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Analysis by IR, XRD, TGA, SEM and EDX for the Study on Zn(II) ions Exchange by Natural Zeolite and it's Adsorbed Derivative

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ABSTRACT

In the present work Stilbite (Natural Zeolite), Na-Zeolite are exchanged with Zn(II). The analysis of the parent zeolite and the exchanged derivative has been carried out using Inductive Couple Plasma-Atomic Emission Spectroscopy (ICP-AES). The exchanged derivative is then used to prepare adsorbed derivatives with N_2 *gas. The structural changes are studied by IR spectroscopy. The exchange percentage of Zn(II) with natural zeolite and Na-zeolite is maximum. In this study Scan Electron Microscopy (SEM) analysis for morphological structure and XRD technique is used to determine the unit cell structure of synthesized and natural zeolite. Also thermal studies of natural zeolite and its exchanged derivative are carried out using TGA (Thermal Gravimetric Analysis). For the same samples FESEM (Field Emission Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray Spectroscopy) analysis is also carried out.*

Keywords: Natural Zeolite (Stilbite), Na-Zeolite, ICP-AES, X-Ray Diffraction, IR, TGA, SEM, EDX etc.

INTRODUCTION

Zeolites are micro porous crystalline solids with well defined structures. Generally they contain silicon, aluminum and oxygen in their pores. Many occurs naturally as minerals and are extensively mined in many parts of the world, Others are synthetic and are made commercially for specific uses, or produced by research scientists trying to understand more about their chemistry. Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tons per annum. In the western country major application is in petrochemical cracking, ion-exchange (water softening and purification) and in the separation and removal of gases and solvents. Multifunctional Zeolite have attracted worldwide attention; zeolites are alluminosilicate crystals with a three dimensional framework of SiO_4 and AlO_4 and are used as ion-exchange materials, shape selective catalysts, petrochemical catalysis and adsorbents [1-3]. Many of the Natural zeolites now serve as petroleum refining, petrochemical and chemical process industries as a selective adsorbent, ion exchanger catalyst [4-5]. These are also used for cleaning up of municipal, industrial and nuclear wastewater [6-7]. The most fundamental consideration regarding the adsorption of chemical species by zeolites is molecular sieving.

Species with a kinetic diameter which makes them too large to pass through a zeolites pore are effectively sieved. This sieve effect can be utilized to produce sharp separations of molecules by size and shape.

The three dimensional crystalline framework of natural zeolite is formed by corner-sharing SiO_4 tetrahedral with the possibility to replace a few SiO_4 units by AlO_4 units, and an equivalent amount of cations to maintain the electronic neutrality of the structure. The cations associated with the Natural zeolite framework have played an important role in the field of catalysis. Natural zeolites are used widely for the adsorption of harmful gases [8]. The catalytic importance of Natural zeolite has prompted several investigations of its physical and chemical nature [9-10]. Because cations are free to migrate in and out of zeolite structures, zeolites are often used to exchange their cations for those of surrounding fluids. The preference of a given zeolite among available cations can be due to ion sieving or due to competition between the zeolite phase and aqueous phase for the cations that are present. The dimension of the channels of natural zeolite and ability to adsorb gases adds a new approach to automobile emission control. Zn(II) ions exchanged zeolites have been found their application in preventing environmental pollution.

The present work is carried out to find the stability and suitability of the natural zeolite and exchange derivatives for catalysis and pollution abatement.

MATERIALS AND METHODS

The natural zeolite (stilbite) used in this work was collected from Dhule and Jalgaon district from Maharashtra (INDIA). These zeolite crystals were kept in contact with the saturated solution of sodium chloride. Heating up to 100^oC for 8 hours, stirring and cooling was continued for 10 days to ensure maximum exchange. The zeolite crystals dried up to 150^oC after the removal of anions. These are then exchanged with Zn(II) ions through the same procedure. Both the parent zeolite and its exchanged derivative are then studied by ICP-AES (Inductive Couple Plasma with Atomic Emission Spectroscopy) for the determination of Na(I), Zn(II), aluminium and silicon contents. The IR spectra of the zeolites and its exchanged derivatives are carried out on FTIR spectrometer model SIMADZU 8400 S PC by using KBr pellet in the region 400-4000 per cm with 4.0 per cm resolution. The adsorbed derivatives have been prepared from exchanged derivatives using continuous flow of N_2 gas. X-ray diffraction patterns are obtained between 2^o angles of 5^o to 80^o using Cu K^0 radiations of wavelength 1.5414 A^o.

Thermo gravimetric Analysis is used to find the thermal stability of exchange and adsorbed derivatives. The analysis is carried out using Perkin-Elmer STA 600 Serial Number: 521A00813090, Thermal Analyzer. The samples are heated from 50°C to 800°C at 20°C min^{-1}. Field emission scan electron microscopy is carried out for characterization of the surface morphology on Hitachi High Technologies Corporation, Japan (model no. S-1800 Type-II). Also energy dispersive X-ray spectroscopy is used to characterize the elemental composition by Bruker AXS GmbH Germany (model X-flash Detector).

RESULTS AND DISCUSSION

The compositional analysis of the Na-metal with the natural zeolite (stilbite) and its exchanged derivatives shows exchange in ppm as shown in table-1 follows. Also its exchanged derivative shows for Zn(II) ions mentioned in the same table.

Table 1. The analysis of metals by ICP-AES

Sr.No.	Name of the Sample	Si in ppm	Al in ppm	Na in ppm	Zn in ppm
1	Zeolite (Stilbite) Crystals	108.7	304.3	---	---
2	Na+Zeolite Sample Crystals	182.2	119.8	961.902	---
3	Zeolite+Zn(II) Sample Crystals	49.3	11.4	---	7956.1
4	Na-Zeolite+Zn(II) Sample Crystals	125.6	27.3	6821.2	22516.5

IR Analysis: The IR spectra of the natural zeolite, Na-zeolite and their derivatives of Zn(II) are shown in the figs.1-4. IR spectroscopy has been used to determine structural changes due to cation exchange and adsorption between 4000 cm^{-1} - 400cm^{-1} in KBr using FTIR spectrometer model SIMADZU 8400 S PC with 4.0 per cm resolution. The IR spectra of the natural zeolite (stilbite) is shown in the (fig.-1), and its parent zeolite (Na-zeolite) is shown in the (fig-2). The IR spectra of the exchange derivatives of natural zeolite and Zn(II) metal (fig-3) are quite similar to the parent zeolite (Na-zeolite) except shifts of O-H and T-O stretching vibrations. The hydroxyl group present in cation-exchanged form of zeolite is responsible for many catalytic properties. A peak in the water region of Na-zeolite contains zeolitic and mobile water (12). A shift of O-H band from 3552 cm^{-1} in Na-zeolite to the lower side of the spectrum has been observed in all the cases, due to decrease in O-H bond strength. The O-H band appears at 3446 cm-1 in Zn(II) ions exchanged Na-zeolite (fig.-4). The bending vibrations of O-H molecules is unaffected by cation substitution, which is substantiated by the cation exchanged derivatives. The position of the peaks observed in IR spectra of all the ion exchanged samples is reported in (Table-2). The frequencies related to the vibrations Si-O-Si and Si-O-Al bands of external linkage vary with cation substitution. The stretching modes are sensitive to Si-Al composition of the framework and vary with the increasing number of tetrahedral aluminium atoms. A shift to higher frequency side is observed for the asymmetric vibrations of external linkage. The spectra of the adsorbed derivatives show the bands due to the adsorption the positions of the peaks for the adsorbed derivatives are given in (Table-2).

Zeolites are crystalline micro-porous, hydrated aluminosilicates that are built from an infinitely extending three-dimensional network of $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetrahedral linked to each other by the sharing of oxygen atom. Generally, their structure can be considered as inorganic polymer built from tetrahedral TO_4 units, where T is Si^{4-} or Al^{3+} ion. Each oxygen (O) atom is shared between two T-atoms.

Table 2 . Result of IR Spectroscopic and Thermo-Gravimetric Analysis of ion-exchanged derivatives

Sr.No.	**Name of Sample**	**Total Wt. Loss (%)**	**IR peaks (cm^{-1}) with assignments**
1	Natural Zeolite	--	3552 (H-O-H stretch), 1691 (O-H bending),1065 (Si-O-Si stretch), 993 (T-O Assym str.), 765 (sym str.), 692 (T-O sym str.) 592 (Double ring), 487 (T-O bending)
2	Zeolite+Na	1.168 %	3552 (H-O-H stretch), 1643 (O-H bending),1047 (Si-O-Si stretch), 960 (T-O Assym str.), 767 (sym str.), 570 (Double ring)
3	Zeolite+Zn(II)	13.395 %	3514,3407,3282,3224 (H-O-H stretch), 1629 (O-H bending), 1364(O-NO stretching), 686 ((T-O sym str.), 505 (Double ring), 484 (T-O bending)
4	Zeolite-Na+Zn(II)	12.338 %	3446,3371,3282,3226 (H-O-H stretching), 1627 (O-H bending), 1425,1386 (O-NO stretching), 931 (T-O Assym str.), 694(T-O sym str.), 540 (Double ring), 466 (T-O bending)

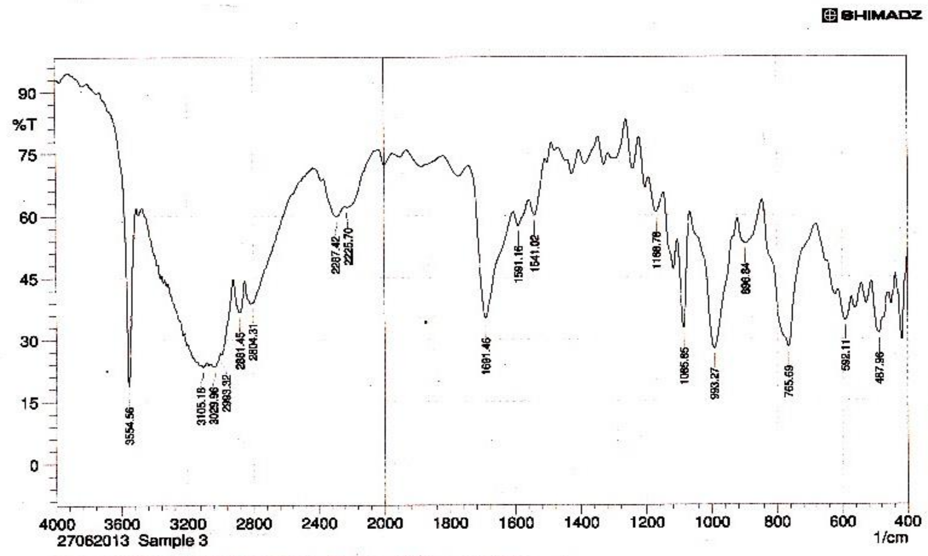

Figure – 1) IR Spectra of Natural Zeolite (Stilbite)

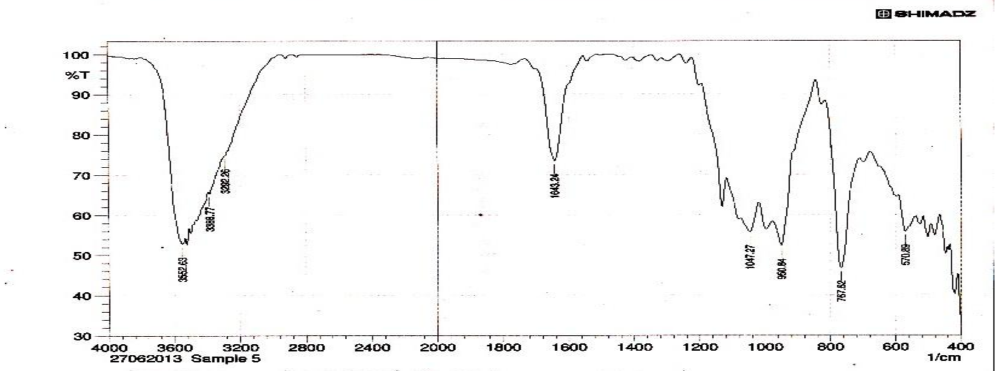

Figure – 2) IR Spectra of Natural Zeolite + Na-metal Mixture

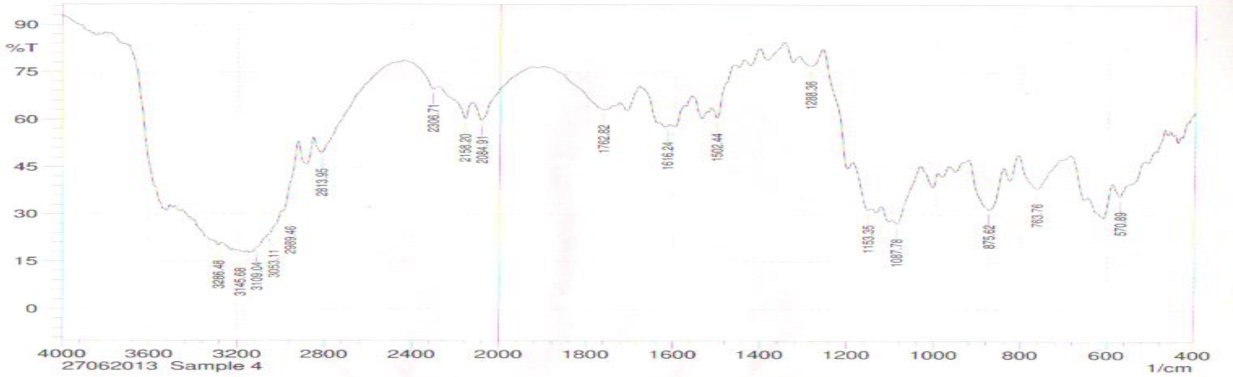

Figure – 3) IR Spectra of Natural Zeolite + Zn(II) metal Mixture

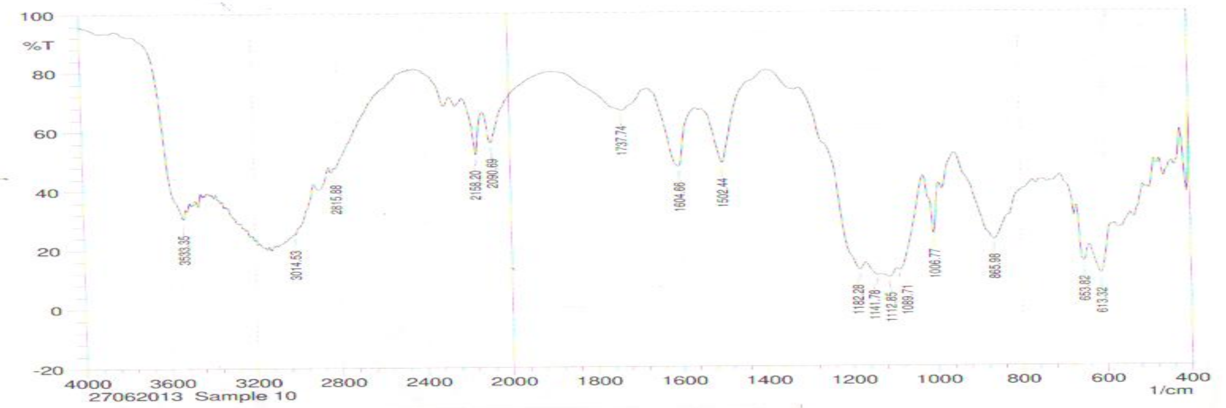

Figure – 4) IR Spectra of Na- Zeolite + Zn(II) metal Mixture

XRD Analysis : The X-ray diffraction pattern of the natural zeolite and its parent Na-zeolite (fig.-5 and fig.-6) shows that it is crystalline and cubic [11]. This is in good agreement with XRD pattern reported [12]. X-ray diffraction patterns of exchanged derivatives show that all the derivatives are cubic and crystalline. No significant change in the zeolite framework is observed during ion-exchange reaction from X-ray diffraction technique. There is no change in d-spacing except the intensities of the peaks are reduced after exchange. From the XRD pattern it is also clear that neither the distortion of the framework nor the elipticity of the double ring has taken place (Fig.7-8). There is slight change in d-spacing due to the entry of larger Zn(II) ions into the framework. The intensity of the peaks are also changed but the structure remains unaffected. The XRD analysis of the natural zeolite and synthesized or exchanged derivative shows crystalline nature. There is no significant change in the zeolite framework is observed, during ion-exchange reaction from XRD analysis.

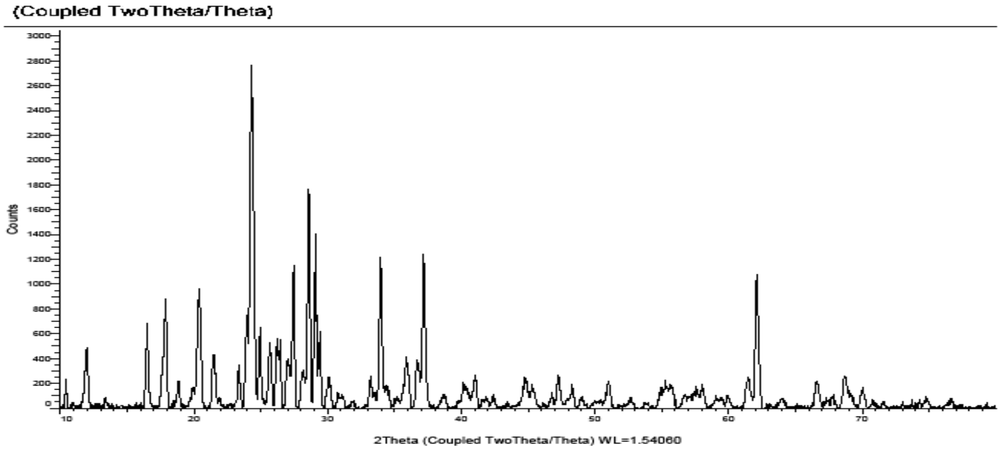

Fig. 5. X-Ray diffraction pattern of Natural-Zeolite

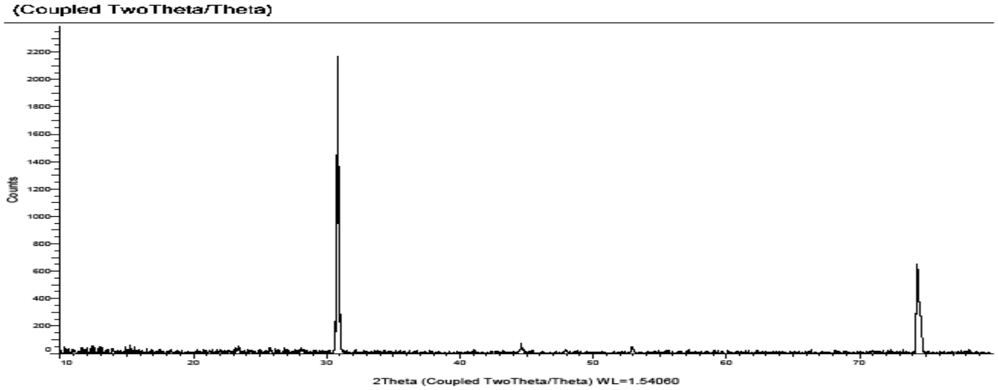

Fig 6. X-Ray diffraction pattern of Na-Zeolite

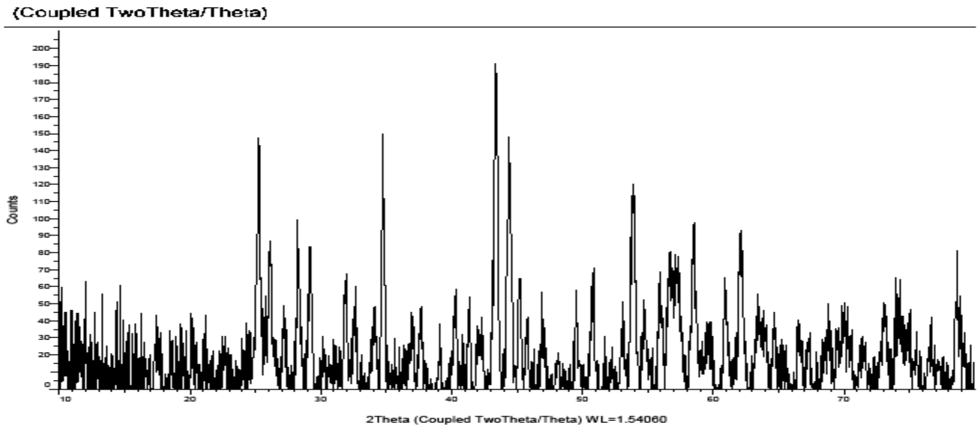

Fig 7. X-Ray diffraction pattern of Natural-Zeolite + Zn(II) metal mixture

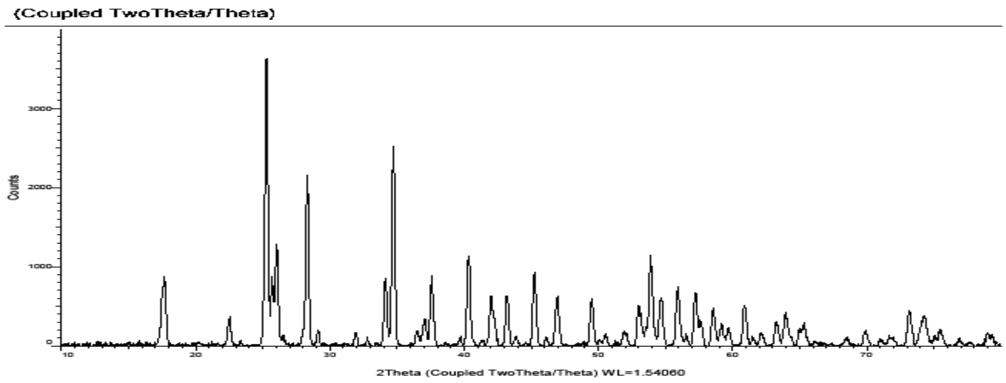

Fig 8. X-Ray diffraction pattern of Na-Zeolite + Zn(II) metal mixture

TGA Analysis: Thermal analysis of Natural zeolite and its derivative helps to understand the effect of dehydration as well as a heat treatment. The thermal stability of host lattice increased with increase in the size of exchanged cations[13]. The TG curve of the derivative of Natural zeolite is Na-zeolite shows the total weight loss of 1.168 % in three steps(Fig-9).In the first step rate of weight loss is 0.368 % which is slow up to the temperature 300^{0}C due to loss of adsorbed water, followed by slowly increased the rate of weight loss up to 0.620% due to dehydration. Followed by in the next third step weight loss is 0.180%, which is very slow. This is a good agreement with the peaks present in Na-zeolite curve showing a strong peak at 270^{0}C. Another small peak is obtained lastly at 760^{0}c showing that there is a weight gain in negligible quantity due to the presence of additional water. The comparative of second TG graph of Natural-zeolite+Zn(II) derivative shows that the total weight loss 13.395 % for Zn(II) in three steps. In Natural-zeolite+Zn(II) derivative TG curve shows strong peak at 250^{0}C (fig-10). The TG curve of derivative of Na-zeolite+Zn(II) shows total loss of 12.338 % which shows the strong peak at 250^{0}C(fig-11). The TG curve of adsorbed derivatives of Na-zeolite+Zn(II) exchanged zeolite shows the faster rate of weight loss after 250^0C to 330^0c due to desorption of N_2 gas. A perusal of the TG curve for N_2 gas adsorbed derivative of Na-Zeolite-Zn(II) the weight loss is 11.711 % up to 600^0C followed by dehydroxylation and desorption upto 760^0C.The TG curves of Natural-Zeolite, Na-Zeolite derivative and its exchanged derivatives shows that the derivatives are thermally stable up to a very high temperature. The Adsorbed derivatives of Zn(II) exchanged sample show great affinity towards N_2 gas adsorption.

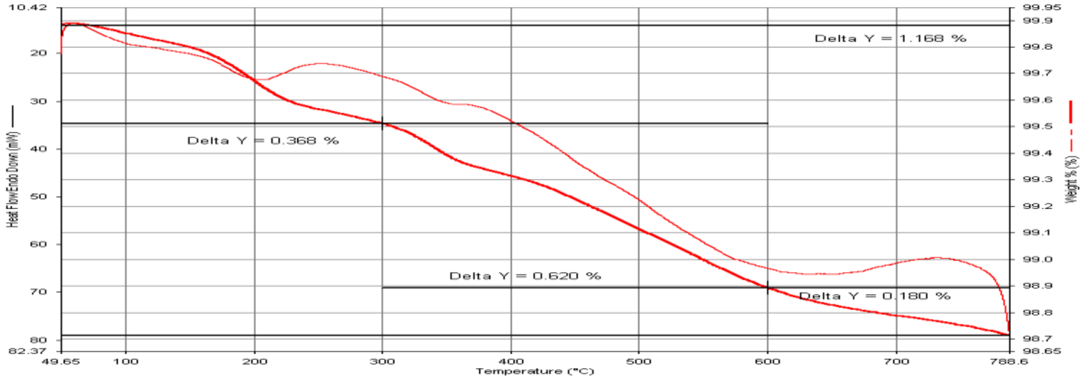

Fig 9 TGA Curve for Na- Zeolite

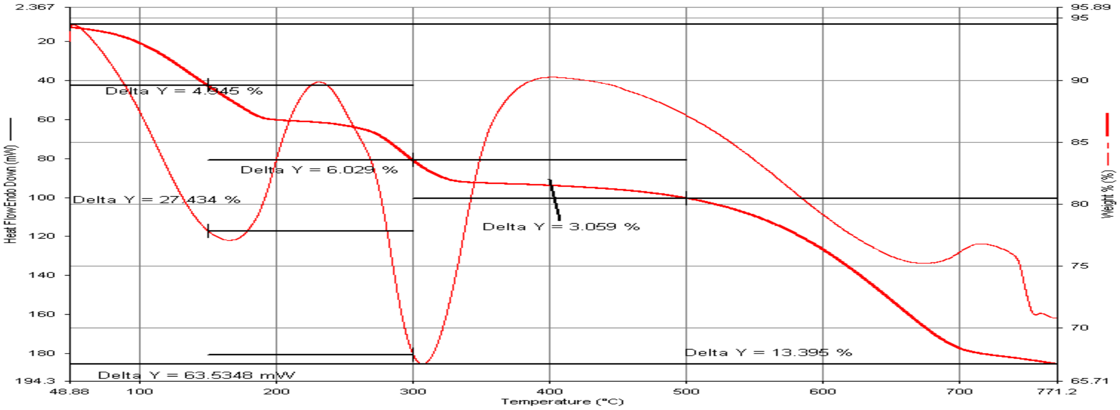

Fig 10. TGA Curve for Natural-Zeolite + Zn(II) metal mixture

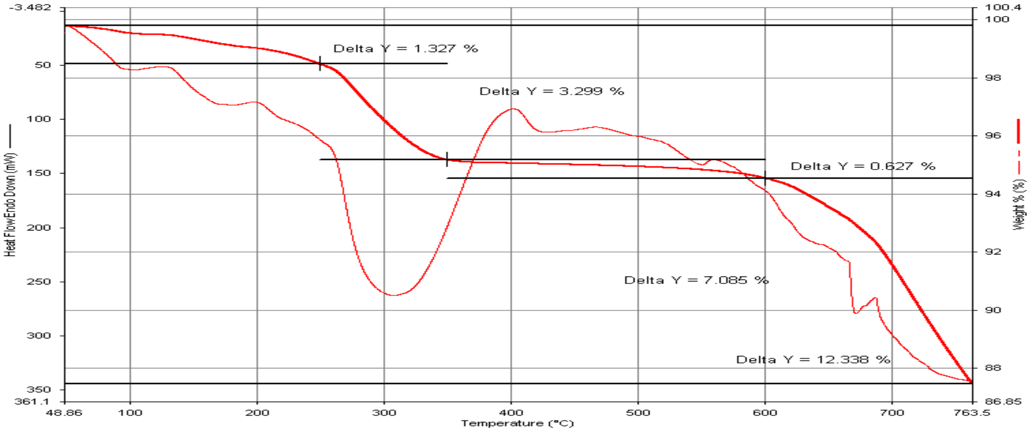

Fig 11. TGA Curve for Na-Zeolite+Zn(II) metal mixture

FESEM Analysis (Field Emission Scan Electron Microscope) : The scanning electron microscopy (SEM) is a primary tool uses for characterization of the surface morphology and fundamental physical properties of natural zeolite and its derivatives. It is useful for determining the particle size, shape, porosity. The SEM analysis is carried out on by Hitachi High Technologies Corporation, Japan (model no. S-4800 Type-II). Scanning electron micrograph of natural zeolite, its derivative Na-zeolite and its exchanged derivatives with Zn(II) metal before and after treatment are shown in figs.(12-15).

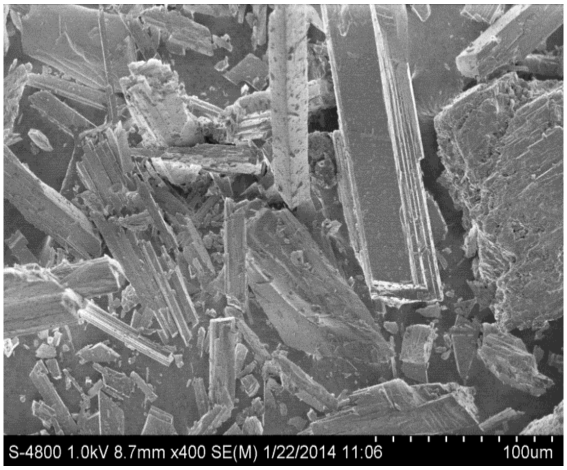

Fig 12. SEM analysis for Natural Zeolite

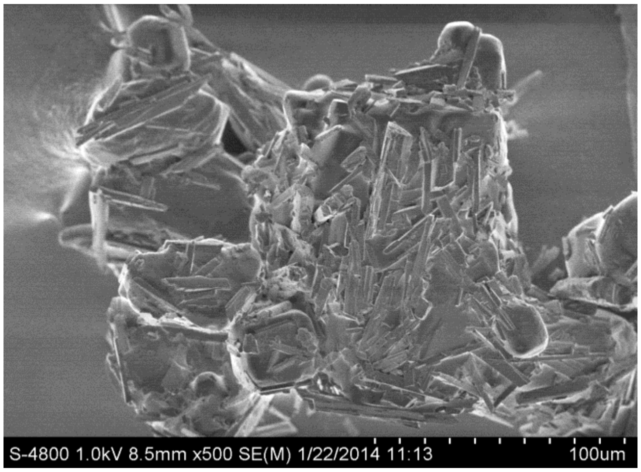

Fig 13. SEM analysis for Na-Zeolite

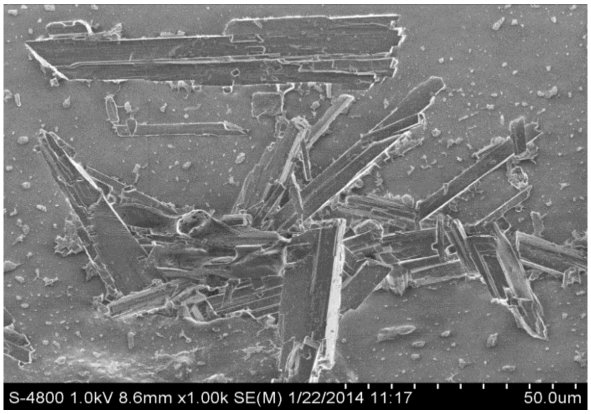

Fig 14. SEM analysis for Zeolite+Zn(II)

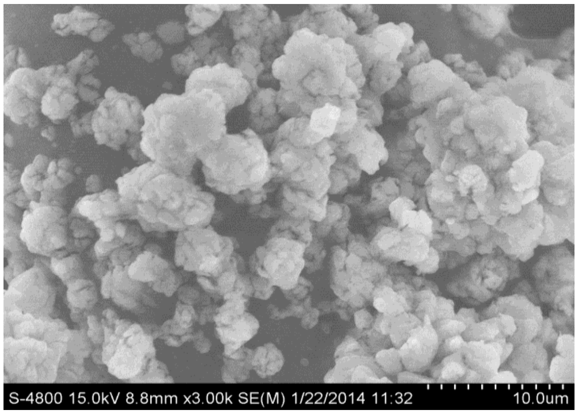

Fig 15. SEM analysis for Na-Zeolite + Zn(II)

EDX Analysis (Energy Dispersive X-ray spectroscopy) : Energy dispersive X-ray spectroscopy is a chemical microanalysis technique used in conjugation with SEM. EDX was used to characterize the elemental composition of the natural zeolite and its parent derivative like Na-zeolite, Zeolite+Zn(II) and Na-zeolite+Zn(II). The typical EDX pattern of the naturl zeolite and its parent derivatives Na-zeolite, Zeolite+Zn(II)metal, and Na-zeolite+Zn(II) metals are shown in figures (16-19).

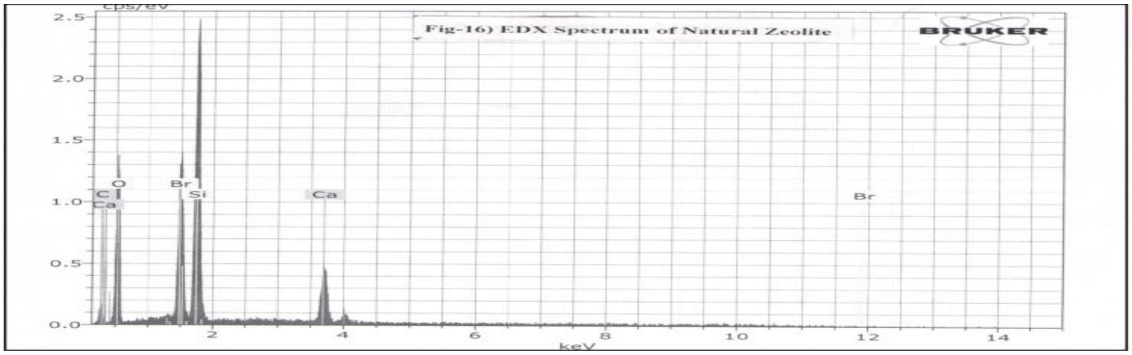

Fig 16.EDX Spectrum of Natural Zeolite

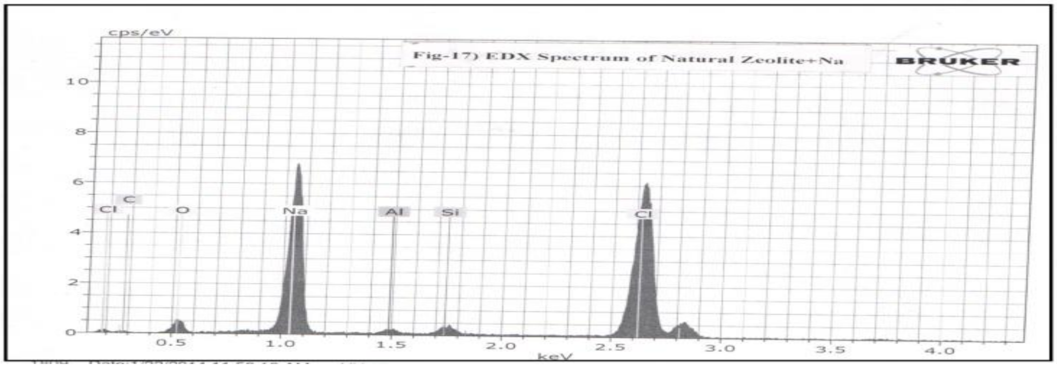

Fig 17.EDX Spectrum of Na-Zeolite

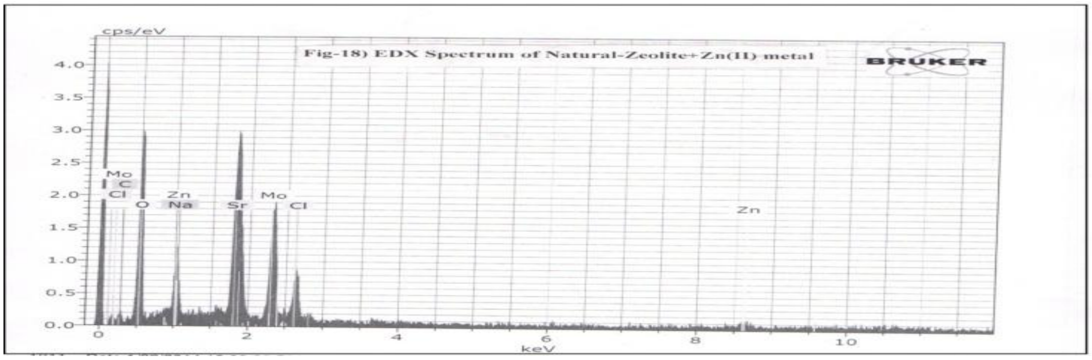

Fig 18. EDX Spectrum of Natural Zeolite+Zn(II) Metal

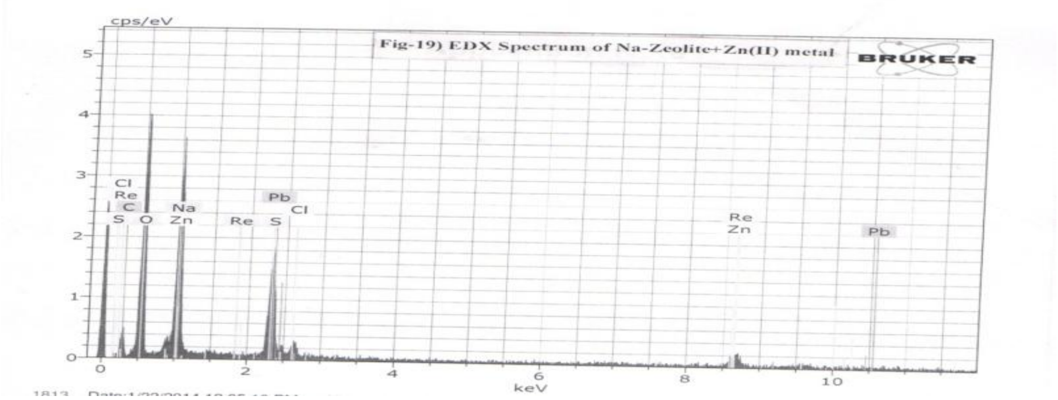

Fig 19. EDX Spectrum of Na-Zeolite+Zn(II) Metal

APPLICATIONS

The natural zeolite and it's adsorbed derivatives are quite useful as adsorbents and also for cleaning up municipal, industrial and nuclear wastewater. The exchanged derivative can be used as catalyst and for pollution control in automobile and chemical industries as it shows greater affinity to remove N_2 gas up to very high temperature.

CONCLUSIONS

The above facts shows that Natural zeolite and Na-zeolite are good ion exchanger for Zn(II) ions. The exchanging capacity Zn(II) ions is maximum. There is no change in the framework structure of zeolite after the exchange. The parent zeolite and its derivatives are thermally stable up to very high temperature. The adsorb derivative of Na-zeolite+Zn(II) and zeolite+Zn(II) shows there stability in case of N_2 gas. The zeolite used in this present work would be quite useful as adsorbent and also for cleaning up municipal, industrial and nuclear wastewater with exchanged derivative can be used as catalyst and for pollution control in automobile and chemical industries as it shows greater affinity to remove N_2 gas up to very high temperature.

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