SORPTION PROPERTIES OF NATURAL ZEOLITES FOR THE REMOVAL OF AMMONIUM AND CHROMIUM IONS IN AQUEOUS SOLUTION

By

Guillaume Ndayambaje

BTech – Cape Peninsula University of Technology

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Supervisor : Prof. Leslie Petrik
Co-supervisors : Prof. T.N Van Der Walt
Dr. Richard Akinyeye

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SORPTION PROPERTIES OF NATURAL ZEOLITES FOR THE REMOVAL OF HAZARDOUS ELEMENTS

KEYWORDS

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Zeolite

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ABSTRACT

There are huge amount of natural clinoptilolite available in South Africa which can be utilised for wastewater treatment of ammonia and chromium if their characteristics are properly known. However, these deposits have not been well characterised but in this study, the untreated clinoptilolite materials were fully characterised using techniques such as SEM-EDS, HRTEM-SAED, XRD, XRF, FTIR and BET. After acid pretreatment with several extractions, the pretreated samples were again characterised using the above mentioned techniques. These pretreated materials were used for NH_4^+ and Cr^{3+} adsorption of wastewater. The three natural South African clinoptilolite samples used in this study were from ECCA Holdings (ESC and EHC samples) and Pratley (PC sample) deposits obtained from Western Cape and KwaZulu-Natal Province respectively.

This study revealed that the chemical composition and mineral phases of South African clinoptilolites vary considerably from site to site, even clinoptilolite mined from the same deposit sites. The XRD analyses showed that Pratley clinoptilolite (PC) was the most pure clinoptilolite sample (81.41 %) compared to the purity of EHC (67.88 %) and ESC (44.0 %) sample. The ECCA Holdings untreated clinoptilolite samples contained dense phases such as quartz which was not found in Pratley sample. Quartz was found to be the most dominant impurity in both ECCA Holding sample. The cation exchange capacity (CEC) of ESC, EHC and PC samples were found to be 1.23, 1.81 and 2.90 meq/g respectively and these results were compared to that of XRF analyses.

The acid solutions of 0.02 and 1.0 M HCl were used to pretreat natural clinoptilolite to determine the optimum acid concentration and number of extractions required to fully replace the exchangeable cations. The pretreatment results showed that 0.02 M HCl was the optimum acid concentration for acid pretreatment of clinoptilolite samples. Between 7 and 22 extractions were required to remove Na^+, K^+, Ca^{2+} and Mg^{2+} without causing much dealumination

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of the framework. Sodium ion was found to be weakly bound cation in the clinoptilolite framework, since it could be completely exchanged by H^+ after 7 extractions with 0.02 M HCl acid solution. Potassium ion was found to be strongly bound in the clinoptilolite framework since it could not be completely exchanged during the acid pretreatment process even after 22 extractions. The HRTEM-SAED and BET results showed that ESC, EHC and PC were all polycrystalline and microporous materials respectively.

It was found that the adsorption capacity of the treated Pratley clinoptilolite sample was increased by 36 % for NH_4^+ removal, compared to that of the untreated PC sample. The adsorption study results showed that the pretreatment of clinoptilolite samples using 150 mL volumes of 0.02 M HCl with 7 acid extractions at 25 °C for ESC pretreated and EHC pretreated. The pretreatment of PC sample at 22 extractions could remove high percentage of NH_4^+ (98.11 %) within a short contact time of 10 min. The pretreated Pratley clinoptilolite sample was found to be the best NH_4^+ adsorbent (98.11 % NH_4^+ removal) compared to EHC treated (93.89 % NH_4^+ removal) and ESC treated (75.00 % NH_4^+ removal) clinoptilolite samples. However, acid-pretreated Pratley clinoptilolite did not sufficiently remove Cr^{3+} (16.10 %) from synthetic wastewater showing that it is not a good adsorbent for this particular metal ion removal.

Despite several studies that have been conducted on clinoptilolite, no study has been carried out on the pretreatment and comparison of sorption capacity of different South African clinoptilolites for the removal of NH_4^+ from wastewater. This study has been able improve on the acid-pretreatment procedure for clinoptilolite. This study demonstrated that it is not only the acid concentration that is important but also the number of extractions needed to remove all the exchangeable cations from the clinoptilolite framework. This study has also been able to prove that South African clinoptilolite can treated ammonia from wastewater.

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DECLARATION

I declare that “***Sorption properties of natural zeolites for the removal of hazardous elements***” is my own work, that it has not been submitted for any degree or examination in any other university, and that all the resources I have used or quoted have been indicated and acknowledged by complete references.

Guillaume Ndayambaje November 2011

Signed...

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DEDICATION

I dedicate this thesis to my late parents Mr and Mrs Naligizente

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LIST OF ABBREVIATIONS

A	Anorthite
AMD	Acid mine drainage
BET	Brunauer–Emmett-Teller
BJH	Barret–Joiner–Halenda
C	Clinoptilolite
C_{ca}	Concentration of cation species
C_e	Equilibrium concentration of the adsorbate (mg/L)
CEC	Cation Exchange Capacity
C_o	Initial concentration of adsorbate (mg/L)
EDS	Energy Dispersive X-ray Spectroscopy
EHC	ECCA Holdings hard clinoptilolite
ENS	Environmental and Nano Sciences
ESC	ECCA Holdings soft clinoptilolite
FTIR	Fourier Transform Infrared
ICP-OES	Inductively Coupled Plasma–Optical Emission spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
LOI	Loss on Ignition
LZC	Lightweight zeolite concrete
M	Muscovite
ND	Not detected
Q	Quartz
Q_e	Adsorption Equilibrium amount of adsorbate (mg/g)
PBU	Primary Building Unit
PC	Pratley clinoptilolite
S	Stilbite
SAED	Selective Area Electron Diffraction
SBU	Secondary Building Unit
SEM	Scanning Electron Microscopy
T	Sanidine

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T-O	Represents AlO_4 or SiO_4 tetrahedral
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
V	Volume (L)
W	Weight (g)

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CHAPTER 1

1.0 INTRODUCTION

This chapter will mainly focus on the background and provide an outline of this study. The first section of this chapter will present a brief background information on the pollution of water by heavy metals, different wastewater treatment technologies and a brief description of natural zeolites. The second section will outline the research questions, problem statement, motivation and objectives, and research approach of this study. In order to highlight the aim of this study, the scope and delimitation of this study will be defined at the end of this chapter followed by the whole thesis outline (structure).

1.1 BACKGROUND

Wastewater discharged from industries such as mining, chemical manufacturing, electroplating, metallurgical and metal finishing and so on contains heavy metals and other hazardous components which are classified as environmental contaminants. When discharged into the environment, the heavy metals in wastewater pollute the surface and groundwater. Heavy metals are well known to be harmful to humans. Some of these metals are carcinogenic or nephrotoxic when a large amount is accumulated in the human body causing cancer and destroying tissues such as the kidneys (Human health fact sheet, 2005). The quality of drinking water in South Africa, especially in Gauteng Province has been negatively affected due to the contamination by heavy metals from the acid mine drainage (AMD) generated by some mining companies (Mohamed *et al*., 1992).

Different treatment technologies such as electrodialysis, precipitation, flocculation, adsorption, ion exchange, chromatography and membrane technologies (reverse, osmosis and ultrafiltration) have been used by different wastewater treatment plants (Mumpton, 1999).

Among these purification processes, some are expensive in terms of their operating system while others have low metal recovery capacity and produce a large amount of sludge which needs to be safely disposed into the environment to avoid further pollution. Adsorption and ion exchange processes have been proved to be reliable, low cost and effective methods for the removal of heavy metals and other contaminants in drinking and wastewaters. The use of natural zeolites (e.g. clinoptilolite) for the removal of heavy metals or ammonia has been considered to be a competitive and effective process due to its low cost, relative simplicity of application and operation and high sorption capacity (Erdem *et al*., 2004; Gedik and Imamoglu 2008). Synthetic resins are used in ion exchange processes and are the most effective sorbents in terms of ion exchange capacity, metal recovery and regeneration compared to that of natural zeolites, but they are costly to acquire and operate. Due to the need experienced by many companies to reduce operating and maintenance costs, many industries prefer to use natural zeolites such as clinoptilolite for economic reasons.

Natural zeolites are crystalline aluminosilicates of group one and two elements. They are mostly composed of SiO_4 and AlO_4 tetrahedral joined into three-dimensional frameworks. Aluminium and silicon are linked together by oxygen atoms to form a large framework structure in which each aluminium atom has a negative charge that is balanced by exchangeable cations such as Na^+, K^+, Mg^{2+} and Ca^{2+} (Kaduk and Faber, 1995; Cakicioglu-Ozkan *et al*., 2005; Faghihian *et al*., 2008). These charge compensating cations in the large channels or cavities of the zeolite framework structure are easily exchanged with other cations present in the solution; depending on the size, charge density and distribution of the exchangeable cations in the porous structure. Among these cations, Na^+ is the most weakly bound cation in the clinoptilolite framework and is therefore easily exchanged with other cations present in the solution. These exchangeable cations play a vital role in the adsorption of metals ions and dyes from wastewaters. In the sorption method, certain parameters are to be considered, such as the pH, concentration, reaction time, sorbent mass and particle size of the sorbents.

Tang *et al*., 2006 reported the increase in sorption capacity of ammonium with the decrease in particle size of sorbents. This was attributed to the fact that the exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the smaller zeolite particle sizes are easily exchanged with the cations in the aqueous solution compared to those in the zeolites with larger particle sizes. Many researchers have reported the pretreatment of clinoptilolite in order to enhance its cation exchange ability using different activating agents at low concentration level such as ammonium acetate, hydrochloric acid, sodium chloride, potassium and sodium hydroxide solution (Akyil *et al*., 2004, Cakicioglu-Ozkan *et al*., 2005; Loizidou *et al*., 1994; Semmens *et al*., 1988; Walker *et al*. and Zamzow *et al*., 1990). Very few studies considered the optimisation of the pretreatment step.

The removal of heavy metals from wastewaters before their discharge has been a major problem for many industries. The world is facing a serious challenge of providing quality drinking water due to the rapid increase of population, change in climate and environmental pollution. It is therefore necessary to remove heavy metals from wastewater before it gets discharged into the surrounding environment and find the most simple ways of purifying water since the purification process currently used is costly. Many researchers have investigated the removal of ammonia using clinoptilolite from aqueous solution (Gaspard *et al*., 1983; Schoeman, 1986; Haralambous *at al*., 1992; Ahmet *et al*., 2000 and Muzenda *et al*., 2011). Koon *et al*., (1975) investigated the removal of ammonia from municipal wastewater using clinoptilolite. Gaspard *et al*., (1983) studied the ammonium uptake characteristics from drinking water using the natural zeolite; clinoptilolite. Schoeman (1986) investigated ammonia uptake from underground mine-water using South African clinoptilolite (mined by Pratley Polymers companies) and then compared it with that of Hector clinoptilolite mined in the United States of America. Muzenda *et al*., (2011) also investigated the removal kinetics of ammonia from synthetic wastewater solutions using South African pretreated clinoptilolite mined by Pratley. Two of these types of clinoptilolites are mined by ECCA Holdings company (soft and hard clinoptilolite samples) in the Western Cape Province, while the third type of clinoptilolite used as comparison,

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was sourced from Pratley from KwaZulu-Natal province in South Africa for the removal of ammonia and chromium from synthetic solutions (see the geology map in Figure 1). The ECCA Holdings deposit has not been extensively studied for its clinoptilolite quality.

1.2 STUDY SITE

The natural adsorbents used in this study were South African clinoptilolites which originated from two different zeolite companies; ECCA Holdings and Pratley. The ECCA Holdings company is located in the Western Cape of Province in South Africa thus its clinoptilolite deposits are located in the Western Cape. The Pratley natural clinoptilolite is mined in Kwazulu-Natal Province in South Africa. Figure 1 blow shows the geological map of the ECCA Holdings clinoptilolite deposits.

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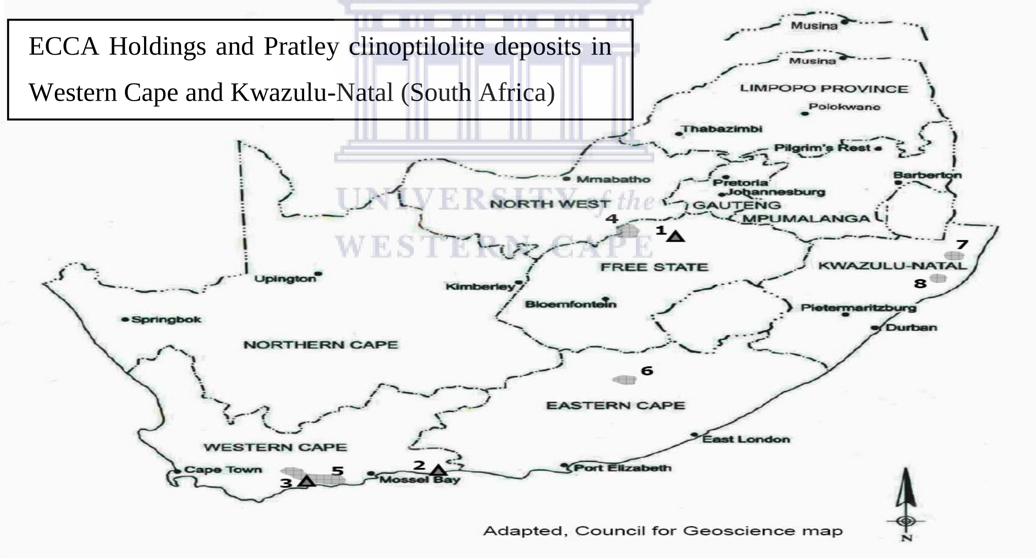
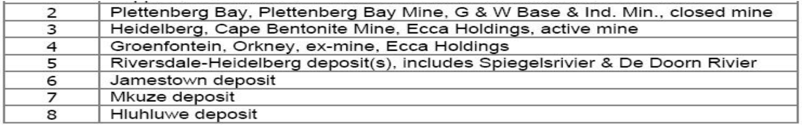


ECCA Holdings and Pratley clinoptilolite deposits in Western Cape and Kwazulu-Natal (South Africa)

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



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: Mining map of clinoptilolite deposits in South Africa (Western Cape and Kwazulu-Natal)

1.3 PROBLEM STATEMENT

The Republic of South Africa is facing the challenge of continuous water pollution resulting from abandoned and active mines, mostly situated in Gauteng Province. Polluted water from these mines contains various heavy metals and cations or anions which contaminate the surrounding surface and ground water. Many dams and rivers are heavily polluted with heavy metals leading to loss of human lives and also aquatic species in the dams and river. It is therefore necessary to find a way of extracting these contaminants from wastewater before discharging it to the environment. There is a need to investigate the use of economically viable natural South African zeolites such as clinoptilolite and explore their potential applications in wastewater treatment processes. The beneficiation of the abundant natural clinoptilolite produced by the South African mining companies such as ECCA Holdings and Pratley requires a thorough investigation of the characteristics of this source of zeolite. Schoeman (1986) and Muzenda *et al*., 2011) investigated the removal of ammonia using South African clinoptilolite mined by Pratley. Schoeman (1987) compared the ammonia removal capacity of South African clinoptilolite to that of Hector from USA. Mamba *et al.*, (2009) also investigated the removal capacity of copper and cobalt from synthetic zeolite using South African clinoptilolite (Pratley). Apart from the study conducted by Schoeman (1986), Muzenda *et al*., (2011) and Mamba *et al*., (2009) on South African Pratley clinoptilolite for the removal of ammonia or other heavy metals from wastewater, no other study has been conducted to compare the sorption capacity of different South African clinoptilolites for the removal of ammonia and chromium from wastewaters. The motivation for this study is therefore to characterize, activate and compare the quality of South African clinoptilolite mined by two different companies and from two different provinces.

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1.4 AIMS AND OBJECTIVES OF THE STUDY

Over the past years, various studies have been conducted on the use of South African clinoptilolite for the removal of ammonia and other heavy metals (Schoeman, (1986); Muzenda *et al*., 2011 and Mamba *et al*., 2009).

However, these studies, there has not been any study done on the comparison of sorption capacity of two different South African clinoptilolites (ECCA Holdings and Pratley) for the removal of ammonia and chromium from wastewater. Therefore, the aims of this study are to characterize natural clinoptilolites from different provinces in South Africa and determine their sorption capacity for the removal of ammonium and chromium ions from aqueous solutions. Moreover none of the existing studies considered the optimization of the process, its effect upon sorption properties of the local clinoptilolite.

The overall objectives of this study are summarised as follows:

- To convert (pretreat) both natural South African clinoptilolites (Pratley and ECCA Holdings) to H^+ form of clinoptilolite using HCl solution.

- To characterize both as-received and pretreated natural South African clinoptilolites (ECCA Holdings and Pratley).

- To investigate the total cation exchange capacity (CEC) of both South African clinoptilolites (ECCA Holdings and Pratley) considering their exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} located in clinoptilolite framework structure.

- To examine the leaching capacity of the exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) using diluted HCl acid solution as a function of time, to optimize the pretreatment procedure.

- To apply both as-received and pretreated ECCA Holdings and Pratley clinoptilolites for the removal of ammonia an chromium from synthetic wastewater.

- To examine the sorption capacity of both Cr^{3+} and NH_4^+ on the as-received and pretreated Pratley and ECCA Holdings clinoptilolites.

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- To investigate the relevant sorption mechanisms for Cr^{3+} and NH_4^+ uptake using both untreated and treated clinoptilolite by focusing on the following sorption mechanisms such as equilibrium and kinetics studies. These mechanisms are based on the sorption parameters such as pH, reaction contact time, sorbate concentration, adsorbent dosage, natural adsorbent mineral phase purity, adsorbent surface area and exchange sites in the adsorbent.

- To model the adsorption kinetics of the zeolites via the Langmuir and Freundlich adsorption isotherms.

1.5 RESEARCH QUESTIONS

The research questions of this study are summarized as follows:

- What are the chemical and mineralogical compositions of natural clinoptilolites from ECCA Holdings and Pratley in South Africa?
- Does cation exchange capacity (CEC) of natural ECCA Holdings and Pratley South African clinoptilolite fall in the specific limit of the accepted clinoptilolite value and what are the optimum conditions?
- Can natural clinoptilolite be converted into H^+ form using HCl without modifying its framework structure?
- Are the South African natural clinoptilolites equally useful as adsorbent for the removal of ammonia from synthetic wastewaters?
- Will the acid-pretreatment of clinoptilolite enhance adsorption capacity?

1.6 RESEARCH APPROACH

In the interest of achieving the above mentioned objectives and choosing the right strategy for preconditioning (pretreatment) of natural South African clinoptilolites and apply them to remove ammonia and chromium from wastewater, the following approaches were considered:

- Choose the parameters to optimise and understand the effects of different acid pretreatment of both South African clinoptilolites (ECCA Holdings and Pratley) based on literature review.

- Compare and explore the chemical and physical properties of both pretreated and as-received South African clinoptilolites (ECCA Holdings and Pratley) using characterization methods adopted from the literature review.

- Investigate whether both South African clinoptilolite (ECCA and Pratley) have the same adsorption capacity for the removal of ammonia and chromium considering different sorption parameters based on the literature review.

Extensive review on the pretreatment of natural clinoptilolite was carried out and features of the proper pretreatment methodology were adopted. The variables most likely to affect the chemical and physical properties of natural South African clinoptilolite during the acid pretreatment process were identified. These variables (acid concentration and treatment time) were optimised and then both pretreated and as-received clinoptilolites were characterised using different techniques such as XRD, XRF, BET, SEM-EDS, HRTEM-SAED, FTIR and BET adopted from the literature review. The results obtained were then compared to those obtained in other clinoptilolite studies since there are significant differences in elemental composition of clinoptilolite mined from different sources. Cation exchange capacity was determined based on the literature review in order to know which adsorbent is the best in terms of ion exchange capacity.

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The second experimental section focused on the adsorption of ammonia using both as-received and pretreated clinoptilolites from Pratley in order to optimize process parameters found for Pratley clinoptilolite. Adsorption experiments were done using a batch method and were divided into four different experiment sets; contact time, pH, dosage and concentration experiment.

The above described adsorption experiments were done sequentially whereby, at each experiment, a single parameter was changed while the other parameter remained constant. Once the effect of one parameter had been determined or optimized, the effect of the next parameter was investigated whilst keeping all the other parameter constant. The obtained kinetics data were compared to those obtained in the literature review. The adsorption of chromium was also done following the same experimental adsorption parameters used in ammonia adsorption experiment. Both ammonia and chromium were analysed in the solution after adsorption experiments using UV/Vis spectroscopy method but each with different sample preparation and at different wavelength.

After optimization of all the adsorption parameters on Pratley clinoptilolite, no optimization experiments were done on ECCA Holding clinoptilolite. Instead, the optimized parameters were applied in the adsorption of ammonia and chromium using ECCA Holdings clinoptilolite for a good comparison of their cation exchange capacities. Adsorption experiments were followed by analysis of the equilibrium kinetics data and then tested for applicability to the Langmuir and Freundlich adsorption isotherms.

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The challenge of this approach was the large number of trials needed to optimize each adsorption parameter especially for contact time and pH experiments. Triplication of some experiments was conducted in order to check the reproducibility of the adsorption study. Ammonia determination using Nessler method of analysis was difficult to achieve.
This is because ammonia is volatile causing the fluctuation of results using UV/Vis method. Ammonia measurements need to be carried out immediately after the adsorption experiment.

1.7 HYPOTHESIS

Pretreatment of natural adsorbents can increase the uptake of pollutants from wastewaters.

1.8 SCOPE AND DELIMITATION OF THE STUDY

The extensive work done by different researchers on clinoptilolite either mined in South Africa or elsewhere around the world, created a good foundation for this study. Owing to the wide scope of the science of natural zeolite such as clinoptilolite, those aspects that seem important to the pretreatment of clinoptilolite were determined and underlined. However, most of the information which is of less relevance to this study was left out or briefly defined. Out of more than 50 known natural zeolites, this study focused prominently on South African clinoptilolite and only referred to some other natural zeolites that had been pretreated for the adsorption study.

In the choice of the adsorption parameters (time, pH, dosage and concentration) during the course of this study, the variables that had shown some significant influence in the studies done previously on the uptake of ammonia and chromium using clinoptilolite were chosen. Owing to the time consuming nature of pretreatment optimization and adsorption experiments, all optimization adsorption parameters were only investigated on the Pratley clinoptilolite sample due to time and the small amount of ECCA Holdings clinoptilolite sample available. Therefore, ammonia adsorption experiments were conducted using both ECCA Holdings and Pratley clinoptilolite samples (untreated and pretreated) whereas chromium was only conducted only on the pretreated Pratley sample. The analyses of elemental composition (exchangeable and heavy metals) of the as-received treated and pretreated clinoptilolite were only done on the exchangeable cations due to high cost of ICP analyses.

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1.9 THESIS OUTLINE

This thesis is divided into six chapters (including this one; Chapter 1) and is structured as follows:

Chapter one: This chapter presents the introduction to the study, the motivation and objectives of the study. This chapter provides an outline of the research framework and contextualizes the study by presenting a brief overview of the background, problem statement and a brief general literature of natural zeolites (clinoptilolite).

Chapter two: This chapter presents the literature review which covers relevant aspects of natural zeolite in general and specifically clinoptilolite. This chapter also presents an overview of zeolites with focus on key natural zeolites (clinoptilolite), their characteristics, applications in different fields, and discusses the factors that affect either zeolite (clinoptilolite) or the solution during the pretreatment and adsorption process. This chapter also describes the mechanisms and isotherms that are attributed to the adsorption study.

Chapter three: This chapter gives an account of the materials used, the study design and methodologies, and gives the rationale behind the selection of the procedure for natural zeolite (clinoptilolite) pretreatment. Details of the actual methodologies and research instruments used and the relevant analysis techniques are presented in this chapter.

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Chapter four: This chapter presents the pretreatment and characterization of pretreated and as-received clinoptilolite and compares ion exchange capacity of different types of South African clinoptilolites with relevant references to literature.

Chapter five: The results and discussion of the adsorption of ammonia and chromium from synthetic wastewater are presented in this chapter. The metal uptake ability of South African clinoptilolite are compared to those obtained from the literature.

Chapter six: The summary of the main findings of the study is presented her. The conclusions and recommendations for possible future work are also presented in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 BACKGROUND

Over the years, studies on properties of natural zeolites have been carried out by many researchers and their findings varied from one another due to the diversity of the nature of zeolites. It is therefore important to understand the origin, background of zeolites and its derivatives. This chapter will cover different aspects such as the origin, the background of natural zeolites and their abundance around the world. Studies on chemical and physical properties of zeolites will be reviewed for a better understanding of their varied applications.

2.2 ORIGIN OF ZEOLITE

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Zeolites were discovered in 1756 by a Swedish mineralogist called Axel Fredrik Cronstedt while heating a material (stilbite). Cronstedt observed steam coming from the sample which was from water absorbed by the material. From this observation, he then named the material; “zeolite”. In Greek, the word zeolite is composed of two different words “zeo” and “lithos” meaning “boil” and “stone” respectively (Newsam, 1986). Since the discovery of zeolite in 1756, natural zeolites have been used in many different applications. Due to the low production of natural zeolites and the inability to meet demands, the use of synthetic zeolites became popular. However, in late 1950s, the business of synthetic zeolite was also put on hold due to the discovery of huge beds of natural zeolite-rich sediments containing about 95 % zeolite mineral. These sediments resulted from the alternation of volcanic ash in lake and marine waters. The first natural zeolite sediments were discovered in the United States of America and later sediments were discussed in the rest of the world. The natural zeolite beds were easily mined and processed for various applications (Mumpton, 1999).

2.3 ABUNDANCE OF ZEOLITES IN THE WORLD

Natural zeolites are found in large quantities in most countries of the world such as Turkey, Russia, New Zealand, Japan, North Korea, USA and Central America. According to the Chamber of Mining Engineers of Turkey (2003), there are forty different types of natural zeolites found in sufficient quantities across the World. The most common of these natural zeolites are clinoptilolite, mordenite, phillipsite, chabazite, eronite, ferrierite and analcime. These zeolites are of high purity and their ion exchange properties have made them useful in different applications (Ouki *et al*., 1994). Clinoptilolite is the most abundant naturally occuring zeolite across the world. It is found in large reserve deposits in different countries and the mined quantity differs from country to country. Turkey is known to have the highest reserve of zeolite deposits in the world (Chamber of Mining Engineers of Turkey, 2003). A study conducted by the Chamber of Mining Engineers of Turkey (2003) has estimated 20 million tons of clinoptilolite in the deposit of Gordes and Manisa in Turkey while 500 million tons was found in Bigadic and Balikesir. In South Africa, the reserves of clinoptilolite deposits are found mainly in the province of Western Cape and Kwazulu-Natal Province (Mamba *et al.*, 2009) (refer to the geological map shown in Figure 1, Chapter 1).

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2.4 PHYSICAL AND CHEMICAL PROPERTIES OF ZEOLITE

2.4.1 Zeolite structure

Zeolites are crystalline hydrated aluminosilicates of group one and two cations (alkaline and alkaline earth). They are mostly composed of SiO_4 and AlO_4 (as $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$) tetrahedrons linked together though oxygen atoms (Barrer, 1979 and Mumpton, 1999). These tetrahedrons are known to be the primary building unit (PBU) in the zeolite framework structure (Figure 2 and 3). The primary building units are then assembled together by oxygen atom bridges to form a secondary building unit (SBU) (Figure 3) which are repeated to form a continuous large framework structure in a unit cell (Barrer, 1982; Flanigen, 1991; Tsitsishvili *et al*., 1992 and Mumpton, 1999).

Zeolites contain both water molecules and extra framework charge balancing cations (normally Na^+, K^+, Mg^{2+} and Ca^{2+}) in their channel cavities. These cations are mainly alkali metal or alkaline earth metals. Zeolites are able to lose and gain water reversibly and exchange their exchangeable cations without causing any destruction or change in the framework structure. In the zeolite unit cell, each aluminium atom carries a negative charge which is compensated by extra-framework charge balancing cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) located together with water molecules in zeolite pores to give electrical neutrality (see Figure 3). These cations are easily exchanged or removed by other cations in a solution leaving aluminium and silicon unchanged under normal standard conditions (Cakicioglu-Ozkan *et al.*, 2005; Kaduk and Faber, 1995; Faghihian *et al.*, 2008 and Mumpton, 1999). The following figures (Figure 2 and 3) describe the primary building unit (PBU) of zeolite framework.

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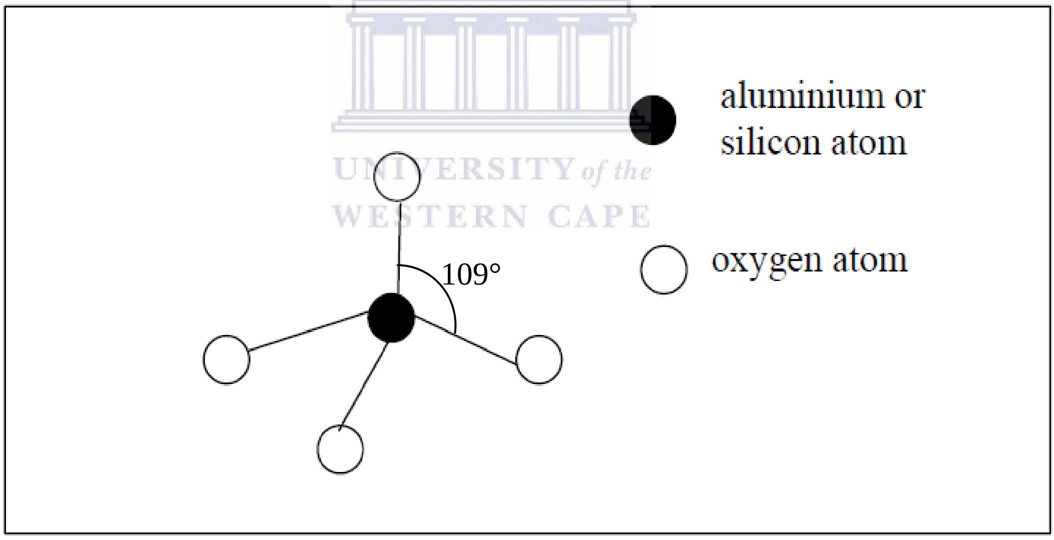

Figure 2: Primary building Unit: $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ (Barrer, 1982)

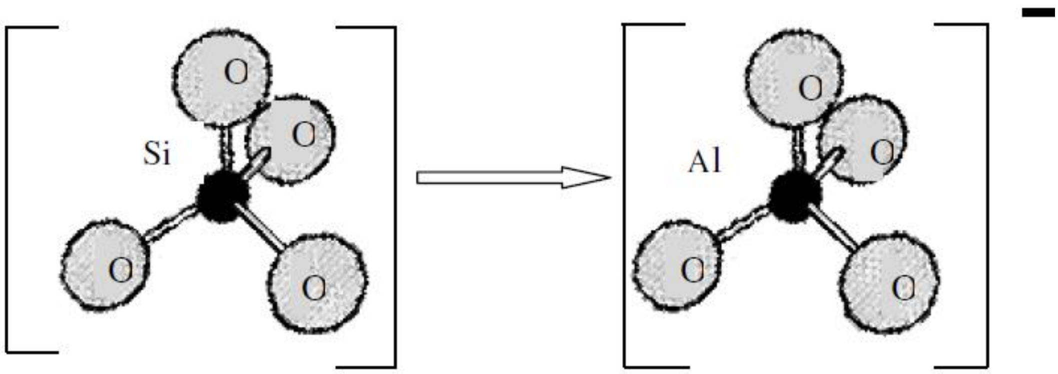

Figure 3: Primary building unit $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons arrangement in the zeolite framework structure showing each Al atom surrounded by a negative ion which balanced by the extra-framework cations present in the zeolite framework (Kapanji *et al*., 2009).

Meier (1996) explained that the secondary building unit (as shown in Figure 4) with different shapes of tetrahedrons are generated from the primary building units during formation depending on the type of zeolite framework. The following are different possible secondary building units that can exist in the course of zeolite framework structure formation.

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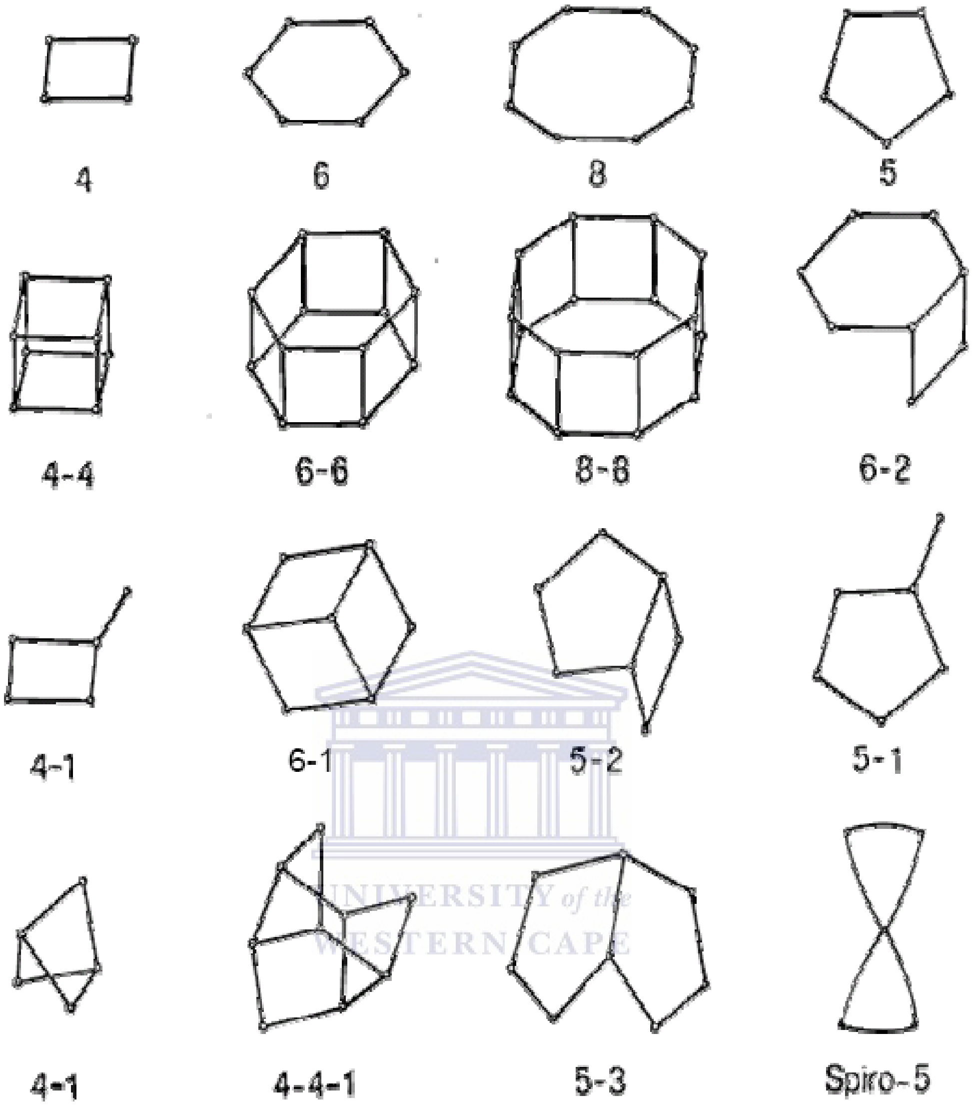

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Figure 4: Secondary building unit (SBU) in the zeolite framework structure (Meier, 1996)

Szostak (1989) described the primary units as the network of tetrahedrons connected to each other by straight lines which schematically represent the T-O-T bridges (Figure 5) where T represents either Si or Al. These tetrahedral are joined so that each of the four bridging oxygens are shared in turn with another tetrahedron, silica or alumina (Figure 5a) to form a wide range of small secondary building units (Figure 5b).

Figure 5c shows zeolite framework structure formed from the continuous repeat of the primary building units (PBU).

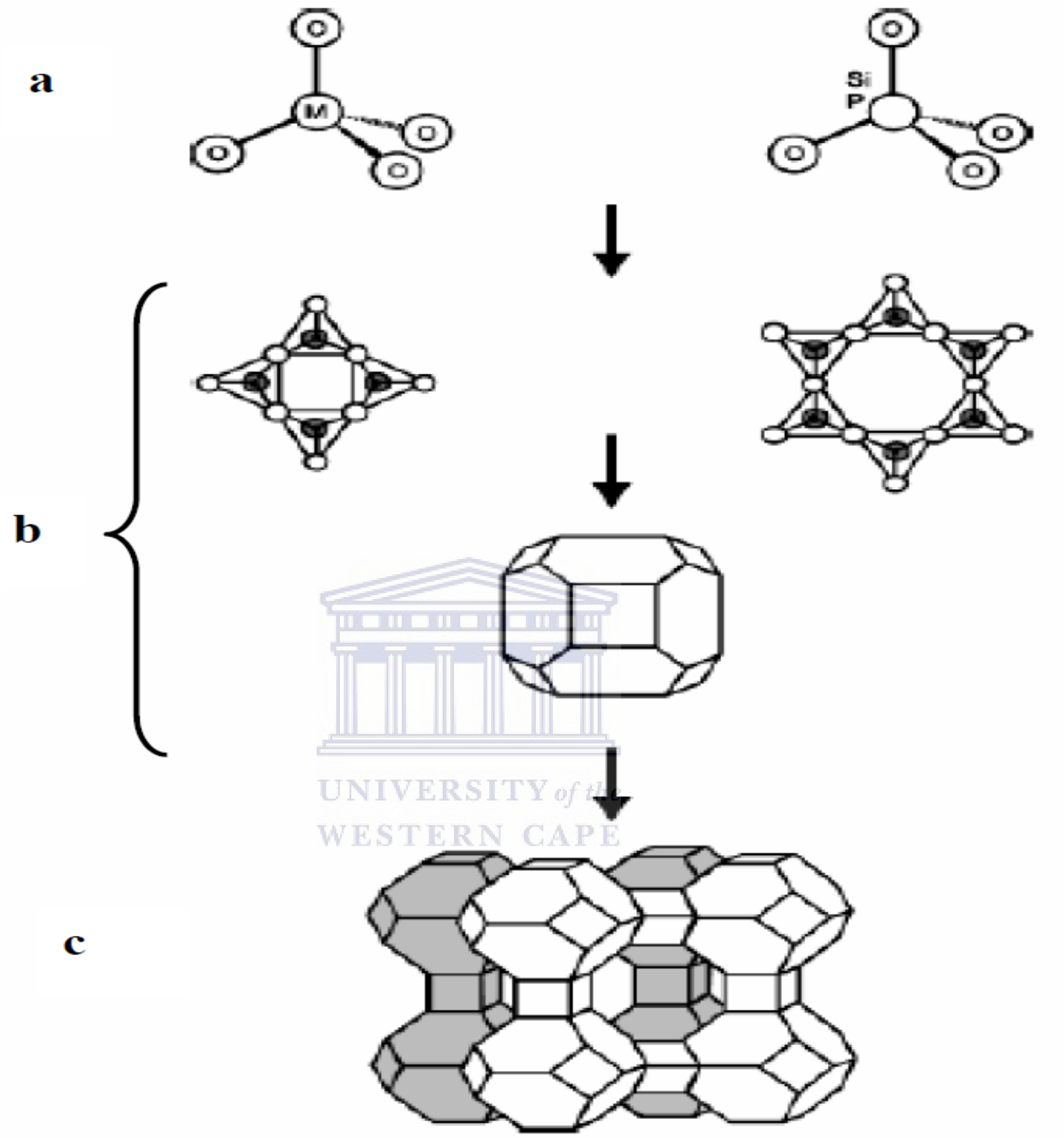

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Figure 5: Schematic representative of the building of zeolite framework (Meier, 1996) where (a) primary build-up units, (b) second build-up and (c) zeolite framework structure

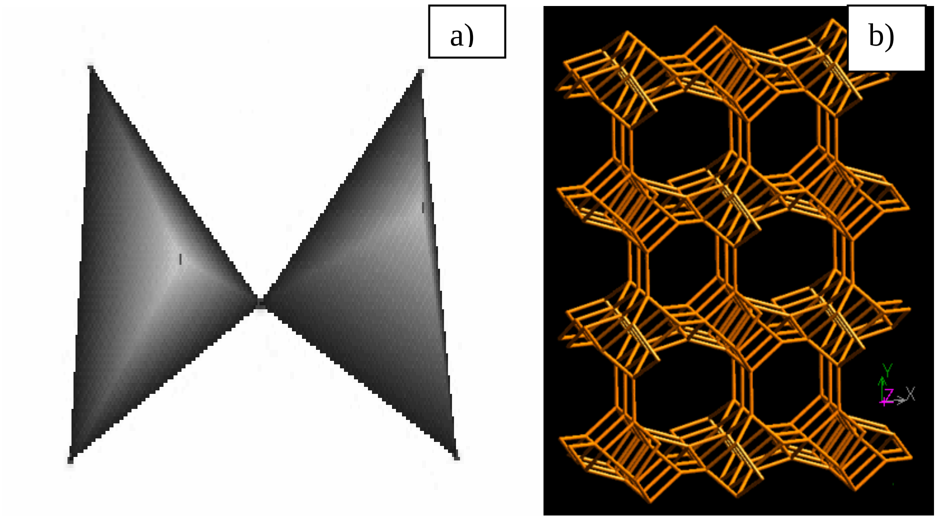

Figure 6: Schematic representation of (a) SiO_4 and AlO_4 tetrahedrons sharing an oxygen atom to form a continuous framework and (b) zeolite framework pore structure in the unit cell (HEU), (Barrer, 1982)

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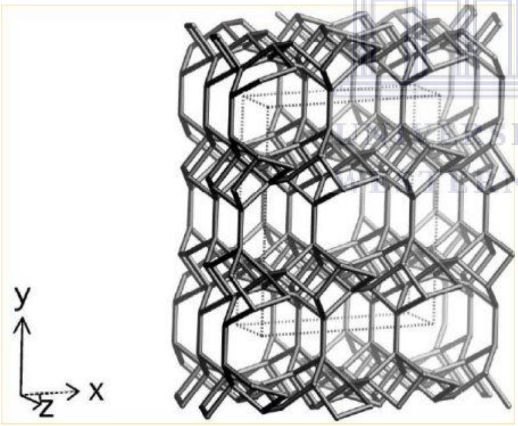

Figure 7: Clinoptilolite framework in a 3-Dimenssion representation showing pores in the framework (Baerlocher *et al*., 2002)

Theoretically, the general chemical formula zeolite per unit cell is expressed as follows (Breck, 1974);

$$Mx/nO[(AlO_2)x.(SiO_2)y].wH_2O \qquad 2.1$$

Where *M*: Exchangeable cation with the valence of n (alkaline and alkaline earth being Na^+, K^+, Mg^{2+} and Ca^{2+}).
W: Number of water molecules present in a unit cell
x and y: Total number of tetrahedra in the unit cell.

The chemical formula of South African natural clinoptilolite is given below (Pratley information sheet, 1977):

$$(MgCaNa_2K_2)_{25}(AlO_2)_7(SiO_2)_{30}.21H_2O \qquad 2.2$$

2.4.2 Chemical properties of zeolites

As mentioned in the previous section, zeolites are composed of alumina-silicates (which are the main constituents), alkaline and alkaline earth cations and water molecules. These extra framework cations and water molecules are both found in the channel or pore cavities of the zeolite framework in a unit cell (Tsitsishvili *et al*., 1992). The main primary build blocks of zeolite are aluminium and silicon which makes up its continuous framework. Its topology consists of stable site of aluminium ions (Al^{3+}) and silicon ions (Si^{4+}). The Si/Al and exchangeable cations ratio are used to determine the properties of different zeolites. According to Tsitsishvili *et al*., (1992), Si/Al ratio lies between the boundaries of 1 to 6 for natural zeolites with the range of 4 to 6 for clinoptilolite and mordenite. Mason and Sand (1960), explained that the characteristics boundary of clinoptilolite is Si/Al ≥ 4.0 with a sum of ($Na^+ + K^+$) exceeding that of ($Ca^{2+} + Sr^{2+} + Ba^{2+}$) in clinoptilolite. Mason and Sand, (1960) compared clinoptilolite and mordenite, and reported that the ratio of Si/Al ≥ 4.0 for clinoptilolite, and the sum of monovalents (Na^+ and K^+) exceeded that of divalents (Ca^{2+} and Mg^{2+}). The ratio of (Na^+ and K^+)/Ca^{2+} was found to be 4.3, and a similar value was reported by Coombs *et al.*, (1997) and Armbruster (1993). However, Coombs (1997) recommended that zeolite minerals should 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). Other properties of zeolite are detailed below.

2.4.3 Cation exchange characteristics of zeolites

The exchangeable cations located in the channel cavities or pores of the zeolite framework are weakly bonded and mobile. They can easily be substituted, removed or exchanged by another cation from aqueous solution. Sorption capacity of zeolites depends on the amount of aluminium that replaces silicon atom in the framework structure. Therefore, the more the aluminium atoms content in the framework, the more exchangeable cation are needed to balance the negative charges in the framework (Mumpton, 1999). Natural zeolites are known to have a theoretical cation ion exchange capacity ranging from 2 to 5.5 meq/g zeolite (see Table 2). Cation exchange behaviour of zeolites depends upon the nature of the cation species, cation size, both anhydrous and hydrated, cation charge, the concentration of the cation species in solution and the structural characteristics of the particular zeolite (Breck, 1974).

2.4.4 Molecular sieve properties of zeolites

Water molecules are located in the channel cavities (voids) of zeolites framework structure. Tsitsishvili *et al.*, (1992) stated that under normal standard conditions, water fills the free volume of channels and cavities in the zeolite framework. According to Ouki *at al.*, (1994), the content of water in the channels and cavities is about 10 to 25 % of their weight in the normal natural of zeolites. Zeolites framework cannels cavities exhibit a phenomenon called “molecular sieve” which takes place when zeolite is heated at about 350 to 400 °C where small water molecules can pass though the entry channel excluding the large molecules (Mumpton, 1999).

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2.4.5 Thermal stability of zeolites

The thermal stability of zeolites is seen to increase with increasing SiO_2/Al_2O_3 ratio of the framework. In low silica zeolites ($SiO_2/Al_2O_3 < 5$), the crystalline decomposition temperature is near 700ºC, while in high silica zeolites the crystalline decomposition temperature can be above 1300ºC. The acid or base stability of zeolites also varies with changes in the framework SiO_2/Al_2O_3 ratio.

Low silica zeolites are fragile in the presence of acids, while high silica zeolites are completely stable in boiling, concentrated mineral acids. Conversely, high silica zeolites are unstable in basic solution, while low silica zeolites show increased stability (Murphy, 1996).

2.4.6 Hydrophobicity of zeolites

High silica zeolites with SiO_2/Al_2O_3 ratio from 20 - ∞ in the zeolite tend to make the zeolite hydrophobic. With increasing silica content and decreasing aluminium, zeolites become more hydrophobic and therefore, the greater the ability of these materials to interact with hydrophobic organic molecules or to exclude hydrophilic molecules, such as water. The transition from hydrophilic to hydrophobic occurs at about $SiO_2/Al_2O_3 = 20$. Whether zeolites are hydrophilic or hydrophobic can have a profound influence on their chemical reactivity (Juttu, 2001).

2.4.7 Acidity of Zeolites

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Acidity is one of the most important characteristics of zeolites which make them very useful in acid catalysis. A good understanding of the nature and number of acid sites which correlates directly with the amount of Aluminium incorporated in the lattice framework in zeolite is needed in developing improved and novel catalysts for applications in the chemical industries (Juttu, 2001). The reactivity and selectivity of zeolites as acid catalysts are determined by the surface acidity of the active sites. It is clear that this activity is related to the acid strength of the Brönsted acid sites (Costa *et al.*, 2000).

The framework aluminium atoms are negatively charged and balanced by extra-framework cations (Na^+, K^+, Mg^{2+} and Ca^{2+}), which represent potential active acid sites (Barrer, 1982). The acidic properties of zeolites are mainly dependent on the Si/Al molar ratio as well as the temperature of activation. In zeolites, acid sites are classified according to the classical Brönsted and Lewis acid models (see Figure 8). Brönsted acidity corresponds to proton donor acidity, while Lewis acidity corresponds to electron pair acceptor.

Brönsted acidity occurs when the cations, used to balance the negatively charged framework, are protons (H^+). A trigonally coordinated aluminium atom possessing a vacant orbital that can accept an electron pair, behaves like a Lewis acid site. To produce the zeolite acid catalysts, it is necessary to replace the cations present in the freshly synthesized or natural material with protons. In zeolite, proton can be introduced by various methods. If an aluminium ion, which is trivalent, is substituted isomorphously for a silicon ion, which is quadrivalent, in a silica lattice comprising silica tetrahedral, the net negative charge must be stabilized by a nearby positive ion such as a proton. This positive ion can be produced by the dissociation of water, forming a hydroxyl group on the aluminium atom. The resulting structure, in which the aluminium and the silicon are both tetrahedrally coordinated side by side, produces the Brönsted acid cite. If this structure is heated, occluded water in the zeolitic framework is driven off followed by condensation process and Brönsted acid sites are converted to Lewis acid sites. The addition of water and heating can convert Lewis acid sites back to Brönsted acid sites (Barrer, 1982). The following is the diagram (Figure 8) describing the mechanism that takes place on the Brönsted and Lewis acid sites.

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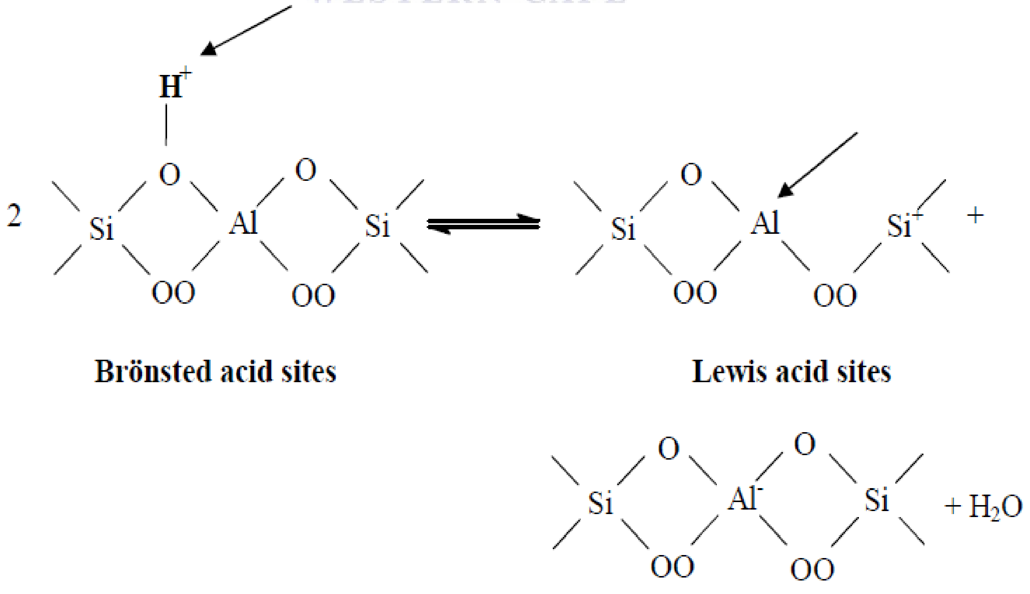

Figure 8: Brönsted and Lewis acid sites in clinoptilolite framework (Barrer, 1982).

Table 1: Representative formulas and selected properties of important zeolites

Zeolite	Representative unit cell formula	Void volume %	Channels dimensions Å	Thermal stability (relatively)	CEC, meq/g
Analcime	$(Na_{10})(Al_{16}Si_{32}O_{96}).16H_2O$	18	2.6	High	4.54
Charbazide	$(Na_2Ca)_6(Al_{12}Si_{24}O_{72}).40H_2O$	47	3.7 x 4.2	High	3.84
Clinoptilolite	$\mathbf{(Na_3K_3)(Al_6Si_{30}O_{72}).24H_2O}$	**34**	**3.9 x 5.4**	**High**	**2.16**
Erionite	$(NaCa_{0.5}K)_9(Al_9Si_{27}O_{72}).27H_2O$	35	3.6 x 5.2	High	3.12
Faujasite	$(Na_{58})(Al_{58}Si_{134}O_{384}).240H_2O$	47	7.4	High	3.39
Ferrierite	$(Na_2Mg_2)(Al_6Si_{30}O_{72}).18H_2O$	28	4.3 x 5.5	High	2.33
Heulandite	$(Ca_4)(Al_8Si_{28}O_{72}).24H_2O$	39	4.0 x 5.5 4.4 x 7.2 4.1 x 4.7	Low	2.91
Laumonitte	$(Ca_4)(Al_8Si_{16}O_{48}).16H_2O$	34	4.6 x 6.3	Low	4.25
Modernite	$(Na_8)(Al_8Si_{40}O_{96}).24H_2O$	28	2.9 x 5.7 6.7 x 7.0	High	2.29
Phillipsite	$(NaK)_5(Al_5Si_{11}O_{72}).20H_2O$	31	4.2 x 4.4 2.8 x 4.8 3.3	Medium	3.31

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Table 1 is a modified table from reference: Breck, 1974 and Meier *et al*., 1971, and presents the summary of physical, chemical properties and the cation exchange capacity of different natural zeolites. The void volume shown in Table 1 was determined from water content in the framework and it was calculated based on the unit cell. Linde A was found to have the highest cation exchange capacity (CEC) with high thermal stability which may be due to the fact that it is a synthetic zeolite. Clinoptilolite has a theoretical total cation exchange capacity (CEC) of 2.16 meq/g with high thermal stability.

2.5 APPLICATIONS OF NATURAL ZEOLITES

Zeolites have attracted the attention of scientists due to their various industrial applications, availability in nature and their unique characteristics (Frost, 2001). Since their commercial discovery in 1950s, natural clinoptilolite has been used in several areas such as water treatment, pollution control, radioactive waste treatment, agriculture, horticulture, aquaculture, natural gas purification and construction (Mumpton, 1999). The following are the overview of different applications of zeolites (clinoptilolite).

2.5.1 Waste water treatment

Among all the above mentioned zeolites applications, the use of zeolites in wastewater treatment is predominant (Frost, 2001). Many researchers have investigated and reported the use of zeolites for the removal of heavy metals from industrial wastewaters (Curkovic *et al*., 1997, Erdem *et al*., 2004, Kapanji and Kutemba., 2009, Mamba *et al*., 2009, Mier *et al*., 2001, Ouki and Kavannagh, 1999 and Ward, 2004).

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Clinoptilolite is been used in water treatment for the removal of heavy metals and toxic elements from wastewater. Researchers have reported that clinoptilolite has a high capacity of removing Pb^{2+}, Zn^{2+}, Cr^{3+}, Cu^{2+}, Cd^{2+} and Ni^{2+} (Curkovic *et al*., 1997, Erdem *et al*., 2004, Kapanji and Kutemba., 2009, Mamba *et al*., 2009, Mier *et al*., 2001, Ouki and Kavannagh, 1999 and Ward, 2004*).* Clinoptilolite can exist in different ionic form; natural as it was mined or in treated Na^+, K^+ and H^+ form. Concerning the adsorption specificity for the extraction of metals from water; clinoptilolite and heulandite are low field strength zeolites for which the cation selectivity series are shown in Table 2. The following (Table 2 is the summary of various metal selectivity series on Na-clinoptilolite reported by different researchers.

Table 2: Selectivity series of different metal ions on Na-clinoptilolite form of zeolite

Selectivity series	**Literature**
Pb^{2+}> NH_4^+ > Cu^{2+} Cd^{2+}, Sr^{2+} > Zn^{2+} > Co^{2+}	Blanchard *et al*., 1984
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 Velokov, 2002
Pb^{2+} > Cr^{2+} > Fe^{2+} ≥ Cu^{2+}	Inglezakis *et al*., 2004
Co^{2+}>Cu^{2+}>Zn^{2+}>Mn^{2+}	Donat, *et al*., 2004

Lead ion has been identified to be the most selective metal ion due to its up-take by clinoptilolite (see Table 2). Many researchers reported high lead ion removal from aqueous solutions using clinoptilolite compared to other metals ions (Curkovic *et al*., 1997, Loizidou *et al*., 1994, Mier *et al*., 2001 and Ward *et a*l., 2004). According to Curkovic *et al*., (1997), the removal of heavy metals from aqueous solution such as wastewater could be attributed to adsorption or ion exchange mechanisms.

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2.5.2 Radioactive waste treatment

Clinoptilolites have been utilized as sorbates for the removal of radionuclides such as ^{90}Sr, Cs and ^{358}U (Akyil 2003). Clinoptilolites serve as filter traps for possible leakages of radionuclides from the containers used to bury radionuclides on dumping sites for the protection of the environment. Zeolites are also used at nuclear weapon test sites to trap possible spills of radionuclide species. According to Frost (2001), clinoptilolite zeolites are effective in the treatment of radionuclide wastes that contain certain isotopes such as ^{90}Sr, ^{89}Sr, ^{137}Cs, ^{134}Cs, ^{60}Co, ^{45}Ca, and ^{51}Cr. Chabazite-rich tuffs are also routinely applied for the decontamination of radioactive wastewater to remove Cs and Sr.

Zeolites are applied to soils to prevent uptake of the radionuclide species by the plant roots. According to a survey conducted by Frost (2001), zeolites have also been used as sorbent to control high levels of nitrogen in soil and serve in the cleaning of chemical waste dumps.

2.5.3 Agriculture and horticulture

Zeolites have shown a potential application in the agriculture industry especially in nurseries and greenhouses. Zeolites remove the slow released nitrogen, potassium, phosphorus and calcium from the fertilizer (Frost, 2001). The removal of the above cited elements (nitrogen phosphorus and calcium) is achieved when soil is mixed with a certain amount of clinoptilolite during cultivation process. The resulting soil is called amended soil and the whole process is called amendment of soil. Soil modification with zeolites is advantageous for turf and green. An extensive research done by Mumpton (1999) in Japan and Cuba, showed that soil amendment has yielded results with significant increases in the yields of wheat (13 – 15 %), eggplant (19 – 55 %), apples (13 – 38 %), and carrots (63 %) when 4 to 8 tons per acre zeolite was used. The benefits of utilizing clinoptilolite in agriculture including controlled release of fertilizers and the ability to be loaded with a fertilizer, exchange and release of inherent potassium ions. Natural clinoptilolites are available at low cost and they are hydrophilic materials. They decrease the need for golf course green top dressing and they increased the yields documented for many crops.

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2.5.4 Aquaculture

Zeolites are known to have a high cation exchange capacity (CEC) making them to be excellent in the removal of hazardous elements (Frost, 2001). According to Frost (2001), the aquaculture industry contributed to about 30 % to the total fish production yielding an increase of 31 % from 1997 to 2000. Natural zeolites play three vital roles in aquaculture and these include; removal of ammonium from hatchery, fish transport, and aquarium waters; generation of oxygen for aeration systems in aquaria and transport; and supplementing fish feed.

2.5.5 Pet litter and odour control

Farmers are faced with serious problems of irritating gaseous by-product such as ammonia and hydrogen sulphide which results from the decomposition of organic matter from food and waste products (Frost, 2001). The use of clinoptilolite in the animal feed for cows, pigs, horses and chicken house has resulted in the improvement of animal health and low mortality. Therefore, zeolites are considered as excellent materials in the elimination of irritating gaseous matters (mostly nitrogen and ammonia emissions) due to their high cation exchange capacity. The use of clinoptilolite as feed additive and bedding mixture has resulted in cleaner chicken houses and healthier animals. For instance, 10 % weight clinoptilolite has been observed to increase the weight of chicken by 20 % without deleterious effect on health. The use of zeolite in the chicken house has been observed to improve the productivity (increase egg-laying and shell thickness), reduce gastrointestinal disease, increase nutrient adsorption, and reduce ammonia emissions (Mohi *et al*., 2005). A shifting effect on nitrogen excretion from urine to faeces in monogastric animals, which resulted in lower aerial ammonia, has been noted (Mohi *et al*., 2005).

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2.5.6 Other application of zeolites

Clinoptilolite is utilized in the purification process of natural gas such as methane. Impurities such as water, carbon dioxide and sulphur dioxide are removed from natural gas using zeolites in order to improve its final quality (Frost, 2001). Clinoptilolite is used in the construction industry in the production of concrete. Light weight zeolite mixed with cement has been used to produce a concrete mixture called lightweight zeolite concrete (LZC). This is due to its ion exchange property, low bulk density, high porosity, homogeneity and close knit texture. The use of zeolites has led to reduction in the cost of cement production (Frost, 2001). During the process of making concrete, the high content of zeolite plays a vital role in neutralizing the excess lime produced by setting concrete.

2.6 MECHANISMS INVOLVED IN THE REMOVAL OF POLLUTANTS FROM WASTEWATER

The up-take of pollutants from water can be achieved though many treatment processes such as ultrafiltration, precipitation, reverse osmosis, electrodialysis, ion exchange and adsorption process. The most commonly used processes are ion exchange and adsorption. Among all the cited processes, this work will only focus on ion exchange and adsorption processes and they are elaborated as follows.

2.6.1 Ion exchange

The ion exchange process is one of the significant mechanisms involved in heavy metal uptake from solution (Mozgawa and Bajda, 2005; Trgo et al., 2003). It is defined as the stoichiometric replacement of one equivalent ion in the solid phase (solute) by an equivalent of another ion (sorbate) in the liquid phase (Petrus and Warchol, 2003; Inglezakis *et al.*, 2004). The ion exchange process takes place between exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) located in the zeolite framework structure and the cations "M^{n+}" in solution. Benhammou *et al*., (2005), theoretically described ion exchange reaction as follows:

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$$\text{Zeolite–n(Na,K)}^+ + M^{n+} \Leftrightarrow \text{Zeolite–}M^{n+} + \text{n(Na,K)}^+ \qquad 2.2$$

$$\text{Zeolite–n(CaMg)}^{2+} + 2M^{n+} \Leftrightarrow \text{Zeolite–2}M^{n+} + \text{n(CaMg)}^{2+} \qquad 2.3$$

According to Doula and Ioannou (2003), the reaction that takes place in the ion exchange process does not involve formation of bonds between metal ions (solute) and zeolite surface (exchanger); hence it is usually rapid and reversibleprocess. During the ion exchange process, metal ions move though the pores and channel cavities located in the zeolite structure and replace the exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} (Curkovic *et al*., 1997). The diffusion of metal ions from the surface to intraparticle sites are considered as the rate controlling step in ion exchange (Helffreich, 1966). Helffreich (1966) stated that diffusion of metal ions (solutes) though zeolite pores is slow due to the unavailability of some exchange sites occupied by exchangeable cations and long diffusion paths causing a slow interaction of metal ions with surface functional groups (i.e. electrostatic attraction, bond formation).

According to Grimshaw *et al*., (1975), ion exchangers are always insoluble in a medium which ion exchange is carried out. This heterogeneity allows an easy separation of ion exchangers from the liquid medium during the filtration process. The particle size of the exchanger (sorbent) is an important factor that requires consideration in ion exchange process. Tang *et al*., (2006); Malliou *et al*., (1994) and Ali and El-Bishtawi (1997) reported the effect of particle size in ion exchange process showing that the smaller the particle size, the higher the ion exchange capacity. This process has been used by several industries such as metal processing and dyes industries for water treatment. Cations or anion in a given solution can only be exchanged with an exchanger of the same cationic or anionic nature. The following are the illustrations of the chemical reactions that take place during cation and anion exchange process.

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$$\text{Zeolite–A}^+ \text{ (solid)} + \text{B}^+ \text{ (solution)} <=> \text{Zeolite–B}^+ \text{ (solid)} + \text{A}^+ \text{ (solution)} \qquad 2.4$$

$$\text{Zeolite–A}^- \text{ (solid)} + \text{B}^- \text{ (solution)} <=> \text{Zeolite–B}^- \text{ (solid)} + \text{A}^- \text{ (solution)} \qquad 2.5$$

The above equations 2.4 and 2.5 represent the cationic and anionic exchanger respectively. In the equation 2.4, cation A^+ is bound onto the solid exchanger whereas cation B^+ is in the solution. The same scenario is represented in equation 2.5 with the anionic format A^- and B^- anions.

2.6.2 Adsorption

Adsorption is a separation process that takes place in sorption mechanism whereby the solutes are favourably removed or extracted from solution by the means of attachment of the solute onto a surface of a solid material (Somorjai, 1993). In adsorption process, two terminologies are frequently used; adsorbent and adsorbate.

The solid material used in the adsorption process is called “adsorbent” whereas the solute to be removed from the solution is called “adsorbate”. The attachment of sorbate (solute) onto the surface of the sorbent occurs by the formation of a bond between sorbate and sorbate. These bonds are formed by two adsorption mechanisms which are called physisorption and chemisorption.

According to Somorjai (1993), physisorption is an adsorption process in which the sorbate or solute is attached or joined to the surface of the sorbent by weak Van der Waals forces. These forces allow the process to be reversible since the adsorption bonds are easily formed or broken due to their low adsorption energy. Adsorption is known to be physisorption process because it requires some energy for the process to take place. On the other hand, Somorjai (1993) described chemisorption as chemical interactions between sorbate molecule and sorbent surface. In this process, ionic and covalent bonds are normally formed having high adsorption energy. This makes the system to be an irreversible process since the bonds formed are semi-permanent.

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There has been confusion whether adsorption and ion exchange are two synonymous terminologies. The difference of the two was explained by Hamdaoui (2009). According to him, sorption processes of ion exchange and adsorption are unit operations, which often share theory, although they have their own special areas of concern. Schoeder (1977) also emphasized that adsorption is the accumulation of materials at an interface, and this interface may be liquid–liquid, liquid–solid, gas–liquid or gas–solid. Ion exchange process is similar to an adsorption system in that a solid, usually porous particle with reactive sites on its surface comes into equilibrium with ions in solution. These reactive sites have exchangeable ions such as Na^+, H^+, Cl^-, OH^- attached, and these ions exchange with ions in solution at equilibrium. The ion exchange and adsorption processes use two different setup methods, which are column and batch methods respectively. In ion exchange process, a column is typically used whereas in the batch method a vessel or tank is used in adsorption process.

In the batch method, an optimum amount of sorbent is mixed with a solution containing the sorbate of interest and shaken in a water bath at a certain speed and temperature. In a column method, the solution containing the sorbate is flowed through a column packed by an optimum amount of sorbent at an optimum operating flow rate and temperature. In order to study the kinetics of the sorbent and modelling adsorption isotherms, certain variable parameters such as contact time, stirring speed, pH of the sorbate solution, temperature, sorbent dosage and sorbate concentration are to be taken in consideration. The effect of all these parameters can be studied using the following kinetic equations:

$$Q_e = \frac{(C_o - C_e)V}{W} \qquad 2.6$$

Where:

Q_e (mg/g) is the amount of sorbate adsorbed by a gram of adsorbent.

C_o (mg/l) represents initial solute (adsorbate) concentration to be adsorbed.

C_{e} (mg/l) is the equilibrium concentration of adsorbate in solution after adsorption

V (L) is the volume of solution used for the adsorption experiment

W (g) is the mass of adsorbent used for the adsorption experiment

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The equilibrium point is where the sorbent reaches the maximum up-take of a given concentration of sorbate onto a certain adsorbent at certain experimental conditions. The equilibrium point can be observed at the point where the up-take concentration of a given adsorbate remains constant. The following is the kinetic equation to determine the percentage removal of the adsorbate after the adsorption process.

$$\%\ removal = \frac{(C_o - C_e)}{C_o} * 100 \qquad 2.7$$

2.6.2.1 Empirical adsorption rate model in batch system

In order to fully understand the mechanism that takes place between solutes (adsorbate) and adsorbents during the adsorption process, adsorption kinetic experiments need to be conducted. In adsorption kinetic experiments, certain adsorption parameters such as adsorbent dosage and adsorbate concentration are taken in consideration. Addition to this, adsorption kinetics can provide a better understanding of the rate-controlling step of the mass transfer process. According to Leyva-Ramos and Geankoplis (1985) Leyva-Ramos *et al.*, (2005), Valsaraj (2000) and Helfferich (1995), the overall rate of adsorption on adsorbents can be well described in three sequential steps. The first step involves the external mass transfer of solutes or adsorbate from the bulk solution though the boundary layer to the surface of the adsorbent (film diffusion), which is commonly identified as an external mass transfer resistance. The second step involves the diffusion of solutes though the adsorbent solid matrix (intra-particle diffusion), associated to intra-particle mass transfer resistance (pore-volume size diffusion or surface diffusion). The third step involves the adsorption of solutes molecules at the active sites. This step evaluates the overall rate of adsorption of a solute by an adsorption reaction model. Valsaraj (2000) described mass transfer resistances on porous adsorbents in the following diagram showing both the first and second step of the above three mentioned steps.

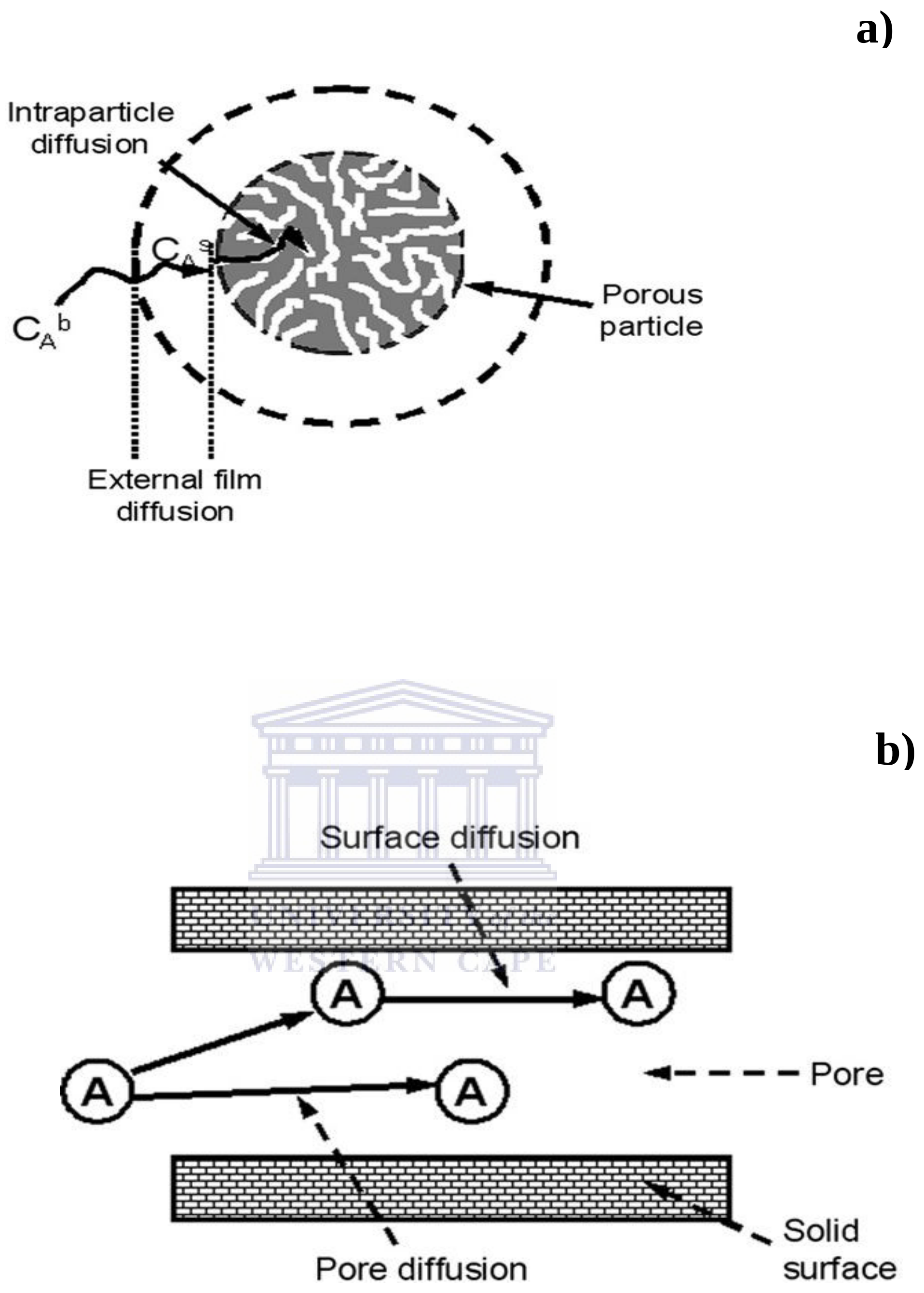

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Figure 9: Diagram describing mass transfer resistances on porous adsorbents. Image (a) illustrates the external resistance due to the boundary layer whereas Image (b) represents intra-particle diffusion due to a gradient concentration (pore-volume diffusion) or hopping diffusion (surface diffusion) (Valsaraj (2000)).

In order to understand the whole mechanism of transfer of solutes from liquid to the adsorbent material, both step one and two exhibit adsorption kinetic models. In step one, the film diffusion model is involved and it is used to determine whether the adsorption of solute from the aqueous solution is limited by the film resistance surrounding the solid adsorbent particles (Figure 9*a*). Step two of mass transfer resistance on porous adsorbents involves the intra-particle pore-volume size diffusion or surface diffusion models. According to Al-Duri and Mckay (1990), the mechanism of intra-particle diffusion depends on different experimental factors such as chemical and physical properties of the solute, structure of the adsorbate, equilibrium behaviour of the solute and the experimental conditions of the whole adsorption system. Pore volume refers to diffusion of solutes molecules though the liquid filled pores to the adsorption sites. The intra-particle diffusion may be governed either by pore-volume diffusion or surface diffusion or the combination of both diffusion models (Figure 9*b*). The third step was described by Helfferich (1995) to be the step in which adsorption of solutes molecules at the active ion exchange sites takes place and to be the fastest step of the three and the solute adsorption rate is limited by diffusion in porous materials.

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2.6.2.2 Adsorption Isotherms

Adsorption isotherms define the degree of equilibrium or distribution of dissolved substances between solution and solid phases at constant temperature. The equations that are often used to describe the experimental isotherm data are given as Langmuir, Freundlich and Brunauer – Emmett - Teller (BET) isotherms (Tchobanoglous and Burton, 1991). Among these, Langmuir and Freundlich are the commonly used adsorption isotherms in the batch method.

2.6.2.2.1 Freundlich isotherm

The Freundlich isotherm is the most widely used non-linear adsorption model which is mathematically expressed as follows:

$$Q_e = K_f C_e^{1/n} \qquad 2.8$$

The Freundlich isotherm equation is shown in equation 2.8, where K_f relates to sorption capacity and n is the sorption intensity. The logarithmic form of the above given equation 2.8 is used to fit the linear plot of the experimental data obtained from batch equilibrium kinetics study which is given as follows:

$$\log Q_e = \log K_f + n \log C_e \qquad 2.9$$

The equation given above (2.9) is used for the batch equilibrium kinetics data analysis where log Q_e is plotted against log C_e which yields a linear plot if the batch data confirm Freundlich isotherm.

2.6.2.2.2 Langmuir isotherm

According to different scientists; Langmuir isotherm model represents one of the first theoretical treatments of non-linear sorption. It has been successfully applied to wide range of systems that exhibit limiting or maximum sorption capacities. It is widely used for heavy metal removal from aqueous solution especially for clinoptilolite systems (Altin *et al.*, 1998; Erdem *et al.*, 2004; Payne and Abdel-Fattah, 2004; Petrus and Warchoł, 2003; Trgo and Peric, 2005; Sheta *et al.*, 2003) since it is simple and capable of describing experimental results in wide ranges of concentrations (Altin *et al.*, 1998). Langmuir isotherm equation is mathematically given as follows:

$$Q_e = \frac{K_L C_e}{1 + aC_e} \qquad 2.10$$

Equation 2.10 is the Langmuir model where K_L and a are Langmuir constants where K_L is related to sorption capacity and n to sorption intensity. Equation 2.10 is usually linearized by rearranging and inversion of equation 2.8 to obtain the following mathematical equation:

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \left(\frac{1}{aK_L}\right)C_e \qquad 2.11$$

Equation given above (2.11) is used for the batch equilibrium kinetics data analysis where C_e/Q_e is plotted against C_e yielding in linear plot if the batch data confirm Langmuir isotherm.

2.7 FACTORS AFFECTING HEAVY METAL UPTAKE FROM AQUEOUS SOLUTION IN SORPTION PROCESS

Several studies on the removal of heavy metal cations from aqueous solution by zeolites have been conducted by many scientists as discussed previously. They found that the removal of heavy metals by adsorption process was affected by factors associated with the solution (including solute) and the solid (adsorbent). The factors associated with the solution include pH, temperature and the presence of other contaminants in the solution.

2.7.1 Solid (adsorbent) factors

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2.7.1.1 Effect of pretreatment of zeolite

The pretreatment applied to natural material (zeolite) aims to improve its ion exchange capacity. For this purpose, certain cations from the structure of the material are removed and more easily removable ones are located (Inglezakis *et al*., 2001). As a result, material is converted to near-homo ionic form with the increase of content in a single cation (Semmens, 1988). Natural clinoptilolite contains Na^+, K^+, Ca^{2+} and Mg^{2+} as extra-framework exchangeable cations in its structure. Among these ions, selectivity of clinoptilolite for Na^+ is the lowest and is the most weakly bound cation on the zeolite framework structure (Stefanovic *et al*., 1996; Semmens *et al*., 1988). Therefore, increasing Na^+ content of clinoptilolite by pre-treatment improves its ion exchange ability. In order to replace K^+, Ca^{2+} and Mg^{2+}, which are strongly held by clinoptilolite (Curkovic *et al*., 1997), with Na^+ ions, extensive exposure of material to high Na^+

concentration is required (Semmens *et al*., 1988; Curkovic *et al*., 1997). However, it is not possible to displace all other exchangeable ions from the structure with Na^+ (Inglezakis *et al*, 2005; Semmens *et al*., 1978; Faghihian *et al*., 1999; Langella *et al*., 2000; Culfaz and Yagiz, 2004). Pretreatment agents used for conversion of clinoptilolite to homo ionic or near-homo ionic form are mainly HCl (Akyil *et al*., 2004; Cakicioglu-Ozkan *et al*., 2005; Mamba *et al*., 2009; Kurama *et al*., 2002 and Spryskyy *et al*., 2005), NaOH (Kang and Egashira, 1997; Ouki *et al*., 1993; Panayatova, 2001) and NaCl being the most used one (Culfaz and Yagiz, 2004; Bektas and Kara, 2004; Semmens *et al*., 1988; Ouki *et al*., 1993; Athanasiadis and Helmreich, 2005 and Inglezakis *et al*., 2001).

In contrast, acid treatment as an activation procedure results in a highly crystalline H-zeolite, but has a slight disadvantage since the acid (at high concentration) can remove some of the aluminium atoms from the framework (Cakicioglu-Ozkan *et al*., 2005; Mamba *et al*., 2009; Tang *et al*., 2006). It was observed by Mamba *et al*., (2009) that the pretreatment of zeolite (clinoptilolite) using less concentrated acid does not destroy zeolite framework. Comparing the concentration range of 0.02, 0.04 and 0.1 M HCl, Mamba found that 0.02 M HCl was the optimum acid concentration for pretreatment of South African clinoptilolite originated from Pratley (Vulture Creek) in Kwazulu-Natal. This was confirmed by the measured FTIR spectra of conditioned clinoptilolite samples pretreated by 0.02 M and 0.04 M HCl. In that experiment, FTIR spectra showed the absence of some zeolitic stretching bands by treating clinoptilolite with 0.04 M HCl. This may be due to the fact that some aluminium atoms were destroyed or washed out by acid whereas, 0.02 M HCl showed no destruction of the zeolite framework and showed a higher exchange percentage compared to that of 0.04 M HCl. In the study conducted by Mamba *et al*., (2009), the uptake percentage of Cu^{2+} and Co^{2+} using 0.02 and 0.04 M HCl were observed to be 79 % and 63 % respectively.

Cakicioglu-Ozkan *et al*., (2005) investigated the effect of HCl treatment on water vapour adsorption characteristics of clinoptilolite and observed an increase in the dealumination effect (removal of aluminium in from the zeolite framework structure) at higher concentration level. The degree of dealumination effect increased from 20.1 % to 57.1 % by increasing the concentration of acid from 0.032 to 0.32 M HCl respectively. The effect of dealumination was observed by looking at the shifting of the zeolitic bands position when compared to that of untreated clinoptilolite Infra-Red spectrum.

Different concentration of NaCl solution used for pre-treatment of natural material has been reported in literature. Inglezakis *et al*., (2001) investigated the effect of NaCl concentration on the effective capacity of the conditioned clinoptilolite in fixed-bed reactors and found that raising the concentration above 0.40 M NaCl has practically no effect on the effective capacity. Most widely used concentration ranges, however, are 0.5 - 2 M NaCl (Culfaz and Yagiz, 2004; Ouki *et al*., 1993; Athanasiadis and Helmreich, 2005; Curkovic *et al*., 1997; Cincotti *et al*., 2001).

Washing after the pretreatment process is critical in order to remove excess NaCl entrapped within the zeolite structure (Ouki and Kavannagh, 1999). Inglezakis *et al*. (2001) emphasized that if no washing is applied, excess NaCl might diffuse out in the solution, leading to unexpected results during capacity determination. They also investigated the effect of washing water quality after the pretreatment process and concluded that the use of tap water and deionized water give the same product quality. Some investigators studied the effect of the conditioning of natural zeolite on the crystal structure of zeolite and found that NaCl conditioning had no effect on the crystal structure of the zeolites (Ouki *et al*., 1993; Culfaz and Yagiz, 2004).

2.7.1.2 *Effect* of zeolite pore clogging

In sorption studies, pore clogging causes the decrease in heavy metal removal by preventing heavy metal ions from entering into zeolite structure. Fine particles on zeolite surface and precipitation as a result of heavy metal accumulation on the surface are the possible causes of pore clogging. Inglezakis *et al*., (1999) stated that pore clogging, resulting from dust particles produced during the grinding process makes clinoptilolite surface and pore openings partially covered and caused slower ion exchange rates of the unwashed against washed clinoptilolite samples. An influence of the dust on the kinetics of the ion exchange process was evident. Furthermore, for the unwashed samples, the smaller particles exhibit slower kinetics.

Athanasiadis and Helmreich (2005) found out that dust particles produced during the grinding process made up 8 % (w/w) of clinoptilolite and suggested the removal of the fine fraction prior to any application of clinoptilolite. Surface precipitation has been observed to probably reduce the ion-exchange ability of the zeolites due to blockage of the pores (Inglezakis *et al*., 2005).

2.7.1.3 Effect of zeolites particle size

According to Tang *et al*., (2006) an increase in NH_4^+ sorption capacity was found with decrease in particle size of three types of zeolites; with values increasing from 68.2 to 72.0 meq/100 g NH_4^+, from 53.2 to 73.2 meq/100 g NH_4^+ and from 43.6 to 56.2 meq/100 g NH_4^+ for the particle size ranges of 8 to 15 and 1.0 to 3.32 mm respectively was observed. This is due to the fact that cations in the smaller zeolites are much easier to diffuse and be exchanged into the aqueous solution. Malliou *et al*., (1994) found that the removal of Pb^{2+} was increased by decreasing the particle size, but at equilibrium the difference was minimized.

On the other hand, Ali and El-Bishtawi (1997) showed that the finer the zeolite particles used, the higher the metal ion removal. Ouki *et al*., (1993) conducted a study on the uptake of $Pb^{2+}$and Cd^{2+} using both pretreated clinoptilolite and chabazite and their results contradicted the outcomes of the study carried out by Tang *et al*., (2006) and Malliou *et al*., (1994). They observed that particle size had no significant effect on the zeolites sorption capacity and therefore suggested that the uptake of metals was not surface controlled but depend on the zeolites pre-condition.

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2.7.1.4 Effect of mineral composition

The chemical composition of zeolites (amount of exchangeable ions, Si/Al ratio), purity of natural material, channel dimensions are among the factors that affect heavy metal removal. According to Godelitsas and Armbruster (2003), the rather low Si/Al ratio and the consequently increased total cation exchange capacity are advantageous for removing dissolved cations from aqueous solutions. In this sense, Ouki and Kavannagh (1999) demonstrated that chabazite is more efficient than clinoptilolite for metals removal due to its larger pore window size that controls access to the pore system and higher Al^{3+} substitution of Si^{4+} providing a negative framework favourable to superior ion exchange capability. The cation exchange capacity of clinoptilolite is markedly dependent on its original chemical composition and sample purity. According to the study carried out by Cincotti *et al*., (2001) on clinoptilolite samples originated from the same source but having different purities (20 % and 50 %), the observed lower capacities with sample having low clinoptilolite content.

Gedik and Imamoglu (2005) compared the Cd^{2+} removal capacity of clinoptilolite from two different sources having different purities and chemical compositions. They observed that higher capacity was attained for the sample having high clinoptilolite and Na^+ ion content, even though its cation exchange capacity was lower.

2.7.2 Solution factors

2.7.2.1 Effect of pH in adsorption process

In adsorption process specifically in zeolites system, pH plays a vital role in the removal of heavy metal from aqueous solution. In a solution, pH influences metal speciation, integrity of zeolites used and H^+ ions are considered as competitive in ion exchange process (Ouki and Kavannagh, 1999 and Mier *et al.*, 2001). Chemical speciation describes the composition, i.e. types of chemical compounds and their concentration in an aqueous solution. According to Ouki and Kavannagh (1999) and Mier *et al*., (2001), speciation in the adsorption or ion exchange process, of any metal ion in the solution whether it is a free or bound to a ligand in a complex, has a significant impact on its uptake by zeolite or any other ion exchanger material. The selectivity of zeolite material for sorption of heavy metal ions is strongly influenced by the type of metal complex that predominates in the solution at a particular pH (Ouki and Kavannagh, 1999). Semmens *et al*., (1978) emphasized that the kinetics of heavy metal ions removal may be affected by the size or bulkiness of the complex which may results in reducing the cation exchange capacity of zeolite.

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Mier *et al*., (2001) emphasized a pronounced effect of pH on metal removal in the adsorption process and stated that the uptake of metals by natural zeolites during the ion exchange process is more effective when the metal species are cationic. Their study showed that Pb^{2+} was completely removed from aqueous solution at near-neutral or acidic pH, but its removal efficiency decreased in the basic pH range. From the same study, Cd^{2+} exhibited similar behaviour. The pH of solution can also affect the removal efficiency by affecting the integrity of zeolite. Mier *et al*., (2001) stated that clinoptilolite is known to be partially destroyed and lose its ion exchange capacity in alkaline media. It was also discovered that the clinoptilolite structure gets destroyed in highly acidic solutions resulting in dealumination of the zeolite (Tsitsishvili *et al*, 1992).

Benhammou *et al.*, (2005) stated that the number of negatively charged sites increases as the solution pH increases as described by the following chemical reaction:

$$\equiv S-OH+OH^{-}\longleftrightarrow S-O^{-}+H_2O \qquad 2.12$$

The above chemical reaction (equation 2.12) favours the adsorption of metal cations and their hydroxides, forming surface metal complexes as described by the following reactions (Benhammou *et al.*, 2005; Doula *et al.*, 2002).

$$\equiv S-O^{-}+M^{2+}\longleftrightarrow S-OM^{+} \qquad 2.13$$

$$\equiv S-O^{-}+M(OM)^{+}\longleftrightarrow S-OM(OH) \qquad 2.14$$

Doula and Ioannou, 2003 emphasized that the protonation of neutral and negative surface hydroxyl groups takes place at low pH values, which is described in the following chemical equations.

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$$\equiv S-O^{-}+H^{+}\longleftrightarrow S-OH \qquad 2.15$$

$$\equiv S-OH+H^{+}\longleftrightarrow S-OH_2^{+} \qquad 2.16$$

Therefore, at near-neutral or neutral pH values, the surface has a low net negative charge due to increase in positively charged surfaces (Doula and Ioannou, 2003; Mozgawa and Bajda,2005). This results in decrease in the ability of the surface groups to form complexes with metal ions (Benhammou *et al.*, 2005; Mozgawa and Bajda, 2005). Although, net negative charge of surface is decreased, it was reported that clinoptilolite surface can maintain its negativity at neutral and even very acidic medium (Ersoy and Çelik, 2002; Englert and Rubio, 2005). Correspondingly, Athanasiadis and Helmreich (2005) noticed that the clinoptilolite surface has a negative charge at pH 3, 5, 6 and 7. In addition, at low pH values, since H^+ ions are considered as competitive in ion exchange, heavy metal uptake is reduced correspondingly (Ouki and Kavannagh, 1999).

Generally, no significant changes were observed in Pb^{2+} uptake at pH range of 3 - 11 (Payne and Abdel Fattah, 2004; Ponizovsky and Tsadilas, 2003; Ouki and Kavannagh, 1999; Um and Papelis, 2004). However, while Ali and El-Bishtawi (1997) observed a decrease in Pb^{2+} uptake with decreasing pH in the range of 2.5 - 4.5, Inglezakis *et al*., (2003) observed that Pb^{2+} removal was almost stable at pH range of 2 - 4. Zeolites are not only influenced by pH but also are capable of affecting the solution pH when they are brought together to form a mixture. It was found that clinoptilolite tends to neutralize the solution by acting as H^+ acceptor or H^+ donor (Rivera *et al.,* 2000; Ersoy and Celik, 2002) as described by equations 2.4, 2.7 and 2.8. Ersoy and Çelik (2002) revealed that clinoptilolite-deionized water suspensions at neutral, acidic and basic pH values exhibited a buffer pH around 9.0 ± 1.

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In the aqueous solution, ammonia may exist in either the non-ionized form (NH_3) and/or ionized form (NH_4^+) depending on the pH and temperature. The ion-exchange process can remove only the ionized form. The equilibrium exchange capacity remains constant up to pH 7. The pH of the aqueous solution must be at/or below 7 for optimum ion-exchange operation in order to avoid the alteration of chemical composition of ammonia (Rahmani *et al*., 2004).

2.7.2.2 Effect of solution temperature

The uptake of heavy metals from aqueous solution mostly wastewater is enhanced by increasing temperature due to activation of metal ions by enhancing adsorption at the coordination sites of zeolites (Babel and Kurniawan 2003).

At higher temperatures, ions become smaller due to their reduced hydration and their movement becomes faster (Inglezakis *et al*., 2004), resulting in higher removal efficiencies. This was experimentally proven by different scientists during their study on the removal of heavy metals from aqueous solution.

Ali and El-Bishtawi (1997) found that the removal of Pb^{2+} was independent of temperature in 20 – 35 °C range, whereas increasing temperature affected Ni^{2+}

removal positively. On the other hand, Payne and Abdel-Fattah (2004) revealed that Pb^{2+} removal increase with temperature in the range of 23-45 °C while Bektas and Kara (2004) observed higher Pb^{2+} removal capacities at temperature ranging between 20 and 50 °C. In addition, Malliou *et al*. (1994) found that Pb^{2+} and Cd^{2+} uptake is favoured by higher temperatures.

2.7.2.3 Presence of other contaminants in the solution

In adsorption process, the uptake of heavy metal ions can be influenced by the presence of inorganic (cations or anions) and organic ions in the solution containing the target solutes. Anions can affect adsorption of heavy metal ions by direct or indirect ways (Doula and Ioannou, 2003). The presence of anions together with heavy metal ions leads to the formation of metal-anion complexes, which may adsorb weakly or not at all to the zeolite surface, thus, resulting in reduced heavy metal uptake (Doula and Ioannou, 2003). As the concentration of the anion increases, participation of the cation in complexes gets higher. Heavy metal–anion complexes may possess negative charge, which, in turn, results in reduced heavy metal removal (Inglezakis *et al*., 2003; 2005).

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The anionic species may interact with surface sites of zeolites leading to increase in surface negative charge (Doula and Ioannou, 2003). This, in turn, would probably enhance heavy metal removal by zeolites. In addition, complex formation with heavy metal ions following adsorption of anion to surface sites (Doula and Ioannou, 2003) is also one of the mechanisms involved in removal process.

Mier, *et al*. (2001) observed that when anions are present in the solution, the efficiency of Pb^{2+} and Cd^{2+} removal would be significantly diminished. They revealed that the presence of Cr^{6+} decreased the removal of Pb^{2+} due to the formation of insoluble complexes, leading to precipitation and blockage of channels in zeolite structure (Mier *et al*., 2001). Inglezakis *et al*. (2003b) examined the effect of SO_4^- and HPO_4^{2-} on ion exchange of Cu^{2+}, Fe^{3+} and Cr^{3+} on clinoptilolite and observed lower uptakes for Cu^{2+}.

On the other hand, Doula and Ioannou (2003) observed that Cu^{2+} uptake was enhanced in the presence of Cl^- and NO_3^- due to possible increase in surface negative charge, which further results in a surface complexation mechanism.

Other than anions, cations present in solutions together with heavy metal ions can affect heavy metal removal due to competition between cations for the sites in clinoptilolite structure. Panayotova and Velikov (2002) investigated the influence of water hardness (Ca^{2+} and Mg^{2+} ions) on uptake of heavy metal ions and stated that Pb^{2+} uptake was not influenced by the presence of Ca^{2+} and Mg^{2+}, whereas lower uptakes were attained for Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} in the presence of Ca^{2+}. Studies carried out by Petruzzelli *et al*., (1999) revealed that Pb^{2+} uptake in tap water and deionized water were different with lower uptake obtained in tap water in the presence of other cations and anions.

Among organic contaminants, phenol has been reported to hinder heavy metal removal (Mier *et al*., 2001). This was attributed to the formation of organometallic complexes that are generally too large to penetrate the channels in the zeolite (Mier *et al*., 2001). Turan *et al*. (2005) in their study observed that the removal of Pb^{2+} was higher in the absence of acetic acid.

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2.7.2.4 Hydrated radii of heavy metal

The hydration radius of cations plays a vital role in the heavy metal removal especially for clinoptilolite system. The movement or penetration of certain metal cations though the zeolite channels depends on their ionic and hydrated radius. The smaller the hydrated radius of cation, the easier it moves or penetrates though the clinoptilolite channels. Among divalent metal cations, Pb^{2+} has been reported to have a high selectivity for clinoptilolite systems, which is due to its small hydrated radius (Table 2.3) (Inglezakis *et al*., 2003, 2004 and Semmens *et al*., 1978).

The dimensions of channels in clinoptilolite structure should be large enough to allow passage or penetration of hydrated metal ions (Castaldi *et al*., 2005;

Semmens *et al.*, 1978). The ions with hydrated radii smaller than the channel size are able to move or penetrate easily within the channel. Although, hydrated radii of ions are related to their preference by clinoptilolite, not only hydration energies can explain selectivity of clinoptilolite. Inglezakis *et al.*, (2004) stated that formation of precipitates, adsorption or fixation of metal complexes on surface sites could reduce uptake of heavy metal cations, lowering their selectivity even if their hydration energies are low. The following is the table (Table 2.3) of ionic and hydrated radius of certain metal cations summarised by Semmens *et al.*, 1978).

Table 3:The ionic and hydrated radius of certain metal cations with their free energy hydration

Cation	**Ionic radius (Å)**	**Hydrated ionic radius (Å)**	**Free hydration energy (Kcal/g-ion)**
NH_4^+	1.43	5.35	-
Pb^{2+}	1.32	4.01	-357.8
Cd^{2+}	1.03	4.26	-430.5
Cu^{2+}	0.82	4.19	-498.7
Zn^{2+}	0.83	4.30	-484.6

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Apart from the above mentioned factors, there are other factors associated with the solid (adsorbent), and these include pre-treatment of zeolite, particle size, mineral composition and pore clogging.

2.8 CHARACTERIZATION METHODS AND TECHNIQUES

The knowledge of the structure, physical and chemical properties of a natural zeolite is important in order to fully understand the chemistry of its pretreatment. Characterisation techniques were carried out in order to investigate the structure and properties of natural zeolites. The techniques used to characterise the zeolite (clinoptilolite) samples including SEM used for morphology analysis, Electron Dispersive Spectroscopy (EDS) for rough determination of surface elemental composition, High Resolution Transmission Electron Microscopy (HTEM) and

Selective Area Electron Diffraction (SAED) for determination the crystallinity. The X-ray Diffraction (XRD) is used for mineral identification and purity, X-ray Fluorescence (XRF) for elemental composition, Fourier Transforms Infrared (FTIR) for determination of the structural configuration and N_2-BET (Brunauer - Emmett – Teller) for determination of the surface area and pore size distribution of clinoptilolite samples before and after acid-pretreatment process. Some characterization techniques are detailed in the following sections.

2.8.1 X-ray Diffraction (XRD)

Zeolites are crystalline solid materials which have a characteristic diffraction pattern that can be used to identify their exact structure and to determine its degree of crystallinity. The diffractions of X-rays from zeolite crystallites produce a scattering pattern which is specific of the periodic arrangement of regular arrays of atoms or ions located within the zeolite structure. Each zeolite has their own specific pattern that can be used as a reference for mineral phase determination and thus can be used as fingerprint for every type of zeolite. This technique can also signify whether the solid sample is in amorphous or crystalline phase. The purity of the solid crystal can then be measured by comparing the X-ray diffractogram pattern of the sample with that of the standard sample. The principal equation used in the analysis of an X-ray powder pattern is the Braggs law which states that;

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$$n\,\lambda = 2\, d_{hkl} \sin\theta \qquad 2.17$$

Where n is the order of diffraction ($n = 1, 2, \ldots$), λ is the wavelength of the incident X-ray beam ($\lambda = 1.54178$ Å for Cu Kα), θ is the Bragg angle between the incident X-ray beam and the crystal planes and d_{hkl} is the interplanar distance on a set of planes (Figure 10). In this case, $n\lambda$ must be less than 2 d_{hkl}. Thus the indices (*hkl*) of a plane in the crystal system, is called Miller-Bravais indices (Cullity, 1956).

$$d_{hkl} = \frac{1}{2} a \sqrt{h^2 + k^2 + l^2} \qquad 2.18$$

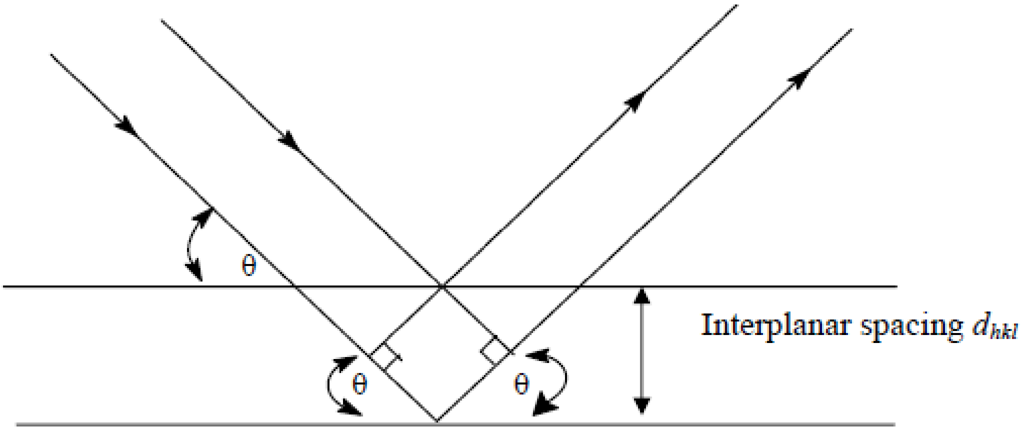

Figure 10: Schematic representation of diffracted beams in crystal lattice

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Mamba, *et al*., (2009) characterized the South African natural clinoptilolite (originated from Vulture Creek deposit I KwaZulu-Natal, South Africa) using XRD method and found the following XRD diffraction patterns.

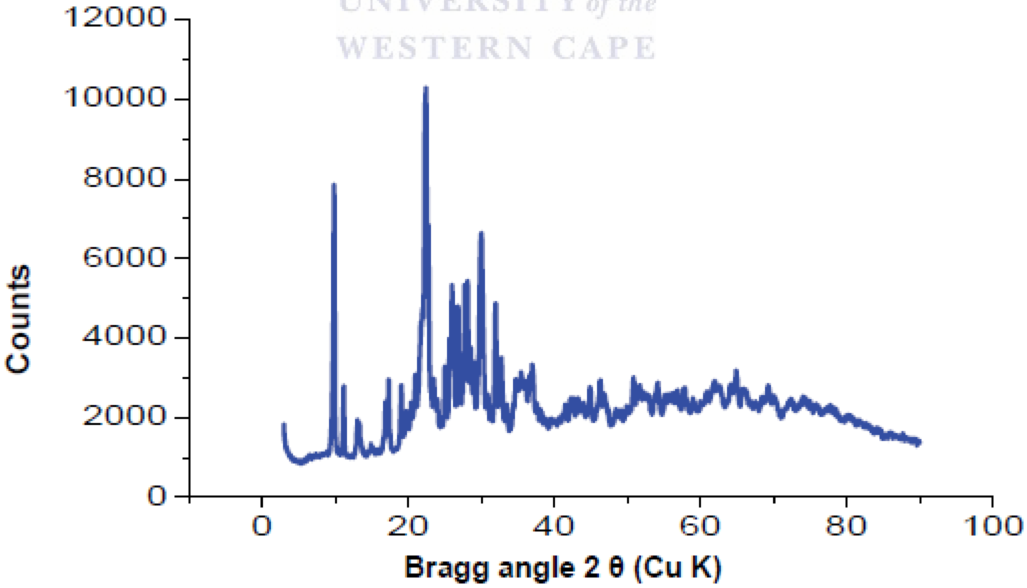

Figure 11: Diffraction pattern of the South African natural clinoptilolite (Mamba *et al*., 2009)

2.8.2 X-Ray Fluorescence (XRF)

The elemental chemical composition of natural zeolites such as clinoptilolite can be determined using the XRF analytical technique. Mamba *et al*., (2009) studied the elemental composition of South African natural clinoptilolite (Pratley) and found the following major oxides: SiO_2 (74 %), Al_2O_3 (12.4 %), K_2O (3.8 %), Fe_2O_3 (1.5 %), CaO (1.5 %), Na_2O (1.3 %), MgO (1.1 %), and TiO_2 (0.2 %),

2.8.3 Infrared Spectroscopy

The main areas of the application of FTIR spectroscopy in zeolite research are the investigation of the framework properties and the study of active sites, Brönsted or Lewis acid sites and also adsorbed molecules in zeolites such as pyridine, ammonia among others (Fierro, 1990). Basically, infrared spectroscopy provides information on short range and long range bond order caused by lattice coupling, electrostatic and other effects such as the destruction of zeolite framework. The technique is based on the possibility to separate the energy of a molecule into three additive components associated with the rotation of the molecule as a whole, the vibration of the constituent atoms and the motion of the electrons in the molecule (Nakamoto, 1962). Theoretically, if a molecule is placed in an electromagnetic field for instance light, a transfer of energy from the field to the molecule will occur in accordance to the Bohr's frequency equation,

$$\Delta E = h\nu \qquad 2.19$$

Where ΔE is the difference in energy between two quantized states, h is Planck's constant and ν is the frequency of the light.

Frequencies range in the infrared spectroscopy can be from 400 to 4000 cm^{-1}, but frequencies of certain framework vibrations of tetrahedral SiO_4 or AlO_4 linkages are in the mid-infrared region of 400 - 1200 cm^{-1}. Figure 12 shows the FTIR spectrum of zeolite (clinoptilolite) framework in the region of 400 - 1200 cm^{-1} which is divided into two groups of vibration, the internal and external vibration.

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The internal vibration of TO_4 tetrahedral (T being the atom at the centre of the tetrahedron e.g. Si, Al) is insensitive to the structure changes and present in each zeolite framework and silica.

The internal vibration includes the T-O asymmetric stretch at 1250 - 950 cm^{-1}, T-O symmetric stretch at 720 - 650 cm^{-1} and T-O bends at 500 - 420 cm^{-1}) (Flanigen, 1976). The T-O stretching is sensitive towards the composition of Al and Si in the zeolite framework. The shifting of the stretching to higher wavenumber occurs when the aluminium contents in the framework decreases. The decrease in aluminium content in the zeolite framework structure is known as "the dealumination effect" (Cakicioglu-Ozkan *et al.*, 2005). The increase of wavenumber with the decrease in aluminium content is related to change of bond length and bond orders. The longer length of Al-O bond and the decrease in the electronegativity of Al results in the decrease of the forces constant and hence the wavenumber.

The dealumination effect causes the destruction of the zeolite framework therefore reducing the ion exchange ability of zeolites. Cakicioglu-Ozkan *et al.*, (2005) reported the dealumination effect while investigating different HCl concentrations and different pretreatment temperatures on Turkish clinoptilolite. According to Cakicioglu-Ozkan *et al.*, (2005), 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 after acid pretreatment. The strong bands were identified to be zeolitic bands and assigned to the asymmetric stretching vibration modes of the internal T-O bands in the SiO_4 and AlO_4 tetrahedral whereas the weak bands were 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 strength during acid-clinoptilolite pretreatment (Cakicioglu-Ozkan *et al.*, 2005; Mamba *et al.*, 2009 and Faghihian, *et al.*, 2008).

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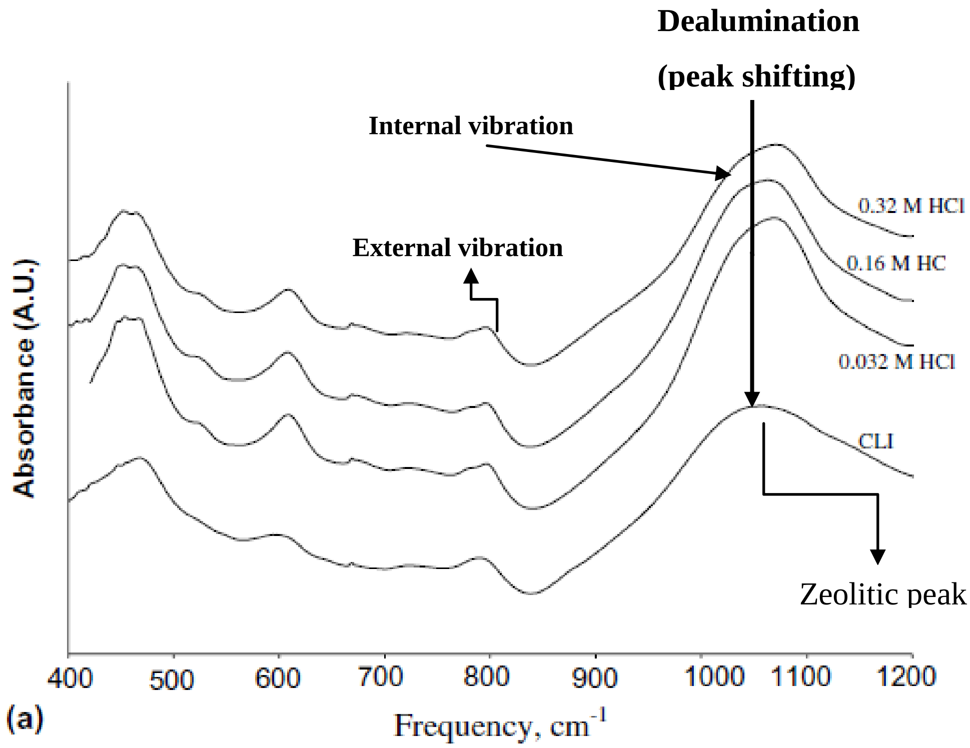

Figure 12: Infrared spectra of different HCl concentrations (0.032, 0.16 and 0.32M HCl) pretreated Turkish clinoptilolite (Cakicioglu-Ozkan *et al.*, 2005).

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The external vibration occurs from the vibration of TO_4 tetrahedral linkages. This vibration is sensitive to the structure changes and tetrahedron linkages. It can be observed at 820 - 750 cm^{-1} and can be assigned to the symmetric stretching for T-O and at 1050 - 1150 cm^{-1} for asymmetric stretching of T-O. The presence of double rings in the zeolites framework gives a strong absorption band at 650 - 500 cm^{-1}. Zeolites which do not have double rings in the framework such as mordenite will give a weak absorption band in the region. Besides, the T-O bending for tetrahedron that formed large pore opening was observed at 420 - 300 cm^{-1}.

2.8.4 N_2 adsorption

Nitrogen gas adsorption at solid surface and pore is a complex phenomenon which involves mass, energy interaction and phase transformation. When a gas (N_2) molecule of adsorbate, such as nitrogen approaches a solid surface of porous material, at a certain temperature, the molecule is initially acted by an attractive force called adsorption. This method can determine the surface area and pore size of materials which are the important properties of zeolites.

The total volume of gaseous that adsorbed and desorbed depends on absolute temperature (T), pressure (P) of the vapours, surface area (Å), pore volume and solid-gas system. When adsorption occurred at constant temperature for gas and certain solid, then a total mole gas, n, only depends on pressure. If gas is under critical temperature, therefore, the following equation is considered.

$$n = f\left(\frac{P}{P_o}\right) \qquad 2.20$$

There are six types of adsorption isotherms which are shown in Figure 13 in the classification originally proposed by Brunauer-Emmett-Teller (BET). These isotherms are obtained when the total volume of gas is adsorbed, V_a is plotted as a function of P/P_o, (see Figure 13) (Gregg and Sing, 1982).

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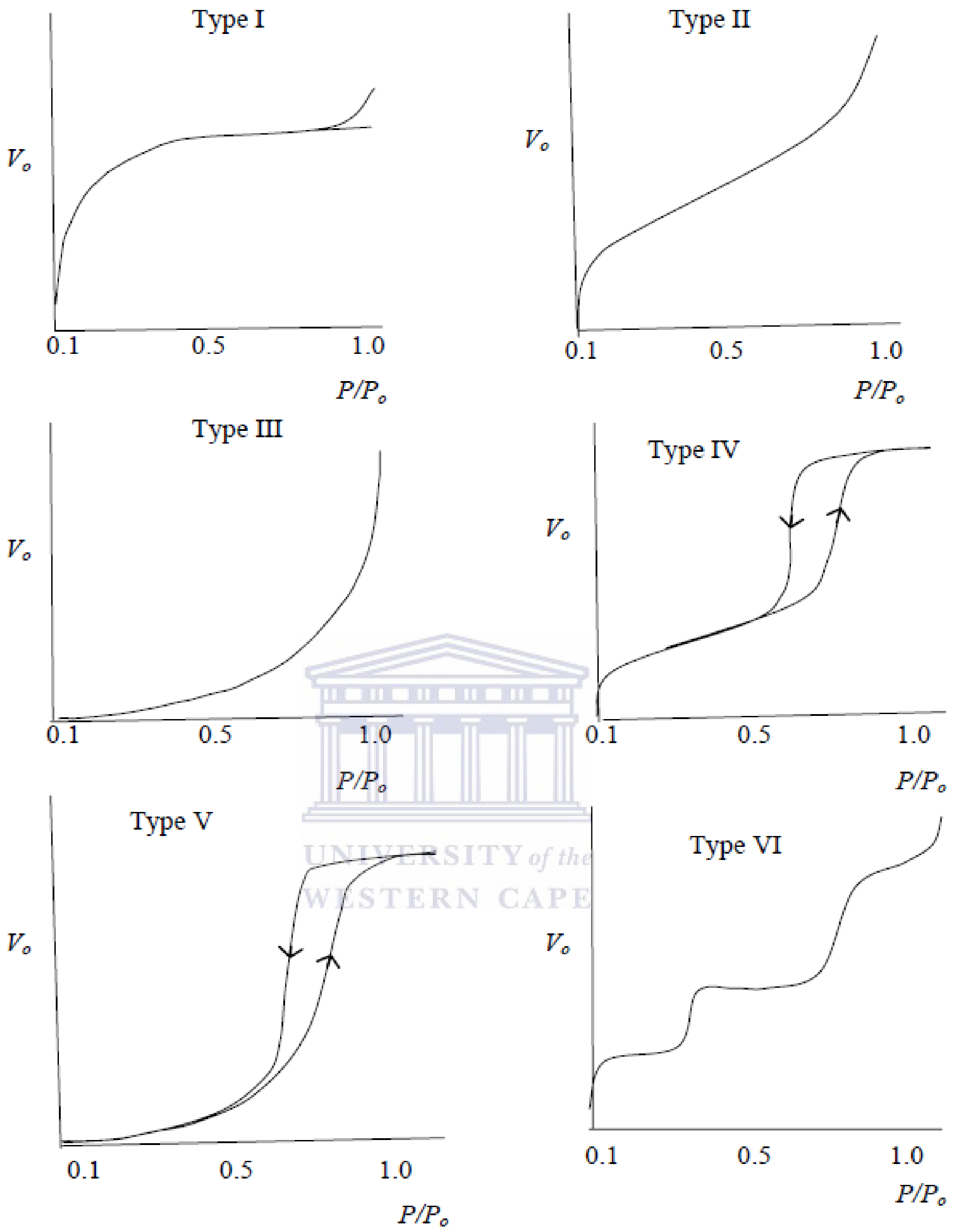

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Figure 13: The six types of adsorption and desorption isotherms for the microporous and mesoporous materials (Gregg and Sing, 1982).

In Figure 13, type I is the characteristic of microporous materials like zeolites. The typical type I isotherm always show high adsorption capacity and very fast reaction saturation, followed by consistent adsorption over a wide range of P/P_o.

Nonporous materials exhibit the adsorption isotherm Type II while type III isotherm is for macroporous materials. Adsorption isotherm for nonporous materials shows high adsorption capacity at low relative pressure (P/P_o), moderate adsorption capacity at the middle and high adsorption capacity at P/P_o in proximity to 1. Type IV isotherm is characteristic of mesoporous materials. Type V isotherm represent when the interaction of nitrogen molecules is stronger than the interaction of nitrogen with solids. Type VI represents nonporous material which has uniform surface.

2.9 CHAPTER SUMMARY

The relevant studies regarding the natural zeolites such as clinoptilolite and their applications have been reviewed in this chapter. Various wastewater technologies have been successfully used to remove metal ions from wastewater, but unfortunately, some technologies are costly in terms of operation and cause the generation of more waste during the treatment process. The disposal of the waste resulting from the treatment technologies could pose an environmental problem. Several studies have shown the potential use of clinoptilolite in waste water treatment. Studies have been conducted on the sorption ability of clinoptilolite as a sorbent for different water pollutants such as heavy metals or ammonia. The obtained results indicated that clinoptilolite has high ion exchange ability on the removal of pollutants such as heavy metals and ammonia at a very low cost and easy regeneration of the sorbent used in the treatment process (Erdem *et al*., 2004).

It was shown by several scientists that the various uses of these zeolite materials depend on their physico-chemical properties. Therefore, adsorption of metal ions and ammonia onto zeolites such as clinoptilolite has more advantages than most other technologies that are used in water treatment process. The use of clinoptilolites as adsorbents in adsorption process was investigated by many scientists and it was established that it has a high ion exchange capacity compared to that of other water treatment processes at a very low cost since the operating setup is simple.

It was observed that in order to achieve high removal of metals using natural adsorbents, natural clinoptilolite should be pretreated prior to its use in sorption application. The pretreatment involves the exchange of the extra framework cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) located in the clinoptilolite framework by an activating agent with a homo ionic ion. The pretreatment agents used for the conversion of clinoptilolite to homo ionic or near-homo ionic form are mainly HCl, NaCl and KCl and NaOH. The use of diluted acid (HCl) has been proven to be the best since it involves H^+, which can easily be exchanged with another ion during the process of adsorption (Akyil *et al*., 2004; Cakicioglu-Ozkan *et al*., 2005; Malliou *et al*., 1994; Mamba *et al*., 2009 and Kurama *et al*., 2002). Schoeman (1986) and Mamba *et al*., (2009) used South African clinoptilolite for the removal of ammonia and heavy metals from wastewater. Mamba *et al*., (2009) studied the sorption capacity of heavy metals (lead and cadmium) on South African acid treated-clinoptilolite (HCl) mined by Pratley Polymers Company. Schoeman (1986) investigated the sorption capacity of South African Pratley clinoptilolite and compared it to that of Hector from United States of America.

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Apart from the study conducted by Schoeman (1986), Muzenda *et al*., (2011) and Mamba *et al*., (2009) on South African Pratley clinoptilolite for the removal of ammonia or other heavy metals from wastewater. No other study has been conducted to compare the sorption capacity of different South African clinoptilolites for the removal of ammonia and chromium from wastewaters. The current study will explore and compare physical and chemical properties as well as sorption capacity of two different types of treated and untreated South African clinoptilolites from both Pratley and ECCA Holding companies. The difference between the current study and the study conducted by Mamba *et al*., (2009) and Muzenda *et al*., 2011) is the pretreatment method of clinoptilolite that they used which is different from the one used in this work. Mamba *et al*., (2009) and Muzenda *et al*., (2011) pretreated clinoptilolite for 8 h with one acid solution extraction which may not exchange all the cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) from clinoptilolite framework.

The acid-pretreatment method in this work will be carried out differently in which numerous acid extractions will be used in order to completely exchange or remove all he exchangeable cations from the clinoptilolite framework. It is therefore assumed that this acid pretreatment will improve the exchange capacity more than that obtained by Mamba *et al*., (2009) Muzenda *et al*., (2011).

The following chapter (Chapter 3) will focus on the material and experimental methodologies. The main areas of focus will be the sample pretreatment, characterization and ends adsorption methodologies of ammonia and chromium on different South African clinoptilolite.

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CHAPTER 3

EXPERIMENTAL

This chapter focuses on the origin of the clinoptilolite materials and details chemicals, equipment and the experimental methods used in the study. The pretreatment methods of natural South African clinoptilolite, characterization techniques and sorption procedures for ammonia and chromium removal using the South African clinoptilolite are highlighted in this chapter.

3.1 MATERIALS

The details if the samples, sources and the sampling procedures are given in this section.

3.1.1 Clinoptilolite sample source

Clinoptilolite samples used in this study originated from two zeolites deposits in South Africa. One sample originated from Pratley clinoptilolite deposit located in Kwazulu-Natal Province and ECCA Holdings clinoptilolite (soft and hard sample) deposit located in the Western Cape Province (refer to study site map in Figure 1).

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3.1.2 Sample handling and storage

Clinoptilolite samples (Table 5) were delivered in sealed plastic (polypropylene) containers and stored in a sealed evacuator desiccator to avoid the uptake of moisture. Clinoptilolite samples from Pratley and ECCA Holdings were milled (using TS-250 Mill machine) to very fine powder. Samples were then sieved into two particle size fractions of 90 – 125 µm and 1000 – 1400 µm for experimental purposes. The sieved clinoptilolite samples were then dried at 50 °C in an oven overnight to remove moisture and then stored in an evacuated desiccator (Akyil *et al*., 2004; Cakicioglu-Ozkan *et al*., 2005; Mamba *et al*., 2009).

The clinoptilolite processed in this way was named as as-received ECCA Holdings (soft and hard) and Pratley clinoptilolite. The list of reagents used in experiments is given in Table 4.

Table 4: List of the reagents used in this study

Reagent	Name	% Purity	Source
HCl	Hydrochloric acid	32	KIMIX
CH_3COOH	Glacial acetic acid	99.8	KIMIX
H_3BO_3	Boric acid	99.8	KIMIX
NaOH	Sodium hydroxide	99.5	KIMIX
CH_3COONH_4	Ammonium acetate	-	Prepared
NH_4OH	Ammonium hydroxide	99.5	KIMIX
NH_4Cl	Ammonium chloride	99.8	KIMIX
CH_3CH_2OH	Ethanol	99.8	KIMIX
$C_{13}H_{14}N_4O$	1.5-diphenyl carbazide	99.8	Merck
HgI_4K_2	Nessler reagent	-	Prepared

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The list of the names and codes of clinoptilolite samples as-received are presented in Table 5.

Table 5: List of sources of South African clinoptilolite samples codes

South African clinoptilolite as-received sample sources				
Clinoptilolite sample name	**Deposit location**	**Physical description**	**Sample code (90–125 μm)**	**Sample code (1000–1400 μm)**
ECCA Holdings soft	Western Cape	Soft	ESC	ESC1
ECCA Holdings hard	Western Cape	Hard	EHC	EHC1
Pratley clinoptilolite	Kwazulu-Natal	Hard	PC	PC1

3.2 EXPERIMENTAL METHODS

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This section presents different experiments carried out on the acid-pretreatment of the clinoptilolite samples. All the characterization were done on both untreated ESC, EHC and PC and acid-pretreated clinoptilolite samples to evaluate the difference before and after their pretreatment (see Table 9). The CEC (see Table 7) and total acid digestion experiments were carried out using untreated as-received samples (ESC, EHC and PC). The acid-pretreated clinoptilolite samples (PC1) (see Table 6) were used in the adsorption of NH_4^+ and then compared its adsorption capacity to that of the untreated as-received clinoptilolite (PC) (see section 3.2.4.1 for the experimental procedure). The chromium adsorption experiments were only carried out on the acid-pretreated Pratley clinoptilolite sample (PC2) due to time and small sample available. The sample names and codes are shown in Table 6.

Table 6: List of the sample names and codes used in the acid-pretreatment experiments

Sample used for acid-pretreatment (particle size of 1000 – 1400 µm)		
Sample name	**Acid-pretreatment (0.02 M HCl)**	**Acid-pretreatment (1.00 M HCl)**
	Code	**Code**
ECCA Soft	ESC2	-
ECCA Hard	EHC2	-
Pratley	PC2	PC3

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The schematic illustration of the experimental protocol of this study is presented in Figure 14 below.

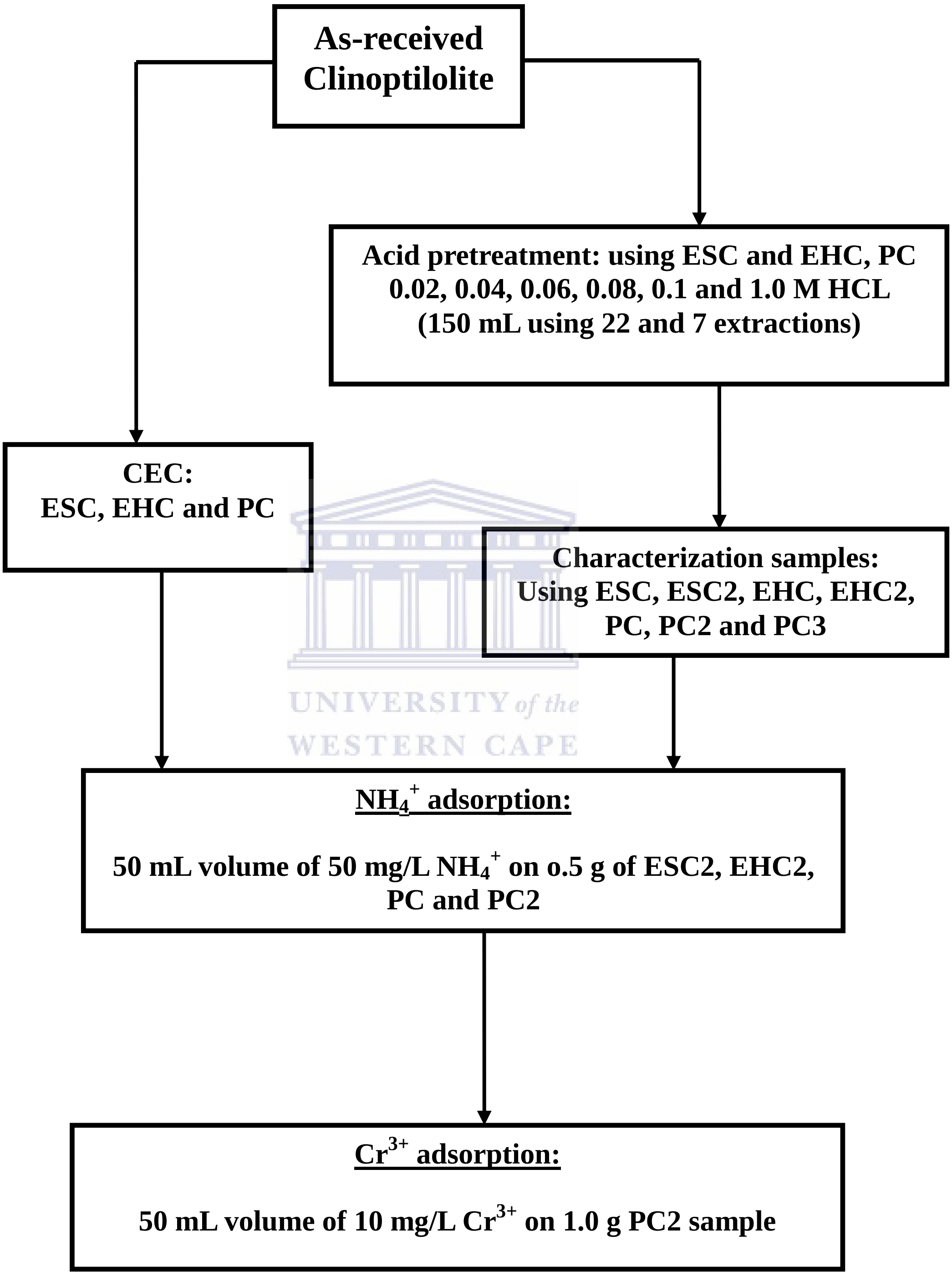

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Figure 14: The experimental schematic of the study

3.2.1 Acid-pretreatment of natural South African clinoptilolite

In order to improve ion exchange capacity of the untreated natural mineral (clinoptilolite), exchangeable cations such as Na^+, K^+, Mg^{2+} and Ca^{2+} of clinoptilolite were removed or exchanged with H^+ (Akyil *et al*., 2004; Cakicioglu-Ozkan *et al*., 2005; Mamba *et al*., 2009; Kurama *et al*., 2002 and Spryskyy *et al*., 2005).

3.2.1.1 Pretreatment of clinoptilolite: optimum HCl concentration

The method used for pretreatment in this study was a modified form of that used by different scientists (Akyil *et al*., 2004, Cakicioglu-Ozkan *et al*., 2005 and Mamba *et a*l., 2009). To pretreat or activate each clinoptilolite sample (ESC, EHC and PC), 10.0 g of zeolite was weighed and transferred into a 250 mL polypropylene plastic container. To this, 150 mL of 0.02 M HCl acid was added and the mixture was initially shaken at 250 rpm for 4 h (optimum time/one extraction fraction) at 25 °C. The sample was centrifuged for 15 min at 6000 rpm and then the supernatant was filtered and recovered using a membrane filter paper (pore size of 0.2 µm). The solid filtered clinoptilolite sample was recovered quantitatively and washed with deionized water till pH 4.5 to 5.0 to remove the excess Cl^- (Akyil *et al*., 2004 and Cakicioglu-Ozkan *et al*., 2005). A 1.0 mL sample of the supernatant from the original HCl wash was set aside to determine the content of exchangeable cations using ICP-OES analysis. The HCl wash procedure was then repeated several times (22 extractions) using the same clinoptilolite sample using the same recovered experimental conditions but for a time of 2 h per extraction fraction till the concentration of the major exchangeable cations was undetected. The final solid filtered clinoptilolite sample was recovered quantitatively and dried in a 50 °C oven, overnight. A similar pretreatment procedure was used with different acid concentrations solutions of 0.04, 0.06, 0.08, 0.1 and 1.0 M HCl (7 extractions for 1.0 M HCl), in order to find the most suitable HCl concentration for pretreatment.

3.2.2 Cation Exchange Capacity determination

The cation exchange capacity (CEC) was determined to measure exchangeable cations present in clinoptilolite samples. The procedure used for CEC determination was adopted from Amrhein *et al*., (1999) and the reagents were prepared as follows.

3.2.2.1 Preparation of 1.0 M ammonium acetate

A volume of 144 mL glacial acetic acid was added into a 2.0 L volumetric flask and was diluted using ultrapure water to about a volume of 1.0 L. The pH of the solution mixture was adjusted using a few drops of glacial acetic acid and ammonium hydroxide solution to adjust the pH to 8.2 (Amrhein *et al.*, (1996). A 138 mL of 0.1 M ammonium hydroxide solution was added and the volumetric flask was topped up to the mark using ultrapure water to a volume of about 2.0 L.

3.2.2.2 Procedure of cation exchange capacity

Cation exchange capacity was determined by contacting 0.5 g of freshly milled and sieved of ESC, EHC and PC samples (90 - 125 µm particle size) with 25 mL of 1.0 M ammonium acetate (pH of 8.2) and each mixture was shaken in a water bath at 250 rpm for 15 min at 25 °C. After the shaking process, the sample was centrifuged for 15 min and the supernatant was then decanted. The extraction was repeated four times (25 mL each extraction for 30 min at 25 °C stirring at 250 rpm) on the same clinoptilolite sample and then the extracted (decanted) aliquots fractions (25 mL each) from each respective sample were accumulated and added together making a total volume of 100 mL for each sample (ESC, EHC and PC samples). A similar set of experiments were done, where the time of shaking was increased to 30 min. All cation exchange capacity experiments were done in triplicate. The concentration of the major exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) was determined using inductively Coupled Plasma-Optical Emission Spectrometry method (ICP-OES). Cation exchange capacity of each major element was calculated and then the summed up to a total CEC of the clinoptilolite sample. The cation exchange capacity (CEC) was calculated using the following equation:

$$CEC(meq) = \left[(V) * \left(\frac{Ca}{mass} \right) / Mw \right] \qquad 3.1$$

Where V is the total accumulated volume (L) of the extracted aliquot, 0.5 being the mass of clinoptilolite expressed in grams (g), *Ca* is the measured concentration of the exchangeable cation (mg/L) and Mw is the molecular weight of the analyte cation (g/mol). Cation exchange capacity was expressed in mili-equivalent per gram of clinoptilolite (meq/g).

Table 7: List of the sample names and codes used in cation exchange capacity

Sample used for CEC determination (particle size of 90 - 125 µm)	
Sample name (as-received sample)	**Code**
ECCA Soft	ESC
ECCA Hard	EHC
Pratley	PC

3.2.3 Total element determination in the samples

The total acid digestion test involves dissolving clinoptilolite (ESC, EHC and PC) with concentrated acid to determine the total concentrations of all elements species in the sample. This test was carried out according to Jackson and Miller (1998). A 2 mL of concentrated hydrofluoric acid (HF) and 5 mL aqua regia were reacted with 0.25 g of each clinoptilolite sample in a digestion vessel (Parr bomb) at 200 °C for 2 h. The sample was allowed to cool after which the excess HF in the digestate was neutralized by the addition of 14 mL of saturated H_3BO_3 solution. The digestate was filtered through 0.2 µm membrane filter and the solution was diluted to 50 mL with de-ionized water. Aqua regia solution was prepared immediately before the total acid digestion experiment.

The solution was obtained by carefully adding three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid with a volume ratio of 3:1. The obtained solution was then prepared for ICP analysis for the analysis of major and minor metal analysis. The results will are presented in appendix B.

3.2.4 Adsorption experimental procedures

Table 8: List of sample name and codes used for adsorption experiments

Sample used for adsorption experiments of NH_4^+ and Cr^{3+}		
Sample name	**Sample used for NH_4^+ adsorption**	**Sample used for Cr^{3+} adsorption**
ECCA Soft	ESC2	-
ECCA Hard	EHC2	-
Pratley	PC1 and PC2	PC2

3.2.4.1 Adsorption of ammonia (NH_4^+)

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The sorption study was conducted using a batch method focusing on the comparison of the three pretreated zeolite samples; ECCA soft and hard sample with Pratley sample, running at the same experimental conditions. The acid-pretreated clinoptilolite samples were dried in an oven over night at 50 °C to remove all moisture before the adsorption experiment. Ammonium ion stock solution of 1000 mg/L was prepared by dissolving an accurately weighed amount of 1.0 g of ammonium chloride (NH_4Cl) powder in one litre using ultrapure water and the solution was kept in the fridge in order to avoid the alteration of its chemical composition.

To determine the effect of contact time in the sorption study of NH_4^+ on the acid-treated clinoptilolite (PC2), 50 mL solution (using 22extractions) of 50 mg/L NH_4^+ solution was mixed with a fixed amount of 0.5 g of pretreated clinoptilolite (PC2) sample and then shaken at 250 rpm at room temperature (25 °C) for a contact time of 1, 2, 4, 6, 8, 10, 30, 60 min.

After the adsorption, samples were filtered using membrane filter (0.2 µm pore size) and the residual NH_4^+ concentration in the recovered supernatant solution was determined spectrophotometrically using Nessler reagent giving a colour range of light yellow to dark brown depending on the ammonia content in the solution (APHA 1980, Ivanova *et al*., 2010, Rahmani *et al*., 2004 and El-Hady *et al.*, 2001). The absorbance of NH_4^+ was measured at 380 nm (obtained by scanning method). A standard sample (50 mg/L) was used as a control which was shaken for the same time as the sample. The percentage removal was calculated using the mathematical equation 2.7 (see section 2.6.2) and the equilibrium amount of NH_4^+ was calculated using equation 2.6 (see section 2.6.2).

To determine the effect of dosage for the adsorption study of NH_4^+ on the acid-pretreated clinoptilolite (PC2) sample, 50 mL solution of 50 mg/L NH_4^+ was mixed with 0.1, 0.3, 0.5, 1.0, 1.5 and 2.0 g of pretreated clinoptilolite (PC2) and then shaken at 250 rpm at room temperature of 25 °C for a constant contact time of 10 minutes (optimum time). After the adsorption, samples were filtered using membrane filter (0.2µm pore size) and the residual NH_4^+ concentration was determined spectrophotometrically using Nesslerization method as described above.

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To determine the effect of the acid-pretreatment of the adsorbents in the sorption study of NH_4^+, 50 mL solution of 50 mg/L NH_4^+ was mixed with 0.5 g of each untreated (PC1) and acid-pretreated (PC2) sample and then shaken at 250 rpm at room temperature of 25 °C for a range of contact times of 1, 2, 4, 6, 8, 10, 30 and 60 min. After each adsorption (10 min), samples were filtered using membrane filter (0.2 µm pore size) and the residual NH_4^+ concentration was determined spectrophotometrically using Nessler reagent.

To determine the effect of the initial concentration of NH_4^+ on the pretreated PC, 50 mL volumes of 10, 20, 30, 40, 50, 60, 100, 150 and 200 mg/L NH_4^+ were each respectively mixed with 0.5 g (optimum dosage) of the acid-pretreated clinoptilolite and then shaken at 250 rpm at room temperature of 25 °C for a constant contact time of 10 min. After the adsorption experiments, samples were filtered using membrane filter and the residual NH_4^+ concentration in the recovered supernatant solutions were determined spectrophotometrically using Nessler reagent. The adsorption isotherms (Langmuir and Freundlich) were modelled from the obtained equilibrium adsorption data.

3.2.4.1.1 Preparation of Nessler reagent

A 100 g HgI_2 and 70 g KI were dissolved in a small quantity of ultra-pure water. The mixture was added, with stirring, to a cool solution of 160 g NaOH in 500 mL water. The mixture was then diluted to 1 L.

The solution was stored in rubber-stopped glassware of sunlight to maintain reagent stability. This method was adapted from the Standard methods for the examination of water and wastewater.

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3.2.4.1.2 Preparation of UV/Vis sample using Nessler reagent

Ammonium solution of 5 mL volume was measured and place into a 15 mL Nessler reagent tube. To this, one drop of Nessler reagent was added and then shaken very well to bring the mixture together. The mixture was allowed to settle for 5 min for the reaction to take a place. After 5 min, about 2 mL of the sample mixture was mixture was poured into a UV/Vis quartz cuvette and then was analysed at the maximum NH_4^+ wavelength of 380 nm. This method was also adapted from the Standard methods for the examination of water and wastewater.

3.2.4.2 Adsorption of chromium (Cr^{3+})

The sorption study of Cr^{3+} was conducted using the batch method which focused on the various sorption parameters such as reaction contact time, pH, sorbent dosage and sorbate concentration. Chromium (III) stock solution of 1000 mg/L was prepared by dissolving the accurately weighed 5.124 g of Chromium chloride hexahydrate ($CrCl_3.6H_2O$) powder using 0.1 M HCl and the solution was kept in a cool and dark place (Vogel, 1978 and Kennedy, 2009). Chromium ion adsorption experiments were only done using pretreated Pratley clinoptilolite not ECCA Holdings soft and hard clinoptilolite because there was not sufficient ECCA

Holding clinoptilolite sample supplied to do both ammonium and chromium ions experiments.

To determine the effect of contact time for the sorption study of Cr^{3+} on the pretreated clinoptilolite, 50 mL of 10 mg/L solution of $Cr^{3+}$was mixed with a constant mass of 2.0 g of PC2 (22 extractions using 50 mL) clinoptilolite then shaken at around 250 rpm at room temperature (25 °C) for a range of contact times of 30 min, 1, 2, 4, 6 and 8 h. After the specific reaction time, samples were filtered using membrane filter (0.2 µm) and the residual Cr^{3+} concentrations were determined spectrophotometrically using 1.5-diphenyl carbazide reagent giving a violet complex solution. The absorbance of Cr^{3+} was measured at 540 nm (Vogel, 1978 and Kennedy, 2009). The chromium ion stock sample was scanned using UV/Vis to confirm the wavelength value given in the literature. A standard sample of Cr^{3+} (10 mg/L) was used as a control which was shaken for the same time as the sample with the longest contact time, which was 24 h. The kinetics study of chromium (III) on clinoptilolite was conducted using the measured absorbance to get the adsorption equilibrium amount of Cr^{3+} per unit mass of clinoptilolite.

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To determine the effect of pH upon the adsorption of Cr^{3+} with the pretreated clinoptilolite (PC2), 50 mL volumes of 10 mg/L solution of Cr^{3+} was adjusted to a pH range of 1.5, 2, 3, 4, 5, 6, 7 and 8 respectively using a diluted NaCl or HCl solutions (drops). The sample of clinoptilolite (2.0 g of PC2) and pH adjusted chromium (III) solution was then shaken at 250 rpm at room temperature (25 °C) for a period of 2 h. The samples were again filtered and prepared for UV/Vis analysis in the same way using 1.5-diphenyl carbazide reagent at 540 nm.

To determine the effect of initial concentration of Cr^{3+} upon the adsorption properties of the pretreated clinoptilolite (PC2; treated using 22 extractions), 50 mL volumes of 10, 20, 30, 40 and 50 mg/L solution concentration of Cr^{3+} were respectively mixed with 2.0 g of clinoptilolite then shaken at 250 rpm at room temperature (25 °C) for a period of 2 h. The samples were again filtered and the recovered supernatant solutions were prepared for UV/Vis analysis in the same way using 1.5-diphenyl carbazide reagent at 540 nm.

3.3 ANALYTICAL METHODS

3.3.1 pH measurement

The pH measurements involve the comparison of the solution potential with the unknown hydrogen ion [H^+] to the known reference potential. This is done when the indicating electrode, which is sensitive to the hydrogen ion, develops a potential directly related to the hydrogen concentration in the solution, and the reference electrode provides a stable potential against which the indicating electrode can be compared. The pH meter converts the potential (voltage) ratio between a reference half-cell and a indicating half-cell to pH values. In acidic or alkaline solutions, the voltage on the outer membrane surface changes proportionally to changes in [H^+]. The pH meter electrode detects the change in potential and determines [H^+] in the unknown solution.

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In this study, the pH measurements of all solutions used were measured using a HANNA HI 991301 portable pH/EC/TDS/Temperature meter. Calibration of the pH meter was done each time before use by using buffer solutions of pH 4.01 and 7.01. The electrode of the pH meter was rinsed with ultrapure water each time before and after pH measurement. The sample solutions were placed in the plastic containers (polypropylene) in which the pH electrode was immerged. The pH measurement was done on the stirred solution for a good and precise measurement. In order to obtain the reproducibility, pH measurements were done on triplicate samples for each type of sample.

3.3.2 Inductively Coupled Plasma-Optical Emission Spectroscopy

Elemental analysis study of the clinoptilolite supernatant filtrates (filtered using 0.45 µm membrane) collected after cation exchange capacity, adsorption procedures and after the pretreatment procedure of the natural clinoptilolite was done in order to gain a better understanding of the trace and major heavy metal species leached into the filtrates from the zeolite, and also to determine which elemental species were trapped in the zeolite sample and which were leached out. The concentrations of ionic species in the post-synthesis aqueous supernatant solution were measured by the use of inductively coupled plasma atomic emission (ICP-OES). The instrument used for the major and trace elements, was a Varian Radial ICP-AES using a High Matrix Introduction (HMI) accessory and He as collision gas. External calibration of the instrument was performed daily, and a quality control standard verifying accuracy was included with every batch of samples analysed. During ICP-OES analysis, internal standards were used to correct the matrix effects and instrument drift. In this case, the mixed standards solutions were used since the metal analytes were to be analysed from a solution containing different metals. Samples were diluted by hundred for major and trace elements since some major elements were high in concentration. The measurements of all metals were done using mixed standard solutions. Triplicate samples were considered in order to achieve the reproducibility of the analysis results.

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3.3.3 Characterization methods of South African clinoptilolite

Table 9: List of the sample name and codes used for characterization

Sample used for characterization experiments	
Sample name (as-received sample)	**Code**
ECCA Soft	ESC, ESC2
ECCA Hard	EHC, EHC2
Pratley	PC, PC2 and PC 3

It is necessary to understand the structure, physical and chemical properties of clinoptilolite before and after its modification. Clinoptilolite (as-received sample and pretreated) was characterized using different techniques in order to investigate its structure and properties. Both as received and pretreated clinoptilolite samples were characterized using X-ray Powder Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier Transform Infrared (FTIR), High Resolution Transmission

Electron Microscopy (HTEM), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

3.3.3.1 Mineralogical Identification: XRD

The samples were characterized by X-ray diffraction in order to confirm the phase identity structure, crystallinity, the purity and quantity of each mineral phase in the as-received and pretreated clinoptilolite samples. The untreated and pretreated clinoptilolite samples of 90 - 125 µm particle size from both Pratley and ECCA Holdings companies were prepared for both qualitative and quantitative XRD analysis using a back loading preparation method. Samples were analysed qualitatively by XRD using a PANalytical X’Pert Pro powder diffractometer with X’Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-K radiation. The relative mineral phases were identified using X’Pert Highscore plus software.

The quantitative minerals identification of mineral phases in clinoptilolite samples was performed using the operating settings shown in the table below (Table 10). The relative phase amounts (weights %) were estimated using the Rietveld method (Autoquan Program). Amorphous phases were not taken into account during quantification.

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Table 10: X-ray diffraction parameters (quantitative)

Radiation source	Co-K
Radiation wavelength (λ)	104 nm
Range	1.54056<2°<<80°
Time constant	1 s
Preset count	1000
Voltage (kV)	40
Current (mA)	25
2 θ range	4°
2 θ/step	0.1°
Anti-scatter	4°

3.3.3.2 Scanning Electron Microscopy (SEM)

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The morphological analysis of as-received and pretreated clinoptilolite samples was done using SEM technique in order to determine the difference of the sample surface before and after pretreatment process. Scanning electron microscopy images of both as-receive and pretreated were generated using a Hitachi X-650 Scanning Electron Microanalyser equipped with a CDU- lead detector at 25 kV. Scanning electron microscopy clinoptilolite samples were done on samples prepared by putting a small amount of clinoptilolite on aluminium stubs coated with a thin carbon film to make the surface conductive and to prevent the charging of the sample to enhance the sample images. The coating process was done by EMITECH K950X carbon coater.

3.3.3.3 High Resolution Transmission Electron Microscopy (HTEM)

This technique was used in order to get a good understanding of the crystallinity and the crystals displacement of clinoptilolite "as-received" and pretreated clinoptilolite samples. Clinoptilolite sample (of 90-125 µm) preparation was done by ultra sonicating a tip of clinoptilolite mixed with approximately 10 mL of ethanol and sonicated for 10 min in order to attain a good suspension of clinoptilolite sample. After ultra-sonication, a small drop of sample was deposited on the sample grid (S147 - 4 Holey carbon film 400 mesh Cu grids). The images were captured using Field Emission gun, lens 1 was used with spot size 3, at 200 kV using HTEM-EDS Tecnai G2 F20 XT winMAT.

3.3.3.4 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy (FTIR) was used to determine the degree of dealumination of as-received and pretreated clinoptilolite samples. Fourier Transform Infrared spectra also provided information about the molecular structure. Fourier Transform Infrared requires virtually no sample preparation so in this case; a small amount of each clinoptilolite sample was placed on the Attenuated Total Reflectance (ATR) sample holder of a Perkin Elmer spectrum 100 FT-IR spectrometer. The clinoptilolite sample of particle size of 90 – 125 µm was scanned in the range of 1800 – 250 cm^{-1} and then the baseline was corrected using the background spectrum obtained without any clinoptilolite sample but with the same operating conditions. Fourier Transform Infrared spectra were then analysed by comparing their main zeolitic stretching bands to those of the literature review. Dealumination effect was determined by looking at the shifting of the main zeolitic band positions after acid pretreatment (Cakicioglu-Ozkan, *et al.*, 2005).

3.3.3.5 X-Ray Fluorescence Spectroscopy (XRF)

In order to understand and analyse chemical compositions of untreated and pretreated clinoptilolite samples, X-ray fluorescence (XRF) was used for determination of multi-element composition of all as-received clinoptilolite samples. Clinoptilolite major elements were analysed using a fused glass bead set at 40 kV and 50 mA tube operating conditions. The trace elements were analysed using a powder briquette set at 50 kV and 40 mA tube operating conditions. Matrix effects in the samples were corrected by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ Phillips software.

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The powder samples were prepared by mixing 8 g of clinoptilolite sample mixed with 2 g of a binder which was made up of 10 % C-wax binder and 90 % electron microscopy unit (EMU) powder). This mixture was then thoroughly shaken, poured into a mould and pelletized at a pressure of 15 tons for about 1 min using a Dickie and Stockler manual pelletizer loss of ignition was measured by placing the samples in the furnace at 1000 °C for at least 45 min. Both major and trace elements were analysed 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. In all the analysis, the gas used was a mixture of 90 % argon and 10 % methane.

3.3.3.6 Surface area and pore size distribution method

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Surface area and pore size distribution analysis of both as-received and pretreated products was conducted by the application of Quantachome; Automated gas sorption analyser; iQ_2 surface analyser. The as-received and pretreated clinoptilolite sample of about 0.27 g was weighed and loaded into the sample cell. The samples were initially heated at 35 °C for 10 min then outgassed with nitrogen gas at 120 °C for 240 min. Quantachome instrument was used with nitrogen as the analysis gas starting at 0.015 points and stopped at 0.994 for adsorption whereas the adsorption process started 0.994 points and stopped at 0.015 points. The starting adsorption pressure was 38.1 mmHg and stopped at 750.1 mmHg vice versa for desorption. The sample was ran for 480 min in total.

CHAPTER 4

PRETREATMENT AND CHARACTERIZATION OF NATURAL SOUTH AFRICAN CLINOPTILOLITES

This chapter is divided in two main sections. The first section (section 4.1) presents and discusses the results of the optimization of the acid-pretreatment method using Pratley clinoptilolite sample then the comparison of acid-pretreatment of ECCA Holdings soft clinoptilolite (ESC) sample, ECCA Holdings hard clinoptilolite (EHC1) with Pratley clinoptilolite (PC) obtained from two different zeolite companies (ECCA Holdings and Pratley). The second section (section 4.2) presents and discusses the results of the characterization carried out on the untreated and pretreated clinoptilolite samples (ESC, EHC and PC) using different analytical techniques such as X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy (SEM), High Resolution Transmittance Electron Microscopy (HTEM) and Brunauer-Emmett–Teller (BET). In Section two, the chemical and physical properties of the three clinoptilolite samples will be compared to determine which has the best capacity for the adsorption of ammonia and chromium from wastewater. The acid-pretreatment experimental results are presented in section 4.1.

4.1 ACID-PRETREATMENT OF CLINOPTILOLITE

In order to improve ion exchange capacity of the as-received clinoptilolite samples, the acid-pretreatment was performed to remove or exchange the charge balancing cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) from clinoptilolite framework and prepare the H^+ form of clinoptilolite (Akyil *et al*., 2004; Cakicioglu-Ozkan *et al*., 2005; Mamba *et al*., 2009; Muzenda *et al*., 2011; Kurama *et al*., 2002 and Spryskyy *et al*., 2005).

4.1.1 Effect of time on the acid pretreatment of the clinoptilolite

The initial pretreatment experiment was done in order to determine the optimum time required for the pretreatment of clinoptilolite by using 0.02 M HCl. The experiment carried out to determine the optimum time for the acid-pretreatment was only carried out on the PC1 sample (Untreated Pratley clinoptilolite with particle size of 1000 – 1400 µm) due to the insufficient quantity of ESC and EHC samples. This experiment was performed in one beaker in which clinoptilolite sample (10.0 g of PC1) was mixed with acid (150 mL volumes of 0.02M HCl) from which a sample of a volume of 1.0 mL was drawn after every 2 h for the analysis of the cations (Na^+, K^+, Mg^{2+} and Ca^{2+}). The obtained analysis results for the extraction of cations during the acid-pretreatment as a function of time are presented in Figure 15 below.

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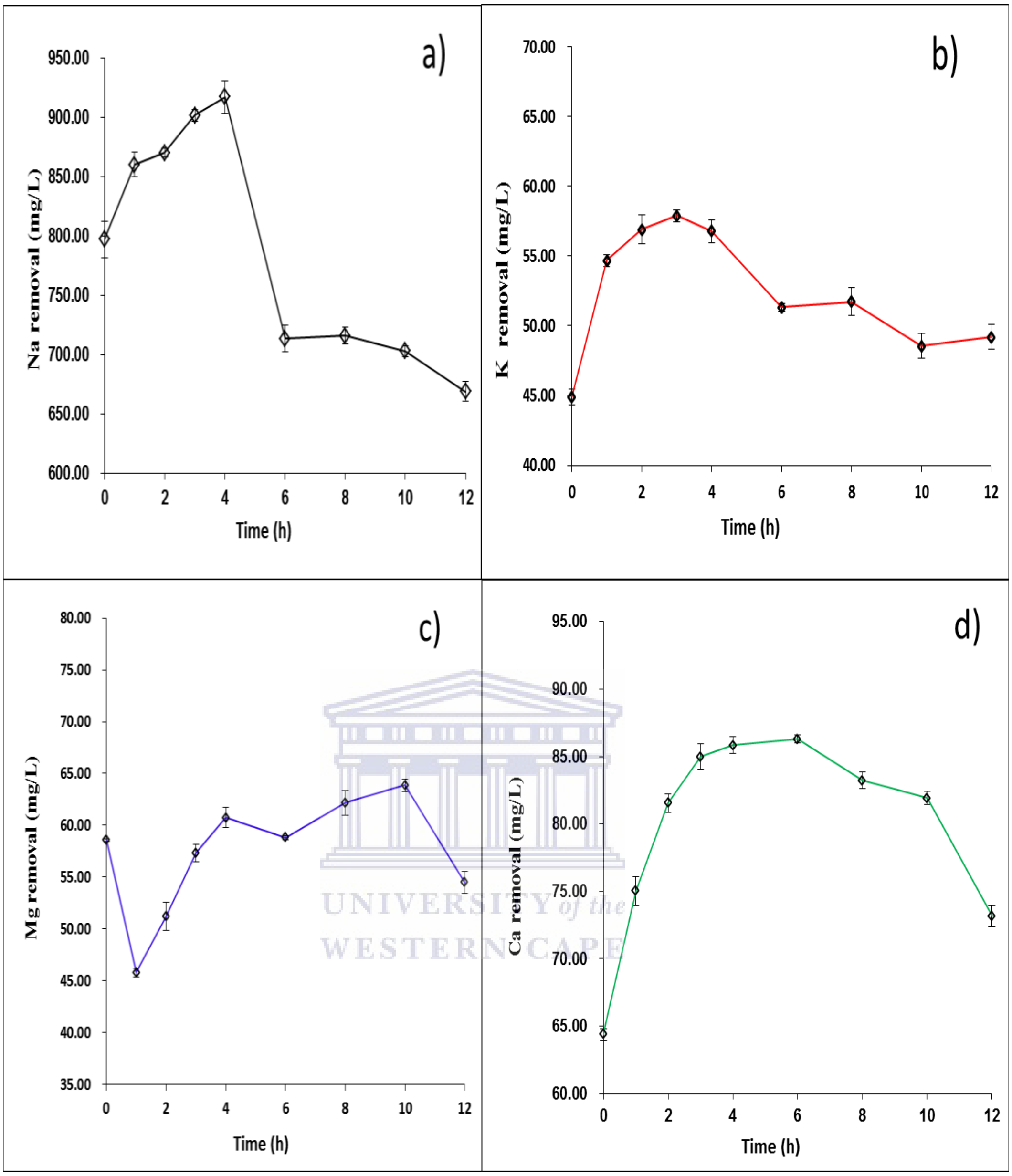

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Figure 15: Extraction of cations from untreated Pratley clinoptilolite (PC1) sample showing the concentration of (a) Na^+, (b) K^+, (c) Mg^{2+} and (d) Ca^{2+} in aliquots extracted from 10 g clinoptilolite using 150 mL of 0.02 M HCl for 12 h.

Figure 15 shows a maximum extraction of the Na^+ ion (917 mg/L) was attained after 4 h (Figure 15a). The decrease in the concentration of the exchanged Na^+ thereafter at 6 h may be due to the cation going back onto the exchange sites within the zeolite framework after the initial competitive desorption. The re-adsorption of Na^+ continued until the end of the experiment with concentration of 668 mg/L. In the case of K^+, the maximum exchange occurred between 3 and 4 h with concentrations of 57.9 mg/L and 56.8 mg/L of K^+ respectively. The re-adsorption of K^+ was observed thereafter and this continued until 10 h (Figure 15 b). The Ca^{2+} showed a similar trend with a maximum exchange of Ca^{2+} into the solution at 4 h with concentration of 85.6 mg/L (Figure 15d). The re-adsorption of Ca^{2+} was observed after 6 h and continued until the end of the experiment. The trend of Mg^{2+} was different from what was observed for the other cations. The maximum concentration of Mg^{2+} was attained at 10 h (Figure 15c). This indicates that the exchange of the Mg^{2+} was a slower process. The Na^+ cation was found to be the most exchangeable of the cations and had the fast exchange rate (Figure 15a). The average optimum time for the acid-pretreatment of the PC1 was found to be 4 h since it is the maximum cation extraction achieved at 4 h. Having determined the optimum time for the pretreatment, further experiment on the pretreatment of all the clinoptilolite samples to determine the optimum concentration of the acid was done at 4 h. The results showing the optimum concentration of acid for the pretreatment of the clinoptilolite are presented in section 4.1.2 below.

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4.1.2 Optimum acid concentration for acid-pretreatment

The optimum acid concentration for the pretreatment was investigated in order to determine the effect of acid strength on the clinoptilolite framework structure for this specific adsorbent (South African clinoptilolite). It is important to optimize the acid pretreatment of natural adsorbents depending on their origin (different composition) despite what other researchers have optimised. The acid-pretreatment of natural clinoptilolites from different deposits should not be uniform, they should be optimized accordingly. The optimum acid concentration to use for pretreatment was evaluated using several concentrations of HCl acid at 4 h (see experimental details in section 3.1.4.2). Optimization of the acid concentration was done on the PC1 (Pratley clinoptilolite with particle size range of 1000 - 1400 µm), sample based on the obtained optimum time (4 h) using acid solutions of different concentrations such as 0.02, 0.04, 0.06, 0.08, 0.1 and 1.0 M HCl but only the results of the pretreatment using 0.02 and 1.0 M HCl are presented in Figure 16.

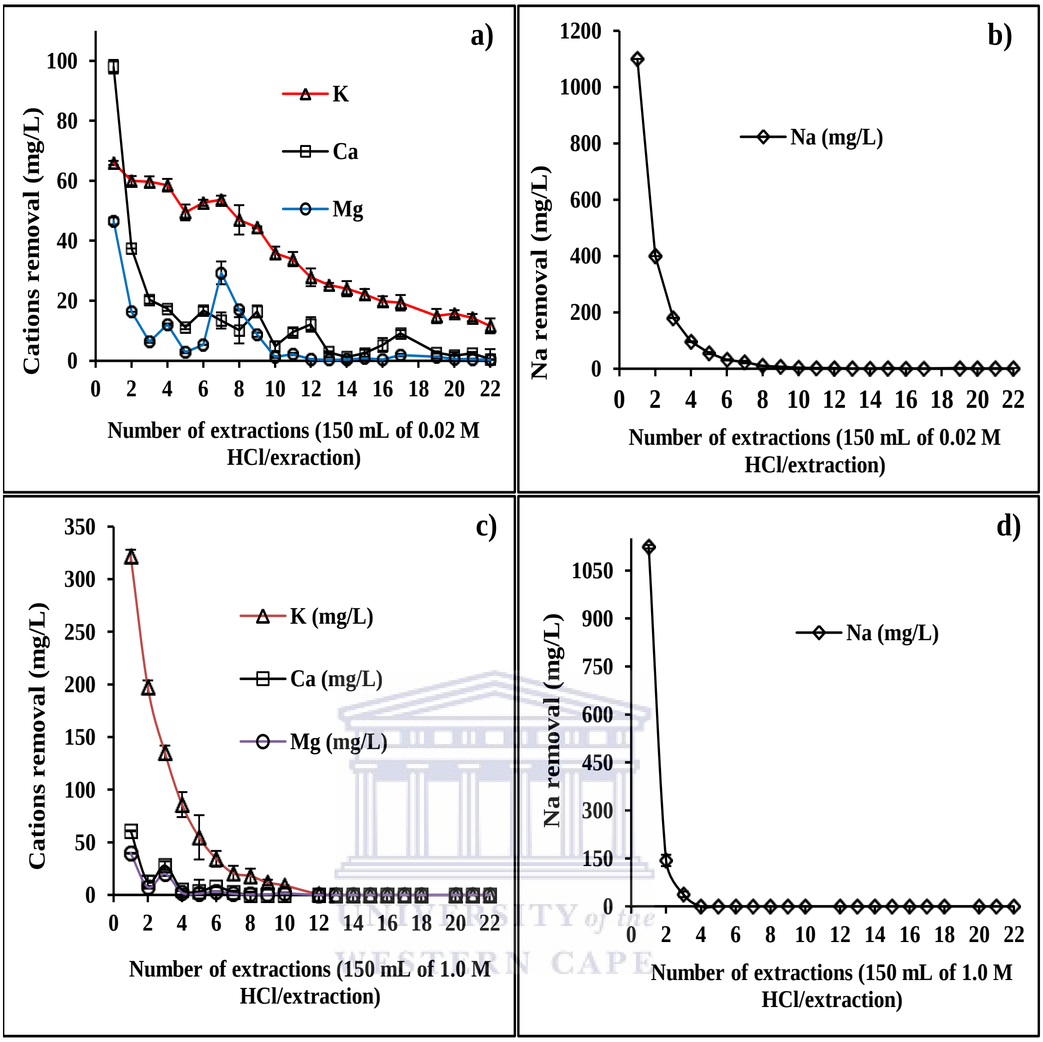

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Figure 16: Extraction of cations from PC1 sample using 22 sequential extraction volumes of 150 mL of 0.02 M HCl (a and b) and 1.0 M HCl (c and d) respectively at 25 °C for 4 h per each extraction.

The results shown in Figure 16a and 16b showed that all cations except the K^+ were below detection limits after 22 extractions when 0.02 M HCl was used. The concentration of Na^+ in the leachate was reduced from 1100 mg/L to 55 mg/L after the 5th extraction. The reduction in the concentration of Na^+ continued until the 8th extraction after which the concentration of Na^+ was below detection limit for the remaining extractions. The concentration of Ca^{2+} in the leachate was reduced from 98 mg/L to 11 mg/L after the 5th extraction, thereafter; the concentration of Ca^{2+} was fluctuating for the remaining extractions.

The Mg^{2+} showed a similar trend as its concentration was reduced from 46.6 mg/L to 6.3 mg/L at the 3rd extraction, after which the concentration of Mg^{2+} fluctuated until the 10th extraction where the Mg^{2+} concentration was below detection limit. The fluctuations observed in the case of the Mg^{2+} and Ca^{2+} ion may be due to the fact that they are strongly bound to the PC1 framework therefore needed more extractions. The K^+ underwent a very gradual decrease from 66 mg/L in the first extraction to 10.8 mg/L on the 22nd extraction with some minor fluctuations. For instance, there was an increase from 49 to 52 mg/L between the 5th and 6th extraction, and an increase from 35.9 to 53.8 mg/L between the 10th and 11th extractions. These are larger cations and maybe slower to diffuse out of clinoptilolite framework through the pores (Pramatha and Dutta *et al*., 2003). The trend of K^+ can be attributed to clinoptilolite preferential selectivity for K^+ (Colella, 1996). The K^+ ion was therefore observed to be the most strongly bound cation among the cations during the mild acid-pretreatment (0.02 M HCl) since its removal from PC1 could not be completely achieved even after 22 acid extractions. This could be due to the large size of K^+ (5.54 Å) causing the slow diffusion through the small pore of clinoptilolite. Zeolites are known to be microporous materials and the pore sizes can vary from 0.2 to 0.8 nm (Pramatha and Dutta *et al*., 2003). The pore size distribution of ESC, EHC and PC samples will be discussed in section 4.2.7. According to the Periodic Table of elements, the atomic size of K^+ is greater than that of the Na^+ (4.46 Å), Ca^{2+} (4.46 Å) and Mg^{2+} (3.44 Å) therefore K^+ diffusion rate is expected to be slower through the clinoptilolite pores during the acid-pretreatment compared to that of other cations. The Na^+ was observed to have the highest concentration and fastest exchange rate since it could be completely removed after the 8th acid-extraction whereas Ca^{2+} and Mg^{2+} were only completely removed after 10 extractions. The content of Na^+ measured from PC sample will be compared to that of ESC and EHC in section 4.1.3.

The same pretreatment experiment (same conditions) was conducted but using a stronger acid concentration (1.0 M HCl; see Figure 16c and 16d). The results of the experiment (Figure 16d) showed that Na^+ concentration was reduced from

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1100 mg/L to below detection limits on the 4th extraction while the Ca^{2+} concentration (Figure 16c) was reduced from 40 mg/L to below the detection limit on the 4th extraction. The concentration Mg^{2+} was reduced from 60 mg/L to below the detection limit on the 4th extraction (Figure 16c) while K^+ concentration was reduced from 330 mg/L to below the detection limit on the 11th extraction.

Considering the pretreatment of PC1 using both 0.02 and 1.0 M HCl, the acid strength played a significant role in the rate of removal of cations. Using 0.02 M HCl, Ca^{2+} and Mg^{2+} were completely removed only after about 10th and 18th extractions respectively, whereas the use of 1.0 M HCl completely removed these two cations at the 4th extraction. The Na^+ was observed to be completely removed at the 8th extraction using 0.02 M HCl and at 4th extraction using 1.0 M HCl. The higher concentration (1.0 M HCl) of acid resulted in fewer extractions to remove all the Na^+ to below detection limits, and a higher concentration of (330 mg/L) was completely exchanged when 1.0 M HCl was used whereas K^+ could not be extracted despite 22 extractions when 0.02 M HCl was applied.

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It could be observed that with higher concentration of acid for the pretreatment of clinoptilolite, the number of extractions required to extract or exchange all the cations from the clinoptilolite sample was reduced. From a green chemistry perspective, this does mean less solvent waste; however, in terms of useful material, higher concentration of acid could remove alumina from clinoptilolite framework, and result in lower cation exchange capacity (CEC). The removal or washing out of aluminium from the framework is known as dealumination.

According to studies, the dealumination occurs when pretreating zeolites with high acid concentrations (Cakicioglu-Ozkan *et al.*, 2005 and Mamba *et al*., 2009). Cakicioglu-Ozkan *et al.*, (2005) used Fourier Transforms Infrared (FTIR) to analyse the dealumination of the pretreatment of clinoptilolite at different acid strength and temperature. They pretreated Turkish clinoptilolite using 0.032, 0.16 and 0.32 M HCl and found that the higher the acid concentration, the higher the degree of dealumination.

They therefore chose 0.032 M HCl as the optimum concentration for Turkish clinoptilolite (Bigadic deposit) based on the degree of zeolitic peak shifting using FTIR method of analysis. Mamba *et al*., (2009) also evaluated the effect of acid-pretreatment on Pratley clinoptilolite and found that 0.02 M was the best concentration compared to that of 0.04 M HCl by considering the dealumination effect and ion exchange capacity of both pretreated form of clinoptilolites. Mamba *et al*., (2009) also used FTIR to analyse the dealumination effect. The dealumination of clinoptilolite in this study is discussed in section 4.5. The PC1 samples obtained after the acid-pretreatment 0.02 and 1.0 M HCl were called PC2 and PC3 respectively. The pretreatment results of ECCA Holdings clinoptilolite samples are discussed in section 4.1.3 below.

4.1.3 Acid-pretreatment of ESC and EHC SAMPLES

The experimental condition (4 h and 0.02 M HCl) optimized during the pretreatment of PC1 sample was applied for the pretreatment of ESC1 and EHC1 and the obtained results are shown in Figure 17.

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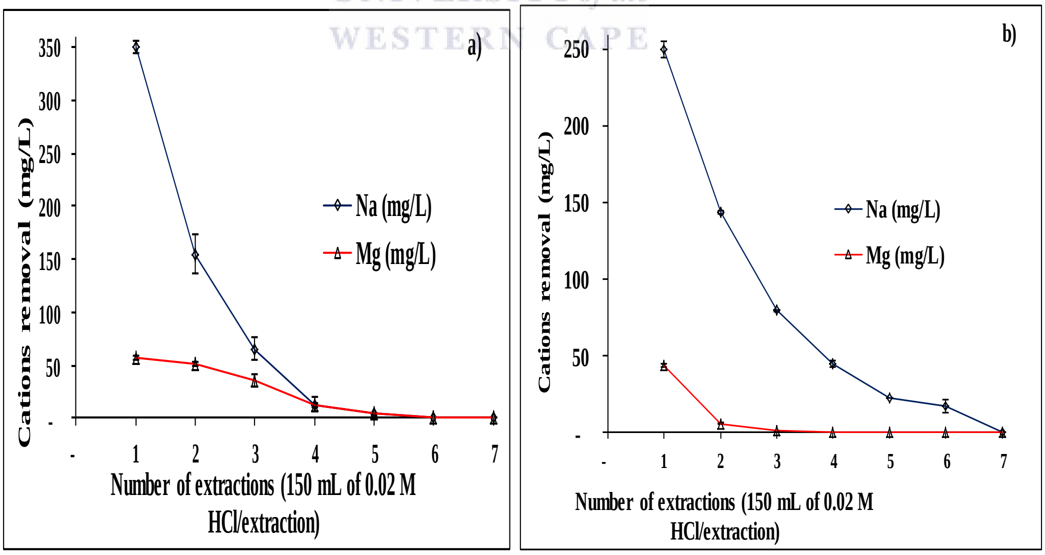

Figure 17: The extraction of cations from 10 g of (a) ESC1,and (b) EHC1 samples using 7 sequential extraction volumes of 150 mL of 0.02 M HCl at 25 °C for 4h per each extraction.

Pretreatment results of both ESC1 and EHC1 samples using several acid extractions are shown in Figure 17a and 17b respectively. Interesting results were generated from both ESC1 and EHC1 samples where only Na^+ and Mg^{2+} could be extracted from the clinoptilolite framework instead of the expected four cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) unlike what happened in the pretreatment of PC1 sample. This means H^+ cannot displace either K^+ and Ca^{2+} at 0.02 M concentration which may be due to the fact that these two are higher in activity series and strongly bound to the clinoptilolite framework whereas Na^+ and Mg^{2+} are weakly bound in it which is due to their small atomic size (see the Periodic Table of elements) compared to that of K^+ therefore making their diffusion rate to be faster through the clinoptilolite pores (Pramatha and Dutta *et al*., 2003). Figures 17a and 17b represent ESC1 and EHC1, showing that the concentration of Na^+ and Mg^{2+} was reduced from 350.96 and 250.31 mg/L to 4.00 and 22.93 mg/L at 5th extraction respectively. At the 6th and 7th extractions of both ESC1 and EHC1 samples respectively, Na^+ was not detected indicating that it was completely removed.

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The concentration of Mg^{2+} of ESC and EHC samples was reduced from 57.08 mg/L and 43.79 mg/L to below the detection limit at the fourth extraction for EHC1 (Figure 17b) and to 12.09 mg/L for ESC1 (Figure 17a). Figure 17b shows a fast exchange of Mg^{2+} in the pretreatment of EHC1 sample compared to that of ESC1 (Figure 17a) because only 3 extractions were enough to completely remove this cation whereas 5 extractions were used to completely remove Mg^{2+} in the case of ESC1 sample. The content of Na^+ removal from PC1 sample was higher than that of ESC and EHC which may due to the fact that Na^+ is weakly bound to the exchangeable sites in the framework (in PC1) than that that of ESC and EHC samples. Another factor is that these samples (ESC1, EHC1 and PC1) are from different deposits and may contain different impurities which may affect the diffusion rate in the removal of Na^+. The purity of the clinoptilolite samples will be discussed in section 4.2.3.

The results shown in Figures 17a and 17b clearly show a significant difference between ECCA Holdings and Pratley clinoptilolites in terms of the cations extraction using the same acid concentration (0.02 M HCl) (Figure 16 and 17). In the pretreatment of PC1 samples, all four expected cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were extracted using 0.02 M HCl at temperature of 25 °C (Figure 16a and 16b) whereas in the pretreatment of ECCA Holdings clinoptilolite samples showed extraction of two cations only; Na^+ and Mg^{2+} (Figure 17a and 17b) extracted at the same experimental conditions. This may be due to the fact that K^+ and Ca^{2+} are more strongly bound to ESC1 and EHC1 exchange sites or the atomic size of K^+ is larger causing the diffusional constrains through the clinoptilolite pores (Pramatha and Dutta *et al.*, 2003). Considering the acid-pretreatment results, the implication is that the acid-pretreatment cannot be applied uniformly but should be optimization for each source of clinoptilolite sample. The ESC1 and EHC1 samples obtained after the acid-pretreatment using 0.02 M HCl were called ESC2 and EHC2 respectively.

4.2 CHARACTERIZATION OF UNTREATED AND PRETREATED ESC, EHC, PC SAMPLES

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This section presents the characterization of untreated and acid-pretreated ESC, EHC and PC samples. Clinoptilolite samples were characterized using different techniques described in Section 3.3. The PC sample was the only fully pretreated and fully characterized clinoptilolite sample using different acid strengths. The results of analysis for the surface morphology carried out using SEM technique are presented in section 4.2.1 below.

4.2.1 Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) was carried out to analyse the effect of acid-pretreatment on the surface morphology and surface chemical composition of ESC, EHC and PC samples. The generated SEM microgram images and EDS spectra are shown in Figure 18, 19 and 20.
The EDS results shown in Table 7 are the average (triplicate) of three different areas of the SEM sample selected during the analysis measurement. All the

figures; Figure 18a, 18a and 20a represent the untreated ESC, EHC and PC samples and Figure 18b, 19b and 20b represent the acid-pretreated ESC2 and EHC2 (treated using 7 acid extractions, 150 mL volumes each at 25 °C; see Figure 17) and PC2 samples treated using 22 acid extractions, 150 mL volumes each at 25 °C; see Figure 16a and 16b). The SEM image and EDS spectrum of untreated (ESC) and 0.02 M HCl-pretreated (ESC2) samples are presented in Figure 18 below.

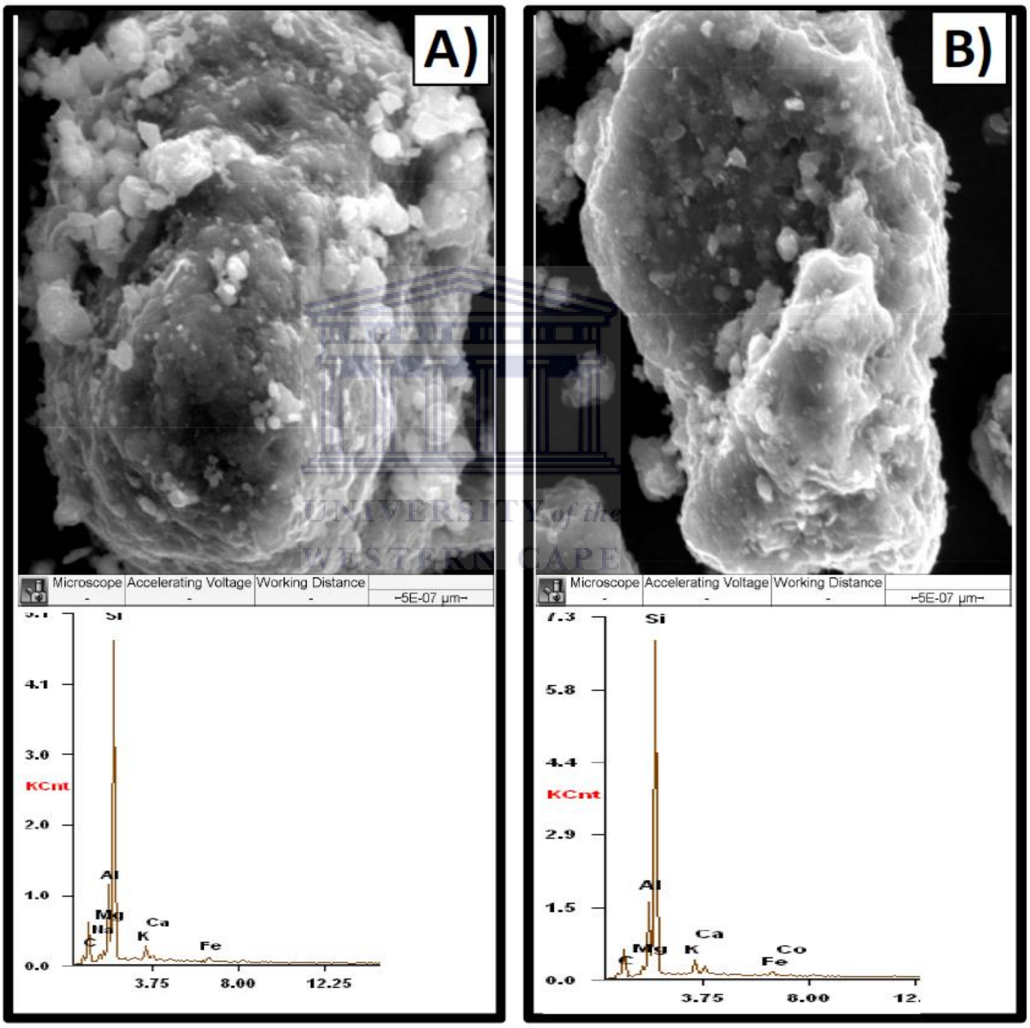

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Figure 18: Scanning electron microscopy images (5 nm scale) of ESC sample (a), untreated, with corresponding EDS spectrum below the micrograph, and (b) 0.02 M HCl-pretreated (ESC2) sample with corresponding EDS spectrum below the micrograph. Images were taken at the same magnification.

In the first panel (Figure 18a), the untreated sample displays an irregular shaped particulate morphology. The pretreated sample (Figure 18b) still displays an irregular shaped morphology. The EDS analysis in the first panel (Figure 18a) shows that the untreated ESC sample has some sodium, while the pretreated sample did not reveal any sodium as expected. The pretreatment step used HCl (0.02 M) acid to exchange the cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} from the various sorption sites available to the zeolite framework. During the pretreatment, the acid solution washed out certain amount of non zeolitic materials (impurities) and lowered cation (Na^+, K^+, Ca^{2+} and Mg^{2+}) content in clinoptilolite by exchanging these cations with H^+. The removal of the non zeolitic materials (impurities) from clinoptilolite samples will be detailed in FTIR analysis results (section 4.2.4). The rough qualitative analysis by EDS (Figure 18) shows that the pretreatment method successfully removed the sodium charge balancing cation from the zeolite pores. The differences in morphology between the untreated and pretreated sample does show that the 0.02 M HCl acid-pretreatment was relatively mild and did not affect the overall topology of the sample. The SEM image and EDS spectrum of untreated (EHC) and 0.02 M HCl-pretreated (EHC2) samples are presented in Figure 19.

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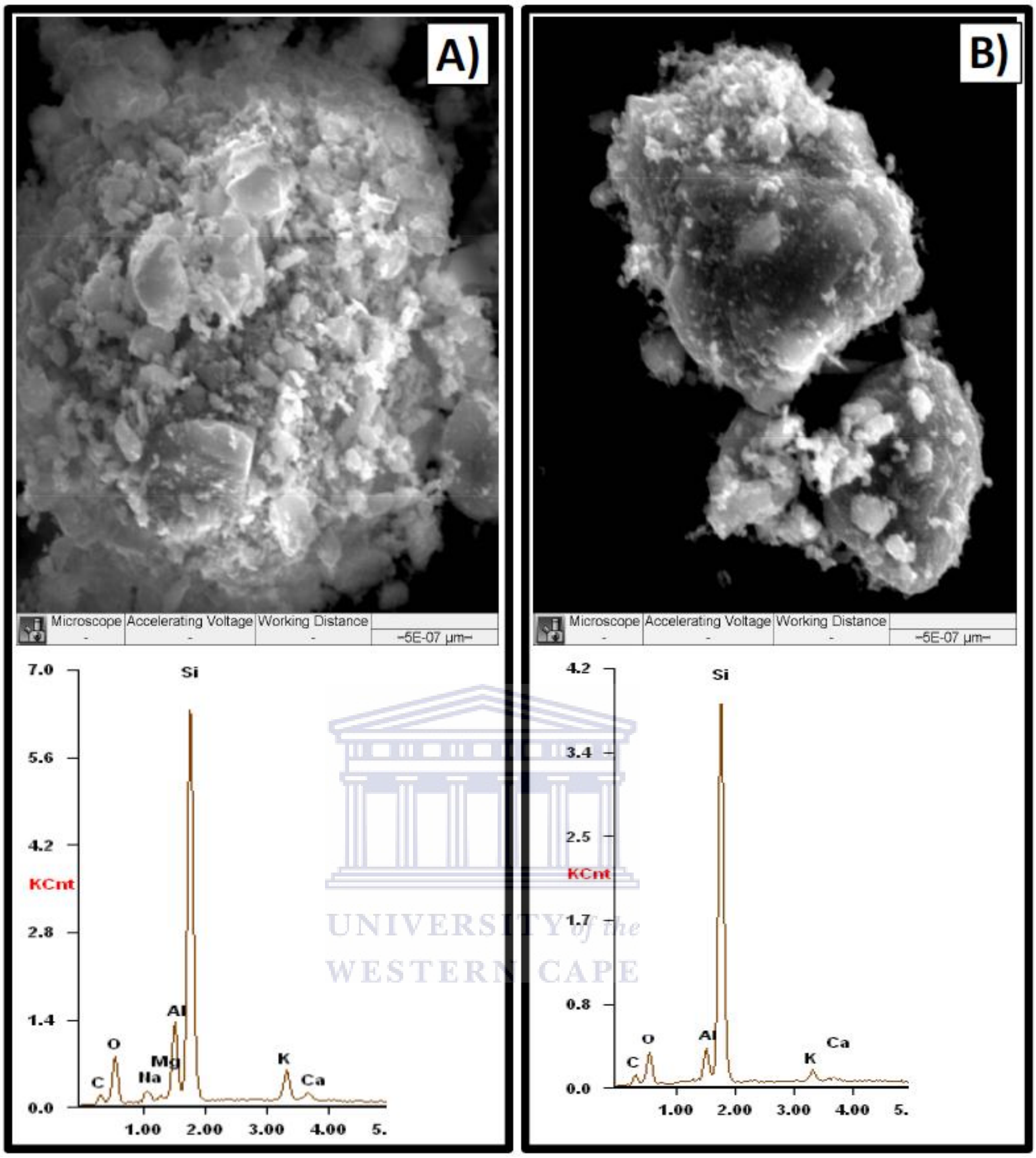

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Figure 19: Scanning electron microscopy images of EHC sample (a) Untreated, with corresponding EDS spectrum below the micrograph, and (b) 0.02 M HCl-pretreated (EHC2) sample with corresponding EDS spectrum below the micrograph. Images were taken at the same magnification.

The EHC sample had a similar irregular morphology when examined by SEM (Figure 19). With the 0.02 M HCl-pretreatment (pretreated with 7 extractions; see Figure 17b) there was little change in the overall morphology. A similar trend with the EDS was observed as with the previous sample; specifically, loss of the sodium peak after treatment, but a noted difference was the additional loss of the magnesium peak (compare panel A) and panel B) in Figure 19). No iron was detected with this sample whereas it was detected in both untreated and treated ESC (Figure 18). The SEM image and EDS spectrum of untreated (PC) and 0.02 M HCl-pretreated (PC2) samples are presented in Figure 20.

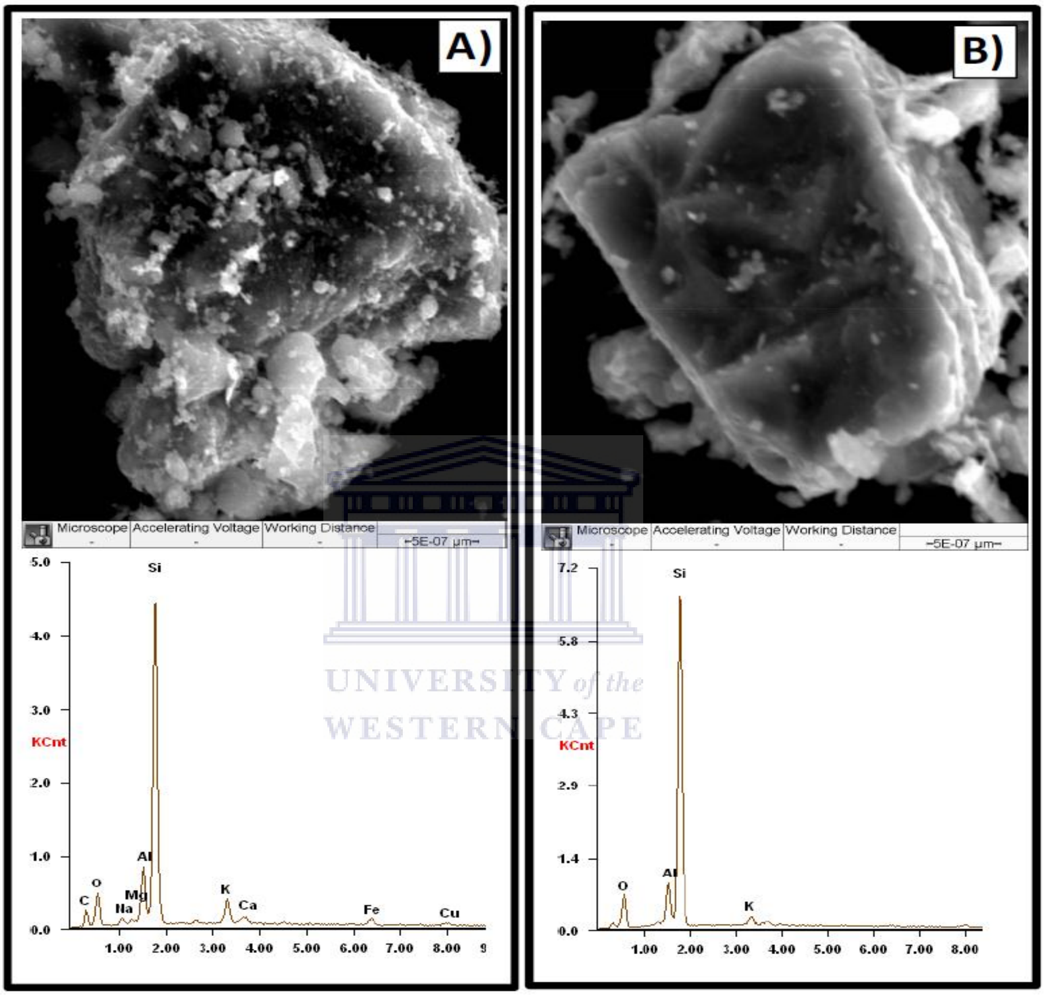

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Figure 20: Scanning electron microscopy images of PC sample (a) untreated, with corresponding EDS spectrum below the micrograph, and (b) 0.02 M HCl-pretreated (PC2) sample (pretreated with 22 extractions) with corresponding EDS spectrum below the micrograph. Images were taken at the same magnification.

The Panel A) and B) in Figure 20 shows the PC sample before and after treatment (see Figure 16a and 16b), with the corresponding EDS spectra. This sample was also characterized by an irregular shape. In the 0.02 M HCl-pretreated PC2 (pretreated with 22 extractions), only K^+ was not completely extracted from its framework whereas other cations (Na^+, Mg^{2+} and Ca^{2+}) were completely extracted. Another difference between this sample and the previous two is the presence of small amounts of iron and copper detected with the EDS before treatment. This can be simply ascribed to the different mining areas or processing steps, and the presence of the metals in the sample will be discussed from the XRF analysis in section 4.2.5. The above discussed SEM-EDS results (Figure 18 to 20; Panel A and B) are supported by the following EDS results presented in Table 11 below (triplicates).

Table 11: Quantitative Energy Dispersive Spectroscopy (EDS) results before and after acid-pretreatment of ESC, EHC and PC samples

Sample name	Na %	K %	Ca %	Mg %
Untreated ESC	1.81 ± 0.05	2.75 ± 0.6	0.88 ± 0.07	1.53 ± 0.04
Pretreated ESC	ND	2.68 ± 0.1	0.76 ± 0.08	0.021 ± 0.001
Untreated EHC	2.42 ± 0.03	4.15 ± 0.3	1.00 ± 0.04	0.87 0.02
Pretreated EHC	ND	4.09 ± 0.2	0.97 ± 0.02	ND
Untreated PC	1.73 ± 0.08	1.06 ± 0.02	1.89 ± 0.05	0.85 ± 0.03
Pretreated PC	ND	0.40 ± 0.04	ND	ND

ND = Not Detected

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Considering the EDS results of both untreated and treated ESC, EHC and PC samples shown in Table 11, all four exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were present before pretreatment. These cations are clearly present in very low content compared to that of aluminium and silicon since these two are the main components of clinoptilolite structure. Na^+ was found to be completely extracted out of the clinoptilolite framework after acid-pretreatment of ESC, EHC and PC samples. Thus, Na^+ was found to be the most weakly bound exchangeable cation since it could be completely exchanged and quickly removed in all the three types clinoptilolite samples (Figure 18 to 19; Panel A and B).

The K^+ was found to be the strongest bound cation among other four exchangeable cations in ESC, EHC and PC samples since it could not be completely exchanged or extracted from clinoptilolite framework. This was earlier shown in acid-pretreatment section 4.1 (Figure 15, 16 and 17). The analyses obtained from EDS are not representative because they represent a very small selected surface area of the sample being analysed. It is therefore, a rough determination of the sample surface elemental composition. It is therefore necessary to use an adequate quantitative analytical technique such as XRF for a better determination of chemical composition of a given zeolite sample. A sample analysed by XRF method gives a true sample representative results. Therefore, the true chemical composition of untreated ESC, EHC and PC samples will be discussed in details in section 4.2.5.

4.2.2 High Resolution Transmission Electron Microscopy (HTEM) analysis

The crystal structure analysis for ESC, EHC and PC samples was carried out using High Resolution Transmittance Electron Microscopy (HTEM) coupled with Selective Area Electron Diffraction (SAED) device. The experimental procedure for HTEM technique is detailed in section 3.3.3.3. The generated HTEM images are presented in Figure 21, 22a, 23a and 24a). The polycrystallinity of clinoptilolite samples was analysed using Selected Area Electron Diffraction (SAED) method and the generated images are shown in the Figure 22b, 23b and 24b below.

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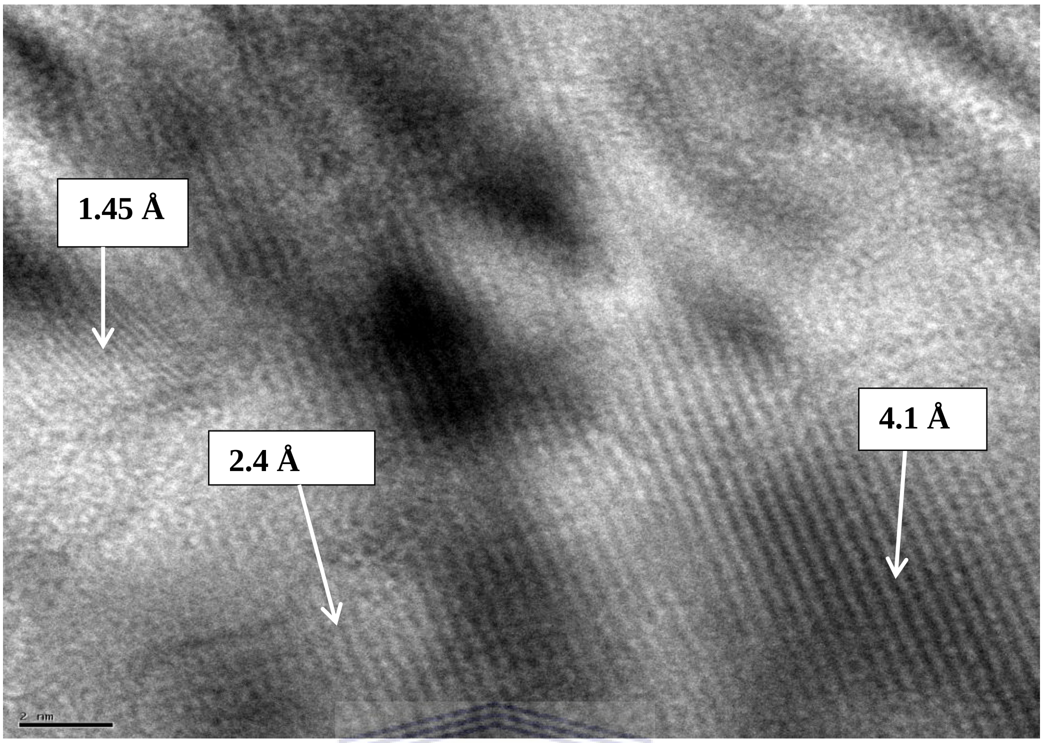

Figure 21: HTEM images of ESC sample scaled at 2 nm showing d-spacing.

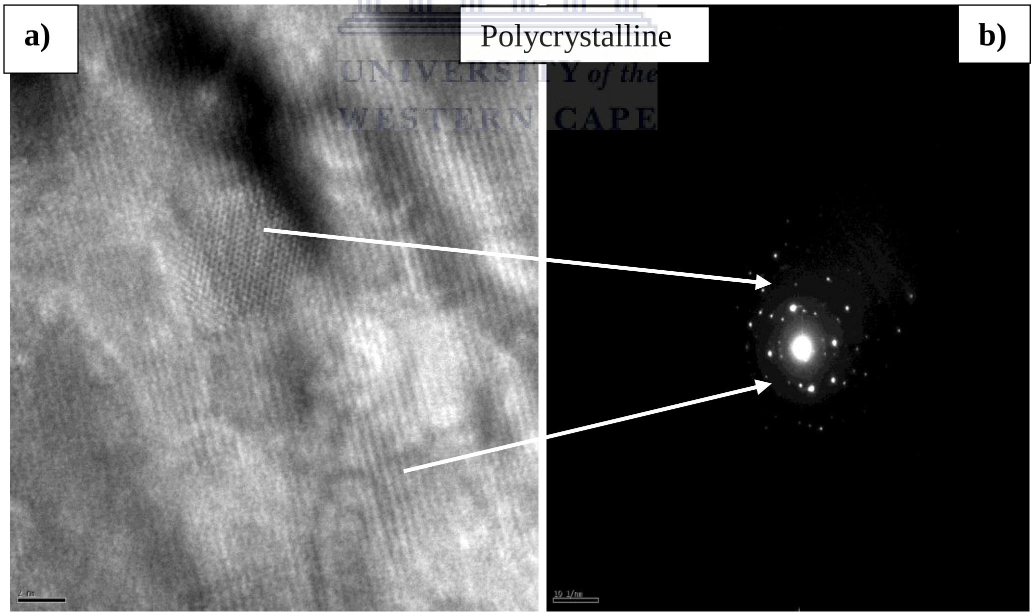

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Figure 22: HTEM image (a) and SAED (b) of untreated soft ESC sample scaled at 2 nm showing polycrystallinity of the sample

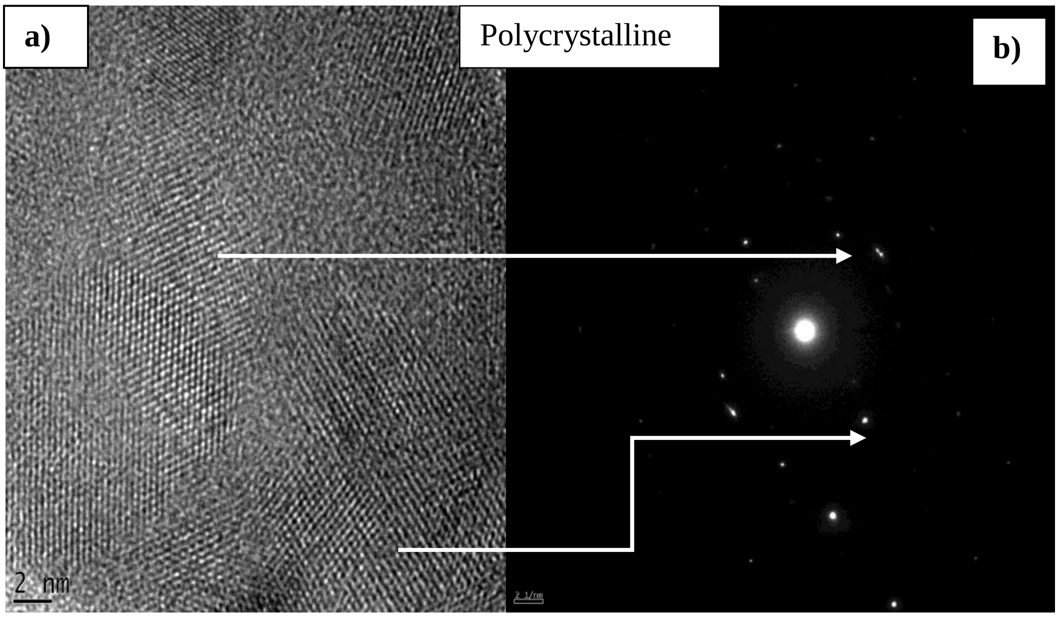

Figure 23: HTEM image (a) and SAED (b) of untreated EHC sample scaled at 2 nm showing polycrystallinity of the sample

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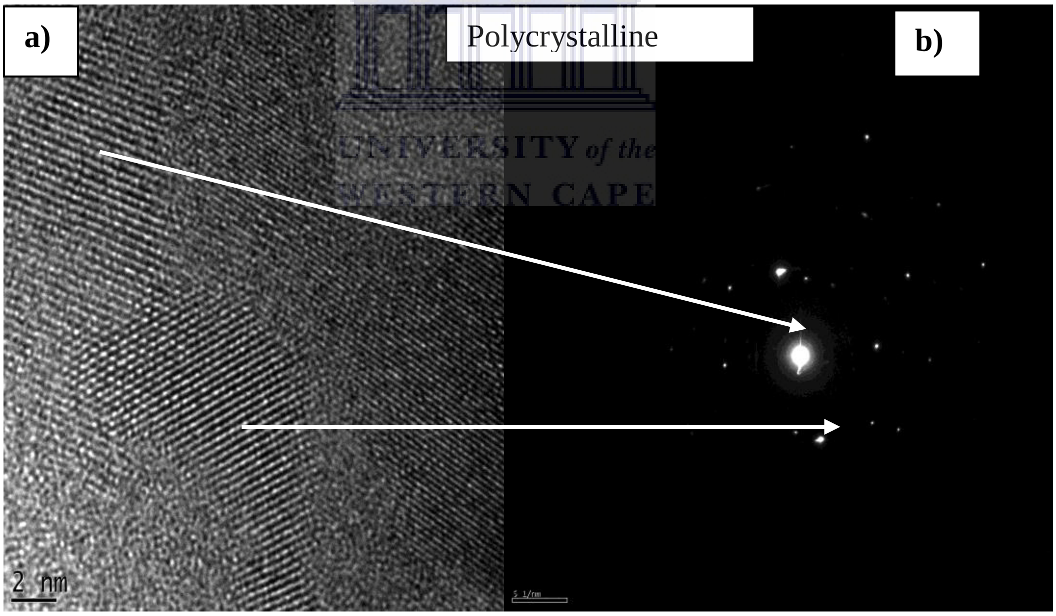

Figure 24: HTEM image (a) diffraction patterns SAED (b) image of untreated PC sample scaled at 2 nm showing polycrystallinity of the sample.

The generated HTEM images of untreated ESC, EHC and PC samples show the structures with different crystals oriented in different directions (Figure 21, 22a, 23a and 24a).

The crystals in HTEM images showed fringes with different inter-distance (d-spacing) depending on the mineralogical association (Figure 21). The highest inter fringes distance was 4.1 Å and the smallest with 1.5 Å. The directions of the crystals are shown by fringes which differ from clinoptilolite, sample to sample. All the three samples (ESC, EHC and PC) were found to be polycrystalline due to different crystal directions (Figure 21, 22a, 23a and 24a). The white dots shown in the SAED images (Figure 22b, 23b and 24b) represent the crystal arrangement in the clinoptilolite framework structure. The white dots are scattered instead of being arranged in the same direction along the central diffuse ring. Polycrystallinity may be due to the fact that all three clinoptilolite samples might not be in pure clinoptilolite form or composed of different mineral phases. The polycrystallinity of these samples may affect the diffusional rate for the removal of cations from the framework during the acid-pretreatment. The measurement of the fringe distances (d-spacing) was done using a digital micrograph program.

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4.2.3 Mineralogy of the clinoptilolite

The X-ray diffraction (XRD) patterns of the untreated and 0.02 M HCl-pretreated ESC and EHC and PC samples used throughout this study are discussed in this section. Mineral phases were identified using the qualitative XRD analytical method as described in section 3.3.3.1. Characteristic clinoptilolite and other mineral phase peaks for ESC, EHC and PC samples in the XRD patterns are assigned in the Figure 25. X-ray diffraction patterns of the untreated ESC, EHC and PC samples are shown in Figure 25.

Qualitative XRD analysis was conducted on untreated ESC, EHC and PC samples to identify their mineral phases, content of clinoptilolite and other mineral phases in all three samples were obtained using quantitative XRD analysis procedure as specified in section 3.3.3.1 for which results are shown in Figure 25, 26, 27 and Table 12.

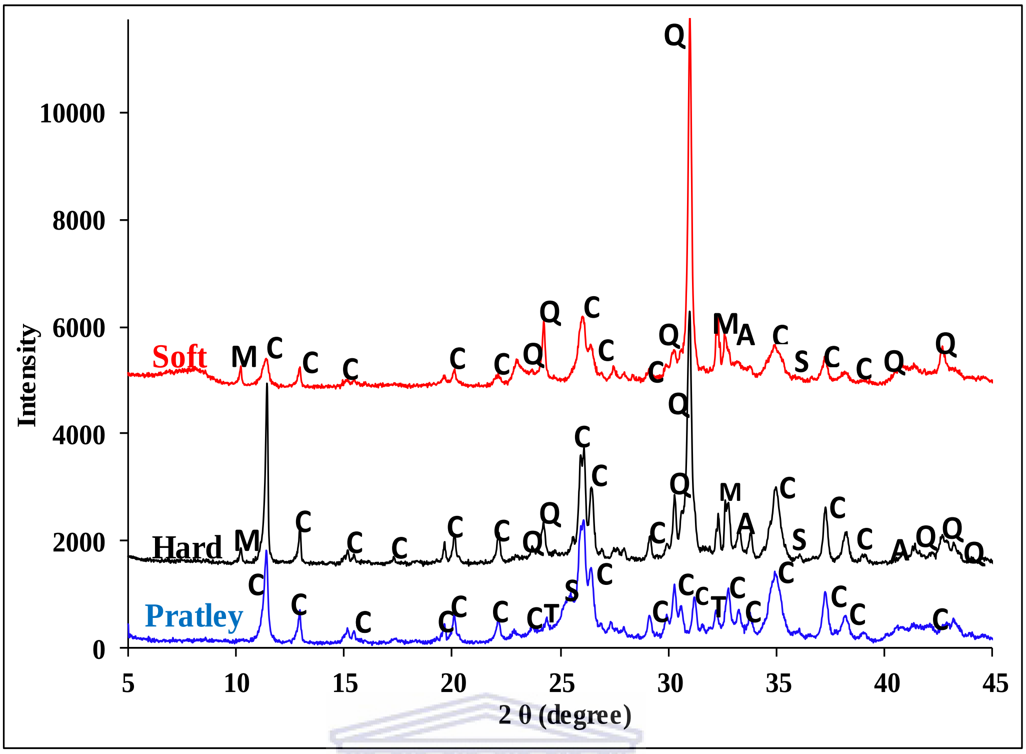

Figure 25: The qualitative X-ray diffraction patterns showing mineral composition of untreated ESC, EHC and PC samples where mineral phase peaks are represented as clinoptilolite (C), Muscovite (M), Anorthite (A) and Quartz (Q), Sanidine (T) and Stilbite (S).

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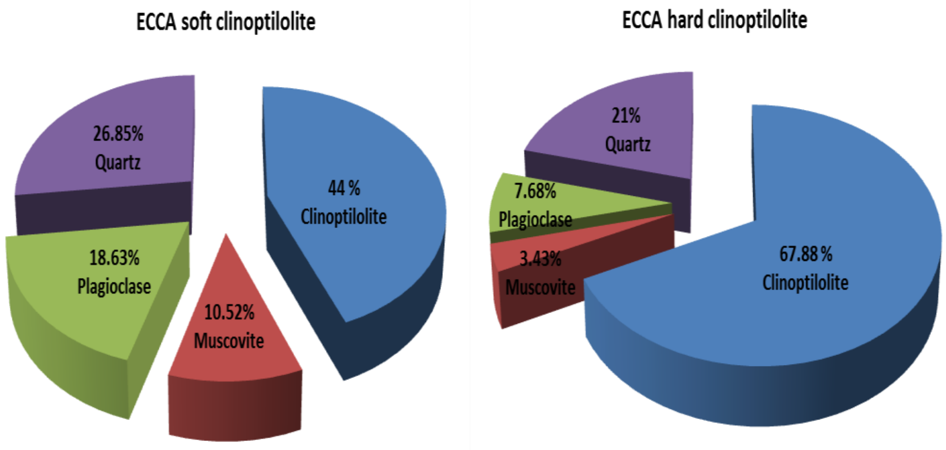

Figure 26: Quantitative X-Ray Diffraction data for ESC and EHC samples

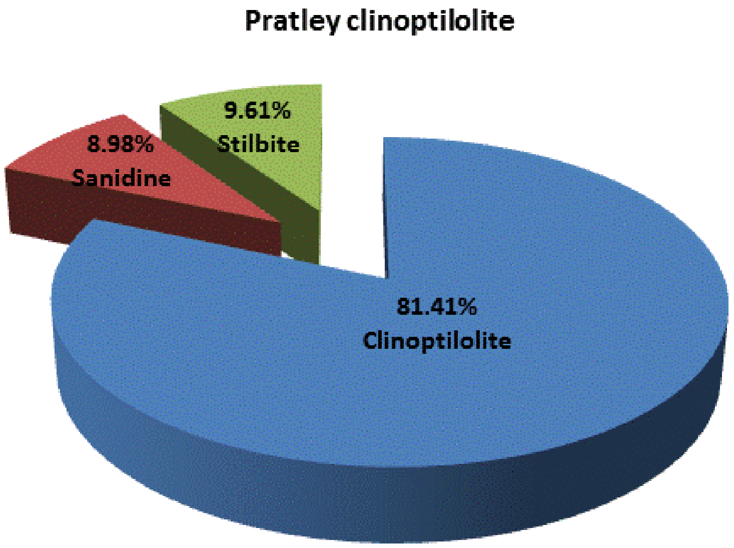

Figure 27: Quantitative X-Ray Diffraction data for PC sample

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Table 12: Quantitative X-Ray Diffraction data of ESC, EHC and PC samples

	ECCA Clinoptilolite			**Pratley Clinoptilolite**
	soft sample	**hard sample**		**pratley**
Mineral phases	**(%)**	**(%)**	**Mineral phases**	**(%)**
Clinoptilolite	44 ± 1.56	67.88 ± 1.17	Clinoptilolite	81.41 ± 1.59
Muscovite	10.52 ± 1.11	3.43 ± 0.66	Sanidine	8.98 ± 0.99
Plagioclase	18.63 ± 1.59	7.68 ± 0.9	Stilbite	9.61 ± 1.32
Quartz	26.85 ± 1.17	21 ± 0.96	-	-

Qualitative XRD analysis was carried out on the untreated samples and analysis of both the untreated ESC and EHC samples is presented in Figure 25, quantitative XRD data showed different mineral phases with their percentage content present in both ESC and EHC samples. Both samples showed common mineral phases but with different peak intensities. Clinoptilolite was found to be the dominant mineral phase in both samples showing stronger peaks than other mineral phases present such as quartz, muscovite and anorthite. Both ESC and EHC samples showed characteristic quartz peaks at around 24 and 32° 2θ and the intensity of the quartz peak at 32° 2θ in the ESC sample was higher than that of EHC sample. The reduction of clinoptilolite quality (or purity) in the ESC sample was due the presence of the high quartz content (Figure 26), as could be seen from quantitative analysis showing only 44.0 % clinoptilolite phase for ESC compared to that of EHS sample (67.88 %).

Qualitative XRD analysis of the untreated PC sample presented in Figure 25 showed high intensities of clinoptilolite peaks with the presence of sanidine and stilbite peaks. This supports the results obtained from quantitative XRD where the clinoptilolite mineral phase in PC was found to be 81.41 % and the rest of the mineral phases (sanidine and stilbite) being only 8.98 and 9.61 % respectively. The quartz mineral phase was not identified in PC sample which makes it to be the highest quality clinoptilolite sample in this study. Quartz mineral is known to be a crystalline mineral phase (physically hard and dense) which does not easily release the containing cations during the ions exchange process (at the normal standard conditions). This affects the exchange capacity of the exchanger such as clinoptilolite. It was observed from the acid pretreatment of ESC and EHC that less cations content could be removed compared to that of PC because PC sample contained no quartz phases. The percentage quartz contents in ESC, EHC and PC samples are presented in the Figure 26 and 27 and Table 12.

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The ESC sample contained low content of clinoptilolite (44 %) with high content of quartz (26.85 %). Quantitative XRD data of the EH C sample showed that the sample contains 67.88 % clinoptilolite and 21.00 % quartz. Both ECCA Holdings clinoptilolite samples were compared to that of PC in terms of clinoptilolite content. Pratley contains high content of clinoptilolite (81.41 %) mineral phase without quartz and was considered to be the most pure phase sample used in this study. More mineral phases such as muscovite and plagioclase have been identified in both ESC and EHC samples but with lower amounts compared to that of quartz. The percentage of muscovite was found to be 18.63 % in the soft and 7.68 % in the EHC sample while the plagioclase phase content was 10.52 % and 3.43 % in both samples respectively. The muscovite mineral phase is known to be part of the mica group of mineral with a chemical formula: $KAl_2(Si_3Al)O_{10}(OH; F)_2$ (Frondel, 1962). Neither of these two minerals phases (muscovite and plagioclase) were found in the PC sample. The Pratley clinoptilolite sample contained sanidine and stilbite mineral phases, with 8.98 % and 9.61 % content respectively. It was observed from acid-pretreatment results that the removal of cations out of less pure clinoptilolite samples (ESC and EHC) was quicker (less diffusional constrains) than that of pure clinoptilolite sample (PC). The diffusional constraints for the removal of cations may be due to the polycrystallinity of the clinoptilolite samples as shown by HRTEM-SAED results (see section 4.2.2).

In order to determine the effect of acid-pretreatment on ESC, EHC and PC samples, X-RD analysis was used to compare the samples mineral phases before and after pretreatment. The obtained XRD patterns for the untreated and acid-pretreated ESC, EHC and PC samples are shown in Figures 28, 29 and 30 respectively.

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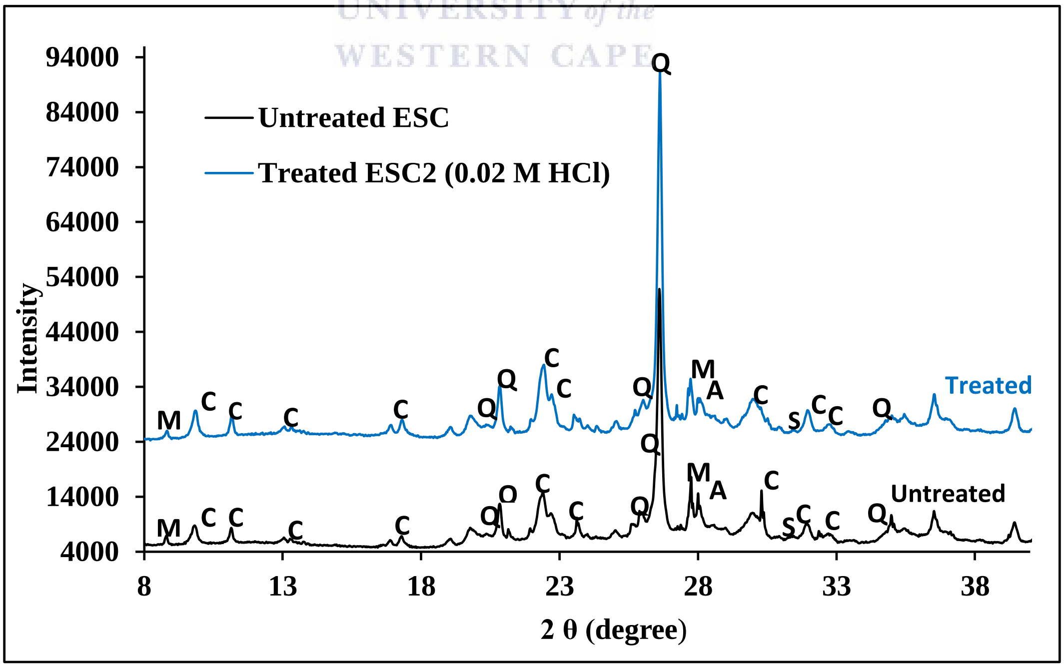

Figure 28: The diffraction patterns of untreated and treated ESC samples, where the mineral phase peaks are represented as clinoptilolite (C), Muscovite (M), Anorthite (A) and Quartz (Q) and Stilbite (S)

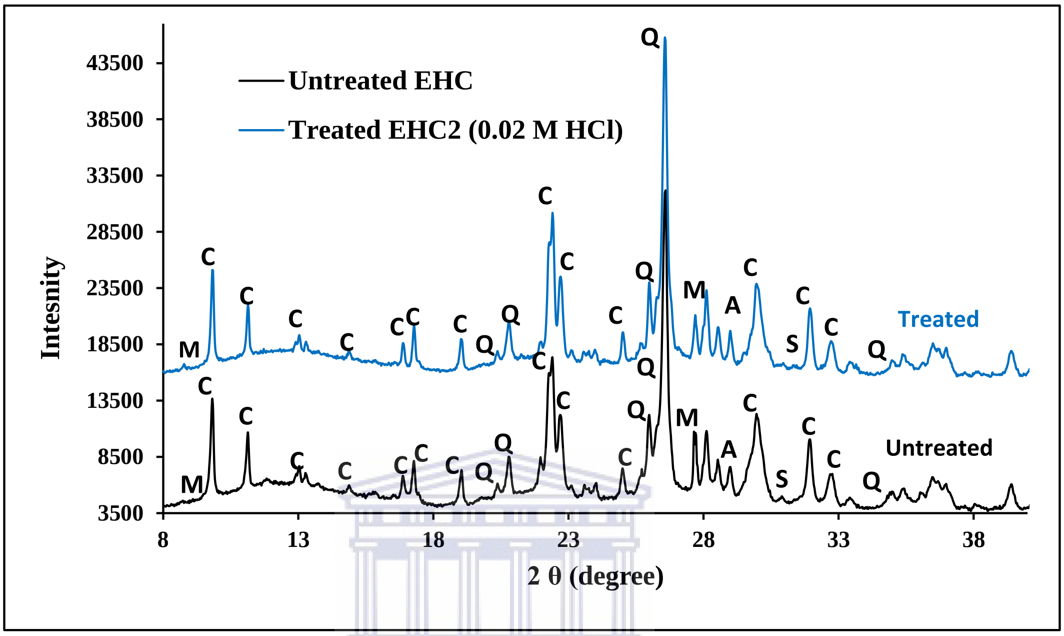

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Figure 29: The X-ray diffraction patterns of untreated EHC samples, where the mineral phase peaks are represented as clinoptilolite (C), Muscovite (M), Anorthite (A) and Quartz (Q) and Stilbite (S)

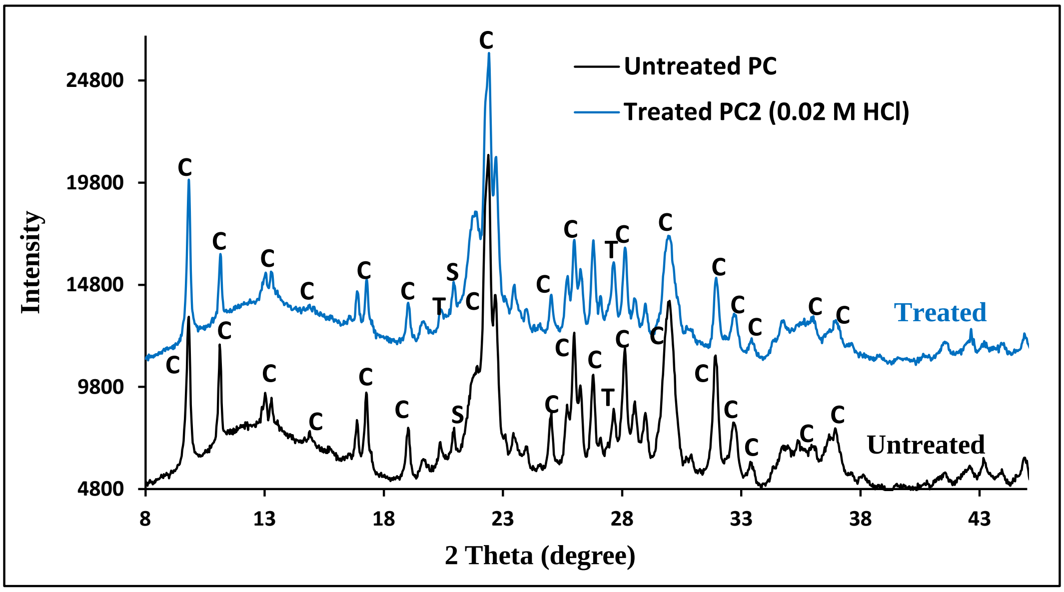

Figure 30: The X-ray diffraction patterns of untreated PC samples, where the mineral phase peaks are represented as clinoptilolite (C), Sanidine (T) and Stilbite (S)

The XRD patterns in Figure 28, 29 and 30 indicate that the XRD analytical technique was not sensitive to alterations in the framework as a result of pretreatment or alternatively, that the 0.02 HCl pretreatment did not impact the overall structure of the zeolite. No changes could be observed in the XRD patterns of ESC, EHC and PC samples before and after the pretreatment process (Figure 28; 29 and 39). Options in terms of ascertaining the extent of dealumination include analysis of the extractions for aluminium, using Fourier Transforms Infra-Red (FTIR) studies. It is possible to pretreat clinoptilolite with diluted acid solution but the dealumination may occur when clinoptilolite is washed many times with acid solution or with high concentration (Cakicioglu-Ozkan, *et al.*, 2005; Mamba, *et al.*, 2009 and Faghihian, *et al.*, 2008). The most favourable option to determine the dealumination effect was thus the FTIR technique, simply due to the ease of access, simplicity in use due to the ATR accessory, and prior success and knowledge of looking at ordered silicates using the FTIR method of analysis. The results obtained from FTIR analyses are presented in section 4.2.4 below.

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4.2.4 Fourier Transforms Infra-Red (FTIR) analysis of PC sample

The Fourier Transforms Infra-Red (FTIR) analytical technique was used to determine the functional groups of untreated and pretreated PC sample as this was the most crystalline and pure clinoptilolite sample. The analysis and FTIR sample preparation were done based on the procedure given in section 3.3.3.4. Perkin Elmer FTIR instrument with an ATR accessory was used to analyse the untreated and pretreated Pratley clinoptilolite samples and the spectra are shown in Figures 31, 32 and Table 13).

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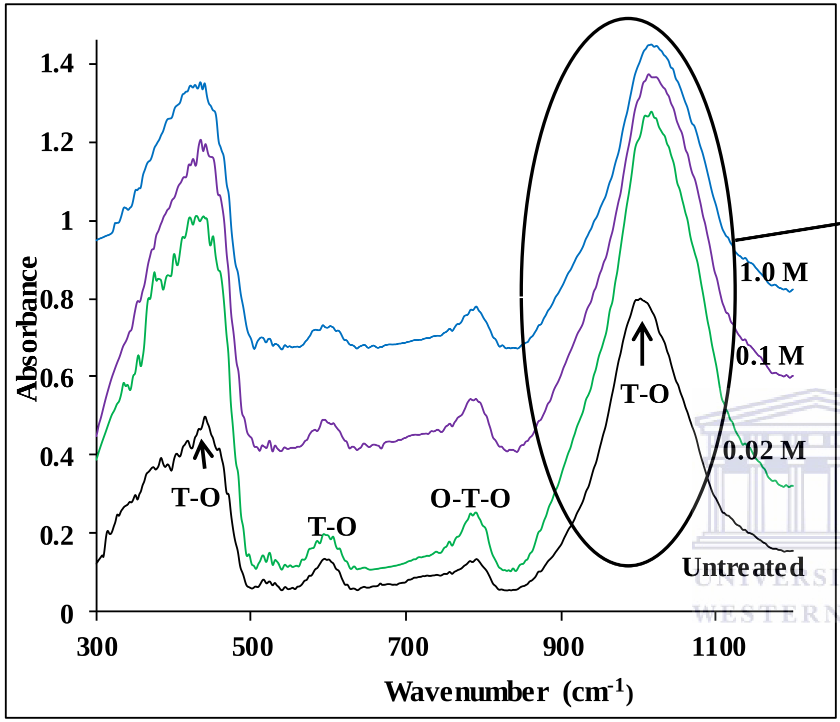

Figure 31: Fourier transforms infrared spectra of untreated and pretreated PC where T represents the stretching bands of Si and Al atoms and O represents oxygen atom.

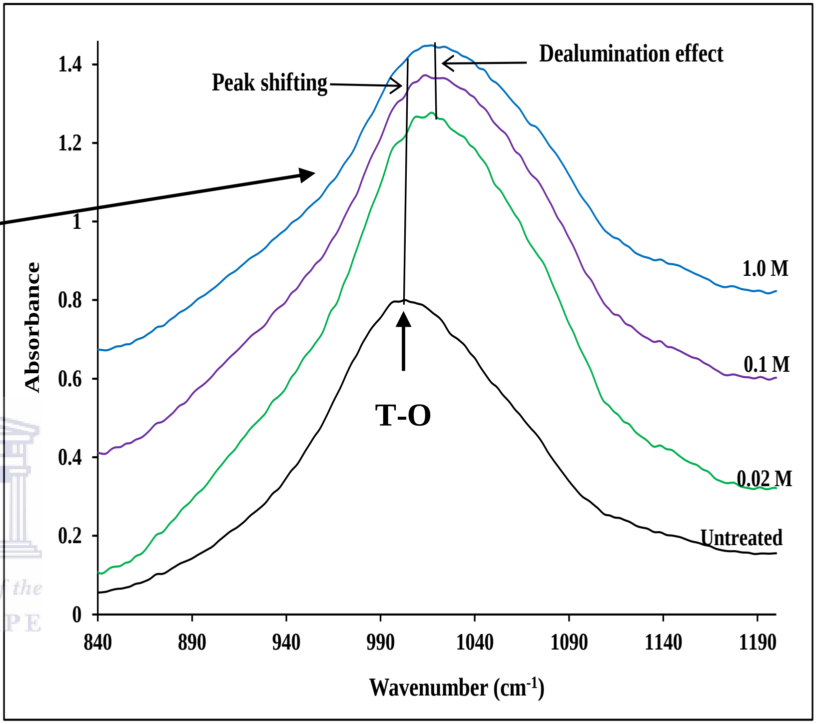

Figure 32: Fourier transforms infrared spectra of untreated and pretreated PC (blown up from 840 to 1200 cm^{-1}) where T represents the stretching bands of Si and Al atoms and O represents oxygen atom.

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Table 13: Summary of the main absorbance bands found in untreated and treated PC samples

Sample (HCl)	T-O (strong) cm^{-1}	O-T-O (weak) cm^{-1}	T-O (weak) cm^{-1}	T-O (strong) cm^{-1}
Untreated	1009	795	601	444
0.02 M	1022	797	602	441
0.1 M	1026	797	603	441
1.0 M	1030	798	607	440

The FTIR spectrum of the untreated PC shown in Figure 31 clearly showed strong bands at 1009 cm^{-1} and 444 cm^{-1} and two weak bands at 795 cm^{-1} and 601 cm^{-1}. These bands are T-O (T represents Si or Al) asymmetric stretching vibration modes of the internal SiO_4 and AlO_4 tetrahedra structure. These strong bands are characteristic of zeolite materials (Flanigen, 1976). The weak bands were the O-T-O stretching vibration modes (795 cm^{-1}) and T-O bending vibration modes (601 cm^{-1}) of the external SiO_4 and AlO_4 tetrahedral. Figure 32 was generated from Figure 31 by enlarging the zeolitic bands around 840 – 1200 cm^{-1} in order to clearly see the shifting of the bands (peaks) after the acid-pretreatment process. The effect of the acid-pretreatment was determined by looking at the degree of shifting of these specific zeolite bands because such shifts are indicative of degradation of the framework (Figure 32) (Cakicioglu-Ozkan, *et al.*, 2005; Mamba, *et al*., 2009; Faghihian, *et al.*, 2008 and Pramatha and Dutta *et al*., 2003). The shifts were observed with T–O stretching vibration mode, from 1009 cm^{-1} (untreated sample) to 1022, 1026 and 1030 cm^{-1} and 1018.7cm^{-1} for treated samples using 0.02, 0.1 and 1.0 M HCl respectively, and are summarized in Table 13. Spectra obtained from the pretreatment of PC using 0.04, 0.06, and 0.08 M HCl are presented in appendix A1 and the same dealumination effect was observed after pretreatment but at a lower degree compared to that of 0.1 and 1.0 M HCl.

The measured FTIR spectra of soft samples also showed a slight peak shifting after acid-pretreatment meaning that these samples also underwent dealumination after pretreatment (see appendix A2). The increase in intensity of the small peaks around 524 to 538 cm^{-1} in the pretreated PC samples may be due to the ring opening of SiO_4 and AlO_4 tetrahedrons in clinoptilolite framework (Cakicioglu-Ozkan, *et al.*, 2005; Mamba, *et al.*, 2009 and Faghihian, *et al.*, 2008). The ring opening may be the result of acid washing of the non zeolitic materials contained in the clinoptilolite framework structure during the pretreatment process. In the untreated sample, these small peaks are shown but with a small absorbance which became more prominent as the sample was treated with increasing acid solutions strength. Dealumination was thus observed by FTIR with an increase in acid strength (Figure 32). The same trend (dealumination) was also observed by Cakicioglu-Ozkan, *et al.*, (2005) (see section 2.8.3). It was therefore decided that 0.02 M HCl was the optimum acid concentration for the pretreatment of clinoptilolite since it showed a lower degree of dealumination, confirmed by only a small shift in the zeolitic peak position. Mamba, *et al.*, (2009) also concluded from their work on the acid-pretreatment of PC that 0.02 M HCl was the optimum acid concentration when using 0.02, 0.04 and 0.1 M HCl. According to them, the degree of dealumination was seen to increase with the increase in acid strength. However this study has improved on the study conducted by Mamba *et al*., (2009) and Cakicioglu-Ozkan, *et al.*, (2005) by showing that it is not only the acid concentration that is important but also the number of extractions required to remove the possible cations from the framework. The more the cations exchanged, the more exchange sites are created and the higher the exchange capacity of the zeolite. In addition, it is also important to optimize natural adsorbents depending on their origin since their mineral and chemical compositions vary considerably.

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Hydrochloric acid at 1.0 M HCl, significantly reduced the extraction numbers, and solvent wastage, but was shown, in subsequent FTIR analysis (appendix A1), to damage the zeolite framework thus milder activation is preferred. X-ray diffraction analysis was not sensitive to changes in the zeolite framework due to acid treatments, but FTIR clearly revealed dealumination with increasing acid concentrations during the pretreatment and activation step.

In order to obtain the chemical composition of clinoptilolite samples, the X-ray fluorescence (XRF) analytical technique was used.

4.2.5 Chemical composition of soft, hard and Pratley clinoptilolite

Chemical composition analyses were performed via X-ray fluorescence (XRF) method of analysis as specified in section 3.3.3.5. The chemical composition of the untreated ESC, EHC and PC samples is presented in Table 14 below.

Table 14: X-ray fluorescence (XRF) data for major oxides in weight % for the untreated ESC, EHC and PC samples

	Normalised to 100 % on a moisture free basis		
Oxides	**ESC %**	**EH %**	**PC %**
SiO_2	70.936 ± 0.754	73.890 ± 0.042	70.393 ± 0.000
TiO_2	0.162 ± 0.003	0.094 ± 0.002	0.133 ± 0.000
Al_2O_3	13.141 ± 0.163	10.489 ± 0.075	12.017 ± 0.017
Fe_2O_3	1.569 ± 0.006	0.335 ± 0.003	0.920 ± 0.001
MnO	0.004 ± 0.002	0.011 ± 0.001	0.007 ± 0.001
MgO	1.563 ± 0.004	0.585 ± 0.001	0.710 ± 0.001
CaO	1.040 ± 0.011	0.873 ± 0.012	0.839 ± 0.007
Na_2O	2.319 ± 0.064	2.581 ± 0.020	2.502 ± 0.003
K_2O	1.828 ± 0.029	2.461 ± 0.025	3.467 ± 0.016
P_2O_5	0.036 ± 0.000	0.025 ± 0.000	0.017 ± 0.001
SO_3	0.281 ± 0.003	0.117 ± 0.008	0.017 ± 0.002
Cr_2O_3	0.003 ± 0.001	0.001 ± 0.001	0.001 ± 0.000
NiO	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
LOI	7.116 ± 1.022	8.537 ± 0.056	8.977 ± 0.014
Total	100.000	100.000	100.000

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The results shown in Table 14 indicate that the major elemental compositions were as follows; 70.94 %, 73.89 % and 70.39 % silica (SiO_2) for ESC, EHC and PC samples respectively. Looking at the content of silica in all three samples, the PC is the lowest followed by the ESC and the EHC sample. This does not mean that the quality of clinoptilolite depends on the high presence of silica but the fact that both ESC and EHC samples contain dense quartz mineral phases. In addition, the content of silica of these natural adsorbents may due to different origin and compositions. Quartz mineral is mainly composed of silica. Alumina (Al_2O_3) content in ESC and PC samples was found to be 13.14 %, 10.49 % and 12.10 % respectively. Si/Al for the three clinoptilolite samples (ESC, EHC and PC) were calculated and found to be 4.8, 6.0 and 5.2 respectively. The EHC sample was found to have a high Si/Al since it contained a higher content of silica (73.89 %). These ratios are within typical limits (4 - 6) for clinoptilolite (Tsitsishvili, 1992).

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Considering the total cation oxides (Na_2O, K_2O, CaO and MgO) results obtained by XRF (Table 14), total cation oxide content (7.52 %) in PC is higher than that of ESC (6.75 %) and EHC (6.50 %) clinoptilolite samples. This makes PC sample to be the most favourable clinoptilolite type for the ion exchange process compared to that of ESC and EHC samples. The ion exchange capacity of an exchanger such as a zeolite usually depends on the amount of extra framework cations; Na^+, K^+, Ca^{2+} and Mg^{2+} present in the framework and how easily they can be exchanged (Breck, 1974). The cation exchange capacity experiment was carried out in order to determine which clinoptilolite sample (ESC, EHC and PC) has high exchange capacity. The CEC experiment aims on the exchange or removal of cations from the framework with a homo ionic ion such as NH_4^+. The percentage removal of cations that could be extracted from the framework (in CEC experiment) will be determined from the percentage cation oxides obtained by XRF (this will be discussed in section 4.2.6).

Mamba *et al.,* (2009) conducted a study on South African clinoptilolite (untreated sample) mined by Pratley company. Their XRF results showed the chemical compositions (majors) as follows: 74 % SiO_2, 12.4 % Al_2O_3, 1.3 % Na_2O, 3.8 % K_2O, 1.5 % CaO, 1.5 % Fe_2O_3 and 1.1 % MgO.

Their results compared well to those of PC sample XRF results (Table 14) obtained in this study. The difference in some major oxides between Mamba's work and this work may be due to the fact that clinoptilolite are mined from different deposits and different times. The content of silica obtained in Mamba *et al.*, (2009) work is about 4 % higher than that of the current results (70.39 %, see Table 14) silica. Alumina and other cation major oxides had almost the same content. 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).

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The differences in elemental composition can simply be explained by the varying geology of the mined area, and the mining process is beyond the scope of this project; however, some references do show that several forms of naturally occurring zeolites can be found at a particular mining site or geographical location (Mason and Sand, 1960). It was determined from Table 14 that ESC contains high content Fe_2O_3 (1.57 %) compared to the EHC (0.34 %) and the PC (0.92 %) sample. According to ECCA Holdings Company, the high content of Fe^{3+} has an effect in manufacturing ceramics which turns their colour dark.

Mason and Sand, (1960) compared clinoptilolite and mordenite and reported that the ratio of $Si/Al \geq 4.0$ for clinoptilolite, and the sum of monovalents (Na^+ and K^+) exceeded that of divalents (Ca^{2+} and Mg^{2+}). The XRF results obtained for ESC, EHC and PC samples shown in the Table 14 show that the sum of the monovalents exceeds that of the divalents for each clinoptilolite sample. This confirms that the samples are zeolites of clinoptilolite type. However Coombs *et al*., (1997) recommended that zeolite minerals should 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. Mamba *et al*.,

(2009) reported Si/Al value of 5.96 which agreed with the clinoptilolite specification limit and confirmed these samples (ESC, EHC and PC) were high clinoptilolite enriched with Na^+, K^+, Ca^{2+} and Mg^{2+}.

The XRF analysis results were also conducted on the untreated ESC, EHC and PC samples for the determination of trace elements. The concentrations of the trace elements are shown in Table 15.

Table 15: X-ray fluorescence (XRF) data for trace elements for untreated ESC, EHC and PC samples

Trace elements	ESC (mg/L)	EHC (mg/L)	PC (mg/L)
Nb	14.77 ± 0.46	14.58 ± 0	33.73 ± 0.20
Zr	129.19 ± 2.60	150.43 ± 0.88	156.99 ± 0.042
Y	19.310± 2.49	18.085 ± 0.96	26.75 ± 0.57
Sr	908.66 ± 2.27	559.015 ± 0.84	507.94 ± 0.085
Rb	37.28 ± 0.042	27.92 ± 0.26	102.25 ± 0.45
U	7.82 ± 0.37	4.18 ± 0.64	1.80 ± 0.32
Th	12.81 ± 0.14	18.24 ± 0.81	17.36 ± 0.83
Pb	21.22 ± 0.46	22.85 ± 0.20	14.75 ± 0.12
Zn	29.60± 0.40	31.39 ± 0.17	30.90 ± 0.062
Cu	1.11 ± 0	ND	4.74 ± 0.13
Mn	180.47 ± 2.47	38.93 ± 0.67	178.56 ± 3.55
Cr	27.64 ± 3.42	21.19 ± 0.53	12.83 ± 0.12
V	13.58 ± 1.64	6.39 ± 0.15	6.95 ± 0.002
Sc	8.061 ± 0.46	4.13 ± 0.26	1.99 ± 0.15
Ba	2506.45 ± 121.72	2711.83 ± 3.57	377.099 ± 0.35
S	497.83 ± 22.50	676.042 ± 0.53	67.44 ± 0.84

ND = Not Detected

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The highest concentrated metals obtained from the untreated ESC, EHC and PC are barium and strontium (> 2000 mg/L), with significant amounts of sulphur (732 mg/L), zirconium (491 mg/L), and some small amounts, above 100 mg/L, of manganese and rubidium. Various other elements are present in amounts below 100 mg/L. Since clinoptilolite is mined, the plausible factors that may account for the distribution can be the geology of the area, the mining process and subsequent packaging. These factors may contribute to the contamination of the above mentioned trace elements in the mined clinoptilolite.

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4.2.6 Determination of cation exchange capacity for ESC, EHC and PC

In order to theoretically determine which of the three untreated clinoptilolite (ESC, EHC and PC) is the best exchanger, cation exchange capacity (CEC) experiment was conducted. The experimental method used is described in section 3.1.5.2 and CEC was calculated using equation 3.1. The calculated total cation exchange capacities of all three clinoptilolite samples are summarized in Table 16 shown below.

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Table 16: Cation exchange capacity (CEC) for ESC, EHC and PC samples

Cation	**ESC**		**EHC**		**PC**	
	Concentration (mg/L)	**CEC (meq/g)**	**Concentration (mg/L)**	**CEC (meq/g)**	**Concentration (mg/L)**	CEC (meq/g)
Na	42.73 ± 0.45	0.74	58.25 ± 1.32	1.01	88.56 ± 5.23	1.54
K	26.98 ± 0.26	0.28	72.50 ± 0.24	0.74	82.90 ± 1.25	0.84
Mg	12.80 ± 1.01	0.21	3.47 ± 1.34	0.057	4.80 ± 0.22	0.158
Ca	ND	ND	ND	ND	18.12 ± 0.10	0.36
Total CEC		**1.23**	Total CEC	**1.81**	Total CEC	**2.90**

ND = Not Detected

The results shown in the above table (Table 16) were obtained from the experiment done utilizing 30 min of contact time to determine the total exchange capacity of untreated ESC, EHC and PC samples. The calculated total CEC of both ESC and EHC samples were determined to be 1.23 and 1.81 meq/g clinoptilolite respectively. The ESC sample was observed to have a low CEC (1.23 meq/g) compared to that of EHC sample (1.81 meq/g). This may be due to the fact that the soft sample had higher quartz content and has less potassium content than the hard sample thereby making it to have a low CEC. The CEC of zeolite depends on the cation contents and how easily they get exchanged with other cations (sorbate) present in the solution. Cation exchange capacity of both ECCA Holdings samples were then compared to that of Pratley clinoptilolite sample (2.9 meq/g) ran at the same experimental conditions. This supported the results obtained from quantitative and qualitative XRD which showed that PC is 81.41 % pure clinoptilolite in terms of mineral phase. The presence of quartz in both ESC and EHC samples may be the cause of the lower CEC.

The CEC values of EHC and PC samples used in this study were compared and observed to be higher than that reported by Schoeman (1986). According to Schoeman, the total CEC value of South African (Pratley) was found to be 1.21 meq/g which was again lower than the theoretical value calculated from the idealized chemical formula of clinoptilolite (2.16 meq/g) (Table 16). This may be due to the fact that the CEC of natural zeolites (clinoptilolite) vary from mines to mines depending on their origin, chemical and mineral compositions. The total CEC of the soft sample (1.23 meq/g) was similar compared to that obtained by Schoeman (1.16 meq/g). The higher values obtained from ESC, EHC and PC samples can be attributed to the smaller particle size used in the current study (90 – 125 µm) compared to 500 – 1000 µm used in the work done by Schoeman, the clinoptilolites samples mined at different areas but in the same deposit (Pratley). In CEC experiments, the particle size of the exchanger (in this case; clinoptilolite) plays a vital role; the smaller the particle size the faster the exchange of cations (Na^+, K^+, Ca^{2+} and Mg^{2+}), the higher the CEC. This is due to the fact that cations in the smaller zeolites (clinoptilolites) are much easier to diffuse and be exchanged into the aqueous solution containing an homo ionic cations (Tang *et al*., 2006).

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The bigger particles affect the diffusional constraints of the cations during the ion exchange process. According to Tang *et al*., (2006) an increase in NH_4^+ sorption capacity was found with decrease in particle size of three types of zeolites; with values increasing from 68.2 to 72.0 meq/100 g NH_4^+, from 53.2 to 73.2 meq/100 g NH_4^+ and from 43.6 to 56.2 meq/100 g NH_4^+ for the particle size ranges of 8 to 15 and 1.0 to 3.32 mm respectively was observed. (see section 2.7.1.3 for more details).

The CEC results obtained from all three clinoptilolite samples showed a good relationship (correlation) to those obtained by XRF method in terms of the total content of cation oxides (Na_2O, K_2O, CaO and MgO). According to XRF analysis, ESC, EHC and PC samples contained lower cation oxides content compared to that of PC (Table 14). These results indicated that PC may have high cation exchange capacity compared to that of ESC and EHC samples which was confirmed by XRF. The results obtained from XRF, CEC and XRD all showed that PC is a good quality clinoptilolite sample in terms of clinoptilolite mineral phase purity and ion exchange capacity. The results obtained in CEC experiment are not compared well with those obtained from XRF (cations oxides). The CEC values represent the amount of cations removed or exchanged from the total given by the XRF, this will be compared in Table 17 presented below. Cation exchange ability of a certain exchanger also depends on its surface area and pore size distribution. Pore size distribution and surface area determination of ESC, EHC and PC samples will be discussed in the following section (section 4.2.7).

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In order to determine the percentage removal (exchange) of each cation (Na^+, K^+, Ca^{2+} and Mg^{2+}) after ion cation exchange capacity study of ESC, EHC and PC samples, XRF (Table 14) and CEC (Table 16) results of cations were used to calculate percentage of each cation from its total percentage content obtained using XRF. The calculated percentage values are presented in Table 17. The percentage content of each cation oxide (Na_2O, K_2O, CaO and MgO) obtained by XRF (Table 14) was first converted into elemental (Na^+, K^+, Ca^{2+} and Mg^{2+})

concentration (mg/g) from which the concentration of cations obtained by CEC (Table 16) were subtracted to get the percentage removal of each element.

Table 17: The percentage exchange of cations by ammonium acetate during cation exchange capacity (CEC) study of ESC, EHC and PC samples

Analyte	Description	**ESC**	**EHC**	**PC**
Na^+	Na_2O (%), obtained from XRF	2.319	2.581	2.502
	Na (mg/g), calculated from XRF	17.204	19.147	18.561
	Na (mg/g), obtained from CEC	0.0427	0.0583	0.0886
	% removed by CEC method	**0.24**	**0.30**	**0.48**
K^+	K_2O (%), obtained from XRF	1.828	2.461	3.467
	K (mg/g), calculated from XRF	15.175	20.430	28.781
	K (mg/g), obtained from CEC	0.0270	0.0725	0.0829
	% removed by CEC method	**0.18**	**0.35**	**0.28**
Ca^{2+}	CaO (%), obtained from XRF	1.040	0.873	0.839
	Ca (mg/g), calculated from XRF	7.433	6.239	5.996
	Ca (mg/g) , obtained from CEC	0	0	0.0181
	% removed by CEC method	**0**	**0**	**0.30**
Mg^{2+}	MgO (%), obtained from XRF	1.563	0.585	0710
	Mg (mg/g), calculated from XRF	9.428	3.529	4.283
	Mg (mg/g), obtained from CEC	0.0128	0.00347	0.0048
	% removed by CEC method	**0.14**	**0.098**	**0.11**
Total	% removal of all cations from 0.25 g/each clinoptilolite sample	**0.56**	**0.75**	**1.17**

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Table 17 shows that ammonia acetate solution (pH of 8.2 at 25 °C) used in CEC experiment to exchange cations with NH_4^+ could only exchange 0.26, 0.31 and 0.50 % of Na^+ calculated from its total content obtained from XRF. The ESC, EHC and PC samples contained 7.20 mg/g, 19.15 mg/g and 18.56 mg/g of Na^+ respectively. The percentage removal of K^+, Ca^{2+} and Mg^{2+} by CEC method were also observed to be very low (>0.38 %) from their total content measured by XRF (see Table 17). The removal of Ca^{2+} (0.32 %) only happened from PC sample calculated from its total content from XRF (5.996 mg/g of Ca^{2+}). Calcium ion concentration was measured below the detection limit from ESC and EHC, this means that Ca^{2+} content in these samples was strongly bound to the clinoptilolite framework or part of other mineral phases.

The same trend was observed in the case of the acid-pretreatment results discussed previously in section 4.1.3. The overall exchange percentage of Na^+ (0.17 %) was again seen to be the highest compared to other cations meaning that Na^+ is the most weakly bound cation in the clinoptilolite framework (Table 13). This was again confirms the acid-pretreatment results using both HCl concentrations (0.02 and 1.0 M) where the percentage removal of Na^+ was higher than that of other cations (Figure 15 to 17). The results obtained by EDS analysis (Figure 18 to 20) also showed the same Na^+ trend, where Na^+ was observed to be completely extracted from all three samples (ESC,EHC and PC). It was therefore observed that the standard cation exchange capacity test can remove a very small percentage of the present cations from clinoptilolite samples using the ammonium acetate method thus should be optimized for microporous materials. This can be explained by the total percentage exchange of the cations by NH_4^+ from ESC, EHC and PC samples giving 0.68, 0.78 and 1.24 % respectively using ammonium acetate. The acid-pretreatment method which involves equilibrium times and sequential extracts of cations is the recommended method of examination of the cation exchange capacity of clinoptilolite since it can completely remove some of the cations from the framework. This was previously shown in section 4.1 where acid washing could almost remove all the 4 cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) from clinoptilolite samples after a certain extraction number depending on the acid concentration.

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4.2.7 Surface area and pore size distribution analyses

N_2-BET (Brunauer - Emmett – Teller) analyses were carried out in order to determine pore size distribution and surface area of the untreated and pretreated ESC, EHC and PC samples. The obtained results of N_2-BET are presented in Table 18, Figure 34, 35 and 36 respectively.

Table 18: The BET surface area of the untreated and treated ESC, EHC and PC samples

Sample	Surface area of untreated (cm^3/g)	Surface area of pretreated (cm^3/g)
ESC	23.95	30.84
EHC	12.39	15.70
PC	17.84	27.75

The surface area of ESC, EHC and PC samples was found to have slightly increased after the acid-pretreatment process from 23.95 to 30.84 cm^3/g for ESC, from 12.39 to 15.70 cm^3/g for EHC and from 17. 84 to 27.75 cm^3/g for PC sample. The improvement of the surface area of these natural adsorbents may be due to the acid-pretreatment that involved the sequential extractions of cations from the framework creating more spaces on the surface area of the treated clinoptilolites. The-acid pretreated PC sample was found to improve its surface area more than other samples (from 17. 84 to 27.75 cm^3/g) followed by ESC sample (23.95 to 30.84 cm^3/g). The EHC was observed to have a lower surface are compared to others samples. All the clinoptilolites samples were found to have a small surface area which is normal for natural zeolites compared to the large surface area material such organic adsorbents (polymeric resins).

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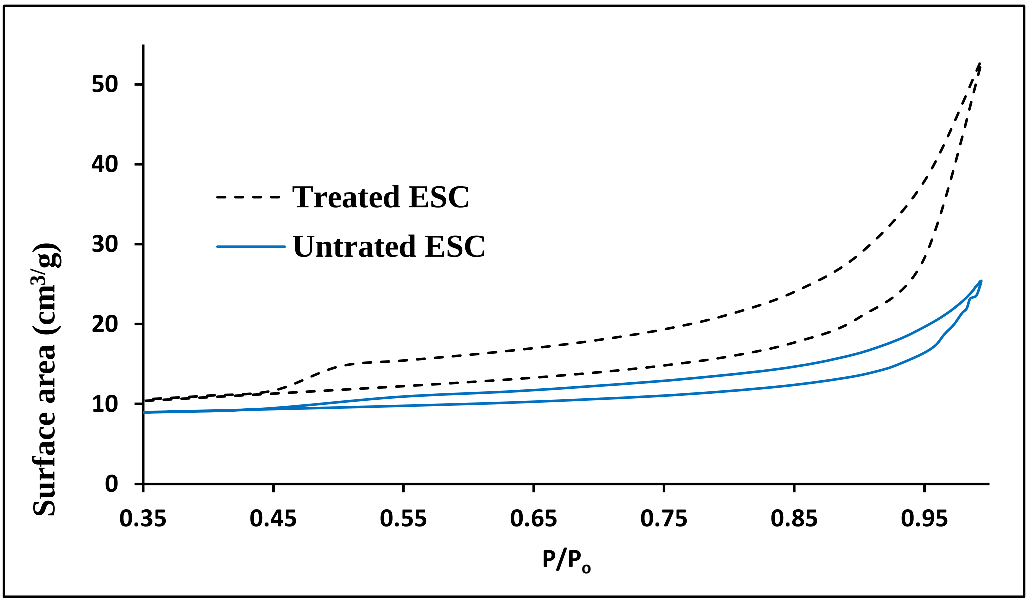

Figure 33: N_2 adsorption and desorption of the untreated and the pretreated ESC

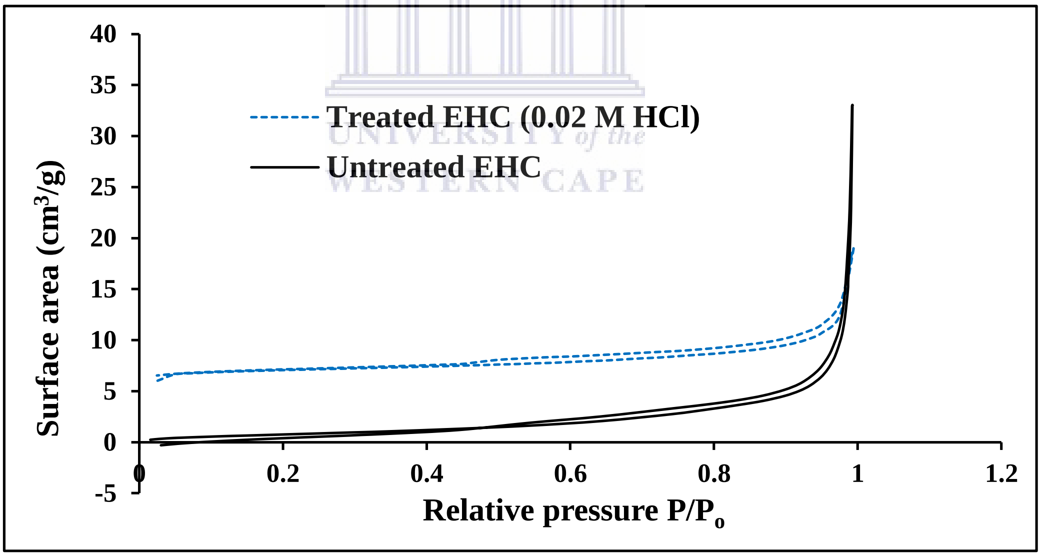

Figure 34: N_2 adsorption and desorption of the untreated and the pretreated EHC

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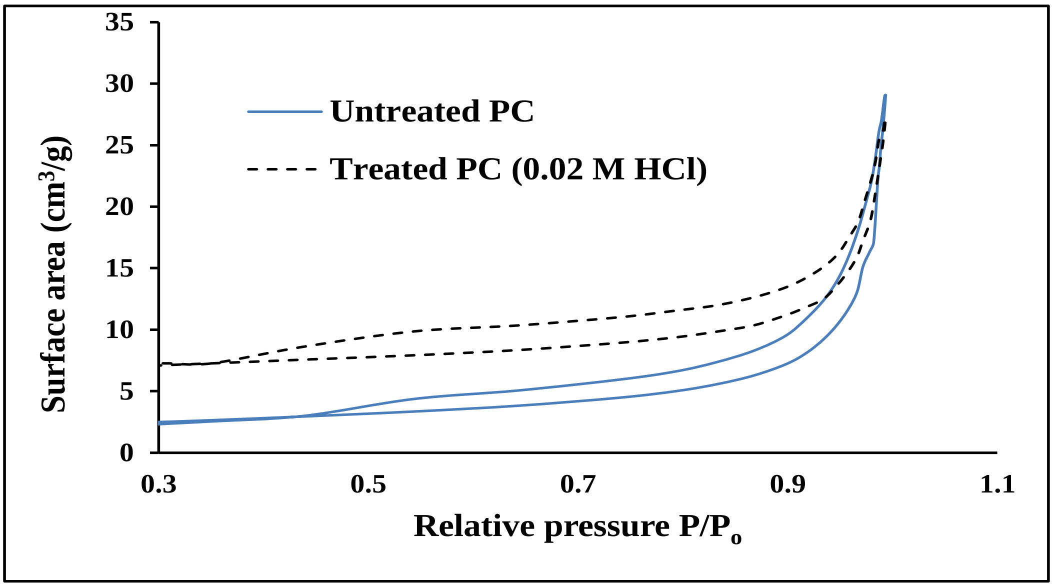

Figure 35: N_2 adsorption and desorption of the untreated and the pretreated PC

The above isotherms were used to calculate the surface area and to classify the adsorption isotherms of the of the untreated and acid-pretreated (0.02 M HCl) using BET method (Figure 33, 34 and 35). The BET adsorption isotherms of the untreated and pretreated clinoptilolite samples were classified based on the classification originally proposed by Brunauer - Emmett - Teller (see section 2.8.4). Based on the BET classification, all three clinoptilolite samples were observed to be type I isotherm. Type I is isotherm is the characteristic of microporous material such as zeolites. The typical type I isotherm always show high adsorption capacity and very fast reaction saturation, followed by consistent adsorption over a wide range of *P/P$_o$* (Gregg and Sing, 1982 and Lowell *et al.*, 2006). The BET isotherm results indicate that ESC, EHC and PC are all microporous material because their inflection points of their hysteresis start after the relative pressure of 0.4 (Figure 33, 34 and 35). Figure 33, 34 and 35 showed a clear difference between adsorption isotherm loop of both untreated and the pretreated samples. The hysteresis loop of the acid-pretreated samples was found to change their shape (wide) compared to those of the untreated samples. These changes are due to the new space created by the acid-pretreatment which extracted the cations and other impurities in the clinoptilolite samples therefore more N_2 gas was adsorbed compared to that of the untreated samples.

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The BET results of pore size distribution of the untreated ESC and EHC samples are presented in Figure 36 whereas the BET pore size distribution results of PC sample is presented in separate Figure (Figure 37) due to its large incremental surface area.

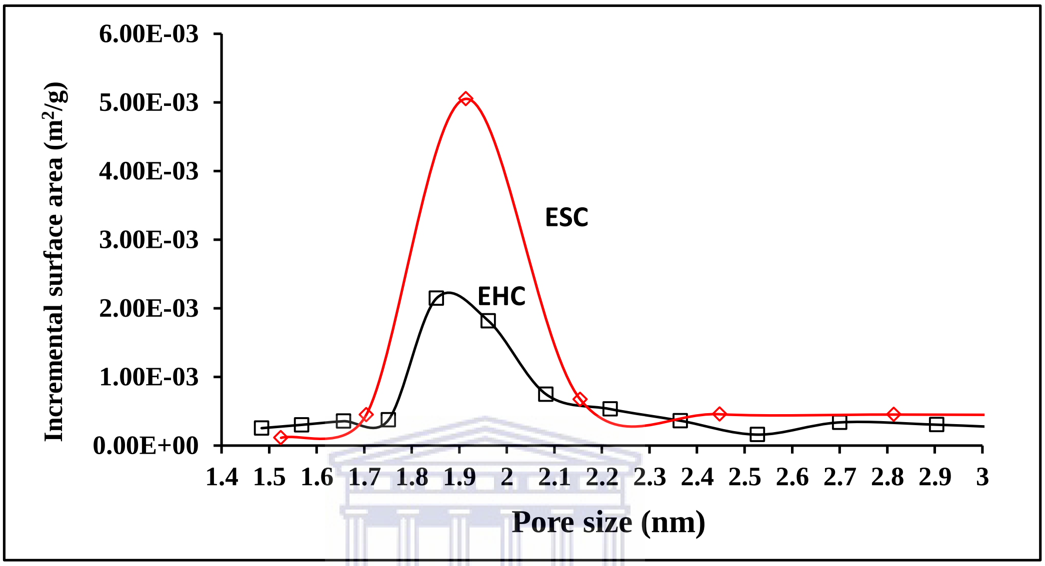

Figure 36: Pore size distribution of the untreated ESC and EHC samples

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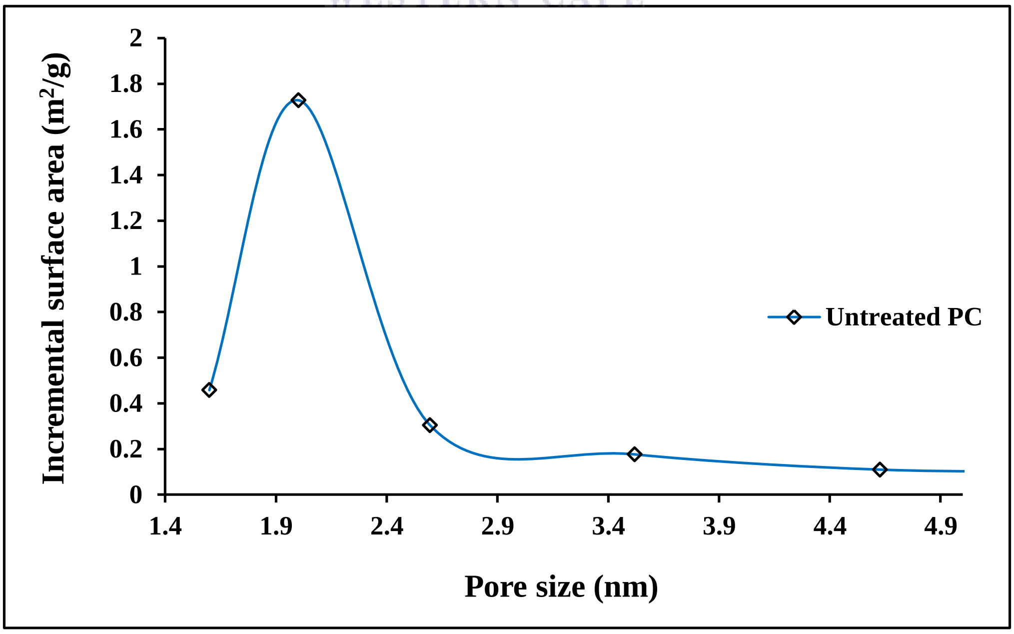

Figure 37: Pore size distribution of the untreated PC

The BET pore size distribution of the untreated ESC, EHC and PC samples was determined using BJH (Barret – Joier – Halenda) method. Figure 36 presents the pore size distribution of the untreated ESC and EHC whereas Figure 37 present the untreated PC sample. It was observed that in both Figure 36 and 37 all the clinoptilolite samples are microporous materials because of their inflection point of their pore size distribution is less than 2 nm which is about 1.9 nm in this case. The BET analysis showed that the untreated PC sample has a higher (1.98 nm) pore size distribution than that of ESC (1.91 nm) and EHC (1.85 nm). The typical pore distribution is specifically for natural zeolites (Gregg and Sing, 1982). Pore sizes of zeolites can vary from 0.2 to 0.8 nm (Pramatha and Dutta *et al*., 2003). It was observed that the untreated PC sample is more porous than ESC and EHC samples (Figure 37). The untreated EHC was again found to have a narrower pore size distribution and to have a lower incremental surface area as if it was seen in in Table 18 and Figure 34. The following section (section 4.3) presents the summary of the work covered in chapter 4.

4.3 CHAPTER SUMMARY

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This chapter dealt with two different experimental sections including acid pretreatment and characterization of the untreated and pretreated ESC, EHC and PC samples. The preliminary acid-pretreatment time optimisation experiments were carried out on the PC sample and the optimum time was found to be 4 h per each extraction fraction. The acid-pretreatment optimization was carried out on PC sample using different acid concentrations in order to determine the optimum concentration of the acid on the clinoptilolite framework structure. The optimum acid concentration was found to be 0.02 M HCl since it did not cause much dealumination of the clinoptilolite framework structure. It was again observed that using acid-pretreatment with highly acid strength reduced the pretreatment time, but caused a significant dealumination of the zeolite. The extent of dealumination was determined with the FTIR technique which showed the increase of dealumination with an increase in the acid strength used for acid-pretreatment.

The same trend of dealumination was reported by Mamba *et al*., (2009) and Cakicioglu-Ozkan, *et al.*, (2005) who observed dealumination during their acid-pretreatment of clinoptilolite (HCl). However this study has improved on the work previously conducted on the acid-pretreatment of clinoptilolite that it is not only the acid concentration that is important but also the number of extractions needed to remove all the possible cations from the clinoptilolite framework. In this study, 22 acid extractions were needed to remove Na$^+$, K$^+$ and Mg^{2+} from 10 g of PC clinoptilolite and 7 extractions used treat ESC and EHC whereas the previous work only considered the acid concentrations to pretreat natural clinoptilolite.

Different characterization techniques were used to analyse the untreated and the pretreated clinoptilolite samples. The analyses done using SEM showed few differences in the morphology of all clinoptilolite samples before or after the pretreatment process. The EDS analyses quantitatively showed that some exchangeable cations were completely removed out of the clinoptilolite framework after the acid-pretreatment process using 0.02 M HCl with 22 extractions. Sodium ion was determined to be the most weakly bound cation in all three clinoptilolite samples because it was completely removed or exchanged from ESC and EHC after 7 extractions and PC samples whereas in the use of the extraction of other cations (K$^+$, Ca^{2+} and Mg^{2+}) was not possible in all cases. The Mg^{2+} and Ca^{2+} ions were also observed to be completely removed out of EHC and PC during acid-pretreatment but not in the case of ESC. The EDS and acid-pretreatment results showed that the K$^+$ ion was observed to be the most strongly bound cation in all the clinoptilolite samples (ESC,EHC and PC) since it could not be completely exchanged or extracted out of the clinoptilolite frameworks. The crystallinity and crystal structure analyses of ESC, EHC and PC samples were carried out using HTEM-SAED and the entire sample were found to be polycrystalline. The mineral identification and quantification of ESC, EHC and PC samples were carried out using qualitative and quantitative XRD respectively and showed that the content of clinoptilolite phase in ESC, EHC and PC samples was 44.00, 67.88 and 81.41 % respectively. These results showed that PC was the purer clinoptilolite sample (81.41 %) compared to ESC and EHC samples.

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Quartz mineral phase was found in ESC (26.85 % quartz) and EHC (21.0 % quartz) samples but not in PC sample. Other mineral phases were muscovite which was found to be 18.63 % in the ESC and 7.68 % in the EHC sample, and the plagioclase phase content was 10.52 % and 3.43 % in both samples respectively. The elemental composition analyses of clinoptilolite samples were carried out using XRF and the obtained results were compared to those of cation exchange capacity. Cation exchange capacity of ESC, EHC and PC samples were 1.23, 1.81 and 2.90 meq/g respectively. It was again observed from this study that the pretreatment of natural adsorbents is not uniform; it varies from mines to mines. It was observed that the deposits of clinoptilolite even from same mine varied (mineral phases composition) considerably. Some sources of clinoptilolite are more pure than phases than others. The standard procedure to determine the exchangeable cations exchange capacity is not a good measure of donnan exclusion effect. The acid-pretreatment using numerous extractions were necessary to remove exchangeable cations from the framework. The BET results showed that ESC, EHC and PC clinoptilolite samples are microporous materials of Type I with a low surface area of 23.95, 12.39 and 17.84 cm^3/g respectively. The acid-pretreatment process of ESC, EHC and PC samples was found to increase the surface area of these clinoptilolite samples from 23.95 to 30.84 cm^3/g for ESC, from 12,39 to 15.70 cm^3/g and from 17.84 to 27.75 cm^3/g. The BET analysis showed that PC sample has a higher (1.98 nm) pore size distribution than that of ESC (1.91 nm) and EHC (1.85 nm). The small pore of these material may have contributed to the diffusional constraints occurred during the removal of cations from clinoptilolite framework.

The following chapter (chapter 5) will present the batch adsorption study of ammonium and chromium ions on South African untreated and pretreated ESC, EHC and PC samples. The adsorption equilibrium of ammonia will be presented and their isotherm will be investigated.

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CHAPTER 5

APPLICATION OF NATURAL SOUTH AFRICAN CLINOPTILOLITE IN ADSORPTION STUDIES

This chapter is divided into two sections. The first section (section 5.1) presents and discusses the adsorption studies results of ammonia on the untreated and acid-pretreated clinoptilolite samples (ESC, EHC and PC). The second section (section 5.2) presents and discusses the results of the adsorption studies of chromium ion on only acid-pretreated PC. In both sections, the adsorption parameters were investigated in order to determine their optimum values for the adsorption of both ammonia and chromium. The results obtained from batch adsorption studies of ammonia are presented in section 5.1 below.

5.1.1 Effect of reaction contact time for ammonia on PC sample

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To determine the effect of contact time for the sorption of NH_4^+ on clinoptilolite, 50 mL solution of 50 mg/L NH_4^+ (prepared concentration not experimental) was mixed with a fixed amount of 0.5 g of PC (acid pretreated using 22 extractions). In order to determine the initial NH_4^+ concentration used in the contact time experiment, the line equation was used and the results are presented in section 5.1.2 below.

5.1 BATCH ADSORPTION EXPERIMENTS OF NH_4^+

Ammonia was adsorbed as ammonium ion (NH_4^+) from a synthetic ammonium chloride solution. In this study (ammonia adsorption), only certain adsorption parameters were considered during the batch adsorption experiments including contact time, effect of adsorbent pretreatment, amount of adsorbents and initial NH_4^+ concentration. The variation of these parameters made it possible to determine the optimum value of each adsorption parameter for the adsorption of ammonia. The contact reaction time experiments results are presented and discussed in section 5.1.1 below.

5.1.2 Determination of the actual initial concentration of NH_4^+ in the standard solutions using line equation method

The initial concentration of NH_4^+ in the standard solution was determined using the standard calibration curve (Figure 38). Table 19 presents the calculated actual experimental initial concentration of NH_4^+ in the standard solution used to determine the initial concentration. The initial concentration was determined from the measured absorbance obtained from UV/Vis analysis (see Table 19).

Table 19: Absorbance versus ammonium ion concentration

Concentration of NH_4^+ mg/L	Absorbance At 380 nm
2.0	0.1887
4.0	0.2671
6.0	0.4982
8.0	0.6098
10.0	0.7737
12.0	0.8856

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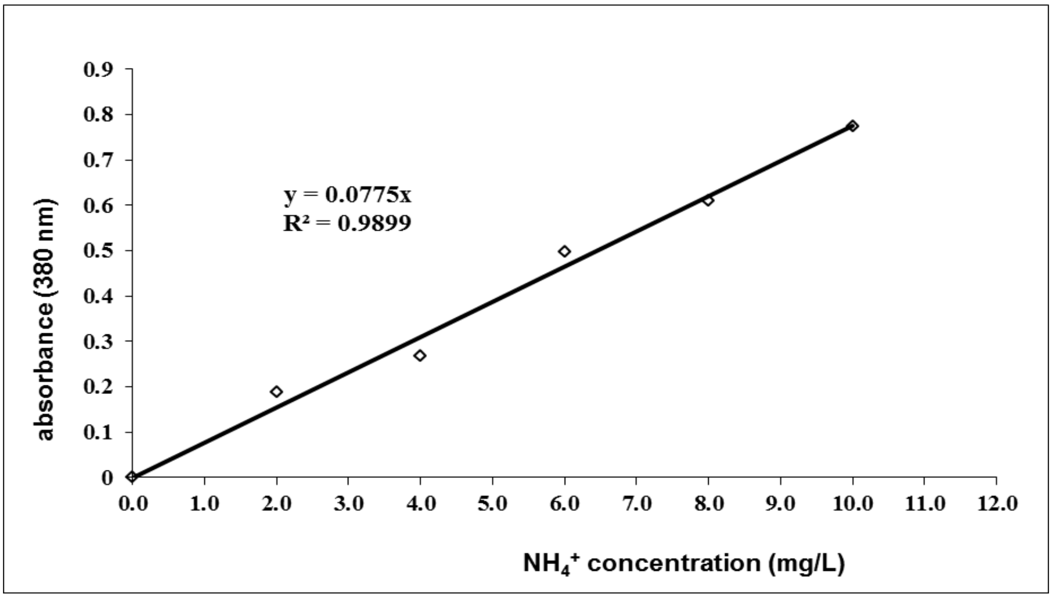

Figure 38: Calibration curve of NH_4^+ used in contact time experiment. Absorbance of NH_4^+ standard solution was measured at 25 °C at 380 nm

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Table 19 and Figure 38 present the obtained adsorption results. In order to calculate the experimental initial concentration of NH_4^+ in the standard ammonium chloride solution, the line equation was used.

$$y = mx + c \qquad 5.1$$

Therefore, $x = 0.775 / 3.861 + 0$

Giving; x = **49.815 mg/L** NH_4^+ (this is the **experimental initial concentration**)

Where y is the measured absorbance (in this case; y = 3.861 of the standard solution of 50 mg/L), m is the slope and x is the remaining concentration measured after adsorption in mg/g and c = 0 in this case. In equilibrium study x represents C_e. The measured absorbance of the blank (control) sample was used to calculate the unknown sample concentration. The blank sample is the sample that contains the highest concentration of the adsorbate that is ran at the same adsorption experimental conditions as other samples but without the adsorbents and shaken for the same time as for the sample with the longest shaking time. In this experiment, the concentration used for the blank sample was 50 mg/L NH_4^+

(prepared concentration) which was the same as the concentration of the NH_4^+ adsorption samples.

The standard calibration curve was observed to be a straight line (Figure 38). The line equation was found to be y = 0.0775 x, and this was used to calculate the actual initial concentration of NH_4^+ in the standard solution where m was obtained to be 0.0775. The initial concentration (x) was calculated to be 49.815 mg/L NH_4^+ being slightly lower than the prepared concentration (50 mg/L). Therefore, the experimental initial concentration on NH_4^+ is 49.815 not 50.0 mg/L. The error may be due to the fact that ammonia is a volatile compound or that the measurement error during solution preparation resulted in fluctuation on absorbance during UV/Vis analysis which causes the m (slope) to be either low or high (Figure 38).

5.1.3 Effect of time on the adsorption of ammonium ion in aqueous solution on PC2 samples

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Adsorption parameters applied in this experiment were 50 mL of about 50 mg/L NH_4^+ at pH of 6.8 and 25 °C treated with 0.5 g of pretreated PC sample over a contact time ranging from 0 to 60 min. The results obtained from the adsorption equilibrium and removals of ammonium ion from aqueous solution are shown in Table 20, Figure 39 and 40.

Table 20: Equilibrium data obtained for adsorption of ammonium ion on the pretreated PC2 sample (a sample calculation for 2 min)

Time **min**	**prepared initial Conc.** **mg/L**	**experimental blank Conc.** **mg/L**	**experimental conc. of stock soln.** **mg/L**	**weight of clino** **g**	**y**	**C_e x=y/0.0775** **x** **(mg/L)**	**adsorbed NH_4^+ by Clino** **mg/L**	**adsorbed NH_4^+ from 50 mL solution** **mg**	**adsorbed NH_4^+ from the solution by clino** **mg NH_4^+/g**	**% removal**
2	50	49.8151	49.8151	0.5007	0.697	8.9935	40.8215	2.0411	4.0764	97.38
2	50	49.8151	49.8151	0.5002	0.6398	8.2555	41.5596	2.0780	4.1543	97.53
2	50	49.8151	49.8151	0.5003	0.6604	8.5213	41.2938	2.0647	4.1270	97.18

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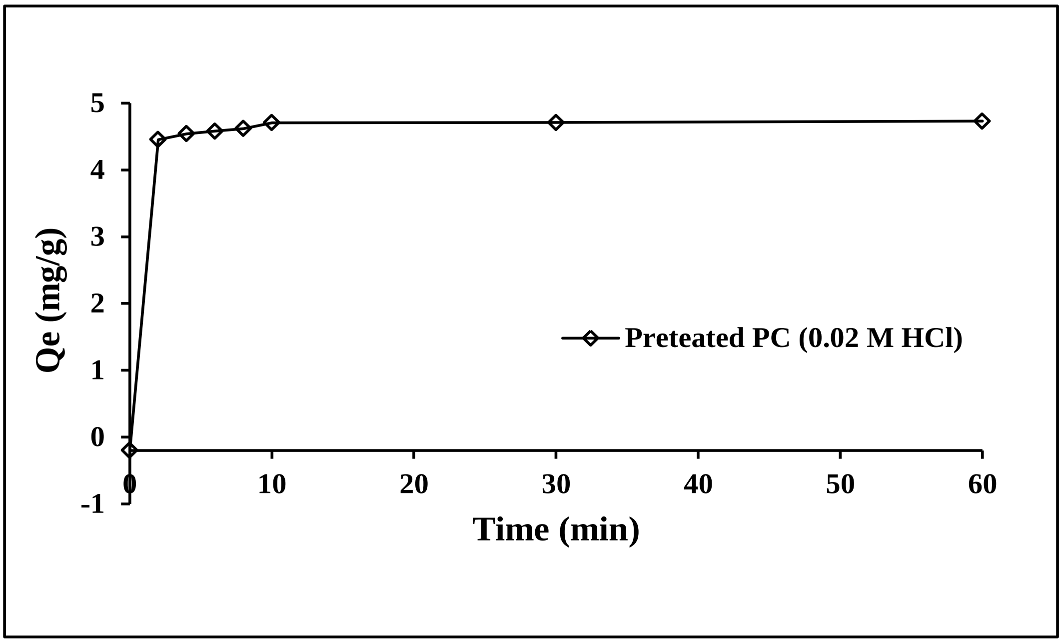

Figure 39: The adsorption equilibrium amount (Q_e) of 50 mL of 49.815 mg/L NH_4^+ on the HCl-pretreated (0.5 g of PC2), conducted at the natural pH of 6.8 at 25 °C for different contact times.

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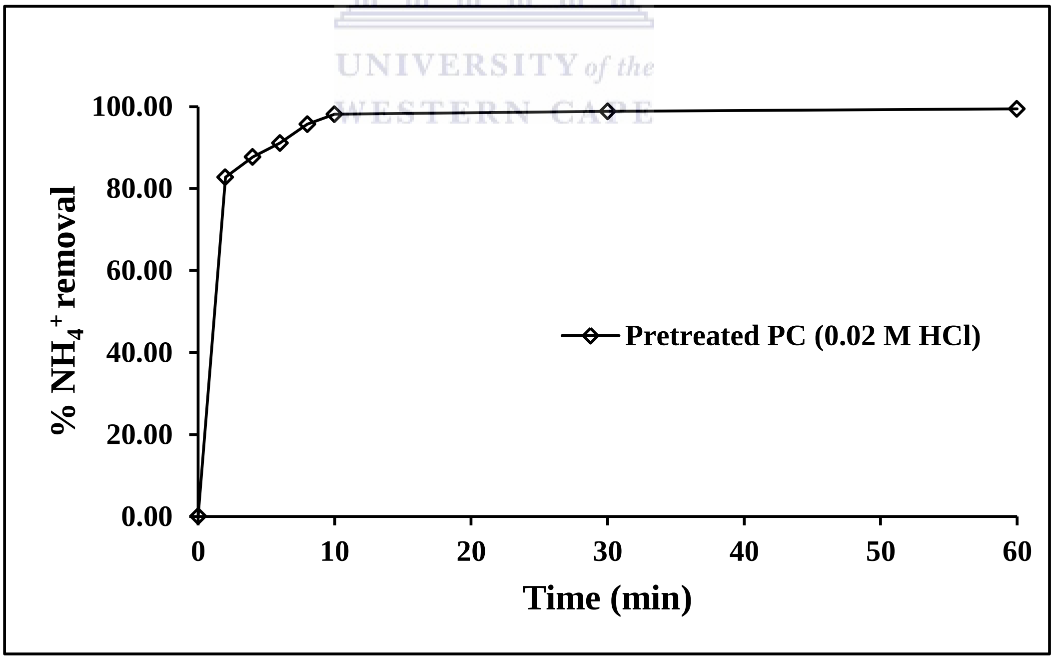

Figure 40: The percentage removal of 50 mL of 49.815 mg/L NH_4^+ with the HCl-pretreated PC (0.5 g PC2), conducted at the natural pH of 6.8 at 25 °C for different contact times

Figure 39 and 40 present the equilibrium amount of NH_4^+ and the percentage removal of NH_4^+ as a function of time respectively. Considering Figure 39, the adsorption equilibrium point was achieved at 10 min with 0.5 g of PC sample (with 98.1 % NH_4^+ removal) after which the removal of NH_4^+ remained almost unchanged. There was no significant difference in the equilibrium amount of NH_4^+ at 30 and 60 min compared to that of 10 min showing that it was unnecessary to run the adsorption experiment for more than 10 min. The same trend (10 min) was observed in Figure 40, where the equilibrium maximum percentage removal of NH_4^+ was achieved after 10 min (98.1 %). These results indicate that the adsorbent (PC) and adsorbate (98.1 %) had reached their adsorption equilibrium point and they indicate that clinoptilolite has high adsorption capacity towards NH_4^+ since about 98.2 % NH_4^+ removal can be achieved within a short contact time of 10 min. The results indicate that natural zeolites such as clinoptilolite have a high ion exchange capacity for the removal of ammonia from aqueous solution. Muzenda *et al.,* (2011) reported a low removal of NH_4^+ (26 % of 0.01 ppm NH_4^+ at pH 7) using South African clinoptilolite from Vulture Creek from Kwazulu-Natal. They used different acid-pretreatment method by only considering the acid concentration not the number of extractions needed to remove all the cations from the framework. The results of NH_4^+ removal was compared with the clinoptilolite selectivity series for the removal of NH_4^+ compared to some other cations. Different researchers such as Semmens and Martins (1988) and Rahmani *et al*., (2004) reported the selectivity series as follows Pb>K>Ba>NH_4>Ca>Cd>Cu>Na and $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$ respectively. The effect of adsorbent pretreatment was determined on the PC sample and the obtained equilibrium results are presented in section 5.1.3 below

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5.1.3 Effect of adsorbent pretreatment

To determine the effect of adsorbent pretreatment and evaluate whether pretreatment enhanced the adsorption capacity of the PC1 sample, batch adsorption experiments were carried out using both untreated PC1 and pretreated PC samples.

In this case, the batch experiments were carried out using 0.5 g of untreated PC1 and pretreated PC2 sample as a function of time in order to compare their adsorption capacity for NH_4^+ (see experimental procedure in section 3.2.4). The equilibrium results of untreated PC1 were then compared to those obtained in the adsorption of NH_4^+ using the pretreated PC2 sample. The results obtained after the adsorption experiment at equilibrium for untreated PC1 and pretreated PC samples are presented in Figure 20 (for the pretreated PC2) and Figure 42 (for the untreated PC1).

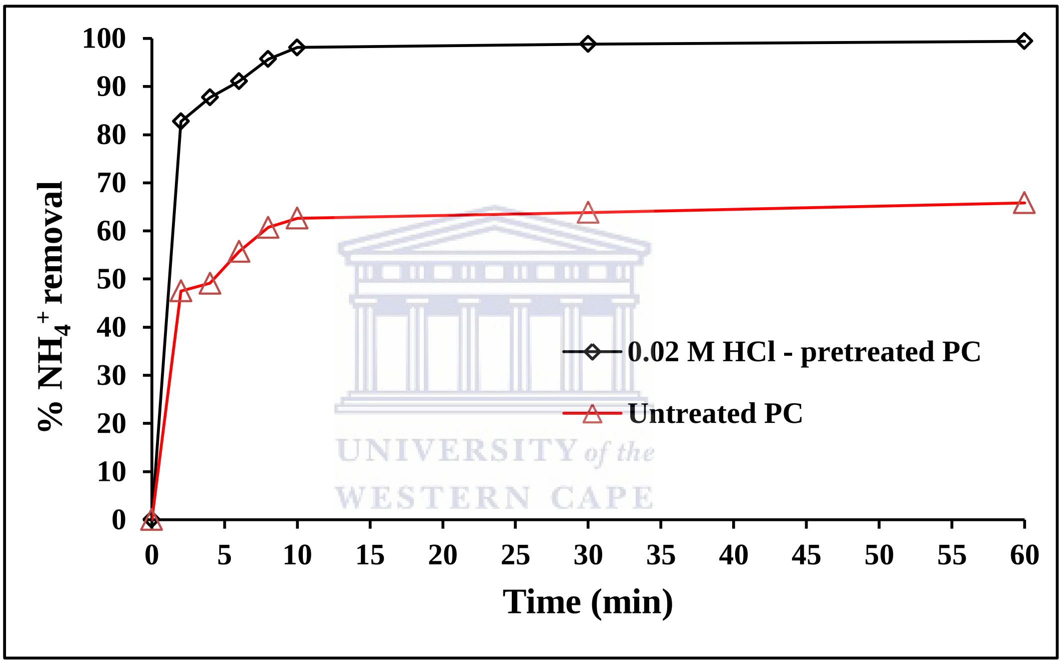

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Figure 41: The percentage removal of 50 mL of 49.984 mg/L NH_4^+ on 0.5 g of untreated PC1 and pretreated PC2 (treated using 22 extractions) conducted at the natural pH of 6.8 at 25 °C for different contact times

The percentage removal and the equilibrium adsorption amount of NH_4^+ on the untreated and pretreated samples results are compared in Figure 41. The equilibrium adsorption amount of NH_4^+ was reached after 10 min (93.09 %) in the case of the pretreated PC2 sample contact time and the percentage removal of NH_4^+ was almost constant thereafter whereas in the case of the untreated PC1 the removal after 10 min was only 62.30 % (Figure 41).

There was no significant difference in the percentage removal of NH_4^+ after 10 min for both samples. The optimum contact time of NH_4^+ with untreated PC1 was therefore determined to be 10 min. Figure 41 shows that the percentage removal of NH_4^+ on the untreated PC2 sample (62.30 %) at 10 min which was about 36 % lower than that of HCl-pretreated PC2 sample (98.11 % at 10 min. These results indicate that the acid-pretreatment with 0.02 M HCl using 22 extractions improved the PC1 adsorption capacity. The results obtained are comparable to those obtained by Muzenda *et al*., (2011) on the pretreated clinoptilolite sample using 0.02 M HCl for 8 h (one extraction). Muzenda *et al*., (2011) also used South African clinoptilolite from Vulture Creek deposits to treat synthetic wastewater supplied from Kwazulu-Natal. According to them, the sorption capacity of the HCl-pretreatment of natural clinoptilolite (0.02 M HCl) improved the sorption capacity of ammonia but pretreatment was performed in different ways (different experimental conditions).

5.1.4 Effect of adsorbent dosage for the removal of ammonium ion from aqueous solution

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In the previous adsorption experiments (section 5.1.3), the optimum contact time to reach the equilibrium point was 10 min to treat 49.0564 mg/L (50 mL volume) of using 0.5 g of acid-pretreated PC2 (Figure 39 and 40). It is therefore necessary to investigate and optimize the amount of PC required to remove the 50 mg/L NH_4^+ within the optimum contact time of 10 min. The results of the adsorption experiment carried out to determine the removal of NH_4^+ from the synthetic solution as a function of adsorbent dosage (mass) are presented in Figure 42 below

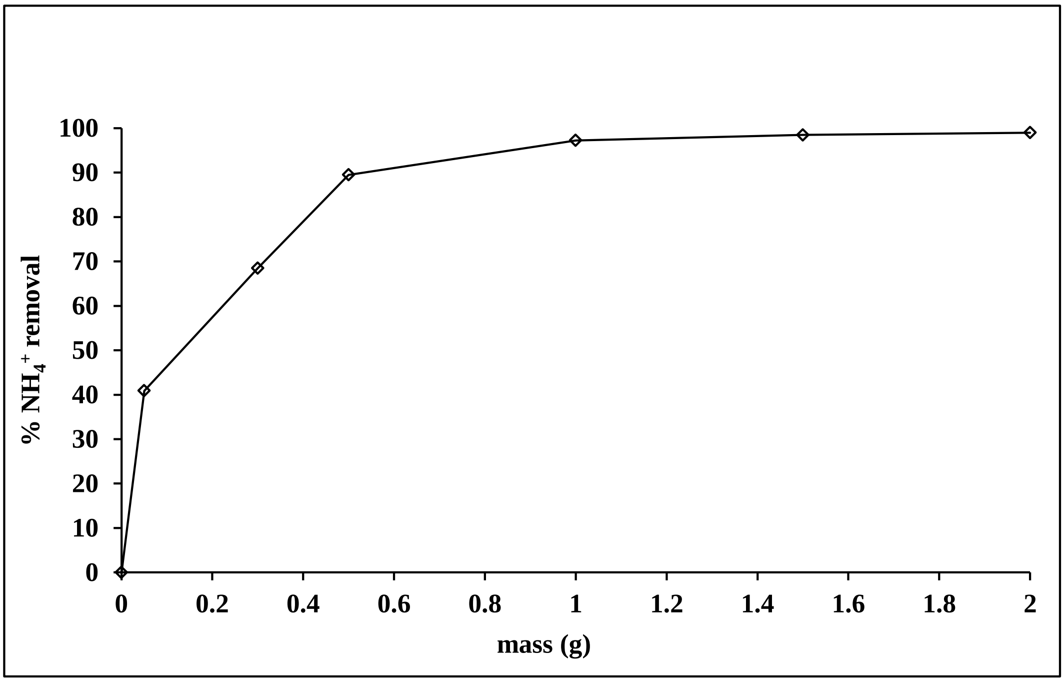

Figure 42: The percentage removal of NH_4^+ at natural pH (6.8) conducted at room temperature (25 °C) on different mass of clinoptilolite for a constant contact time of 10 min and 50 mL of adsorbate (NH_4^+) with concentration of 49.0564 mg/L

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The results in Figure 42 show a low percentage removal of NH_4^+ with the sorbent mass of 0.05 g (40.9 %) and 0.1 g (41.9 %). Ammonia percentage removal increased with an increase in adsorbent mass where 0.3 g of pretreated PC2 sample removed about 68.5 % NH_4^+ and 0.5 g with 89.5 % NH_4^+ removal. The maximum equilibrium removal of NH_4^+ was reached at an adsorbent mass of 0.5 g (89.5 %) after which the percentage removal remained almost constant until the end of the experiment. Considering the amount of sorbent used to reach the maximum removal of ammonia; the dosage of 0.5 g seems to be the optimum dosage since it can remove about 89.5 % (Figure 42).

The dosage of 1.0 g of the pretreated PC sample for the removal of 49.0564 mg/L of NH_4^+ will be just a waste of sorbent since 0.5 g of PC sample can remove 89.5 % NH_4^+ at the same operating conditions. Therefore, 0.5 g of PC2 was found to be the optimum adsorbent dosage for the removal of 50 mg/L NH_4^+ from 50 mL synthetic solution for a reaction contact time of 10 min (25 °C). After the optimization of the contact time and adsorbent dosage for the removal NH_4^+, it was therefore necessary to determine the optimum initial NH_4^+ concentration for full optimization of the adsorption parameters.

5.1.5 The effect of initial NH_4^+ concentration on pretreated PC sample

To determine the effect of the initial concentration of NH_4^+ on its removal by the pretreated PC2, 50 mL of about 10, 20, 30, 40, 50, 60, 100, 150, and 200 mg/L NH_4^+ were each mixed with 0.5 g (optimum adsorbent dosage) of acid-pretreated PC2 (treated with 22 extractions) and then shaken at 250 rpm at room temperature of 25 °C for a constant contact time of 10 min (see the experimental procedure in section 3.2.4.1). The equilibrium adsorption results obtained are presented in Figure 43 and Figure 44 below.

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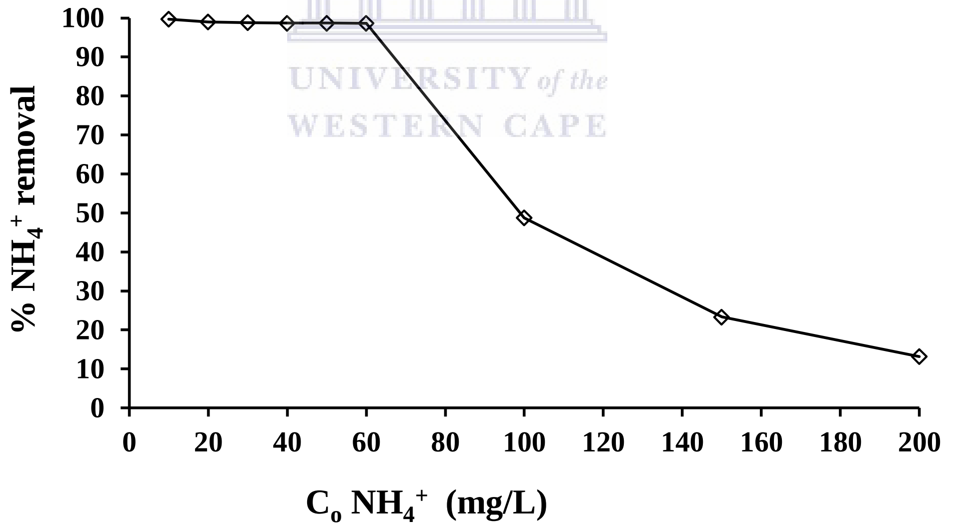

Figure 43: Percentage removal of NH_4^+ with function of initial NH_4^+ concentration on 0.5 g of the acid-pretreated PC2 sample (treated with 22 extractions) at natural pH conducted at 25 °C for 10 min.

In Figure 43, the removal of NH_4^+ was observed to decrease with an increase in NH_4^+ concentration (Figure 43). The removal of NH_4^+ was observed to be high from the low concentration of 10 to 60 mg/L (98.64 %) which means that there was an excess of exchange sites (limited by the amount of sites) with low amount of NH_4^+ present in the solution. These changes in the rate of removal of NH_4^+ might be due to the fact that, initially, more adsorbent sites were vacant and the adsorbate (NH_4^+) concentration was low. Afterwards, the ammonium uptake rate by the PC2 sample decreased significantly due to decrease in exchange sites. The removal of NH_4^+ started decreasing with a concentration of 100 mg/L NH_4^+ (48.75 %) to 200 mg/L NH_4^+ (13.19 %) indicating that there were too low exchange sites available on 0.5 g of PC2 sample for the removal of high amount of NH_4^+ present in the solution.

A decreasing removal rate, particularly towards the high concentration, indicated a possible monolayer of ammonium ions on the outer surface and pores of the zeolite and pore diffusion onto the inner surface of clinoptilolite particles through the film due to continuous agitation maintained during the experiment. The adsorption equilibrium amount of NH_4^+ was observed to be between 50 and 60 mg/L, which was the optimum NH_4^+ concentration for a dosage of 0.5 g of PC2 sample. These results show that all the previous adsorption experiments (using about 50 mg/L NH_4^+ on 0.5 g PC2 sample) were limited by the amount of NH_4^+ present in the solution. Ahmet *et al.*, (2002) observed the same NH_4^+ removal trend on the Turkish clinoptilolite where the NH_4^+ removal decreased with increasing the concentration of NH_4^+ in the solution during batch adsorption experiment. The equilibrium isotherm results obtained from the adsorption experiment as a function of concentration are presented in Figure 44 below.

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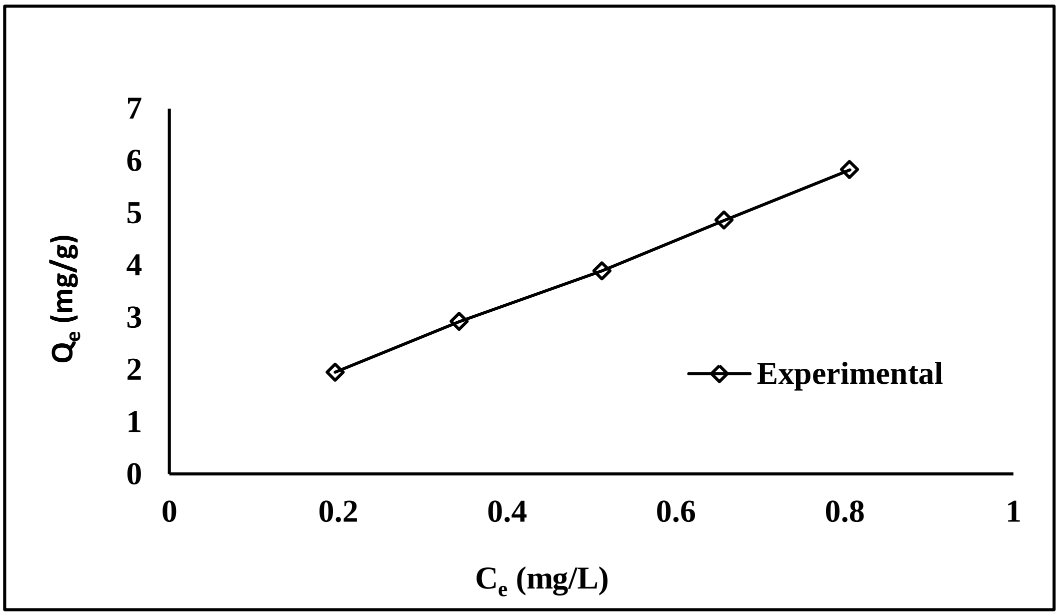

Figure 44: The adsorption experimental isotherm of NH_4^+ on 0.5 g of the pretreated PC2 sample at natural pH (6.8) and at 25 °C

The adsorption equilibrium isotherm of NH_4^+ on the pretreated PC2 sample results (Figure 44) shows that the equilibrium concentration of NH_4^+ is directly proportional to the adsorption capacity from 20 mg/L to 60 mg/L.

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In order to analyse the obtained equilibrium adsorption data for NH_4^+, the modeling of the adsorption isotherms are necessary and the results are discussed in section 5.1.6 below.

5.1.6 Adsorption equilibrium isotherms

The equilibrium data obtained from the adsorption equilibrium experiments of NH_4^+ on the pretreated PC sample was analysed using the linearized Langmuir and Freundlich adsorption isotherms. The linearized Langmuir and Freundlich equations were shown and explained in section 2.7.2.2. The results obtained are presented in Table 21 and Figure 45 and 24. The Langmuir adsorption isotherm was tested using two different linearized equations (equation 5.2 and 5.3) and their R^2 values are compared to evaluate which equation fits the isotherm best. The linearized Langmuir equations are shown below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_o} + \frac{1}{bQ_o} \qquad 5.2$$

$$\frac{1}{Q_e} = \frac{1}{bQ_oC_e} + \frac{1}{Q_o} \qquad 5.3$$

Where Ce is the measure concentration at the at the equilibrium (mg/L)
Qe represents the adsorption equilibrium amount of NH_4^+ (mg/g clinoptilolite)
Qo is the equilibrium Langmuir capacity of PC2 sample for the removal of NH_4^+
b is the Langmuir parameter (constant)

Freundlich model is described by the following formula

$$\left[\ln q_{eq} = \ln K_F + \frac{1}{n}\ln C_{eq} \right] \qquad 5.4$$

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In that equation C_e (mg*L^{-1}) and Q_e (mg/g) are equilibrium liquid and solid dye concentrations, K_F and n are Freundlich constants, n shows the favourability of the adsorption and K_F [(mg*g^{-1})*$(L/mg)^n$] showing the adsorption capacity of the adsorbent. The values of n and K_F are calculated from the slope and intercept of the plots of ln Q_e vs ln C_e . The n value between 1 and 10 means that adsorption is favourable.

Table 21: The equilibrium adsorption data obtained from the linearized Langmuir adsorption isotherms equations

Experimental			**Langmuir I**			**Langmuir II**			
			$\frac{C_e}{Q_e} = \frac{C_e}{Q_o} + \frac{1}{bQ_o}$ **Equation 5.2**			$\frac{1}{Q_e} = \frac{1}{bQ_oC_e} + \frac{1}{Q_o}$ **Equation 5.3**			
			Theoretical			**Theoretical**			
			y = 0.0607x + 0.0943			y = 0.0873x + 0.0761			
C_o (mg/L)	**C_e (mg/L)**	**Q_e**	**C_e/Q_e**	**C_e/Q_e**	**Q_e**	**$1/C_e$**	**$1/Q_e$**	**$1/Q_e$**	**Q_e**
10	0.0284	0.9818	0.0289	0.0600	0.4728	35.2477	1.0186		
20	0.1965	1.9484	0.1009	0.1062	1.8502	5.0878	0.5132	0.5203	1.9221
30	0.3434	2.9184	0.1177	0.1151	2.9823	2.9121	0.3427	0.3303	3.0273
40	0.5126	3.8885	0.1318	0.1254	4.0875	1.9507	0.2572	0.2464	4.0585
50	0.6575	4.8596	0.1353	0.1342	4.8990	1.5209	0.2058	0.2089	4.7875
60	0.8061	5.8264	0.1384	0.1432	5.6282	1.2405	0.1716	0.1844	5.4232
Langmuir isotherms parameters	**R^2**		0.8943			0.9934			
	Q_o		16.4743 NH_4^+ mg/g			13.1406 NH_4^+ mg/g			
	b		0.6437			1.7434			

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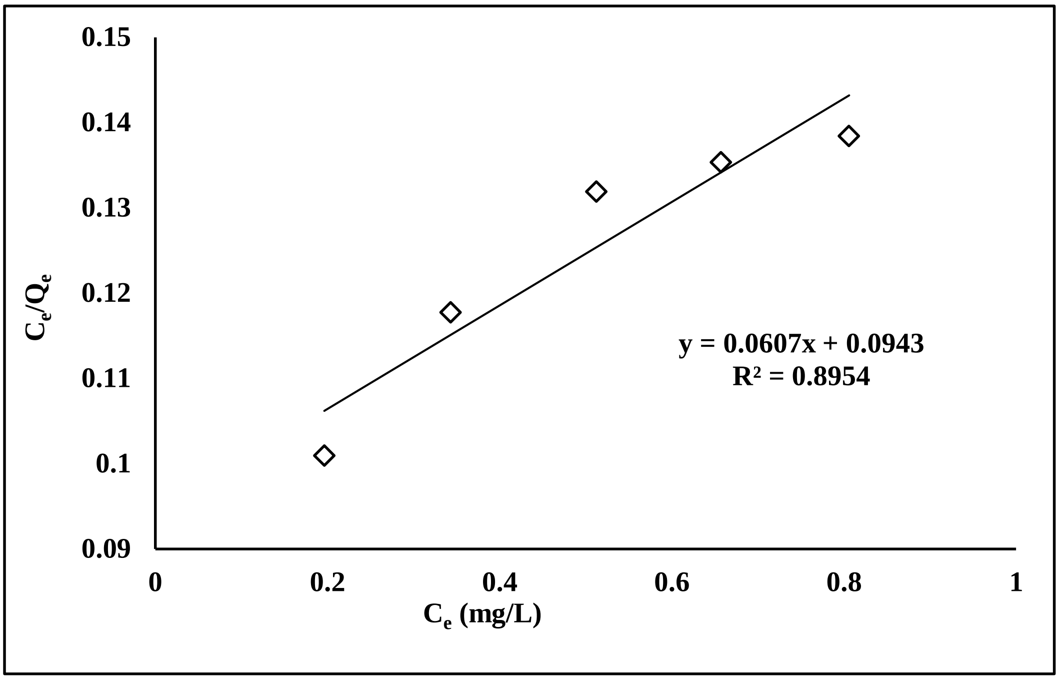

Figure 45: Linearized form of Langmuir (I) model (Equation I, see Table 24) of NH_4^+ on 0.5 g of the pretreated PC2 sample at natural pH and at 25 °C

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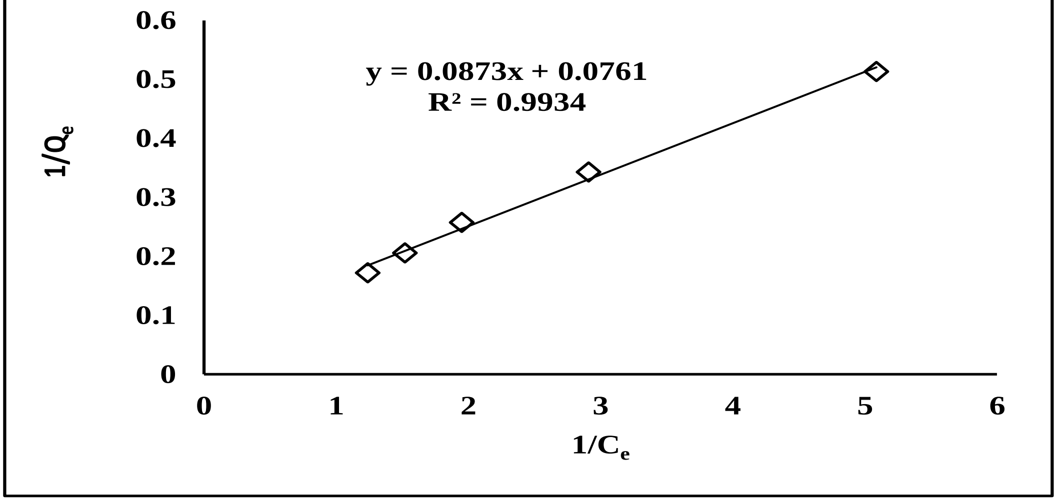

Figure 46: Linearized form of Langmuir (II) model (Equation II, see Table 21) of NH_4^+ on 0.5 g of the pretreated PC2 sample at natural pH and at 25 °C

Both Figure 45 and Figure 46 represent Langmuir adsorption isotherms obtained using two linearized form of Langmuir equations (equation 5.2 and 5.3, see Table 21). The first and second linearized forms of the Langmuir in this case are called Langmuir I and Langmuir II respectively. The correlation coefficient for the linear regression fit of Langmuir I and Langmuir II forms were found to be 0.8943 and 0.9934 for pretreated PC2 sample, respectively. The linear plot of C_e/Q_e versus C_e and the linear plot of $1/Q_e$ versus $1/C_e$ were both found to obey the Langmuir isotherm but with different linear regression (R^2) values; 0.8943 and 0.9934 respectively (Table 21 and Figure 45 and 46). Considering the linear regression (R^2) Langmuir values (Figure 5.8 and Figure 5.9), the adsorbent shows a better fit for Langmuir II shows a better fit for adsorption system compared to that of Langmuir I since its R^2 (0.9934) is greater than that of Langmuir I (0.8943). The experimental equilibrium adsorption data were compared to that of both the theoretical Langmuir isotherm forms (I and II) and they are presented in Figure 47 and Figure 48. The adsorption capacity (Q_o) of the pretreated PC2 sample for the removal of NH_4^+ was calculated from the obtained linear equations of Langmuir form I and II shown in Figure 45 and Figure 46. The calculated NH_4^+ adsorption capacity of Langmuir form I (16.47 mg/g PC sample) was found to be higher than that of Langmuir form II (13.47 mg/g PC2). The sample calculations of all isotherm parameters are shown in the appendix 7. The comparison of the experimental and theoretical adsorption data for the Langmuir isotherms I and II is presented in Figure 47 and 48 below.

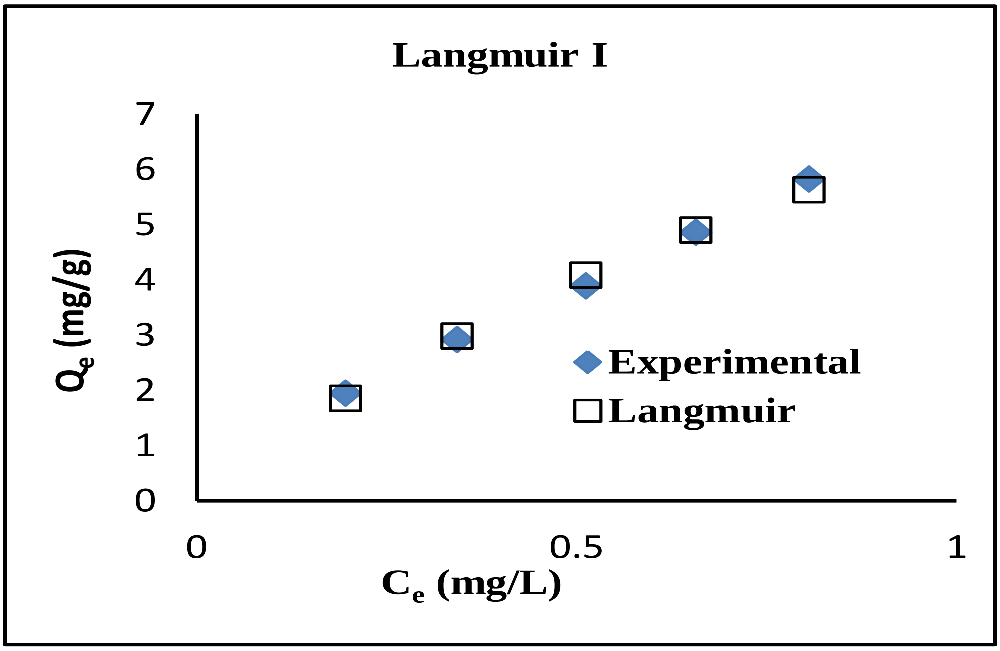

Figure 47: The comparison of the experimental and theoretical adsorption data for Langmuir isotherm I

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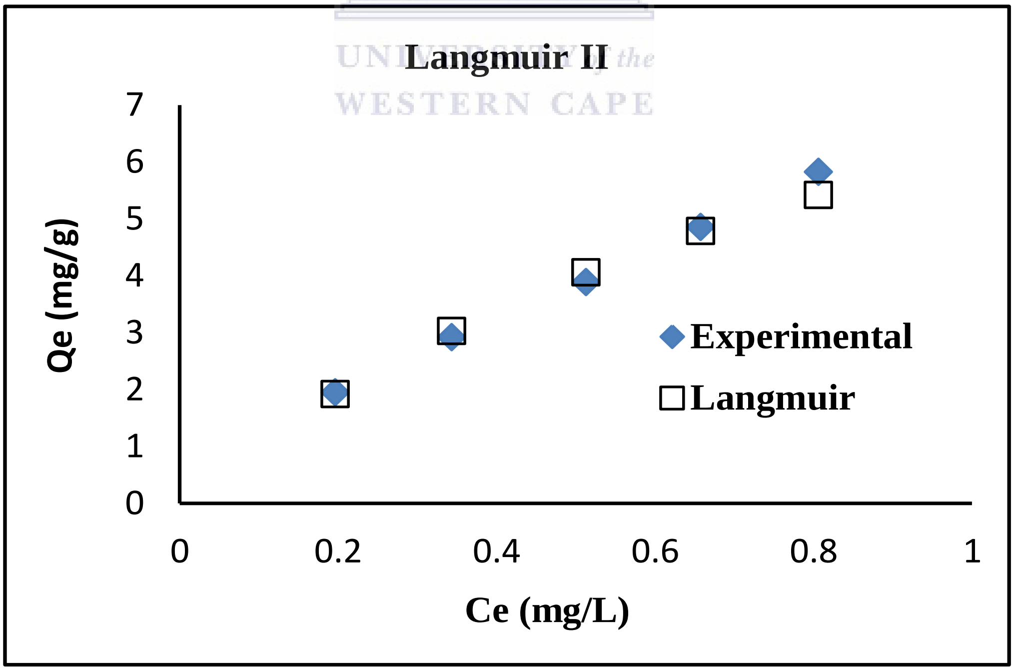

Figure 48: The comparison of the experimental and theoretical adsorption data for Langmuir isotherm I

The theoretical curves of both Langmuir isotherms (Form I and II) show the similarities with the experimental equilibrium curve indicating that there is a strong relationship with the equilibrium data and the Langmuir model mechanism (Figure 47 and 48). A slight difference was observed on the Langmuir II curve where the last two points are not well fitted compared to those of Langmuir I. Both Langmuir data fitted all the adsorption data well-meaning that the surface of the adsorbent (acid-pretreated PC2 sample) is homogeneous. It was therefore observed that the pretreated PC2 sample has great adsorption efficiency towards ammonia removal since the maximum removal can be reached within a short contact time of 10 min on 0.5 g of PC2 sample (treated using 22 extractions).

Figure 49 shows that the adsorption data of ammonium ion on the pretreated PC2 sample fitted well to the Freundlich model (R^2 0.9974). The model constants K_F and n were found as 6.7093 and 1.2990, respectively.

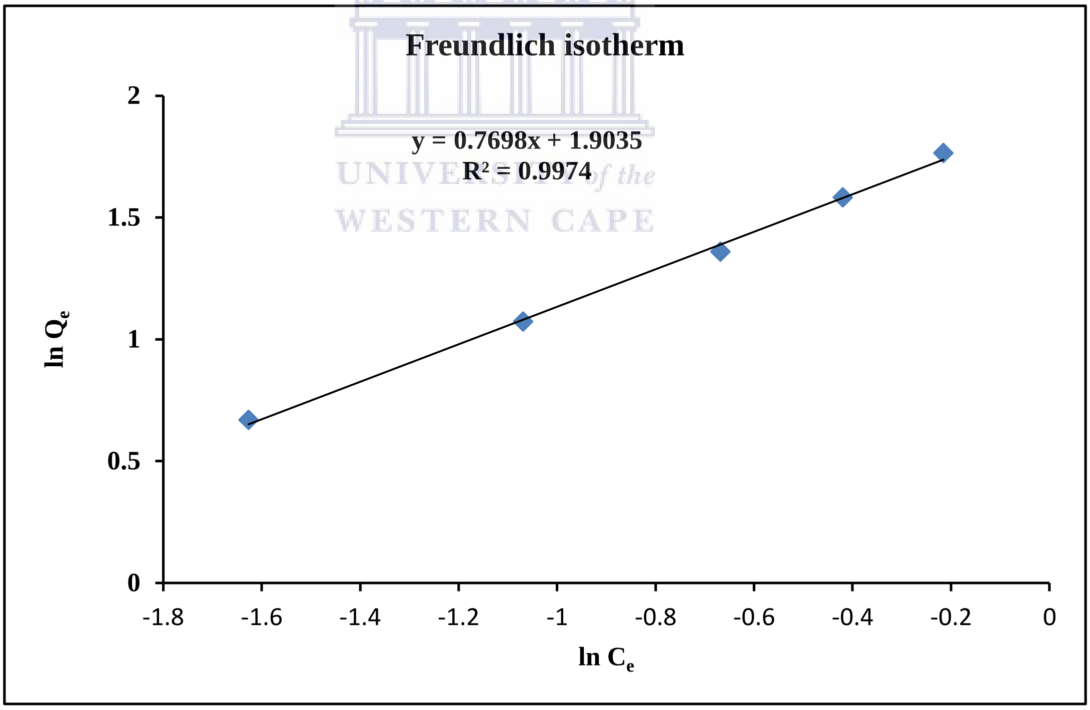

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Figure 49: Linearized form of Freundlich model of NH_4^+ on the pretreated PC2 sample at natural pH and at 25°C

In order to determine the best adsorbent (ESC2, EH2C and PC2) used in this study, the adsorption experiments of NH_4^+ were carried out using acid-pretreated ESC2, EHC2 and PC2 samples. The experimental obtained results are discussed in section 5.1.7 below.

5.1.7 Comparison of adsorption capacity of NH_4^+ on the pretreated ESC, EHC and PC samples

The adsorption experiment was carried out using sorbent mass of 0.5 g of each type of acid pretreated ESC2 and EHC2 samples (7 extractions) and PC2 (22 extractions) keeping both sorbate (50 mL of about 50 mg/L NH_4^+) and the contact time constant (10 min). The aim of this experiment was to invistigate the adsorption capacity of these adsorbents for the removal of 50 mg/L NH_4^+ within an optimum contact time of 10 min at 25 °C. The equilibrium adsorption results are presented in Figure 50 below.

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Table 22: Equilibrium results obtained from the adsorption of NH_4^+ on ESC, EHC and PC sample

Clinoptilolite sample	% NH_4^+ removal
ESC	75.00
EHC	93.89
PC	95.48

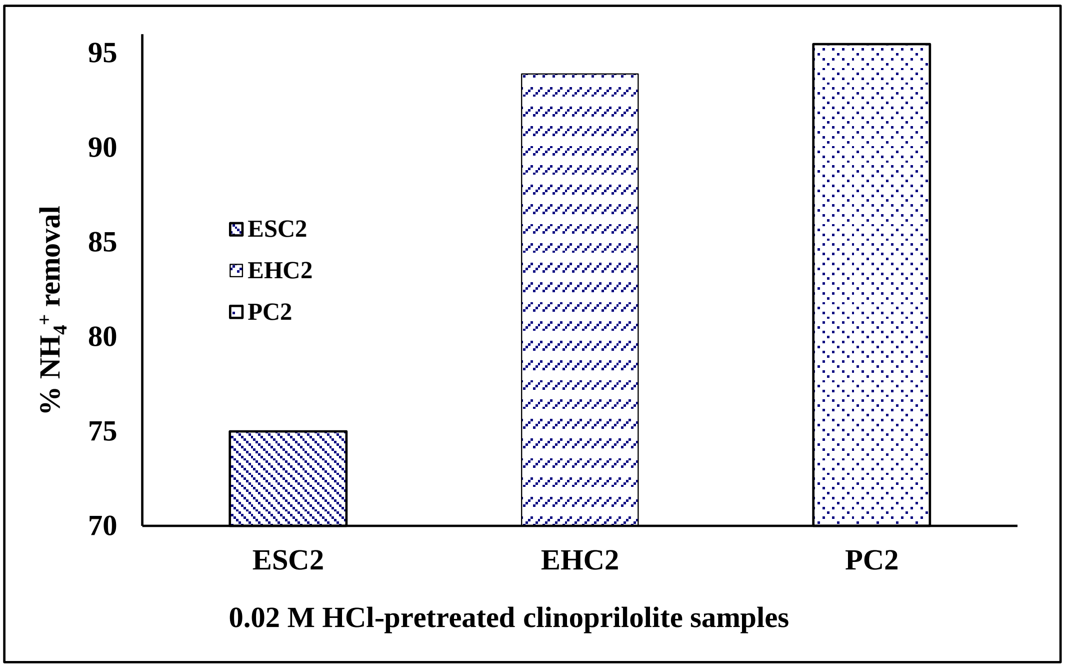

Figure 50: The percentage removal of NH_4^+ (at pH 6.8) conducted at room temperature (25 °C) on pretreated ESC, EHC and PC samples at a constant contact time of 10 min and 50 mL of about 50 mg/L NH_4^+.

The results in Figure 50 and Table 22 show the lowest percentage removal of NH_4^+ was obtained on the ESC2 (75.48 %). The NH_4^+ percentage removal increased using the HCl-pretreated EHC and PC2 samples by removing 93.89 % and 95.50 % NH_4^+ respectively. It was therefore determined that PC2 sample has the highest quality of the clinoptilolite sample for the NH_4^+ removal compared to that of ESC2 and EHC2 samples because of its high NH_4^+ adsorption capacity. These results are compared to those obtained from the characterization carried out for the determination of CEC (section 4.2.6) and it shows that Pratley has a high CEC (2.9 meq/g of PC) followed by EHC with 1.81 meq/g EHC and the lowest CEC was ESC (1.23 meq/g of ESC). These results are again supported by the purity of the clinoptilolite phase of the samples obtained by qualitative and quantitative XRD which shows that PC sample was the most pure clinoptilolite sample (81.10 % purity) follwed by EHC with 67.88 % the ESC with 44.00 %. The acid-pretreatment results also support these results since more cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) could be easily exchanged by H^+ generating more proton exchange sites in the pretreated PC2 sample compared to those in ESC2 and

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EHC2. These results shows that ion exchange capacity depends on the purity of the mineral phase of the sample. The acid washing or pretreatment results for both ECCA Holdings samples (ESC2 and EHC2) only showed the removal of Na^+ and Mg^{2+} but with low concentration compared to that of PC sample.

5.2 BATCH ADSORPTION EXPERIMENTS OF Cr^{3+}

Chromium adsorption was carried out using experimental method described in section 3.2.4.2. Chromium ion was adsorbed as chromium ion (Cr^{3+}) from the synthetic chromium chloride hexahydrate solution. The pretreated PC2 sample was the only adsorbent used in batch adsorption experiments of Cr^{3+}. Only certain adsorption parameters were considered during batch adsorption experiments including reaction contact time, amount of adsorbents (dosage) and the solution pH. The contact time experimental results are presented and discussed in section 5.2.1 below.

5.2.1 Effect of contact time for the removal Cr^{3+}

The contact time of Cr^{3+} (prepared concentration of 10 mg/L) on the acid-pretreated PC2 sample was carried out following the procedure described in section 3.2.4.2. The experimental initial concentration of Cr^{3+} in the standard solution was determined using the standard calibration curve method (line equation) in the same way as it was done in section 5.1.2. The adsorption equilibrium experimental results were carried and are shown in Figure 51 and 52 below.

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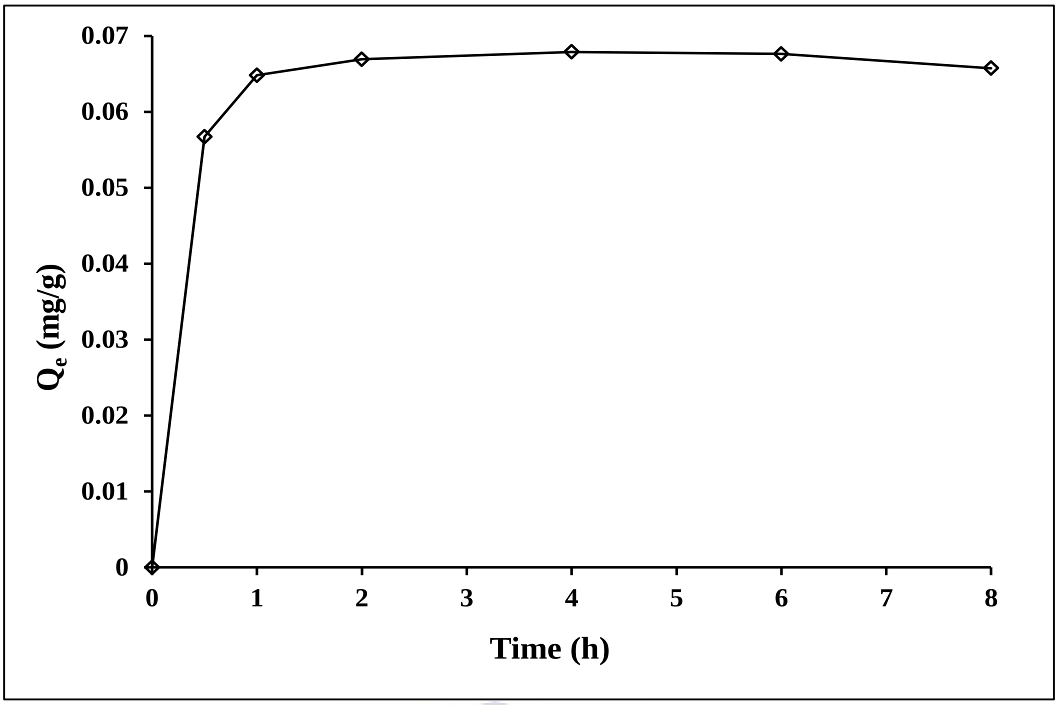

Figure 51: The adsorption equilibrium amount (Q_e) of 10.0 mg/L Cr^{3+} (50 mL) on 1.0 g of pretreated PC2 sample, conducted at 25 °C and natural pH (2.0) varied at different contact time

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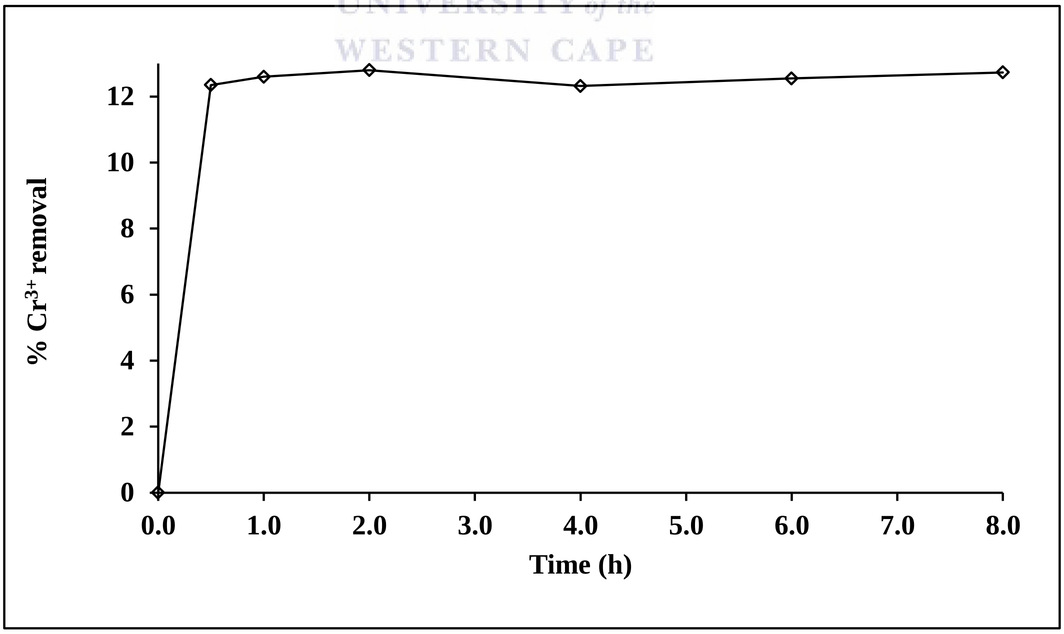

Figure 52: The percentage removal of 10.0 mg/L Cr^{3+} (50 mL) on 1.0 g of pretreated PC2 sample, conducted at 25 °C and natural pH (2.0) varied at different contact time

In Figure 51, the adsorption equilibrium point was achieved within 2 h after which the removal of Cr^{3+} remained almost unchanged till end of the experiment (at 8th h). These results shows that the adsorbent (PC2 sample) and adsorbate (Cr^{3+}) had reached their adsorption equilibrium point after 2 h of the adsorption time. This indicates that clinoptilolite may not be a suitable adsorbent for the removal of Cr^{3+} from aqueous solution as the percentage Cr^{3+} removal at 2 h was 12.8 % from 10 mg/L Cr^{3+} (Figure 52). The poor removal of Cr^{3+} may be due to the large size of Cr^{3+} and speciation of chromium. The natural clinoptilolite is known to be a microporous material (shown by BET), they have small pores (1.9 nm) in their framework therefore Cr^{3+} do not easily fit in the pores during the ion exchange process resulting in having poor adsorption capacity. This is an indication that natural zeolites such as clinoptilolite may have a low ion exchange capacity for the removal of some heavy metals in aqueous solution. Silva *et al.,* (2008) suggested that it is better to use biomass as adsorbent in order to enhance the removal of chromium (III) from aqueous solution. The removal of Cr^{3+} on any adsorbents strongly depends on the pH of the solution which changes its speciation (Silva *et al*., 2008 and Faghihian and Bowman, 2005). The effect of pH for the removal of Cr^{3+} will be discussed in section 5.2.5.

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5.2.5 Effect of pH on the removal of Cr^{3+}

The previous experiment carried out on the effect of the contact time on the removal of Cr^{3+} shows that the optimum contact time for Cr^{3+} removal when the pretreated PC2 sample was applied as adsorbent, was 2 h. Therefore, another batch experiment was carried out in order to determine the effect of pH for the removal of 10 mg/L Cr^{3+} (50 mL) from synthetic solution at a contact time of 2 h at different pH of 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 (experimental procedure found in section 3.2.4.2) with 1.0 g of the acid-pretreated PC2 sample (treated with 22 extractions). The results obtained in the pH experiment for the removal of Cr^{3+} are presented in Figure 53 below.

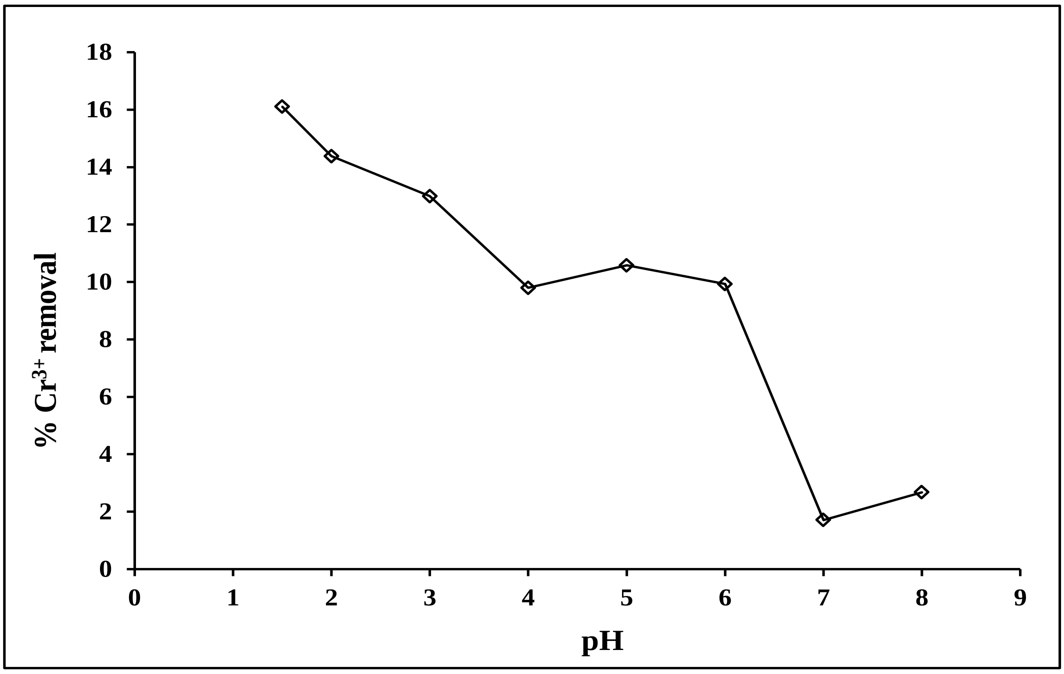

Figure 53: The percentage removal of 10 mg/L Cr^{3+} (50 mL) on 1.0 g of pretreated PC2 sample sample shaken for 2 h at pH range of 1.5 to 8.

The adsorption of Cr^{3+} strongly depends on the pH of the solution. The results obtained in Figure 53 shows the effect of pH on the removal of Cr^{3+} using 1.0 g of the pretreated PC2 sample. It was clearly observed that the Cr^{3+} removal decreased with an increase in the solution pH after a maximun removal at the pH of 1.5 (16.1%). The pH of 1.5 was thus found to be the optimum pH at which a maximum concentration of Cr^{3+} was removed by PC2 sample. The percentage removal of Cr^{3+} on the pretreated PC drastically decreased as the pH increased. The maximum Cr^{3+} removal was observed at the pH of 1.5 with 16.10 %. Silva *et al*., (2008) reported the maximum removal of Cr^{3+} on the biomass adsorbents at pH 1.0 and 2.0 where the chromium III concentration was calculated by the difference between the total Cr and Cr (VI) concentration. The speciation of chromium changes with changing pH of the solution. According to Silva *et al.*, (2008), Cr^{3+} species exist at lower pH (1.0 to 2.0) and the Cr (VI) species at pH 4. It is therefore necessary to control the pH of chromium solution.

5.3 CHAPTER SUMMARY

This chapter dealt with the batch adsorption of NH_4^+ or Cr_3^+ from synthetic wastewater. The determination of different adsorption parameters were investigated in batch studies. The maximum removal (89.5 %) of about 50 mg/L NH_4^+ (volume of 50 mL) in batch adsorption experiment was achieved within a short contact time of 10 min with an optimum mass of 0.5 g of the pretreated PC2 sample shaken at 250 rpm, at 25 °C and at natural pH of 6. The percentage removal of NH_4^+ on the untreated PC sample (62.30 %) at 10 min was around 36 % lower than that of acid-pretreated PC2 sample (98.11 % at 10 min). These results shows that even the untreated clinoptilolite sample can remove a lot of NH_4^+ (62.30 %). These results revealed that the acid-pretreatment with 0.02 M HCl using 22 extractions improved the PC adsorption capacity for the removal of NH_4^+. It was therefore observed that this study has improved (high removal of NH_4^+) on the work previously conducted on the acid-pretreatment of clinoptilolite and that it is not only the acid concentration that is important but also the number of extractions needed to remove all the possible cations from the clinoptilolite framework. The numerous extractions of the cations during the acid-pretreatment of clinoptilolite increased the number of exchange sites in the framework. In this study, 22 acid extractions were needed to remove Na^+, K^+ and Mg^{2+} from 10 g of PC clinoptilolite and 7 extractions used to pretreat ESC and EHC whereas the previous work only considered the acid concentrations to pretreat natural clinoptilolite. Langmuir isotherm was found to fit with the adsorption equilibrium NH_4^+ data system better than that of the Freundlich model for the pretreated PC2 sample. Langmuir data fitted all the adsorption data well-meaning that the surface and exchange sites of the adsorbent (acid-pretreated PC2) are homogeneous.

The pretreated Pratley clinoptilolite sample was found to have the highest capacity for the removal of ammonia from synthetic solutions compared to clinoptilolite samples ECCA Holdings. These results compared to those obtained from the characterization carried out for the determination of cation exchange capacity (section 4.2.6) which showed that Pratley has a high CEC (2.9 meq/g)

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followed by EHC with 1.81 meq/g and the lowest CEC was ESC (1.23 meq/g). These results are again supported by the purity of the clinoptilolite phase of the samples obtained by qualitative and quantitative XRD which shows that PC sample was the most pure clinoptilolite sample (81.10 % purity) follwed by EHC with 67.88 % the ESC with 44.00 %. These results indicate that the ion exchange capacity of a natural adsorbent depends on the purity of the sample. It was determined that South African clinoptilolite is a good adsorbent for NH_4^+ removal from aqueous solutions since it has high efficiency for its removal.

The adsorption of Cr^{3+} results show that the maximum removal of 16.10 % Cr^{3+} could be achieved within a contact time of 2 h at natural pH of around 1.5. It was found that the percentage removal of Cr^{3+} decreases with increasing in pH of the solution. It was therefore determined that natural clinoptilolite is not an appropriate adsorbent for the removal of Cr^{3+} from aqueous solutions since only a maximum adsorption of 16.10 % could be achieved using 1.0 g of PC2 sample for 2 h. The poor removal of Cr^{3+} may be also due to the size of Cr^{3+} and speciation of chromium.

The natural clinoptilolites were determined to be microporous materials (shown by BET), they have small pores (about 1.9 nm) in their framework therefore Cr^{3+} cannot easily fit in the pores during the ion exchange process resulting in having low adsorption capacity.

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CHAPTER 6

CONCLUSION

In this study, three sources of natural South African clinoptilolite were characterized and it was found that these natural materials characteristics vary considerably even from the same deposit. The clinoptilolite samples mined by two companies are ECCA Holdings soft (ESC), ECCA Holdings hard (EHC) and Pratley (PC) samples. The five major findings of this study were natural sources of South African clinoptilolite vary a lot, the pretreatment of natural clinoptilolites needs optimization, the repeated extraction needed, acid-pretreatment could not remove all the cations from clinoptilolite framework and the removal of NH_4^+ worked but not for Cr^{3+}.

The XRD results revealed that PC sample was the most pure clinoptilolite sample compared to the purity of EHC and ESC sample. This study revealed that the quality of these natural adsorbents depends on their mineral phase impurities content. The ECCA Holdings clinoptilolite samples were found to contain dense phases such as quartz which was found to be the most dominant impurity but it was not present in PC sample. Cation exchange capacity of ECCA Holdings and Pratley samples varies from mines to mines depending on their origin, chemical and mineral compositions showing that Pratley sample has the highest CEC value.

It was found that the standard CEC test can only remove a very small percentage of the present cations from clinoptilolite samples using the ammonium acetate method thus should be optimized further for microporous materials. The polycrystallinity of theses natural adsorbents were found to affect the diffusion of cations through the pores of clinoptilolite during the sample pretreatment process.

The optimum acid for the pretreatment of these adsorbents was found to be 0.02 M HCl using 22 extractions of 50 mL volumes since these conditions did not cause much dealumination of the clinoptilolite framework structure. It was found that using acid-pretreatment with highly concentrated acid solution (1.0 M HCl) reduced the pretreatment time, but caused a significant dealumination of the zeolite framework. However this study has improved the acid-pretreatment procedure for clinoptilolite because it demonstrated that it is not only the acid concentration that is important but also the number of extractions needed to remove all the exchangeable cations from the clinoptilolite framework. The Na^+ was found to be the most weakly bound cation in all three clinoptilolite samples because it was completely removed from ESC and EHC even after 7 acid extractions.

The Mg^{2+} and Ca^{2+} ions were also observed to be completely removed out of EHC and PC sample during acid-pretreatment but not in the case of ESC sample. It was revealed by the EDS and acid-pretreatment results that the K^+ is the most strongly bound cation in all the clinoptilolite samples (ESC, EHC and PC) since it could not be completely removed out of the clinoptilolite frameworks using 0.02 M HCl even after 22 extractions. It was found that the acid-pretreatment using numerous extractions were necessary to remove exchangeable cations from the framework. This study found that natural South African clinoptilolites were pretreated and converted into H^+ form of clinoptilolite achieved by exchanging the cations from the framework using 0.02 M HCl after 22 extractions.

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It was found that the acid-pretreatment procedure cannot be applied uniformly but should be optimization for each source of clinoptilolite sample. This study found that the CEC and the acid-pretreatment results have a correlation with those obtained by XRD analyses confirming that the purity of the clinoptilolite phase affects the diffusion of cations through the pores of clinoptilolite. The polycrystallinity of the clinoptilolite sample was also found to cause the diffusional constraints of the cations through the pores of clinoptilolite.

The percentage removal of NH_4^+ on the untreated PC sample was found to be 36 % lower than that of acid-pretreated PC2 sample. It was therefore found that the acid-pretreatment using sequential extractions improved the PC sample adsorption capacity for the removal of NH_4^+. It was found that the adsorption capacity of a natural adsorbents depends on the purity of the clinoptilolite sample.

This study found that natural clinoptilolite is not an appropriate adsorbent for the removal of Cr^{3+} from aqueous solutions since only a miximum adsorption of 16.10 % could be achieved. The poor removal of Cr^{3+} was due to the larger size of Cr^{3+} and its speciation.

Despite several studies that have been conducted on clinoptilolite, no study has been carried out on the pretreatment and comparison of sorption capacity of different South African clinoptilolites for the removal of NH_4^+ from wastewater. This study has been able improve the acid-pretreatment procedure for clinoptilolite. This study demonstrated that it is not only the acid concentration that is important but also the number of extractions needed to remove all the exchangeable cations from the clinoptilolite framework. This study also has been able to prove that South African clinoptilolite can treated ammonia from wastewater.

6.2 RECOMMENDATIONS AND FUTURE WORK

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The natural South African clinoptilolites mined by ECCA Holdings and Pratley companies from Western Cape and Kwazulu Natal provinces respectively, have been explored for their application for the removal of NH_4^+ and Cr^{3+} from synthetic wastewater. However some other adsorption and ion exchange parameters still need to be investigated for a better understanding of these materials. It is suggested that South African clinoptilolites should be pretreated using other pretreatment methods so that their sorption capacity of Cr^{3+} can be enhanced. It is suggested that the acid-pretreatment of natural clinoptilolites from different deposits should not be uniform, they should be optimized accordingly. It is again suggested that the standard CEC method using ammonium acetate is not a good method to use because it extracts a very small amount of cations present in the sample.

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APPENDIX A1: FTIR SPECTRA OF UNTREATED AND PRETREATED PRATLEY CLINOPTILOLITE

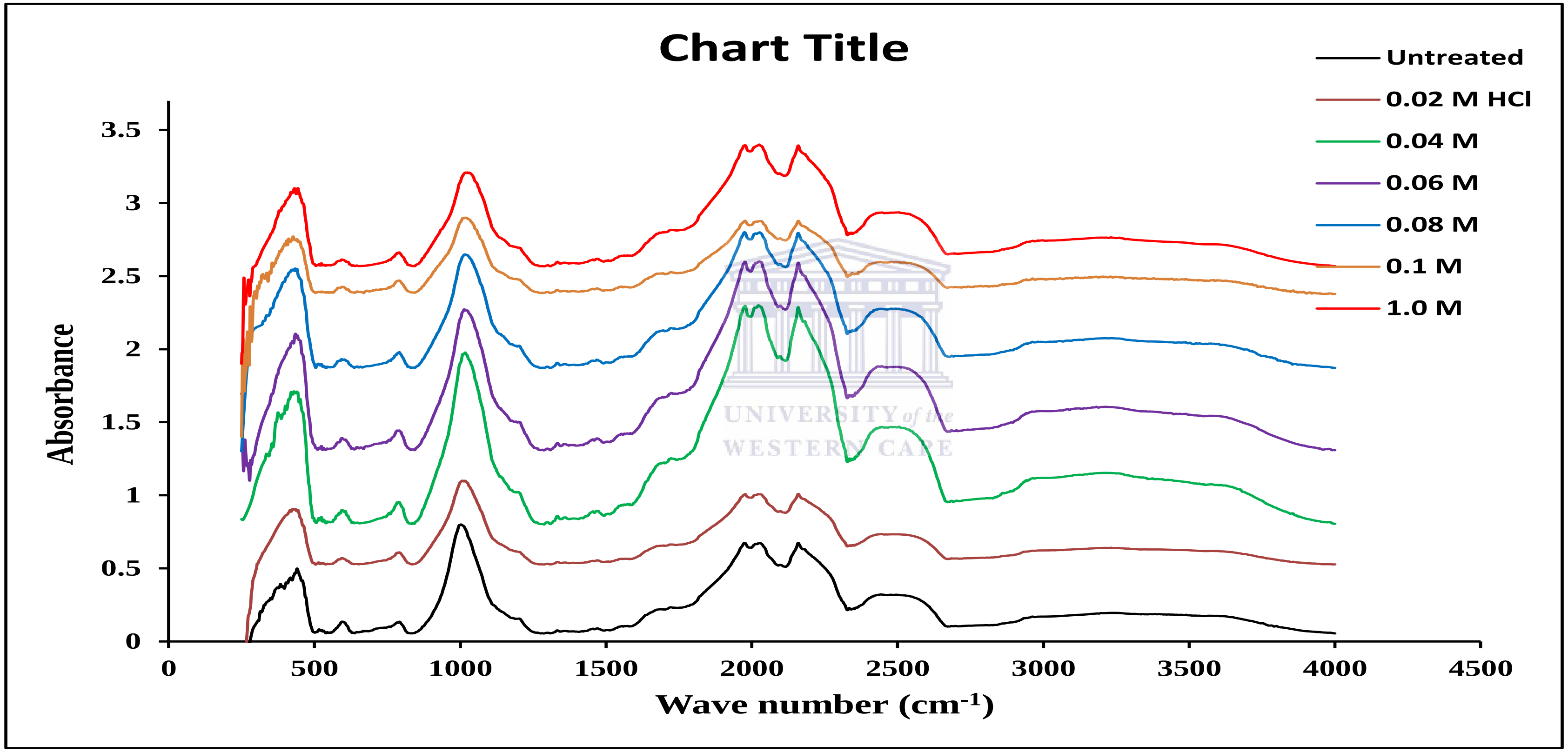

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Figure 54: FTIR spectra of untreated and acid-pretreated of Pratley clinoptilolite using different acid concentrations

APPENDIX A2: FTIR SPECTRA OF UNTREATED AND PRETREATED OF ECCA HOLDINGS SOFT SA CLINOPTILOLITE SAMPLE

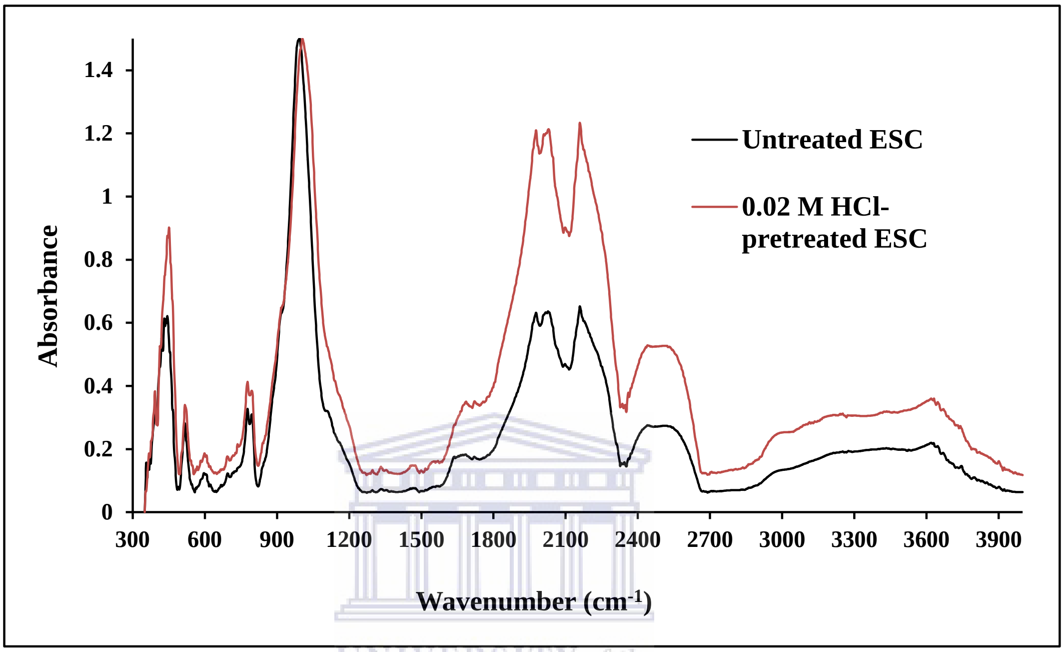

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Figure 55: FTIR spectra of untreated and pretreated ESC (0.02 M HCl)

APPENDIX B: TOTAL DIGESTED METAL CONCENTRATION FOR THE UNTREATED ESC, EHC AND PC SAMPLES

Element	**ECCA Holdings soft clinoptilolite (mg/L)**	**ECCA Holdings Hard clinoptilolite (mg/L)**	**Pratley clinoptilolite (mg/L)**
Al	681.50 ± 91.02	410.81 ± 35.15	279.014 ± 28.22
As	1.14 ± 0.56	0.84 ± 0.45	0.90 ± 0
Ba	19.71 ± 2.93	18.75 ± 3.0	2.99 ± 0.30
Be	0.032 ± 0.011	0.011 ± 0.0043	0.047 ± 0.0003
Ca	31.48 ± 0	8.33 ± 3.79	ND
Cd	0.047 ± 0.016	0.029 ± 0.012	0.053 ± 0.0021
Ce	0.57 ± 0.11	0.46 ± 0.12	0.15 ± 0.078
Cr	0.052 ± 0	ND	0.079 ± 0
Co	0.015 ± 0	ND	0.034 ± 0
Cu	ND	ND	1.051 ± 0
Fe	87.59 ± 12.032	31.024 ± 2.13	49.24 ± 6.28
Hg	1.43 ± 1.32	1.7591 ± 0.47	0.70 ± 0.079
K	106.10 ± 6.037	149.2733 ± 5.33	1.83 ± 13.72
Li	0.22 ± 0.017	0.1251 ± 0.020	0.14 ± 0.0016
Mg	73.16 ± 6.037	19.2531 ± 6.67	4.70 ± 1.72
Mn	1.73 ± 0.093	0.5983 ± 0.05394	1.91 ± 0.84
Mo	ND	0.2135 ± 0	0.18 ± 0.082
Na	130.28 ± 9.99	137.89 ± 11.41	125.97 ± 20.86
Ni	0.074 ± 0.047	0.14 ± 0.0491	0.057 ± 0
P	0.80 ± 0.54	1.25 ± 0.1064	0.29 ± 0
Rb	0.057 ± 0.027	0.047 ± 0	0.051 ± 0
Se	0.912 ± 0.54	0.55 ± 0.086	0.44 ± 0
Si	2 451.49 ± 190.38	2 596.023 ± 141.17	2 425.30 ± 116.70
Sr	4.2461 ± 0.086	5.68 ± 0.89	0.92 ± 0.022
Th	0.1935 ± 0	0.047 ± 0	ND
Ti	5.93 ± 0.58	3.56± 0.15	5.018 ± 0.42
V	0.13 ± 0.056	0.10 ± 0.057	0.068 ± 0.035
Y	0.094 ± 0.021	0.085 ± 0.0087	0.047 ± 0.015
Zr	0.74 ± 0.089	0.5762 ± 0.068	0.99± 0.045

ND = Not Detected

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