

# A Study of South African Natural Zeolites Properties and Applications

Palesa. P. Diale, Edison Muzenda, *Member, IAENG*, and Josephat Zimba

**Abstract**— The morphology and chemistry of natural zeolites, whose occurrence is ubiquitous to the South African provinces of Kwa-Zulu Natal (KZN) and Western Cape (WC), were studied using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), X-ray fluorescence (XRF) and the Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption technique. The stability of these zeolites in varying pH conditions and their cation exchange capacity (CEC) was also investigated. The main mineral constituent of the natural zeolites was found to be clinoptilolite, with plagioclase, quartz and muscovite being the common impurities. The zeolite footprint was not altered after treatment with a hydrochloric (HCl) acid. The BET surface area ranged from 65.5 to 33.22 m<sup>2</sup>/g while the pore size ranged from 3 to 10 nm for the natural zeolites. These properties make them good prospective materials for application in biomedicines, environmental preservation and agriculture.

**Keywords**— Clinoptilolite, Ion exchange, Mineral, Particle morphology, Zeolites

## I. INTRODUCTION

Zeolite minerals were first discovered in 1756 by a Swedish mineralogist Freiherr Axel Frederick Cronstedt. Upon observing boiling and frothing of the collected zeolite mineral, when heated by means of blow flame, he named the mineral using two Greek words *zein* and *lithos* (meaning boiling stone) [1]. For almost 200 years since the mineral was discovered, geologists considered the zeolite mineral to occur as fairly large crystals in the vugs and cavities of basalts and other traprock formations [2].

The growth of the synthetic zeolite market began to take hold in the late 1950s and that ignited the curiosity of the natural form of the mineral. Numerous discoveries of huge beds were made including the reserves in the western United States of America and elsewhere in the world. The beds were found to comprise at least 95 % of a single zeolite. Since then, considerable efforts have been made to develop applications based on their unique adsorption, cation-

exchange, dehydration-rehydration and catalytic properties [2].

Globally, natural occurring zeolites are used for, among other applications: biomedical purposes; the removal of caesium (Cs) and strontium (Sr) from nuclear waste and for soil amendments in agriculture. The commercial use of natural zeolite from Roman times, as a construction material to recent successes in the healing of cuts and wounds, has confirmed that zeolites are fully-fledged mineral commodities, whose uses can potentially be expanded.

South Africa's (SA) wealth is influenced extensively by its natural resources sector specifically mining, farming and its developed industrial sector. The mining industry is one of the best developed in the world and forms a crucial part of SA's economy. Although the mineral production is dominated by gold, diamond, platinum-group metals (PGMs) and chromium: industrial minerals also feature strongly in SA's mining industry. Industrial minerals found in SA largely consist of alumino-silicates in the form of andalusite, bentonite and natural zeolites. The zeolite mineral, despite possessing numerous valuable properties has not enjoyed a lofty market demand like its counterparts. This study explores the composition and quality of selected natural zeolites, with a view of expanding its applications in various industries.

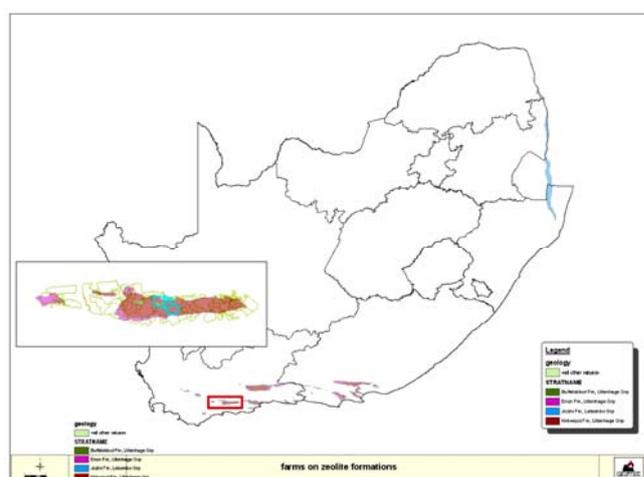


Fig. 1 Geological scan of SA zeolites

This paper discusses the chemistry and properties of natural zeolites found in South Africa, in the provinces of Western Cape and Kwa-Zulu Natal. The specific areas from where the samples were obtained are shown in Fig 1.

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P. P. Diale is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg 2028 (email: palesadoll@yahoo.com).

E. Muzenda is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg, South Africa, 2028 (corresponding author phone: +27 11 5596817; fax: +27 11 5596430; emuzenda@uj.ac.za).

J. Zimba is with Salene Technologies, Bryanston, 2021, South Africa (email: joezimbal@yahoo.com).

## II. MATERIALS AND METHODS

### A. Research Material

Three zeolite-rich samples from volcanic tuffs of the Heidelberg-Riversdale Area in the Western Cape labelled as WC-Akwa; WC-Duminy and WC-Jadico were studied. One zeolite-rich sample from volcanic tuffs of Nxwala Estate in the Northern KwaZulu-Natal labelled as KZN-PO1 Prior to all analysis, except for SEM, the samples were crushed and pulverised to 75 µm.

### B. X-ray Diffraction Analysis of Natural Zeolites and HZSM-5

The phases within the zeolites were determined using X-ray diffraction of powder samples. For all samples a Siemens D500 diffractometer, with Ni-filter, Cu K<sub>α</sub> radiation, operating at 40 kV, 30 mA was used. A step size of 0.02° 2θ and a counting time of 4 second per step were applied over a 2θ range of 3° to 90°.

### C. Porosimetry of the Natural Zeolites and HZSM-5

The zeolites pore size and distribution was determined using a Micromeritics ASAP 2010 surface area analyzer. For the adsorption-desorption curves the adsorbate was N<sub>2</sub> and pore size distribution was calculated from the desorption branch using the Barret-Joyner-Halenda (BJH) model. Prior to the pore measurement, the samples were pre-treated by degassing at -196 °C.

### D. SEM Analysis of the Natural Zeolites and HZSM-5

A Leica-Cambridge Scanning Electron Microscope (Model S420-1) was used to study the morphology of the zeolites. The zeolite samples were not coated prior to examination using the SEM as it was felt this could occlude some of the salient features, instead, a low acceleration voltage was used to avoid charging in the samples. This approach resulted in a good resolution of the zeolite features.

### E. pH Stability Analysis Method

In order to determine the stability of the zeolites under acidic conditions, the different zeolite samples were immersed in aqueous acidic solutions of pH 1.2 and 4. These were intimately mixed for 24 hrs and samples were then dried at 60 °C. Different acidic aqueous solutions of varying pH levels were prepared. The natural and synthetic zeolites were exposed to diluted HCl of pH 1; 2 and 4.

### F. Moisture Content Analysis

The pH titration method was used to determine the cation and anion exchange capacity of the natural and synthetic zeolites. The test work involved measurement of the moisture content, total cation and total anion exchange capacities. For moisture content determination a pill vial was weighed with a lid closed, then an amount of zeolite (1-2 g) was placed

inside and weighed again. The pill vial with the sample was placed open into the oven for 24 hours at 60°C. Upon the removal of the pill vial from the oven, the pill vial was weighed with a closed lid and a dried sample. The moisture content of each sample was calculated using Eq. 1.

$$\text{Moisture } W (\%) = (m_2 - m_3) / (m_2 - m_1) * 100 \quad (1)$$

Where; m<sub>1</sub> - weight of pill vial with lid, m<sub>2</sub> - weight of closed pill vial with (1 – 2 g) zeolite and m<sub>3</sub> - weight closed pill vial with dried zeolite sample.

### G. Ion Exchange Capacity Analysis

The capacity of ion exchangers in literature is defined in terms of the number of functional groups in the material. Cation exchangers in a form of H<sup>+</sup> form and anion exchangers in OH<sup>-</sup> form are considered as insoluble acids and bases. An insoluble acid was therefore used to determine the exchange capacity of the natural and synthetic zeolites. The method of capacity determination is called pH titration.

For the total cation exchange capacity (CEC) test, 5 g of pulverized sample of zeolite was mixed with 500 ml of 0.1 M HCl for 24 hours in a rolling bottle. Solids were separated from solution by filtration. A 10 ml filtrate was titrated with 0.1 M NaOH solution to determine the HCl concentration after adsorption. Three drops of a mixed indicator were added to the 10 ml filtrate solution and the solution turned from colourless to purple. Upon titrating with NaOH the solution turned green. Eqs (2) and (3) were used to calculate the CEC.

$$C2_{HCL} = C_{NaOH} \times \frac{V_{NaOH}}{V_s} \quad (2)$$

$$Q(\text{total cat} \frac{\text{meg}}{\text{g}}) = (C1_{HCL} - C2_{HCL})(V)(100 - W) / \frac{100}{m} \quad (3)$$

Where: C1<sub>HCL</sub> - initial concentration of HCl (0.1 M); C2<sub>HCL</sub> - concentration of HCl after cation exchange (M); C<sub>NaOH</sub> - concentration of NaOH (0.1 M); V<sub>NaOH</sub> - volume of NaOH required for titration of the sample of filtrate (ml); V<sub>s</sub> - volume of filtrate for titration (10 ml); V - volume of HCl solution (500ml); m - mass of zeolite (5g) and W defined by Eqn 1.

The determination of the anion exchange capacity (AEC) involved thoroughly mixing 5 g of a pulverized sample of zeolite with 500 ml of 0.1 M NaOH for 24 hours in rolling bottle. 10 ml of filtrate was titrated with 0.1 M HCl solution to determine the HCl concentration after adsorption. Phenolphthalein was used as an indicator. About 3 drops were added to the 10 ml solution, which remained colourless until the addition of HCl. The end point was reached when the solution turned pink. Equations (4) and (5) were used to determine the AEC.

$$C_{2NaOH} = C_{HCl} \times V_{HCl} / V_s \quad (4)$$

$$Q(\text{total an, meq/g}) = (C_{1NaOH} - C_{2NaOH})(V)(100 - W) / \frac{100}{m}$$

(5)

Where:  $C_{1NaOH}$  - initial concentration of NaOH (0.1 M);  $C_{2NaOH}$  - concentration of NaOH after anion exchange (M);  $C_{HCl}$  - concentration of HCl (0.1M);  $V_{HCl}$  - volume of HCl required for titration of the sample of filtrate (ml)  $V_s$  - volume of the sample titrated (10 ml);  $V$  - volume of NaOH solution (500ml);  $m$  - mass of zeolite (5g) and  $W$  defined by Eqn 1.

### III. RESULTS AND DISCUSSION

#### A. XRD Study of the Natural Zeolites and HZSM-5

The XRD patterns of the four natural are shown in Figs 2 - 5. Two major peaks were found in all natural zeolites studied. The first peak was obtained in the region of 0-5 2θ and the second peak in the 10 -20 2θ. A broad curve was observed in samples Akwa, Duminy and Jadico.

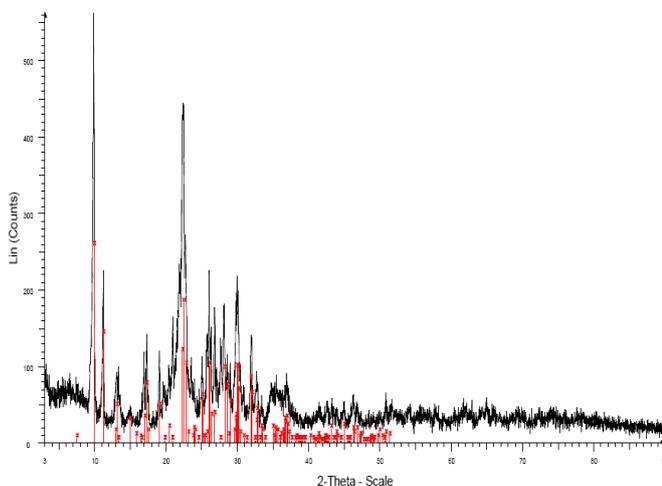


Fig. 2 XRD pattern for KZN-PO1 sample

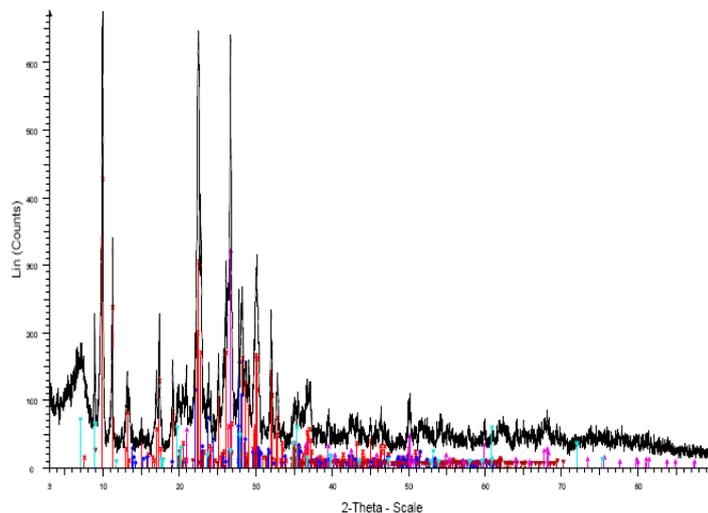


Fig. 3 XRD pattern for WC-Akwa sample

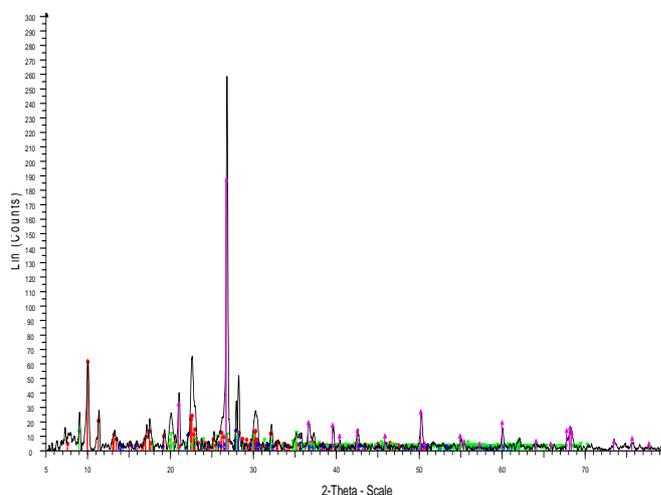


Fig. 4 XRD pattern for WC-Duminy

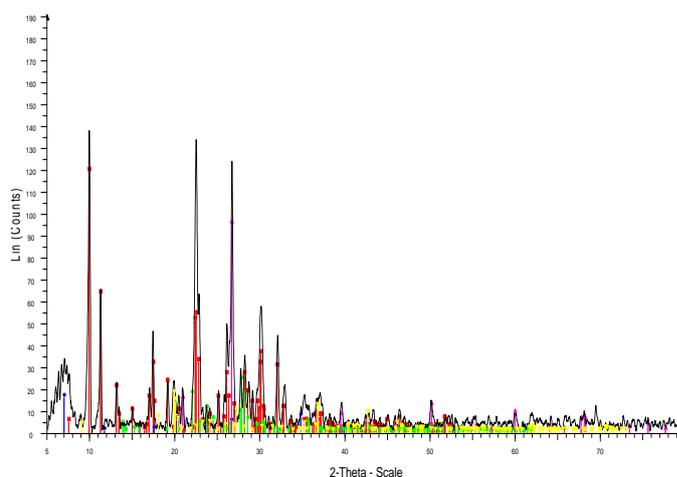


Fig. 5 XRD pattern for HZSM-5 sample

The two largest peaks in the patterns of all the natural zeolites corresponded to clinoptilolite the zeolite. The remaining peaks in the patterns of the natural zeolites may be attributed to the presence of mordenite, sepiolite and quartz. Mordenite was specifically observed in the WC-Akwa zeolite sample. The co-existence of significant amounts of mordenite with the clinoptilolite in zeolites has also been observed by Elaiopoulous et al. [3]. The synthetic zeolite was found to be identical to a natural zeolite called mutinaite, a zeolite from the tectosilicate zeolite group. The zeolite is related to mordenite in that it is an orthorhombic crystal. Plagioclase, quartz, sepolite and muscovite were identified as impurities in the three natural zeolites: Akwa; Duminy and Jadico. The northern KZN zeolite (PO1) showed negligible traces of impurities.

*B. XRF Study of the Natural Zeolites and HZSM-5*

XRF was used to distinguish whether the natural zeolites were heulandite or clinoptilolite type and whether they are hydrophobic or hydrophilic. The XRF analysis results of the natural zeolites presented in Table 1. The results showed a high composition of silicon in all natural zeolites. Potassium (K) and calcium (Ca) were the major single extra-framework cations in the natural zeolites.

TABLE I

XRF ANALYSIS OF THE NATURAL ZEOLITES

CONSTITUENT						
S	Si	Al	Fe	Ca	P	Ti
<b>PO1</b>	20.4	2.6	1.0	0.7	0.3	0.1
<b>Akwa</b>	19.6	2.6	1.2	0.7	0.2	0.0
<b>Duminy</b>	19.2	2.8	1.2	0.5	0.3	0.1
<b>Jadico</b>	17.8	2.7	1.3	0.7	0.3	0.1

According to the International Mineralogical Association, Commission on New Minerals and Mineral Names's (IMA CONMMN) third rule, only heulandite and clinoptilolite zeolites can solely be distinguished on the basis of the silica and aluminium framework [4]. Heulandite has a Si/Al ratio of less than 4, whilst clinoptilolite has a Si/Al of equal or more than 4. The Si/Al ratio of the natural zeolites PO1; Akwa; Duminy and Jadico were found to be 7.96; 7.56; 6.93 and 6.57, respectively, as shown in Table 4. All natural zeolites have a Si/Al ratio of more than 4, thus making them clinoptilolite type. The advantage of high Si/Al ratios is that in low pH environments, the structure is less likely to be damaged [5,8].

The most abundant single extra-framework cation in all natural samples was found to be potassium (K), making the zeolite type Clinoptilolite-K. The "potassium clinoptilolite" is monoclinic, C2/m, C2, or Cm, a 17.688(16), b 17.902 (9), c 7.409(7) Å, β 116.50(7) ° [6].

Zeolites of low Si/Al ratio (less than 4), meaning with high aluminium atoms content, tend to be hydrophilic and organophilic, while a high silica zeolite will tend to be hydrophobic. The XRF results of all natural zeolites showed

that the Si/Al ratio was above 4, therefore making the natural zeolites hydrophobic. SEM Study of the Natural Zeolites

Figs 6 – 9 show the morphologies of the natural and synthetic zeolites that were observed using a scanning electron microscope (SEM).

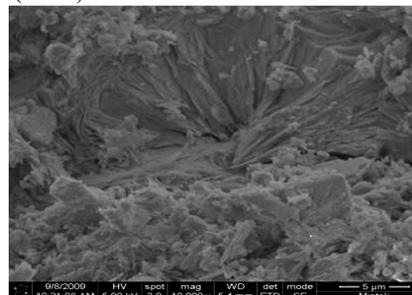


Fig. 6 Scanning electron micrograph of clustered clinoptilolite crystals (A) from KZN. (Sample PO1)

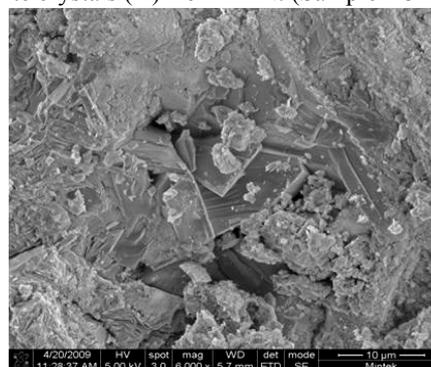


Fig. 7 Scanning electron micrograph of clustered clinoptilolite crystals from WC tuffs. (Sample Akwa)

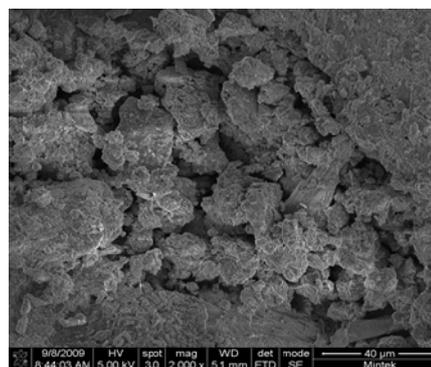


Fig. 8 Scanning electron micrograph of a flaky sample from the WC. (Sample Duminy)

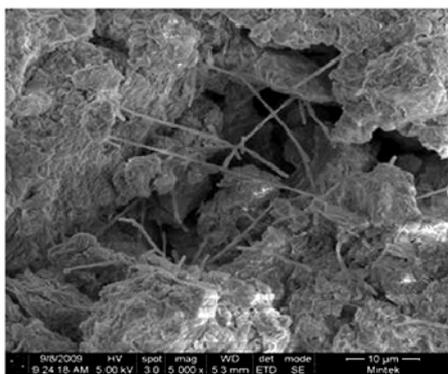


Fig. 9 Scanning electron micrograph of fibres in a material from WC. (Sample Jadico)

Fig 6 of the zeolite sample PO1 showed conglomerates of compact crystals, with thin fibres. The Akwa sample had monoclinic symmetrical blades with a coffin-like shape. The Duminy sample composed mainly of flaky material with little crystals on sight. Thin fibres were also observed in the Jadico sample. Clinoptilolite generally occurs in monoclinic symmetries with coffin-shaped crystals [7]. The SEM scan results of the natural zeolite from PO1 showed clustered crystals, which are a resemblance of clinoptilolite crystal plates, as seen in Figure 6. The Akwa deposit displayed crystals of coffin-like shape resembling clinoptilolite in Figure 7. The crystal assemblage occurs as plates clustered closely together. The flaky material co-existing with the crystals indicate the possible presence of muscovite and clay, which is consistent with the XRD results. Fig 8 shows the Duminy ore sample with a large amount of flaky material. The picture of the natural zeolite suggests that the Duminy deposit is highly impure, because only a small amount of clinoptilolite crystals were found. This is consistent with the XRD scan that the Duminy sample has a low mass percent of about 47.3 % of the heulandite group. The Jadico deposit sample did not depict any coarse grained crystals resembling clinoptilolite; however few thin fibres synonymous with the presence of mordenite were observed, as seen in Fig 9.

#### D. Porosimetric Study of the Natural Zeolites

Adsorption / desorption isotherm curves were used to determine zeolite pore morphology. The different zeolite material's specific surface area were measured using the Brunauer-Emmett-Teller (BET) equation isotherm. The pore size distribution (PSD) was estimated using Barret-Joyner-Halenda (BJH) model. The adsorption / desorption isotherms of the natural zeolites was obtained. It shows that the desorption and adsorption branches meet to form a closed loop for all zeolite samples investigated in the study. A typical plot of the relationship between pore size and pore volume for natural zeolites is depicted in Fig 10.

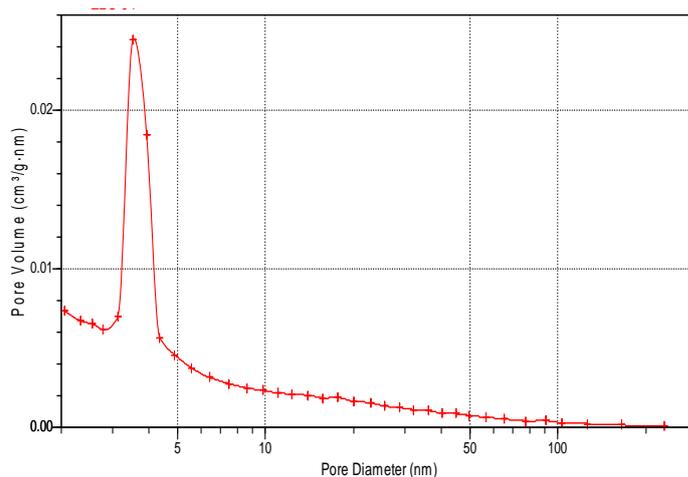


Fig. 10 Pore volume and pore diameter plot showing most of the pores generally fall within a diameter of 2-10 nm.

A summary of the specific surface area and average pore diameter is shown in Table 2.

TABLE II  
 PORE SIZE AND SURFACE AREA RELATIONSHIP FOR  
 THE NATURAL ZEOLITES AND HZSM - 5

Samples	BHP Desorption Ave Pore D (nm)	BET surface area (m <sup>2</sup> /g)
POI	17.78	37.2
Akwa	14.23	33.4
Dummy	9.83	55.8
Jadico	10.36	65.48

There are significant implications to be derived from the results of pore size and surface area measurement: according to literature, common industrial adsorbents like activated carbon have surface areas in the range of 500 – 2000 m<sup>2</sup>/g, with polymeric adsorbents having 150 – 1000 m<sup>2</sup>/g. For the natural zeolites analysed the surface areas were found to be in the range of 33.4 - 65.5 m<sup>2</sup>/g. These surface areas are generally lower than those of adsorbents currently used in the catalysis industry. This could imply that the use of natural zeolites in such applications may not be ideal. According to literature clinoptilolite zeolites with a pore size range of 2 nm – 5 nm can be used for biomedicine purposes. Since the pore sizes of all natural zeolites are in the range of 2 – 5 nm, these zeolites can be candidates for use in biomedicine. This however, needs to be investigated further, particularly the effect of various impurities on the biocompatibility of the zeolites.

E. Study on the Ion Exchange Capacity

The results of the determined total cation and anion exchange capacities are summarised in Table 3.

TABLE III  
 ION EXCHANGE CAPACITY ANALYSIS RESULTS

Samples	Total cation exchange (meq/g)	Total anion exchange (meq/g)
POI	0.39	0.03
Akwa	0.38	0.01
Dummy	0.37	0.02
Jadico	0.41	0.001

The natural zeolites analysed have a low but acceptable cation exchange capacity compared to the theoretical capacity of clinoptilolite (according to literature CEC is 2.16 meq/g). The synthetic zeolite had the lowest cation exchange capacity of 0.32 meq/g. The anion exchange capacity of the natural zeolites proved to be extremely low, confirming that natural zeolites are not ideal for anion exchanging, unless modified or pre-treated. According to these results the natural zeolites could potentially be used as cation exchangers, but not anion exchangers.

IV. CONCLUSION

Having characterised the natural zeolites from the Kwa-Zulu Natal and Western Cape area, by X-ray diffraction, X-ray fluorescence, SEM, BET nitrogen desorption/adsorption method and evaluating their ion exchange capacity. The following conclusions can be made: The zeolitic tuffs of KZN area contain zeolite minerals (>50 mass %), as well as other accessory minerals. The zeolitic tuffs of the WC area contain zeolite minerals in the range 50 < mass % < 20, with sepiolite, albite, quartz, muscovite and mordenite as accessory minerals. The HZSM-5 is akin to the natural zeolite mutinaite; The zeolite tuffs from both KZN and WC are hydrophobic. The surface area of the zeolitic tuffs of KZN is about 37.2 m<sup>2</sup>/g and the pore size distribution is 2 – 10 nm; The WC zeolitic tuffs have a surface areas of 33.4 m<sup>2</sup>/g, 55.8 m<sup>2</sup>/g and 65.48 m<sup>2</sup>/g, with a pore size distribution of 2 – 10 nm; The total CEC of natural zeolites ranged from 0.37 meq/g to 0.41 meq/g, while that of synthetic zeolite was approximately 0.32 meq/g; The zeolite clinoptilolite type studied can potentially be used in industries such as agriculture, horticulture and for environmental protection.

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