixed feed had a higher percentage cadmium uptake than the single feed (20% difference). The order of cadmium uptake was Na⁺ > K⁺ > Ca²⁺ for the single feeds and Na⁺ > K⁺ \geq Ca²⁺ (very similar to the sequence observed at 50 mg/L for mixed feeds).

iii. Lead

The percentage removal data for Pb^{2+} ions by Na⁺, K⁺ and Ca²⁺ form RSA and USA clinoptilolite from 500 mg/L mixed feed solutions has been plotted in Figure 4.14.

The percentage lead removal was similar at 500 mg/L feed concentrations compared to 50 mg/L and 150mg/L feeds, for both the single and mixed feeds and for all the zeolite forms; at about 90 to 99% for the Na⁺, K⁺ and Ca²⁺ clinoptilolite.

In summary, it was observed that the percentage metal uptake was affected by the initial feed concentration. At higher concentrations, the available sites of adsorption decrease in relation to the adsorbates and hence the percentage removal of metal ions is also dependent on the initial concentration (Yu et al., 2003). This indicates that less favourable sites become involved with increasing metal concentrations in aqueous solution (Erdem et al., 2004).

4.6 Equilibrium adsorption capacities

The loading capacity of the zeolites and single and mixed component feeds were determined, giving the maximum equilibrium capacities reached at equilibrium, as shown in Tables 4.2 to 4.4. The RSA and USA Na⁺ form clinoptilolite obtained the maximum equilibrium adsorption capacities for 50 mg/L mixed feed for nickel, cadmium and lead and was found to be 2.31, 2.58 and 2.69 mg/g respectively (Pb²⁺ > Cd²⁺ > Ni²⁺).

For the 500 mg/L mixed feed and 2g Na⁺ clinoptilolite samples, the loading capacity of nickel, cadmium and lead was 8.23, 12.99 and 26.67 mg/g respectively ($Pb^{2+} > Cd^{2+} > Ni^{2+}$) (Table 4.4) for RSA and USA. Lead metal ions had the highest loading capacity feeds at 50 mg/L, 150 mg/L and 500 mg/L. Clearly, the Na⁺ clinoptilolite has a higher

affinity for Pb²⁺ ions than Cd²⁺ and Ni²⁺ ions, regardless of the initial feed concentration. The Na⁺ form clinoptilolite has higher loading capacity than the K⁺ and Ca^{2+} zeolites as shown in Tables 4.2 to 4.4. The Na⁺ form clinoptilolite also exhibits affinities for cadmium ions at 50, 150 and 500 mg/L in both single and mixed feeds. This can be explained in terms of the ease with which Na⁺ counter ions are displaced and so leads to improved loading capacities. There is also an increase in the availability of accessible Na⁺ sites (Panyotova and Velikov, 2003; Sprynskyy et al., 2006; Coruh, 2008). The Ca²⁺- form clinoptilolite loading capacities for Pb²⁺ decreased slightly compared to Na⁺- form clinoptilolite at 50, 150 and 500 mg/L; from 2.69 to 2.53 mg/g, 8.08 to 7.79 and 26.84 to 26.67 mg/g respectively, and also for Ni²⁺ ions, at 500 mg/L feed concentrations; from 8.23 to 2.77 mg/g for the RSA clinoptilolite in mixed waterwater. This reduction in capacity when Ca^{2+} form clinoptilolite is used may be attributed to the difficulty in displacing Ca²⁺ ions from the zeolites due to its low enthalpy of hydration. This then leads to the reduced loading capacities as observed in most of the experiments. In the both the mixed feed and single ion solution, the Na⁺form clinoptilolite (RSA and USA) has the highest selectivity for lead ions and then for cadmium ions and lastly nickel ions $(Pb^{2+} > Cd^{2+} > Ni^{2+})$, at 50, 150 and 500 mg/L concentration, so that the order of selectivity was the same with the K^+ and Ca^{2+} clinotilolite at the same feed concentration.

The noted discrepancies on adsorption capacities with the published data can be attributed to factors such as the mineralogy and chemical features of the used sorbents as well as by experimental parameters such as sorbent–solution ratios (Sprynskyy et al., 2006 and Erdem et al., 2004).

Table 4. 2

Equilibrium adsorption capacity, q_e (mg/g)					
RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca
2.31	2.20	1.87	2.53	2.31	2.20
2.58	2.53	2.42	2.69	2.53	2.47
2.69	2.53	2.53	2.69	2.58	2.53
2.58	2.1	1.76	2.53	1.87	2.25
2.64	2.58	1.98	2.69	1.81	2.58
2.75	2.64	2.42	2.75	2.25	2.58
	RSA-Na 2.31 2.58 2.69 2.58 2.64 2.75	Equilibr RSA-Na RSA-K 2.31 2.20 2.58 2.53 2.69 2.53 2.58 2.1 2.58 2.1 2.64 2.58 2.75 2.64	Equilibrium adsorpti RSA-Na RSA-K RSA-Ca 2.31 2.20 1.87 2.58 2.53 2.42 2.69 2.53 2.53 2.58 2.1 1.76 2.64 2.58 1.98 2.75 2.64 2.42	Equilibrium adsorption capacity, qRSA-NaRSA-KRSA-CaUSA-Na2.312.201.872.532.582.532.422.692.692.532.532.692.582.11.762.532.642.581.982.692.752.642.422.75	Equilibrium adsorption capacity, qe (mg/g)RSA-NaRSA-KRSA-CaUSA-NaUSA-K2.312.201.872.532.312.582.532.422.692.532.692.532.532.692.582.582.11.762.531.872.642.581.982.691.812.752.642.422.752.25

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 50 mg/l wastewater

Adsorbent mass = 2 g

Table 4.3

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 150 mg/l wastewater

Equilibrium adsorption capacity, q_e (mg/g)					
RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca
2.91	1.84	1.55	4.96	5.09	1.89
7.81	5.52	4.19	7.81	7.15	6.10
8.08	7.77	7.79	8.08	7.81	7.91
7.24	6.67	6.36	5.72	7.32	7.13
7.93	7.81	8.11	7.95	7.91	7.91
8.14	7.96	7.94	8.08	8.01	7.98
	RSA-Na 2.91 7.81 8.08 7.24 7.93 8.14	Equilibrit RSA-Na RSA-K 2.91 1.84 7.81 5.52 8.08 7.77 7.24 6.67 7.93 7.81 8.14 7.96	Equilibrium adsorpt RSA-Na RSA-K RSA-Ca 2.91 1.84 1.55 7.81 5.52 4.19 8.08 7.77 7.79 7.24 6.67 6.36 7.93 7.81 8.11 8.14 7.96 7.94	Equilibrium adsorption capacity, q RSA-Na RSA-K RSA-Ca USA-Na 2.91 1.84 1.55 4.96 7.81 5.52 4.19 7.81 8.08 7.77 7.79 8.08 7.24 6.67 6.36 5.72 7.93 7.81 8.11 7.95 8.14 7.96 7.94 8.08	Equilibrium adsorption capacity, qe (mg/g)RSA-NaRSA-KRSA-CaUSA-NaUSA-K2.911.841.554.965.097.815.524.197.817.158.087.777.798.087.817.246.676.365.727.327.937.818.117.957.918.147.967.948.088.01

Adsorbent mass = 2 g

Table 4.4

Adsorbate	Equilibrium adsorption capacity, q_e (mg/g)					
	RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca
Mixed						
Ni	8.23	3.20	2.77	11.07	7.18	3.74
Cd	12.99	7.62	5.95	12.99	8.72	8.97
Pb	26.84	25.96	26.84	26.70	25.63	26.62
Single						
Ni	19.86	18.45	17.85	20.73	18.09	8.74
Cd	23.34	20.66	19.77	24.50	20.39	10.67
Pb	26.94	26.98	26.45	27.11	27.06	26.84

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 500 mg/l wastewater

Adsorbent mass = 2 g

4.7 Modelling

The adsorption isotherm data were correlated with the Langmuir and Freundlich isotherm models by a non-linear regression analysis and the experimental data showed to be adjusted well to both isotherms models which were presented by the following equations: Freundlich equation is written in logarithmic form:

$$\log q_e = \log k_F + \left(\frac{1}{n}\right) \log C_e \tag{4.2}$$

Langmuir equation can be expressed as:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\max}}\right) \frac{1}{C_e} + \frac{1}{q_{\max}}$$
(4.3)

Figures 4.15 and 4.16 show that both mathematical models, either Langmuir or Freundlich, fit well the data obtained with correlation coefficient values of R^2 =0.99 and R^2 =0.99 respectively. The plots were plotted using 2g, 4g and 10g clinoptilolite samples of Na⁺-form using a concentration of 50 mg/L. The data did fit well at low concentration and this is in agreement with Kapanji (2009). Both the Langmuir model and Freundlich model showed better adjustment, which appears to indicate a monolayer adsorption mechanism. The parameters of both models are illustrated on Tables 4.5 and 4.6.



4.7.1 Langmuir isotherm

Figure 4.15 Langumuir isotherm of RSA Na⁺ clinoptilolite


Figure 4.16 Freundlich isotherm of RSA Na⁺ clinoptilolite

The experimental data were fitted to these equations by non-linear regression analysis. Table 4.5 shows the results of the analysis, describing the coefficient values. Acceptable adjustment of data was also obtained by using these two models; these models presented slightly deviations and correlation coefficients. The value of n was between 2 and 10 and this shows that clinoptilolite had good adsorption (Ederm et al., 2004). This Freundlich model has been generally applied to heterogeneous adsorbents which are the case of the zeolitic material used in this work, and it is reasonable to support that the retention of heavy metals in the zeolitic material takes place by chemisorptions.

Table 4.5

Adsorbate	Langmuir			Freundlich		
	q_{max} (mg/g)	K_L (L/m	(ag) R^2	1/n	$K_F (mg/g)$	R^2
Single ions						
Ni ²⁺	7.1685	0.0859	0.9846	0.9184	0.21697	0.9701
Cd ²⁺	9.2678	0.05565	0.994	0.8622	0.4681	0.9894
Pb ²⁺	19.8413	0.0154	0.9955	0.8849	0.3299	0.9877
Mixed ions						
Ni ²⁺	10.341	0.01686	0.9975	0.9281	0.1771	0.9968
Cd ²⁺	5.8411	0.0.0837	0.9942	0.8462	0.4496	0.994
Pb ²⁺	12.1065	0.0228	0.9997	0.8895	0.2901	0.9977

Langmuir and Freundlich isotherm constants for RSA clinoptilolite treated with Na⁺

Table 4.6

Adsorbate	Langmuir			Freundlich			
	q_{max} (mg/g)	K_L (L/m	ng) R^2	1/n	$K_F (mg/g)$	R^2	
Single ions							
Ni ²⁺	8.4388	0.0332	0.9941	0.9152	0.2727	0.991	
Cd ²⁺	10.8225	0.05810	0.998	0.9192	0.5858	0.9979	
Pb ²⁺	4.01123	0.12796	0.9955	0.7419	0.4643	0.991	
Mixed ions							
Ni ²⁺	3.7779	0.0805	0.9907	0.784	0.2955	0.9686	
Cd ²⁺	11.4547	0.04911	0.9966	0.9362	0.5269	0.9949	
Pb ²⁺	3.7285	0.11867	0.9798	0.7446	0.4066	0.993	

Selectivity series of modified clinoptilolites 4.8

The following metal ion selectivity series (based on the percentage removals) of single components and multi-components was observed at 50 mg/L, 150 mg/L and 500 mg/L feeds using 2g, 4g and 10g zeolite samples. The selectivity series at 50 mg/L mixed feed was $Pb^{2+} > Cd^{2+} > Ni^{2+}$ for Na⁺ form, K⁺ form and Ca²⁺ form clinoptilolite. At 150 and 500 mg/L, the same order of selectivity was obtained for the Na⁺ form, K⁺ form and Ca²⁺ forms. When the Na⁺ form zeolite was converted to Na⁺, there was no change in the order of selectivity for the metal ions at 50 mg/L (order remained $Pb^{2+} > Cd^{2+} >$ Ni²⁺). The counter ions (Na⁺) sitting in the zeolite framework did not affect the accessibility of incoming ions ions. However, when the natural zeolite at 50 mg/L was converted to Ca^{2+} form (single feed), the order of selectivity was the same $Pb^{2+} > Cd^{2+} > Ni^{2+}$. This implies that the Ca^{2+} ions sitting in the zeolite framework affect the availability and accessibility of exchange sites for incoming cations, possibly by an alteration of the pore sizes of the zeolite channels. This shows that both feed concentration and the exchange ions sitting in the zeolite framework affect the order of selectivity of metal ions in solution. This agrees with the findings of Jewell and Kapanji (2009) for adsorption of Co, Ni, and Cu on Na⁺, K⁺ and Ca²⁺ RSA and USA clinoptilolite.

Not much information has been documented on the effect of Ca^{2+} form clinoptilolite on the selectivity for metal ions. In this research, it was observed that Ca^{2+} form clinoptilolite exhibits selectivity that is significantly different from Na⁺ form and K⁺ zeolite. The total loading capacities dropped in both single and multi-component feeds for all three ions at 50, 150 and 500 mg/L feed concentrations. In general, the selectivity series could be the result of various factors like pH and temperature which can influence adsorption behaviour of zeolites. According to the model, it a cation exchanger such as zeolite is placed in a solution containing several different metal salts, the preference of the exchanger for one metal over another depends on whether the difference in their hydration free energy or interaction with fixed anionic exchange sites predominates.

4.8 Summary of discussion and results

A comparison of the two clinoptilolites indicates that RSA clinoptilolite has a higher surface area than the USA clinoptilolite. However, USA clinoptilolite adsorb heavy metals better than the RSA. This can be explained by the inaccessibility of the crystallite because of occlusion in the RSA clinoptilolite.

As observed from the nitrogen adsorption isotherms and the pore size distributions, clinoptilolite from the two countries have mesopores. In general clinoptilolite performed poorly in the case of Ni²⁺ (maximum removal efficiency of 20-90%) and better in the case of cadmium (92% maximum removal efficiency). However Pb²⁺ removal efficiency was around 99% and was achieved in most cases.

The hydration enthalpies of Na⁺ of -405kJ/mol and K⁺ -321kJ/mol (Atkins, 1988) are much lower than the hydration enthalpy of Ca²⁺ of -1577kJ/mol (Panayotova and Velikov, 2003). Thus in metal solution, the Na⁺ and K⁺ ions are both displaced more easily than the Ca²⁺ from the zeolite and this is the reason for the inability of heavy metals to displace Ca²⁺ from the clinoptilolite.

The effect Ca^{2+} on the uptake of Pb^{2+} is slightly diminished compared to the uptake of Pb^{2+} on the Na⁺ and K⁺ forms of zeolite. Whereas Cd^{2+} and Ni²⁺ uptake decreased strongly when using Ca^{2+} modified clinoptilolite, which is comparable with the results of Kesraoui-Ouki and Kavannagh, (1997) on Cd^{2+} uptake. These findings can be explained by different preferences of the modified clinoptilolite for different cations (Wingenfelder et al., 2005). Because of its high Si:A1 ration, clinoptilolite has a low structural charge density. Therefore divalent cations with low hydration enthalpies are sorbed preferentially compared to cations with high hydration enthalpies (Collela, 1996). The Gibbs free enthalpies of hydration are -1577kJ/mol for Ca^{2+} , -2105kJ/mol

(Panayotova and Velikov, 2003) for Ni²⁺, -1755kJ/mol for Cd²⁺ and -1425kJ/mol for Pb²⁺ (Marcus, 1991). This explains why Pb²⁺ uptake was only slightly influenced when using Ca²⁺ modified clinoptilolite, whereas Cd²⁺ and Ni²⁺ uptake was significantly reduced at when using Ca²⁺ modified clinoptilolite. According to the hydration enthalpies, the zeolite will prefer Pb²⁺ over Cd²⁺ and Ni in both single and mixed feeds. Therefore, the zeolite yields a high Pb²⁺ removal. The relatively poor removal of Ni²⁺ by the zeolite has been attributed to the high stability of its aqueous complex (Mondale et al., 1995).

The modification of natural clinoptilolite with sodium chloride solutions was found to improve the effective exchange capacity, and therefore its performance for Pb^{2+} , Cd^{2+} and Ni^{2+} . The improvement in the removal efficiency was attributed to the increase of easily removable Na^{2+} ions in the zeolite structure (Inglezakis et al., 2004). Moreover, it is observed that sodium form zeolite gives rise to a better heavy metal removal compared to the K⁺ and Ca²⁺ form zeolites, as is clearly shown in Figures 4.12 to 4.14. It is worth noting that sodium conversion enhances removal of some metals more potassium and calcium converted zeolites.

5.0 CHAPTER FIVE

5.1 Conclusion

In the experimental work carried out, the USA clinoptilolite had a higher adsorption capacity for Pb²⁺, Cd²⁺ and Ni²⁺ than the RSA clinoptilolite though RSA clinoptilolite had a higher specific surface area and pore volume. This might be due to the source of the zeolite and pretreatment procedures of the USA Na⁺ as received form. The results presented in this research report clearly document the dependence of measured zeolite capacity and selectivity data upon the manner in which the zeolite is treated prior to testing. Modified zeolites were found to be excellent in adsorption of heavy metals. In this work, the adsoption capacities for the removal of Ni²⁺, Cd²⁺ and Pb²⁺ by clinoptilolite were altered when the zeolite homoionic form was modified from Na⁺ to K⁺ and Ca²⁺. The selectivity series of the Na⁺-, K⁺- and Ca²⁺- form clinoptilolite has the same selectivity series: Pb²⁺ > Cd²⁺ > Ni²⁺ for 50 mg/L, 150 mg/L and 500mg/L. We conclude that a selectivity series for a zeolite in its natural form is meaningless unless the counter ions are known. The order for the selectivity of the ions of the same valence can be explained by the enthalpies of hydration of the cations.

5.2 Recommendations

The addition of a metal salt solution as a modification medium used in this study has produced promising results; however, there are a number of areas that need further investigation. In order to improve the adsorption capacities of the zeolite, further modification experiments must be carried out to increase the physico-chemical properties such as specific surface area, pore volume and active sites. For instance, the effect of pH and temperature must be carried out on the modification of zeolite so as to increase the adsorption capacity of zeolite. Futher research could be done on the regeneration capacity of the modified zeolites to assess the effectiveness of regeneration capacity on adsorption.

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Figure A1 Adsorption-desorption isotherms of nitrogen on the RSA clinoptilolite modified with Na⁺.



Figure A2 Adsorption-desorption isotherms of nitrogen on the RSA clinoptilolite modified with $K^{\!+}$



Figure A3 Adsorption-desorption isotherms of nitrogen on the RSA clinoptilolite modified with Ca^{2+}



Figure A4 Adsorption-desorption isotherms of nitrogen on the USA clinoptilolite modified with $\mathrm{Na}^{\mathrm{+}}$



Figure A5 Adsorption-desorption isotherms of nitrogen on the USA clinoptilolite modified with $\mathrm{K}^{\!+}$



Figure A6 Adsorption-desorption isotherms of nitrogen on the USA clinoptilolite modified with $\rm Ca^{2+}$

Appendix B: Single metal ions adsorption



Figure B1 Removal of Ni^{2+} , Cd^{2+} and Pb^{2+} from individual solution (50 mg/L) using 2g RSA (1a to c) and 2g USA (2a to c) zeolites modified with Na^+ , K^+ and Ca^{2+}



Figure B2 Removal of Ni^{2+} , Cd^{2+} and Pb^{2+} from individual solution (150 mg/L) using 2g RSA (1a to c) and 2g USA (2a to c) zeolites modified with Na^+ , K^+ and Ca^{2+}



Figure B3 Removal of Ni^{2+} , Cd^{2+} and Pb^{2+} from individual solution (500 mg/L) using 2g RSA (1a to c) and 2g USA (2a to c) zeolites modified with Na^+ , K^+ and Ca^{2+}

Appendix C: Equilibrium adsorption capacities

Table C1

Equilibrium	adsorption capacities fo	r RSA and USA	A clinoptilolite at 50) mg/l
wastewater				
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Adsorbate		Equilibrium adsorption capacity, q_e (mg/g)					
	RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca	
Mixed							
Ni	1.29	1.18	1.15	1.23	1.18	1.18	
Cd	1.34	1.29	1.18	1.34	1.29	1.23	
Pb	1.34	1.26	1.26	1.37	1.29	1.29	
Single							
Ni	1.29	1.21	1.12	1.29	1.21	1.15	
Cd	1.37	1.26	1.15	1.34	1.29	1.23	
Pb	1.37	1.32	1.26	1.34	1.32	1.29	

Adsorbent mass = 4 g

Table C2

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 150 mg/l wastewater

Adsorbate	Equilibrium adsorption capacity, q_e (mg/g)								
	RSA-Na	RSA-Na RSA-K RSA-Ca USA-Na USA-K USA-Ca							
Mixed									
Ni	1.73	1.25	0.94	2.35	2.03	1.40			
Cd	4.03	3.31	2.71	3.96	3.54	2.80			
Pb	3.72	3.94	3.85	3.98	3.98	3.82			
Single									
Ni	3.93	3.58	3.37	2.75	2.29	3.35			
Cd	3.98	3.94	3.80	4.01	3.83	3.71			
Pb	4.04	3.99	3.74	4.07	3.99	3.82			

Adsorbent mass = 4 g

Table C3

wastewater								
Adsorbate		Equilibrium adsorption capacity, q_e (mg/g)						
	RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca		
Mixed								
Ni	5.02	3.54	3.43	5.47	4.53	2.27		
Cd	8.90	5.71	4.40	9.32	7.14	5.50		
Pb	13.14	13.09	13.09	13.33	13.17	13.25		
Single								
Ni	10.32	9.78	9.41	11.05	10.70	10.15		
Cd	12.25	10.89	10.38	12.43	11.44	10.97		
Pb	13.42	13.28	13.31	13.42	13.40	13.31		

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 500 mg/l wastewater

Adsorbent mass = 4 g

Table C4

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 50 mg/l wastewater

Adsorbate	Equilibrium adsorption capacity, $q_e (mg/g)$					
	RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca
Mixed						
Ni	0.51	0.48	0.46	0.52	0.50	0.48
Cd	0.53	0.51	0.48	0.53	0.51	0.49
Pb	0.55	0.53	0.50	0.53	0.52	0.51
Single						
Ni	0.52	0.50	0.46	0.52	0.50	0.50
Cd	0.53	0.51	0.50	0.55	0.52	0.50
Pb	0.55	0.53	0.51	0.55	0.53	0.52

Adsorbent mass = 10 g

Table 7

Adsorbate	Equilibrium adsorption capacity, $q_e (mg/g)$						
	RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca	
Mixed							
Ni	1.61	0.81	0.54	1.35	1.24	0.57	
Cd	1.61	1.41	1.08	1.62	1.54	1.17	
Pb	1.57	1.57	1.53	1.62	1.57	1.52	
Single							
Ni	1.63	1.50	1.38	1.44	1.32	0.85	
Cd	1.60	1.57	1.56	1.63	1.54	1.24	
Pb	1.62	1.62	1.51	1.63	1.60	1.52	

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 150 mg/l wastewater

Adsorbent mass = 10 g

Table C6

Equilibrium adsorption capacities for RSA and USA clinoptilolite at 500 mg/l wastewater

Adsorbate		Equilibrium adsorption capacity, q_e (mg/g)					
	RSA-Na	RSA-K	RSA-Ca	USA-Na	USA-K	USA-Ca	
Mixed							
Ni	1.26	0.89	0.95	1.26	1.36	1.23	
Cd	4.24	2.93	2.14	4.37	3.15	2.25	
Pb	5.34	5.24	5.10	5.32	5.24	5.13	
Single							
Ni	4.65	4.29	4.09	4.76	4.29	4.16	
Cd	5.08	4.65	4.24	5.17	4.77	4.46	
Pb	5.3	5.29	5.14	5.39	5.29	5.10	

Adsorbent mass = 10 g

Appendix D: Linear Regression analysis for USA Na⁺ clinoptilolite



Figure D1 Langmuir isotherm for USA Na⁺ clinoptilolite



Figure D2 Freundlich isotherm for USA Na⁺ clinoptilolite