

A Cost Effective Natural Zeolite and Fly Ash Zeolite¹ Used For the Removal of NH_4^+ Ions From NH_4Cl Aqueous Solution : As a New Adsorbents



Chemistry

KEYWORDS : Natural zeolite, Fly ash zeolite¹, Adsorption, Ammonium ions.

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ABSTRACT

The adsorption studies on the removal of ammonium ions from aqueous solution of ammonium chloride using non treated natural zeolite and treated fly ash zeolite¹ as a new adsorbent, both are locally available and cost effective was carried out under varying experimental conditions. The maximum adsorption was observed to be a function of solution of pH, contact time and initial concentration of solution has been found out that specific surface of natural zeolite as well as fly ash zeolite¹ takes leading part at the adsorption of ammonium ions from aqueous solutions at room temperature with different concentrations. Natural zeolite showed maximum adsorptive removal of ammonium ions at about pH 3 and doses 1 gm per 50 ml solution in 2.5 hours while the fly ash zeolite¹ showed maximum adsorptive removal of ammonium ions at pH 3, doses 0.2 mg per 50 ml aqueous solution in 60 minutes. Ion exchange is probably one of the major adsorptive mechanisms for binding of NH_4^+ ions on the surface of natural zeolite as well as fly ash zeolite¹. This hypothesis is strongly supported by experimental analysis. On the basis of experimental results it can be said that the adsorbent natural zeolite and fly ash zeolite¹ may be used in developing an adsorptive technology for the removal of ammonium ions.

Introduction:

The widespread use of chemical fertilizers and contamination of water sources with industrial wastes increases the concentration of nitrogenous compounds in water bodies. These compounds, especially ammonium ions in high concentration, adversely affect the purity of water, lowering its quality, increasing algae and contaminating lakes, ponds and rivers. According to existing norms in drinking water ammonium concentration should not exceed 0.5 ppm.

The removal of nitrogenous compounds from wastes can be performed using physico-chemical methods. This includes adsorption by activated charcoal, chemical coagulation, ion-exchange etc. These methods have both advantages and disadvantages (1). Use of ion exchange resins for removal of ammonium ions on large scale is practically difficult due to high input costs and subsequent regeneration of resins.

Zeolites belonging to platy family possess selective ion exchange property for ammonium ions. Most of the zeolites possess high selective exchange property towards ammonium ions. It has been used to remove NH_3/NH_4^+ from wastewater, in wastewater treatment facilities mostly as pilot plants in Hungary, Japan, South Africa and the United States (2-4).

Zeolites are microporous crystalline solids with well defined structures. Generally they contain silicon, aluminium and oxygen in their pores. Many occur naturally as minerals and are extensively mined in many parts of the world. Others are synthetic and ore 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 variety of applications with a global market of several million tons per annum. In the western world major application is in petrochemical cracking, ion-exchange and in the separation and removal of gases and solvents. Apart from this agriculture, animal husbandry and construction they are often also referred to as molecular sieves (5-6).

MATERIAL AND METHOD :

Ion Exchange Property :

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.

Natural zeolites are uniquely effective in adsorbing ammonia and also adsorb hydrogen sulfide. These properties make natural zeolites ideal for use in pet litter to prevent emanation of irritating odors. For similar reasons, natural zeolites can be used for effective control of irritating gases in horse stalls, bams, kennels, etc.

Zeolites are used in ammonia filtration in fish hatcheries and also as biofilter media. In a fish farm the load of the water with fish can be very high. This results in a quick pollution of the water and as a result the concentrations of toxic substances can increase rapidly. Therefore, extensive water purification is necessary. The zeolites can be used in various steps of the purification process; as a secondary filtration unit after biological purification and / or aeration; as a support material for bacteria; as a filter medium for the removal of unwanted ions at the same time.

The objective of this study was to investigate the feasibility of adsorption for removal of NH_4^+ ions from aqueous solution utilizing natural zeolite and fly ash based zeolite¹.

In the previous work number of adsorbents used were Clarified sludge, Rice husk ash, Sawdust (tea wood origin), Activated carbon and a mixture of Fly ash and Activated Carbon (7-12). The adsorbents were selected on the basis of their cost effectiveness and ready availability. Many reports have appeared in literature on the development of low-cost adsorbents developed from cheaper and readily available materials (13-18).

Previously various types of zeolites were crushed and sieves and municipal waste water has been used for the study. Presence of ammonium ions was determined by Nesslerization method (19).

Collection of Fly Ash:

In this present work the fly ash used was collected from thermal power plant Eklahare, Nashik, Maharashtra (INDIA) which was used after treatment.

EXPERIMENTAL:

Preparation of Fly Ash Zeolite¹:

The material used in this study was the fly ash, a waste product resulted in thermal power plant from burning of pit coal. About 500 gm of ash sample (fly ash) have been manually collected at different sites (plants) from the warehouse of a power plant located at Eklahare, Nashik, Maharashtra. (INDIA).

Fly Ash zeolite1 material was obtained by direct alkaline conversion processes in autoclaves at 353 K and at time interval 8 hours. The flyash was added to a 2M NaOH solution. The zeolite obtained was filtered, washed and dried for 4 hours at 373 K. The experimental condition was the mixture continuously stirred.

Preparation of NH₄Cl solution:

All chemicals used were of analytical grade. In order to assess the performance of the low cost adsorbent collected and to avoid interference by other contaminants in waste water, the experiments were conducted with aqueous solution of NH₄Cl prepared by dissolving 3.12gms of ammonium chloride in one liter of double distilled water which makes 1000 ppm solution. Then prepare the 5, 10, 15, 20, 25 and 30 ppm solutions by diluting appropriate 1000 ppm solution.

Equipments:

- 1) ME-MAX Digital pH meter model ME-962-P was used to measure pH.
- 2) The magnetic stirrer was used for continuous stirring.
- 3) Remi R4 laboratory centrifuge was used for separating solution containing adsorbent and adsorbate.

RESULT AND DISCUSSION :

ADSORPTION METHOD AND THE REMOVAL OF NH₄Cl FROM AQUEOUS SOLUTION :

In general, the structure of natural zeolite contains specific size and shape. The porous material is therefore useful for adsorbing transition metals inside the porous material. The most of NH₄Cl are adsorbed very fast from a model solution within 1.5 hours. After this time generally no increase has been occurred, while the adsorption results are interested during first 60 minutes. The removal of NH₄Cl ions over zeolite through adsorption depends mainly on the thermodynamics parameters like temperatures, concentration of adsorbate and the environmental conditions of the adsorbent surface.

EFFECT on pH of various concentrations of NH₄Cl solution and contact time on the adsorption of NH₄Cl by Natural Zeolite :

50 ml of NH₄Cl solutions of various ppm concentrations (5, 10, 15, 20, 25 and 30 ppm) solutions of NH₄Cl were added with 1 gm of Natural zeolite as a adsorbent taken in a Borosil beaker and the mixtures were continuously stirred on the magnetic stirrer. The pH of NH₄Cl solutions were adjusted to about 3.5 by adding 1% HCl solution. The solutions were continuously stirred and the values of pH were recorded on digital pH meter ME-MAX model ME-962-P with contact time of 5 minute interval. The readings were recorded from 0 to 150 minutes.

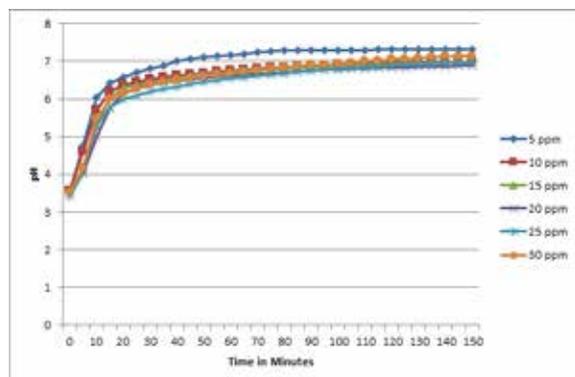


Fig.1) Effect of adsorption contact time (min) on the pH of the NH₄Cl solution at different concentration by using Natural Zeolite

As shown in Fig.1, as increasing the adsorption contact time, the pH of the remaining aqueous solution increases up to a maximum value of 7.32 at 2.5 hours. We observe that in the first 60 minutes pH rapidly increases up to 7.0 and the pH of the remaining aqueous solution slightly increases over the time from 60 minute to 2.5 hours at room temperature. This is due to the adsorption and/or cation exchange equilibrium.

EFFECT on pH of various concentrations of NH₄Cl solution and contact time on the adsorption of NH₄Cl by Fly ash Zeolite1 :

50 ml of NH₄Cl solutions of various ppm concentrations (5,10,15,20,25 and 30 ppm) solutions of NH₄Cl were added with 100 mg of treated fly ash zeolite1, as a adsorbent taken in a Borosil beaker and the mixtures were continuously stirred on the magnetic stirrer. The pH of NH₄Cl solutions were adjusted to 3.0 by adding 1% HCl solution. The solutions were continuously stirred and the values of pH were recorded on digital pH meter ME-MAX model ME-962-P with contact time of 5 minute interval. The readings were recorded from 0 to 60 minutes.

As shown in the following fig.2 as increasing the adsorption contact time, the pH of the remaining aqueous solution increases up to a maximum value of 4.5 in 60 minutes at room temperature. This is due to the adsorption and/or cation exchange equilibrium.

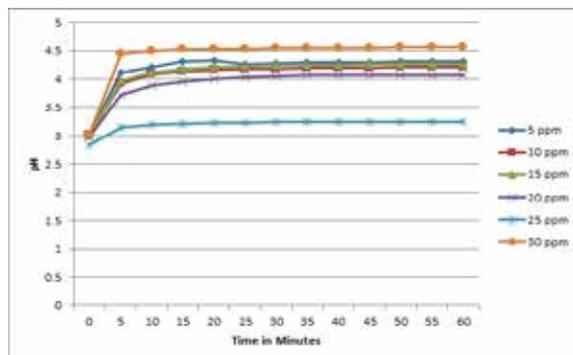


Fig.2) Effect of adsorption contact time (min) on the pH of the residual NH₄Cl solution at different adsorption time by using Fly Ash Zeolite1.

CHARACTERIZATION OF NATURAL ZEOLITE BY USING THE TECHNIQUE LIKE XRD, SEM AND EDX:

XRD Analysis :

The X-ray diffraction pattern of the natural zeolite doped with NH₄Cl solution (Fig.3) and the X-ray diffraction pattern of the Fly Ash zeolite1 doped with NH₄Cl solution (Fig.4) shows that it is crystalline, monoclinic and orthorhombic (20-21). The intensity of the peaks are also changed but the XRD analysis of the natural zeolite shows crystalline nature(22).

Fig.3) X-Ray diffraction pattern of Natural-Zeolite (Before Treatment) :

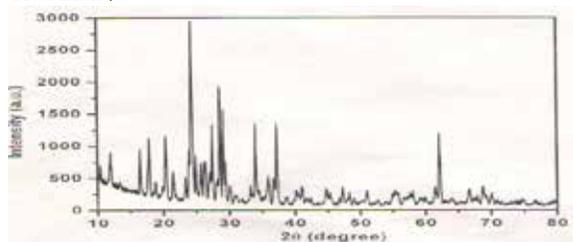


Fig.4) X-Ray diffraction pattern of Natural-Zeolite doped with NH₄Cl solution (After Treatment) :

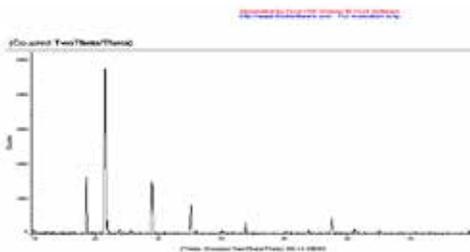
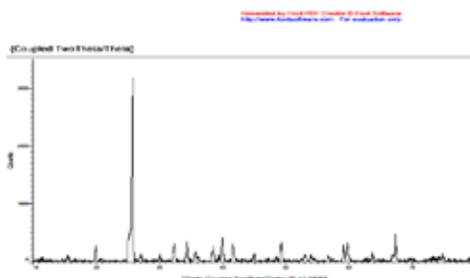


Fig.5) X-Ray diffraction pattern of Fly Ash Zeolite1 doped with NH4Cl solution (After Treatment) :



In order to study crystal structure of natural zeolite, X-ray diffractogram of the samples were examined with $2\theta = 100$ to $2\theta = 800$. The calculated and standard d values, 2theta values of natural zeolite, natural zeolite doped with NH_4Cl solution and Fly Ash Zeolite1 doped with NH_4Cl solution are reported in table-2.

Table 2 : Result of XRD Analysis of Natural Zeolite and Fly Ash Zeolite1:

Sample	2 Theta	Standard d	Calculated d
Natural Zeolite	16.32	5.3719	5.4285
	17.73	4.9690	5.1115
	20.41	4.3533	4.3471
	24.33	3.6548	3.6560
	28.57	3.1213	3.1224
	33.91	2.6365	2.6416
	37.05	2.4146	2.4246
	62.06	1.4926	1.4943
Natural Zeolite doped with NH_4Cl solution	18.64	4.7566	4.7567
	21.59	4.1133	4.1133
	29.05	3.0712	3.0711
	35.23	2.5458	2.5458
	43.86	2.0626	2.0626
	53.85	1.7010	1.7009
	57.52	1.6011	1.6011
	65.08	1.4320	1.4320
Fly Ash Zeolite1 doped with NH_4Cl solution	19.95	4.4469	4.4469
	25.74	3.4583	3.4576
	30.07	2.9692	2.9691
	32.31	2.7683	2.7683
	34.36	2.6080	2.6080
	38.51	2.3361	2.3362
	39.97	2.2538	2.2538
	41.62	2.1681	2.1681
	44.97	2.0144	2.0144
	49.27	1.8480	1.8480
	54.02	1.6961	1.6963
	59.11	1.5618	1.5618
	59.78	1.5457	1.5457
67.37	1.3889	1.3888	

In order to study crystal structure of natural zeolite, doped with NH_4Cl solution and NH_4Cl doped with fly ash zeolite1, X-ray diffractogram of the samples were examined with $2\theta=100$ to $2\theta=800$. X-ray pattern reveal that all the samples are polycrystalline and monoclinic in nature. The maximum observed and calculated d values for the samples were tabulated in the following table-3.

Table-3) The observed and calculated 'd' values for the samples:

Sr.No.	Sample Name	d (observed) value	d (calculated) value
1.	Natural Zeolite	3.6572	2.6500
2.	Natural zeolite doped with NH_4Cl solution	4.1136	2.4606
3.	Fly Ash zeolite1 doped with NH_4Cl solution	3.4573	2.3516

The crystalline size D of the samples have been evaluated by using Scherrers's formule where K is constant ($K=0.9$), λ is the wavelength of X-ray, β is full width at half of the peak maximum in radians and θ is the Bragg's angle. It is observed that the crystalline size observed and calculated are tabulated in the table-4.

Table-4) Crystalline size "D" of the samples :

Sr.No.	Sample Name	(observed) D value in nm	(calculated) D value in nm
1.	Natural Zeolite	25.2 nm	24.26 nm
2.	Natural zeolite doped with NH_4Cl solution	410.8 nm	356.77 nm
3.	Fly Ash zeolite1 doped with NH_4Cl solution	388.8 nm	374.16 nm

The % crystallinity for natural zeolite was 88.1%, while % atmosporosity was 11.9%, while the % crystallinity for natural zeolite doped with NH_4Cl solution was 86.7 % and the % atmosporosity was 13.3 %. Similarly the % crystallinity for fly ash zeolite doped with NH_4Cl solution was 73.1% and the % atmosporosity was 26.9 %.

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. It is useful for determining the particle size, shape, porosity. Scanning electron micrograph of natural zeolite, natural zeolite doped with NH_4Cl and Fly Ash zeolite1dopped with NH_4Cl solution is shown in fig. 6 to fig.8 respectively, the image was taken on the external surfaces of the natural zeolite. All the structures of natural zeolite after treatment can be observed and shows clearly crystalline and micro pores.

Fig.6) SEM Analysis of Natural Zeolite (Before Treatment) :

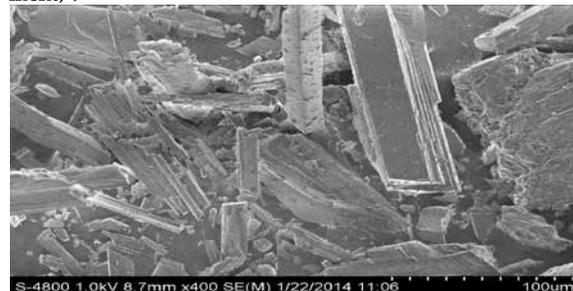
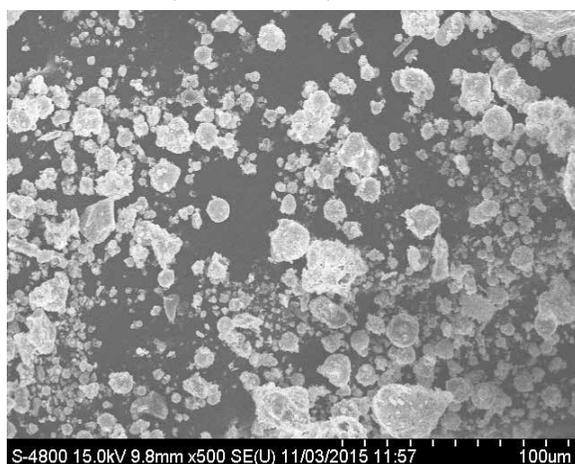


Fig. 7) SEM analysis of Natural Zeolite doped with NH₄Cl solution (After treatment) :



Fig. 8) SEM analysis of Fly Ash Zeolite1 doped with NH₄Cl solution (After treatment) :



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

Energy dispersive X-ray spectroscopy is a chemical microanalysis technique used in conjunction with SEM (23-24). EDX was used to characterize the elemental composition of the natural zeolite. The typical EDX pattern of the natural zeolite doped with NH₄Cl solution and Fly Ash zeolite1 are shown in (Fig.9,10). EDX data obtain from characterization shows some other elements are detected in analysis such as Si, Ca, K, C, O etc (25-27). As shown in Fig. 9 EDX spectrum of natural zeolite doped with NH₄Cl solution. The fig.10 shows the EDX pattern of Fly Ash Zeolite1 doped with NH₄Cl solution, shows the presence of Si, Al, Fe, Br, C, O elements detected.

Fig. 9) EDX Spectrum of Natural Zeolite doped with NH₄Cl solution:

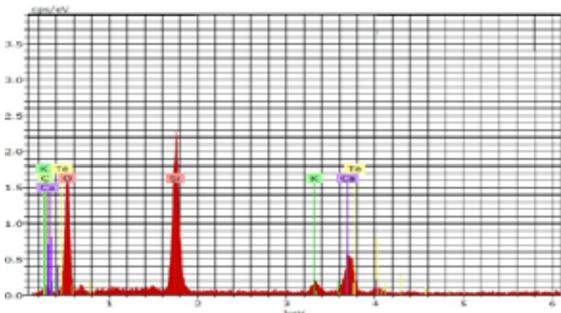
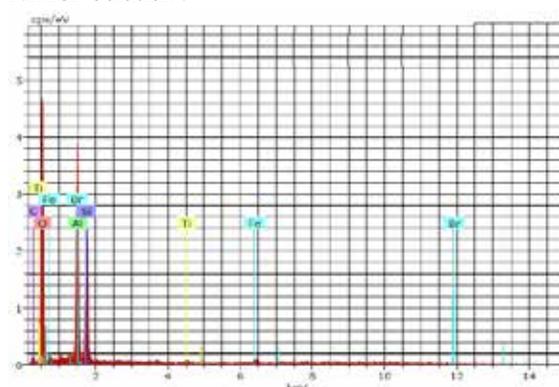


Fig. 10) EDX Spectrum of Fly Ash Zeolite1 doped with NH₄Cl Solution :



TGA Analysis :

The TGA curve of natural zeolite shows the total weight loss of 16.414% in three steps (fig.9). In the first step total weight loss is 11.665 % of which initial rate of weight loss is higher up to the temperature of 280oC due to loss of adsorbed water followed by rate of weight loss decreased up to temperature 800oC due to dehydration. At last from 390oC temperature against loss in weight of sample observed up to 600oC temperature which is about 4.745% 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 NH₄Cl 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 (28). The TGA curve of natural zeolite treated with NH₄Cl solution shows the total weight loss of 15.584% in three steps (fig.10). In the first step total weight loss is 10.584% of which initial rate of weight loss is higher up to the temperature of 280oC due to loss of adsorbed water followed by rate of weight loss decreased up to temperature 763oC due to dehydration. At last from 380oC temperature against loss in weight of sample observed up to 500oC temperature which is about 5.100% 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.

Similarly thermal analysis of fly ash zeolite1 treated with NH₄Cl 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 fly ash zeolite1 treated with NH₄Cl solution shows the total weight loss of 10.843% in three steps (fig.11). In the first step total weight loss is 10.843% of which initial rate of weight loss is higher up to the temperature of 400oC due to loss of adsorbed water followed by rate of weight loss decreased up to temperature 763oC due to dehydration. At last from 400oC up to 763oC temperature there is no weight loss. 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 (29).

Fig.9) TGA graph of Natural Zeolite :

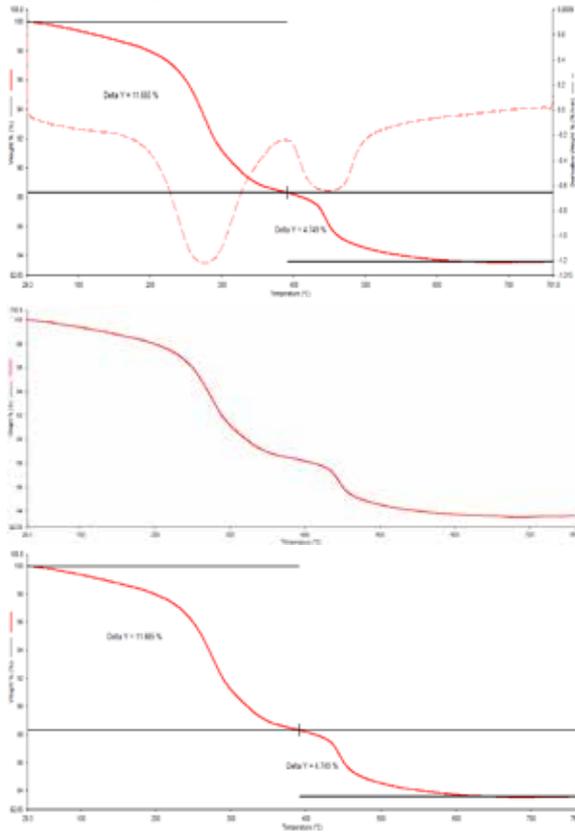


Fig.10) TGA Analysis of NH4Cl solution treated with Natural Zeolite (After Treatment):

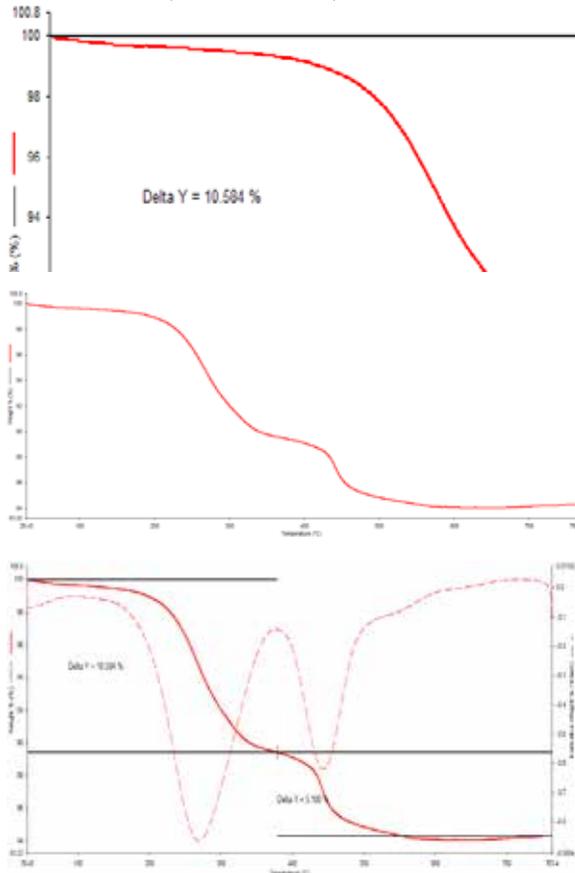
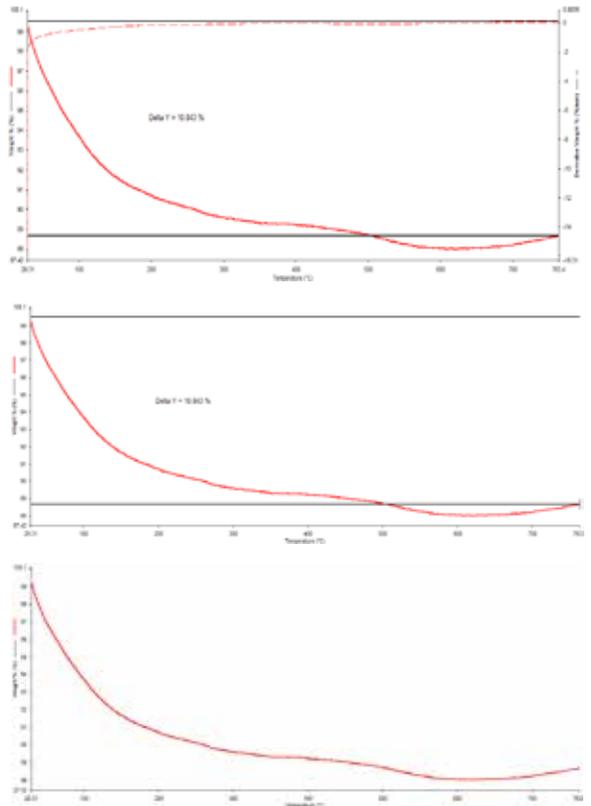


Fig. 11) TGA Analysis of NH4Cl solution treated with Fly Ash Zeolite1(After Treatment):



Conclusion :

In this present work natural zeolite and fly ash zeolite1 have been successfully used for the removal of ammonium ions from aqueous solution of 1000 ppm at a correlation of liquid to solid phase, v:g = 50:1 for natural zeolite while the correlation for fly ash zeolite1 it is v:mg = 50:100. It has been found out that the best adsorption environment at room temperature. The adsorption efficiency of NH4+ ions is slightly constant at the contact time 60 to 150 for natural zeolite and for fly ash zeolite1 it is slightly constant at time 30 to 60 minutes. The result shows that the natural zeolite and fly ash zeolite1 both are good ion exchanger for NH4+ ions.

Applications:

The natural zeolite and fly ash zeolite1 are good adsorbents and can be applied for cleaning up municipal, industrial waste water for the removal of heavy metals.

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