



## **Indian Natural Zeolite: A Low Cost Adsorbent for the Removal of Fe (III) Metal Ions from Aqueous Model Solution**

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### **ABSTRACT**

*The adsorption studies on the removal of iron from aqueous solution using non-treated natural zeolite; locally available was carried out under varying experimental conditions. The maximum adsorption was observed to be a function of solution of pH, contact time, initial concentration of ions and temperature, has been found out that specific surface of zeolite takes leading part at the adsorption of iron from aqueous solution with different concentrations. Natural zeolite showed maximum adsorptive removal of iron at about pH 3 and doses 1 gm 50 ml for iron aqueous solution in 2.5 hours contact time. Ion exchange is probably one of the major adsorption mechanisms for binding of Fe(III) ions on the surface of natural zeolite. The experimental results strongly support this hypothesis. On the basis of experimental results as well as the model parameters, it can be said that the adsorbent natural zeolite may be used in developing an adsorptive technology for the removal of iron.*

**Keywords:** Indian Natural Zeolite (INZ), Iron(III) ions, Adsorption.

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### **INTRODUCTION**

Iron is one of the heavy metals present in the potable water in India, in which iron is found to be much higher than the permissible limits ( $0.3\text{mg L}^{-1}$ ) in many parts of the country. It can cause serious environmental contamination if it present at high level [1]. The main source of  $\text{Fe}^{+3}$  present in the soil as well as corrosive water which will pick up iron ions from pipes [2]. This soluble iron in the potable water may be in the form of ferrous carbonate which causes unaccepted taste, odor and discoloration of washing clothes, utensils, textiles, paper and plumbing fixtures and encrustation in water system[3]. Iron as an element may not be causing any significant health hazards. But when water containing colorless dissolved  $\text{Fe}^{+3}$  is allowed to stand in a cooking container or comes in contact with a sink or bath tub, the  $\text{Fe}^{+3}$  combines with oxygen from the air to form reddish-brown particles (rust). These impurities can give a metallic taste to water or to food [4].  $\text{Fe}^{+3}$  deposits can built-up in pressure tanks, water heaters and pipe-lines, reducing the quantity and pressure of water supply. Due to that special attention should be paid to the problem. Therefore purification is one of the widest spread technological processes [5]. For the up take iron metals, different methods are employed, such as physicochemical [6] and biological methods [7]. In

which the removal is usually achieved through ion exchange and/or adsorption. There are a number of inorganic adsorptive are used, for example, zeolite [8-11], rice husk, bone powder, activated charcoal, saw dust, waste tea leaves, coconut fiber pith, fly ash, feldspar [12] etc.

A perspective method for purification of wastewater is adsorption using zeolite [4-5, 8-11]. Zeolites are highly selective scavengers of a variety of metal cations that can be removed from liquid effluents through the process of adsorption.

## MATERIALS AND METHODS

**Adsorbent:** Natural zeolite of India was collected from Dhule and Jalgaon district (M.S.) India. The zeolites are generally built from  $(AlO_4)$  and  $(SiO_4)$  tetrahedrons, which have three dimensional structures. The natural zeolite exhibits considerable ion exchange capacity due to exchanging functional group like hydroxyl group and its porous nature which is present in zeolite. Natural zeolite obtained was crushed and sieved for desirable particle size. These particles were dried and stored in glass bottle. Natural zeolite was used as an adsorbent material without any pre-treatment.

**Chemicals:** Analytical grade ferrous nitrate was purchased from Chemox chemicals, Nashik, and it was used for iron source. Concentrated Nitric acid (1%  $HNO_3$ ) and pH buffer solutions were used to adjust pH values of adsorptive solution samples. Double distilled water was used in all experimental work.

**Stock Solution:** A stock solution of 1000 ppm was prepared by dissolving 1.80 g of ferric nitrate  $[Fe(NO_3)_3 \cdot 9H_2O]$  in 250 mL double distilled water. The stock solution was further diluted with distilled water to desired concentration for obtaining the test solutions.

### Experimental:

**Determination of Residual Metal Concentration:** Conductivity and pH was measured using digital conductivity meter and digital pH meter respectively, conductivity meter (Equiptronics) with magnetic stirrer (model no. EQ-664) and pH meter ME-MAX DIGITAL pH meter with magnetic stirrer (model no. ME-963-P) equipped with temperature probe. The residual metal concentration in the solution was measured using the atomic absorption spectrophotometer Systronics model-118.

**Adsorption And The Removal of Iron (III) Ions:** A set of laboratory scale experiments was performed in which the INZ was contaminated with acidic media 1%  $HNO_3$  model solution of  $Fe(NO_3)_3 \cdot 9H_2O$  in constant doses (50mL  $1g^{-1}$ ). The contact between the INZ and the model solution is realized in static conditions with the help of magnetic stirrer in correlation liquid: solid, v:g=50:1 for all experiments. Adsorption experiments were performed in 100  $cm^3$  Borosil beaker by mixing 50  $cm^3$  of  $Fe(NO_3)_3 \cdot 9H_2O$  solution with 1 g of zeolite at constant pH of 1%  $HNO_3$ . Variant temperatures are carried out. For adsorption studies, some competitive methods will be carried out e.g. stirring, temperature, contact time, as well as reported one [13]. The dipping of zeolite through water model solution involves over a period of 5 min to 150 min.

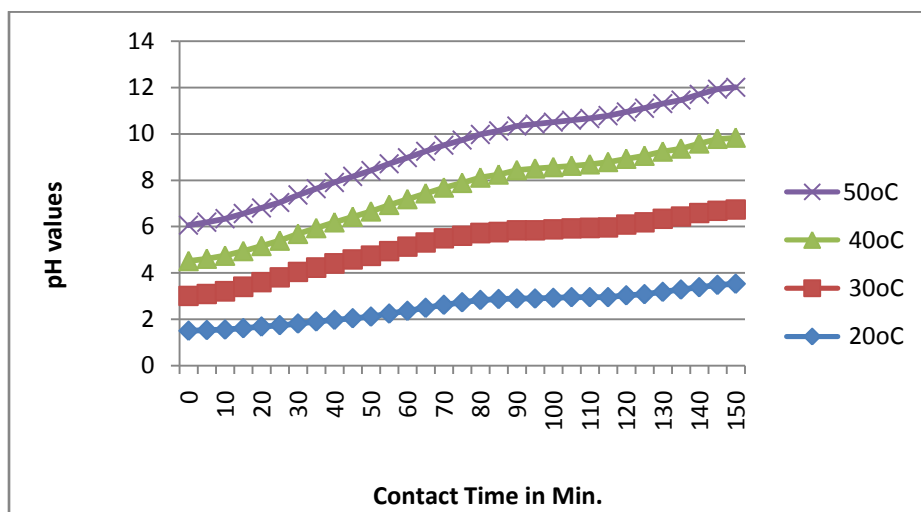
**pH and Conductivity Method:** The samples are poured into two separate clean beakers. The electrodes of the pH or conductivity indicator are then submerged into the beakers contains the samples and the readings are recorded.

## RESULTS AND DISCUSSION

**Adsorption Method and The Removal of  $Fe^{+3}$  From Aqueous Solution:** In general, the structure of INZ contains specific size and shape. The porous material is therefore useful for adsorbing transition metals inside the porous material. The most of  $Fe^{+3}$  are adsorbed very fast from a model solution within 1.5 h. After this time generally no increase has been occurred, while the adsorption results are interested during first 60 min. The removal of Fe (III) ions over zeolite through adsorption depends mainly on the

thermodynamics parameters like temperatures, concentration of adsorptive [14] and the environmental conditions of the adsorbent surface.

**pH And Conductivity for The Residual  $\text{Fe}^{+3}$  Solution:** The first test conducted is the pH test, which test the acidity of the remaining solution. As seen from the results (Fig 1), the pH values of the samples increased from the value 1.5 (1%  $\text{HNO}_3$  initial solution) towards the pH 3.0 after 2.5 h of the adsorption contact time. This shows after the adsorption process, the sample becomes less acidity. This give high recommended materials, due to that, most of the industrial process which use the water, most likely to be less acidity to prevent the corrosions.

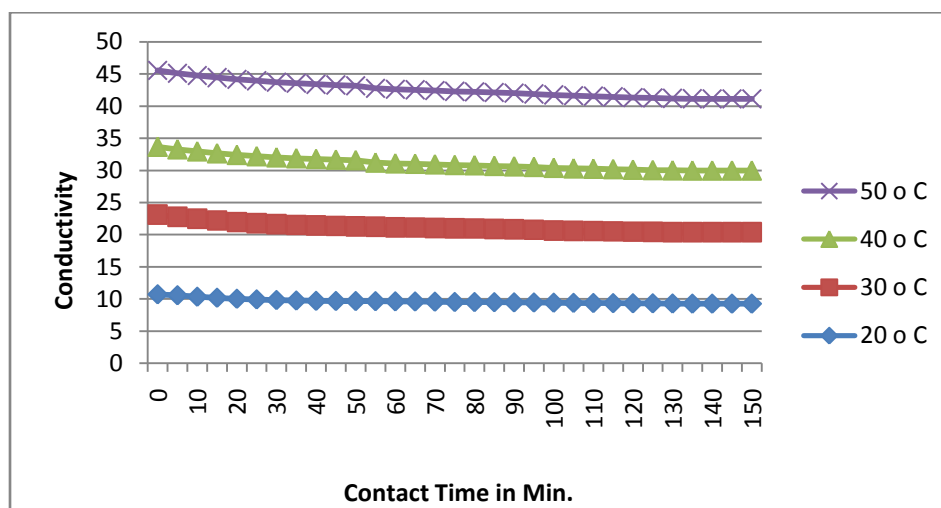


**Fig. 2** Effect of adsorption contact time (min) on the pH of the residual  $\text{Fe}^{+3}$  solution at different adsorption temperature

As shown in fig. 1 as increasing the adsorption contact, the pH of the remaining aqueous solution increases up to a maximum value of 3.5 at 2.5 hours. We observe that the pH of the remaining aqueous solution slightly increases over the time from 60 min to 2.5 h in various temperatures from 20° to 50°C. This is due to the adsorption and/or ion exchange equilibrium.

The next test conducted is a conductivity, which indicated how a sample could conduct electricity. As shown in fig. 2 the conductivity of remaining aqueous solution decreases as increases the contact time of adsorption over several temperature ranges.

It can be seen from results (fig. 2) the conductivity of the model solution has been decreased after going through the increasing of the adsorption contact time. This shows that the number of iron present is decreased after the adsorption process of  $\text{Fe}^{+3}$  of the model solution.

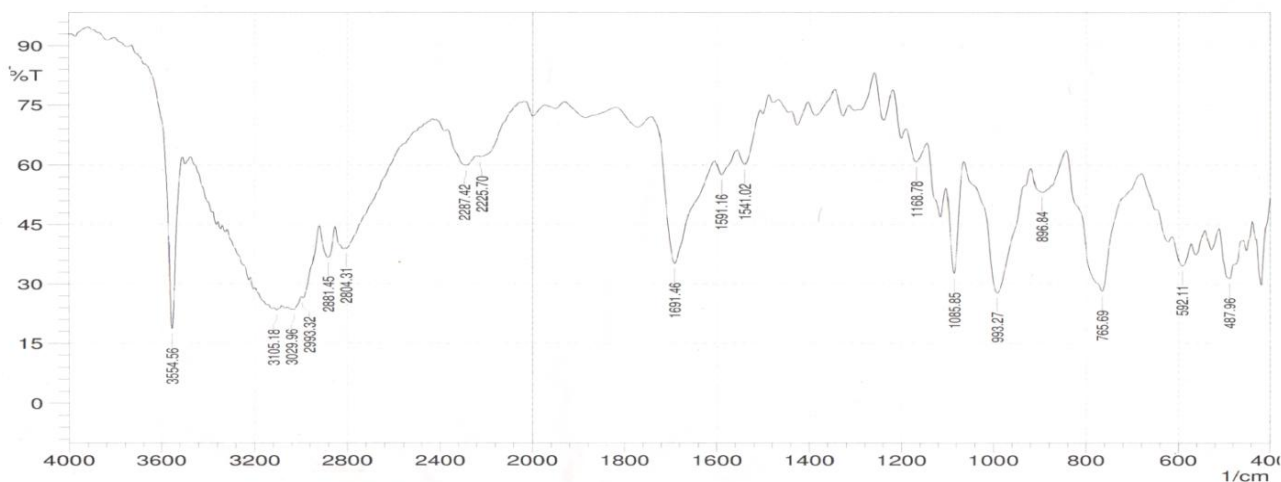


**Fig.2** Effect of adsorption contact time (min) on the conductivity of the residual  $\text{Fe}^{+3}$  solution at different adsorption temperature

**Contact Time Effect:** Figs.1, 2 shows the removals of  $\text{Fe}^{+3}$  VS the contact time at temperature  $30^\circ\text{C}$  and  $300\text{ rpm}$ , the maximum removal of  $\text{Fe}^{+3}$  is found to be around 50% at the first 50 min of contact time. As the adsorption contact time increases the concentration of  $\text{Fe}^{+3}$  in the model solution decreases. It can be seen that 70% of  $\text{Fe}^{+3}$  is adsorbed first 5 min while 15 % in the contact time interval of 5 min to 2.5 h.

#### Characterization of Indian Natural Zeolite

**IR Analysis:** The IR spectra of the Indian Natural Zeolite before treatment and after treatment with ferric nitrate solution are shown in the fig.3 and fig.4. IR spectroscopy can be used to determine structural changes due to cation exchange and adsorption  $4000\text{cm}^{-1}$  to  $400\text{cm}^{-1}$  with KBr using spectrometer model SIMADZU-8400S PC with  $400\text{ cm}^{-1}$  resolution. The IR spectra of the Indian Natural Zeolite before treatment and after treatment are shown in figs.3, 4. Results of IR Spectroscopy Analysis of Natural Zeolite are shown in table 1.



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

**Figure 3**

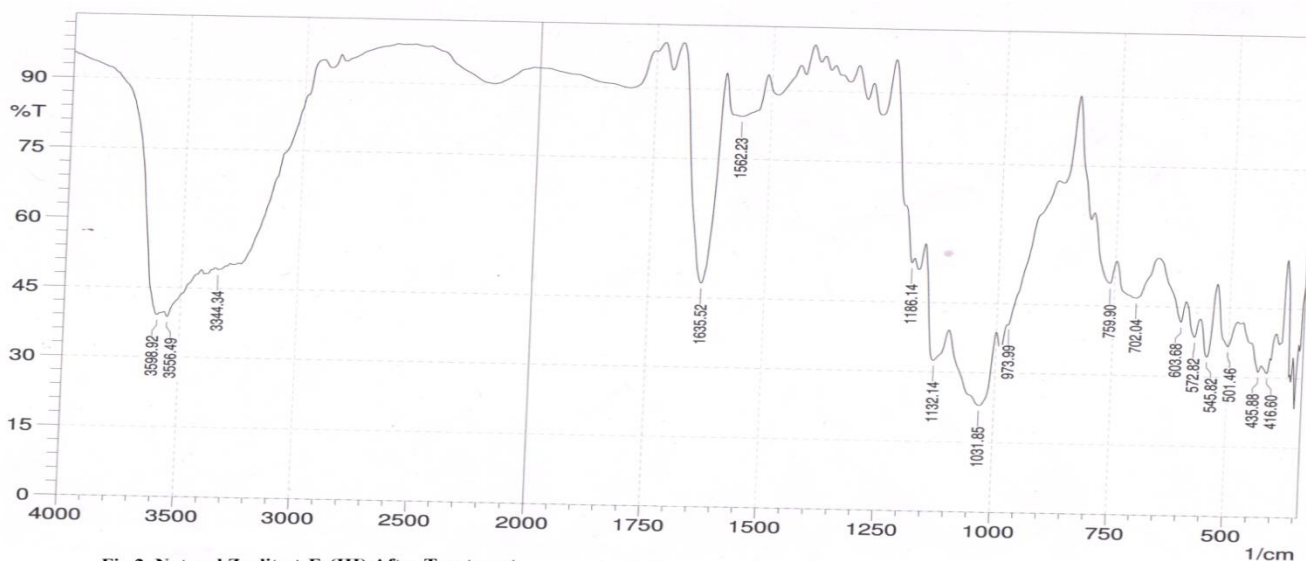


Fig.2. Natural Zeolite + Fe(III) After Treatment

Figure 4

Table -1 Results of IR Spectroscopy Analysis of Natural Zeolite

S No	Name of Sample	IR peaks (cm-1) with assignment
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)

**XRD Analysis:** The X-ray diffraction pattern of the natural zeolite before and after treatment (fig. 5 and 6) shows that it is crystalline and cubic [15-16]. This is good agreement with XRD pattern reported [17]. In order to study crystal structure of natural zeolite and natural zeolite doped with Fe(III) metal ion, X-ray diffractogram of these samples were examined with  $2\theta=10^\circ$  to  $2\theta=80^\circ$ . X-ray pattern reveal that both the samples were polycrystalline in nature with orthorhombic crystal structure for natural zeolite match with JCPDS card no. 83-1566. While natural zeolite doped with Fe(III) metal ion the crystal structure was crystalline and cubic, match with JCPDS card no. 85-2499. The % crystallinity for natural zeolite was 88.1%, while % amorphosity was 11.9%, while the % crystallinity for natural zeolite doped with Fe(III) metal ion was 88.9% and the % amorphosity was 11.1%.

The crystalline size D of the samples have been evaluated by using Scherer's formula

$$D = K\lambda/\beta\cos\theta$$

where K is constant ( $K=0.9$ ),  $\lambda$  is the wavelength of X-ray,  $\beta$  is full width at half of the peak maximum in radians and  $\theta$  is the Bragg's angle. It is observed that the crystalline size observed and calculated is tabulated in the table-2.

Table-2 Crystalline size D of the Samples

Sr. No.	Sample	Observed D value in nm	Calculated D value in nm
1.	Natural Zeolite	25.2 nm	24.26 nm
2.	Natural zeolite doped with Fe(III) metal ion	17.3 nm	16.84 nm

From the result tabulated in table 2, it is observed that the crystalline size of natural size changes when doped with Fe (III) metal ion. The Results of XRD Analysis of Natural zeolite and zeolite doped with Fe(III) metal ion are presented in table 3.

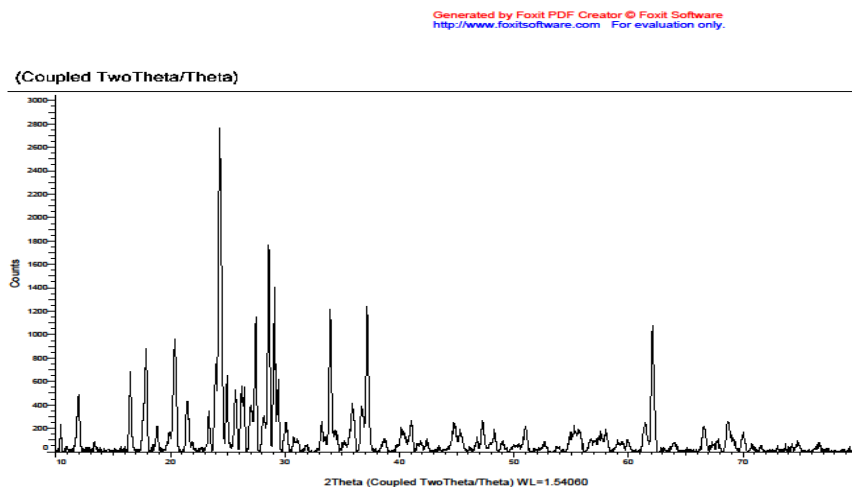


Fig. 3 XRD Analysis Before Treatment

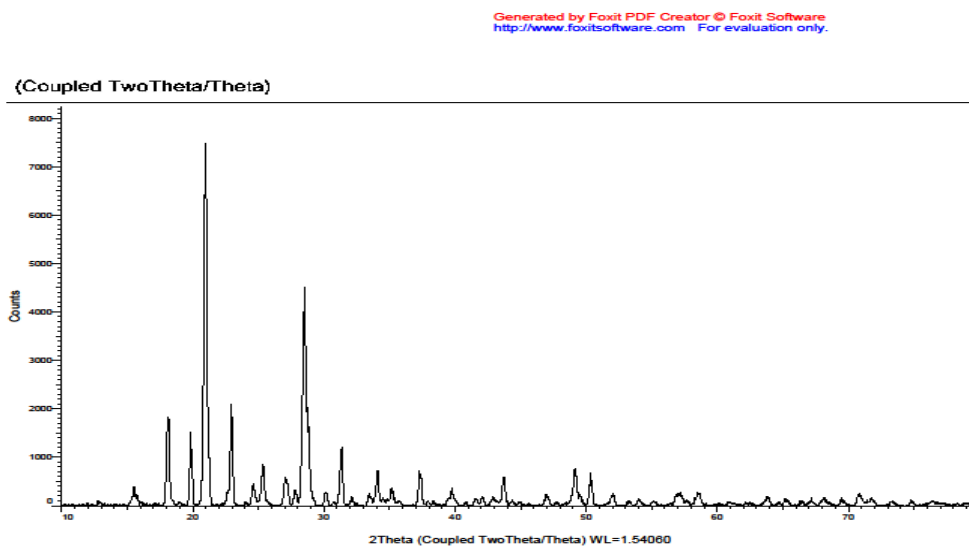


Fig.4 XRD Analysis after Treatment

**Table 3:** Results of XRD Analysis of Natural zeolite and zeolite doped with Fe (III) metal ion

Sample	2 Theta	h k l	Standard d value	Calculated d value	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	4.3553	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 Fe(III) metal ion	18.963	2 1 1	4.6771	4.6756	85-2499
	20.971	2 2 0	4.2327	4.2324	
	22.953	2 2 0	3.8716	3.8816	
	24.141	--	3.6837	3.6839	
	25.340	--	3.5120	3.5117	
	27.113	3 2 1	3.2862	3.2863	
	28.519	3 2 1	3.1273	3.1275	
	31.328	4 0 0	2.8530	2.8530	
	34.085	4 2 0	2.6282	2.6281	
	37.338	4 2 2	2.4064	2.4064	
	40.831	4 3 1	2.2638	2.2081	
	43.717	4 4 0	2.0689	2.0690	
	49.418	6 2 0	1.8428	1.8428	
	50.355	5 4 1	1.8107	1.8108	
58.564	7 2 1	1.5749	1.5749		

**FESEM Analysis (Field Emission Scan Electron Microscope) :** The scanning electron microscopy (SEM) is a primary tool used for characterization of the surface morphology and fundamental physical properties (18-19) of natural zeolite and its exchanged (after treatment) derivative. It is useful for determining the particle size, shape and 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 before and after treatment is shown in fig.7 and 8.

**Fig.7** SEM Analysis before Treatment

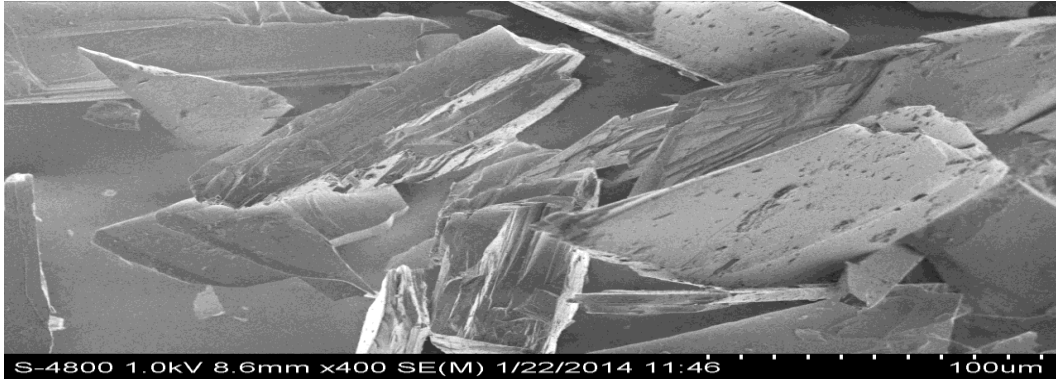


Fig.8 SEM Analysis after Treatment

**EDX Analysis (Energy Dispersive X-ray Spectroscopy):** Energy dispersive X-ray spectroscopy is a chemical microanalysis technique used in conjunction with SEM. EDX is used to characterize the elemental composition [20] of the natural zeolite before and after treatment. The typical EDX pattern of the natural zeolite before treatment and its parent derivative after treatment with Fe(III) metal ions are shown in figs.9 and 10. The EDX analysis of fig.9 shows the major elements of zeolite are Si and Ca before treatment while fig.9 shows the major elements Si, Ca and Fe after treatment. This results that Fe<sup>3+</sup> ions are adsorbed on the zeolite surface.

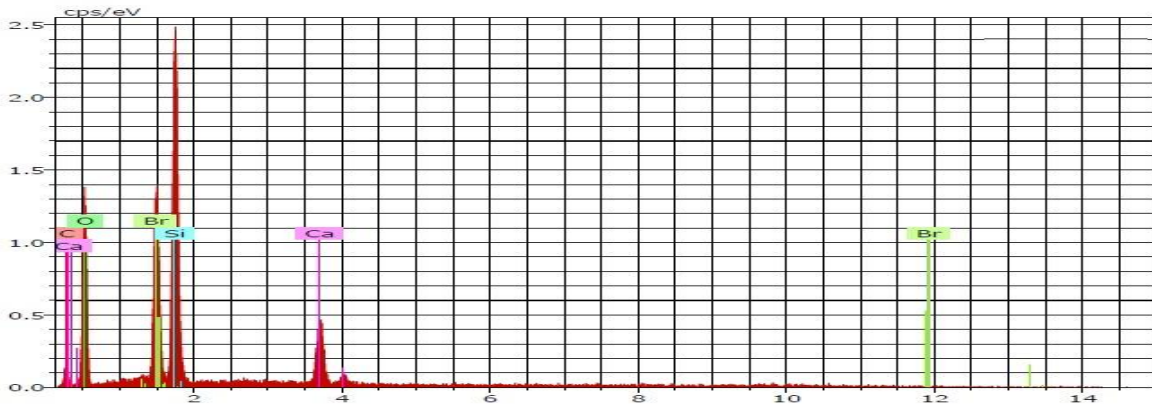


Fig.9 EDAX Analysis before Treatment

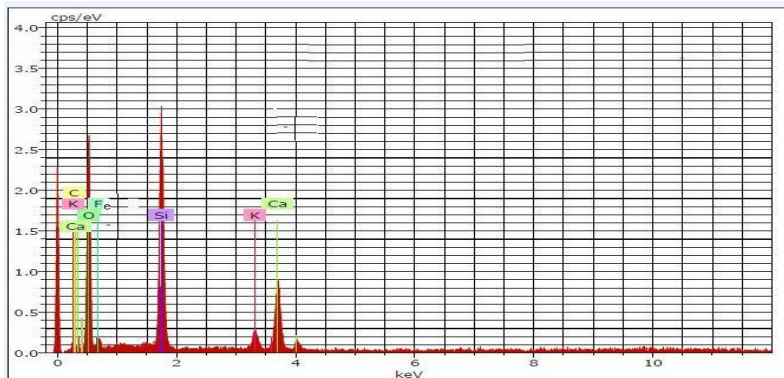
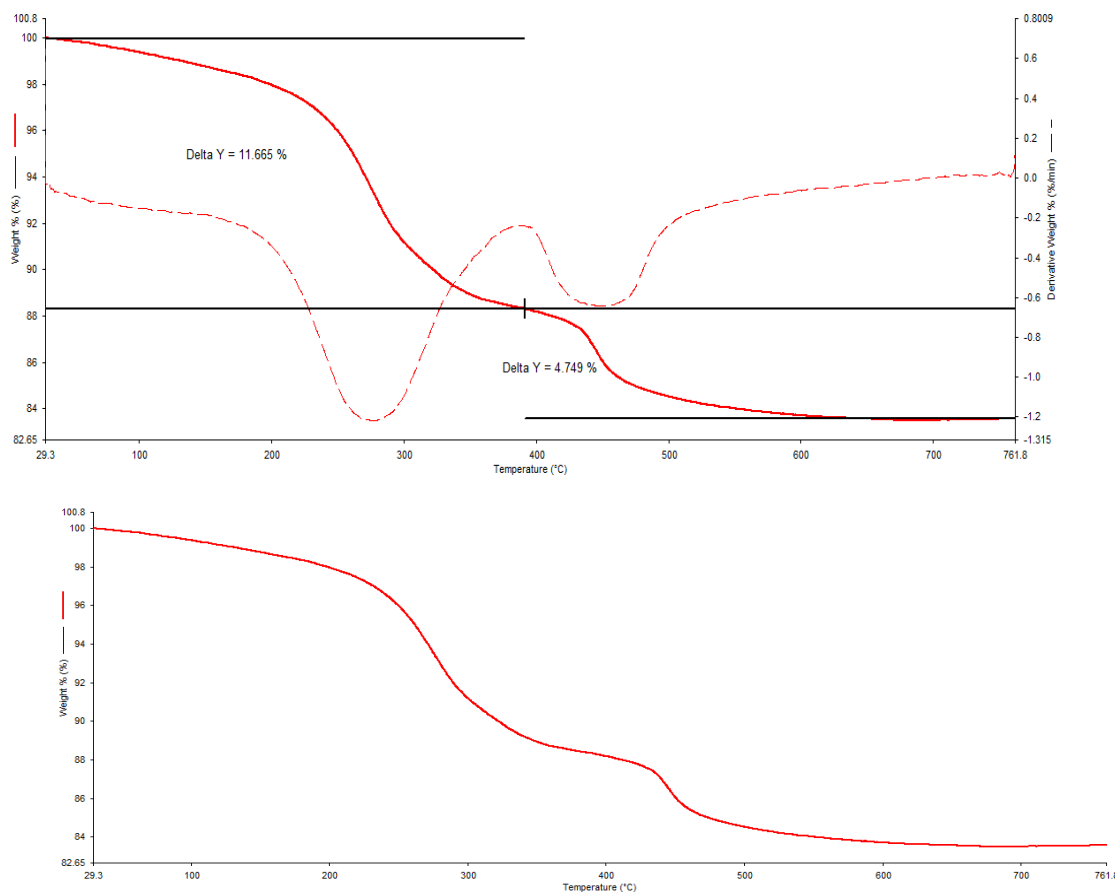


Fig.10 EDAX Analysis after Treatment



**TGA Analysis:** The TGA curve of natural zeolite shows the total weight loss of 16.414 % in three steps (Fig.11). In the first step total weight loss is 11.665 % of which initial rate of weight loss is higher up to the temperature of 280°C due to loss of adsorbed water followed by rate of weight loss decreased up to temperature 800°C due to dehydration. At last from 390°C temperature against loss in weight of sample observed up to 600°C temperature which is about 0.620% may be due to dehydration present in the core of zeolite. Followed by as the temperature increases there is no loss of weight and the graph becomes a straight line.

Thermal analysis of natural zeolite treated with Fe (III) metal ion solution helps to understand the effect of dehydration as well as heat treatment. The thermal stability of host lattice increased with increase in the size of exchanged cations [26]. The TGA curve of natural zeolite treated with Fe (III) metal ion solution shows the total weight loss of 16.091 % in three steps (Fig.12). In the first step total weight loss is 15.471 % of which initial rate of weight loss is higher up to the temperature of 140°C due to loss of adsorbed water followed by rate of weight loss decreased up to temperature 300°C due to dehydration. At last from 420°C temperature against loss in weight of sample observed up to 600°C temperature which is about 0.620% may be due to dehydration present in the core of zeolite. Followed by as the temperature increases there is no loss of weight and the graph becomes a straight line. The result of thermal stability of zeolite studied in our core is in good agreement with previous reports [27].



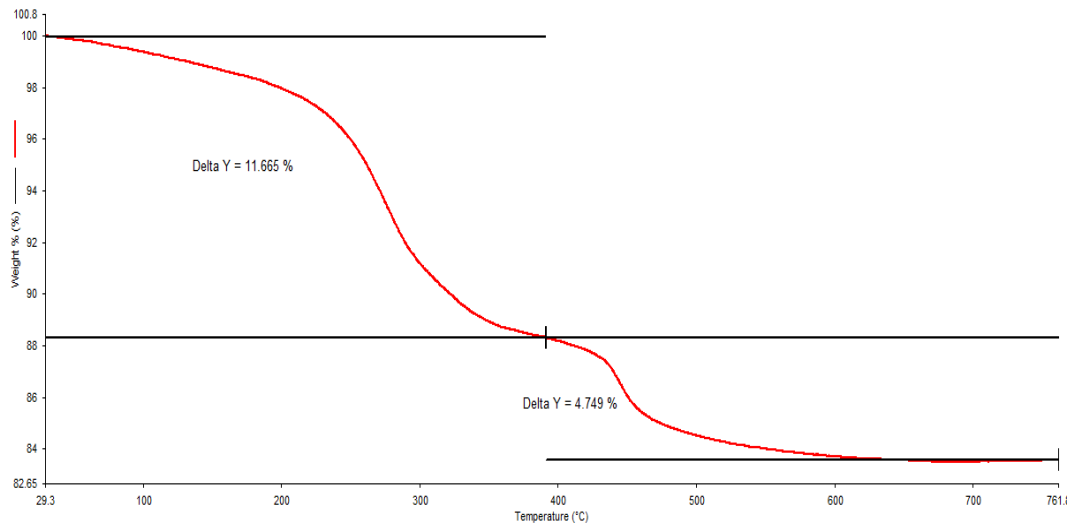
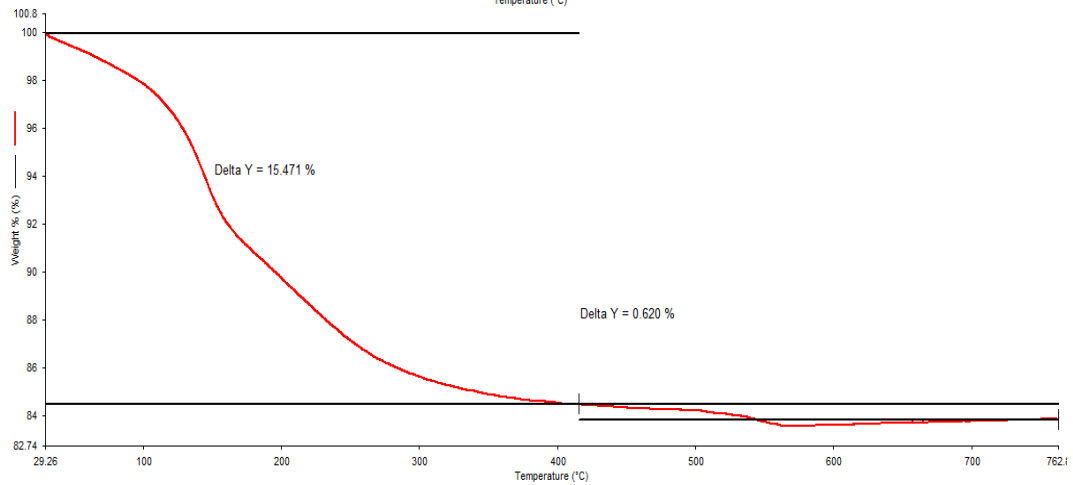
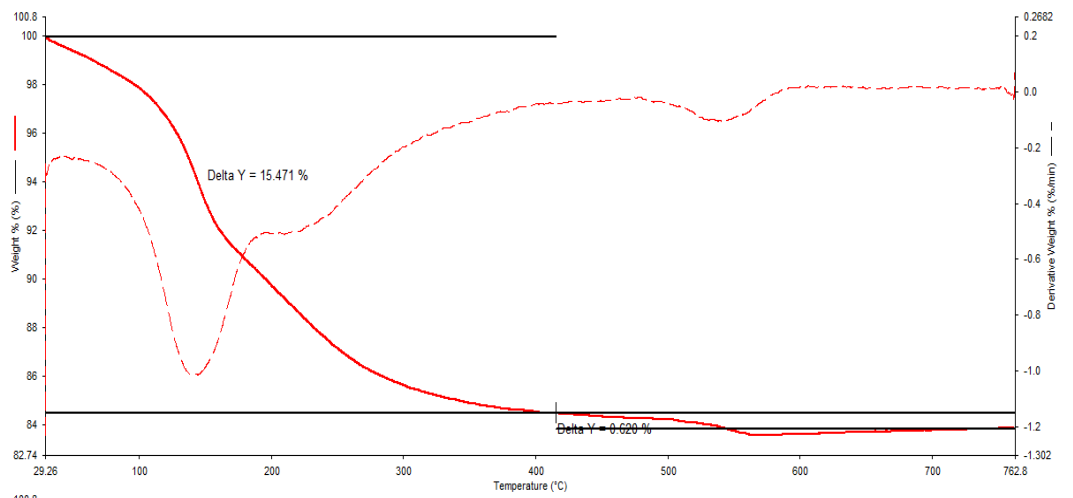


Fig.11 TGA graph of Natural Zeolite



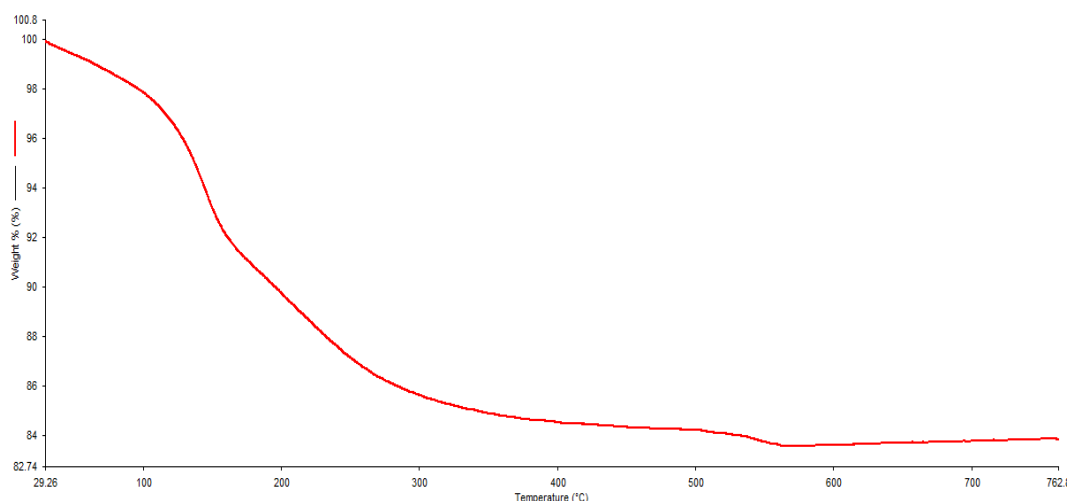


Fig.12 TGA Graph of Natural zeolite treated with Fe(III) metal ion solution (After Treatment)

**Magnetic Susceptibility:** The most commonly used method for measuring magnetic susceptibility is that introduced by Gouy method [21-26].  $\text{Fe}^{3+}$  has five unpaired electrons ( $d^5$ ) which caused magnetic properties. As it is expected that if the  $\text{Fe}^{3+}$  is entered the zeolite, the material will be improved and increased their magnetic properties. As increasing of contact time, the weight susceptibility will be increased, because the residual concentration of  $\text{Fe}^{3+}$  is decreased as shown in the fig.13. Natural zeolite has been successfully used for the removal of  $\text{Fe}^{3+}$  from a model solution at  $30^\circ\text{C}$ . The magnetic property of the residual zeolite increases as the contact time increase. This indication of successfully increase of the  $\text{Fe}^{3+}$  from the solution towards the zeolite particles.

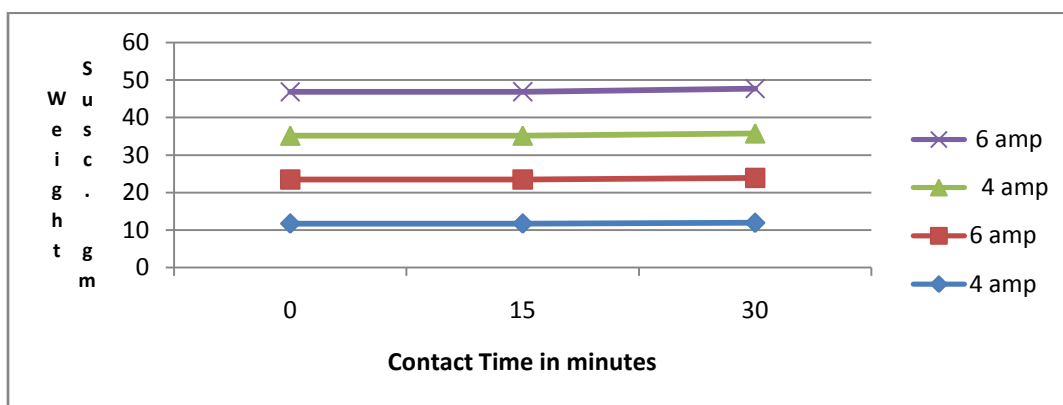


Fig.13 Effect of the adsorption contact time (min) on the weight susceptibility of the natural Zeolite on the sample 1 and sample 2.

The natural zeolites are quite useful as adsorbents and also useful for cleaning up municipal, industrial waste water. The natural zeolites can be used as a catalyst.

In this present work Indian Natural Zeolite have been successfully used for the removal of  $\text{Fe}^{+3}$  from a model solution of 1000 ppm, (1%  $\text{HNO}_3$ ) at a correlation of liquid to solid phases, v:g = 50:1. It has been found out that the best adsorption environment  $30^\circ\text{-}40^\circ\text{C}$ . The adsorption efficiency of  $\text{Fe}^{+3}$  is slightly constant at the contact time from 50 to 150 min. The conductivity of remaining solution is decreased as the contact time is increased. The results show that the natural zeolites are good ion exchanger for Fe (III) ions. The exchanging capacity Fe (III) ion at temperatures between  $30^\circ$  to  $40^\circ\text{C}$  at contact time interval from 50 to 150 min is maximum. The weight susceptibility of Natural Zeolite increases as contact time

increases. There is no change in the framework structure of zeolite after treatment. The natural zeolite used in this present work would be quite useful as adsorbent and also for cleaning up municipal, industrial waste water for the removal of heavy metals.

### APPLICATIONS

The natural zeolite is a good adsorbent and can be applied for cleaning up municipal, industrial waste water for the removal of heavy metals.

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