# STUDY OF THE REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTE WATER OF INDUSTRIAL ZONE OF BALOCHISTAN USING ZEOLITES.

**Zahoor Ahmad[1], Manzoor Iqbal Khattak[2] , Adnan Afridi[3], Munnaza Saeed and Shaheen Wali[3]**
1-3 Chemistry Department, University of Balochistan, Quetta.
Email; Manzoor Iqbal @yahoo.com

***ABSTRACT:*** *The aim of this work to present the study of the removal of $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$ and $Zn^{2+}$ from synthetic metal solutions using natural zeolite. Laboratory experiments were used to investigate the efficiency of adsorbents in the uptake of heavy metals from industrial wastewater because of the popular aluminosilicate minerals called zeolites have been utilized extensively as adsorbents in the separation, purification, and reduction of environmental contamination processes. Due to their superior cation-exchange capacity, molecular sieve, and catalytic capabilities, zeolites are used in a wide range of industrial applications. Zeolite (natural & synthetic) were used for purification of wastewater in order to reduce adsorbents disposal and lower acquisition costs. The distinctive qualities and uses of adsorbents are also covered, along with the benefits and drawbacks of each method. The results show that the removal of $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$, and $Zn^{2+}$ from synthetic metal solutions using natural zeolite is very friendly.*

**Keywords:** Zeolites, Heavy Metals, EP&ICPOE Spectrometer.

## INTRODUCTION

It has become a global worry that a significant amount of harmful material is accumulating. Pollution from wastewater is part of this issue. Fresh water is essential for maintaining life on our planet, but owing to a lack of clean, fresh water supply, the globe is now experiencing a water crisis. Freshwater worries are growing daily as a result of the escalating demands for the production of food and energy [1]. In the environment, pollutants are discharged on a global scale. These wastes come from numerous sources, including domestic, industrial, transportation, mining, and agricultural wastes. [2]; Burton and Tchobanoglous, [3–4]. Regular waste generation occurs without sufficient sustainable and effective treatment. As these activities have increased, dangerous inorganic and organic pollutants have been released in massive amounts into aquatic systems [5]. As a result, these accumulated toxins in the water might pose a risk to human health and the environment's ecology [6].

Keeping clean water and managing its quality have become imperative tasks for preventing illnesses of all kinds and further environmental deterioration [7]. There is broad agreement regarding the difficulties in treating wastewater for a sustainable future all throughout the globe. Wastewater may have negative short- and long-term effects on ecological systems and human health [8].

There are a number of international laws and rules to address this issue, including the International Kyoto Protocol (United Nations Framework Convention on Climate Change, [9]). Terms like "wastewater," were commonplace by the turn of the century [10–11]. Since then, both developing and developed nations have begun to take certain actions to lower the danger of polluted water systems. When the concentration of contaminants surpasses specified thresholds, rapid cleanup measures are required, according to research by Peng et al. [12].

Currently, it is thought that removing dissolved heavy metals via the process of adsorption is an efficient, inexpensive ,and quick method. The success of the approach, according to Babel and Kurniawan [13], largely relies on the traits and qualities of an effective adsorbent. The utilisation of natural zeolites and their modified forms has the benefits of being inexpensive and widely accessible in many regions of the globe, even if a variety of materials and processes have been used for these objectives [14–17]. As a result, extensively used adsorbents (zeolites) have been employed for the removal of ions during the treatment of wastewater [18–20].

As was already said, the most popular approaches that have drawn growing attention from many businesses are adsorption and ion exchange. Additionally, synthetic zeolites were created because they outperformed natural zeolites in terms of their superior adsorption capacity, although they are often highly costly [21–22]. While being less expensive than synthetic zeolites and having a higher adsorption capacity than natural zeolites [23]. Numerous studies have shown the strong adsorption capabilities of zeolites for the removal of contaminants from solutions and their ability to quickly attain adsorption equilibrium levels [24—26].

Natural zeolites come in a variety of forms; some are relatively frequent, including laumontite, chabazite, stilbite, analcime phillipsite, mordenite, clinoptilolite, while others are far less common, like paulingite, off retite, mazzite, and barrerite [27]. Clinoptilolite, according to Galli [28], is the naturally occurring zeolite that is most prevalent. Its distinctive tabular morphology reveals an open, easily accessible reticular structure made up of open channels created by 8- to 10-membered rings. Clinoptilolite is extensively utilised across the globe and has strong adsorption properties, according to Argun [26]. However, depending on their physicochemical characteristics, several varieties of zeolite have varying adsorption capabilities [29].

A major issue on a worldwide scale is the decrease of heavy metal pollution in aquatic systems [30]. Meanwhile, it has grown to be very difficult to remediate industrial effluent that has been polluted with heavy metals. The wastewater that is collected from communities, businesses, and municipalities has to be cleaned before being released back into the environment, say Bish and Ming [29]. According to Patterson [31], polluting firms must adhere to ever-stricter environmental rules in industrialised nations. Salam et al. [30], stated that overuse of pesticide, operations of mining, nuclear waste production, operations of metal plating, wastages of treated wood, paints, glass industries, vehicle emissions, mining operations, battery wastages, micro-plastics are primary sources of pollution heavy metals. Considering that they do not biodegrade and cause a wide range of illnesses and problems [32, 33]. In organisms, the metals accumulate and cause a wide range of illnesses and disorders including Pb2+, $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$, and $Cr^{3+}$ [34]. Heavy metals-containing wastewater has to be treated before being released into the environment [35].

Wang [36] recommended a number of procedures that may be utilised to decrease/remove metals. Numerous of these approaches have complex operating requirements and substantial energy costs. They could also produce a lot of difficult-to-treat sludge that has to be treated. A few methods also prevent the recovery of metals or materials [37]. Clinoptilolite has the advantages of being inexpensive, readily available, sustainable, and ecologically friendly, according to Panayotova and Velikov [37]. When changed, it has increased adsorption capabilities [38–40]. Natural zeolites are used to clean up the environment because of their ion exchange capabilities [41].

Heavy metals have the ability to adhere to the surface of bacteria and may even enter the cell's inside. As the microbe employs chemical processes to break down food, heavy metals inside the microorganism might undergo chemical changes. The capacity of certain bacteria to transform mercury into methylmercury, a modified form of mercury, is a well-known example. Methyl mercury may enter the body of insects and other tiny creatures far more readily than mercury can. The concentration of heavy metals increases when larger living beings devour the smaller living species that make up the food chain [42].

## MATERIALS AND METHOD

$Fe^{3+}$, $Cu^{2+}$, $Pb^{2+}$, and $Zn^{2+}$ were chosen for study because these ions are found abundant volume in wastewater. The initial ion’s level in industrial effluent was measured from Hub, Balochistan. Deionized water was utilized throughout the experiment. pH meter was used for measuring solution pH, afterward corrected and checked level of pH by addition of HCl or NaOH until end of the experiment.

Zeolite (natural and synthetic) was utilized for ions removal. A ZEISS EVO50 scanning electron microscope was used to examine the surface topography and morphology of the raw and zeolitic materials. An Emscope SC500 sputter coater was used to provide a gold coating to the samples. Images were captured uutilizingthe secondary electron detector in a high vacuum environment.

The elemental analysis or chemical characterization of the materials was done in this research using the Energy Dispersive Spectroscopy analytical method. A chemical microanalysis method called EDS may be used in conjunction with SEM. The samples were prepared similarly to how the SEM samples were for the EDS study. X-ray diffraction (XRD) method was used for natural zeolite identification. XRF analysis method was used for zeolite composition.

The measurement of changes in the physical and chemical characteristics while continuously raising the temperature was done using the thermo gravimetric analysis method. Thermogravimetry was used to analyse the raw materials between 30 and 1000 °C using a Perkin Elmer TGA7 thermobalance. The TGA was heated at a rate of 20 °C min-1 with nitrogen as the environment. For TGA testing, 10-15 mg of pulverised sample was immediately added to the crucible. The TGA crucible was thoroughly cleaned both before and after each test. At each level, the TGA patterns' findings were analysed and evaluated. This analytical method proved extremely helpful in determining the thermal stability of goods made from synthetic zeolite and thermally treated zeolite.

In this investigation, a materials examination was carried out using an FTIR Platinum ATR single-reflection diamond module made by ALPHA. A sample's fingerprint is represented by an infrared spectrum.

Before analysis, samples were filtered using Whatman filter sheets to get rid of any particulates they could have contained. To make a blank solution and dilute all samples and standards, 2 percent nitric acid was utilised. Acid concentrations in the samples were diluted to fall within the desired range of less than 5%. 10 ml of the material were placed in a 15 ml centrifuge vial before being examined.

## RESULTS AND DISCUSSION

In this investigation, native zeolite, kaolinite, and synthesis product samples were examined using a variety of analytical methods.

The diverse natural zeolite materials' surf ace morphologies both before and after alteration were examined. The micrographs of the "as received" natural zeolite samples are shown in Figure 1.

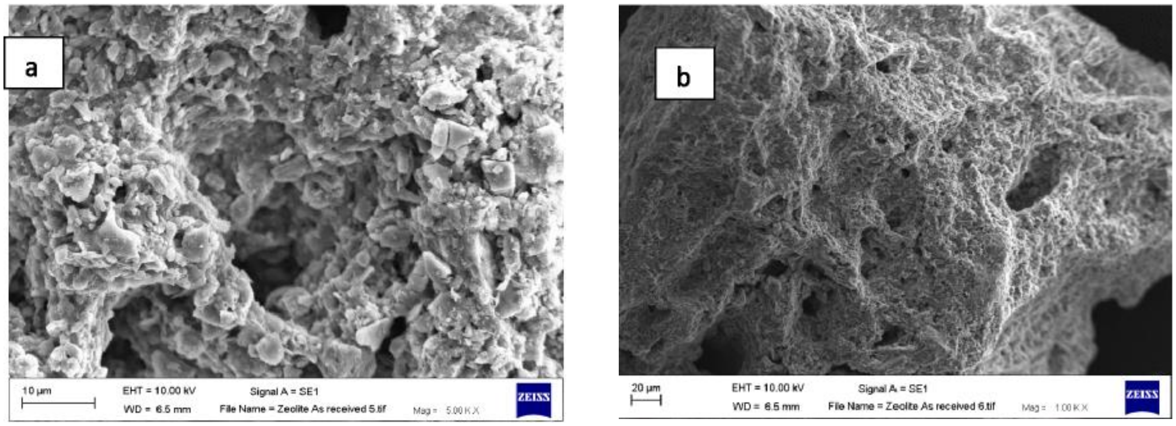


**Figure:1** **displaying natural zeolite (a) 50x and (b) 100x.**

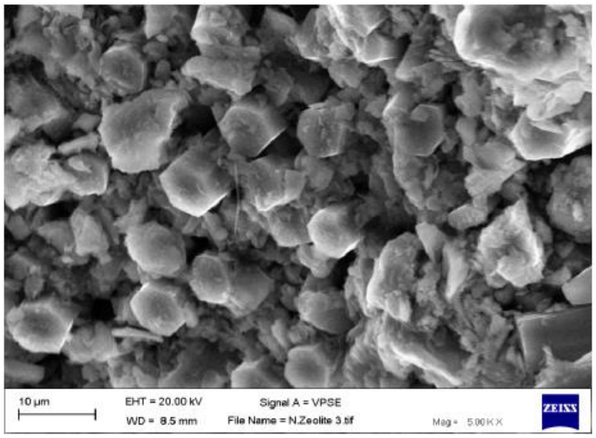


**Figure: 2** **Highlight zeolite (natural) the crystal structure.**

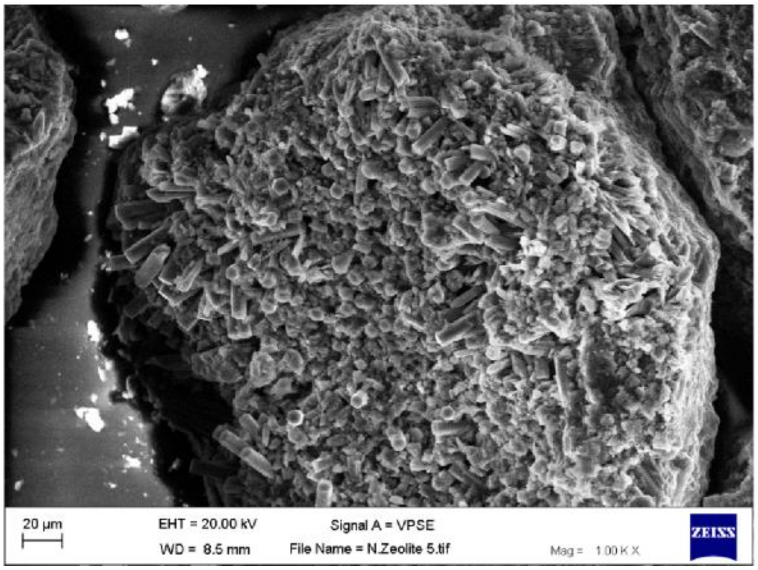


**Figure: 3 Highlighting the crystalline character of natural zeolite.**

As shown in figure 4, well defined structures of clinoptiloite has a clear surface in micrographs.

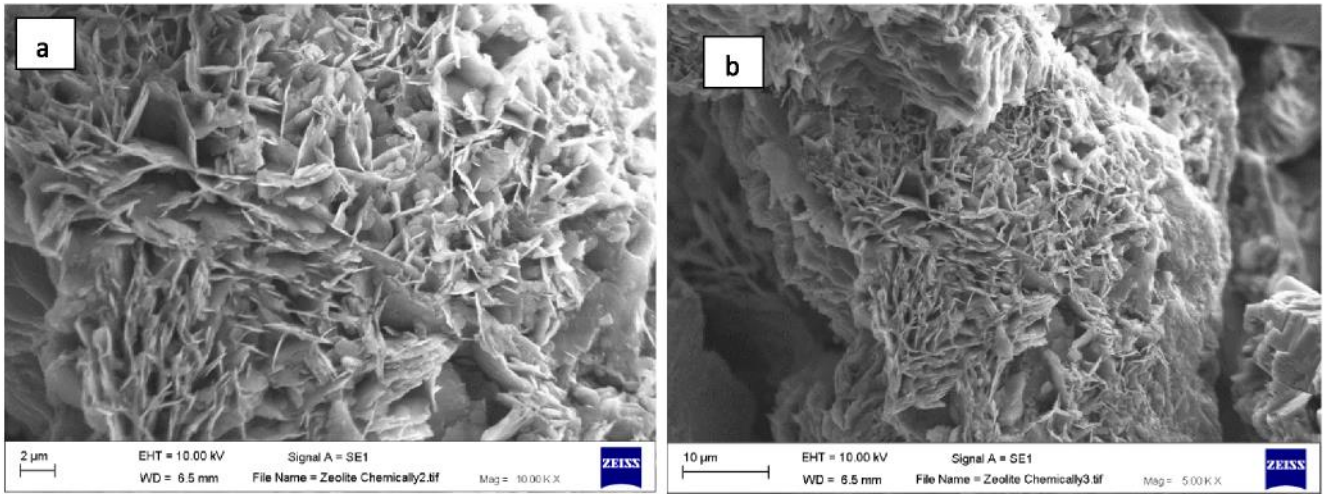


**Figure** 4: **SEM micrographs of natural zeolite (Clinoptilolite) (a) 10x and (b) 50x.**

Natural zeolite samples were heated for 30 minutes at 200, 400, and 600°C in a furnace. The whole undesirable volatile material was removed from zeolite via thermal pre-treatment, but eventually, the structure of the material was lost. Figure 5(a) demonstrates that thermally treated natural zeolite at 200ºC did not significantly alter its microstructure. The crystals' surfaces seem to have significantly disintegrated after being heated directly at 400ºC. (b). The unique crystal structures of clinoptilolite have vanished.

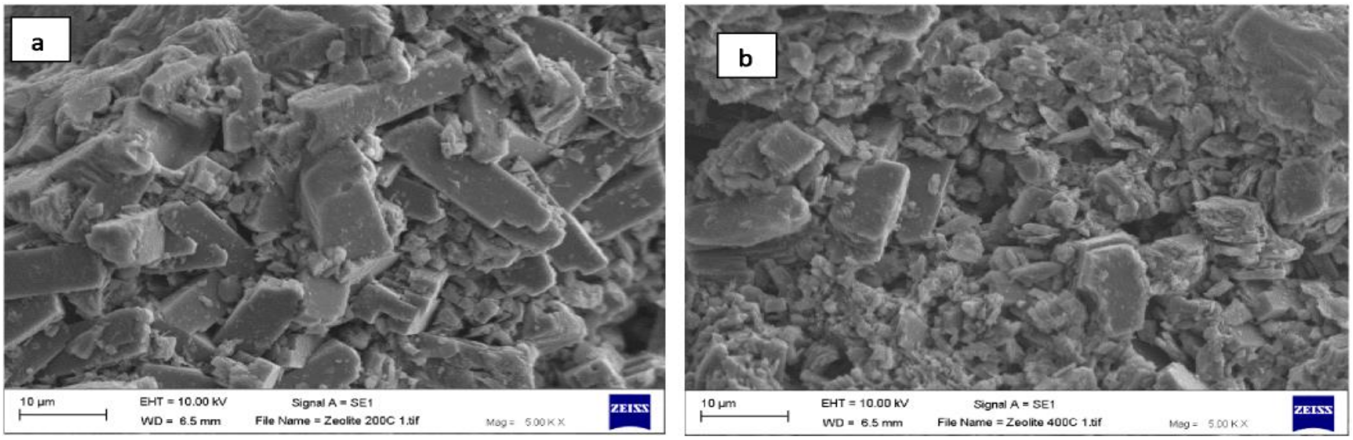


**Figure** 5: Natural zeolite's SEM microstructure after heat pretreatment.

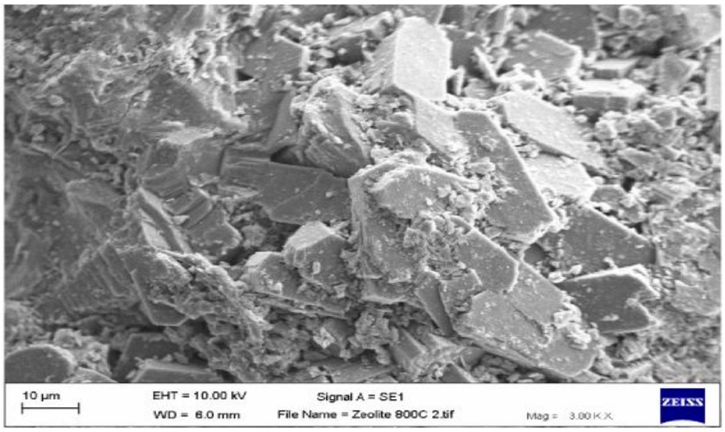


**Figure 6: Demonstrate zeolite (natural) collapse at 600ºC.**

Figure 7 makes clear how the various components of the sample were examined. All natural zeolite samples' elemental compositions were quickly revealed in the meanwhile. EDS was used to identify the primary elements and their associated oxides. In appendix A, four analysed locations are localised and given numerical designations, along with a typical EDS spectrum.

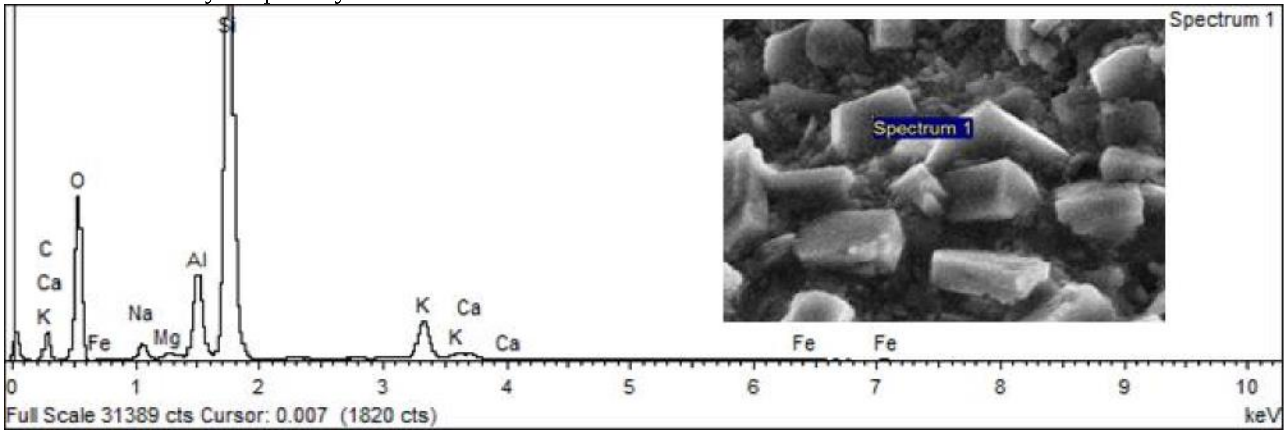


**Figure 7: EDS study displaying natural zeolite's scanned picture and elemental makeup.**

According to the EDS analysis findings, $Na^+$, $Mg^{2+}$, $K^+$, and $Ca^{2+}$ were discovered to be the main exchangeable cations in the natural zeolite structure. The bulk of the sample was found to contain clinoptilolite, according to the XRD results (Figure 8).

**Table 1: Natural zeolite elemental composition and scanning process as shown by EDS study.**

| Element | Na2O % | MgO % | Al2O3 % | SiO2 % | K2O % | CaO % | TiO2 % | Fe2O3 % |
|---|---|---|---|---|---|---|---|---|
| wt.% | 1.33 | 0.29 | 3.93 | 21.22 | 2.39 | 0.31 | 0.06 | 0.34 |

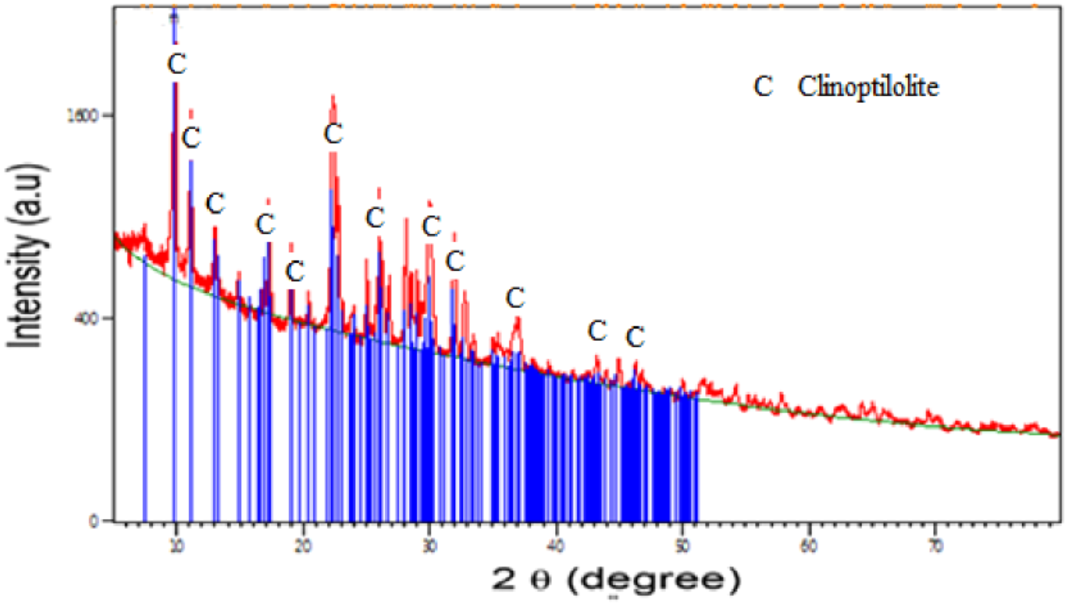


**Figure 8: Clinoptilolite's mineralogical analysis as seen by an X-ray diffractogram (Natural Zeolite).**

Table 2 displays the findings of the XRF study. In contrast to the findings of the EDS study, the results demonstrate that $SiO_2$, $Al_2O_3$, $Na_2$, and $K_2O$ are the primary components of natural zeolite. The findings of the EDS study also revealed that $Na^+$, $Mg^{2+}$, $K^+$, and $Ca^{2+}$ were the most common cations which are ex-changeable.

**Table2: Natural zeolite's chemical makeup, expressed as a percentage.**

| Element | $Na_2O$ % | MgO % | $Al_2O_3$ % | $SiO_2$ % | $K_2O$ % | CaO % | $TiO_2$ % | $Fe_2O_3$ % |
|---|---|---|---|---|---|---|---|---|
| **wt.%** | 4.12 | 0.89 | 4.53 | 37.97 | 2.12 | 0.96 | 0.06 | 0.74 |

After heating at high temp: there were loss of weight has been observed continuously in clinoptilolite samples (Fig 9). de-hydroxylation and de-hydrations are both process which are involved in major loss of weight [43–45].Dehydroxylation occurred between 400 and 600 °C [46-47] and two types of hydroxyl groups and water molecules were found.

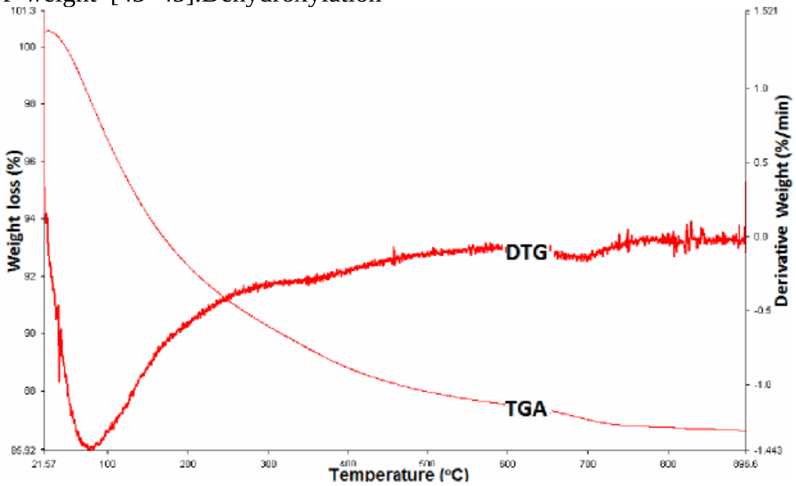


Figure 9: **TGA of clinoptilolite.**

According to the findings, water was responsible for any loss below 400 °C in zeolitic materials. The thermogravimetric study revealed a total loss of 13 weight percent. Other writers [48–50] also got results that were comparable. The development of sodalite may be the cause of a new peak in the DTG pattern of clinoptilolite around 750–800ºC.

For the purposes of this study's materials investigation, the structure of zeolites is investigated using FTIR spectroscopy.

In this work, FTIR is used to characterise zeolites. Only the 1200-400 cm-1 range was examined; all spectra indicated notable variations in this area. All of the adsorbents exhibit a wide band between 3500 and 3700 cm-1. Results from FT-IR analysis show that zeolites are considerably hydrated (Figure 10). These findings coincide with those of other writers [51–55].

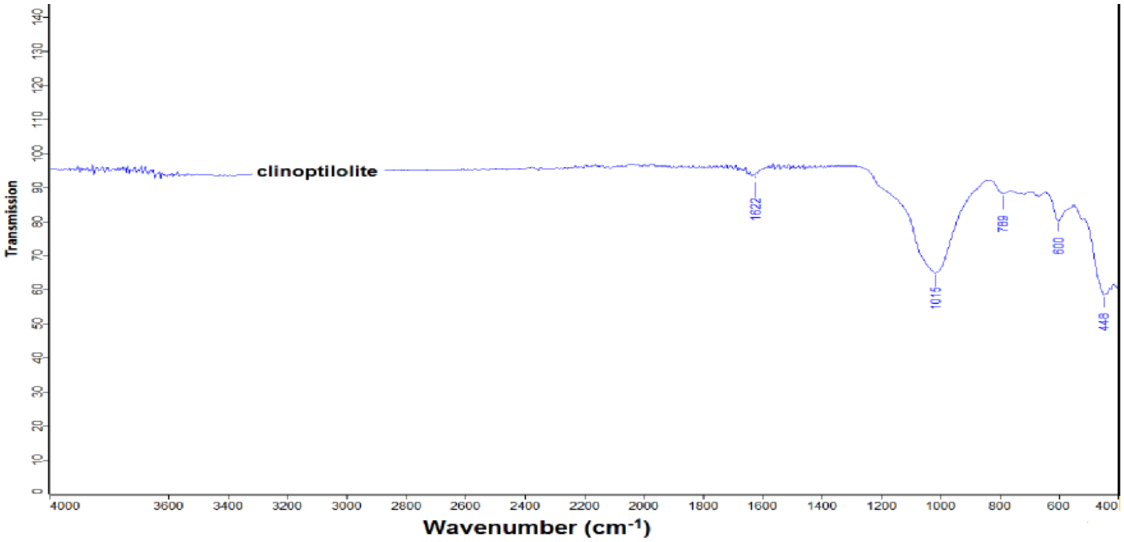


**Figure 10: demonstrates the FT-I R spectrum analysis of the cli noptilolite as received.**

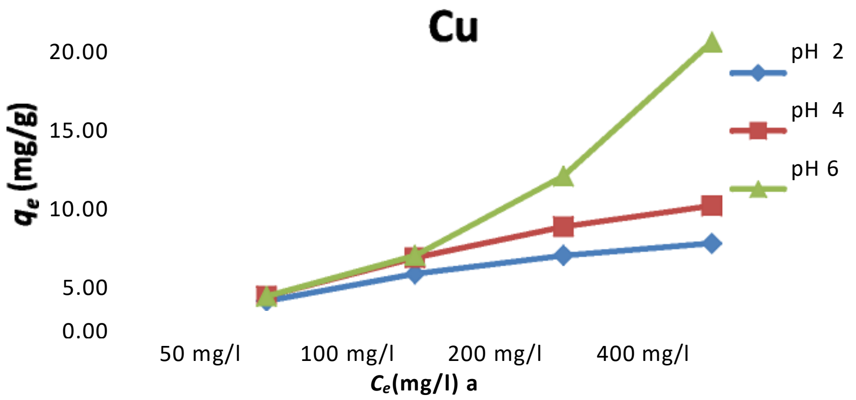
ICPOES was used to calculate the amounts of heavy metal ions in the waste water solution. The outcomes were shown in below (table-3).

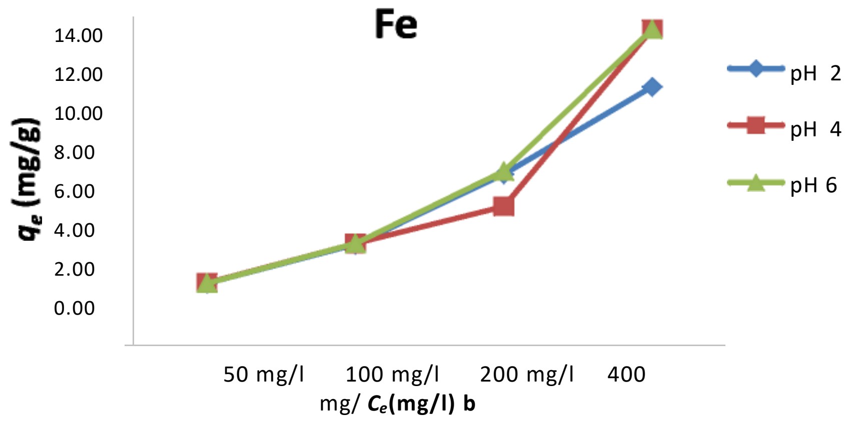
**Table 3 Equilibrium adsorption calculations.**

| composition of material | Initial pH | Langmuir | | |
|---|---|---|---|---|
| | | Q(mg/g) | b (l/mg) | Correlation coefficient ($r^2$) |
| **$Cu^{2+}$** | 2 | 6.33 | 1.506 | 0.99 |
| | 4 | 8.896 | 2.155 | 0.99 |
| | 6 | 22.83 | 3.325 | 0.93 |
| **$Fe^{3+}$** | 2 | 8.13 | 2.414 | 0.99 |
| | 4 | 14.92 | 5.449 | 0.98 |
| | 6 | 14.71 | 7.131 | 0.99 |
| **$Pb^{2+}$** | 2 | 13.70 | 198.5 | 0.99 |
| | 4 | 1.039 | 0.28 | 0.99 |
| | 6 | 14.49 | 216.3 | 0.93 |
| **$Zn^{2+}$** | 2 | 13.33 | 3.07 | 0.93 |
| | 4 | 13.89 | 3.54 | 0.94 |
| | 6 | 17.54 | 6.34 | 0.96 |
| | | | | |

The Langmuir isotherms for the removal of metals from solution provide a straight line, as shown in Table 3. When the pH of the original solution rises, the adsorption capacity often rises as well. The sorption data with all r2 values more than 0.93 were successfully and substantially shown using the Langmuir model. $Cu^{2+}>Zn^{2+}>Fe^{3+}>Pb^{2+}$ was created via sorption on the zeolite, according to the Q parameter.

Figure 11 below demonstrates how more metal is adsorbing into the natural zeolite surface (qe).





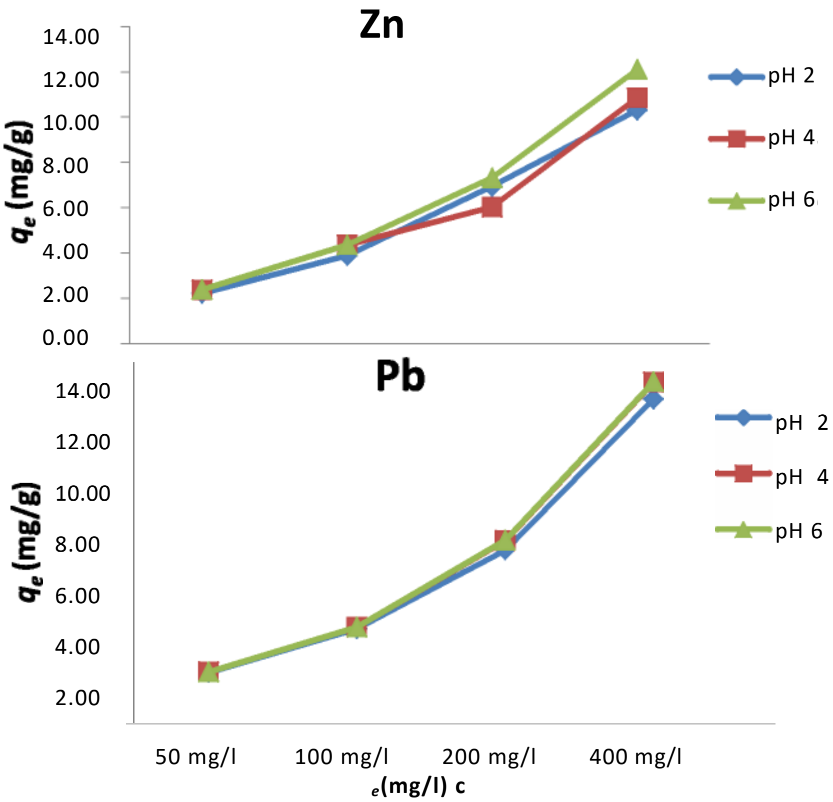
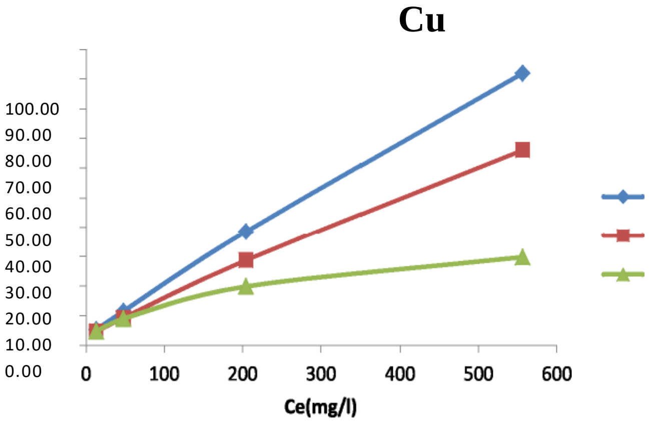


**Figure11:-a,b,c&d** **displaying the results of an experiment on the elimination of metals at various pH levels.**

Figure 11 also graphically displays the natural zeolite's ability to adsorb $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$, and $Zn^{2+}$ at various starting solution pH values. It is evident that the adsorption capacity of the adsorbent increases as the pH of the solution rises. The concentration of $H^+$ ions has decreased, which is mostly to blame.



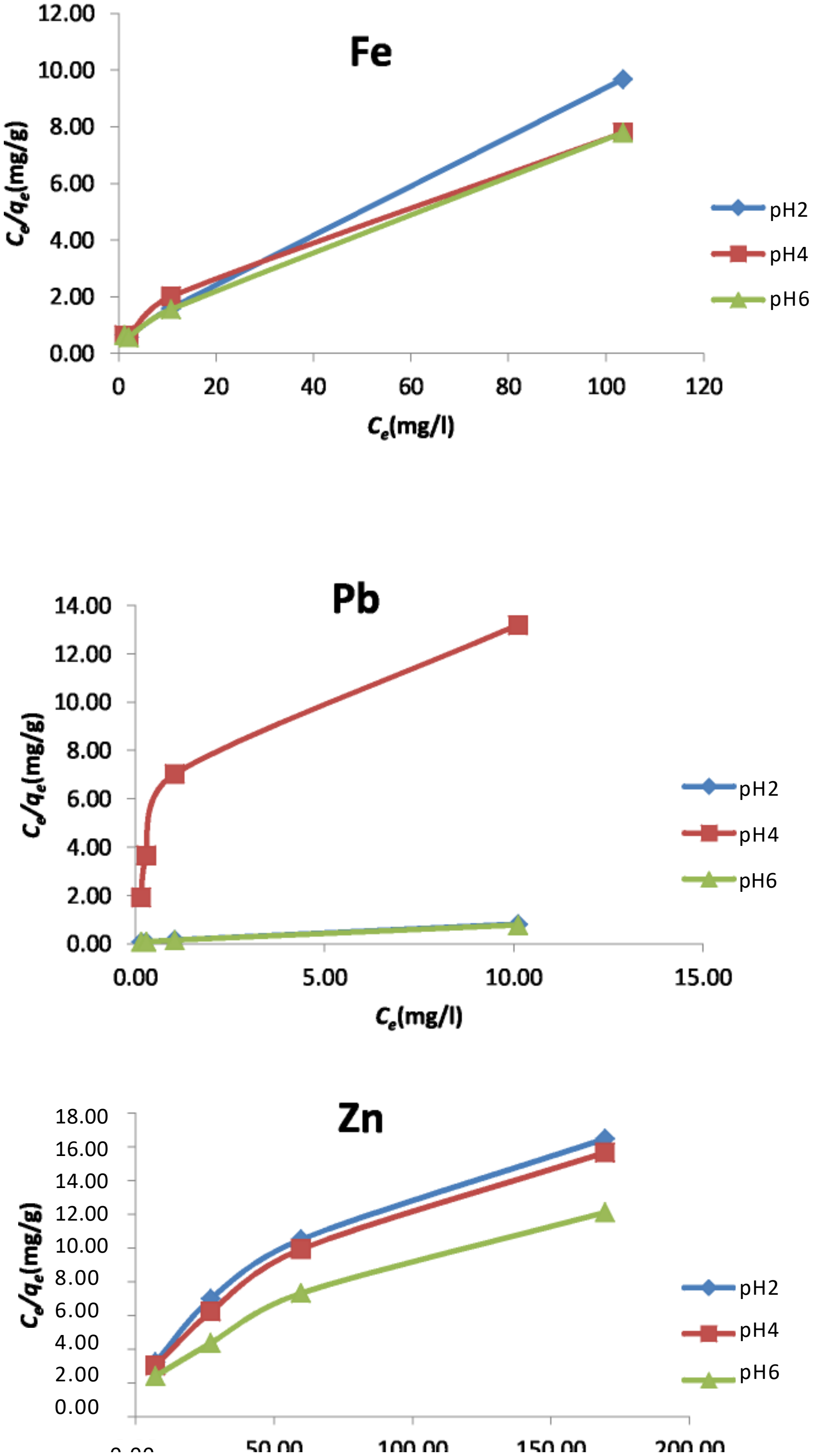


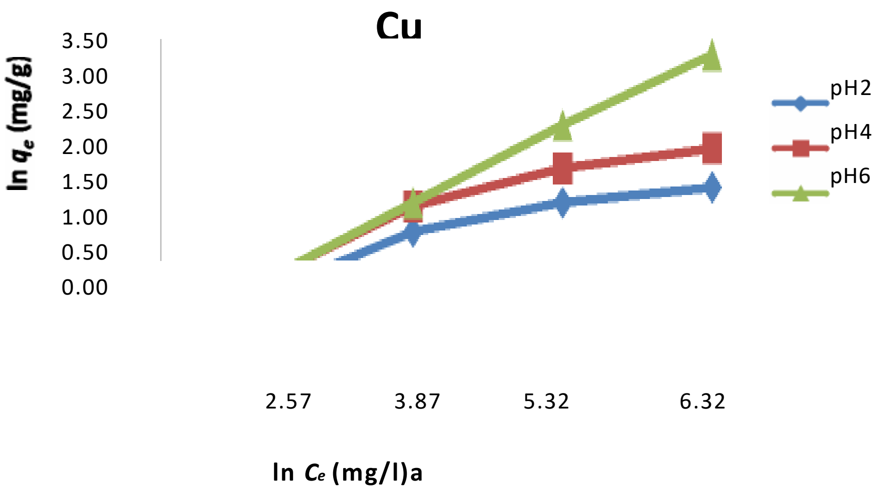
**Figure: 12**Removal of metals via equilibrium adsorption utilising Langmuir isotherm constants

Figure 12 shows that there is a fluctuation in pH values, the often higher values in equilibrium than the original pH adjustments. This could be brought on by the rising initial concentrations of investigated metals. When the values of k and n were determined and the relationship between lnqe and lnCe was plotted throughout the whole concentration range of the metal ions studied, a linear plot was produced. (Table 2

**Table-4 Equilibrium adsorption calculations ion removal from solution using Freundlich isotherm constants.**

| composition of material ppm | Initial pH | Freundlich | | |
|---|---|---|---|---|
| | | *k* (l/mg) | *1/n* | Correlation coefficient ( *r2)* |
| $Cu^{2+}$ | 2 | 1.47 | 0.24 | 0.93 |
| | 4 | 1.45 | 0.29 | 0.94 |
| | 6 | 1.33 | 0.50 | 0.99 |
| $Fe^{3+}$ | 2 | 2.29 | 0.36 | 0.90 |
| | 4 | 2.13 | 0.95 | 0.95 |
| | 6 | 2.23 | 0.41 | 0.94 |
| $Pb^{2+}$ | 2 | 3.22 | 1.85 | 0.95 |
| | 4 | 3.22 | 1.82 | 0.96 |
| | 6 | 3.20 | 1.81 | 0.96 |
| $Zn^{2+}$ | 2 | 1.23 | 0.50 | 0.97 |
| | 4 | 1.10 | 0.47 | 0.99 |
| | 6 | 1.20 | 0.52 | 0.99 |

The Freundlich isotherms for the adsorption of $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$, and $Zn^{2+}$ from solution provided excellent fits for the experimental findings, as shown in Table 4. The correlation coefficient, or r2 value, ranged from 0.90 to 0.99, which amply demonstrated this. Table 4's findings reveal that all of the metals $Fe^{3+}$, $Cu^{2+}$, and $Zn^{2+}$ have numerical values of 1/n 1, with the exception of $Pb^{2+}$, which has a value of 1/n > 1, n values ranged 2-10 for zeolite correlated excellent adsoprtion [56–57]. The findings demonstrate that the pH of the solutions gradually rose during the equilibrium studies. Figures (11), (12), and (13), respectively, show how the pH changes as a function of the equilibrium concentrations of $Cu^{2+}$, $Fe^{+}3$, $Pb^{2+}$, and $Zn^{2+}$.



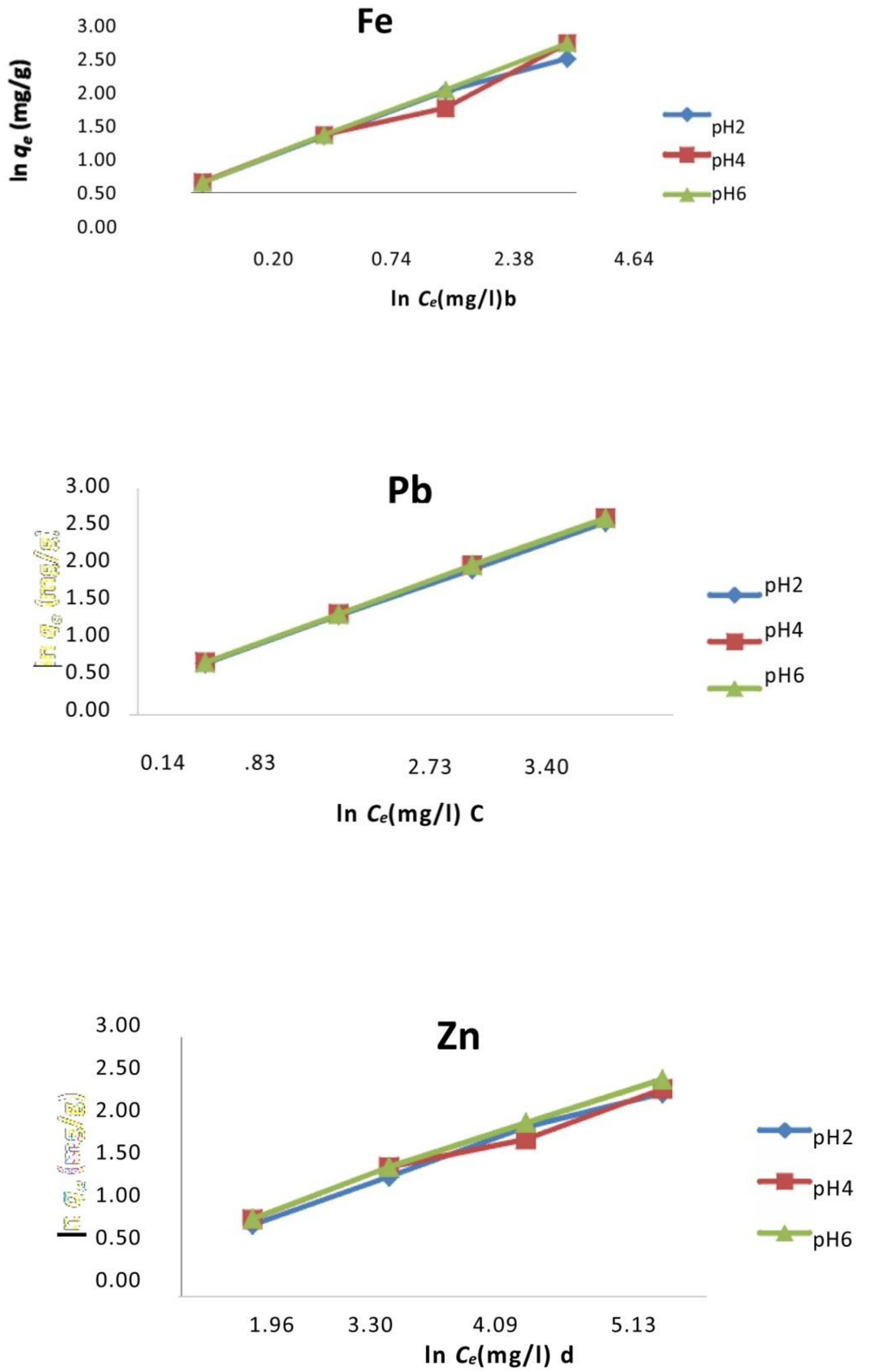


**Figure:13**-a,b,c&d **Equilibrium adsorption is used in conjunction with Freundlich isotherm constants.**

## CONCLUSION

To learn more about the properties of natural zeolite samples, various analytical techniques were used in this study.

SEM was used to analyses the surface morphology of the various natural zeolite samples. The "as received" natural zeolite micrographs display a variety of different size macro-pores (1 m d 2 m) within the zeolite structure. The majority of the natural zeolite crystals in the micrographs are clearly defined.

The SEM images depict some clearly defined zeolite crystals at 200 $^{0}$C, but further thermal processing causes some of the crystals' surface porosity to be lost and some of their crystalline structure to be decomposed.

The zeolite was chemically pre-treated using acidic NaCl solutions.

The results of the EDS and XRF analyses revealed that the primary elements of natural zeolite were SiO2, Al2O3, Na2O, and K2O. The research also reveals that Na+, Mg2+, K+, and Ca2+ were the most common exchangeable cations in the natural zeolite structure.

Results demonstrate that when undergoing dehydroxylation and dehydration, clinoptilolite samples are continuously losing weight.

The equilibrium experiments showed that natural zeolite was effective in removing heavy metals from mixtures of different components.

The experimental results were represented using the Langmuir and Freundlich isotherm models, and the models suited the data perfectly.

## REFERENCES

1. Pandey, P., Sambi, S.S., Sharma, S.K. and Singh, S. (2009) Batch Adsorption Studies for the Removal of Cu (II) Ions by ZeoliteNaX from Aqueous Stream. *Proceedings of the World Congress on Engineering and Computer Science*, **I,** San Francisco, USA
2. Misaelides, M (2011) Application of natural zeolites in environmental remediation: A short review. *Microporous and Mesoporous Materials,* **144,** pp. 15–18.
3. Tchobanoglous G. and Burton F.L. (1991) *Wastewater Engineering: Treatment, Disposal, Reuse.* 3rd ed. Signapore: McGraw-Hill International Editions.
4. Papageorgiou, K.S., Katsaros, K.F., Kouvelos, P.E., Nolan, W.J., LeDeit, H. and Kanellopoulos, K.N. (2006) Heavy metal sorption by calcium alginate beads from Laminaria digitata. *Journal of Hazardous Materials,* **B137,** pp.1765 – 1772.
5. Milton (1968) Molecular Sieves. *Journal of the Society of Chemical Industry,* **68,** pp. 199– 203.
6. Alvarez-Ayuso, E., Garcia-Sanchez, A., and Querol, X. (2003) Purification of metal electroplating waste waters using zeolites. *Water Research,* **37,** pp. 4855-4862.
7. Peric, J., Trgo, M. and Medvidovic, N.V. (2004) Removal of zinc, copper and lead by natural zeolite-a comparison of adsorption isotherms. *Water Research,* **38,** pp. 1893-1899.
8. Mulligan, C. N., Yong, R. N., Gibbs, B. F. (2001) Heavy metal removal from sediments by biosurfactants. *Journal of Hazardous Materials, **85,*** pp.111–125.
9. United Nations Framework Convention on Climate Change (2007) updated.[online].[accessed 10 August 2016] Available at: <http://unfccc.int/kyoto_protocol/items/2830>.
10. Deunert, R., Lennart, B. and Tiemeyer, B. (2007) Legislative effects on the development of surface water quality in rural areas in Northern Germany. *Cleaner Production,* **15(16),** pp. 1507 – 1513.
11. Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D. (1999) A review of potentially low– cost sorbents for heavy metals. *Water Research,* **11(33),** pp. 2469 – 2479.
12. Peng, J., Song, Y., Yuan, P., Cui, X. and Qiu, G. (2009) The remediation of heavy metals contaminated sediment. *Journal of Hazardous Materials,* **161**(2 **-** 3), pp. 633 – 640.
13. Babel, S. and Kurniawan, T.A. (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials,* **97(1),** pp.219 – 243.
14. Millennium Development Goals (2000) Global Water Supply and Sanitation Assessment Report 2000, WHO, Geneva, Switzerland [On line] [Accessed 5th November 2016]. available at< http://www.who.int/water_sanitation_health/monitoring/jmp2000.pdf >.
15. Payra S. and Dutta P. K. (2003) Handbook of Zeolite Science and Technology, Marcel Dekker :New York, pp. 1–19.
16. Crini, G. (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science,* **30,** pp.38-70.
17. Inglezakis, V.J., Loizidou, M.M. and Grigoropoulou, H.P. (2004) Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility. *Journal of Colloid and Interface Science,* **275(2),** pp. 570 – 576.
18. Margeta, K., Logar, N.Z., Šiljeg, M. and Farkaš, A.(2013) Natural Zeolites in Water Treatment – How Effective is Their Use, Chapter 5 [online][accessed on 08 November 2016] available at: <http://www.intechopen.com/books/water-treatment/natural-zeolites-in-watertreatment-how-effective-is-their-use>.
19. Payne, K.B. and Abdel-Fattah,T.M. (2004) Adsorption of Divalent Lead Ions by Zeolites and Activated Carbon: Effects of pH, Temperature, and Ionic Strength. *Journal of Environmental Science and Health,* **39(9),** pp.2275-91
20. Baccouche, A., Srasra, E. and Maaoui, M.E. (1998) Preparation of Na-P1 and sodalite octahydrate zeolites from interstratified illite-smectite. *Applied Clay Sciences,* **13,** pp.255-273.
21. Inglezakis, V.J., Loizidou, M.D. and Grigoropoulou, H.P. (2002) Equilibrium and kinetic ion exchange studies of $Pb^{2+}$, $Cr^{3+}$, $Fe^{3+}$ and $Cu^{2+}$ on natural clinoptilolite. *Water Research,* **36,** pp.2784-2792.
22. Oztas, N.N., Karabakan, A. and Topal, O. (2008) Removal of Fe (III) ion from aqueous solution by adsorption on raw and treated clinoptilolite samples. *Journal of Microporous and Mesoporous Materials,* **111**(1 **–** 3), pp. 200 – 205.

23. Colella, C. (2007) Environmental applications of natural zeolitic materials based on their ion exchange properties. *Natural Microporous Materials in Environmental Technology,* **362,** pp 207-224.
24. Blanchard, G., Maunaye, M. and Martin, G. (1984) Removal of heavy metals from waters by means of natural zeolites. *Water research,* **18(12),** pp. 1501 -1507.
25. Erdem, E., Karapinar, N. and Donat, R. (2004) The removal of heavy metal cations by natural zeolites. *Journal of colloidal and Interface Science,* **280(2),** pp. 309 – 314.
26. Inglezakis, V.J., Hadjiandreou, K.J., Loizidou, M.D., Grigoropoulou, H.P. (2001) Pretreatment of natural clinoptilolite in a laboratory-scale ion exchange packed bed. *Water Research,* **35 (9),** pp. 2161-2166.
27. Breck, D.W. (1974) *Zeolite Molecular Sieves: Structure, Chemistry and Use,* 1st ed. John Wiley: New York.
28. Galli, E., Gottardi, G., Mayer, H., Preisinger, A., Passaglia, E. (1983) crystallography journals,[online] **.B 39,** pp.189.< http://journals.iucr.org>.
29. Inglezakis, V.J., Stylianou, M .A., Gkantzou, D. and Loizidou, M.D. (2007) Removal of Pb (II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents. *Desalination,* **210(3),** pp. 248 - 256.
30. Ouki, S. K. and Kavannagh, M. (1999) Treatment of metals contaminated wastewaters by use of natural zeolites. *Water Science and Technology,* **39**(10-11), pp.115 – 122.
31. Patterson, J.W. (1987) *Metal Speciation Separation and Recovery,* Chelsea: Lewis Publishers.
32. Ozaydin, S., Kocar, G. and Hepbasli, A. (2006) Natural zeolites in energy applications, *Energy Sources Part A: Recovery Utilization and Environmental Efects.* **28,** pp. 1425-1431.
33. Tien, C. (1994) *Adsorption calculations and modelling.* Butterworth – Heinemann: New York.
34. Inglezakis, V.J., Zorpas, A.A., Loizidou, M.D., Grigoropoulou, H.P. (2003) Simultaneous removal of metals Cu2+, Fe3+ and Cr3+ with anions SO42- and HPO42- using clinoptilolite. *Microporous and Mesoporous Materials,* **61,** pp. 167-171.
35. Kesraoui, O.S., Cheeseman, C. R. and Perry, R. (1994) Natural zeolite utilisation in pollution control: A review of applications to metals' effluents. *Journal of Chemical Technology & Biotechnolog,* **59(2),** pp. 121-126.
36. Wang, S.B, Ang, H.M. and Tadé, M.O. (2008) Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes. *Chemosphere,* **72,** pp. 1621-1635.
37. Amarasinghe, B.M.W. and Williams, R.A. (2004) Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal,* **132,** pp.299 – 309.
38. Panayotova, M. and Velikov, B. (2003) Influence of zeolite transformation in the homoionic form on the removal of some metal ions from wastewater. *Journal Science and Health,* **A38(3),** pp. 545 – 554.
39. Gunay, A., Arslankaya, E. and Tosun, I. (2007) Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials,* vol. **146(2),** pp. 362 – 371
40. Gedik, K and Imamoglu, I. (2008) Removal of cadmium from aqueous solutions using clinoptilolite: Influence of pretreatment and regeneration. *Journal of Hazardous Material,* **155(2),** pp. 385 – 392.
41. Colella, C. (1999) Natural zeolites in environmentally friendly processes and applications. *Studies in Surface Science and Catalysis.* **125,** pp. 641–655.
42. In Depth Tutorials and Information (2017) Bioaccumulation of Heavy Metals (Water Science)available at [http://what-when-how .com/water-science/bioaccumulation-of -heavymetals-water-science/].
43. Sprynskyy, M., Boguslaw B., Terzyk, A.P. and Namiesnik, J. (2006) Study of the selection mechanism of heavy metal ($Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Cd^{2+}$) adsorption on clinoptilolite. *Journal of Colloid and Interface Science,* **304,** pp.21 -28.
44. Dyer, A. (1988) *An introduction to zeolite molecular sieves.* GB: John Wiley& Sons Ltd.
45. Gottardi, G. and Galli, E. (1985) *Natural Zeolites.* Berlin Heidelberg: Springer Verlag.
46. Colella, C. and Wise, W.S. (2014) The IZA Handbook of Natural Zeolites: A tool of knowledge on the most important family of porous minerals. *Microporous and Mesoporous Materials,* **189,** pp.4–10.
47. Ribero, F.R, Rodrigues,A.E., Rollmann, L.D. and Naccache, C. (1984) *Zeolite:Science and Technology.* Lancaster: Martinus Nijhoff.
48. Korkuna, O., Leboda, R., Skubiszewska-Ziemba, J., Vrublevska, T., Gunko, V.M. and Ryczkowski, J. (2006) Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. *Microporous and Mesoporous Materials,* **87,** pp. 243.
49. Al-Dwairi, R.A. (2009) The Use of Expendable Local Zeolite Deposits for NH4 Removal in Municipal Wastewater. *Jordan Journal of Civil Engineering,* **3(3),** pp. 256 -263.
50. Ugal, J.R., Hassan, K.H. and Ali, I.H. (2010) Preparation of type 4A zeolite from Iraqi kaolin: Characterization and properties measurements. *Journal of the Association of Arab Universities for Basic and Applied Sciences,* **9,** pp. 2–5.
51. Li, G. (2005) FT-IR studies of zeolite materials: characterization and environmental applications." PhD diss., University of Iowa.<http://ir.uiowa.edu/etd/96>.
52. Wilson, M .J. (1994) *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods.* Chapman and Hall: New York, 1994.
53. Tanaka, H., Yamasaki, N., Muratani, M.and Hino, R. (2003) Structure and formation process of (K, Na) - clinoptilolite. *Materials Research Bulletin,* **38,** PP.713.
54. Olad, A. and Naseri, B. (2010) Preparation, characterization and anticorrosive properties of a novel polyaniline/clinoptilolite nanocomposite. *Progress in Organic Coatings,* **67,** pp.233 - 238.

55. Perraki, T. and Orfanoudaki, A. (2004) Mineralogical study of zeolites from Pentalofos area. *Applied Clay Science,* **25,** pp.9-6.
56. Faghihian H., Marageh M.G., Kazemian H. (1999) The use of clinoptilolite and its sodium form for removal of cesium and strontium from nuclear wastewater and $Pb^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Ba^{2+}$ from municipal wastewater. *Applied Radiation and Isotopes,* **50,** pp.655 – 660.
57. Panday K.K., Prasad, G. and Singh V.N. ( 1985) Copper(II) removal from aqueous solutions by fly ash. *Water Reserch,* **19(7),** pp.869–73.