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The Study of Sr(II) Metal Ion Exchange by Stilbite a Natural Zeolite and It's Adsorbed Derivative

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Authors' contributions

This work was carried out in collaboration between both authors. Author PPT designed the study, performed the statistical analysis and synthesis and characterization of natural zeolite (stilbite) and its parent Na-zeolite doped with Sr(II) metal ion, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches under the guidance of author PMY. Authors PPT and PMY managed the analyses of the study and literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

In the present work Stilbite (Natural Zeolite), Na-Zeolite are exchanged with Sr(II) metal ion to study the removal of heavy metal ions from the industrial waste water. 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 Sr(II) metal ion. The structural changes are studied by IR spectroscopy. The exchange percentage of Sr(II) metal ion with natural zeolite is maximum than Na-zeolite. In this study Scan

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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 EDAX analysis is also carried out. We successfully exchanged Sr(II) metal ions with Stilbite-natural zeolite and doped Na-zeolite.

Keywords: Natural zeolite; Na-zeolite; ICP-AES; XRD; IR; TGA; SEM; EDAX.

1. INTRODUCTION

Zeolites are micro porous crystalline solids with well defined structures [1]. Generally they contain silicon, aluminum and oxygen in their pores. Many occur 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 [2-4]. Many of the Natural zeolites now serve as petroleum refining, petrochemical and chemical process industries as a selective adsorbent, ion exchanger catalyst [5-6]. These are also used for cleaning up of municipal, industrial and nuclear waste water [7-8].

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 [9].

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 [10]. The catalytic importance of Natural zeolite has prompted several investigations of its physical and chemical nature [11-12]. 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. Sr(II) ions exchanged zeolites have been found their application in preventing environmental pollution [13].

Most of the industries have discharged their effluents which are being added to aquatic system. The moieties present in industrial effluents accumulate in different region as soil, ground water and various parts of animals or plants [14]. In the industrial area most of the industries are being discharged the effluent into the open places, rivers and sea. Most of the industrial waste water is containing organic, inorganic matter and hazardous metals [15]. These heavy metals and organic compounds affect the quality of soil and ground water. Heavy metal enters in the human body by different pathways and causes harmful effects. The organics and heavy metals like Cu, Zn, Sr, Cd, Pb, Fe, Ni, Cr, Mn, Co etc. and some water soluble pollutants percolate into the ground water. The removal of these heavy metals from waste can be performed using physico chemical methods. Zeolites play an important role for the ion exchange property for the removal of heavy metals [16].

The present work is carried out to find the stability and suitability of the natural zeolite and exchange derivatives for catalysis and pollution abatement. In addition the zeolites were also characterized by FESEM and EDAX by BET technique, atomic force microscopy [17].

2. EXPERIMENTAL

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 100ºC for 8 hours, stirring and cooling was continued for 10 days to ensure maximum exchange. These zeolite crystals were filtered and dried up to 150ºC in an oven. Then natural zeolite and Na-zeolite derivatives were treated with saturated solution of $SrCO_3$ by the same procedure, for the adsorption of Sr(II) ions. Both the parent zeolite and its exchanged derivatives were then studied by ICP-AES (Inductive Couple Plasma with Atomic Emission Spectroscopy) for the determination of Na(I), Sr(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. X-ray diffraction patterns are obtained between 2º angles of 5º to 80º using CuKº radiations of wavelength 1.5414 Aº.

The XRD patterns are taken on Bruker company, model D8- advance, Germany at Department of Physics, North Maharashtra University, Jalgaon, Cu-k alpha radiation of wavelength 1.5406 A used. 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 50.00ºC to 800.00ºC at 20.00ºC/min. While the SEM analysis is carried out on by HITACHI High Technologies Corporation (model no.S-4800 Type-II). Also the EDX analysis is carried out on Bruker AXS Gmbh Germany (model no.D-98) with X-flash detector.

3. 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 Sr(II) ions mentioned in the same table.

3.1 IR Analysis

The IR spectra of the natural zeolite, Na-zeolite and their derivatives of Sr(II) 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) and its parent zeolite (Na-zeolite) with the IR spectra of the exchange derivatives of natural zeolite doped with Sr(II) metal 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 [18]. 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 Sr(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.

3.2 XRD Analysis

The X-ray diffraction pattern of the natural zeolite and its parent Na-zeolite (Figs. 1 and 2) shows that it is crystalline, monoclinic and orthorhombic [19-20]. X-ray diffraction patterns of exchanged derivatives are shown in (Figs. 3 and 4). There is slight change in d-spacing due to the entry of larger Sr(II) ions into the framework. The intensity of the peaks are also changed but the XRD analysis of the natural zeolite and synthesized or exchanged derivative shows crystalline nature [21].

In order to study crystal structure of natural zeolite, Na-zeolite derivative, natural zeolite doped with Sr(II) metal ion and Na-zeolite doped with Sr(II) metal ion, X-ray diffractogram of the samples were examined with 2Θ=10 to 2Θ=80º. X-ray pattern for natural zeolite and for Na-zeolite match with JCPDS card no. 83-1566 and 81-2081 and for a natural-zeolite doped with Sr(II) metal ion the crystal structure is monoclinic match with JCPDS card no. 38-1454 also Na-zeolite doped with Sr(II) metal ion the crystal structure is monoclinic match with JCPDS card no. 38-1454 and 83-1618. The standard and calculated d values of the samples with h k l values are given in Table 3.

Table 1. The analysis of metals by ICP-AES

Sr. No.	Name of the sample	Si in ppm	Al in ppm	Na in ppm	Sr in ppm
1	Zeolite (Stilbite) Crystals	108.7	304.3	---	---
2	Na doped Zeolite Sample Crystals	182.2	119.8	961.902	---
3	Zeolite doped with Sr(II) Sample Crystals	101.3	15.3	---	1514.8
4	Na-Zeolite doped with Sr(II) Sample Crystals	403.6	303.7	1832.6	22672.6

Table 2. Result of IR Spectroscopy Analysis of Natural Zeolite and its derivatives

Sr. No.	Name of sample	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.	Natural Zeolite doped with Na	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.	Natural Zeolite doped with Sr(II)	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.	Na-Zeolite doped with Sr(II)	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)

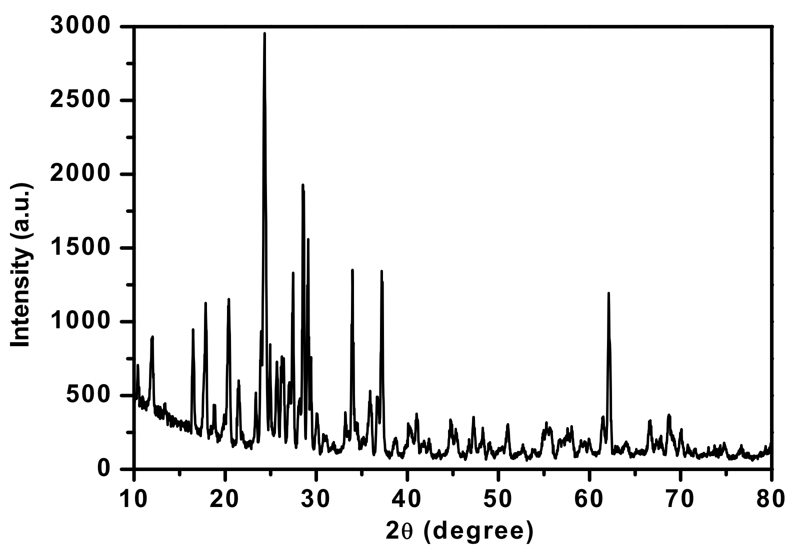

Fig. 1. X-Ray diffraction pattern of Natural-Zeolite

Table 3. Result of XRD analysis of natural zeolite and its derivatives

Sample	2 Theta	h k l	Standard d	Calculated d	JCPDS card no.
Natural Zeolite	16.32	1 1 0	5.3719	5.4285	83-1566
	17.73	1 0 1	4.9690	5.1115	
	20.41	1 0 1	4.3533	4.3471	
	24.33	2 0 0	3.6548	3.6560	
	28.57	0 2 1	3.1213	3.1224	
	33.91	2 2 0	2.6365	2.6416	
	37.05	3 1 0	2.4146	2.4246	
	62.06	3 1 3	1.4926	1.4943	
Natural-Zeolite doped with Na(I) metal	30.77	2 3 1	2.8956	2.9035	81-2081
	44.61	3 1 2	2.0291	2.0300	
	52.79	4 6 0	1.7275	1.7326	
	74.31	1 1 4	1.2738	1.2753	
Natural Zeolite doped with Sr(II) metal	24.26	1 3 1	3.6716	3.6663	38-1454
	30.20	0 4 1	2.9468	2.9570	
	32.95	1 3 2	2.7118	2.7161	
	39.96	3 3 2	2.2500	2.2543	
	44.75	3 1 1	2.0242	2.0234	
	51.90	4 4 1	1.7598	1.7599	
	59.47	2 2 3	1.5524	1.5704	
	71.26	2 6 2	1.3217	1.3224	
	74.28		1.2755	1.2757	
Na-Zeolite doped with Sr(II) metal	17.75		4.8312	4.8355	38-1454
	18.83	0 2 1	4.7346	4.7084	
	21.65	2 0 1	4.1216	4.3082	And
	26.70	2 2 0	3.3136	3.3361	
	31.16	0 4 1	2.8579	2.8678	83-1618
	32.76	1 3 2	2.7207	2.7316	
	35.40	3 1 2	2.5335	2.5339	
	38.82	1 1 3	2.3105	2.3181	
	42.27	0 0 3	2.4105	2.1484	
	45.30	3 1 1	1.9987	2.0003	
	47.32	2 6 1	1.9119	1.9195	
	51.77	2 0 4	1.7597	1.7643	
	60.66	0 6 3	1.5226	1.5253	
	62.08	4 6 2	1.4805	1.4940	
	77.83	4 8 0	1.2250	1.2262	

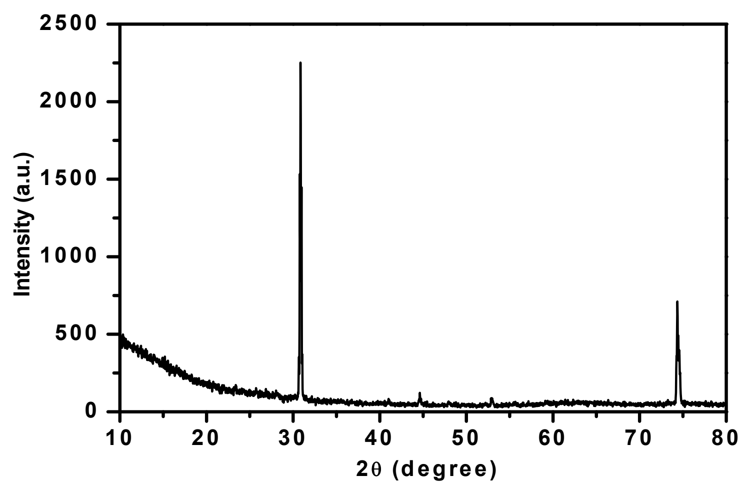

Fig. 2. X-Ray diffraction pattern of Na-Zeolite

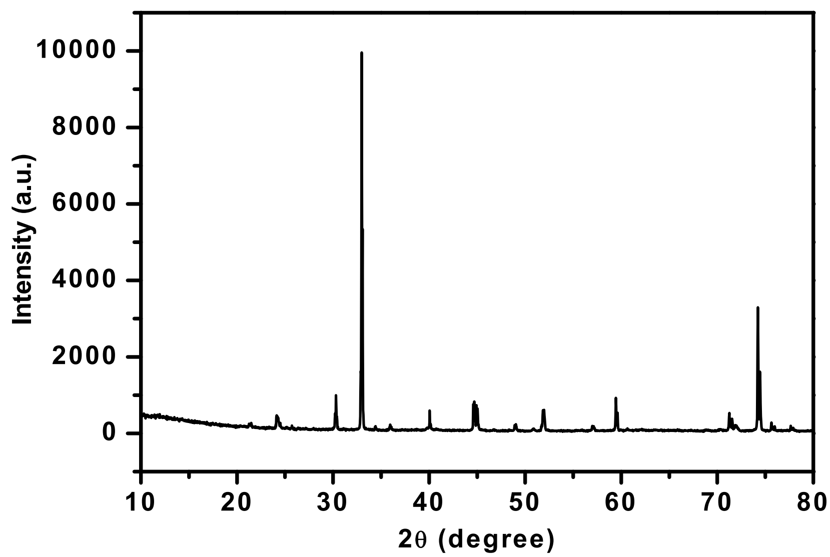

Fig. 3. X-Ray diffraction pattern of Natural-Zeolite doped with Sr(II) metal ion

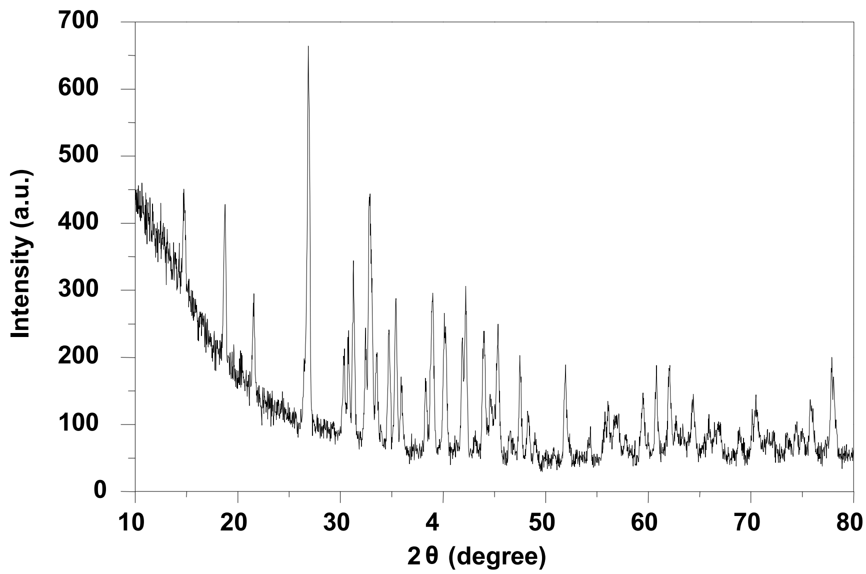

Fig. 4. X-Ray diffraction pattern of Na-Zeolite doped with Sr(II) metal ion

3.3 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 [22]. The TG curve of the derivative of Natural zeolite is Na-zeolite shows the total weight loss of 1.168% in three steps (Fig. 5). In the first step rate of weight loss is 0.368% which is slow up to the temperature 300ºC 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 270ºC. Another small peak is obtained lastly at 760ºc showing that there is a weight gain in negligible quantity due to the presence of additional water [23].

The comparative study of second TGA graph of Natural-zeolite doped with Sr(II) derivative shows that the total weight loss 15.377% for Sr(II) in three steps. In Natural-zeolite doped with Sr(II) derivative TG curve shows strong peak at 180ºC (Fig. 6). The TG curve of derivative of Na-zeolite doped with Sr(II) shows total loss of 13.003% which shows the strong peak at 180ºC (Fig. 7). The TG curve of adsorbed derivatives of Na-zeolite doped with Sr(II) exchanged zeolite shows the faster rate of weight loss after 180ºC to 250ºc due to desorption of N_2 gas. A perusal of the TG curve for N_2 gas adsorbed derivative of Na-Zeolite doped with Sr(II) the weight loss is 12.095% up to 250ºC followed by dehydroxylation and desorption up to 600ºC.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 results are shown in the Table 4.

3.4 FESEM Analysis (Field Emission Scan Electron Microscopy)

The field emission scanning electron microscopy (SEM) is a primary tool uses for characterization of surface morphology and fundamental physical properties of natural zeolite and its derivatives. It is useful for determining the particle size, shape, porosity. Scanning electron micrograph of natural zeolite, its derivative Na-zeolite and its exchanged derivatives with Sr(II) metal before and after treatment are shown in (Figs. 8-11). The images were taken on the external surfaces of the natural zeolite and its derivatives. The crystalline and micro pores structures could be observed and shows clear exchange of Sr(II) with natural zeolile.

Table 4. Results of thermo gravimetric analysis of Natural Zeolite and its derivatives

Sr. No.	Name of the sample	Total weight loss in percentage
1.	Natural Zeolite	----
2.	Natural zeolite doped with Na	1.168%
3.	Natural Zeolite doped with Sr(II)	15.377%
4.	Na-Zeolite doped with Sr(II)	13.03

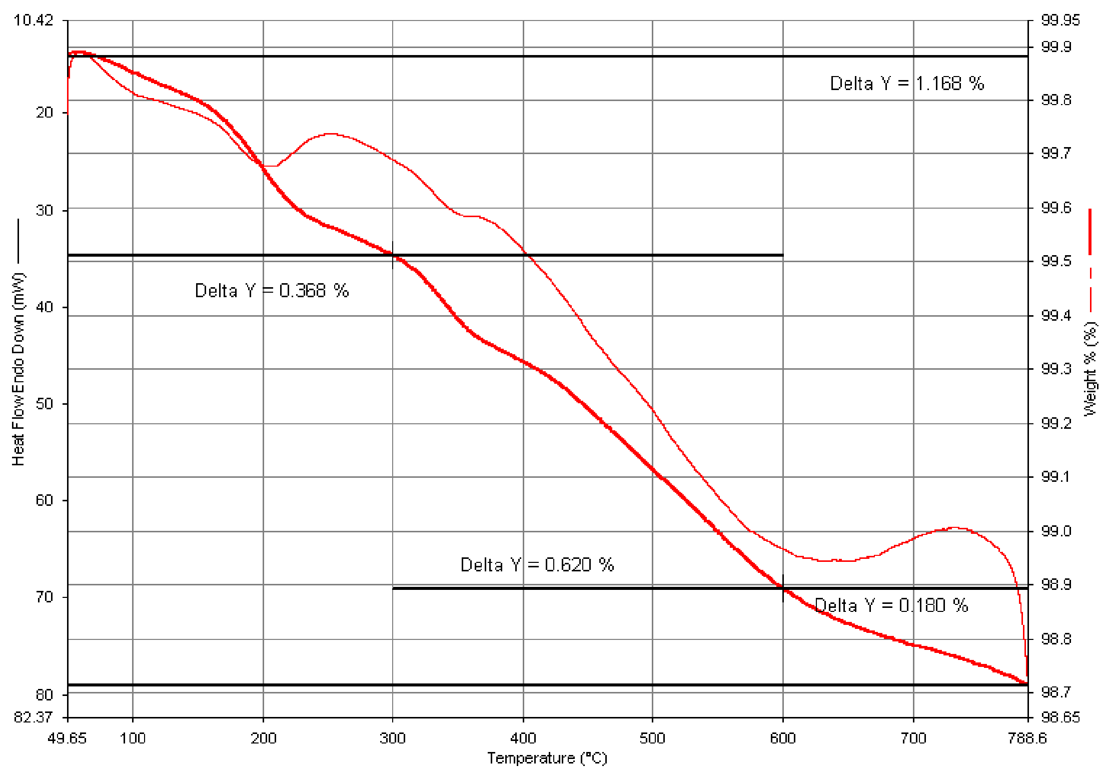

Fig. 5. Thermo-gravimetric curve of Na-zeolite

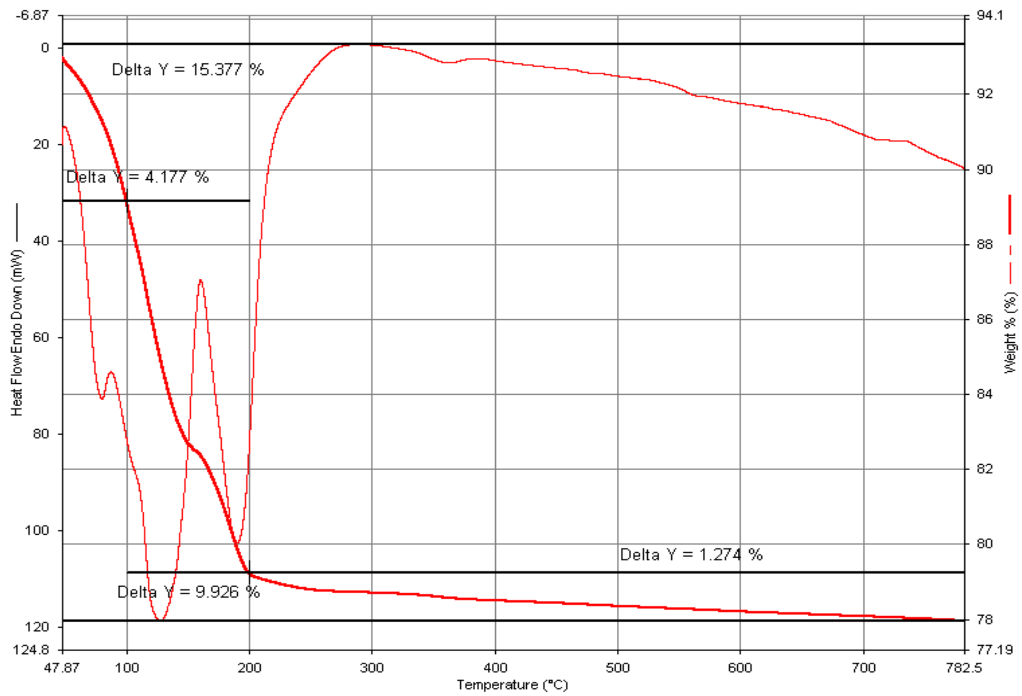

Fig. 6. Thermo-gravimetric curve of Natural-zeolite doped with Sr(II) metal ion

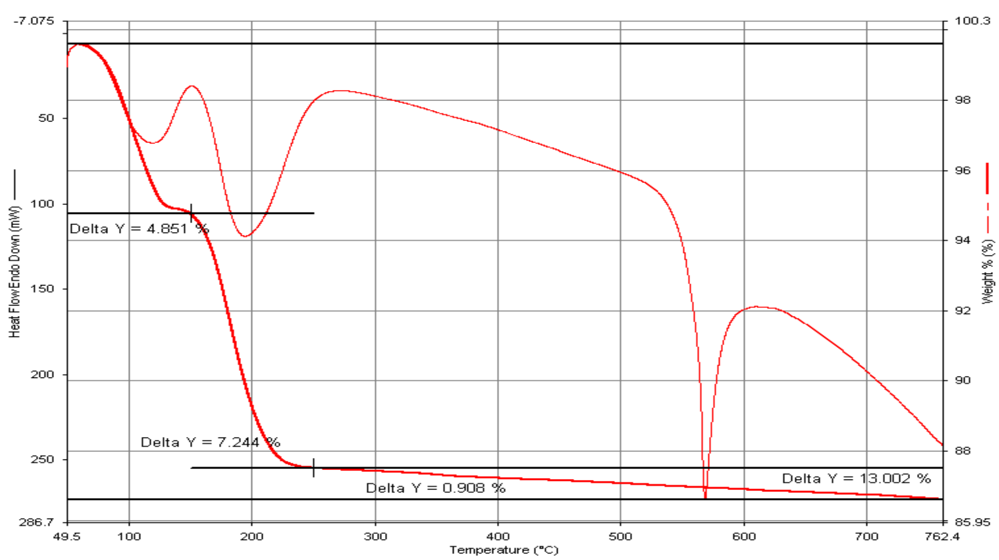

Fig. 7. Thermo-gravimetric curve of Na-Zeolite doped with Sr(II) metal ion

3.5 EDX or EDS Analysis (Energy Dispersive X-ray spectroscopy)

Energy dispersive X-ray spectroscopy is a chemical microanalysis technique used in conjugation with SEM. [18] EDX was used to characterize the elemental composition of the natural zeolite and its parent derivative like Na-zeolite, Zeolite doped with Sr(II) and Na-zeolite doped with Sr(II). The typical EDX pattern of the naturl zeolite and its parent derivatives Na-zeolite, Zeolite doped with Sr(II) metal, and Na-zeolite doped with Sr(II) metals are shown in (Figs. 12-15). EDS data obtain from characterization shows there is exchange takes place between natural zeolites and Sr(II). Also some other elements are detected in analysis such as Si, O, Al, Ca, Cl, Br, Na, Sr etc. [24-32] The removal of Si metal ions by Na metal ion and Sr(II) metal ions are shown in the Table 5.

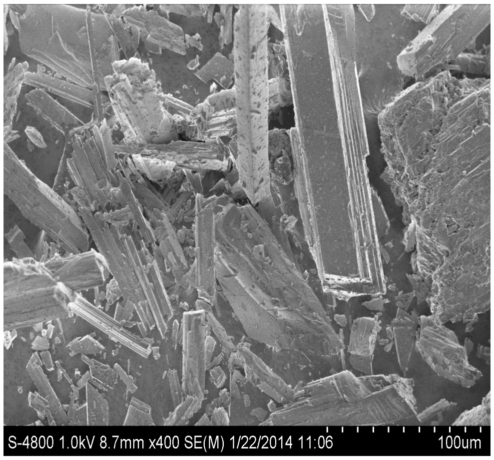

Fig. 8. SEM analysis for Natural Zeolite

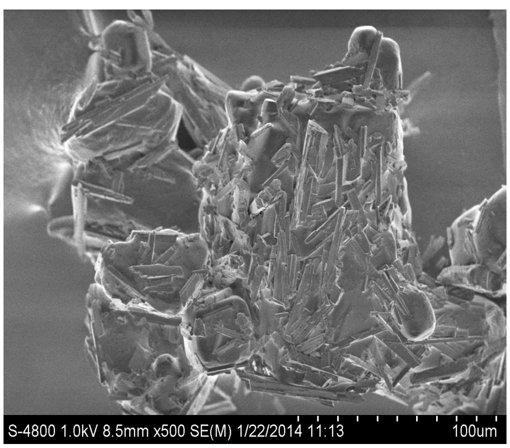

Fig. 9. SEM analysis for Na-Zeolite

As shown in above Fig. 12 shows EDX spectrum of natural zeolite and the Fig. 13 shows EDX spectrum of natural zeolite doped with Na-metal ion replaces the Na ion up to 90.55%. Si ions adsorbed by Na metal. In Fig. 14 EDX spectrum of natural zeolite doped with Sr(II) metal ion which replaces ion by Sr(II) ion up to 55.68%, while Fig. 15 EDX spectrum of Na-zeolite doped with Sr(II) metal ion which adsorbed Sr(II) metal ion up to 45.35%. Sr(II) metal ion adsorbed by natural zeolite is more than it's Na-zeolite derivative.

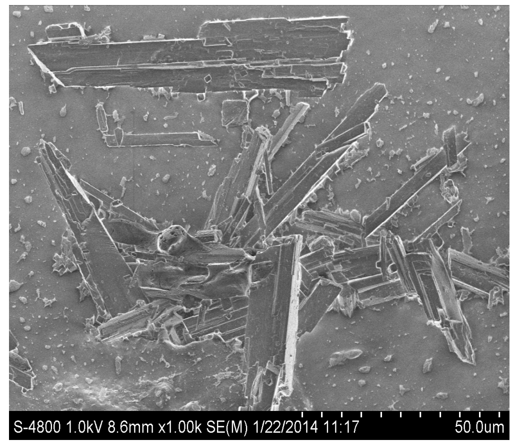

Fig. 10. SEM analysis for Zeolite doped with Sr(II)ion

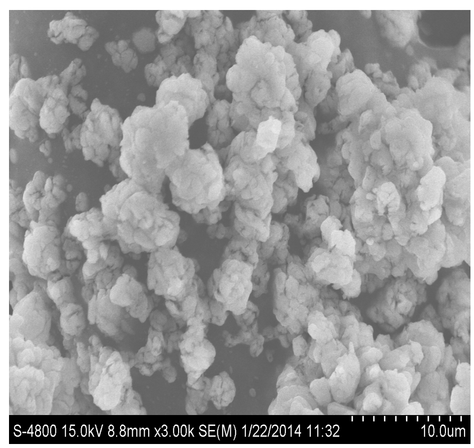

Fig. 11. SEM analysis for Na-Zeolite doped with Sr(II) ion

Table 5. Results for removal of Si ions by Na metal and Sr(II) metal ions from Zeolite

Sr. No.	Name of the sample	Removal of metal Ions	
		Na	**Sr(II)**
1.	Natural Zeolite	--	--
2.	Natural zeolite doped with Na metal	90.55%	--
3.	Natural Zeolite doped with Sr(II) metal	--	55.68%
4.	Na-zeolite doped with Sr(II) metal	--	45.35%

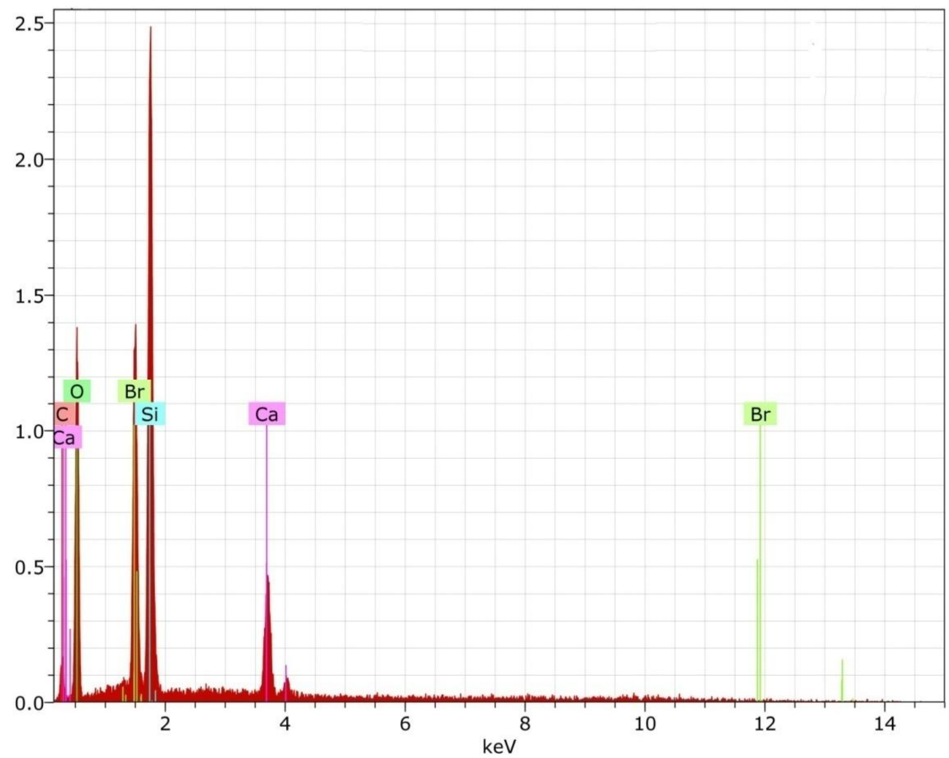

Fig. 12. EDX spectrum of natural zeolite

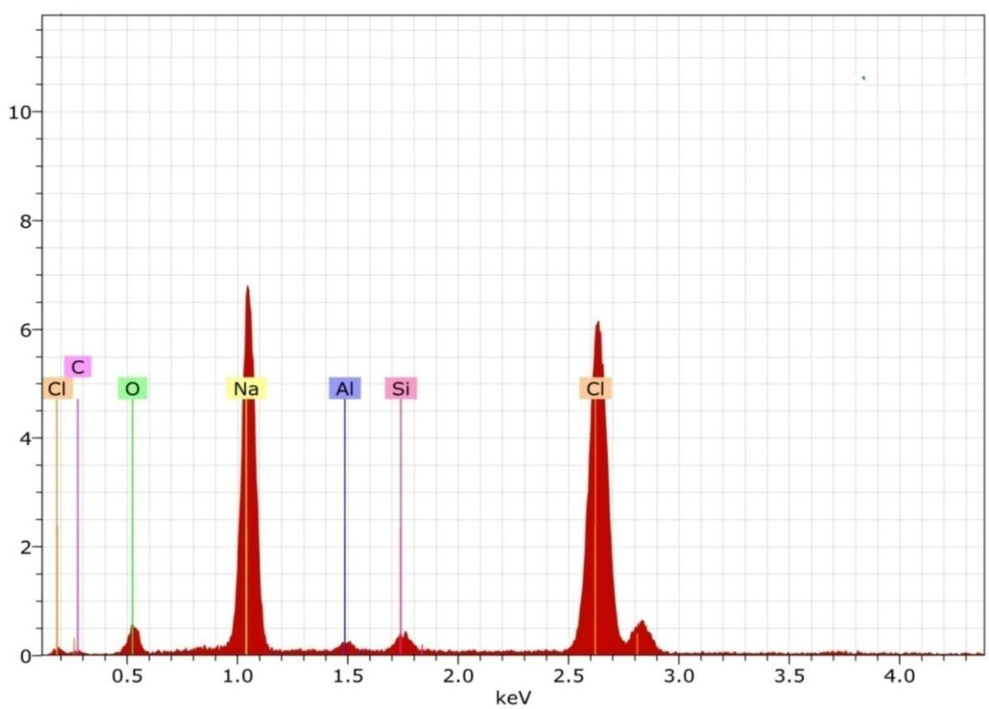

Fig. 13. EDX spectrum of natural zeolite doped with Na metal ion

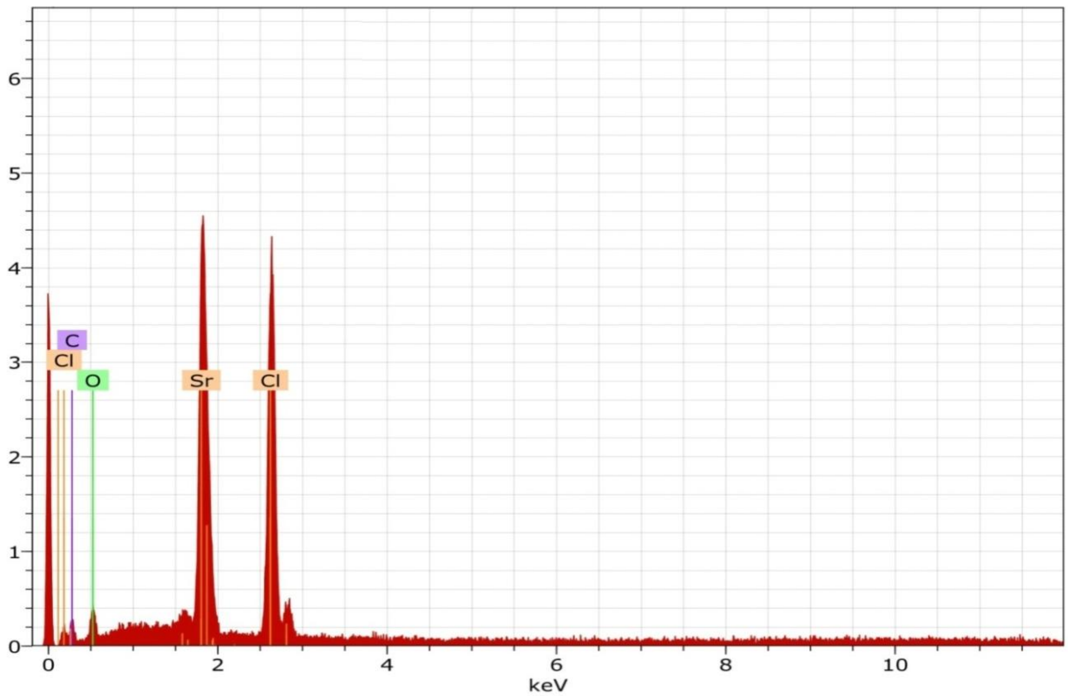

Fig. 14. EDX spectrum of natural zeolite doped with Sr(II) metal ion

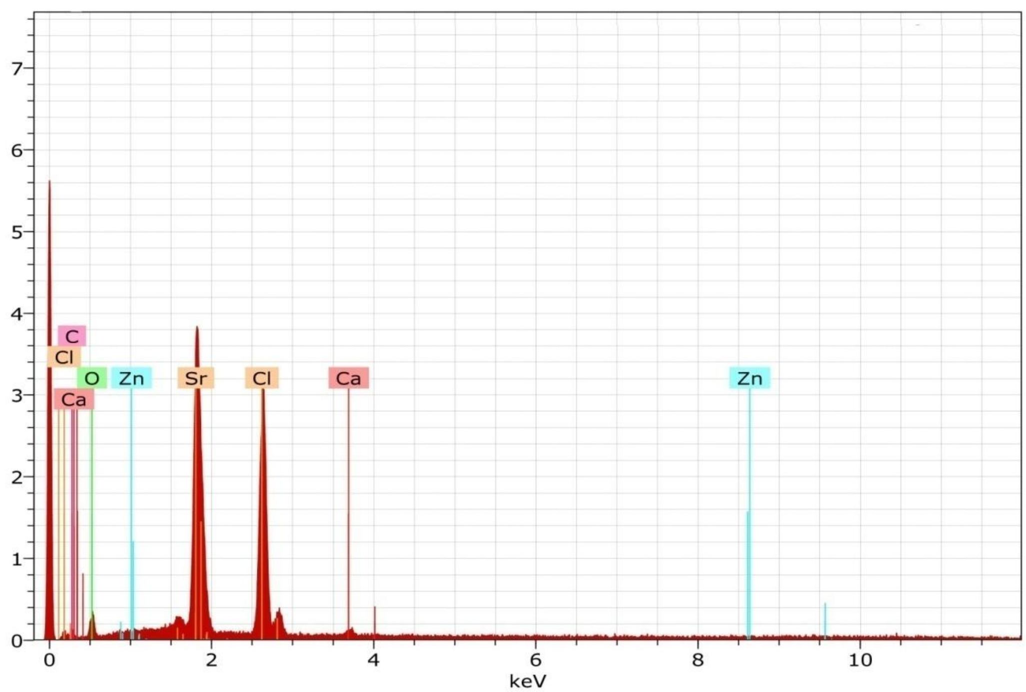

Fig. 15. EDX Spectrum of Na-Zeolite doped with Sr(II) Metal ion

4. CONCLUSION

The above facts shows that Natural zeolite and Na-zeolite are good cation exchanger for Sr(II) ions. Natural zeolites adsorbs Sr(II) ions more than Na-Zeolite. That is exchanging capacity of Sr(II) ions is maximum by natural zeolite than Na-Zeolite derivative. There is a change in the framework structure of zeolite after the exchange of cations. The parent zeolite and its derivatives are thermally stable up to maximum temperature (800ºC). The zeolite used in this present work would be quite useful as adsorbent and as a catalyst [31-32].

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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