Brine treatment using natural adsorbents

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A thesis submitted in fulfillment of the requirements for the degree of Magister of Scientiae in the Department of Chemistry, University of the Western Cape

TITLE PAGE

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May 2011

ABSTRACT

Studies involving the use of natural clays such as bentonite, montmorillonite and natural zeolite clinoptilolite in water treatment have been reported. Researchers suggested cost effective processes, such as ion-exchange and adsorption for the removal of heavy metals from waste waters by using naturally occurring and synthetic materials. The current study investigated application of natural adsorbents in brine treatment. Brines are hypersaline waters generated in power stations and mining industries rich in Mg^{2+}, K^+, Ca^{2+}, Na^+, SO_4^{2-}, Cl^- and traces of heavy metals, thus there is a need for these brines to be treated to recover potable water and remove problematic elements. Natural adsorbents have been successfully used in waste water treatment because of their high surface area and high adsorptive properties when they are conditioned with acid or base.

The natural adsorbents used in this study were obtained from Ecca Holdings company (Cape bentonite mine) Western Cape in South Africa, comprising bentonite clay and natural zeolite (clinoptilolite) and another clinoptilolite sample was obtained from Turkey. These adsorbents were investigated in their natural and pretreated form for removal of toxic elements in brine water. The pretreatment was aimed at removing Na^+, K^+, Ca^{2+}, Mg^{2+} from the clinoptilolite as well as the bentonite and replacing these cations with the H^+ cation to activate the materials.

The cation exchange capacity (CEC) of natural zeolite from South Africa was found to be 2.14 meq/g, Turkish Clinoptilolite was 2.98 meq/g while South African bentonite was 1.73 meq/g. at 25ºC using ammonium acetate (pH 8.2) method. Characterization of these natural adsorbents was done prior to pretreatment and after the treatment. ICP-AES analysis was used for determination of toxic elements in brines before and after sorption. The morphology of clays was characterized by X-ray diffraction (XRD), Brunauer Emmett Teller (N_2-BET) and Scanning electron microscopy (SEM) for confirmatory purposes and X-ray Fluorescent spectroscopy

(XRF) was used for the composition analysis of the natural adsorbent. The results from batch experiments prior to pretreatment of the natural adsorbents showed that these natural adsorbents contained Mg^{2+}, K^{+}, Ca^{2+}, Na^{+} in their structures as charge balancing cations, thus needed pretreatment to remove the cations. The natural adsorbents were pre-treated with 0.02M HCl. After the pretreatment of natural adsorbents it was possible to enhance the percentage removal of the major cations from brine, and the Na^{+} and Mg^{2+} removal achieved (86 % and 85% respectively) from brine was more than Co^{2+} (70%) the SC was the adsorbent one that gave highest removal of cations in the brines. Trace elements removal was high with $Cu^{2+}$and Zn^{2+} being the highest of toxic elements in brine. The optimum contact for the toxic element removal was found to be 30 min for the Turkish clinoptilolite and 1 hr for the South African clinoptilolite and South African bentonite clay. Leaching of Al^{3+} and Si^{4+} during adsorption was also investigated and it was found that less than 1 ppm of Al^{3+} and Si^{4+} were leached into the solution during adsorption experiments indicating that these materials were stable. The investigation of pH showed that natural adsorbents did not perform well at low pH of 4 and 6. The adsorbents were able to work efficiently at the natural pH of 8.52 of the brine solution. These results show that natural adsorbents hold great potential to remove cationic major components and selected heavy metal species from industrial brine wastewater. Heterogeneity of natural adsorbents samples, even when they have the same origin, could be a problem when wastewater treatment systems utilizing natural clinoptilolite and bentonite are planned to be developed. Therefore, it is very important to characterize the reserves fully in order to make them attractive in developing treatment technologies.

Brine treatment using natural adsorbents

KEYWORDS

Clays
Clinoptilolite
Bentonite
Zeolite
Ion exchange
Adsorption
Cation exchange
Major and trace elements
Brine
Adsorbents

DECLARATION

I declare that “*Brine treatment using natural adsorbents*” is my own work, that it has not been submitted before for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated or acknowledged as complete references.

Bonelwa Mabovu May 2011

Signed………………

ACKNOWLEDGEMENTS

Firstly I would like to thank Lord Almighty who is the reason why I am alive, thanking him for everything he made possible for me.

I would like to thank my supervisor Dr. Leslie Petrik, for allowing me to be the part of Environmental and Nanoscience Research group (ENS) and for all the support during the difficult times I encountered during the course of my study and Dr. Gillian Balfour, Dr Wilson Gitari, Dr Patrick Ndungu and Dr. Olanrewaju Fatoba for their guidance.

I wish to thank my colleagues at ENS for their continuous support and believing in me when I did not believe in myself.

I would also like to thank NRF, WRC, Coaltech and ENS for financial support

I would like to sincere thank everyone in the Chemistry department for being a helping hand. Special thanks goes to my mother Noahlile Ivy Mabovu who never stopped believing in me. I would like to say I love her very much.

Lastly I would like to thank my entire family and encouraging friends.

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LIST OF ABBREVIATION

BET	Brunauer Emmett Teller
BJH	Barrett-Joiner-Halenda method
C_{ca}	Concentration of cationic species
CEC	Cation exchange capacity
DWA	Department of Water Affairs
EC	Electrical Conductivity
ED	Electro Dialysis
ENS	Environmental and Nano Sciences research group
FTIR	Fourier transform infrared spectroscopy
HEU	Heundanlite
HRTEM	High resolution transmission electron microscopy
IC	Ion Chromatography
ICP-AES	Inductively coupled plasma atomic emission spectrometry
JCPDS	Joint Committee on Powder Diffraction Standards
LO	Loss on ignition
M	Montmorillonite
Meq	Milliequivalents
MED	Multi-effect distillation
MSF	Multi-stage-flash distillation
Q	Quartz
SB	South African bentonite
SBU	Secondary building blocks
SC	South African clinoptilolite
SEM-EDS	Scanning Elecron Microscopy-Energy Dispersive X-ray Spectroscopy
Stdev	Standard deviation
T-Atoms	Si and Al (Silicon and Aluminium)

TDS	Total dissolved solids
TC	Turkish clinoptilolite
RO	Reverse Osmosis
XRD	X-ray Diffraction Spectroscopy
XRF	X-ray fluorescent Spectroscopy
Wt	Weight

OUTLINE OF THE THESIS

This thesis consists of five chapters and is structured as follows:

Chapter 1: *Background*

This chapter outlines the introduction, brief overview of the background, motivation of the study objectives of the study, problem statement, hypothesis, research approach, scope and delimitations together with research frame work.

Chapter 2: Literature review

This chapter gives insight on the significance, and general literature on clays, brines and applications and characteristics of clays and natural zeolites, the impact of brine on the environment, the methods used in brine treatment.

Chapter 3: Methodology

This chapter details the methodological approach and characterization of the clays using various characterization tools such as X-ray diffraction, N_2-BET analysis, Cation Exchange capacity and the research design as well as procedures selected for the adsorption experiments, instruments used and motivation of the choice of the adsorption methods and techniques used.

Chapter 4: Results and Discussion

In this chapter the results of characterization, adsorption, equilibrium of adsorption process for natural clays and natural zeolites are presented and discussed with relevant references to literature.

Chapter 5: Conclusion and Recommendations

This chapter draws the conclusion of this thesis by summarising all the main points, highlights and recommendations. It also outlines future research from the results obtained in this study.

CHAPTER 1

INTRODUCTION

CHAPTER 1

1 INTRODUCTION

This chapter presents the background, problem statement, aims and objectives, motivation of the study, research questions, hypothesis, research approach and scope and delimitations of the thesis. The study will to a great extent focus on the preparation of natural clay and natural zeolite materials and their uses as adsorbents in waste water.

1.1 Background

Water treatment has been the subject of much interest due to pollution of water by heavy metals and toxic elements. Hence, many researchers have suggested a cost effective process, such as ion-exchange, to remove heavy metals from waste waters by using naturally occurring and synthetic materials (Szostak *et al*., 1989; Zamzow *et al.,* 1992); Zoumis *et al*., 2000). The term heavy metal refers to metals such as Cd, Cr, Hg, Ni, Pb and Zn which are commonly associated with pollution and toxicity problems (Griffin, 1988).

Several methods of water purification such as ion-exchange, adsorption, precipitation, ultra filtration, reverse osmosis, phytoextraction and electrodialysis have been studied (Morali, 2006; Mamba *et al.*, 2009). However industrial water such as mine water and effluents such as brines often contain toxic metals or elements that impose cost restraints when it comes to their purification. Ion-exchange and adsorption are two main methods that are well-known for heavy metal removal by natural clays and zeolites (Morali, 2006).

Brines are hyper saline waters that contain high concentrations of salts and toxic elements. They are problematic effluents created by the desalination processes such as Reverse Osmosis (RO), electrodialysis (ED), used for coal and gold mining, evaporative cooling power stations and process industries. Such brines are also found in nature in the interior of earth, and they are also found on the earth's surface as byproducts of mining, gas production and oil production (Ndlovu-Yalala, 2010). The mine drainage arising from mining operations has a daily contribution of chlorides and sulphates to water streams or rivers. The high salt content in mine water prevents its use in agriculture and for consumption and causes tremendous economic losses due to corrosion attacks on pipes and machines etc (Ericsson, 1996).

Clay refers to naturally occurring minerals composed mainly of fine grained minerals that make up colloid fraction (particle size of ~2 µm) which possess plasticity when exposed to water and harden when dried (Guggenheim, 1995). There are several clay types, among others there are smectites, chlorite, illite and kaolin. The low cost material such as fly ash and clays were studied for waste water treatment (Sanchez *et al*., 1997). Clays have high surface areas which previously had been suggested as sites where concentration and catalysis can take place (Jiang *et al*., 2004). Natural zeolites have open, three dimensional structures that help in losing and gaining water reversibly and to exchange extra framework cations, both without change of crystal structure (Mumpton, 1999). For this reason natural clay and natural zeolite have been of interest in water treatment studies among other adsorbent. In the current study clays and zeolites were chosen because of their unique properties to adsorb toxic metals in the layered and swelling structure of clays and zeolites for their open three dimensional structures from concentrate water such as brine and cost effectiveness because of their abundance all over the world.

1.2 Problem statement

There is a need for cost effective ion exchangers to purify effluents with lower cost and beneficial outcomes (Sanchez *et al*., 1997).

Recent studies have focused on wastewater and brine treatment using low cost ion exchangers such as natural zeolites and clays (Vega *et al*., 2005; Mamba *et al*., 2010; Bhattacharya *et al*., 2008). Some of these studies showed removal of heavy metal and toxic elements from waste waters from mining industries all over the world including South Africa. Clays play an important role in the environment by acting as natural scavenger by taking up some elements through ion exchange or adsorption (Bhattacharya *et al*., 2008). Zeolites act as molecular sieves also natural scavengers, have properties including adsorption, cation exchange, catalysis and dehydration and rehydration (Mumpton, 2009). In South Africa there are large deposits of these natural zeolites and natural clays in Kwazulu Natal, Gauteng and Western Cape provinces. However these natural materials have not been used intensively in South Africa for treatment of waste waters as compared to other countries where the use of the natural materials have been extensively studied.

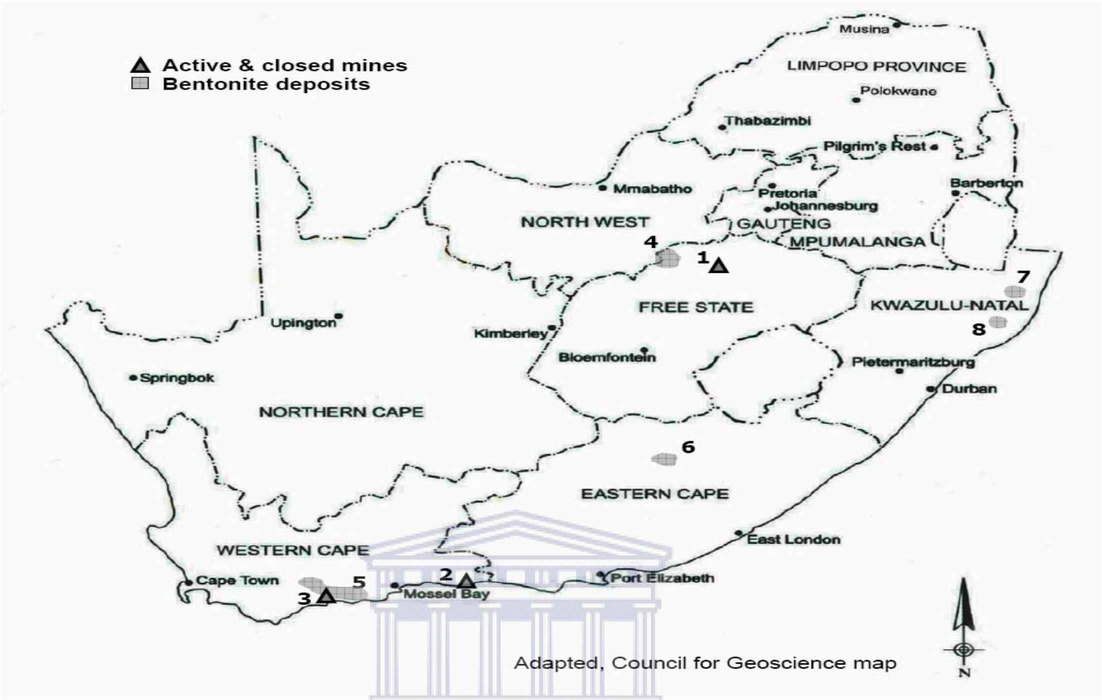
The disposal of brines known as hypersaline waters has been a challenge to South African power utilities and mines due to the large volumes generated and the high concentration of contaminants in the wastewaters. To combat this problem several methods are used to treat this kind of water but many of the methods used for purification end up releasing two types of water, clean water and the concentrated reject brine. Thus there is a need for their remediation and purification of water using less expensive and abundantly available materials.

Mine water can be broadly classified into two distinct groups, the one kind which has a scaling potential with $CaSO_4$ and those waters which do not. These concentrated process brines also need to be treated to obtain clean water from them as South Africa is a country that has water shortages. The major disadvantage for waste water treatment utilization comes from economic consideration, since other adsorbents such activated carbons or ion exchange materials such as commercial resins are quite expensive therefore rendering them costly for large scale operation (Putra *et al*., 2009). Acid water treatments plants, such as Emalahleni water treatment plant near Mpumalanga, have provided a challenge of how to recover residue water left in the brines and to develop a process to produce saleable by-product from brines (Coaltech, 2008).

1.2.1 Study area

The source of brine studied in this research was a stage 3 effluent waste from Emalahleni water desalination plant in Mpumalanga province in South Africa. The feed source to the reverse osmosis plant (RO) is a large volume of excess coal mine water with a high salt concentration from four fully operational coal mines in the Mpumalanga area which water is associated with ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-} [neutral type of water] or is slightly acidic associated with iron, manganese and aluminum metal (Ndlovu-Yalala, 2010). Natural adsorbents are of interest in treatment of waste water streams because of their abundance in all over the world, cost effectiveness and success in recovering metal ions in waste streams.

The natural clay (bentonite) and natural zeolite (clinoptilolite) from Ecca Holdings Company in South Africa and natural zeolite (clinoptilolite) from Turkey and also attapulgite clay from South Africa were used in the treatment of Stage 3 brine effluent from Emalahleni water desalination (RO) plant, which effluent is high in salt. This RO treatment plant is fed by acidic, saline mine waters from four different coal mines in the Witbank area. The natural adsorbents, bentonite and clinoptilolite from South Africa were obtained from the Ecca holdings Holdings Company from the Western Cape displayed in the geology map below.



Adapted, Council for Geoscience map

Deposit	Nearest district / town
1	Koppies, Ocean Mine, G & W Base & Industrial Minerals, active mine
2	Plettenberg Bay, Plettenberg Bay Mine, G & W Base & Ind. Min., closed mine
3	Heidelberg, Cape Bentonite Mine, Ecca Holdings, active mine
4	Groenfontein, Orkney, ex-mine, Ecca Holdings
5	Riversdale-Heidelberg deposit(s), includes Spiegelsrivier & De Doorn Rivier
6	Jamestown deposit
7	Mkuze deposit
8	Hluhluwe deposit

Figure 1.1: Map displaying bentonite and clinoptilolite and active mines in South Africa (DME, 2004)

1.3 Motivation of the study

Several studies (Onyango *et al*., 2010; Langella *et al*., 2000) have been reported on the use of natural and functionalized adsorbents materials such as natural zeolite clinoptilolite and bentonite to adsorb contaminants from wastewaters. This study was motivated by studies carried out by Sanchez *et al*., (2007) and Hamidpour *et al*., (2010) who explored the use of natural adsorbents such as clays and zeolites for the removal of heavy metals from wastewaters. It has been shown that the edges and faces of clay particles can adsorb anions, cations, non-ionic and polar contaminants from natural water or contaminated water. The contaminants accumulate on the clay surface leading to their immobilization through the processes of ion exchange, coordination or ion-dipole interactions (Bhattacharya *et al*., 2008). Extensive research has been conducted on different natural adsorbents such as bentonite clays as well clinoptilolite under laboratory such studies are lacking on zeolites and clays from South Africa. This study, therefore investigates the use of natural zeolites (clinoptilolite) and clays from South Africa in the treatment of waste water. Turkish natural zeolite (clinoptilolite) was used as comparison. Addition of using the Turkish natural zeolite in this process would be useful.

1.4 Aims and objectives of the research

The main aim of this research was to investigate the possibility of using different low-cost natural adsorbents materials mined in South Africa for the treatment of brine generated by power and mining industries in South Africa.

The objectives of this study included the following:

i. Understand the mineralogical, physicochemical characteristics and surface areas of the different natural South African clays and zeolite as adsorbents
ii. Determine the effect of untreated natural adsorbents materials and pretreated adsorbents in toxic elements removal from industrial waste water (brines).
iii. Compare characteristics of naturally occurring South African zeolites and clays to adsorbent from Turkey
iv. Compare the adsorption capacity of South African natural adsorbents with the natural zeolite from Turkey
v. Investigate the use of several natural adsorbents for the uptake of toxic elements and heavy metals in the stage 3 brine effluent from Emalahleni power plant.

1.5 Research questions

To achieve the above objectives the following questions need to be answered:

1. What is the chemical composition of brines produced by industrial power stations?
2. What are the mineral and chemical composition and characteristics of natural adsorbents?
3. What is the best method to activate these natural adsorbents in order to enhance their adsorption capacity without destroying their structure?
4. What is the adsorption capacity of these adsorbents materials for both treated and untreated?
5. Can the natural clays effectively remove alkali/alkaline earth elements/species in brines
6. What are the mechanisms involved in the removal of the species from brine by the clay material?
7. Do the natural adsorbents leach?

1.6 Research Approach

The experimental approach was divided into four stages. The first stage involved the characterization of natural clays and zeolites. The second stage involved the preliminary adsorption experiments of adsorbents (before activation) using the stage 3 brine solutions obtained from Emalahleni water reclamation plant. The third stage involved the pretreatment of clays and zeolites for improved sorption capacity. The last stage involved the actual adsorption experiments after pretreatment with acid and the comparison of the various materials before and after activation.

Adsorption experiments performed included the investigation of various parameters such as temperature, contact time and pH and adsorption experiments were studied to understand the adsorption capacity for Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} of the various locally sourced natural adsorbents. The suite of toxic elements such as Cu^{2+}, Zn^{2+}, Pb^{2+} that could be removed by these materials was also evaluated

The study was carried out by focusing on the following:

- ✓ Characterization of the natural clay and zeolite material
- ✓ Pretreatment of the natural adsorbents
- ✓ Comparative batch adsorption experiments comparing clays and zeolites
- ✓ Investigation of metals that leached during adsorption.

1.6.1 Characterization of the natural clay and zeolite materials

In the first stage of the experimental procedure, the clays and zeolites used were obtained via Ecca Holdings Company mined in the Cape bentonite mine in South Africa and the other natural zeolite used was obtained from Turkey. The choice for the use of the natural clays from Ecca Holdings is because limited research has been carried out on this deposit compared to the natural zeolite (clinoptilolite) from Kwazulu Natal sold by Pratleys Company. Turkish zeolite was used based on the previous study by (Cakicioglu-Ozkan *et al*., 2005). It proved to be a high-silica clinoptilolite that meant it was a reasonably pure zeolite. The natural zeolites and bentonite clay were characterized by using different techniques such as X-ray diffraction (XRD) for mineralogy of the materials, X-ray fluorescence (XRF) for elemental composition, scanning electron microscopy (SEM) for morphology, adsorption-desorption Nitrogen N_2 BET for surface area and pore size, cation exchange capacity (CEC) for the exchange capacity.

1.6.2 Preliminary adsorption experiments

The second stage of the study involved the preliminary adsorption experiments of clays (before activation) using the stage 3 brine solutions obtained from the Emalahleni RO water reclamation plant. In the second stage of the experimental procedure, the preliminary adsorption experiments were performed using these natural clays and zeolites to remove major cations or toxic elements from brines obtained from Emalahleni water reclamation plant. The parameters that showed a significant experimental influence in the first stage and also those parameters of importance as identified from the literature were investigated in more detail. It was important to vary the contact time to see if time had an effect on the adsorption capacity of natural zeolites and clays.

These first two stages of the study were all geared towards obtaining percentage purity of each material, information on mineral phases present; obtain cation exchange capacity and adsorption capacity. The last two stages were geared towards obtaining improved adsorption capacity by natural clays and natural zeolites. Among other clays attapulgite (palygorskite) was also briefly investigated in this study since it also consist of smecticte clay. Replication of some experiments was conducted to check the reproducibility of adsorption procedures. To carry out adsorption experiments, the cation exchange capacity of the clays had to be investigated first to better understand the exchange sites of the clays, and thus identify which activation method to use and also to identify their baseline ion exchange capacity before activation. The application of untreated clays and zeolites was carried out to understand the effect of pretreatment and activation on improvement of the adsorption capacity.

1.6.3 Pretreatment of clays (activation)

The third stage involved the pretreatment of clays for improved sorption capacity. This section of the study was motivated by results reported by (Mamba *et al*., 2009); (Cakicioglu-Ozkan *et al*., 2005) who used HCl in the activation of zeolites and found that they adsorb Co^{2+}, Cu^{2+} and water vapour respectively when the zeolites were treated with HCl as compared to NaCl and KCl treated zeolites.

1.6.4 Adsorption experiments after pretreatment

The last stage involved the actual adsorption experiments after pretreatment with the acid and the comparison of the various materials before and after activation. This section of the study involved obtaining optimum contact time and pH for effective adsorption of cations and toxic elements.

1.7 Scope and delimitations of the study

All the relevant work to this study has been highlighted and acknowledged. Due to time constraints this study mainly focused on one type of natural clay out of more than 50 natural and 200 synthetic zeolites. The smectite clay and natural zeolite (clinoptilolite) were chosen for the current study. The smectite clay also known as swelling clay or bentonite and natural zeolite clinoptilolite from South Africa chosen for this study were obtained from Ecca Holdings Company in South Africa, and for comparison purposes, the natural zeolite clinoptilolite from Turkey. The choice of these clay materials was motivated by the outcome of relevant studies from literature and the fact that they are cost effective adsorbent and locally available.

In the current study the following areas were not investigated:

- Modification of clays for heavy metal removal
- Effect of adsorbent dose
- Kinetics of adsorption because of time constraints
- Modeling of solutions

Factorial design

1.8 Hypothesis

Natural South African minerals can be optimized for effective adsorption of toxic cations and elements from brine wastewaters.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

It is important in this section to discuss brines, the origin of the clay materials and natural zeolites, their background in use as adsorbents as well as their applications and properties. This chapter is going to present the relevant literature on use of clays and zeolites as alternative adsorbents in waste water treatment as well as brines.

2.1 Water Pollution

Water is the essence of life and its scarcity causes huge problems for populations and societies. All over the world preservation of water is crucial. South Africa is a semi-arid country with water shortages and the need for fresh water is increasing because of rapidly increasing population. In South Africa the greatest pollution of water comes from mining industries. Industrial power plants handle large volume of process waters, which are contaminated with fines, chemicals, metal ions, and other materials (Feng, 2004). These streams often contain heavy metals and these heavy metals are very common in electroplating, electrolytic refining plants and acid mine drainage waters. Brine is water saturated with dissolved salts such as sodium, calcium, potassium, chlorides, sulphates and nitrates ions and high total dissolved solids (> 1,500 mg/kg TDS). Since brine is a by-product of various water treatment processes such as desalination, mine water, power generating station it needs proper handling when disposed because of its potential to pollute ground water. Surface water pollution resulting in salinity levels in excess of the Department of Water Affairs and Forestry (DWAF)' limits (Guther *et al.*, 2008).

2.2 Brines

Brines are saline waters that are saturated or near saturation with dissolved salts such as Na^+, Cl^-, Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-} and NO_2^- ions (Sonqishe *et al.*, 2009), thus brines consist of high concentrations of dissolved components such as sodium and magnesium. Brines are of commercial interest, especially in the production of table salt. Brines also occur in nature and are found in the interior of the earth as well as on earth's surface as salts lakes or by-products of mining, gas production and oil production.

The feed source of South African brine produced from coal mining industries in the Witbank region is a large volume of excess ground water with considerably high salt concentration from coal mines which are either associated with Ca, Mg, SO_4^{2-} (neutral type of water) or is slightly acidic (associated with Fe, Mn and Al metals) (Ndlovu-Yalala, 2010). Brines have many applications besides the production of salts. Studies have shown that brines can also be used in oil production. In the USA crude oil and processed hydrocarbons are easily stored in caverns produced in domes by solution mining salt. These hydrocarbons float on brines within the cavern and are readily recovered by simply pumping brine back into the well (Varjian, 2003). Subsurface caverns especially those used for the mining of table salt, saline lakes and the saltwater ocean are three principal sources of brine for commercial use. Even though brines have economic value in some circumstances, brines may cause considerable problems where they leak into potable drinkable water supplies or contaminate water for drinking or irrigation water used for animals, crops, gardens, or agricultural land. The most problematic brines are those that contain toxic elements released from industry or mines. The mine drainage of water arising from mines has a daily contribution of Cl^- and SO_4^{2-} to water streams or rivers. The high salt content in water prevents its use from agriculture and for consumption and causes tremendous economic losses due to corrosion attacks on pipes and machines, etc (Ericsson, 1996).

To combat this problem several methods are used to treat saline waters but many of the methods used for purification end up releasing two kinds of water, clean water and the even more concentrated reject brine. The removal of metal cations from aqueous solutions can be achieved by several processes such as solvent extraction, precipitation, adsorption and ion exchange (Tehrani, 2005). There is a need to recover salts and potable water from brines produced by industries in South Africa due to water shortages. Acid water treatments plants such as the Emalahleni plant near Mpumalanga has provided a challenge of how to recover residue water left in the brines and to develop a process to produce saleable by-product from reject brines (Coaltech, 2008). This study is focused on the treatment of brines produced at the Emalahleni plant using natural adsorbents.

Figure 2.1: Emalahleni Water Reclamation plant (www.mmma.org.za/presentations)

2.2.1 Brine Formation

Brine is formed as result of water treatment when a Tubular Reverse Osmosis (TRO) process takes places to treat wastewater such as the case at the Emalahleni treatment plant. It is a concentrate stream that contains a TDS concentration greater than 36 g/L. Brines may also contain low amounts of certain chemicals used during pretreatment and post-treatment (cleaning). Concentrates are high in salinity and may contain low concentrations of various chemical as well as elevated temperatures pose a threat to riverside habitats and receiving water environments. TRO is a pressure-driven membrane process operating at about 4000 kPa (Juby, 1992). The membranes available in this configuration are made of cellulose acetate thinly coated on the inside of synthetic support tubes of 12 mm diameter. The membrane allows water to pass through it but rejects up to 95 per cent of the salts, which remain inside the tubes as the brine stream (Juby, 1992). In this study the brine studied was an effluent waste from Emalahleni water (RO) desalination plant, stage three brine effluents.

2.2.2 Desalination processes

Desalination is the process whereby salty water is turned into fresh water. Water re-use and desalination emerged because of limited water resources to support daily fresh water supplies in many countries. Greenlee *et al*, (2009) define fresh water as containing less than 1000 mg/L of salts or total dissolved solids (TDS). The desalination processes give rise to a concentrated brine stream after the treatment of salty water. In the production of fresh water, dissolved salts are concentrated to produce saline stream or concentrate brine which must be disposed of. Currently potable water production by desalination is increasing world-wide because of increasing population and demand for water. Fresh water resources like groundwater, rivers and lakes are misused or overused, and as result these resources are diminishing or becoming saline. Desalination of water had been used to provide water for uses in irrigation, power plant cooling water, industrial process water and ground water recharge and has been accepted as a method for indirect drinking water production. Desalination methods consist of two main categories, (1) thermal processes or (2) membrane processes. There are three membrane processes available for desalination, electrodialyis (ED), reverse osmosis (RO) and nanofiltration (NF). Electrodialysis membranes operate under a electric field that causes ions to move through parallel membranes and are typically only used for brackish water desalination. Nanofiltration membranes are newer technology developed in the mid-1980s and have been tested on a range of salt concentrations. It has been shown through research that NF is a singular process that cannot reduce seawater salinity to drinking water standards; however NF has been successfully used to treat mildly brackish water feed water. Together with RO, NF can be used to treat seawater. Nanofiltration is mainly used for removal of divalent ion such as $Ca-^{2+}$, Mg^{2+} that contribute to water hardness as well as dissolved organic material whereas RO is able to reject monovalent ions such as sodium and chloride (Greenlee *et al*., 2009).

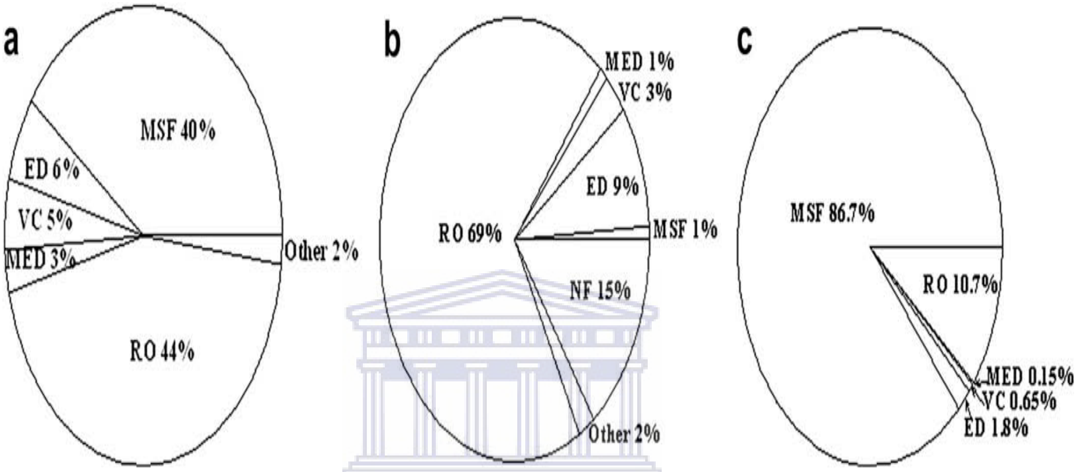


Figure 2.2 : Distribution of desalination production capacity by process technology for (a) the world, (b) the United States and (c) the Middle East(countries include Arabia, Kuwait, United Arab Emirates, Qatar, Bahrain, and Oman (Greenlee *et al*., 2009)

Various technologies are used in water treatment Reverse osmosis (RO), Electrodialyis (ED), Multi-stage-flash (MSF), Multi-effect-distillation (MED), Vapor compression (VC), Nanofiltration (NF) apart from electrodialysis desalination and reverse osmosis. Ultra filtration, ion exchange, adsorption, nanofiltration, filtration or coagulation and other types of micro-filtration and membrane processes are used for purification of effluent from secondary or tertiary level effluents generated at wastewater treatment systems. RO membranes can reject the smallest contaminants, monovalent ions while other membranes, including nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) are designed to remove materials of increasing size. The current study focuses on brine water from RO processes because the Emalahleni treatment plant is a reverse osmosis water treatment.

2.2.2.1 Thermal Processes

Distillation or thermal desalination has been the main distillation process for hundreds of years for production of fresh water, however large-scale municipal drinking water distillation plants began to operate during 1950s. The countries in the Middle East are the ones that initiated the design and implementation of thermal distillation; they firstly used a process called multi-effect distillation (MED) and then later developed a process called multi-stage-flash (MSF) distillation. Greenlee *et al.*, (2009) states that currently Middle East holds about 50% of world's desalination capacity and primary uses of MSF technology. The thermal desalination technology is being surpassed by the development of membrane processes in the Middle East since 1960s because of new plants installations. However countries in the Middle East still use thermal desalination due to easily accessible fossil fuel resources and poor water quality of the local feed water. Thermal desalination helps when feed water is more concentrated at high temperatures (Greenlee *et al.*, 2009).

2.2.2.2 Reverse Osmosis

Reverse Osmosis is one of the basic treatment technologies of membrane desalination. In the reverse osmosis separation process pressure is applied and forces water through a membrane overcoming the natural osmotic pressure, to divide the water into dilute product stream and a concentrated brine stream. Water molecules pass through the membrane while contaminants are flushed along the surface of membrane and come out as concentrate brine in a separate stream. RO membranes have a negative surface charge and repel negatively charged ions or molecules and more cations are then present near the membrane surface, thus an electric potential that is known as the Donnan potential, is created (Greenlee *et al.*,2009). This whole process of the creation of the Donnan potential helps in repelling ions by the membrane; however increasing salinity or divalent ions decreases the Donnan potential effect on membrane salt rejection. RO membranes typically achieve NaCl rejections of 98-99.8%. Figure 2.3 illustrates a schematic diagram of a typical RO process.

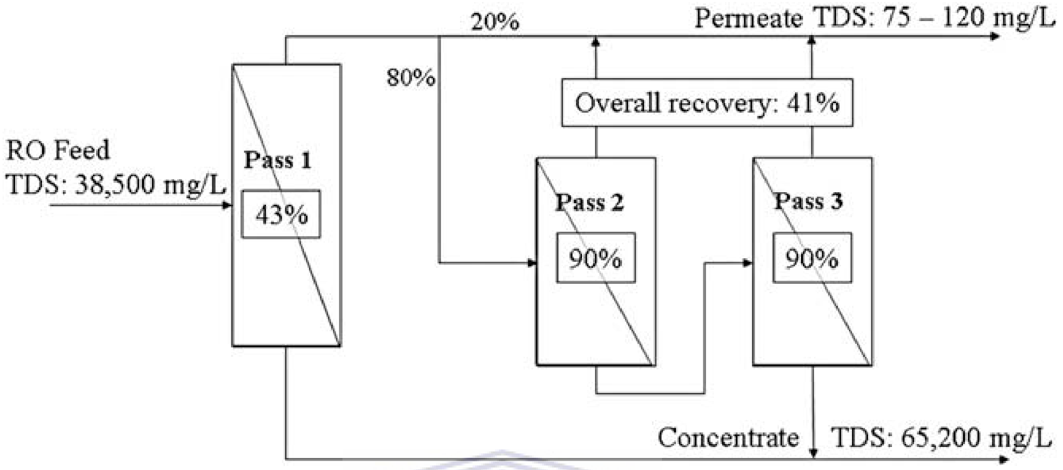


Figure 2.3: Schematic diagram of Reverse Osmosis (RO) sea water plant. Each box represents one RO pass, and the recovery (in %) is shown for each pass (Greenlee *et al.*, 2009)

2.2.2.3 Eletrodialysis (ED)

Electrodialysis removes contaminants from water by using an electric current field to pull ionic impurities through ion selective membranes and away from the purified water. ED is cost competitive with reverse osmosis especially when used to make drinkable water from relatively clean brackish feed water. The ED process is effective for salt removal from feed water because cathode attracts the sodium ions and anode attracts chloride ions. The recovery rate is high and the ED process can remove 75 to 98 % of total dissolved solids from the feed water (Chamier, 2007). However the ED process has several drawbacks when producing laboratory grade water and is rarely used in laboratory settings. First it is limited in the contaminants it can remove. It cannot remove organics, pyrogens and elemental metals which have weak or nonexistent surface charges because they are attached to the membranes. Secondly, the system requires a skilled operator and routine maintenance. Some colloids and detergents can plug the membranes' pores reducing their ionic transport ability and thus membranes requiring frequent cleaning (Korngold *et al*., 2009). Figure 2.4 illustrates a schematic diagram for a typical electrodialyis desalination cell.

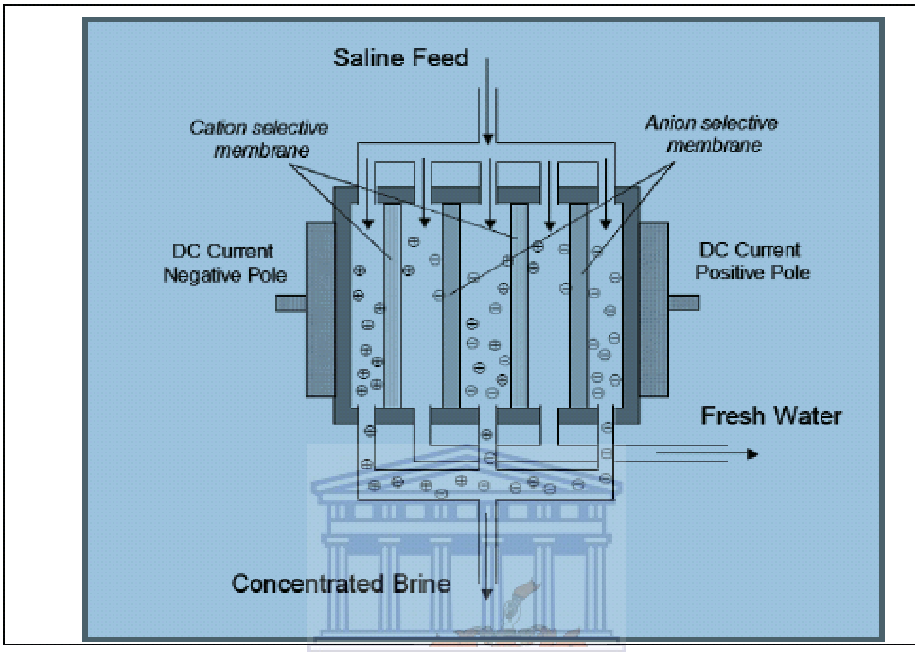


Figure 2.4: Schematic diagram of electrodialysis desalination process (Chamier, 2007)

A study conducted by (Korngold *et al*., 2009) revealed that brine concentration can be increased from 1.5% to 10% using electrodialysis in combating the volume of brine effluent and the cost of its disposal. Korngold showed that ED has a drawbacks when producing laboratory grade water and is rarely used in laboratory settings because of $CaSO_4$ precipitation on the membrane during brine concentration. The overall study of Korngold showed that the ED process combined with continuous $CaSO_4$ precipitation could be successfully carried out under reverse polarity in a non-continuous operation.

2.2.2.4 Impact of brine on the environment

The only aspect of desalination which has been relatively neglected is the environment and impact of the process. There are some methods applied in the disposal of brine and each method has disadvantages and advantages and often represents a compromise between cost, local available resources, environmental impact and technology. Desalination and the environment, with the main issue being solutions for brine disposal, should be brought into more focus. The most important environmental issues for a desalination plant are the location of the plant, brine disposal and energy considerations. The plant location is an obvious issue where selection of site should be determined by considerations of the energy supply available and the distance in relation to feed water intake, brine disposal site and water end-user (Svensson, 2005).

2.2.2.5 Brine Disposal

Brine disposal is a major problem because of development and execution of environmental policies that are protecting the environment from pollution hence rendering the current disposal methods prohibited. New methods for use in brine disposal are vital. There are two completely different ways regarding brine disposal which is determined by the location of the plant. There are brine disposal in inland areas and in coastal areas with the main difference being possibility for discharge to a large saltwater body, i.e. the sea. Ocean disposal is recognized as the most simple and least costly method and is therefore almost solely used wherever it is possible. However, in inland locations too far from the sea, alternative methods have to be used, increasing both the economical and environmental impacts of brine disposal (Sabah *et al*, 2009).

Land disposal can have a negative impact because of water pollution that results when concentrated brine is discharged into fresh water sources and unprotected wells. Chemistry of brines has an impact on soils which become saline and thus prevents crop growth because of the plant’s intolerance to salt. Absorption of soil water decreases from plants in contaminated ground water thus polluting drinking waters (Svensson, 2005).

2.3 Clays

Since clays have attracted much research in their use for water treatment they are of interest for treatment of brines or sludges which are the waste products from mining industries when treating water in processes such reverse osmosis and desalination. This section presents formation of natural clays, classification, properties and uses of clays.

2.3.1 Formation of clays

In the definition by Guggenheim (1995), clay is used to refer to naturally occurring minerals composed mainly of fine grained minerals that make up the colloid fraction (particle size of ~2 µm) which possess plasticity when exposed to water and harden when dried. Clays also have other materials in them that do not impart plasticity and organic matter, formed over long periods of time by gradual chemical weathering of rocks, usually silicate bearing (Tehrani, 2005). They are also grouped to approximately 4 groups, namely smectites, illite, chlorite and kaolin. Among this variety of clays this present study focused on smectites because of their unique properties as adsorbents (Hofmann *et al*., 2004). Natural clays exhibit specific surface properties such as cation exchange capacity and adsorptive affinity for some organic and inorganic compounds.

Natural clays can easily adsorb heavy metals via ion exchange reactions (McBride, 1994). Recent studies showed the use of clays such as bentonite as adsorbents in waste water and have been found to be cost effective (Sanchez *et al*., 1997). Several studies showed many processes exist for removing dissolved heavy metals including but not limited to, ion exchange, precipitation, ultrafiltration, reverse osmosis, electrodialysis and adsorption (Morali, 2006; Mamba *et al*., 2009)

Water pollution involving waste spills and contamination of water is a great challenge. Clays as common adsorbent for removal of hazardous contaminants have been studied. The potential use of clays as adsorbents for treating heavy metals and organic pollutants, or as coagulant aids for improving the settling performance in water treatment has been studied (Zhao *et al*., 2007).

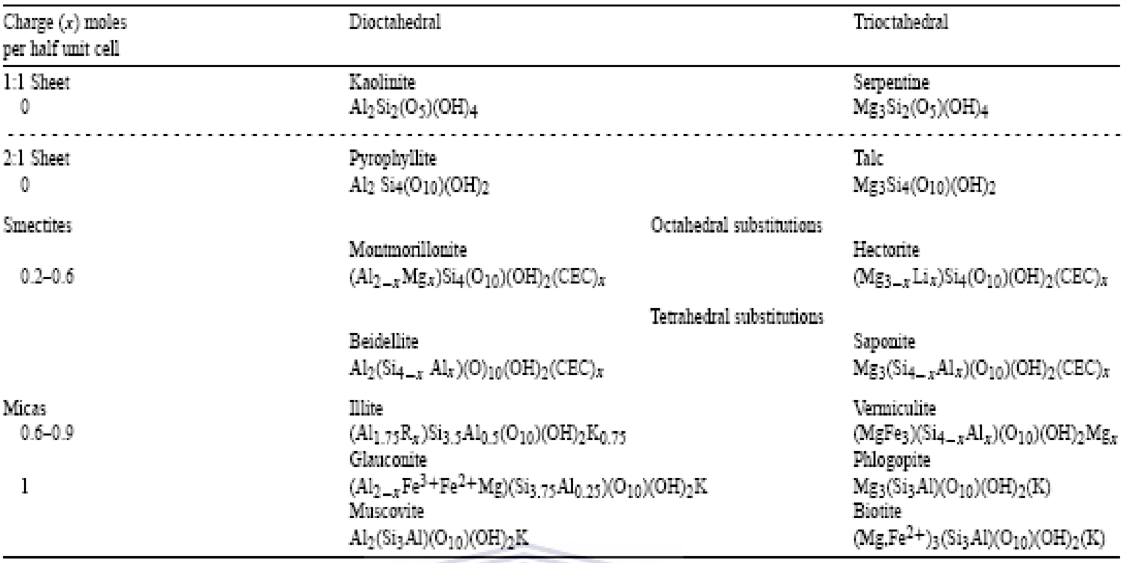
Activated carbon has been extensively studied as an adsorbent because it exhibits good capacity for removing pollutants from waste and drinking water but this process is expensive and thus requires regeneration. The low cost material such as fly ash and clays were studied by various researchers for waste water treatment (Guggenheim, 1995).

2.3.2 Classification of clays

Since they fall within the larger class of silicate minerals known as the phyllosilicates/layered silicates, clays are generally classified in terms of the differences in the layered structures that make up the clay material. Different classes of clays include smectites (beidellite, montmorillonite, nontronite, saponite and hectorite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (Gre'gorio, 2006).

The main minerals in bentonites are smectites such as montmorillonite, beidellite, saponite, nontrolinte and hectorite. Smecticte clay is 2:1 layer clay mineral and has two silica tetrahedral (T) sheets bonded to a central aluminium octahedral (O) sheet. These clays contain $Mg^{2+}$and Fe^{2+} ion in the octahedral sites and Si^{4+} and Al^{3+} in the tetrahedral sites and charges are balanced by the cations such as Na^+ and Ca^{2+} located between the layers and surrounding edges. All smectites have very high cation exchange capacity when activated with strong acids (Onal *et al*., 2002).

Table 2.1: Phyllosillicates/Layered silicates classifications (Myriam *et al*., 2005)



Charge (x) moles per half unit cell	Dioctahedral		Trioctahedral
1:1 Sheet 0	Kaolinite $Al_2Si_2(O_5)(OH)_4$		Serpentine $Mg_3Si_2(O_5)(OH)_4$
2:1 Sheet 0	Pyrophyllite $Al_2\ Si_4(O_{10})(OH)_2$		Talc $Mg_3Si_4(O_{10})(OH)_2$
Smectites		Octahedral substitutions	
0.2–0.6	Montmorillonite $(Al_{2-x}Mg_x)Si_4(O_{10})(OH)_2(CEC)_x$		Hectorite $(Mg_{3-x}Li_x)Si_4(O_{10})(OH)_2(CEC)_x$
		Tetrahedral substitutions	
	Beidellite $Al_2(Si_{4-x}\ Al_x)(O)_{10}(OH)_2(CEC)_x$		Saponite $Mg_3(Si_{4-x}Al_x)(O_{10})(OH)_2(CEC)_x$
Micas 0.6–0.9	Illite $(Al_{1.75}R_x)Si_{3.5}Al_{0.5}(O_{10})(OH)_2K_{0.75}$		Vermiculite $(MgFe_3)(Si_{4-x}Al_x)(O_{10})(OH)_2Mg_x$
1	Glauconite $(Al_{2-x}Fe^{3+}+Fe^{2+}+Mg)(Si_{3.75}Al_{0.25})(O_{10})(OH)_2K$		Phlogopite $Mg_3(Si_3Al)(O_{10})(OH)_2(K)$
	Muscovite $Al_2(Si_3Al)(O_{10})(OH)_2K$		Biotite $(Mg,Fe^{2+})_3(Si_3Al)(O_{10})(OH)_2(K)$

between 8 and 145 minerals. The most common sub family is montmorillonite. Further along the montmorillonite family tree are the various bentonites. Montmorillonite is a well known crystal that consists of an aluminum sheet between two silica sheets, for example 2:1 mineral in the montmorillonite structure. Interlayer swelling occurs when it is exposed to water. There are 2 types of montmorillonite namely a Na montmorillonite and Ca montmorillonite. Na montmorillonite is also known as bentonite. Bentonite is particularly useful industrially in drilling muds, for moulds in foundries, for pelletizing iron ores, in civil engineering and as absorbents in pet litters among other uses (DME, 2004).

Smectite clays are of interest in water treatment as they have swelling properties. The schematic diagram presented in (figure 2.3). These smectite clays are among the important solids that contain natural mesopores and they also contain small amounts of micro pores (Turek *et al*., 1995). Bentonite is colloidal; aluminosilicate clay derived from weathered volcanic ash and largely composed of montmorillonite. It consists of flat platelets that have high specific surface area, high plasticity, expand when wet and is a non toxic material on the clay surface leads to immobilization of toxic or contaminant species through the processes of ion exchange, coordination or ion-dipole interactions (Bhattacharya *et al*., 2008). The following table is adapted from a selected number of reviews that have highlighted the use of clays for the treatment of simulated waste waters containing dyes or inorganic contaminants. None of the examples given used complex systems such as brine or acid mine drainage water.

Table 2.2 a)-2.3 b): Examples of studies on the adsorption of different metals using natural adsorbents adopted from (Fiset *et al*., 2008)

Aluminium (Al) (III)	Crist *et al.* (1994), Orhan and Büyükg üngör (1993), Cui *et al.* (2006)
Antimony (Sb) (III))	Coupal and Lalancette (1976), Masri and Friedman (1974
Arsenic (As) (II, V)	Loukidou *et al.* (2003), Masri and Friedman (1974)
Barium (Ba) (II)	Crist *et al.* (1994), Smith *et al.* (1977)
Bismuth (Bi) (III)	Masri and Friedman (1974), Shimizu and Takada (1997)
Cadmium (Cd) (II)	Volesk y and Prasetyo (1994), YU *et al.* (1999)
Calcium (Ca) (II)	Fiset *et al.* (2002), Fourest and Volesk y (1997)
Cerium (Ce) (III)	Masri and Friedman (1974)
Chromium (Cr)(III, VI)	Bailey *et al.* (1992), Fisher *et al.* (1984)
Cobalt (Co) (II)	Flynn *et al.* (1980), Kuyucak and Volesk y (1988)
Copper (Cu) (I, II)	Mckay *et al.* (1999), yu *et al.* (1999), CUI *et al.* (2006)
Europium (Eu) (III)	Andres *et al.* (1993)
Gold (Au) (III)	Kuyucak and Volesk y (1988), Nakajima (2003)
Iridium (Ir) (IV)	Ruiz *et al.* (2003)
Iron (Fe) (II, III)	Fiset *et al.* (2002), Nassar *et al.* (2004), CUI *et al.* (2006)
Lanthanum (La) (III)	Bloom and mcbride (1979), Crist *et al.* (1994)
Lead (Pb) (II)	Holan and Volesk y (1994),YU *et al.*(1999), Murathan and Bütün (2006)
Magnesium (Mg) (II)	Crist *et al.* (1994), Fiset *et al.* (2002), CUI *et al.* (2006)
Manganese (Mn) (II)	Fiset *et al.* (2002), Nassar *et al.* (2004), CUI *et al.* (2006)
Mercury (Hg) (I, II)	Fisher *et al.* (1984), Virarag havan and Kapoor (1994)

Molybdenum (Mo) (VI)	Guibal *et al.* (1999), Sakagushi *et al.* (1981)
Nickel (Ni) (II)	Flynn *et al*. (1980), Leusch *et al.* (1995)
Osmium (Os) (IV)	Ruiz *et al.* (2003)
Palladium (Pd) (II)	Baba and Hirakawa (1992), Guibal *et al.* (2001)
Platinum (Pt) (IV)	Baba and Hirakawa (1992), Guibal *et al.* (2001)
Radium (Ra) (II)	Tsezos (1997), Tsezos And Keller (1983)
Silver (Ag) (I)	Fisher *et al.* (1984), Flynn *et al.* (1980)
Sodium (Na) (I)	Fiset *et al.* (2002), Spinti *et al.* (1995)
Strontium (Sr) (II)	Shimizu and Takada (1997); Small *et al.* (1999)
Technetium (Tc) (VII)	Garnham *et al.* (1992a, 1993b)
Thallium (Tl) (I)	Masri and Friedman (1974)
Titanium (Ti) (IV)	Parkash and Brown (1976)
Vanadium (V) (V)	Guibal *et al.* (1994)
Ytterbium (Yb) (III)	Andres *et al.* (1993)
Zinc (Zn) (II)	Artola and Rigola (1992); Kuyucak and Volesky (1988)

Previous studies have demonstrated that using clays in water treatment can be effective and less expensive technology (Zhao *et al*., 1998). Natural clays can easily adsorb heavy metals via ion exchange reactions (McBride, 1994). They are also grouped in approximately 4 groups namely smectites, illite, chlorite and kaolin. Adsorption is considered to be very effective to remove contaminants within waste or wastewater even at very low concentration (1 mg/L) (Putra *et al*., 2009). The major advantage for waste water treatment utilization comes from economic consideration, since other adsorbents such as activated carbons are quite expensive therefore rendering them infeasible for large scale operation (Putra *et al*., 2009).

2.3.3 South African Clays as Low Cost Adsorbents

In terms of South African clays, there are very few publications in the open literature. Potgieter *et al*., 2006 studied the use of palygorskite clay, mined in Gauteng province, for the adsorption of Pb (II), Ni (II), Cr (VI) and Cu (II) from separate solutions with the individual metal ions. From the batch adsorption experiments done, they found that the adsorption of metals from the single-metal solutions followed the order of: Pb^{2+}> Cr^{4+} > Ni^{2+} > Cu^{2+}. Increasing the pH from 3 – 10 increased the amount of metal ion absorbed, and 100% removal was obtained using 0.5 g absorbent on a 20 mg/L solution of Pb^{2+}, 0.25 g absorbent on 20 mg/L Ni (II), 0.25 g absorbent with 80 mg/L Cr (VI), and 1.0 g absorbent with 20 mg/L Cu (II) (Potgieter *et al*., 2006).

Coetzee *et al*., 2003 studied the use of kaolin, palygorskite, and bentonites from Kwazulu – Natal, Free State, Gauteng, and Mpumalanga for the removal of fluoride from NaF stock solutions. The absorption capacities for of fluorine were 0.03 mg/g for kaolinite, 0.1 mg/g for bentonite, varied between 0.21 – 0.29 mg/g for palygorskite, and 0.2 mg/g for goethite/kaolinite. These fluoride removal values were generally lower than a commercial activated alumina (0.5 mg/g). The pH dependence was as expected with the best fluoride adsorption properties seen between pH 3 & 8. Activation of the clays prior to their use was done by heat treatment, chemical treatment with 1% Na_2O_3 or 1% HCl, and use of either treatment only had a marginal effect on the clays. Overall the study concluded that natural clays were not a good option for the removal of fluoride ions from the model solutions used (Coetzee *et al*., 2003).

2.3.4 Characterization of clays

Montmorillonite is a well known bentonite with lamellar structure (Hocine *et al*., 2004). It is a clay mineral with substantial isomorphic substitution, since it is 2:1 layer silicate the ions in the layer are balanced by isomorphic substitution. This montmorillonite is composed of units made up of two silica tetrahedral sheets with central alumina octahedral sheet. The swelling of smectites, such as montmorillonite, occurs when the material is dispersed in water, and the interlamellar spaces absorb enough water and result in the aggregates disintegrating into elementary sheets.

The amount of swelling depends on the size and charge of the cations and the cation exchange capacity (CEC) of the clay. The maximum amount of swelling is observed with small univalent cations such as Li^+ and Na^+, whereas polyvalent cations such as Ca^{2+} or Mg^{2+} result in incomplete swelling due to strong interactions between the cation and water. When the interlamellar layer contains at least a single layer of water, virtually any cation can be exchanged irrespective of the size and charge; such as, heavy metals, organic cations, dyes and cationic polymers (Gre´gorio, 2006). Schematic on the general structure and swelling of smectites is given below.

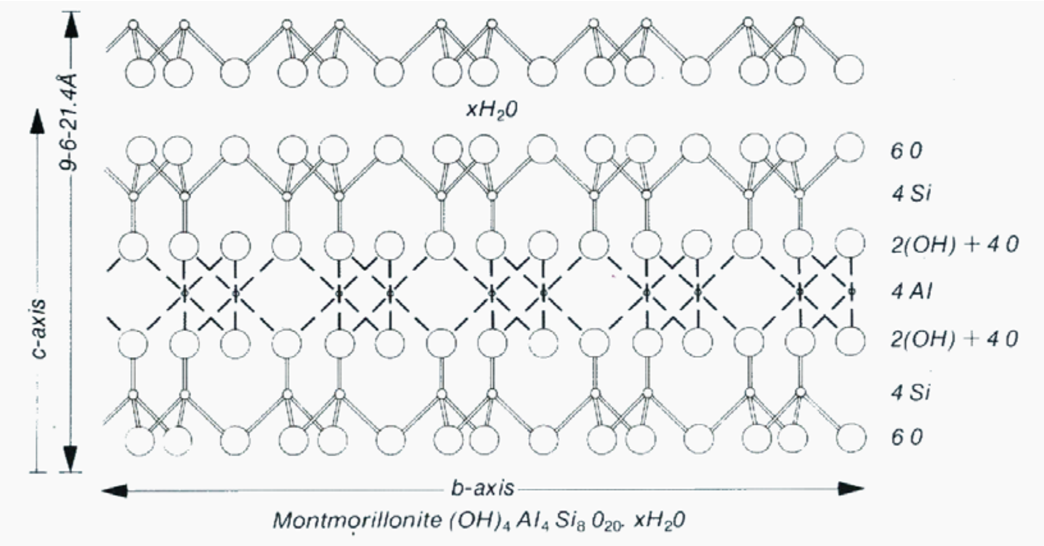


Figure 2.5: Structure of smectites, showing ingress of water in the interlamellar region (DME ,2004).

In figure 2.5 exchanges of cations occurs in the interlamellar region after at least a monolayer of water has penetrated this region, montmorillonite (Ca& Na bentonite) structure. Bentonites are clays whose basic clay mineral is a montmorillonite or smectite. It may also have other mineral phases present in it such as quartz, kaolinite, mica, feldspar, and pyrite and illite. The quality of bentonite raw materials depends on several parameters such as colour, rheological properties, and swelling behavior (Kaufhold *et al*., 2002). Bentonite clays consisting mainly of montmorillonite are widely utilized in various engineering applications. After special treatment or modification bentonite can become a good adsorbent material (DME, 2004).

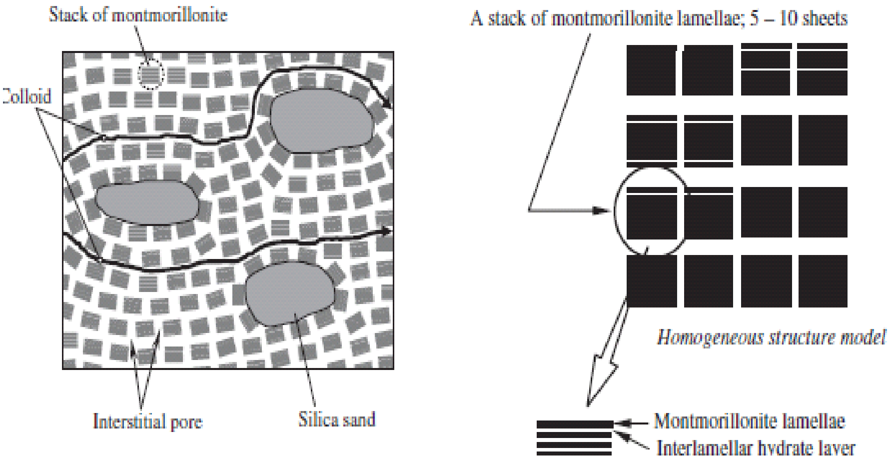


Figure 2.6: Schematic diagram of bentonite porosity (Kurosawa *et al*., 2006)

2.3.4.1 Bentonite

More than 75% of bentonite consumed in South Africa is produced by two open cast mines, Cape Bentonite mine owned by Ecca Holdings near Heidelberg in the Western Cape and the Ocean Bentonite mine owned by G & W Base & Industrial Minerals near Koppies in the Free State (DME, 2004). Bentonite is natural clay that occurs in abundant amounts in South Africa. It is an aluminium phyllosilicate, and generally impure clay consisting mostly of montmorillonite. Bentonite consists of aggregates of flat platelets that have high specific area, plasticity, expand when wet and is inert and non-toxic.

Since bentonite is of smectite group of clays it has a wide variety of industrial applications. A particular feature of this group of minerals is the substitution of Si^{4+} and Al^{4+} in the crystal structure by lower valency cations, thus unsatisfied negative charges are balanced by loosely-held ‘exchangeable’ cations such as Na^{+}. There are a few types of bentonites and their names depend on the dominant elements present in the structure such as K^{+}, Ca^{2+}, Na^{+} and Al^{3+}. Bentonite is valued for its sorptive properties, catalytic action, bonding power and cation exchangeability. Quartz is a non-clay material found in most bentonites but traces of feldspars, biotite, muscovite, pyrites, calcite and other minerals can also be found in it. The two types of bentonite sodium and calcium are three-layered aluminosilicate clays with water molecules between their layers (DME, 2004). Deposits sites of bentonite in South Africa are shown in a map in (section 1.2.1).

2.3.4.2 Na-Bentonite

Sodium-bentonite expands when wet possibly absorbing several times its dry mass in water. Sodium has this property because of its excellent colloidal properties. The swelling property of sodium bentonite also makes it useful as a sealant, especially for sealing subsurface disposal systems for spent nuclear fuel and quarantine metal pollutants of ground water (DME, 2004).

2.3.4.3 Calcium- Bentonite

Calcium-bentonite is also mined like Na bentonite but its swelling properties are lower than that of the sodium type. The Ca bentonites are best suited for acid activation (exclusively H^+ activation) which enhances surface area. When both types of bentonites come in contact with water sodium-bentonite expands more than calcium bentonite, this is because Na^+ can hydrolyse more than Ca^{2+} (DME, 2004).

2.3.4.4 Applications of Bentonite

Bentonites are applied in various industry uses such as binder, pelletising agent, and clarifying agent for wines, adsorbent of cat litter and toxic elements, pharmaceuticals as well as animal feed (Kawatra *et al*., 1999).

The importance of these practical applications is related to the rheological properties of clays. Sodium montmorillonite clay is particularly of interest due to its high swelling capacity and formation of a gel (Amorima *et al*., 2004).

2.3.4.5 Attapulgite

Attapulgite is a hydrated magnesium aluminum silicate present in nature as a fibrillar clay mineral containing ribbons of a 2:1 structure. Attapulgite has permanent negative charges on its surface, which enable it to be modified by cationic surfactants, to enhance contaminant retention, and to retard contaminant migration. Several studies have been presented on the adsorption of heavy metals from aqueous solutions by attapulgite (Chiu *et al*., 2009). Attapulgite also contains many structural hydroxyl groups (such as Al-OH and Mg-OH). In addition, some isomorphic substitutions in the tetrahedral layer, such as $Al^{3+}$for Si^{4+}, develop negatively charged adsorption sites to electro-statically adsorb cation ions.

Attapulgite has been intensively investigated as adsorbent in the removal of organic contaminants and heavy metal ions from the solutions and heavy metal polluted soils in the natural environment (Fan *et al*., 2008). Attapulgite has three kinds of water at room temperature adsorption water on the mineral surface by physical effect, zeolitic water that is weakly bound in the micro-channel; and crystalline water that is tightly bound water molecules completing the coordination of the (Mg, Al) cations at the borders of each octahedral layer structural water.

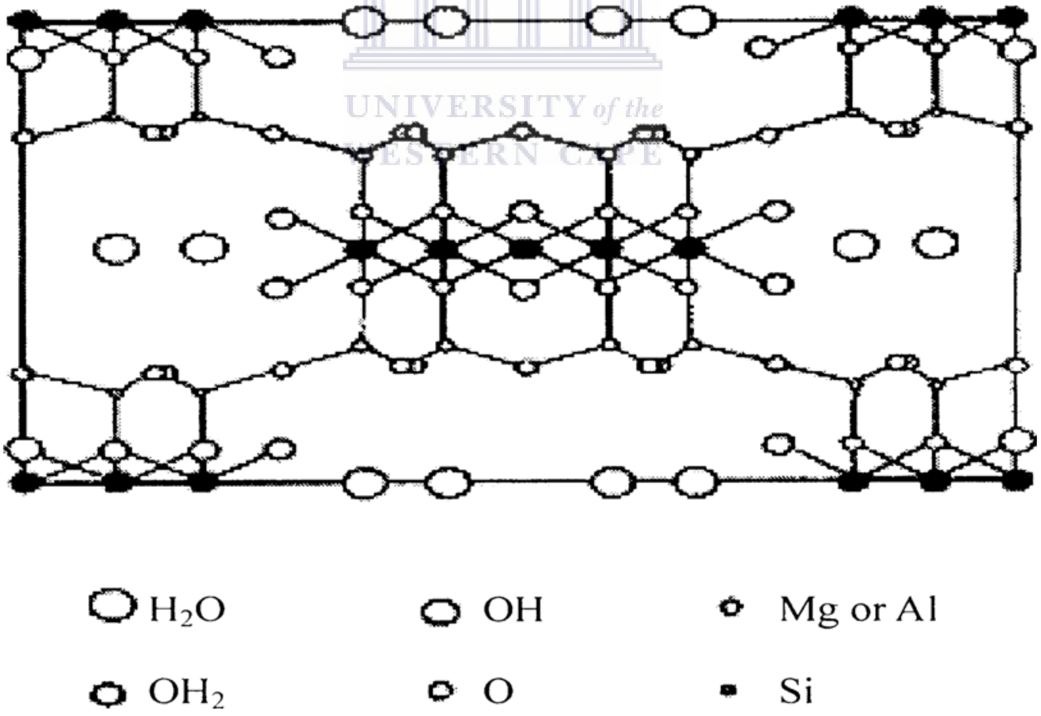


Figure 2.7: Schematic diagram of attapulgite that shows water molecules, Si, Mg, Al and O in the structure of attapulgite (Ping *et al*., 2004).

Attapulgite has been briefly studied as well in this study for comparative characterization purposes only not adsorption.

2.4 Zeolites

Zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth cations having an infinite, open, and three dimensional structures. There are further able to lose and gain water reversibly and to exchange extra framework cations, both without change of crystal structure (Mumpton, 1999). Clinoptilolite is the most well known natural zeolite and is one of the more useful. It is used in many applications such as a chemical sieve, a gas absorber, a feed additive, a food additive, an odor control agent and as a water filter for municipal and residential drinking water and aquariums. It is well suited for these applications due to its large amount of pore space, high resistance to extreme temperatures and chemically neutral basic structure. Clinoptilolite can easily absorb ammonia and other toxic gases from air and water and thus can be used in filters (Tehrani, 2005).

2.4.1 Description of Zeolites

They are two main types of zeolites, synthetic and the natural zeolites. Zeolites names were discovered by Axel F Crownsted from Sweden who was a mineralogist in 1756 (Musyoka, 2009). It is well known that about 40 natural zeolites were identified 200 years ago with clinoptilolite, chabazite, erionite, analcime, ferrite, heulandite, limonite, mordenite and phillisite being the most important types. More than 150 zeolites have been synthesized including type A, X, Y and ZMS-5 being the most common. Zeolites have attracted scientist's attention for their commercial use because of their adsorption, ion exchange, molecular sieves and catalytic properties (Zhao *et al*., 2007). Natural zeolites are abundantly found all over the world and are of commercial interest because they are easily mineable and they are low cost adsorbents and thus have gained attention by many researchers (Morali, 2006).

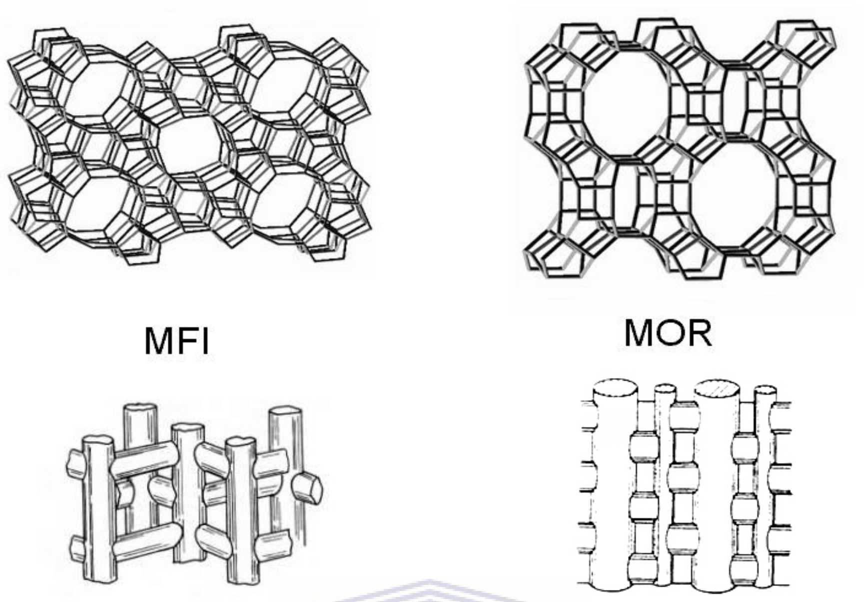
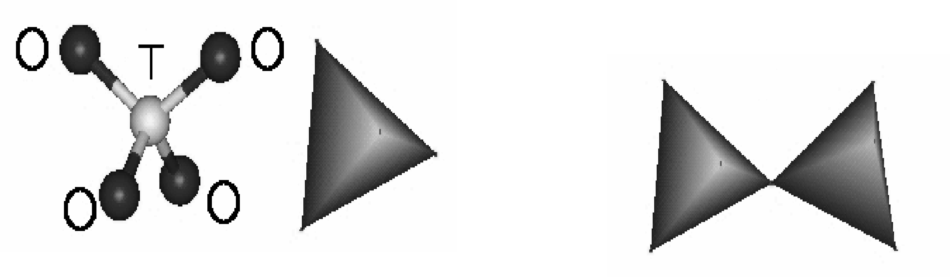


Figure 2.8: Examples of zeolite framework and pore system: MFI and MOR topologies (Houssin, 2003) showing voids and channels which defines the specific properties of the zeolite mineral

Zeolites are crystalline, hydrated alumina silicates of group 1 and group 2 elements that consists of SiO_4 and AlO_4^- tetrahedra linked by oxygen atoms to compose the framework. The aluminum atoms introduce a negative charge on the framework which must be balanced by an exchangeable cation ($Ca^{2+,}$ Mg^{2+}, Na^+, K^+ and others). These cations located as charge balancing elements to stabilize the framework play an important role in the adsorption and thermal properties of the zeolites (Cakicioglu-Ozkan *et al*., 2004). Zeolites are able to gain or lose water without a change in crystal structure (Ivkovic *et al*., 2004).

The most important feature of the zeolite structure is the presence of voids and channels which defines the specific properties of the zeolite mineral. These structural cavities and channels are occupied by the charge balancing alkaline and alkaline-earth cations and water molecules. The physicochemical properties displayed by the zeolite, many of which are of potential in the industrial.



(a) (b)

Figure 2.9: Illustration of (a) primary building block of zeolite (b) two tetrahedral sharing oxygen atoms (Morali, 2006)

The general chemical composition formula of zeolites can be expressed as:
$(M^{+}, M^{2+})\,O.Al_2O_3.gSiO_2.zH_2O$
M^{+} is usually Na^{+} or K^{+} and M^{2+} is Mg^{2+}, Ca^{2+} or Fe^{2+}; unusually but Li^{+}, Sr^{2+} or Ba^{2+} may substitute for M^{+} or M^{2+}. Fe^{3+} is commonly assumed to substitute into the tetrahedral framework position. Zeolite structure is mainly composed of three components (Morali, 2006): (1) Aluminosilicate frame work. (2) Exchangeable cations. (3) Zeolite water

Almost every application of zeolites has been driven by environmental concerns, or plays a significant role in reducing toxic waste (Weitkamp *et al.*, 2007) and stabilizing hyper saline solutions like brines.

Table 2.3: Different generic types of natural zeolites generated from (Musyoka, 2009)

Hydrothermal-geothermal deposits	Alteration of basaltic lava as a result hydrothermal or hotspring activity
Saline, alkaline lake type deposits volcanic	Zeolites formed by alteration of sediments deposited in saline lakes
Deposits from open hydrological systems	Formed when water with high pH and salt content flows through vitric volcanic ash causing crystal growth
Saline, alkaline salts deposits	Formed at land surface in saline soils as a result of evapotransporation in arid and semi-arid regions
Zeolite in marine deposits	Result from alterations of volcanic or non-volcanic material in seabeds due to low temperature or hydrothermal alteration of marine sediments
Burial diagenesis	This is a low grade metamorphism involving reactions pathway influenced by circulation of ground water and transportation of reactants

2.4.2 Clinoptilolite

The typical chemical formula of clinoptilolite is (Na_6 [$Al_6Si_{30}O_{72}$]. $24H_2O$). Natural zeolite clinoptilolite is abundant in many countries, and the interesting properties and varieties of the application have attracted so many areas, it possesses the heulandite (HEU) type framework (Inglezakis *et al.*, 2001). The HEU topology contains a ten-member ring channel pore system with eight-member ring cross channels. The higher silica member of this family is identified as clinoptilolite. Clinoptilolite can be classified by Si/Al ratio. If this ratio is between 4-5 bigger than 4, it can be classified as clinoptilolite. Zeolites also can be classified as clinoptilolite if the criteria of (Na+K) > Ca is available. The difference between natural heulandite and clinoptilolite is its thermal stability. While clinoptilolite is thermally stable above 500°C, heulandite is stable up to 350°C because its structure collapses at temperatures higher than 350°C can offer environmental protection through sorption and binding toxic elements because of its extraordinary ion exchange capacity (YetGin *et al*., 2006).

The negative charge of the clinoptilolite framework comes from tetrahedral coordinated aluminum. Clinoptilolite zeolites have CEC values between 100 and 400 meq 100 g^{-1} (Grim, 1968). It is mostly applicable in soil benefaction, in water and waste water treatment. Clinoptilolite has been widely studied for removal of ammonium from waste water and municipal water streams. It has been proved to be the most attractive material for ammonium removal, the removal of ammonium occurs via cation exchange from the structure of zeolite or through adsorption in pores of the aluminosilicates system. (Sprynskyy *et al*., 2004). The clinoptilolite is a member of heulandite group and has framework structure that consists of three channels. The channel A and B, 10-member rings, respectively, are parallel to each other while channel C, 8-member ring intersects the channel A and B. (Cakicioglu-Ozkan *et al*., 2005). The structure of clinoptilolite is as shown in the Figure 2.8

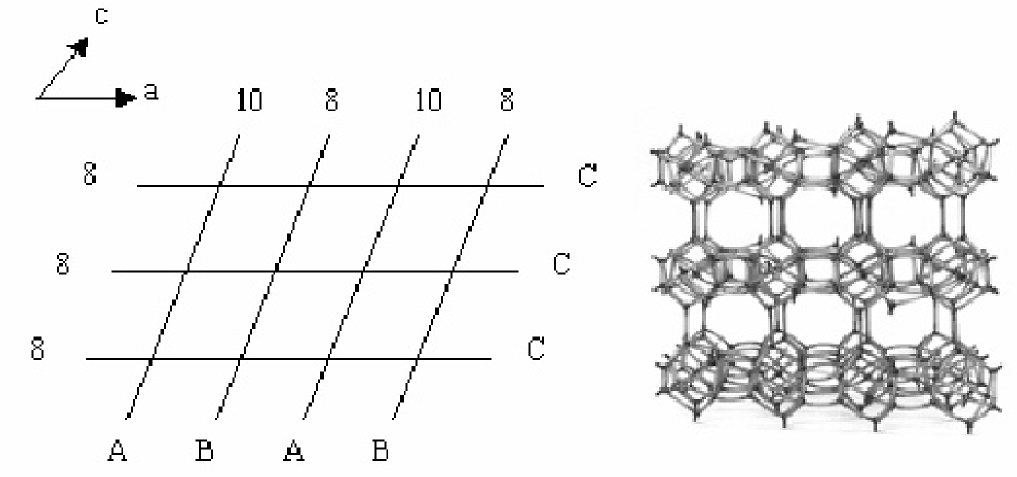


Figure 2.10: a) Orientation of clinoptilolite channel axis b) Model framework for the structure of clinoptilolite (YetGin *et al*., 2006)

2.4.3 Abundant Reserves

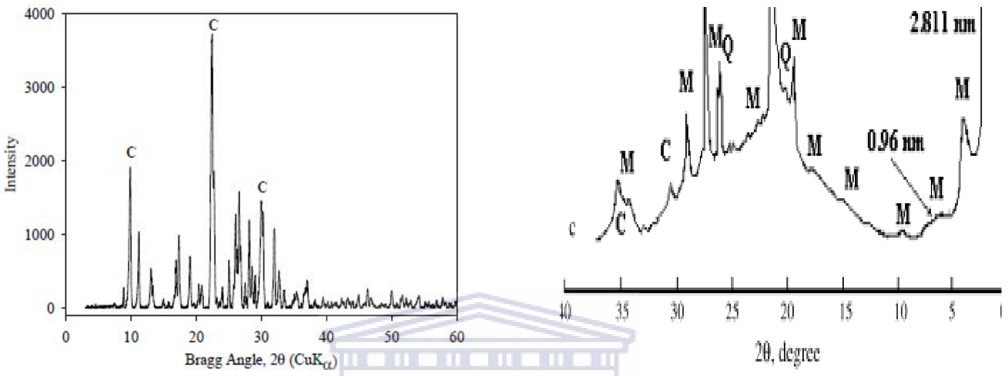
Natural zeolites are abundant all over the world, however only seven zeolites occur in sufficient quantity and purity to be considered as exploitable natural resources. These are namely, clinoptilolite, mordenite, phillipsite, chabazite, eronite, ferrerite and analcime. Clinoptilolte is a widely distributed natural zeolite and thus huge occurrences of clinoptilolite are mined in many countries (Morali, 2006). In South Africa clinoptilolite is found in reserves such as Cape Bentonite mine in the Western Cape and in Kwazulu Natal. In this study the clinoptilolite used was obtained from the Cape Bentonite mine in the Western Cape and the other source of clinoptilolite was from Turkey.

2.5 Characterization of natural clays and natural zeolites

Natural clays and natural zeolites need to be characterized before their use in order to understand the framework, purity, ion exchange capacity and the capacity to perform when used in adsorption studies. This section gives overview the methods used to characterize clays and zeolites.

2.5.1 Mineralogy and crystallinity by X-ray diffraction spectroscopy

X-ray diffraction (XRD) can be used for identification of the clay and zeolite framework structure which is the common method to determine identity and crystallinity of material and this method gives a unique fingerprint of each mineral phase.



a) b)

Figure 2.11: Representation of XRD spectra a) Clinoptilolite and b) Bentonite (Morali, 2006; Vlasova *et al*., 2007).

2.5.2 Structural configuration by infra red spectroscopy

Infra Red spectroscopy (IR) provides vibrational spectroscopic information on a molecular level. This technique can be used to provide direct information about the nature of surfaces and adsorbed surface species.

2.5.3 Morphology by microscopy

There are different techniques in the field of electron optical instrumentation available to provide information concerning crystal shape and particle size and as well as other characteristics of clays and zeolites. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) used in conjunction with scanning microprobe analysis which yields a great deal of information on zeolites are the most important ones applied in zeolite research (Szostak, 1989)

2.5.3.1. Scanning Electron Microscopy

In Scanning Electron Microscopy (SEM), an electron probe is used to scan the surface of a specimen using deflection coils. The interaction between the primary beam and the specimen produces various signals from back scattered electrons, secondary electrons, X-rays, etc. which may be utilized to form an image of the surface..

2.5.3.2. Transmission electron microscopy

Transmission Electron Microscope (TEM) can achieve resolution of about 3Å at a magnification of approximately 106 µm. The resolution can be improved by using special imaging techniques known as bright field, dark field, or lattice imaging. High resolution microscopy can provide information on structural defects within molecular sieve crystals and also generate information on the planar spacing and arrangement of channels and pores within the clay and zeolite when enhanced with computer imaging (Szostak, 1989).

2.5.4 Elemental composition by X-Ray fluorescence spectroscopy

X-ray fluorescence (XRF) is the emission of characteristic secondary (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays by which electrons are expelled from the different atoms leaving “holes” in the low lying orbitals. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. XRF is used for multielement analysis of zeolite and clay starting materials as well as products of synthesis. Si and Al in clinoptilolite obtained by various authors (Morali, 2006) SiO_2 of 71.83% and Al_2O_3 with 11.68%; (Mamba *et al*., 2009) with SiO_2 74% and $Al_2O_3$12.4%; Inglezakis *et al*., 2001) and Si and Al in bentonite by various authors (Hamidpour *et al*., 2009 with 59.6% SiO_2 and 12.5% Al_2O_3).

2.5.5 Cation exchange capacity

Cation Exchange Capacity (CEC) can be defined as a measure of the charge compensating cations per unit of weight of the zeolite or clay. It represents the number of exchangeable extra framework cations available for exchange from the zeolite

2.5.6 Other characterization technique

2.5.6.1. Thermal analysis

Thermal analysis of zeolite or clay can be used to give information on the water content and the amount of organic templating molecules which are occluded in the cavities and pores of clays and zeolites during the synthesis process. This technique can also be used to determine thermal stability of a zeolite since exothermic heat flows over 600 ºC is a general characteristic of the structural collapse of zeolites (YetGin *et al*., 2006)

2.6 Applications of zeolites

Abundance of natural zeolites all over the world makes them an attractive and cost effective tool for removal of toxic elements and heavy metals from waste waters. The value of zeolites depends primarily on their ion exchange and adsorption properties, which have been the focus of studies carried by a number of researchers. The applications of natural zeolites and synthetic zeolites have been widely studied in several fields such as pollution control, energy conservation, agriculture, catalysis etc. Zeolites in both cation-exchange and adsorption applications should be mechanically strong to resist abrasion and disintegration, highly porous to allow solutions and gases to diffuse readily in and out of the rock, and soft enough to be crushed. The applications of natural zeolites in the environment have been studied by various researchers :water pollution (Zhao et al., 2007; Mamba *et al*., 2009; Ouki and Kavannagh, 1999). Air pollution (Tehrani, 2005). NH_4^+ removal from municipal wastewaters (Langella *et al*., 2000).

2.6.1 Catalysis

Mainly synthetic zeolites have been studied for catalysis. Due to lack of purity, applications such as in catalysis and other potential uses based on the adsorption properties of natural zeolites are in general limited in catalysis (Musyoka, 2009). However natural zeolites like erionite-clinoptilolite have also been studied as a selective-reforming catalyst by Mobil Corporation. A hydrogen exchanged natural mordenite was studied for hydrocarbon conversion catalyst for the disproportionate of toluene to benzene and xylene. Cation-exchanged clinoptilolite from Tokaj, Hungary was used for the hydromethylation of toluene, and clinoptilolite catalysts were applied for the isomerization of n-butene, the dehydration of methanol to dimethyl ether, and the hydration of acetylene to acetaldehyde (Mumpton, 1999).

2.6.2 Ion exchange

Ion exchange is one of the methods used for the removal of several toxic substances, including heavy metals and toxic elements from industrial and municipal wastewater. It is defined as stiochiometric replacement of one equivalent of an ion in solid phase by an equivalent of another ion in liquid phase. The application of zeolites for ion exchange is simple and safe because of mild operating conditions. The ion exchange reaction takes place between exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) located in the zeolite structure and cations in the water (Inglezakis *et al*., 2001). Ion exchange capacity is among the most important properties of microporous materials. The ion-exchange capacity of zeolites depends on: the nature of the cation species in the liquid phase, for example, the cation size and valence, the pore size in the crystalline structure, and the number of exchangeable cations bonded to the zeolite framework. This property enables zeolites to exchange their cations with those of the surrounding fluid during the process of cleaning waste water containing heavy metals (Musyoka, 2009).

2.6.3 Use as adsorbents

Natural zeolites have been used as adsorbents because of their unique structures as molecular sieves. The adsorption mechanism involves the uptake of heavy metals, unlike ion exchange, formation of bonds which are mainly covalent and some combinations of covalent and ionic bonding are involved in this mechanism. The adsorption mechanism is sometimes referred to as chemisorptions or inner sphere complexation. In zeolite particles adsorption is defined as reaction of heavy metal species with surface functional groups forming a chemical bond. This mechanism is however difficult due to the porous structure of inner and outer charged surfaces , mineralogical heterogeneity, existence of crystal edges, broken bonds and imperfections on the surface of zeolite (Morali, 2006). Natural zeolite clinoptilolite since is abundant in high purity in many parts of the world and in South Africa, it was used in this study.

Table 2.4: Selectivity series for various heavy metal ions (generated from (Morali, 2006)

Selectivity Series	Reference
$Pb^{2+} > Cd^{2+} > Cs^{+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$	Zamzow et al. (1990)
$Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+}$	Ouki and Kavannagh (1999)
$Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$	Panayotova and Velikov (2002)
$Pb^{2+} > Cr^{2+} > Fe^{2+} > Cu^{2+}$	Inglezakis and Grigoropoulou (2004)
$Pb^{2+} > NH_4^{+} > Cu^{2+}, Cd^{2+}, Sr^{2+} > Zn^{2+} > Co^{2+}$	Blanchard et al. (1984)
$Pb^{2+} > K^{+} > Ba > NH_4^{+} > Ca^{2+} > Cd^{2+} > Cu^{2+} > Na^{+}$	Semmens and Martins (1988)

In table 2.4 above selectivity of clinoptilolite in heavy metals removal is summarised with studies carried out by various researchers. Depending on the metal ions tested and the origin of clinoptilolite, the selectivity series tend to show variations. A common finding, however, is the high selectivity of clinoptilolite for Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr^{2+} and Zn^{2+}.

2.7 Factors affecting removal of toxic elements

Toxic element removal by zeolite and clay in aqueous solutions is affected by a number of factors, thus this section discuss some of these factors. Temperature, pH, pretreatment applied to zeolites and clays, particle size, pore clogging, mineral properties and presence of other contaminants in the solution (Morali, 2006). The current study focused review effect of temperature, pretreatment, contact time and pH among the other factors. The reason for reviewing these factors is because of the information obtained from literature about zeolites material behaving differently under different conditions in ion exchange and adsorption studies (Inglezakis *et al*., 2004).

2.7.1 Effect of Temperature

Many studies conducted using zeolites and clays as adsorbents or ion exchangers showed that temperature can be one the factors affecting removal of heavy metal in aqueous solution. In many of the studies carried out, researchers found that removal of Pb^{2+} was independent of temperature, however other studies showed that increasing the temperature affected Ni^{2+} removal positively, whereas Pb^{2+} removal increases when temperature range is between 23-45 °C (Morali, 2006). On the other hand (Cakicioglu-Ozkan *et al*., 2005) revealed that an increase in temperature and concentration caused an increase in removal of univalent cations such as Mg^{2+}, Fe^{3+} and Ca^{2+}. Heavy metal removal is enhanced by the increase in temperature due to activation of metal ions by enhancing adsorption at coordination sites of zeolites and at higher temperatures ions becomes smaller due to their reduced hydration spheres and their movement become faster resulting in higher removal efficiencies (Morali, 2006). High temperatures can also cause dealumination in zeolites. The high operation temperature heat breaks the aluminium-oxygen bonds and the aluminium atom is expelled from the zeolite frame work (YetGin *et al*., 2006).

2.7.2 Effect of pH

The effect of pH has been investigated in many studies (Onyango *et al*., 2010) ; Inglezakis *et al*., 2001) among other factors affecting efficient removal of toxic elements in wastewater and has a significant impact on heavy metal removal by zeolites since it can influence metal speciation, integrity of zeolite and also H^+ ions considered as competitive in ion exchange. Solution pH is one of the factors that have been found to affect the sorption process significantly. Onyango *et al*., (2010) practically revealed that nitrate removal is affected by pH. Adsorption processes using zeolites and clays are not only influenced by pH but zeolite or clay addition is also capable of affecting the solution pH. Clinoptilolite tends to neutralize the solution to be treated by acting as H^+ acceptor or donor (Morali, 2006).

2.7.3 Effect of pre-treatment

Zeolites and clays can be tailored to obtain better properties. Some modification can be based on creation of secondary pores by either dealumination or acid leaching (Nagy and Nairn, 1998), or by modifying external surface area or internal pore volume by unblocking pores and also by varying the chemical composition by isomorphous substitution of Al or Si by elements with ionic radii and coordination requirements which are compatible with the tetrahedral sites in the structures of the zeolite. Pretreatment of zeolite has been widely studied and frequently is considered as a first step for zeolites in adsorption and ion exchange studies. Pretreatment aims at removing certain ions from the structure of zeolite material and locate more easily results in the zeolite material being converted to the homoionic form to increase content of single cation (Semmens *et al*., 1988). Mumpton F.A, (1999) stated that modifying of zeolite with quaternary amines may enhance their adsorption capacity.

The significance of pre-treatment to the homoionic or near homoionic state in the case of zeolites was found to improve their effective exchange capacity and performance in ion exchange applications (Inglezakis *et al*., 2001). Clinoptilolite has selectivity among ions and Na^+ is the lowest selectivity and thus increasing the Na^+ content of clinoptilolite by pre-treatment improves its ion exchange ability. Semmens and Martin, (1988) presented the series Pb^{2+}>K^+>Ba^{2+}>NH_4^+>Ca^{2+}>Cd^{2+}>Cu^{2+}>Na^+ respectively meaning clinoptilolite has a high selectivity for Pb^{2+} than for Na^+.

Previous studies investigated the use of hydrochloric acid, sodium chloride, ammonium acetate, potassium hydroxide and sodium hydroxide as activating or pre-treatment agents (Inglezakis *et al*., 2001; Cakicioglu-Ozkan *et al*., 2005; Langella *et al*., 2000) to replace K^+, Ca^{2+} and Mg^{2+}which are strongly held by clinoptilolite with Na^+ ions. Even with extensive exposure of the zeolite clinoptilolite material to high Na^+ concentration on the other hand, it was found not possible to replace all other exchangeable ions from the structure with Na^+ (Langella *et al*., 2000).

However, acid treatment as an activation procedure results in a highly crystalline H-form of the zeolite, but has a slight disadvantage since the acid (depending on the concentration used) can remove some of the alumina from the framework (Mamba *et al*., 2010). Washing after pre-treatment is essential in order to remove excess activating agent entrapped in zeolite structure. Some researchers found that pre-treatment of the natural zeolite with acid has no effect on the crystal structure of zeolites (Mamba, 2010).

2.7.4 Effect of pore clogging and presence of other contaminants

Pore clogging has an effect in the adsorption of heavy metal uptake by preventing heavy metal ions from entering the zeolite pore structure, and that causes a decrease in their removal. Fine particles on zeolite surface and precipitation as a result of heavy metal accumulation on the surface are possible causes of pore clogging. Researchers such as Inglezakis *et al*., (2004) stated that pore clogging as result of dust particles produced during grinding makes clinoptilolite surface and pore opening partially covered resulting slower ion exchange rates.

2.8 Chapter summary

Significant information related to brines, clays and natural zeolites has been presented in this chapter. The applications of the natural adsorbents bentonite and clinoptilolite for removal of contaminants from waste water have also been highlighted. Desalination for water supply has grown steadily since the 1960s. Since then, many plants have been created in various parts of the world as containing innovations in seawater and industrial waste water desalination technology continue to reduce the effective cost of produced water (Ericsson and Hallmans, 2009; Colin *et al*., 1997; Korngold *et al*., 2009; Grenlee *et al*., 2009). Although there are many benefits the desalination technology offers, concerns arise over potential negative impacts of desalination activity on the environment particularly the disposal of the reject brine released after desalination of wastewater to clean water (Mohamed *et al*., 2005; Glater and Cohen, 2003; Amhed *et al*., 2001). Key issues are the brine discharges to the marine environment, impacts caused by feed water intake, the emissions of air pollutants, land disposal and the energy demand of the processes (Younos, 2005). Desalination processes produces two streams of water. One, the product water, is fresh water. The other is concentrate water containing salts also known as reject water, reject brine or wastewater. The concentrate consists of highly concentrated salts that can stress the environment (Sabah *et al.,* 2009). In both the RO and the thermal plants, the salinity of the concentrate is higher than source feed water salinity.

The salinity of the concentrate stream will vary with the type of desalting plant. Thus this chapter informed the current study on the gaps or weakness that the desalination processes have on the treatment of waste water, by not considering how to treat their reject brine before disposing it and the choice for research questions, research approach, the study site chosen and materials used. Natural adsorbents on the other hand are potential adsorbents of the toxic elements or salts present in the reject brine because of their abundance all over the world and in South Africa, cost effectiveness and unique properties to adsorb (Sanchez *et al*., 1997)

CHAPTER 3

EXPERIMENTAL

CHAPTER 3

EXPERIMENTAL

This chapter is divided to several parts. The first section is on materials and the methods used to characterise clays and zeolites before execution of adsorption experiments. The second section deals with preliminary adsorption experiments. The third section deals the activation or pretreatment of clays required to get a better adsorption capacity. The last section deals with the actual adsorption experiments using the pre-treated natural adsorbents for brine treatment.

3.1 Materials

Natural clay bentonite and natural zeolite clinoptilolite were obtained from Ecca Holdings Company in the Western Cape from the Cape Bentonite mine (see section 1.2.1) For Comparison purposes the other clinoptilolite source from Balıkesir-Bigadiçi deposit, Turkey and also attapulgite clay from South Africa.

Table 3.1: Reagents used

Chemical	Percentage purity	Suppliers
Ammonium acetate	98.50%	Kimix
Acetic Acid	99.8%	Kimix
Nitric Acid	55%	Merck Chemicals
Propan- 1-ol	99%	Merck Chemicals
Hydrochloric acid	32%	Sigma Aldrich

3.2 Methods

3.2.1 Sample preparation

Natural adsorbents were firstly used without any chemical modifications they were milled, sieved to 106 µm particle size and dried in an oven at 105ºC for 24 hours prior adsorption. The 106 µm particle size was used for the natural adsorbents throughout the study.

3.2.2 Brine analysis

The brine sample used in this study was collected from the highly saline retentate stream of the reverse osmosis (RO) desalination plant at Emalahleni RO plant, South Africa. The brine was not simulated or diluted it was used as a raw as it was obtained from RO plant. Emalahleni brine was chosen for this study because of the high concentrations of the major species such as Na^+, Cl^- and SO_4^{2-}, and in order to avoid inconsistency. The brine sample was collected in plastic containers and stored in a refrigerator at 4 °C. The brine sample used for this study was sampled at once because of the large variability found over time. The chemical composition (Table 4.4and 4.5) of the two brine solutions used in this study was analyzed using ICP-AES and IC for cation and anion respectively.

3.2.3 Characterization of natural adsorbents

It is necessary to characterize every adsorbent material before its use or application. Characterization makes it possible to match the physical and chemical properties of the material to the environment in which it must operate. Characterization begins at the clay/zeolite deposit. This means the clay or zeolite mineral material deposit must be thoroughly explored to determine its extent, continuity and quality. Both the mined and processed product must be carefully sampled to insure the buyer a dependable supply of clay/zeolite that is of a uniform quality.

The characterization of clay and zeolite minerals initially requires carefully screening techniques to identify the clay and zeolite and gangue minerals and determine the percentage of each present in the product. The following techniques are the appropriate methods used to determine elemental and mineralogy of the clay and zeolite materials. The initial screening involves mineralogical characterization and chemical analysis, pore size determination and the determination of cation exchange capacity. These methods will be briefly given in the following section.

3.2.4. Mineralogical characterization by X-ray Diffraction Spectroscopy

3.2.4.1 Qualitative X-ray Diffraction Spectroscopy analysis

Clays and zeolites have a characteristic X-ray-powder-diffraction pattern (XRD), which is used for phase identification and also to determine the phase purity or quality of clay or zeolite present. By comparing the spectra generated by XRD characterization with that of a reference sample, it is possible to identify the mineralogical phases present in the clay and even determine its purity by checking whether it is a mixture of phases or one pure mineral phase. Natural clays and natural zeolites were grounded to fine powder and were placed in sample holder and the crystalline phases were evaluated using Phillips X-ray diffractometer with Cu-Kα radiation. The XRD instrument operating conditions were given as table 3.2 below:

Table 3.2: The XRD operating parameters

Radiation source	Cu-Kα
Radiation Wavelength (λ)	104
Range	1.54056< 2°<80°
Time constant	1 s
Preset (counts/s)	1000
Voltage (kV)	40
Current (mA)	25
2θ range	4°
$2\ \theta$/step	0.1°
Anti-scatter	4°

Identification of phases present in the clays and zeolites was performed by searching and matching obtained spectra with powder diffraction files from the data base with the help of JCPDS (Joint committee of powder diffraction standards) files for inorganic compounds.

3.2.4.2 Quantification of mineral phases of clays and zeolites

Quantitative X-ray Diffraction (XRD) was performed to identify the percentage of clay or zeolite material present in one adsorbent in order to tell how much of other minerals are present in that particular clay or zeolite. The samples were prepared for XRD analysis using a back loading preparation method. They were analysed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weights %) were estimated using the Rietveld method (Autoquan Program). Errors are on the 3 sigma level in the column to the right of the amount.

3.2.5. Surface area and pore determination

Surface areas and pore size of clays and zeolites were determined using the gravimetric nitrogen Brunauner-Emmett-Teller (N_2-BET) surface analysis technique. The sample to be analysed (0.3- 0.5g) was outgassed at 110° C for 14 hours on the Flow Prep 060 using helium gas The Micromeritics Tristar instrument was used with nitrogen as the analysis gas based on a 5 point with 30 adsorption and 30 desorption points together with total pore size measurement.

3.2.6 Elemental analysis

3.2.6.1 X-Ray Fluorescence Spectroscopy (XRF)

In this study X-ray fluorescence (XRF) was used for multi-element analysis of starting adsorbent materials of clays and natural zeolite clinoptilolite. Major elements were analyzed on a fused glass bead at 40 kV and 50 mA tube operating conditions and trace elements were analyzed on a powder briquette at 50 kV and 40 mA, tube operating conditions. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ Phillips software. The powder samples were prepared by mixing 8 g of clay with 2 g of a binder (which was made up of 10 % C-wax binder and 90% electron microscopy unit (EMU) powder) and this mixture was then thoroughly shaken, poured into a mould and pelletized at a pressure of 15 tons for about 1 minute using a Dickie and Stockler manual pelletizer of ignition was measured by placing the samples in the furnace at 1000 ºC for at least 45 minutes. All elemental analyses were done using a Phillips PW 1480 X-ray spectrometer. The spectrometer was fitted with a chromium tube, five LIF 200, LIF, 220, GE, PE and PX and the detectors are a combination of gas-flow proportional counter and a scintillation detector. The gas used was a mixture of 90 % argon and 10 % methane.

3.2.6.2 Inductively Coupled Plasma Spectrometry (ICP-AES)

Elemental analysis study of the zeolite and clay filtrates collected after cation exchange capacity, adsorption procedure and after activation procedure of the natural adsorbents was done in order to gain a better understanding of the trace and major heavy metal species contained in the filtrates, and also to determine which element species stays trapped in the zeolite sample and which are released. The concentrations of ionic species in the post-synthesis aqueous supernatant solution were measured by the use of inductively coupled plasma atomic emission (ICP-AES). The instrument used for the majors and traces, is a Varian Radial ICP-AES using a High Matrix Introduction (HMI) accessory and He as collision gas. The instrument, external calibration was performed daily, and results of a quality control standard verifying accuracy was included with every batch of samples analyzed. For ICP-AES analysis, internal standards were used to correct for matrix effects and instrument drift. Samples were diluted thousand times for majors and traces, with data corrected for dilution factor

3.2.7 Cation Exchange Capacity

This method is used for determining cation exchange capacity and measuring exchangeable cations and it is the method of interest in this study. The procedure used adopted from Amrhein *et al*., (1999) and the reagents were prepared as follows;

(i) Sodium acetate: 136 g of $Na_2C_2H_2O_2.3H_2O$ was diluted in water into a volume of 1,000 mL .The pH was adjusted to 8.2 with a few drops of acetic acid or NaOH and this was time-consuming because it was difficult to maintain the pH of 8.2

(ii) Ammonium acetate: 114 mL of glacial acetic acid (99.5%) was diluted with water to a volume of approximately 1 liter, 138 mL of concentrated (NH_4OH) was added and made up with water to obtain a volume of about 1,980 mL. The pH was maintained to 8.2 and more NH_4OH was added to obtain a pH of 8.2.The procedure was adopted from (Amrhein and Torre 1996) for fly ash. The CEC was determined by extracting 0.5 g of bentonite clay and clinoptilolite with four 25-mL aliquots of 1.0M ammonium acetate (pH 8.2). Bentonite and clinoptilolite samples were continuously shaken with the extracting solution for 15 min, then centrifuged for 15 min, to separate the solids and then the supernatant was decanted. This extraction was repeated a total of four times. The cumulative extract was brought to 100 mL and then analyzed for major cations by ICP-AES and major anions by IC, traces were determined using ICP-AES.

3.2.8 Physical characterization by morphological analysis

3.2.8.1 Scanning Electron Microscopy

The morphology and particle size of the clays and zeolites used in this investigation untreated and treated clays and zeolite was obtained using a Hitachi X-650 scanning Electron Microanalyser equipped with a CDU- lead detector at 25kV. Samples were mounted on Aluminum pegs and coated with a thin film of gold to make them conductive.

3.2.8.2 Transmission Electron Microscopy

To get an insight on the crystalinity of the material TEM was used to as analysis tool for packed rings that shows crystalinity. Samples were prepared by diluting the suspension clay/zeolite in ethanol, ultra sonicating and depositing a drop onto S147-4 Holey carbon film 400 mesh Cu grids. 200 kV

Field Emission gun lens 1 was used with spot size 3, at 200 kV using HRTEM Tecnai G2 F20 XT winMAT.

3.2.9 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy (FT-IR) was used to monitor evolution of crystallinity during pretreatment and also provide information about molecular structure. FT-IR requires virtually no sample preparation so in this case, approximately 15 mg of the zeolite sample was placed on the Attenuated Total Reflectance (ATR) sample holder of a Perkin Elmer spectrum 100 FT-IR spectrometer. The sample was recorded in the range of 1800 – 250 cm^{-1}, baseline was corrected and the spectra smoothened. Vibrations common to zeolites and clays were identified. The use of diamond cells with beam condenser or microscope allowed adjustment of the thickness of a sample by squeezing which enables analysis of microgram samples to be performed.

3.3 Batch adsorption studies

3.3.1 Preliminary Batch Adsorption experiment

The main purpose of this experiment was to establish if the natural adsorbents can remove toxic elements from brine without pretreatment or being modified.

3.3.1.1 Sample preparation

Natural adsorbents were firstly used without any chemical modifications they were milled, sieved to 106 µm particle size and dried in an oven at 105ºC for 24 hours prior adsorption. The 106 µm particle size was used for the natural adsorbents throughout the study.

3.3.1.2 Materials and methods

Standard batch adsorption experiments were carried out at room temperature 25 ºC. A total of four samples, two clay samples (bentonite and attapulgite) and two zeolite samples were used namely South African clinoptilolite (SC) and South African bentonite (SB) sourced from Ecca Holdings Company in the Western Cape South Africa, as well as a clinoptilolite sample originating from a mineral deposit in Turkey (TC) and attapulgite clay (AS) from South Africa.

About 0.5 g clay absorbent was weighed on a 100ml Erlenmeyer flask and 50 ml of Emalahleni brine effluent was added. All experiments were performed in duplicate. The mixture was shaken for 2 and 24 hr respectively in water bath at 25 ºC. Initially the preliminary batch experiments were done using only the Emalahleni brine with no adjustment to its pH (i.e. natural pH). After contacting the brine with the absorbent, the absorbent was removed via filtration, and the recovered aqueous solutions were analyzed with an ICP – AES.

3.3.2 Leaching experiments

The purpose was to establish which elements are leaching from the clay or zeolite and at what concentration thus was necessary to estimate what elements could be removed from the brine versus what elements originated from the adsorbent and may leach upon contact with water.

3.3.2.1 Materials and methods

Total of four samples, two clay samples (bentonite and attapulgite) and two zeolite samples were used namely clinoptilolite from South Africa, as well as a clinoptilolite from Turkey. Firstly all clay samples were milled, sieved to 106 µm and dried in an oven at 105 ºC for 24 hours prior to the leaching experiments. About 0.5 g clay absorbent was weighed on a 100 ml Erlenmeyer flask and 50 ml of deionised water was added. All experiments were done in duplicate. The mixture was shaken for 1hr and 2hr respectively in a water bath at 25 ºC. After contacting water for the set period with the absorbent, the absorbent was removed via filtration, and the recovered water was analyzed with an ICP – AES.

3.4 Pre-treatment of natural adsorbents

The purpose was to remove the major cations that originated from the natural adsorbents so that they will thus adsorb the cations that are present in the brine effluent. Secondly pretreatment was done to increase surface area by creating more pores.

3.4.1 Activation of natural adsorbents

The method for activation used was adapted from (Mamba 2009) and was optimised. The bentonite and clinoptilolite samples were milled and then sieved to <106 µm. South African clinoptilolite, South African bentonite and Turkish clinoptilolite were contacted with 0.02 M HCl. In a typical experiment, 5.0 g of the natural adsorbent was mixed with 100 ml of 0.02M HCl in a 250.0 ml Erlenmeyer flask. The flask was placed in water bath shaker for a set period of time at a temperature of 25 ˚C and a constant agitation setting of 250 rpm. Samples were washed six times with 0.02M HCl by initially agitating for 2hr, 1hr and thereafter 4 times for 30 min. With each washing, a fresh aliquot of HCl was used the supernatant recovered for further analysis. After the last HCl wash, samples were washed with distilled water until a pH 4.5 – 5.0 was obtained. Samples were then filtered with a 0.45 µm membrane filter paper and analysed then dried in the oven for 24hrs at 105˚C.

3.4.2 Batch Adsorption experiment after pretreatment

The purpose was to establish the effect of pretreatment on the adsorption capacity of the natural adsorbents on toxic elements, to determine optimum contact time of the adsorbent with Emalahleni brine and to also determine optimum pH for toxic element removal. The pH study was done on Tutuka brine solution not on the Emalahleni brine because the Emalahleni brine sample was not enough.

3.4.3 Materials

A total of three adsorbent samples, bentonite clay and two zeolite samples were used namely clinoptilolite from Ecca Holdings Company in South Africa, as well as clinoptilolite from Turkey pretreated with the 0.02 M HCl for better adsorption capacity and removal of cations in the natural adsorbents and then tested for their adsorption capacity using a real raw Emalahleni RO brine obtained from the stage 3 reject stream and Tutuka brine from ESKOM’s RO plant in South Africa.

3.4.4 Determination of optimum contact time

All three treated natural adsorbents (SC, TC and SB) samples were dried in an oven at 105 ºC for 24 hours prior to adsorption experiment as set out in and then were applied in adsorption studies. About 0.5g clay absorbent was exactly weighed into a 100 ml Erlenmeyer flask and 50ml of stage 3 Emalahleni brine concentration in triplicates for replicability. The mixture was shaken for 30 min, or 1, 2, 6, 8 and 24 hr respectively in water bath at 25 ºC. Initially experiments were done using only the brine with no adjustment to its pH (i.e. natural pH) the pH adjustment was checked by experiment outlined in (section 3.4.5). After contacting the brine with the absorbent, the absorbent was removed via filtration using 0.45µm membrane filter paper, and the supernatant solutions were analyzed for components with an ICP – AES.

3.4.5 Determination of optimum pH

All three treated natural adsorbents samples (SC, TC and SB) were dried in an oven at 105 ºC for 24 hours prior to adsorption experiment and then were applied in adsorption studies. About 0.5 g clay absorbent was exactly weighed into a 100 ml Erlenmeyer flask and 50 ml of Tutuka brine concentration in triplicates for replicability. The mixture was shaken for 30 min for South African clinoptilolite and bentonite clay respectively and shaken 1 hr for the Turkish clinoptilolite in water bath at 25 ºC. The initial Tutuka brine pH was adjusted to pH 4 and 6 using 32% hydrochloric acid. After contacting the brine with the absorbent, the absorbent was removed via filtration using 0.45µm membrane filter paper, and the supernatant solutions were analyzed for components with an ICP – AES.

CHAPTER 4

RESULTS AND DISSCUSION

CHAPTER 4

RESULTS AND DISSCUSION

This chapter is divided into four sections. The first section deals with characterization results of as received and treated clays and zeolites before execution of adsorption experiments. The second section deals with preliminary adsorption results prior to pre-treatment to establish baseline data. The third section deals the activation or pretreatment of clays and zeolites in order to get a better adsorption capacity by removing cation originating from the natural adsorbents that block the pores during adsorption. The last section presents the actual adsorption results using the pretreated adsorbents for brine treatment.

4.1 Characterization results

This section presents characterization of the natural adsorbents using different characterization techniques such XRF for elemental analysis, SEM for morphology, XRD for phase identity and purity, N_2-BET to obtain surface area and pore volume, CEC for cation exchange capacity, FTIR for structural configuration, by peak identity and peak shift in wave numbers, and HRTEM for confirmation of the crystalinity of the material.

4.1.1 Elemental composition of the different clays

The X-ray Fluorescence Spectroscopy (XRF) data showing the elemental composition of bentonite clay and clinoptilolite according to Section 3.2.3.1 is presented in Table 4.1 (a-b), Table 4.2(a-b) and Table 4.3 (a-b) showing Si/Al ratio of the South African clinoptilolite (SC),Turkish (TC) and South African bentonite (SB).

Table 4.1a): Major oxides analysis of the South African clinoptilolite untreated (SC-U) and treated South African clinoptilolite (SC-T) and Standard deviations (STDEV) from XRF

Majors wt %	**SC-U1**	**SC-U2**	**Mean**	**STDEV**	**SC-T1**	**SC-T2**	**Mean**	**STDEV**
SiO_2	67.80	63.28	65.54	3.1970	69.83	69.55	69.69	0.2007
TiO_2	0.27	0.24	0.26	0.0214	0.22	0.22	0.22	0.0007
Al_2O_3	13.61	12.33	12.97	0.9077	13.68	13.82	13.75	0.0981
Fe_2O_3	2.30	2.05	2.18	0.1727	1.85	1.84	1.84	0.0060
MnO	0.03	0.03	0.03	0.0007	0.00	0.00	0.00	0.0000
MgO	1.69	1.45	1.57	0.1690	1.20	1.20	1.20	0.0008
CaO	1.24	1.16	1.20	0.0538	0.94	0.95	0.94	0.0085
Na_2O	1.86	1.69	1.77	0.1202	0.62	0.60	0.61	0.0141
K_2O	2.90	2.65	2.78	0.1757	2.56	2.60	2.58	0.0292
P_2O_5	0.03	0.07	0.05	0.0281	0.03	0.02	0.03	0.0005
SO_3	0.12	0.21	0.17	0.0667	0.04	0.04	0.04	0.0030
Cr_2O_3	0.01	0.01	0.01	0.0007	0.00	0.00	0.00	0.0013
NiO	0.01	0.01	0.01	0.0009	0.00	0.00	0.00	0.0000
LOI	7.28	8.07	7.67	0.5577	9.04	9.17	9.10	0.0897
Si/Al			6.29				5.74	
Total	99.14	99.58	99.36	0.3154	100.00	100.00	100.00	0.0000

Table 4.1 b): Trace elemental analysis of the South African clinoptilolite (SC) obtained from XRF.

	Traces in ppm
Ba	2129.88±4
Sr	2285±70
Zr	491.7±1
Mn	139.7±1
Rb	139.4±5
Zn	70.8±1.4
Pb	63.1±0.7
Y	61.6±0.7
Cr	26.5±1.4
Ni	20.8±0.7
V	13.6±0.1
U	11.7±0.7
Sc	6.8±0.1
Cu	6.2±0.1
Co	5.3±0.1
Mo	1.1±0.7

Table4.2 a): Major oxides and analysis of the Turkish clinoptilolite untreated (TC–U) treated Turkish clinoptilolite (TC-T) and Standard deviations (STDEV) from XRF

Majors wt %	**CT-U1**	**CT-U2**	**Mean**	**STDEV**	**CT-T1**	**CT-T2**	**Mean**	**STDEV**
SiO_2	69.11	70.12	69.62	0.7173	71.64	71.54	71.59	0.0740
TiO_2	0.08	0.13	0.10	0.0345	0.09	0.08	0.08	0.0013
Al_2O_3	11.73	11.78	11.76	0.0383	11.52	11.54	11.53	0.0156
Fe_2O_3	0.97	1.39	1.18	0.2984	0.96	0.96	0.96	0.0068
MnO	0.04	0.06	0.05	0.0134	0.01	0.01	0.01	0.0006
MgO	1.06	1.31	1.18	0.1758	0.96	0.95	0.95	0.0043
CaO	2.99	3.10	3.04	0.0778	2.04	2.06	2.05	0.0162
Na_2O	0.56	0.41	0.49	0.1006	0.17	0.18	0.18	0.0044
K_2O	2.40	2.52	2.46	0.0865	2.11	2.10	2.11	0.0048
P_2O_5	0.03	0.03	0.03	0.0054	0.02	0.02	0.02	0.0006
SO_3	0.01	0.04	0.03	0.0189	0.02	0.02	0.02	0.0006
Cr_2O_3	0.00	0.00	0.00	0.0020	0.00	0.00	0.00	0.0013
NiO	0.00	0.00	0.00	0.0013	0.00	0.00	0.00	0.0006
LOI	11.02	8.83	9.92	1.5442	10.45	10.53	10.49	0.0550
Si/Al			3.26				3.41	
Total	100.00	99.74	99.87	0.1860	100.00	100.00	100.00	0.0000

Table 4.2 b): Trace elemental analysis of the Turkish clinoptilolite obtained from XRF

	Traces in ppm
Sr	1042.6±1
Mn	380.4±1
Rb	346.9±1
Ba	301.79±1
Zr	266.6±2
Pb	125.3±1
Th	85.1±0.5
Y	70.1±1.2
Nb	55.3±1.2
Zn	45.3±0.4
S	34.5±1.4
Mo	15.9±0.6
U	12.4±0.3
Cr	7.7±0.1
Sc	5.0±0.6
V	3.1±0.1
Co	2.4±0.2
Cu	1.3 ±0.1

Table4.3 a): Major oxides analysis of the South African bentonite untreated (SB-U))) and treated South African bentonite (SB-T) and Standard deviations (STDEV) from XRF

Majors wt %	**SB-U2**	**SB-U1**	**Mean**	**STDEV**	**SB-T2**	**SB-T2**	**Mean**	**STDEV**
SiO_2	59.27	65.15	62.21	4.1574	63.17	67.60	65.38	3.1289
TiO_2	0.18	0.17	0.17	0.0098	0.17	0.18	0.18	0.0085
Al_2O_3	14.42	15.86	15.14	1.0169	15.03	16.09	15.56	0.7447
Fe_2O_3	2.56	2.44	2.50	0.0842	2.26	2.42	2.34	0.1121
MnO	0.08	0.06	0.07	0.0152	0.04	0.04	0.04	0.0019
MgO	2.76	2.97	2.87	0.1499	2.28	2.44	2.36	0.1129
CaO	1.74	1.77	1.75	0.0197	0.79	0.85	0.82	0.0392
Na_2O	1.31	1.76	1.53	0.3221	0.59	0.63	0.61	0.0290
K_2O	0.87	0.95	0.91	0.0557	0.86	0.92	0.89	0.0425
P_2O_5	0.03	0.04	0.03	0.0082	0.02	0.02	0.02	0.0008
SO_3	0.19	0.12	0.16	0.0512	0.04	0.04	0.04	0.0018
Cr_2O_3	0.01	0.01	0.01	0.0031	0.00	0.00	0.00	0.0000
NiO	0.00	0.00	0.00	0.0011	0.00	0.00	0.00	0.0000
LOI	9.37	8.70	9.04	0.4740	6.217	8.782	7.499	1.8134
Si/Al			2.20				2.31	
Total	100.00	100.00			100.00	100.00	1.98	

Table 4.3 b): Trace elements analysis of the South African bentonite from XRF

Trace elements (ppm)	
Ba	776.05±1
Sr	249.25±1
Mn	186.20±1
Zr	147.23±1
Cr	101.52±1
Zn	58.27±0.7
Pb	24.35±0.7
Rb	24.09±0.7
Y	23.91±0.7
Th	21.03±0.1
Nb	15.26±0.1
Sc	6.59±0.1
Ni	5.87±0.1
Cu	3.69±0.1
U	3.6±0.1
V	1.71±0.1
Mo	1.1±0.5

Tables 4.1 a-b) and 4.3a-b) show that the natural clinoptilolite and bentonite clays are mainly composed of Si, Al and Fe with exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+}. The Si/Al ratio of South African clinoptilolite (SC) was 6.29 for the untreated sample and 5.74 for the treated sample. The South African clinoptilolite showed highest sodium content of 1.77 wt% before pretreatment and 0.61 wt% after acid treatment. High potassium content was observed before and after treatment with concentration of 2.78 wt% and 2.58 wt% respectively. The Si/Al ratio of SC decreased after pretreatment and that could be attributed to dealumination due to acid treatment but the Si/Al ratio decrease was not observed in the TC and SB. Instead an increase in Si/Al ratio was observed for TC and SB after pretreatment.

The minor elements found in the South African clinoptilolite are presented (Table 4.1 b). The highest concentrations were recorded for barium and strontium (> 2000 ppm), with significant amounts of zirconium (491 ppm), and some small amounts, above 100 ppm, of manganese and rubidium. Various other elements are present in amounts below 100 ppm. The material is mined, the plausible factors that may account for the distribution includes the geology of the area, the mining process and subsequent packaging.

The average Si/Al ratio for Turkish clinoptilolite (TC) was 3.26 before pretreatment and 3.41 after pretreatment. Turkish clinoptilolite has a low sodium content of 0.56 wt% before pretreatment and 0.18 wt% after pretreatment the treated sample. However the Turkish sample showed a high calcium content of untreated sample (3.04 wt%) , and 2.05 wt% for the treated sample and high potassium content of 2.46 wt% before pretreatment and 2.11 wt% after pretreatment. The minor elements found in the Turkish clinoptilolite are presented (Table 4.1 b). The highest concentrations are strontium (>1000 ppm), with significant amounts of manganese (380 ppm), barium (346 ppm), zirconium (266 ppm), and some small amounts of lead, (>100 ppm). Various other elements such as Zn, Cr, Cu, Co and Nb are present in amounts below 100 ppm.

The average Si/Al ratio of South African bentonite was found to be 2.20 and 2.31 for untreated and treated respectively. The South African bentonite showed highest magnesium content of 2.87 wt% before pretreatment and 2.36 wt% after pretreatment. Sodium content before pretreatment was found to 1.53 wt % but reduced to 0.61 wt% after treatment. Similar trend was observed for K where the concentration before pretreatment was 0.87 and 0.89 wt% after treatment. Ca in the bentonite was 1.75 wt% before treatment and reduced to 0.82 wt% after pretreatment. The minor elements found in the South African bentonite are presented in Table 4.3 b. The high concentrations of barium (776 ppm) and strontium (249 ppm), zirconium

(141 ppm), Chromium (>100 ppm) and various other elements are present in amounts below 100 ppm. It is clear that the South African clinoptilolite has a higher Si/Al ratio than Turkish clinoptilolite and the bentonite clay from South Africa before and after pretreatment with acid. The presence of CaO and MgO for natural zeolites is important when considering their exchange capacity because Ca^{2+} and Mg^{2+} act as exchangeable cations in the adsorption of heavy metals.

Mamba *et al*., (2010) reported on the chemical composition of naturally occurring, and extensively mined South African clinoptilolite obtained from Vulture creek, Kwazulu-Natal province, the major components reported were 70% SiO_2, 12% Al_2O_3, 2% Na_2O, 5% K_2O, 2% CaO and 2.5% Fe_2O_3 with a Si/Al ratio of 5.96 and the (Na+K)/Ca ratio of 3.4 (Mamba 2010). The higher Si/Al ratio and Ca content reported in their study did suggest that this was not the isostructural form heulandite, but may have been mordenite, and could possibly explain the large disparity between their and the current results. In addition, it should be noted that there are no 'hard and fast' rules when classifying natural zeolites, and recommendations on naming and classification are to be treated as a guideline (Coombs, 1997). Manson and Sand, (1960) compared clinoptilolite and mordernite, and reported a ratio of Si/Al≥4.0 for clinoptilolite, and they found that the sum of monovalents (Na and K) exceeded that of the divalent. The ratio of (Na and K)/Ca were found to be 4.3 and similar value was reported by Coombs *et al*., 1997). However Coombs *et al*., (1997) did advise that zeolite minerals could not be distinguished based on the Si/Al ratio but an exception can be made with heulandite and clinoptilolite due to the distinct framework topology inherent to these zeolites (Coombs *et al*., 1997)

Whether the differences can simply be explained by the geology of the area, and the mining process is beyond the scope of this project. However, some references did show that several forms of naturally occurring zeolites can be found at a particular mining site or geographical location (Manson and Sand, 1960). Clinoptilolite can be classified by Si/Al ratio. If this ratio is between 4 and 5 or greater than 4, it can be classified as clinoptilolite. Zeolites also can be classified as clinoptilolite if the criteria of (Na+K) > Ca is available (Inglezakis *et al*., 2001). In this study South African clinoptilolite could be classified as clinoptilolite according to Si/Al ratio of 6.29 for the untreated sample and 5.74 samples which is greater than 5. The Si/Al ratio of Turkish clinoptilolite was 3.26 before pretreatment and 3.41 after pretreatment and these values are below 5 thus could not be classified according to its Si/Al and also the (Na+K)> Ca criteria was not met by the Turkish. However Coombs *et al*., (1997) did advise that zeolite minerals could not be distinguished based only on the Si/Al ratio. In appendix A1, A2, A3 it observed that after pretreatment of natural adsorbents with acid the Al and Si are still present the adsorbents with some cations such Mg, Ca and K meaning the acid washing did remove all the cations and didn’t remove Si and Al.

4.1.2 Brine Composition

The brine solutions (see section 3.2.2 for analysis details) collected from the Emalahleni RO plant and RO desalination plant at Tutuka power station was adopted from (Fatoba, 2011) for comparison South Africa were analysed by ICP-AES. The initial Emalahleni brine and Tutuka brine compositions prior contact with the adsorbents (SC, TC and SB) are provided in Tables 4.4 and 4.5 respectively.

Table 4.4 a): Composition of the Emalahleni RO brine (concentration in ppm except pH and EC (mS/cm)) major and minor elements

Major elements	Concentration (ppm)
B	8.24 ±2.0
Ca	71.71 ±0.9
K	108.75 ±1
Mg	133.66 ±1
Na	4323.71 ±95
Cl	17.55 ± 0.3
SO_4^{2-}	65.93± 0.3
pH	8.54± 0.0
EC (mS/cm)	15.83 ± 0.5

Table 4.4 b) Minor elements analysis of the Emalahleni RO plant

Minor elements	Concentration (ppm)
Al	1.14 ± 0.1
As	0.13 ± 0.3
Ba	0.05 ± 0.0
Cd	0.03 ± 0.1
Co	0.03 ± 1.4
Cr	0.06 ± 0.1
Cu	0.39 ±0.1
Fe	0.10 ± 0.1
Mn	0.01 ± 0.1
Mo	0.25 ± 0.1
Ni	0.20 ± 0.1
P	1.80 ± 0.7
Se	0.24 ± 0.9
Sr	3.30± 0.3
Ti	0.05 ± 0.2
V	0.13 ±0.2
Zn	0.46 ± 0.1

Table 4.4 c): Elemental composition Emalahleni brine (stage 3)

Anions	Concentration (ppm)
Bromide	0.249 ± 0.005
Chloride	17.5 ±0.308
Fluoride	0049 ±0.003
Sulfate	65.25 ± 0.320

The chemical composition (major, minor and trace species) of Emalahleni brine used in this study was determined using ICP-AES and IC analytical techniques and the results are presented in Table 4.4(a-c) above. It was observed that the concentration of major species Na was 4323.71 ppm. The other major elements are Mg, Ca and K in the range of 100 to 700 to ppm. The minor and trace elements present in the brine are B, Al, P, Fe, Sr, Li, Ti, Hg, Mn, Ni, Cu, Zn, Mo, Ba and P (concentrations ranging between 0.1 to 66 ppm).

Table 4.5 : Composition of the Tutuka RO (concentration in ppm except pH and EC (mS/cm)) major and minor elements adopted from (Fatoba, 2011)

Major elements (ppm)	
Al	0.045 ± 0.1
Ca	106.99 ± 12
K	106.2 ± 1
Mg	163.36 ± 1
Na	4804.88 ± 3
Si	13.11 ± 0.1
Cl	2424 ± 17
SO_4^{2-}	8858 ± 86
pH	7.75 ± 0.0
EC (mS/cm)	16.69 ± 0.5
TDS	5400± 283
Minor elements (ppm)	
B	2.24 ± 0.0
As	0.0068 ± 0.0
Ba	0.057 ± 0.0
Cd	0.00017 ± 0.0
Co	0.014 ± 0.0
Cr	0.014 ± 0.0
Cu	0.26 ± 0.1
Fe	0.24 ± 0.2
Mn	0.0017 ± 0.0
P	0.82 ± 0.3
Pb	0.0039 ± 0.0
Se	0.0049 ± 0.0
Sr	3.055 ± 0.1
Ti	0.00069 ± 0.0
V	0.019 ± 0.0
Zn	0.13 ± 0.0

It was observed that the Emalahleni brine and Tutuka brine are not significantly different in terms of their chemical composition. However the Tutuka brine composition has higher concentrations of Na, Ca, Mg and K than the Emalahleni brine and also has higher S composition. The Tutuka brine was used only to study optimum pH in this study because there was not enough sample of the Emalahleni brine to conduct this particular test, whereas Emalahleni brine was used throughout the study. However the Emalahleni brine pH is slightly higher than the Tutuka brine with 8.54 and 7.75 respectively. The Emalahleni brine used in this study was less saline than the Tutuka brine.

4.1.3 Morphology characterization of the natural adsorbents

The morphology analysis of natural adsorbents before and after acid treatment was done using scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM).

4.1.3.1 Scanning electron microscopy analysis

The SEM analysis was performed in order to determine the morphological changes brought about by acid treatment. Figure 4.1 shows the scanning electron microscope (SEM) images of the South African clinoptilolite (SC), Turkish clinoptilolite (TC) and South African bentonite (SB) aggregated particles.

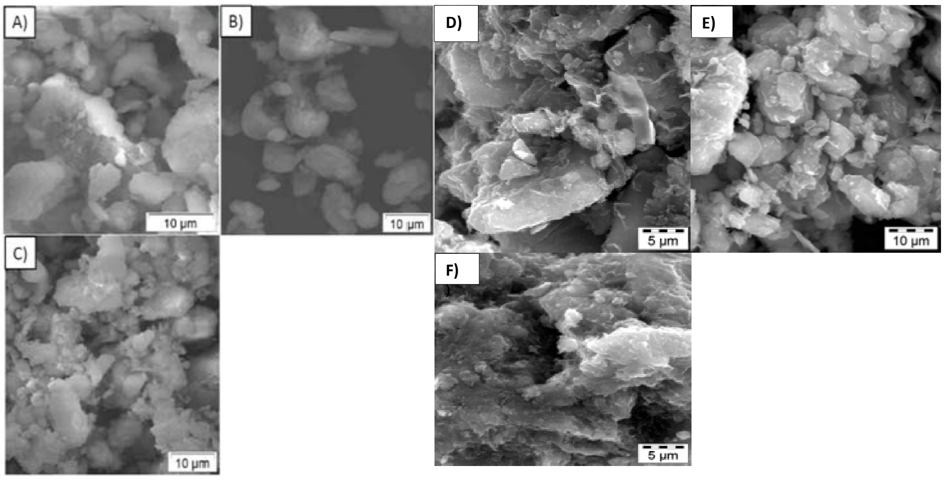


Figure 4.1: Scanning electron microscopy micrographs of untreated a) SC, (b) TC and (c) SB and Figure 4.2 : 0.02 M HCl treated d) SC, (e) TC and (f) SB.

Figure 4.1 (a & b) shows the original clinoptilolite from South Africa and Turkey respectively. There was no crystalinity observed on the surfaces of the adsorbents. The crystalline calcium sites are where most ion-exchange takes place, in the case of original clinoptilolite (Mamba *et al*., 2010). All three images shown in Figure 4.1 show various sized agglomerated particles with different geometries, however the characteristic layered structure of clay platelets expected for the bentonite sample which is often seen with clay minerals is not visible at this resolution. The crystal structures of the clinoptilolite material from South Africa are also not clear. This could be attributed to the impure mineral phase in the South African clinoptilolite as it will be shown in the qualitative and quantitative XRD in section 4.2.

After pretreatment the SC image before and after treatment are not the same there is a noticeable change in morphology from smooth surface into holes and voids on Figure 4.1 image A and Figure 4.2 image A in the surface. And it was also stated by Mamba *et al*., (2010) stated that HCl-treatment is able to eliminate the particles that clog the pores of the natural adsorbent thus improving its adsorption and ion-exchange properties However the South African materials did not show an open structure after acid treatment at this resolution. The crystalinity of the natural adsorbents was also studied with HRTEM in the next section. Pretreatment of the natural adsorbents was expected to have an effect on their morphology, to open more pores by exchange of cations.

4.1.3.2 High resolution transmission emission microscopy analysis

The porous well structured crystalline zeolitic material and natural clays formed during the pretreatment was also confirmed by the use of High Resolution Transmission Microscopy (HRTEM) analysis as shown in Figure 4.3

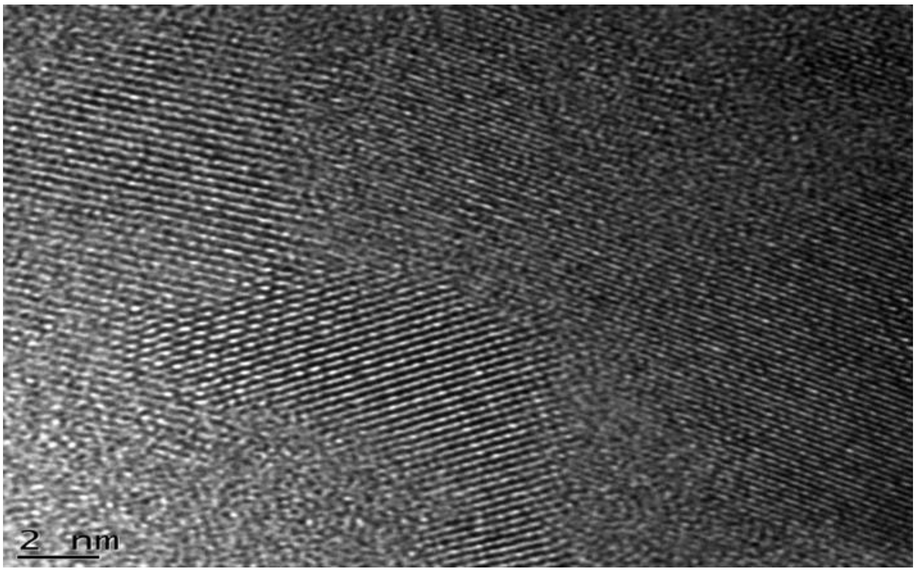


Figure 4.3: HRTEM images of untreated SC

Figure 4.4: HRTEM images of 0.02 M HCl treated a) SC, b) TC and c) SB

Figure 4.3 above shows untreated sample of SC with aligned fringes in one direction showing that the material is polycryastalline , however the Figure 4.4 a) above, the SC shows that fringes are changing in different directions which indicates that the material structure is not monocrystalline, but polycrystalline and as indicated in Figure 4.5. This indicates that the material is crystalline. Figures 4.4 b) and 4.4 c) showed that the materials are electron sensitive under the beam (Terasaki, 1993). The images did not show fringes that are aligned but TC shows crystalinity as shown in selective area diffraction images given in Figure 4.4 b) below where the diffraction spots are aligned and not random showing large crystals whereas the other materials show diffuse rings indicating polycrystallinity

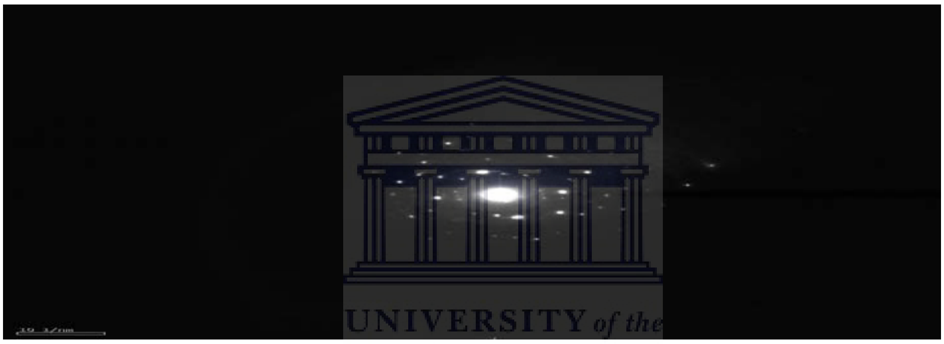


Figure 4.5: Diffraction images of untreated SC showing crystalinity

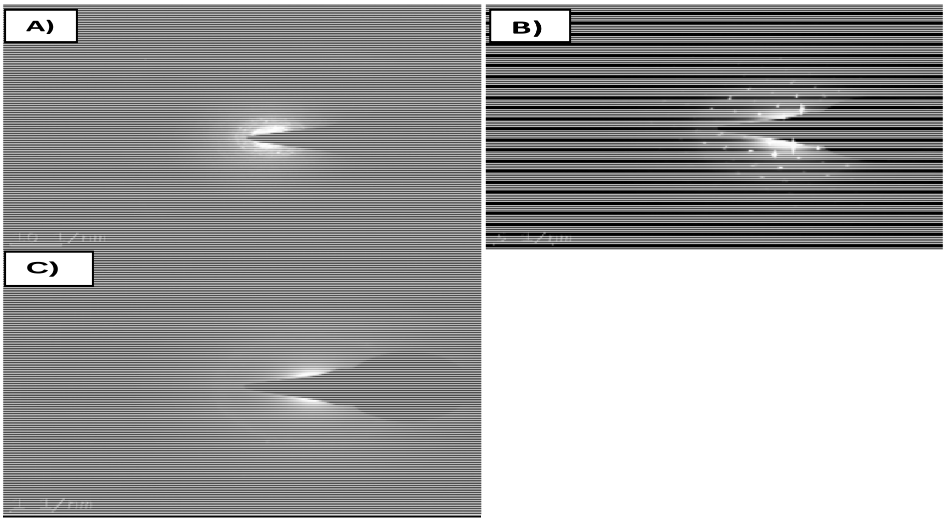


Figure 4.6: Diffraction images of 0.02 M HCl treated a) SC, b) TC and c) SB showing crystalinity

Figure 4.6 above shows diffraction images of the three natural adsorbents (SC, TC and SB). The TC is the one that shows more ordered crystalinity with the spots in figure 4.6 b) the material is considered monocrystalline. In figure 4.6 a) the SC shows crystalinity but the material shows that it is polycrystalline while SB is not showing any crystalinity in the diffraction images above. The natural clinoptilolites from both South Africa and Turkey were thus crystalline as shown by the HRTEM analysis whereas bentonite clay's crystalinity was not clearly observed.

4.2 Qualitative XRD spectra analysis

The mineral phases identified by X-ray Diffraction (XRD) in the natural adsorbents, bentonite clay (SB), clinoptilolite (SC and TC) and attapulgite clay (AS) are presented in the sections that follow.

4.2.1 Mineralogical composition of natural zeolites and natural clays

The qualitative and quantitative X-ray diffraction (XRD) patterns of the samples used throughout the studies is demonstrated in Figure 4.7 (a-d). Characteristic clinoptilolite and bentonite peaks in the XRD pattern are indicated on the Figure 4.7 (a-d) below.

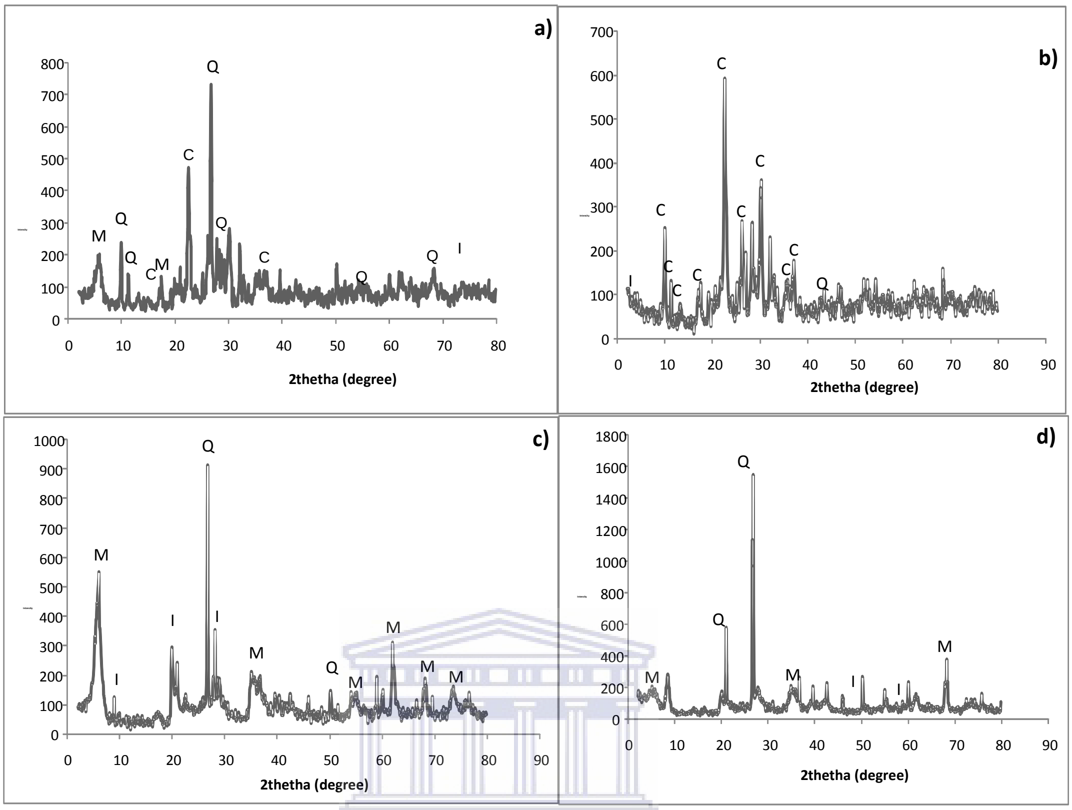


Figure 4.7: X-ray diffraction spectra a) SC b) TC c) SB and d) AS (Q=Quartz, C= clinoptilolite, M = montmorillonite and I= illite)

The above X-ray diffraction data clearly shows that the clinoptilolite from Turkey is more pure than the clinoptilolite from South Africa which contained some quartz as an impurity as can be seen in figure 4.7 a) above. The bentonite from South Africa has some non-clay mineral impurities such as quartz. From the above Figures it observed that TC is more pure than SC and the bentonite clay has more Montmorillonite phases than impurities such quartz and illite.

4.2.2 Quantitative X-ray diffraction analysis

Quantitative X-ray Diffraction (XRD) was performed to identify the percentage of clay or zeolite material present in one adsorbent in order to determine how much of other minerals are present in clay or zeolite. The samples were prepared as described in section 3.2.3.1 a). The quantitative X-ray diffraction (XRD) data of natural clays and natural zeolite shows that the natural materials were not pure mineral phases as can be seen from Figure 4.8-4.11 below.

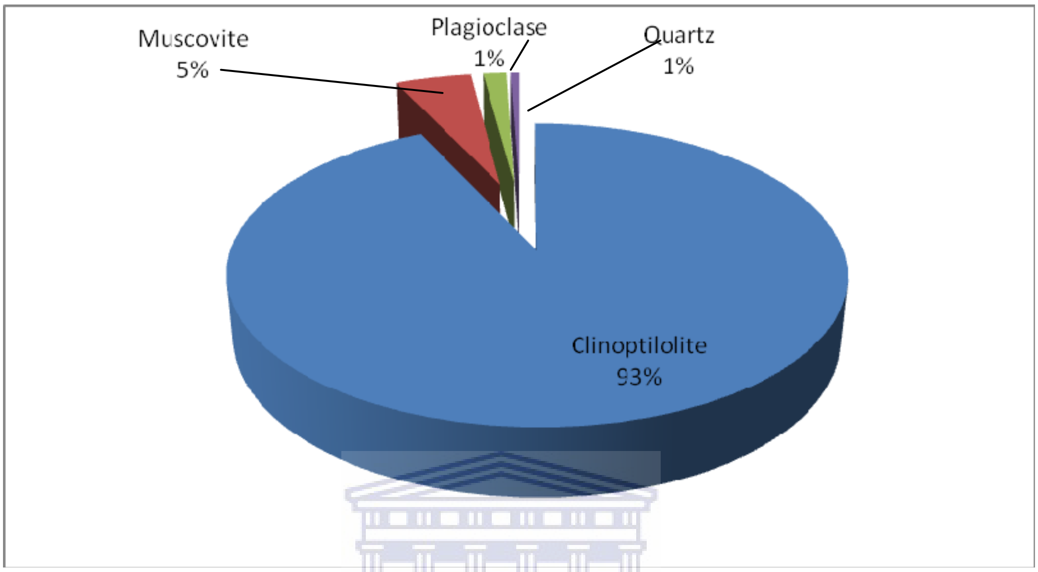


Figure 4.8: Quantitative XRD of Turkish clinoptilolite (TC)

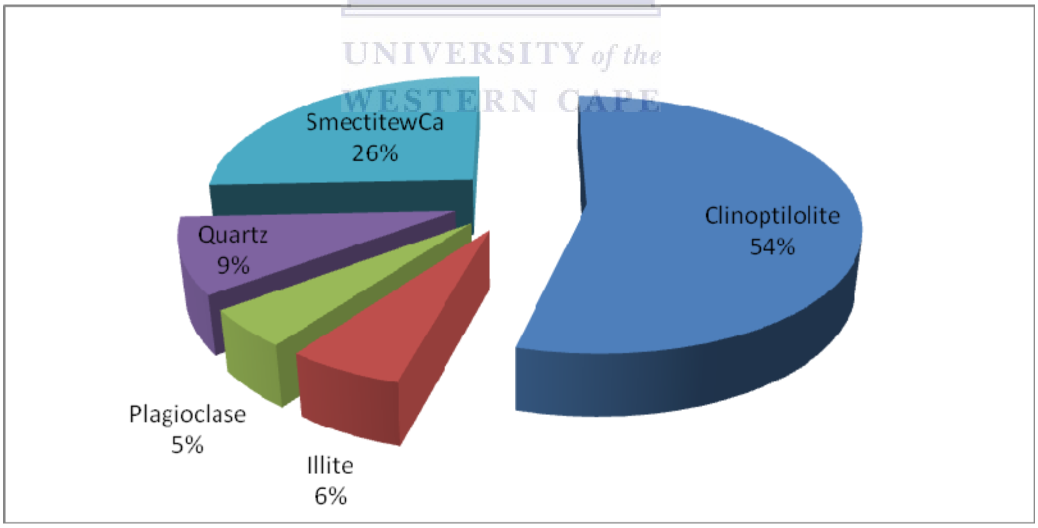


Figure 4.9: Quantitative XRD of South African clinoptilolite (SC)

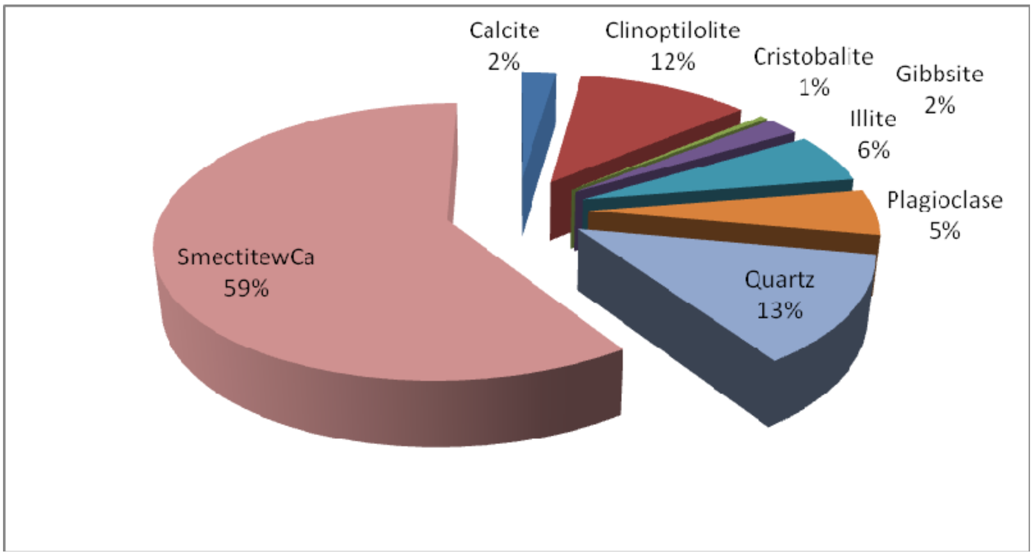


Figure 4.10: Quantitative XRD of South African bentonite (SB)

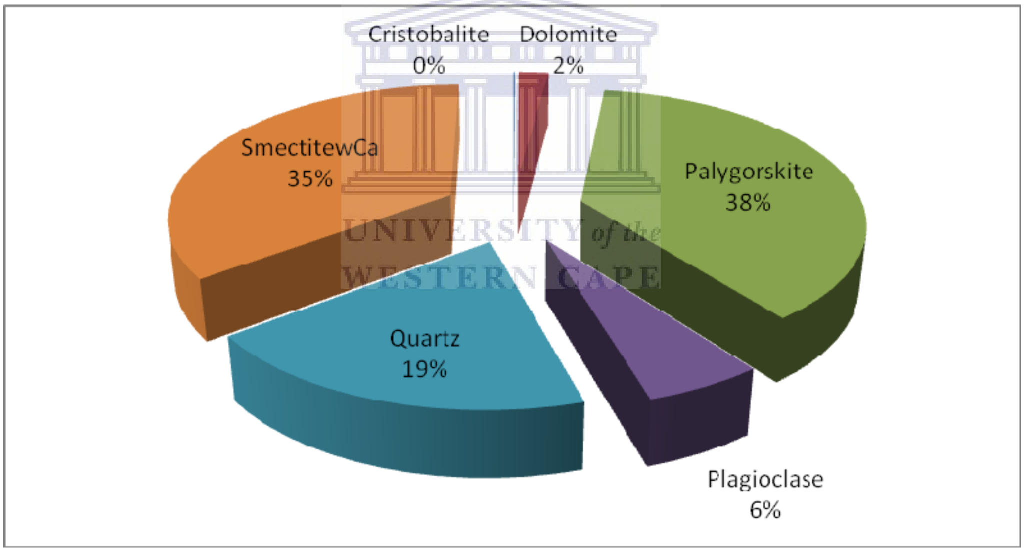


Figure 4.11: Quantitative XRD of South African attapulgite (AS)

(Smectitedi1wMg) denotes lower smectite spacing with magnesium and (Smectitedi1wCa) denotes denotes lower smectite spacing with calcium. Quantitative XRD showed that the South African deposits of clinoptilolite and bentonite contained significant amounts of other dimensional phases such as smectite, quartz and illite, compared to the Turkish clinoptilolite. Hence it would be necessary to establish the cation exchange capacity and the performance as adsorbent of these locally mined materials. As shown in Figures 4.8 and 4.9 Turkish clinoptilolite is more pure containing 93% clinoptilolite than the South African clinoptilolite which only contained 54% of clinoptilolite. South African clinoptilolite also contains quartz; this result was confirmed by the qualitative XRD where other phases were present and not only clinoptilolite phases, and also by the Cation exchange capacity (CEC) results (in section 4.3.1) which show Turkish clinoptilolite having higher CEC than the South African clays and natural zeolite.

4.3 Determination of cation exchange capacity

This method was used for determining cation exchange capacity and measuring exchangeable cations and it is the method of interest in this study. The weight of the zeolite sample used to determine the cation exchange capacity was 0.5 g as specified in (Section 3.2.7) (Radojević & Bashkin, 1999).

4.3.1 Cation exchange capacity

In this section, the results obtained during CEC experiments (see section 3.2.7) which were conducted to determine the cation exchange capacity of natural clays and natural zeolite are discussed. The concentrations of cations obtained from ICP-AES analysis were converted to meq (milliequivalents) per gram of sample as follows (Radojević & Bashkin, 1999)

Mass (mg) of cation per gram of zeolite = Volume (L) x C_{ca} / (weight of zeolite sample used)

Where C_{ca} is the concentration of cationic species in the sample extract in mg/l^{-1}

Therefore, meq of cation g^{-1} of sample = [Volume (L) x C_{ca}/ (weight of zeolite sample used)] / (equivalent weight of the cation)

Equivalent weight of the cation is the mass needed to provide 1 mole of charge or atomic weight divided by the valence.

Therefore:

MeqCa g^{-1} sample = [0.1 x C_{ca} / 0.5] / 40.0

Meq Mg g^{-1} sample = [0.1 x C_{ca} / 0.5] / 24.4

Meq Na g^{-1} sample = [0.1 x C_{ca} / 0.5] / 23.0

Meq K g^{-1} sample = [0.1 x C_{ca} / 0.5] / 39.1

The calculated milliequivalents per g of each cation (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) was summed up to get the total cation exchange capacity (CEC) of the zeolitic and clay material.

Various zeolites including clinoptilolite have been shown to have a preference for the ammonium ion over Na^+, Ca^{2+} and Mg^{2+}; but having a greater selectivity for K^+ than the ammonium ion (Collela, 1996). It is this selectivity that can be exploited in determining the CEC of zeolites. Figure 4.12 gives a comparison of the CEC values obtained for natural zeolite clinoptilolite from South Africa (SC), natural zeolite clinoptilolite from Turkey (TC), bentonite clay from South Africa (SB) and attapulgite clay from South Africa (AS). The procedure used to obtain the CEC results was adopted from (Amrhein *et al*., 1996) and optimised because the procedure was for fly ash not clays or zeolites. The experiment was performed in triplicate for reproducibility

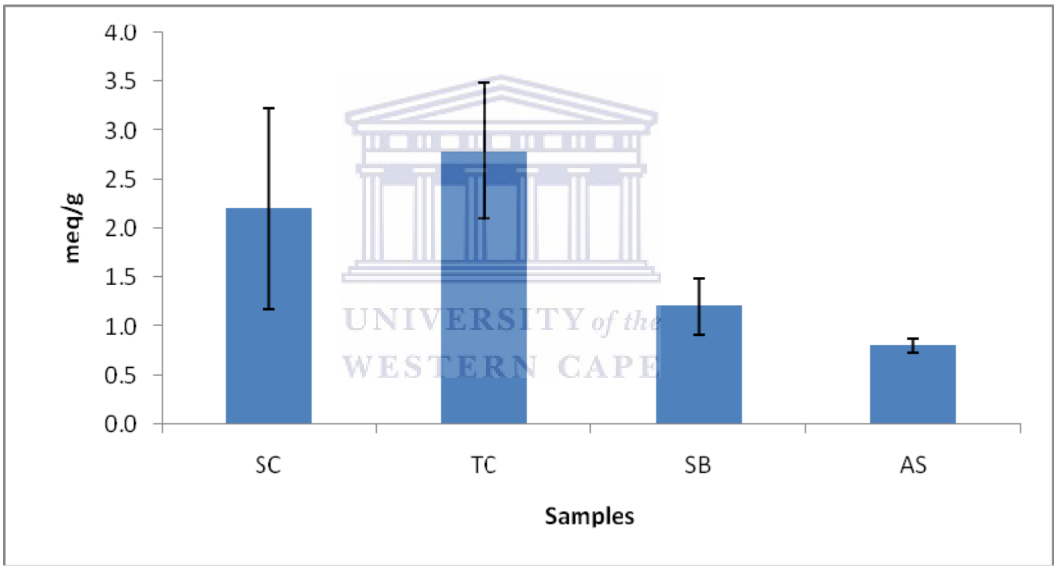


Figure 4.12: Total cation exchange of South African clinoptilolite (SC), Turkish clinoptilolite (CT), South African bentonite (SB) and South Africa attapulgite (AS)

In Figure 4.12 above, the results of CEC for natural adsorbents showed that the Turkish clinoptilolite have a higher cation exchange capacity of 2.8 meq/g than the South African clinoptilolite which had a CEC of 2.2 meq/g and South African bentonite (SB) which had a CEC of 1.2 meq/g and attapulgite clay (AS) with the lowest CEC value of 0.8 meq/g.

Natural zeolites have CECs from 2 to 4 milliequivalents (meq/g), about twice the CEC of bentonite clay (Mumpton, 1999). Unlike most non crystalline ionexchangers, e.g. organic resins and inorganic aluminosilicate gels (mislabelled in the trade as ‘‘zeolites’’), the framework of a crystalline zeolite dictates its selectivity toward competing ions such as K^+, Ca^{2+}, Mg^{2+} and Na^+. The hydration spheres of high field-strength cations prevent their close approach to the seat of charge in the framework; hence, cations of low field strength are generally more tightly held and selectively exchanged by the zeolite than other ions.

Clinoptilolite is reported to have a relatively small CEC (2.25 meq/g) but within the range of 2 to 4 (meq/g) according to Mumpton, (1999), but its cation selectivity is $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$ (Mumpton, 1999). The CEC values obtained for South African clinoptilolite in this study are higher than those reported by Schoeman, (1986). The higher values obtained can be attributed to the smaller particle size of the adsorbents (106 μm) used in this study compared to the particle size 500 – 1000 μm of the adsorbents in the work reported by Schoeman, (1986), and the deviation from theoretical values is most likely due to imperfections and impurities in the natural sample and diffusional constraints in larger particle sizes. The particle size has an effect on CEC, the smaller the particle the higher the CEC. The Turkish clinoptilolite showed higher CEC than South African clinoptilolite and that could be attributed to its purity as shown by the XRD.

4.4 N_2- BET (Brunauer-Emmett-Teller)

Figure 4.13-4.14 presents the results obtained for N_2-BET surface area, pore diameter and volume of the natural zeolite (clinoptilolite) from South Africa (SC), natural zeolite clinoptilolite from Turkey (TC), bentonite clay from South Africa (SB) and attapulite clay from South Africa (AS).

Table 4.6: The BET Surface area, micropore, mesopore and macropore untreated of natural adsorbents.

Adsorbent	**BET surface area m^2/g**	**Micropore m^2/g**	**Mesopore m^2/g**
SC	51.21	12.792	38.42
TC	38.80	3.139	35.66
SB	56.15	9.617	46.53
AS	125.96	2.526	23.431

Table 4.6 shows that the surface area of the material before pretreatment of SC (51.21 m^2/g), TC (38.80 m^2/g), SB (56.15 m^2/g) and AS (125.96 m^2/g). However these natural adsorbents needed to be activated to increase their surface areas before they can be used for adsorption purposes as it can be seen above their surface areas are low in the natural form without pretreatment. Attapulgite is the natural adsorbent with a higher surface area. However South African clinoptilolite showed higher surface area than the Turkish clinoptilolite. The SC has more micropores than the TC, SB and AS, however it was observed that SB has more mesopores and the SC has more mesopores than the TC as seen in Table 4.6 above showing the South African adsorbents are more porous than the Turkish adsorbent.

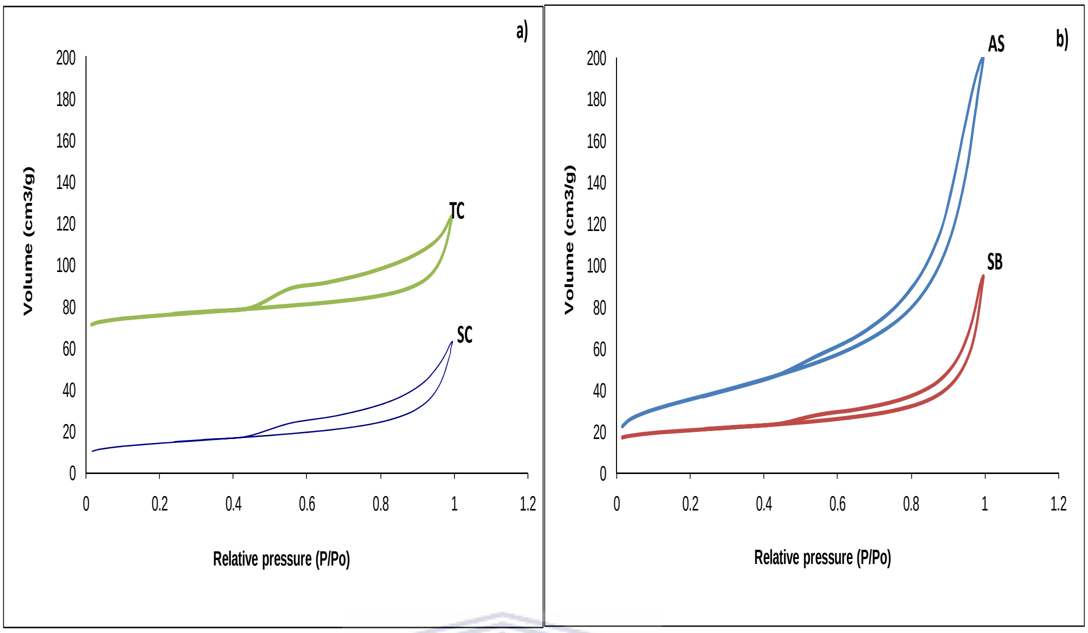


Figure 4.13: Adsorption/desorption isotherms for the SC, TC, SB and AS

These isotherms were used to calculate the specific surface area by the BET method. Zeolites are microporous materials with voids smaller than 2 nm in diameters. The zeolite pore space is filled in volumetric manner rather than a layer-layer mechanism because of proximity of the surrounding pore walls to the adsorbate molecules. The sorption uptake increases with pressure, saturation of each pore domain with adsorbate molecules depends not only on the size and shape of microporous channels and cavities, but also size and geometry of the adsorbate molecules (Korkuna *et al*., 2006). Based on the classification the adsorption isotherms, all the measured isotherms for the natural adsorbents can be considered as isotherms type V. The BET results shown above indicate that these natural adsorbents are microporous because of their hysteresis loops starting above 0.4. Figure 4.13 a) and b) shows that these natural adsorbents show type V isotherms that shows condensation and hysteresis. The initial part of these isotherms shows micropore filling (Lowell *et al*., 2006). Type V isotherm observed for water vapour adsorption.

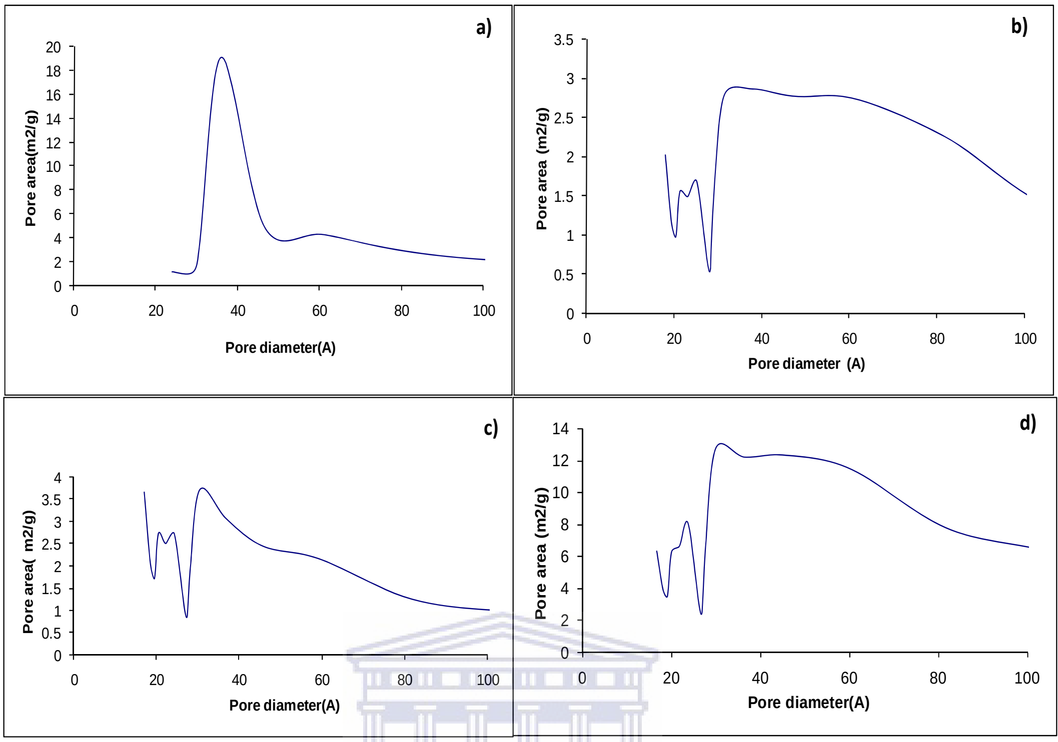


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Figure 4.14: BJH dA/dV pore area of a) SC, b) TC, c) SB and d) AS

The pore distribution was determined by BJH method. The BET results shown above indicate that these natural adsorbents are microporous as well as mesoporous because they have hysteresis loop and their pore size distribution is between 20 and 80 Å. The SC in Figure 4.14 a) shows a mesoporous pore size distribution before pretreatment.

4.5 Preliminary adsorption experiments

The results for the preliminary adsorption experiment (experimental details in section 3.3.1) are discussed in this section. The experiment was performed with 50 ppm initial concentration of brine and 0.5 g adsorbent dose. Figure 4.15 (a-d) shows the removal of major elements from Emalahleni brine at 2 hr and 24 hr contact time.

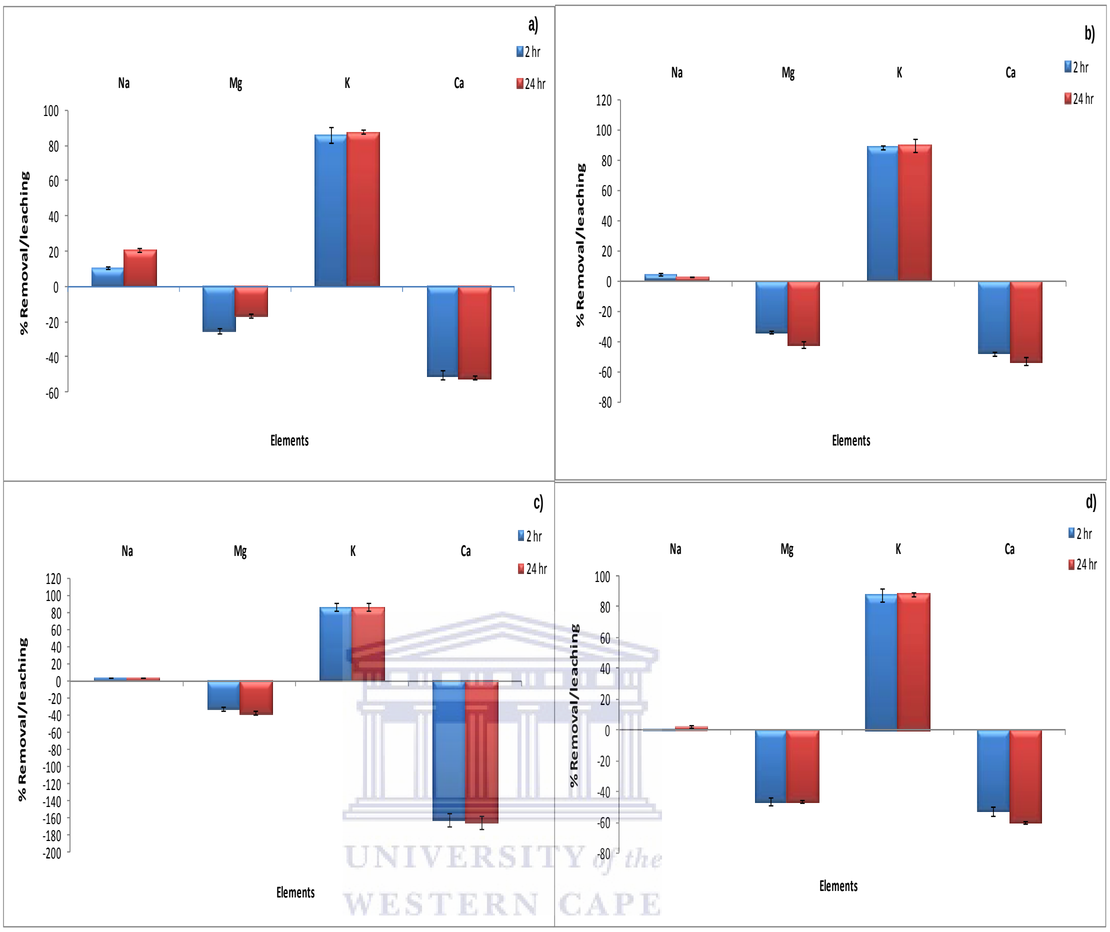

Figure 4.15: Percentage removal efficiency of major elements from brine using a) SC b) CT c) SB and d) AS

The removal of major elements from Emalahleni brine is shown in Figure 4.15 (a-d) above. Significant amounts of the major exchangeable cations Mg^{2+} and Ca^{2+}, contained in the adsorbents were leached/exchanged out of the adsorbents during the testing period. Clinoptilolite from South Africa showed above 20 % Na^{+} removal in 24 hr contact time and the bentonite from South Africa showed highest removal efficiency of K^{+}. It is evident that these natural adsorbents are able to adsorb univalent elements when they are untreated and leaches out divalent ions such as Mg^{2+} and Ca^{2+}. The results above are consistent with the XRF results. The untreated Turkish clinoptilolite (TC-U) was able to adsorb about 5 % of Na^{+} and about 86 % of K^{+} however leaching Ca^{2+} (162 %) and Mg^{2+} (37 %) into the solution was observed.

The XRF results showed that the Turkish adsorbent has high Ca^{2+} content compared to the South African clinoptilolite. South African clinoptilolite XRF data showed that this adsorbent has high Na^+ and K^+content but it was able to adsorb the cations instead of leaching them out, thus there was competitive adsorption. These natural adsorbent thus needs activation prior adsorption because it clearly observed that they leach more elements than adsorbing in their untreated form. Figure 4.16 (a-d) shows preliminary changes in concentration of selected trace elements in Emalahleni. Elements that did not vary by at least 1 ppm from the real brine concentration from Emalahleni are not included in the figure. Initial (Init) represents the raw brine, 2 hr represents after contacting the adsorbent with the raw brine for 2 hr and 24hr represents after contacting the adsorbent with the raw brine for 24hr.

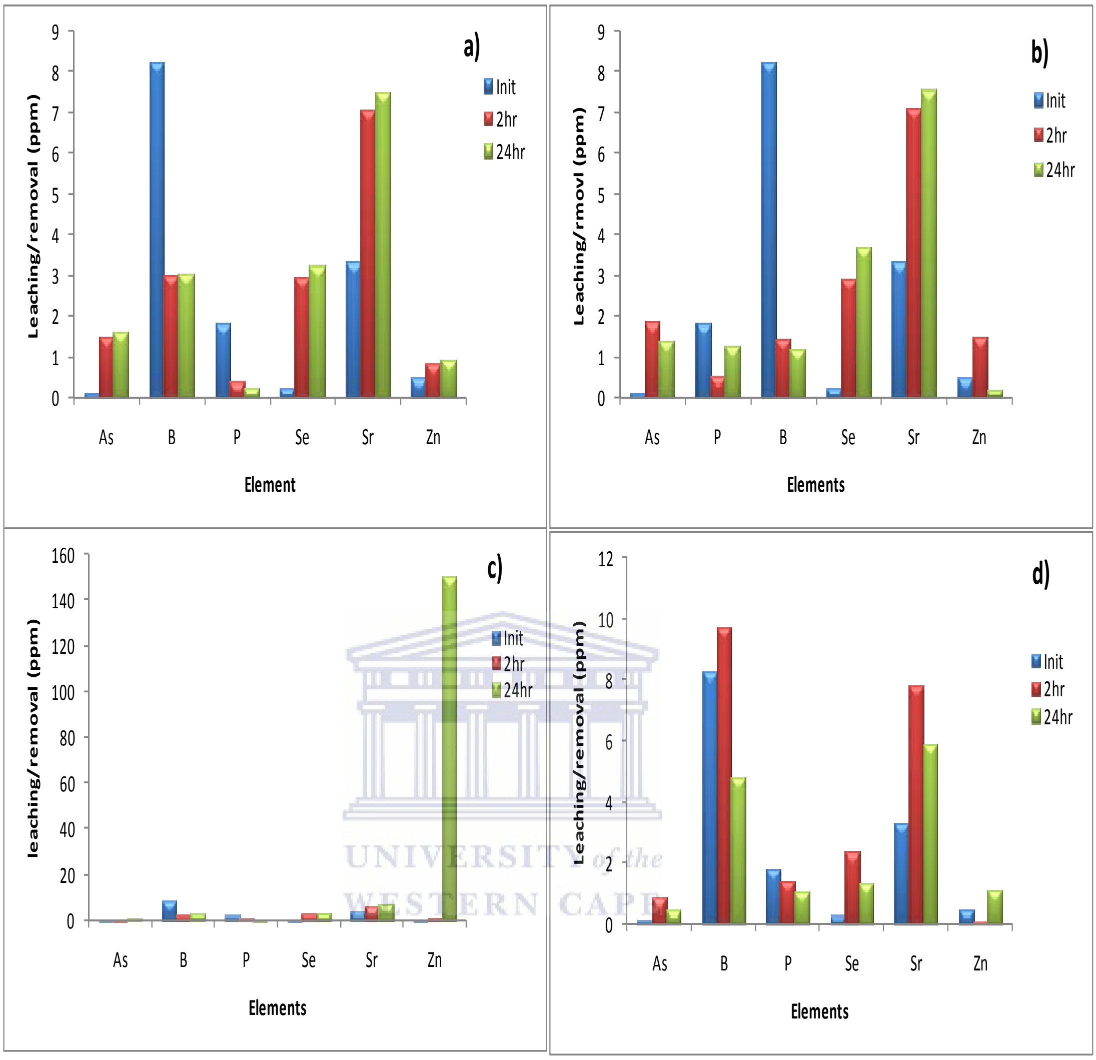

Figure 4.16: Changes in concentration of selected trace elements after a) SC b) TC c) SB and d) AS adsorbents are contacted with the raw brine (Init), after 2hr and 24hr contact times.

Figure 4.16 d) shows that B was not adsorbed at 2hr instead it leached out but was adsorbed again after 24hr, and Figure 4.16 a, b and d) shows that some trace elements (Se, Sr and B) were leached from the natural clinoptilolite and bentonite clay however these natural adsorbents were able to adsorb B in the 2 hr and 24 hr contact time in Figure 4.16 (a,b and c) shown above. South African clinoptilolite and attapulgite clay were able to adsorb P. Some of the clays and zeolite were able to reduce the concentration of some metals (Table 4.7); which is a promising result for these low cost materials. This aspect will require further optimization. The bentonite and attapulgite clay from South Africa leaches out Fe and V respectively after 2 hr and 24 hr contact time, meaning that the V is leaching from the attapugite clay. However the concentration of metals leached were below the target DWAF limit

Table 4.7: Change in brine concentration of iron and vanadium (ppm)

Element	Initial brine content	2hr contact	24 hr contact	Adsorbent
V	0.129	0.557	0.306	Attapulgite SA
V	0.129	0.000	0.000	Clinoptilolite Turkish
Fe	0.097	0.000	0.000	Attapulgite SA
Fe	0.097	0.000	0.000	Clinoptilolite Turkish

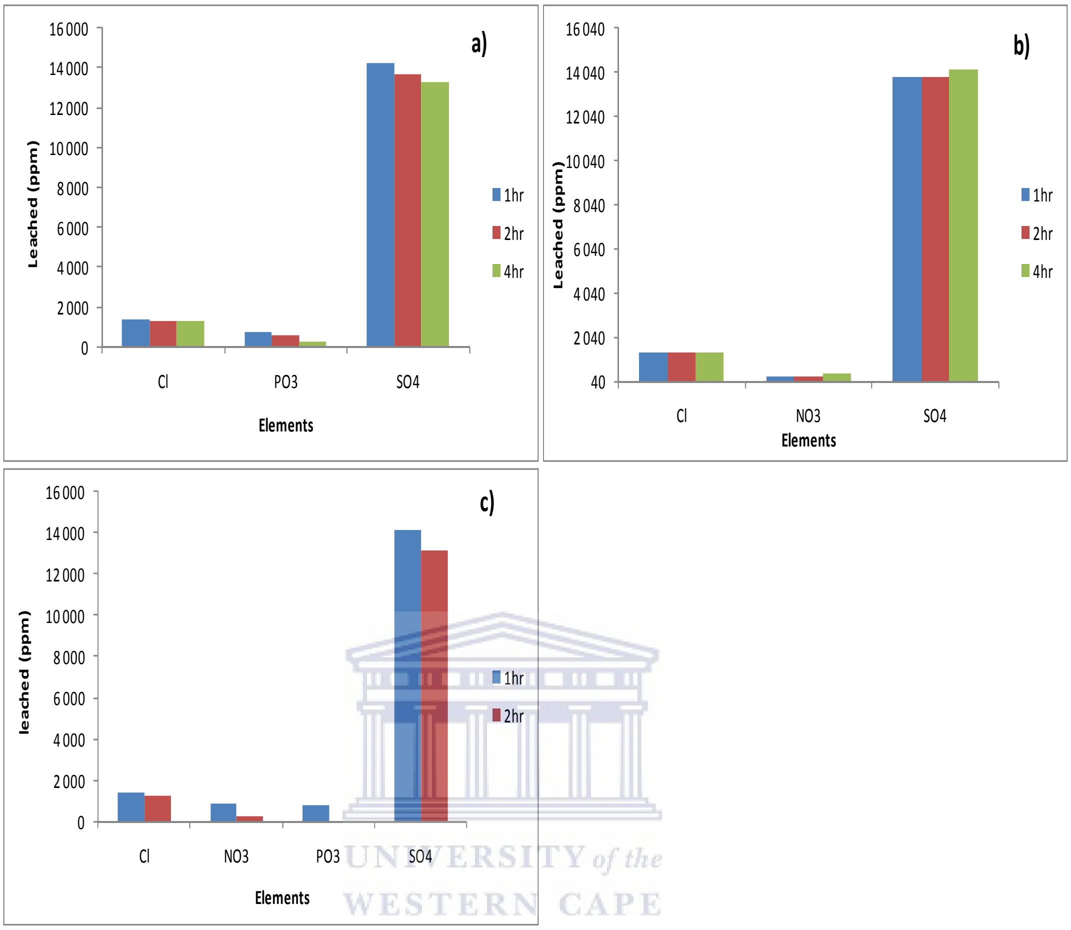

Figure 4.17: Leaching of anions from a) SC b) TC c) SB after contact with brine

The removal of anions using SC, TC and SB natural adsorbents in Figure 4.17 (a-c) above shows that Turkish clinoptilolite and South African bentonite were not able to adsorb anions that were in the Stage 3 brine from Emalahleni in the 2 hr and 4hr contact time. These natural adsorbents leached phosphate and chloride into the brine solution instead of adsorbing and that is because of high pH of the brine thus when in contact with the natural adsorbents the surface of the adsorbents became negative and repelled anions and could only adsorb cations.

The toxic element leachability is an important factor as zeolite and clays should not contaminate the water they intend to treat (Petrik *et al.*, 2007). The conducted experiments using the dosage (50 g/mL) of impure zeolite P showed some toxic elements such as Pb , Cd, Mn, Mo and Sr leached out from the impure phase zeolite P into the treated water solution. Chlorides and phosphate in this study were found to be leaching out of these adsorbents (SC, CT and SB) as shown in figure 4.17 (a-c).

4.6 Leaching experiments

The results for the leaching experiments based on details in the section 3.3.2 are discussed in this section. These experiments were conducted to investigate what elements are being leached out by the natural clays and natural zeolites during adsorption. The negative values in the graphs below shows that elements were readsorbed or removed by the natural adsorbents.

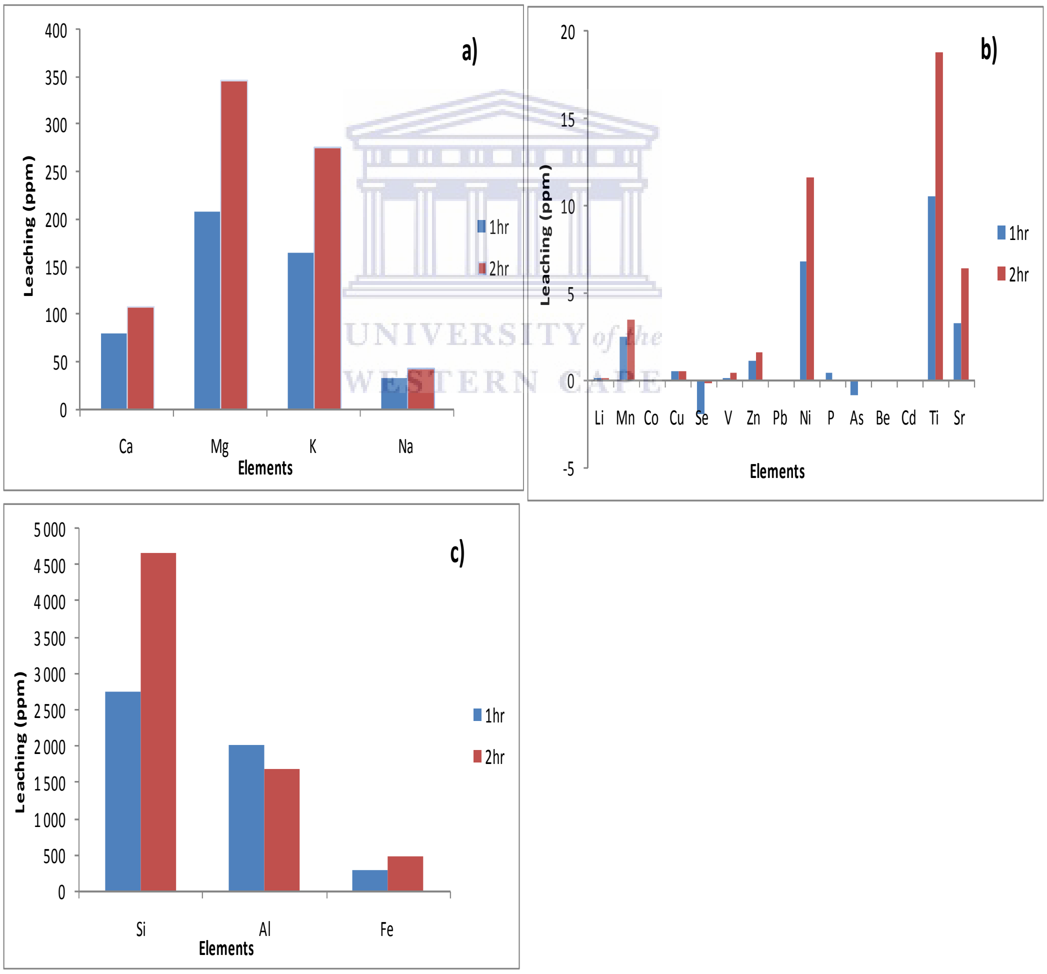

Figure 4.18: Leaching of a) major elements b) trace elements c) Si, Al and Fe from the South African clinoptilolite after contact with deionised water.

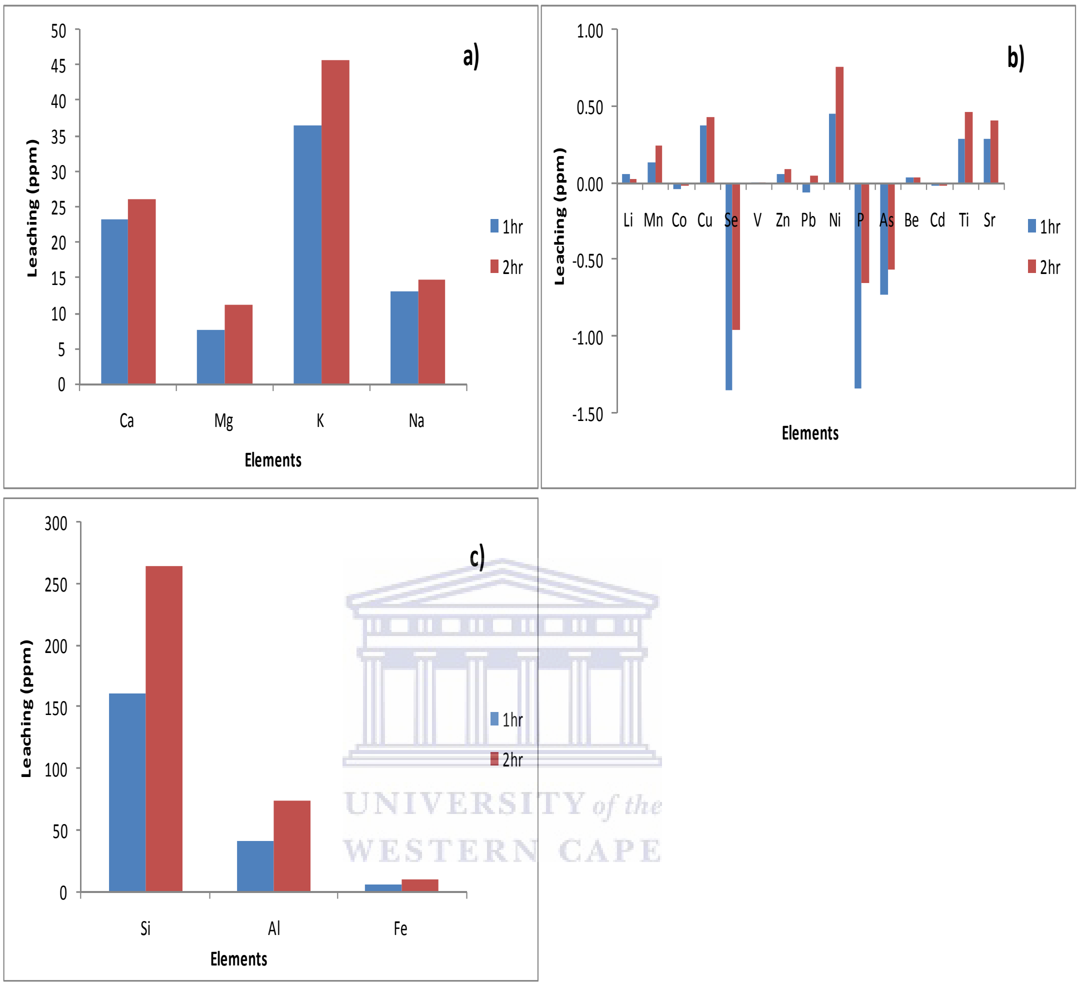

Figure 4.19: Leaching of a) major elements b) trace elements c) Si, Al and Fe from the Turkish clinoptilolite after contact with deionised water

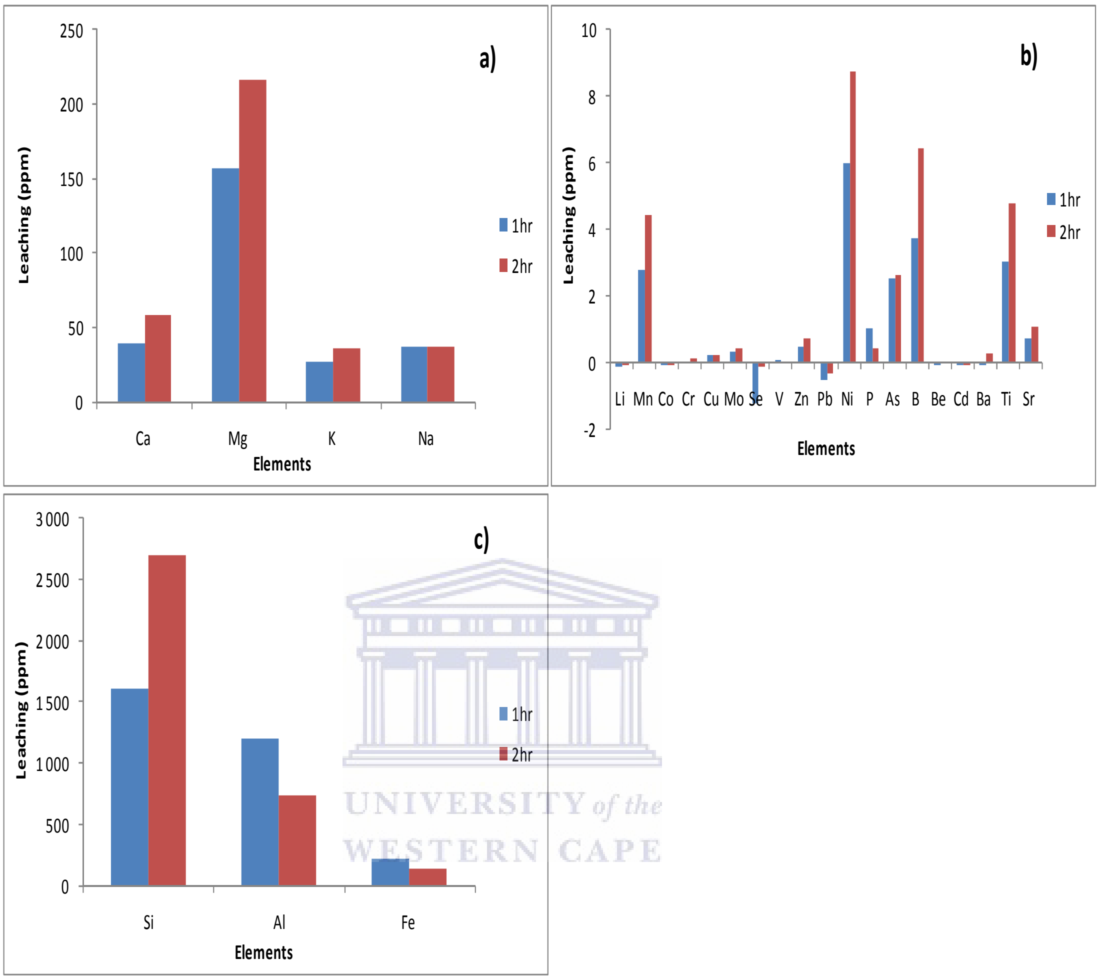

Figure 4.20: Leaching of a) major elements b) trace elements c) Si, Al and Fe from the South African bentonite after contact with deionised water

From the figures 4.18-4.20 shown above it was observed that these natural adsorbents have higher amounts of readily soluble and thus leachable silica and aluminium species than other elements and trace elements. It is also shown that calcium and magnesium are leached in higher amounts than elements due to the solubility of these elements from the clay and zeolite adsorbents, which indicates their presence in the natural materials as soluble salts. It is important to conduct leaching experiments so that we can know what these natural adsorbents are leaching to solution during adsorption studies. The leaching of Si after 2hr shows that some Si was not bound on the zeolite frame work. Figure 4.18-4.20 above. Shows Mg and K are soluble because they leached out more with deionised water in the South clinoptilolite and South African bentonite adsorbents. In the Turkish clinoptilolite less Si was leached. South African clinotilolite leached more Sr, because the zeolites contain Sr observed in the XRF data in section 4.1.1. but the Sr leached was still below the Target water quality range (TWQR) by the Department of Water Affairs (DWA).

4.7 Pretreatment results

In this section, the results of the pretreatment experiments based on the experimental procedure set out in section 3.3 are presented and discussed. These experiments were conducted to activate the natural adsorbents to remove Na^+, K^+, Ca^{2+} and Mg^{2+} to enhance adsorption and prevent leaching. The results below represent the extraction of four major cations, magnesium (Mg), sodium (Na), potassium (K) and calcium (Ca) from the clinoptilolite sample from Turkey. This was compared to natural zeolite (clinoptilolite) and natural clay (bentonite) from South Africa. These samples were obtained from Ecca Holdings Company, Heidelberg, Western Cape in South Africa. In figures 4.21-4.23 the Na^+, K^+, Ca^{2+} and Mg^{2+} concentration remaining in the leachates after each of several extractions are presented. Aliquots were taken after contacting 5 g natural adsorbents with 100 ml 0.02 M HCl for 2 hr, 1 hr and 30 min (x4) represented as (a), (b), (c) and (d) respectively. These experiments were carried out in duplicate for reproducibility.

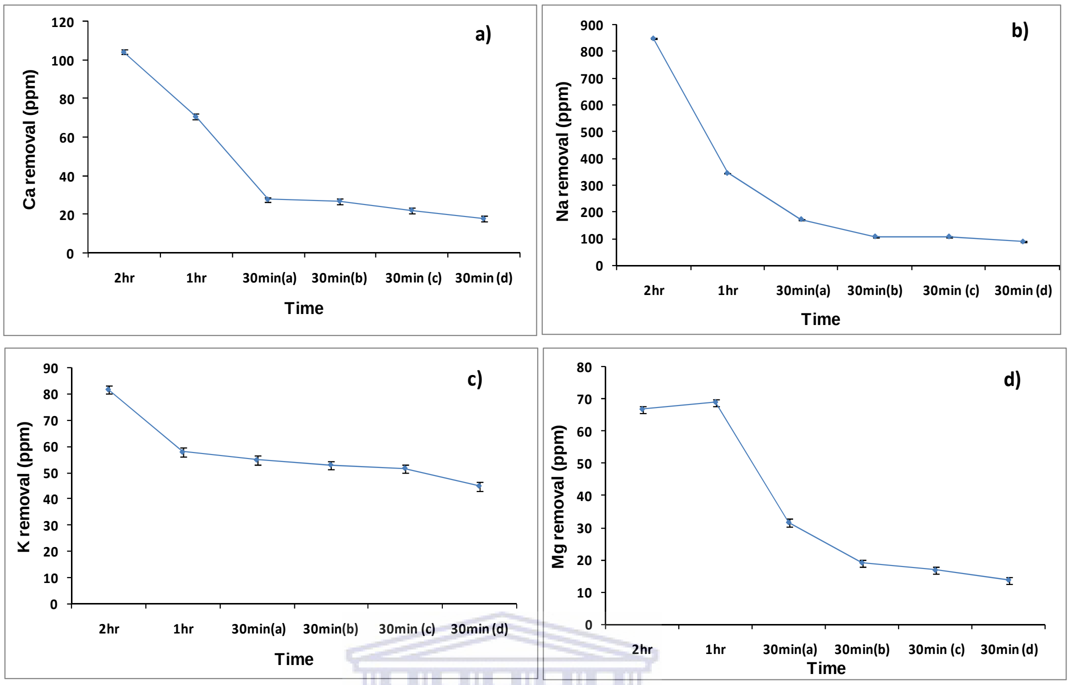

Figure 4.21: Removal of major cations from South African clinoptilolite after contacting 5 g SC with 100 mL, 0.02 M HCl: a) Ca removal b) Na removal c) K removal and d) Mg removal

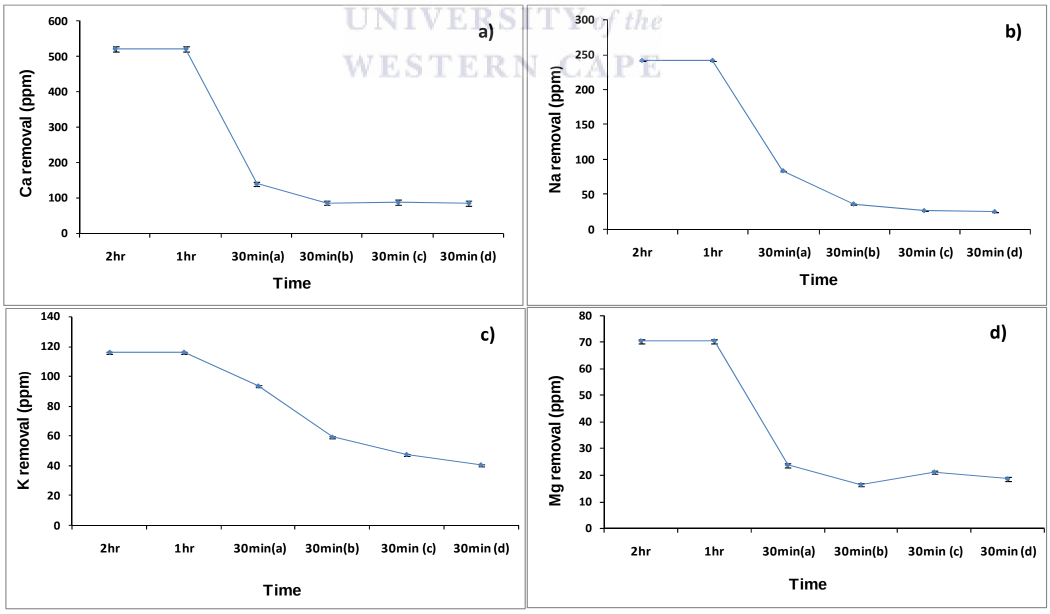

Figure 4.22: Removal of major cations from Turkish clinoptilolite after contacting 5 g TC with 100 mL, 0.02 M HCl: a) Ca removal b) Na removal c) K removal and d) Mg removal

The pretreatment applied to the natural material was aimed at improving its ion exchange capability. After six extractions of the South African clinoptilolite in figure 4.21 (a-d) the content of all cations in the extraction solution (0.02 M HCl) decreased. Sodium reached a plateau at 87 ppm on the sixth extraction (initially at 849 ppm) and this is a good extraction in terms of sodium. These results are consistent with the XRF data showing high sodium but not all sodium can come out easily because of the presence of other phases. Calcium reached 17 ppm on the sixth extraction, from an initial value of 104 ppm on the first extraction, potassium showed an initial good extraction from 81 ppm to 60 ppm. However the extraction of potassium showed steady low incremental removal after initial release and plateaued at 50 ppm, (from the XRF data initial potassium was high at 2.78 (% wt). Magnesium showed easy extraction (from (66 to 13 ppm).

It is evident that the South African clinoptilolite contained higher amounts of sodium, but it can also been seen that 0.02 M HCl can extract the cationic sodium almost completely from the SA clinoptilolite with sufficient extractions. In the case of the Turkish clinoptilolite, the content of all cations decreased in the extraction solution of 0.02 M HCl (figure 4.22 (a-d). It can be observed that Turkish clinoptilolite contained high amounts of calcium as exchangeable cation because the calcium content in the leachant was 522 ppm after the first extraction whereas in the last extraction calcium content was 85 ppm. These results are consistent with the XRF data of untreated Turkish clinoptilolite with calcium content being 3% wt and the highest. Sodium showed a very high extraction with the first extraction of 241 ppm and the sixth extraction down to 25 ppm. Magnesium showed similar good extraction (from 73 to 18 ppm with the first extraction). Potassium underwent a very gradual decrease from 119 ppm in the first extraction, to 40 ppm on the sixth extraction.

Extraction was generally nearly complete after the second extraction hence activation by HCl extraction of the zeolite adsorbents was shown to be generally effective after 2 extractions. These results obtained in this study show that the activation step requires optimization, whereas literature activation studies, such as reported by

(Mamba *et al*., 2009 and Cakicioglu-Ozkan and Ulku, 2009), only showed that activation using HCl enhanced adsorption of clinoptilolite for trace elements and vapour respectively and did not report exactly how much HCl extracts are necessary to displace the major cations in natural zeolite clinoptilolite. The study also showed that the extraction achieved was different for purities of natural clinoptilolite, thus the extraction/ activation step should be optimized specifically for each particular adsorbent material. Potassium was shown to be the least readily removed from the zeolite because in the XRF data the South African clinoptilolite showed highest K content and clinoptilolite has high affinity for K so it was not easily exchanged with H^+ ion. The removal values differ from XRF data which gave the total wt % and showed that not all of each cation is exchangeable, they maybe entrapped in other mineral phases. Continuous extraction for long time maybe a better solution rather than 6 extractions but concentration of the acid needs to be monitored.

Natural bentonite obtained from Ecca Holdings Company in South Africa mined at the Cape bentonite mine was studied under the same conditions as the clinoptilolite to extract major cations from the bentonite. Figure 4.23 shows the removal of major cations from South African bentonite.

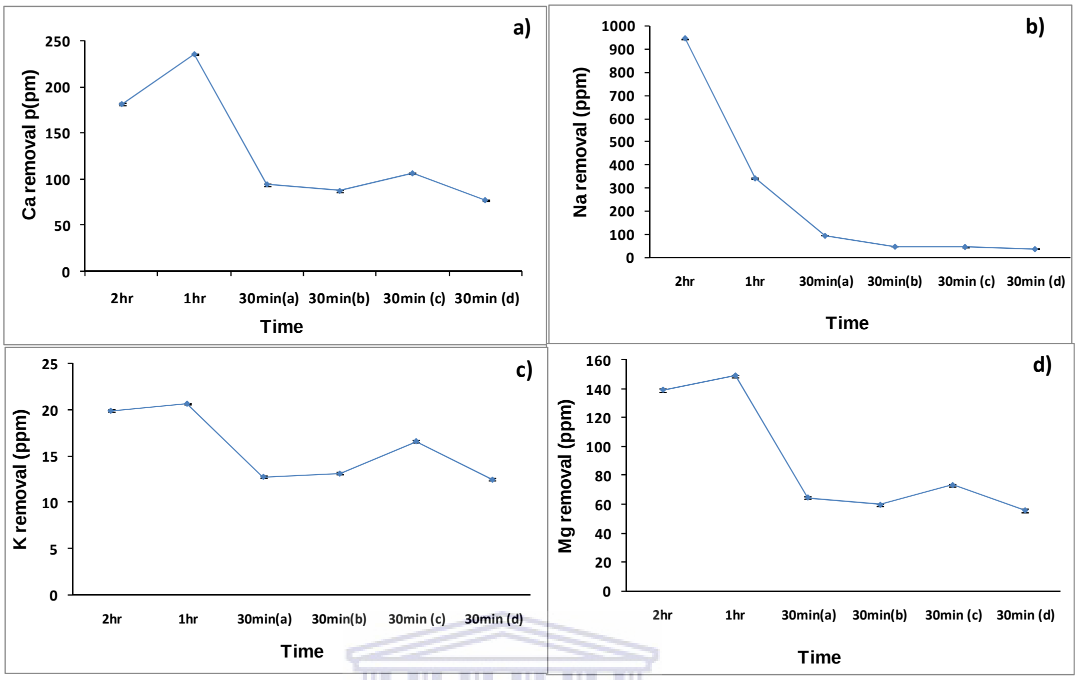

Figure 4.23: Removal of major cations from South African bentonite after contacting 5 g SB with 100 mL, 0.02 M HCl: a) Ca removal b) Na removal c) K removal and d) Mg removal.

A fairly high removal of all cations was observed after six extractions of South African bentonite in Figure 4.23 (a-d). Sodium reached 37 ppm on the sixth extraction whereas the amount was high in leachate after the first extraction (942 ppm) and the XRF data is not consistent with this result because in the XRF data the sodium content was lower than magnesium and that means sodium is easier to exchange than magnesium. Calcium reached 77 ppm on the sixth extraction, from an initial value of 167 ppm on the first extraction, and underwent various fluctuations in concentration with each successive extraction showing competitive readsorption until other cations were extracted, or that it could only come out after sodium was removed from pores as bigger cation moves more slowly. Magnesium showed similar good extraction (from 139 – 55 ppm with the first extraction) with fluctuations between the 4th and the 5th extraction (13 ppm in the 4th extraction and 77 ppm in the 5th extraction. Potassium decreased from low levels of 19 ppm in the first extraction, to

12 ppm on the 3rd extraction; with some minor fluctuations e.g. an increase from 12.5 to 16 ppm between the 4th and 5th extractions. SB showed more fluctuations than the natural zeolite and that could be because the SB is a swelling clay so it adsorbs and swells and takes longer to release the acid again.

The results obtained in Figure 4.21-4.23 show that it was not possible to extract the full cation load in one extraction with HCl in any case. Several extractions with 0.02 M HCl were required in most cases to displace the available cations. South African bentonite also had high sodium content as well as high calcium content with 942 and 167 ppm respectively. ICP was used to analyse the cations from the leachate solution. However it can be seen from the decreasing trends in these extractions from different materials that the 0.02 M HCl worked well as leachant in effectively extracting the cations from the clay and zeolite material.

The extractions were done six times to check to what extent the exchangeable cations would be removed, and it is evident that on the 5th extraction a large part of the available cations had been removed from the clay and zeolite materials. It is possible to remove all the cations from the natural adsorbents using the 0.02 M HCl but dealumination can occur if the natural adsorbents are washed too many times with an acid or with higher concentration of HCl (Mamba *et al*., 2009) and that can also be seen in the shift on the FTIR bands results presented in section 4.6. The XRF data in section 4.1.1 showed that the total load of cation could not be removed but only about 65% of sodium, 7% potassium, 24% magnesium and 22% calcium were extracted based upon the initial XRF data for the South African clinoptilolite. In the case of Turkish clinoptilolite 63% sodium, 14 % potassium, 32% and 20% magnesium were extracted. In the extraction of cations with the bentonite clay 60% sodium, 2% potassium, 53% calcium and 15% magnesium were extracted. It is notable in all three adsorbents that sodium is the most easily extracted cation even though the initial content was high and that could be because of the size of the ion since it a univalent and is easily exchangeable or is present as a soluble salt. The bentonite clay showed highest removal of calcium of about 53% but low potassium removal based upon initial XRF data. XRD shows that these materials contained impurities and were not only clinoptilolite or clay, thus some of Na^{+}, Ca^{2+}. Mg^{2+} and K^{+} could be entrapped in the other mineral phases. The fact that the major cations were easily removed is because some of these cations are soluble salts, thus easily washed away by the acid. From the CEC data more Na^{+} and Ca^{2+} was exchanged. The extraction of major elements using HCl was different from leaching of elements with deionized water. The extraction fluactions might be due to the instrumental error.

4.8 Fourier Transform Infra Red analyses

The FTIR technique was used to determine the functionalities in the HCl-treated and original forms of natural adsorbents. This characterization was done in order to ascertain whether acid treatment of natural adsorbents exposed other latent functional groups. The Fourier Transform Infra – Red Spectroscopy (FT-IR) vibration bands from the analysis of natural adsorbents, that were prepared according to the procedure highlighted in section 3.2.9, were assigned in accordance to the generally accepted practice for silicates and the zeolite family of compounds as shown in (figures 4.24-4.28).

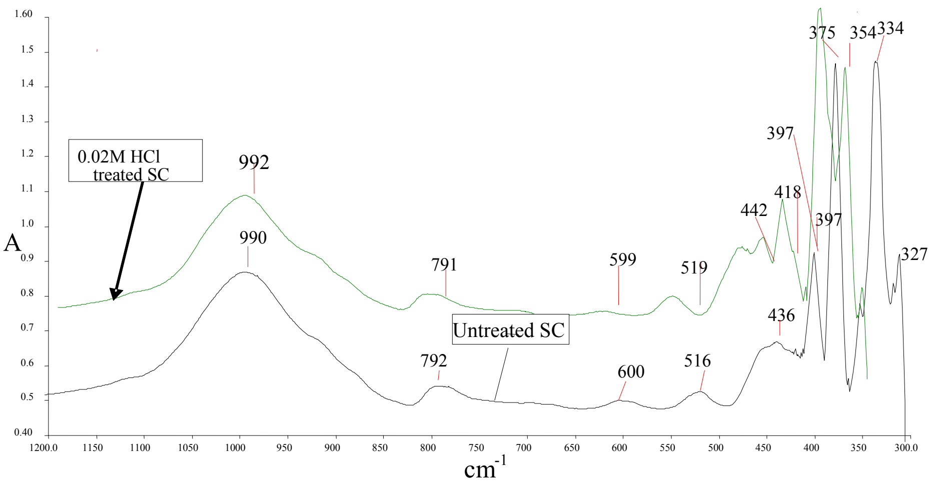

Figure 4.24: The expanded region FTIR spectra for untreated and 0.02 M HCl treated SC between 1300 and 300 cm^{-1}

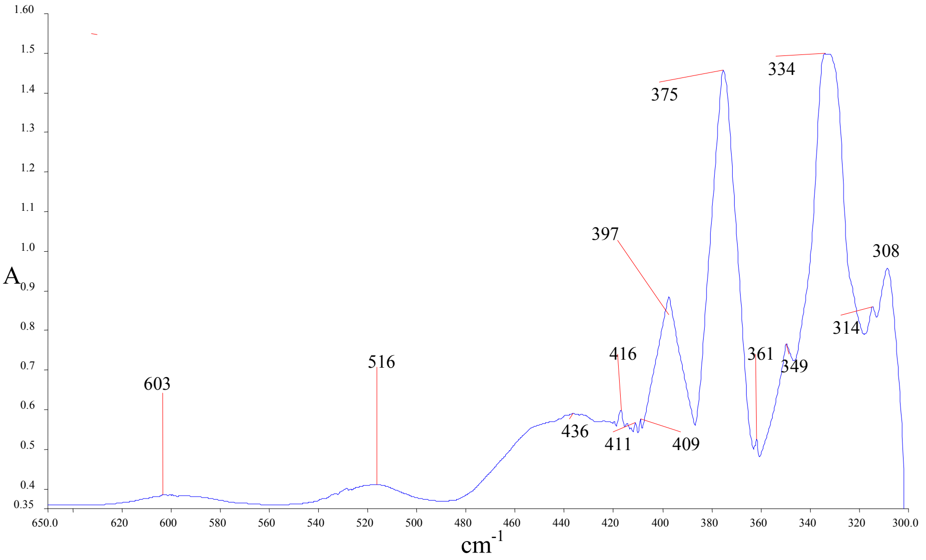

Figure 4.25: The FTIR spectra for untreated SC (600 and 300 cm^{-1})

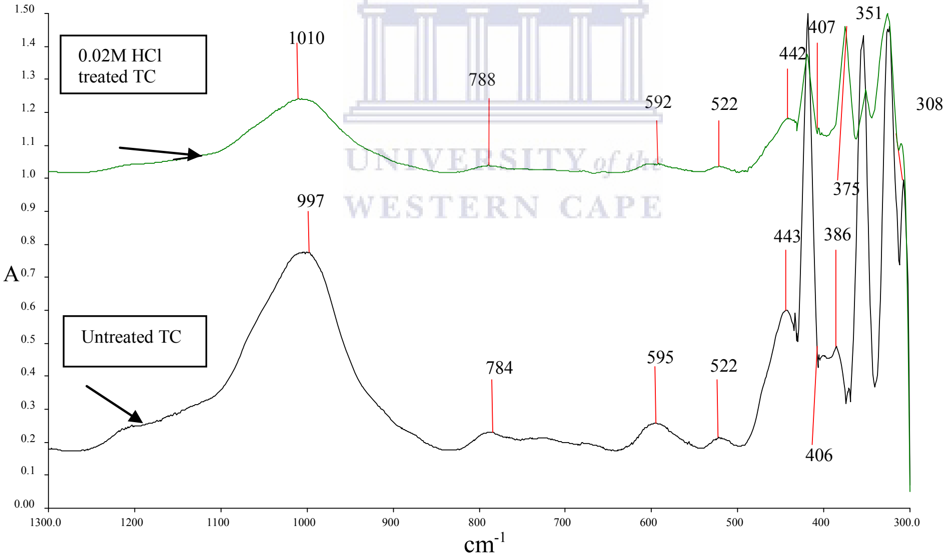

Figure 4.26: The expanded region FTIR spectra for untreated and 0.02 M HCl treated TC between 600 and 300 cm^{-1}

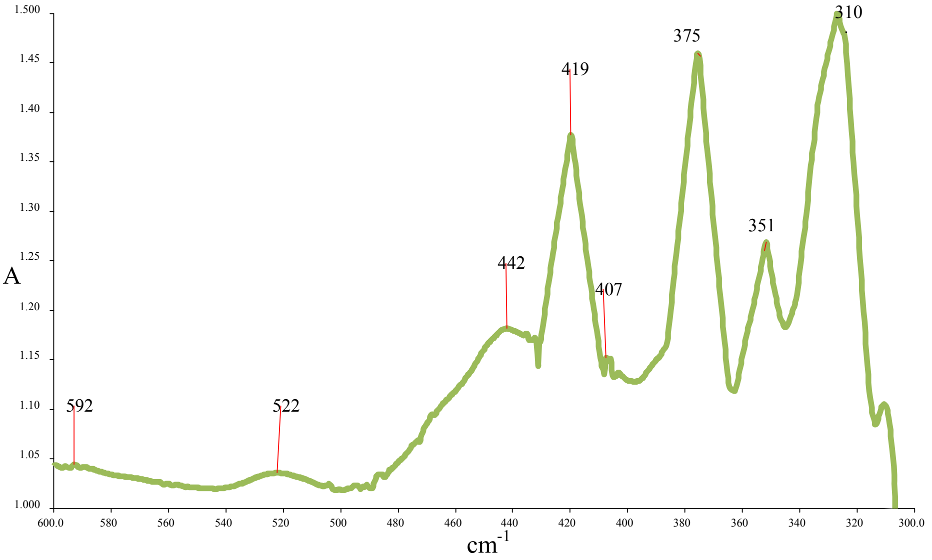

Figure 4.27: The FTIR spectra untreated TC between 600 and 300 cm^{-1}

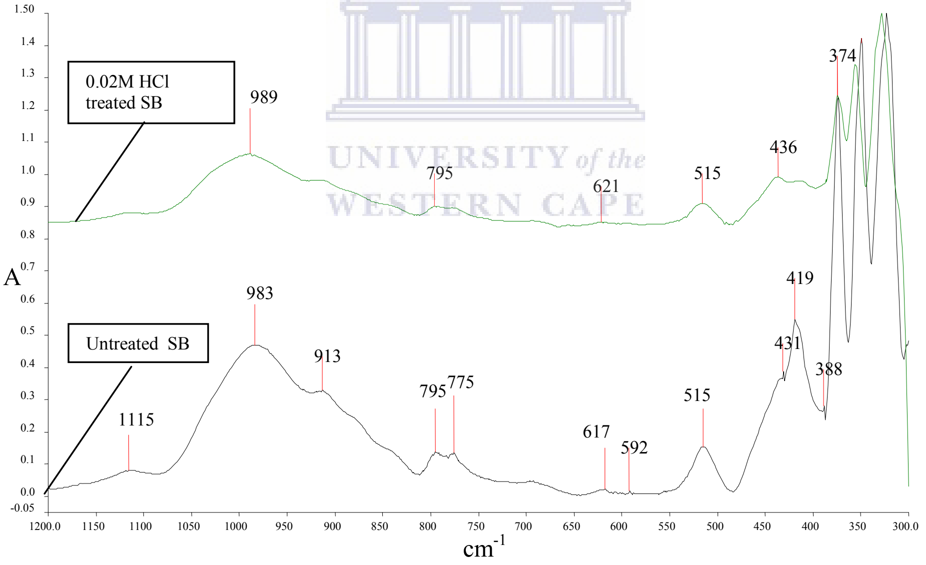

Figure 4.28: The expanded region FTIR spectra for untreated and 0.02 M HCl treated SB between 1200 and 300 cm^{-1}

FTIR spectra of the untreated natural zeolite clinoptilolite from South Africa in Figure 4.24 clearly showed strong bands at 990 and 516 cm^{-1}and two weak bands at 599 and 436 cm^{-1}. These bands are T-O (Tetrahedral-Oxygen) asymmetric stretching vibration modes of the internal SiO_4 and AlO_4 tetrahedral structure. These strong bands are characteristic of zeolite materials. The weak bands (600 cm^{-1}) are the O-T-O stretching vibration modes and T-O bending vibration modes (436 cm^{-1}) of the external SiO_4 and AlO_4 tetrahedral. The effect of the acid was determined by looking at shifts in the position of these specific zeolite bands, such shifts are indicative of degradation of the framework. The shifts were observed with T–O stretching vibration mode, from 990 cm^{-1} (untreated SC) to 992 cm^{-1}(treated SC sample), and as shown in (figure 4.24). The generation of the sharp peaks around 418 to 300 cm^{-1} in the treated samples may be due to the ring opening of SiO_4 and AlO_4 tetrahedra in the zeolite framework. These peaks are not seen in the untreated South African clinoptilolite sample where the peaks around 436 to 300 cm^{-1} appear to be weak. Cakicioglu-Ozkan *et al*., (2005) reported on the effect of different HCl concentrations and different treatment temperatures on Turkish Clinoptilolite. The strong bands were found to appear near 1056 and 451.2 cm^{-1} and weak bands at 790 and 604.8 cm^{-1} in the untreated sample. The strong bands were identified to be zeolite bands and assigned to the asymmetric stretching vibration modes of the internal T-O bands in the SiO4 and AlO_4 tetrahedral whereas the weak bands are assigned to the stretching vibration modes of O-T-O bands and bending vibration modes of T-O in the external tetrahedral structure of zeolite. The degree of dealumination was found to increase with increasing acid concentration during acid-zeolite treatment (Cakicioglu-Ozkan *et al*., 2005).

The vibrations common to all zeolites are the asymmetric stretching modes, which appear in the region 950–1250 cm^{-1}. The broad peaks observed in Figure 4.26 which depicts FTIR spectra for the original and treated natural zeolite (clinoptilolite) from Turkey shows strong bands for original and treated clinoptilolite from 997 to 443 cm^{-1} and 1010 to 407 cm^{-1} respectively and weak bands from 784 to 306 cm^{-1} and 788 to 592 cm^{-1} respectively. These results for the Turkish clinoptilolite are comparable to results by (Cakicioglu-Ozkan *et al*., 2005). FTIR spectra of the untreated natural clay (bentonite) from South Africa in figure 4.26 showed strong bands at 983 and 515 cm^{-}

^{1}and two weak bands at 1115 and 592cm^{-1}. The peak at 1115 cm^{-1} has disappeared in the treated bentonite and the peak at 983 cm^{-1}has shifted to 989 cm^{-1}, and the peak at 913 cm^{-1} in the treated bentonite is not observed in Figure 4.28. Dealumination is observed when wave numbers shift (Cakicioglu-Ozkan *et al*., 2005) , thus in all three samples, dealumination occurred but in a small degree due to the use of low concentrations of HCl in activation . In this study it was observed that pretreatment of the natural adsorbents by 0.02 M HCl did not cause much dealumination because of the small shift in wave numbers observed in the figures above.

4.9 Adsorption after pretreatment with 0.02 M HCl

This section presents adsorption results Figure 4.29 4.40 after the pretreatment of the natural adsorbents with 0.02 M HCl in the experimental method shown in section 3.4.2. Batch adsorption studies on Emalahleni brine on natural adsorbents were conducted at room 25°C by varying contact time and pH.

4.9.1 Determination of optimum contact time

This section presents adsorption Figure 4.29 4.37 results after the pretreatment of the natural adsorbents with 0.02 M HCl in the experimental method shown in section 3.4.2. Batch adsorption studies on Emalahleni brine on natural adsorbents were conducted at room 25°C by varying contact time and pH.

Initially experiments were done using only the brine with no adjustment to its pH (i.e. natural pH of 8.52) to obtain optimum contact time by natural adsorbents for adsorption of toxic elements from Emalahleni brine.

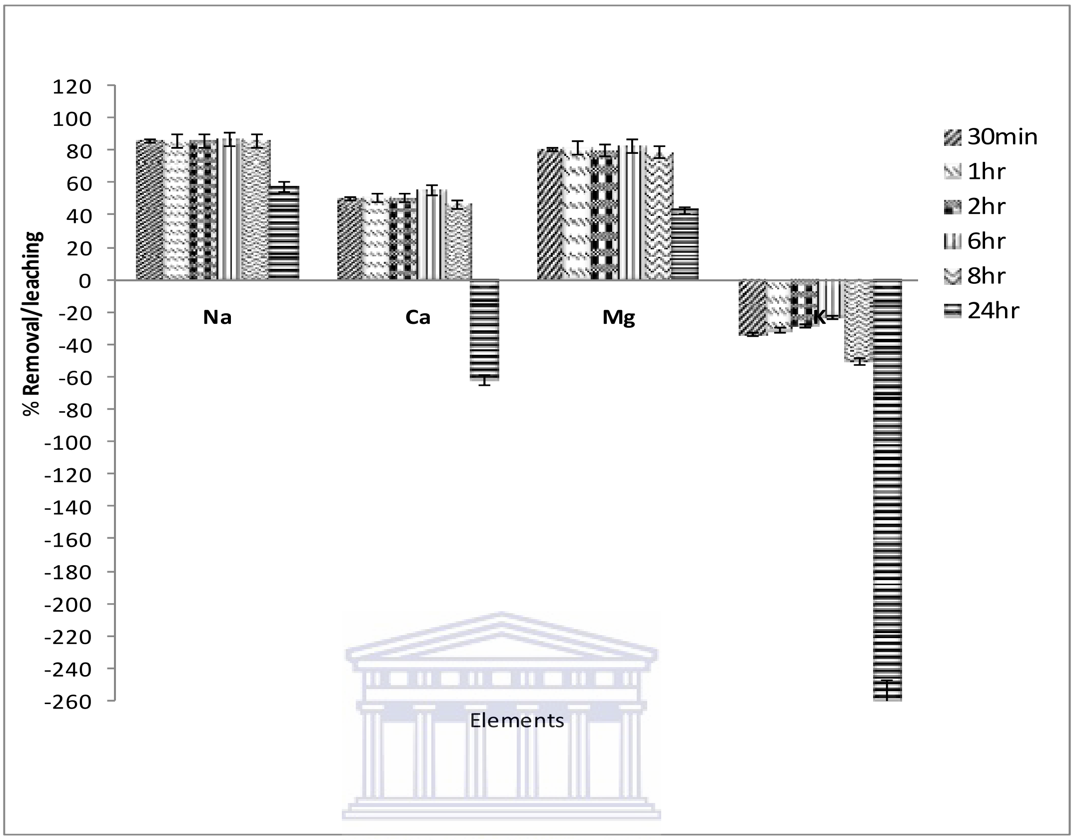

Figure 4.29 a): Removal /leaching of major elements from brine after contacting with 0.02 M HCl treated SC.

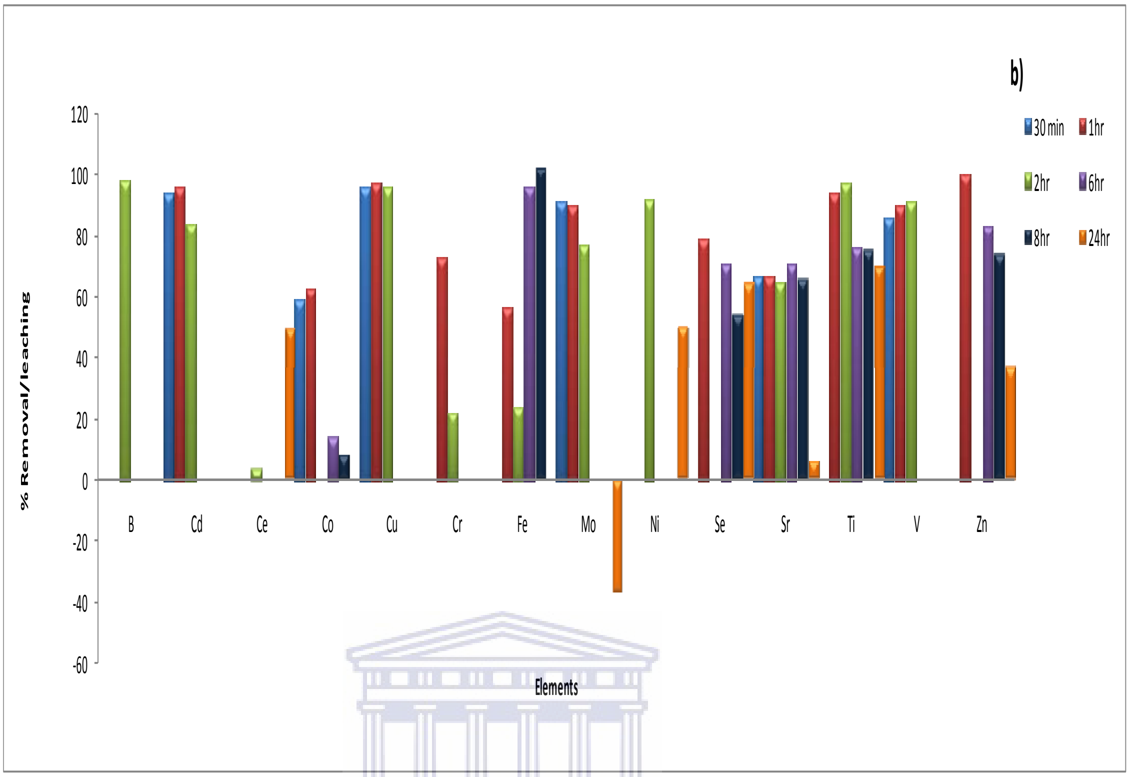

Figure 4.29 b): Removal /leaching of trace elements from brine after contacting with 0.02 M HCl treated SC

The South African clinoptilolite from Ecca Holdings Company performed well for brine treatment after 30 min following the pretreatment with 0.02 M HCl. From the results in figures 4.29 a) and 4.29 b), the optimum time for element removal was found to be 1 hr, as it can be seen that after 1 hr, clinoptilolite is adsorbing Na^+, Mg^{2+}, Ca^{2+} but leaches out more K^+ and some trace elements as well. This trend of percentage removal was expected after the pretreatment of the clinoptilolite to adsorb more metals, however leaching of K^+ was not expected as it has been reported that the clinoptilolite has a greater affinity for K^+ than Na^+ (Langella *et al*., 2000). In this study it was found that Na^+ removal was the highest after the pretreatment of clinoptilolite as about 86% Na^+ removal was obtained, compared to the untreated South African clinoptilolite which removed only about 20% Na^+ from brine. High removal of 80% of Mg^{2+} was also found whereas on the untreated clinoptilolite Mg could not be adsorbed and Mg^{2+} leached out onto the solution. Ca^{2+} removal was about 51% and this was a good removal because on the untreated sample the, Ca^{2+} was leached out and not being adsorbed. After the 24 hr contact time it was observed that Na^{+} and Mg^{2+} removal was low and that in the case of Ca^{2+}, what was adsorbed at 2 hr contact was leached out into the solution over time. More K^{+} was also released into the solution. Only B and trace elements removal was high as well; Cu^{2+} 96%, Zn^{2+} 96%, with Mo 77%, B 96%, Ni 98% removal was obtained. Mamba et al., reported removal of Cu^{2+} of 79% in 1hr contact time using 0.02 M HCl treated clinoptilolite (Mamba *et al*., 2010).

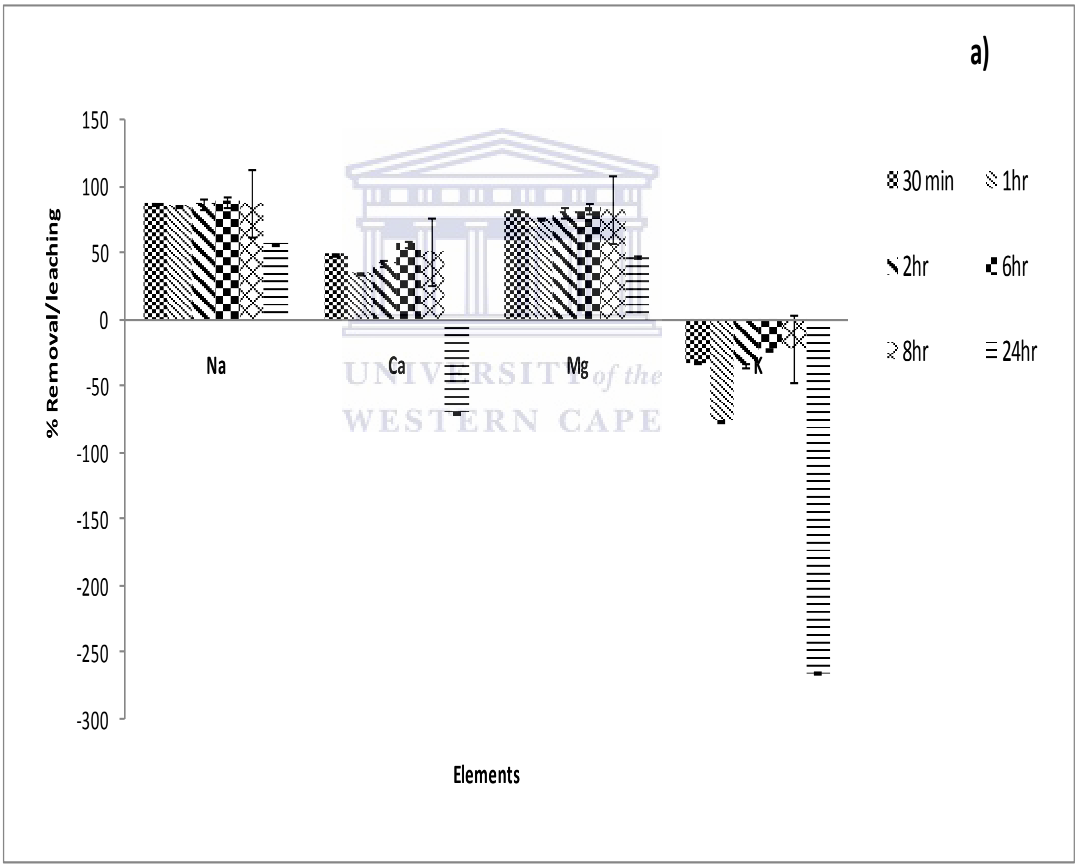

Figure 4.30 a): Removal /leaching of major elements from brine after contacting with 0.02 M HCl treated TC

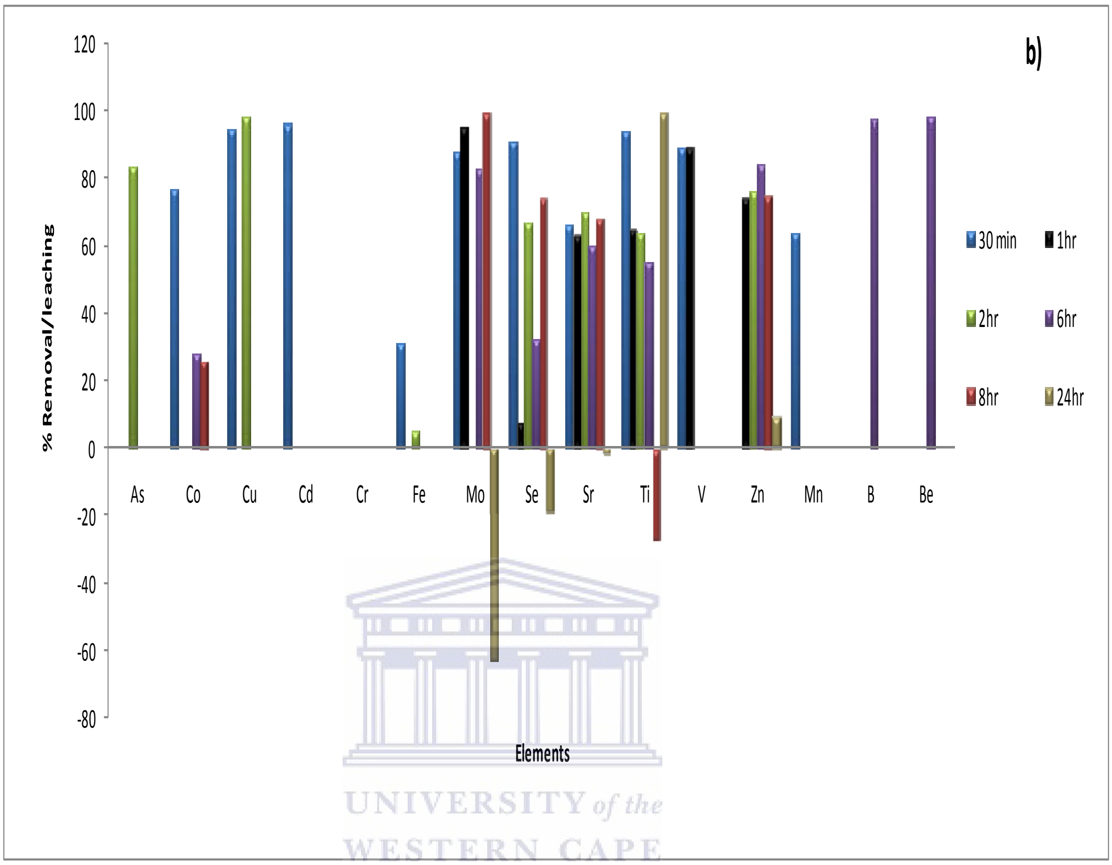

Figure 4.30 b): Removal /leaching of trace elements from brine after contacting with 0.02 M HCl treated TC

In the first 30 min contact time the Turkish clinoptilolite showed highest removal of major elements and trace elements, leaching few in elements in small concentrations onto the solution. Na^+ and Mg^{2+} were also the highest removal obtained with 86 and 81% removal respectively. About 42% removal of Ca^{2+} was obtained and this was lower percentage removal and it can explained by the fact that Turkish clinoptilolite has high Ca^{2+} content from XRD data as well as pretreatment of natural adsorbents data, it was thus difficult to adsorb what was already in the clinoptilolite material. The order of major elements ion selectivity for both (SC and TC) is Na^+>Mg^+>Ca^{2+}). The trace element ion selectivity for SC is B>Ti>Cu>Zn>V>Cd>Mo. The Turkish clinoptilolite trace elements ion selectivity is Cd>Cu>Ti>Se>V>Mo>Co.

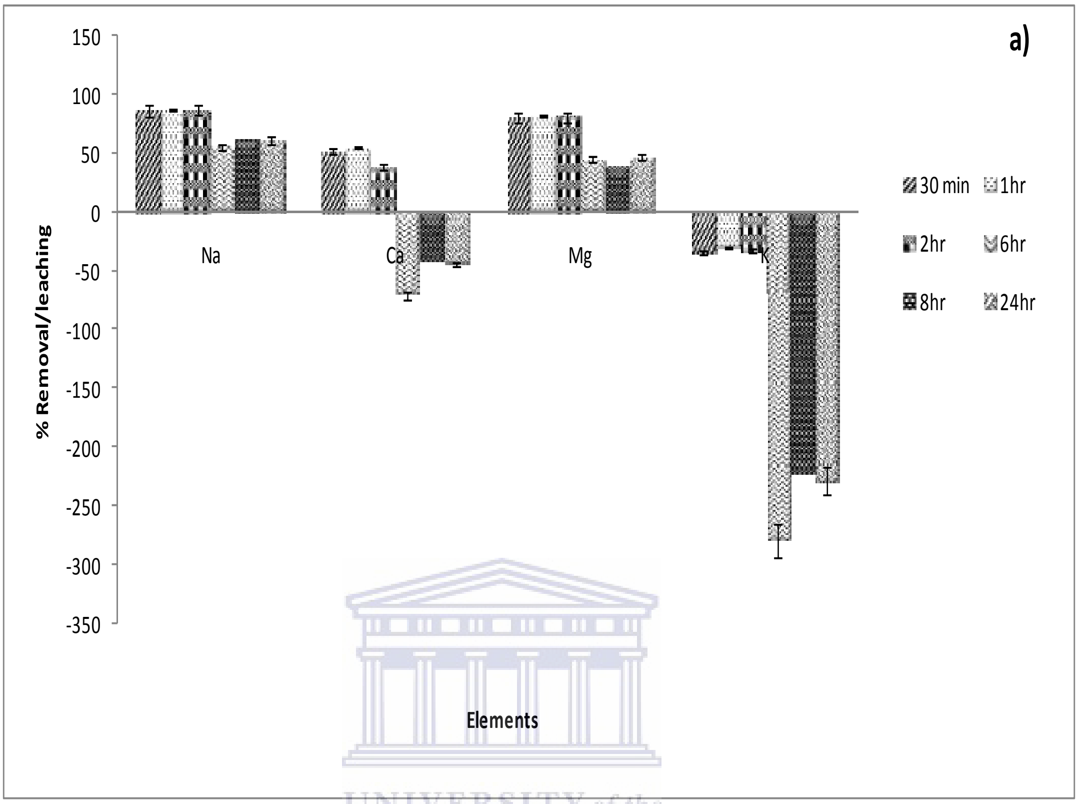

Figure 4.31 a): Removal /leaching of major element from brine after contacting with 0.02 M HCl treated SB

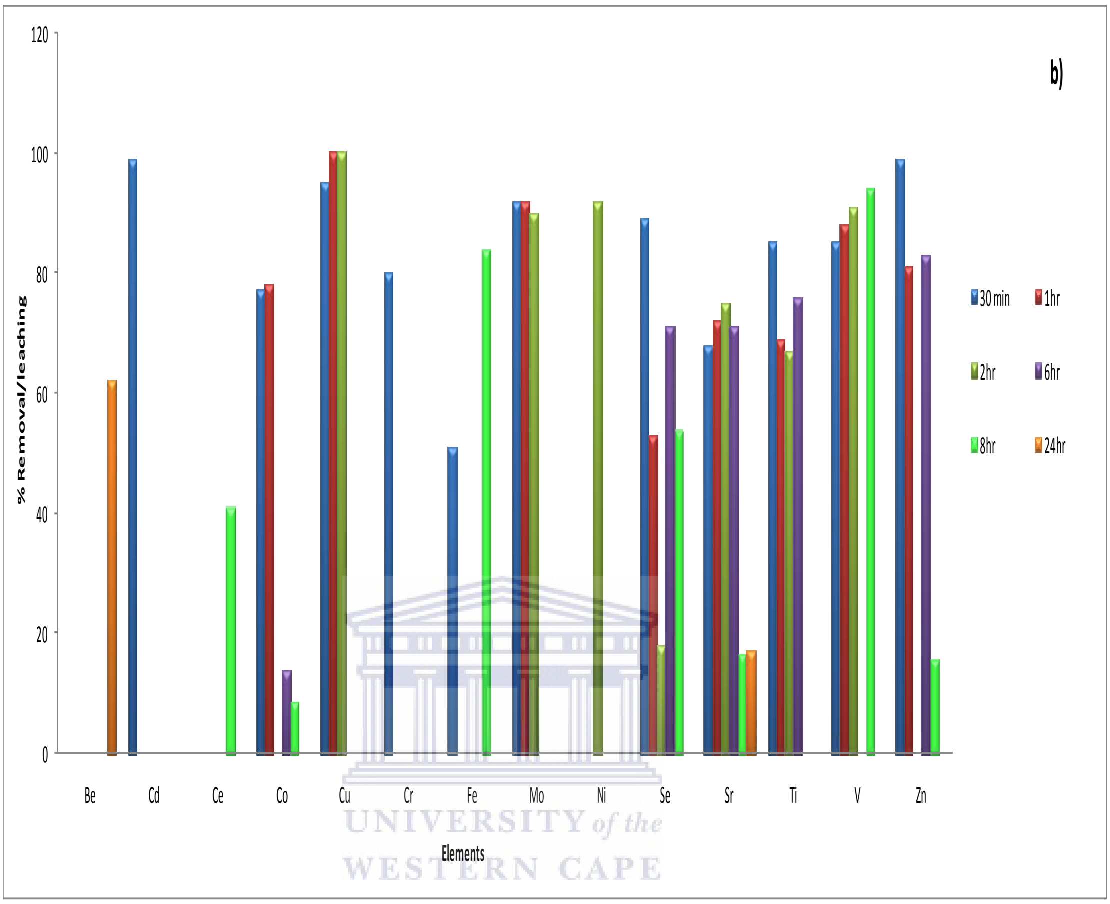

Figure 4.31 b): Removal /leaching of trace elements from brine after contacting with 0.02 M HCl treated SB

In the first 30 min contact time the South African bentonite showed highest removal of major elements and trace elements, leaching few in elements in small concentrations onto the solution. Na^+ and Mg^{2+} had the highest removal obtained with 86 and 81% removal respectively. The major elements ion selectivity for the SB is $Na^+>Mg^{2+}>Ca^{2+}$ and the trace elements ion selectivity is $Cu^{2+}>Mo>V>Zn^{2+}>Co^{2+}>Sr^{2+}>Ti^+$. About 42% removal of Ca^{2+} was obtained and this was lower percentage removal and it can explained by the fact that Turkish clinoptilolite has high Ca^{2+} content from XRD data as well as pretreatment of natural adsorbents data, it was thus difficult to adsorb what was already in the clinoptilolite material.

Figure 4.32 a, b and c) below presents results of leaching of trace elements from the natural adsorbents (SC, TC & SB) after acid treatment and after the brine adsorption. These results were obtained by analysis of the brine by ICP AES after the adsorption experiments.

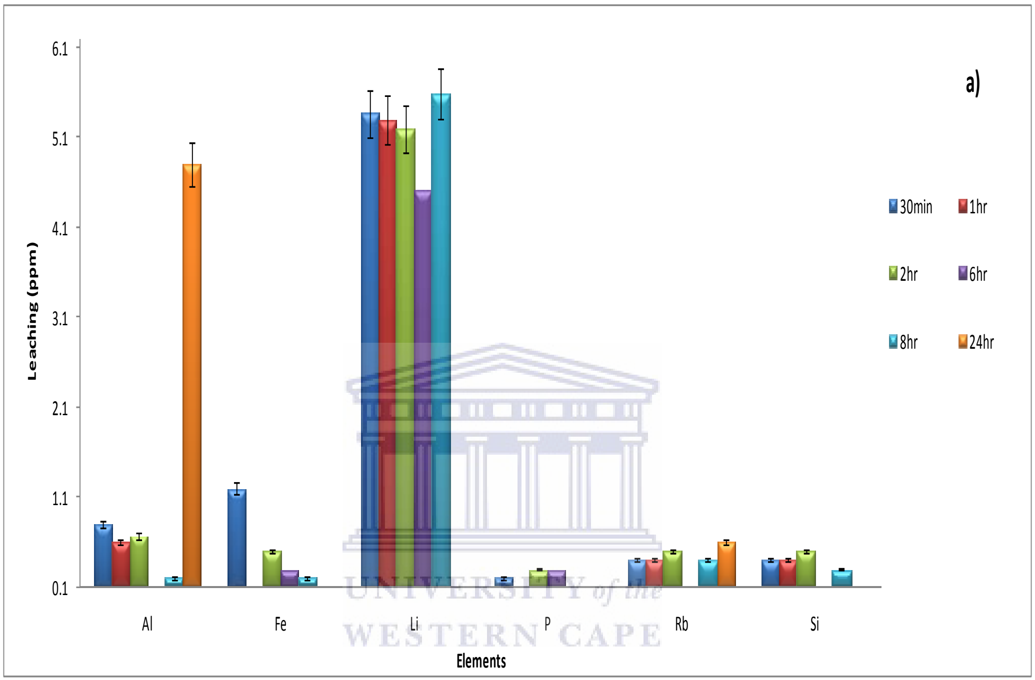

Figure 4.32a): Leaching of trace elements from SC during adsorption

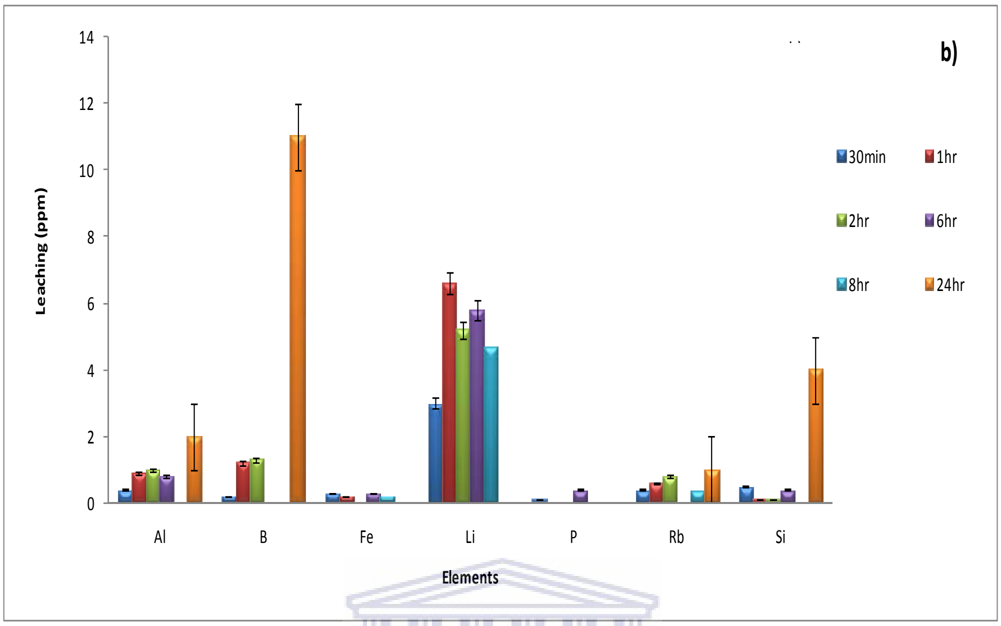

Figure 4.32 b): Leaching of trace elements from TC during adsorption

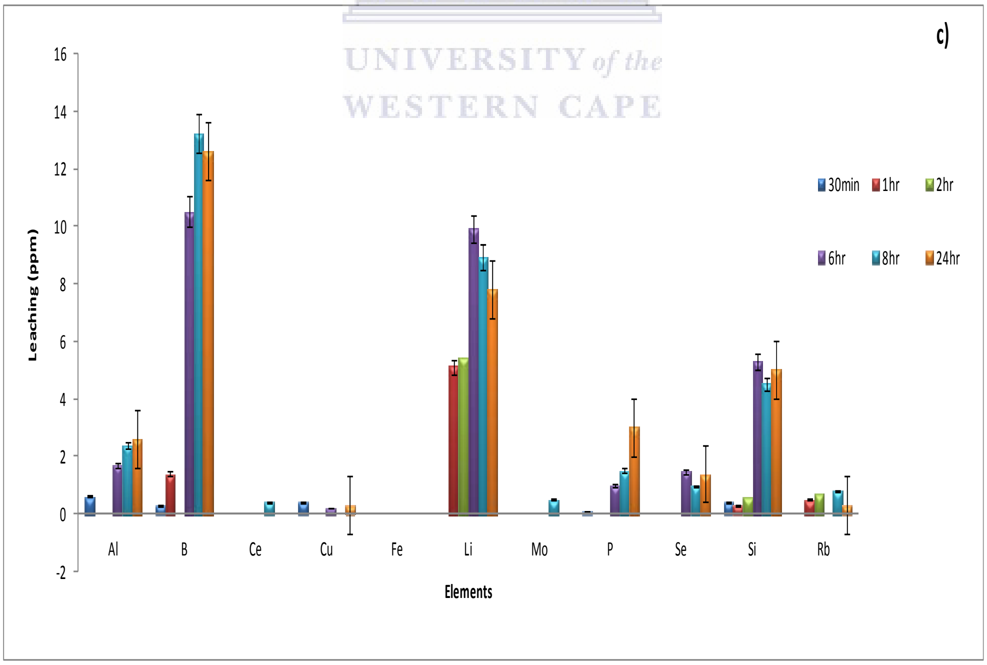

Figure 4.32 c): Leaching of trace elements from SB during adsorption

The South African clinoptilolite in Figure 4.32 a) above leached about 5.8 ppm of lithium in 8 hr contact whereas in 1 hr contact it leached about 5.4ppm of lithium. The SC also leached Al and Si in low concentrations of less than 1ppm in 5 hr contact time, however more Al and Si leached (about 4.8 ppm) after the 24 hr contact time. South African clinoptilolite leached Fe and Rb. The Turkish clinoptilolite in Figure (4.32 b) shows leaching of 11 ppm of Li in 24 hr contact time and less than 4 ppm of Li was leached in 1hr and 30 min contact time. Leaching of Si and Al by TC was less than 1 ppm at 30 min contact time and above 2 ppm of Al was leached in the 24hr contact time. TC leached about 4 ppm of Si in the 24 hr contact time. Other elements leached in low concentrations i.e. less than 1 ppm, such Fe, Rb, B and P. The South African bentonite in Figure (4.32 c) leached about 13 ppm of B in 8 hr and 12.5 ppm in 24 hr. However less than 1 ppm of B was leached in the 30 min and 1 hr contact time by SB. Leaching Si of Al was less than 1 ppm in 30 min and the 1 hr contact time, however Si leaching was above 4 ppm in the 6 hr, 8 hr and 24 hr contact time. The studies carried out on leaching of metals from natural adsorbents (Petrakakis *et al*., 2007; Tomasevic-Canovic, 2005) both studies were conducted in leaching of lead from clinoptilolite.

The high Si/Al ration of clinoptilolite results in typical low anionic field that gives rise to good selectivity towards cations of lower charge e.g Na^+ and poor selectivity towards cations of higher charge i.e. divalent cations (Langella *et al*., 2000). It can be concluded that these natural adsorbents .The structure of natural adsorbents was not destroyed because leaching of Al^{3+} and Si during adsorption was less than 1 ppm.

4.9.2 Determination of optimum pH

The initial Tutuka brine pH was adjusted to pH 4 and 6 using hydrochloric acid according to section 3.4.3. These values have been selected because pH values lower than 4 would induce protonation of clinoptilolite binding sites (Morali, 2006) and high pH values would lead to precipitation of metal ions. Percentage removal of major elements and leaching/removal of trace elements from Tutuka brine using the natural adsorbents (SC, TC and SB) are shown in the figure 4.32-4.34 below.

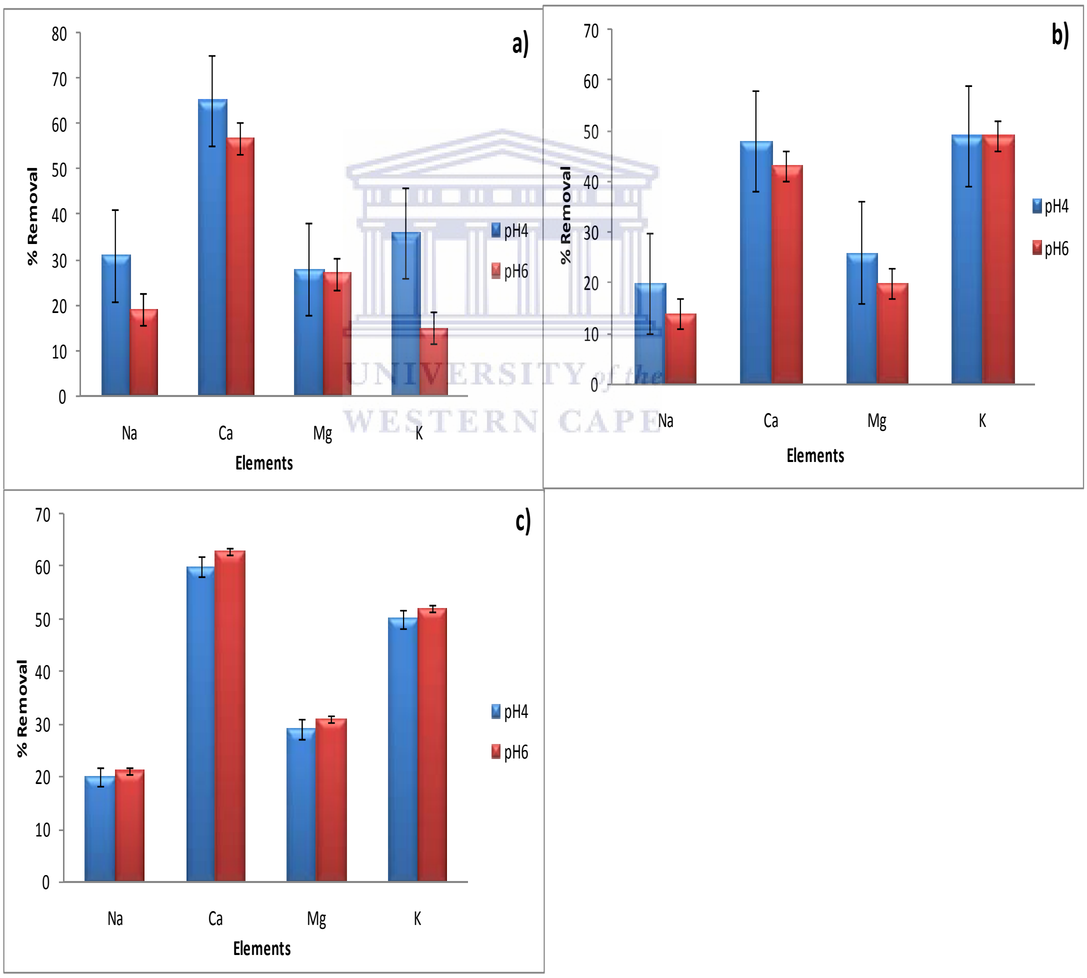

Figure 4.33: Percentage removal of major elements by a) SC b) TC c) SB at pH4 and pH6

It was observed that highest calcium removal from Tutuka brine was obtained in both pH 4 and pH 6 using South African clinoptilolite in Figure (4.33 a). However at pH 4 about 30% of sodium was removed whereas in pH 6 only 20% sodium removal was obtained. Potassium removal was 28% in pH 4 and 15% in pH 6 was obtained. The Turkish clinoptilolite (Figure 4.33 b) showed about 50% removal of potassium and calcium at both pHs with about 20% removal of sodium and less than 10% removal of magnesium in both pHs. The South Africa bentonite (Figure 4.33 c) showed highest removal of calcium and potassium at both pH4 and pH 6. Above 60% removal of calcium was obtained for pH 4 and pH 6 and magnesium removal of 50% was obtained at both pH 4 and pH 6.

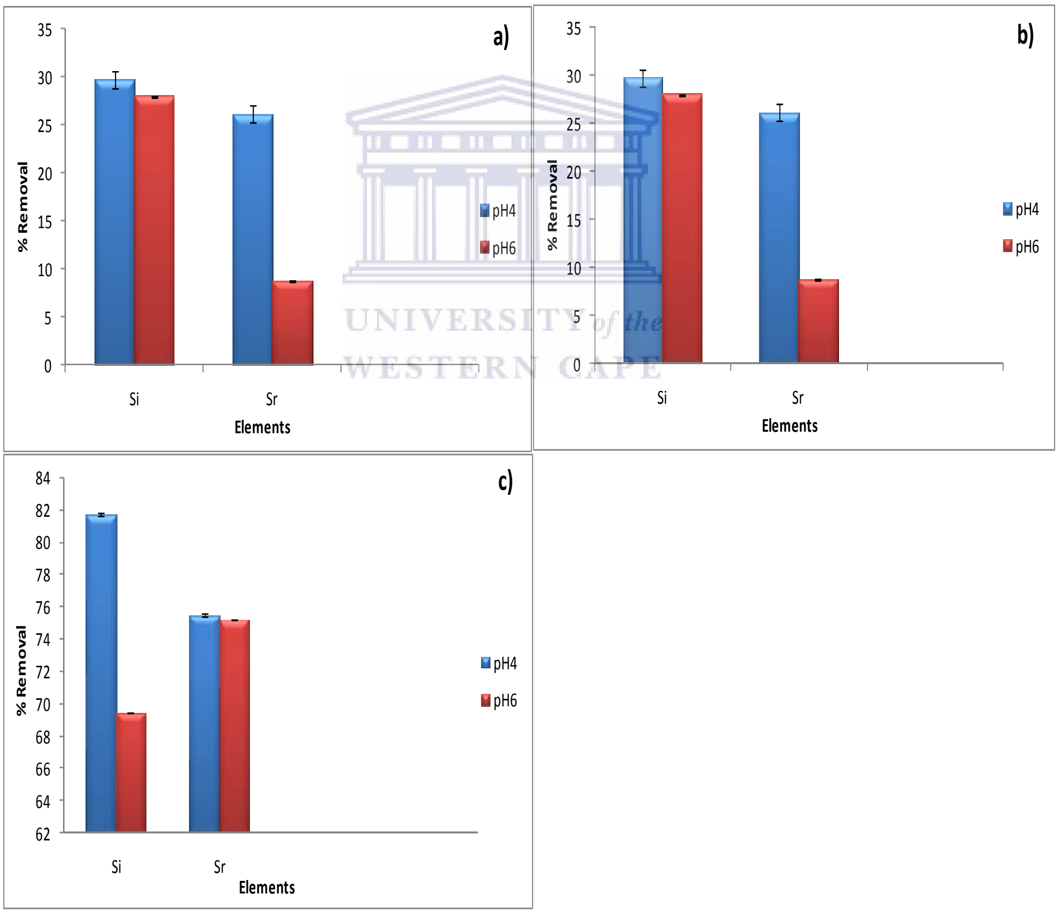

Figure 4.34: Percentage removal of trace elements by a) SC b) TC c) SB at pH4 and pH6

Removal of trace elements is shown in Figure 4.34 (a-c), it was observed that both Turkish and South African clinoptilolites could only remove about 30% of Si in the brine and this can be explained by the fact that these two clinoptilolites have a high Si content in their structure as shown in the XRF data in section 4.1.1 and in the leaching experiments in section 4.6, showed that Si leaching occurred in high concentrations in these two materials. The South African clinoptilolite and Turkish clinoptilolite both removed less than 10% Sr present in the brine at pH 6 whereas above 25% Sr removal was obtained for pH 4. In the case of the South African bentonite clay, about 82 % removal of Si was obtained at pH 4 and about 69% Si removal was obtained at pH 6. The bentonite clay was also able to remove about 75% of Sr at both pH 4 and pH 6 as shown in Figure 4.34 (c) above. From the results obtained in Figure 4.33(a-c) and Figure 4.34 (a-c) it was observed that bentonite clay performed well removing Ca, K, Si and Sr at both pH 4 and pH 6. At higher pH metals could also precipitate so it could only be adsorption.

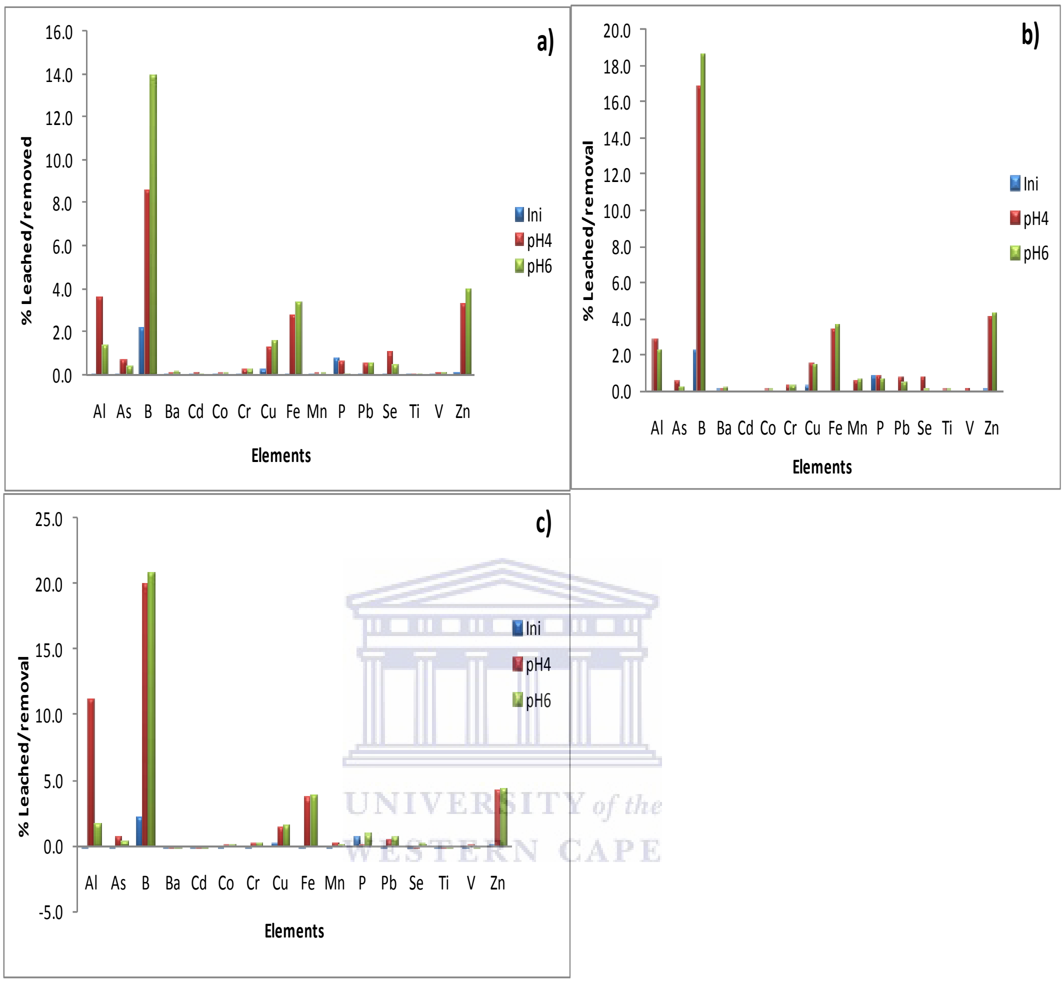

Figure 4.35: Leaching or removal of trace elements by a) SC b) TC c) SB at pH4 and pH6

The results obtained for trace elements removal is shown in Figure 4.35 (a-c) above. It was observed that none of the natural adsorbents used was able to remove the trace elements from the Tutuka brine; instead trace elements were leached from the natural adsorbents into the solution. It was observed that boron was leached out in high concentration when compared with the initial concentration in the Tutuka brine. The concentration increased to 8 ppm at pH 4 and 14 ppm at pH 6 from the South African clinoptilolite. About 4 ppm of aluminium was leached at pH 4 and ≤ 2 ppm at pH 6 by the South African clinoptilolite. Cu^{2+}, Zn^{2+}, Fe^{3+}, Pb^{2+}, Se were leached in concentrations above 1 ppm from the South African clinoptilolite. The Turkish clinoptilolite (Figure 4.35 b) showed high concentration of B of about 20 ppm, Al^{3+} was 2 ppm, Fe^{3+} and Cu^{2+} had above 2 ppm leached into the solution. The South African bentonite clay leached the highest concentrations B of about 18 ppm at pH 4 and 20 ppm at pH 6, the bentonite clay also leached about 10 ppm of Al^{3+} at pH 4 and less 2 ppm at pH 6 but leaching Fe^{3+}, Zn^{2+}, Cu^{2+} and Pb^{2+} in concentrations above 1 ppm. The fact that these elements were leached instead of being removed from Tutuka brine could be explained by the fact that the natural adsorbents at low pH become positively charged thereby negatively affected the adsorption of cations due to repulsive forces. However in natural pH of brine which was 8.55 the major and trace elements were adsorbed within the 1 hr contact time of natural adsorbents with the Emalahleni brine as shown in Figures 4.33 (a-b) 4.35 (a-b) above.

At natural pH the surface of natural adsorbents becomes negatively charged, thus force of attraction occurs and more cations are adsorbed. On the other hand it can also be noted that when removing toxic elements from waste waters, the optimum pH for removal of the particular element needs to be established before executing the adsorption of that element.

Onyango *et al*., (2010) revealed that solution pH is one of the factors that have been found to significantly affect sorption process. Different elements are adsorbed at different pHs and there is also what is known as competitive adsorption, where by bigger ions will fill the exchange sites and smaller ions will not be adsorbed. Several studies conducted on the effect of pH in heavy metal removal (Najim *et al*., 2009; Undabeytia *et al*., 1998: Marzal *et al*., 1996) showed that the increase in pH causes an increase in adsoption, thus the higher the pH solution the higher the adsorption. Najim et al., (2008) reported that adsorption of metal ions were pH dependent and the results indicated the optimum pH for the removal of Fe^{2+} was found to be pH 5.0 and that of Cu^{2+} was 7.0. The effect of pH was studied by Marzal *et al* ., (1996) in removal of Zn^{2+} and Cd^{2+} using granular activated carbon, he found that increasing pH from 4-8 , Cd^{2+} and Zn^{2+} were adsorbed at higher pH. Undabeytia *et al*., (1998) studied adsorption-desorption of Cd^{2+} on Ca^{2+} montmorrilonite and reported that the number of high preference sites for heavy metal adsorption increased with the pH. Clinoptilolite is known to attract metals, which are not expected to leach out at neutral and alkaline conditions. Studies conducted by Aslam *et al*., (2004) also indicated that heavy metals removal proved highly effective as removal efficiency increased with increasing pH while it decreased with increasing metals concentration. The removal efficiency was quite high for copper ranging from 97 to 70%. The only possibility for leaching is during contact with acid solutions, as for example acid rain or acid leachates from industrial and municipal landfills. Acidity is known to influence heavy metal removal since H^+ can be considered as competitive cation in ion exchange processes (Petrakakis *et al*., 2007). In this study it was found that the natural adsorbents were able to adsorb the heavy elements from the brine at its natural pH. and also observed that removal of toxic elements is pH dependent.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER 5

This chapter summarizes the major issues addressed in this thesis. This is followed by a consideration of possible guidelines for future work and a summary of the main contributions made in this thesis.

5.1 GENERAL CONCLUSIONS

In this study, the natural zeolite clinoptilolite and bentonite clay originated from Cape Bentonite Mine deposit, South Africa and the other clinoptilolite originated from Balıkesir-Bigadiçi deposit, Turkey were found to be effective for major elements and trace elements removal from Emalahleni brine solution in their pretreated form. The heavy metal removal was conducted by batch experiments; the untreated natural adsorbents did not sufficiently remove the toxic elements from brine. The pretreatment was aimed at removing the cations in the natural adsorbents and replacing with the H^+ ion for easy ion exchange although lower capacities were attained for major cations in the preliminary adsorption experiments of the untreated adsorbents. It was found that the conditioning or pretreatment of the natural adsorbents improved the capacity of clinoptilolite and bentonite clay for Na^+, Ca^{2+}, Mg^{2+} removal relatively well. However K^+ was leached out by these three adsorbents after their pretreatment and this could be attributed to the competitive adsorption on the sites.

In this study it was also found that these natural adsorbents can also leach some major component elements as well as toxic elements into the solution during adsorption processes. Therefore the use of these natural adsorbents for removal of toxic elements from waste water needs to be thoroughly investigated and optimized where possible. The research approach developed in this study has resulted in better understanding of elemental composition of the natural adsorbents, their purity, surface areas and their cation ion exchange capacity. Investigation of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) released from clinoptilolite structure after pretreatment with 0.02 M HCl indicated that these cations cannot be completely removed. It was observed from the XRF data after pretreatment that the continuous treatment of the natural adsorbents for longer periods would lead to dealumination in their structures. Although irregular trends were observed, the amount of exchangeable ions released to solution was increased with increase in the contact time and the best contact time was 1 hr. During batch adsorption studies, the amounts of exchangeable ions released from clinoptilolite and clay structures were shown to increase with time. However, it was found out that this increase could not only be attributed to ion exchange only. Additionally, ions were released as a result of dissolution of soluble species or of the framework of clinoptilolite structure, which was indicated by increase in Si^{4+} concentration in solution with time.

For trace elements at initial time of uptake by clinoptilolite, electrostatic attraction between positively charged cations and negatively charged surfaces presumably occur and this was followed by ion exchange as the metal ions move through the pores and channels of the clinoptilolite and clay. The pH studies revealed that these natural adsorbents perform better a higher or solution pH than at pH 4 and pH 6 for toxic element removal from the brine.

Heterogeneity of natural adsorbents samples, even when they have the same origin, could be a problem when wastewater treatment systems utilizing natural clinoptilolite and bentonite are planned to be developed. Therefore, it is very important to characterize the reserves fully in order to make them attractive in developing treatment technologies.

5.2 RECOMMENDATION AND FUTURE WORK

In this study, natural adsorbents clinoptilolite and bentonite clay originated from Cape Bentonite Mine deposit, South Africa and the other clinoptilolite originated from Balıkesir-Bigadiçi deposit, Turkey been investigated for their effectiveness in removing major and trace elements from Emalahleni brine solution. However in actual systems, together with these ions, some inorganics and organics could be present. Therefore, effect of presence of inorganics and organics on removal of these heavy metal ions should be investigated. Kinetic and equilibrium studies should be performed as a further study; Column experiments on the adsorption of toxic elements should also be done to confirm the removal efficiency especially for trace elements.

In order to simulate full scale applications, investigation of recovery of heavy metals from clinoptilolite and bentonite clay and examination of regeneration potential of clinoptilolite and bentonite clay could be a guide to real applications. Mass balances should be done in future studies to determine the efficiency and mobility and fate of trace elements during adsorption.

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APPENDIX

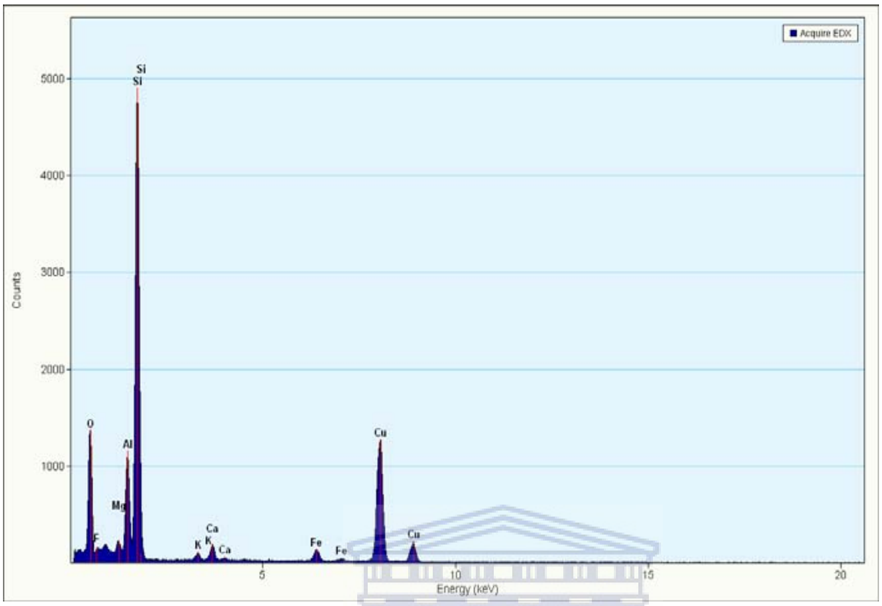

Figure A1: EDS of 0.02 M HCl treated South African clinoptilolite

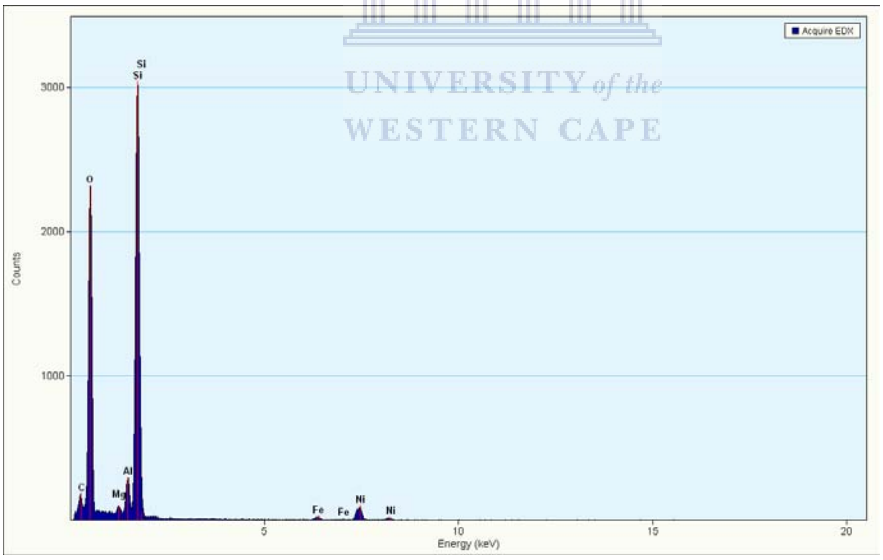

Figure A2: EDS of 0.02 M HCl treated South African bentonite

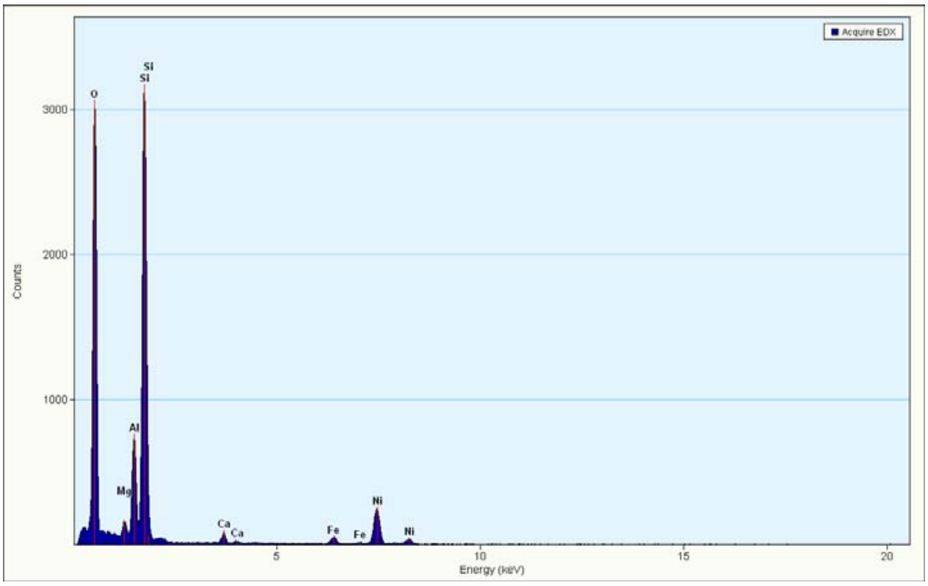

Figure A3: EDSof 0.02 M HCl treated Turkish clinoptilolite