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A Low Cost Adsorbent Natural Zeolite and Fly Ash Zeolite1 for the Removal of Methylene Blue dye, Fe(III) Metal Ions and NH₄⁺ Ions from their Model Solution : A Comparative Analysis by IR, XRD, SEM, EDX and TGA

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ABSTRACT: The adsorption studies on the removal of methylene blue dye, ammonium ions and iron from there aqueous solutions using non treated natural zeolite and treated fly ash zeolite1 as a new adsorbent, both are locally available and lowcost, 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 on natural zeolite as well as fly ash zeolite1 takes leading part at the adsorption of methylene blue dye, ammonium ions and iron from aqueous solutions at room temperature with different concentrations. Natural zeolite showed maximum adsorptive removal of ammonium ions and iron at about pH 3 and doses 1 gm per 50 ml solution in 2.5 hours contact time, 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, methylene blue dye and Fe(III) ions on the surface of natural zeolite as well as fly ash zeolite1. The 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 methylene blue dye, ammonium ions and Fe(III) ions.

KEYWORDS :Natural zeolite, Fly ash zeolite1, Methylene blue dye, Ammonium ions, Fe(III) ions, Adsorption

I. INTRODUCTION

Paper, plastic, leather and textile industries consume large amount of water mainly use in colour for dyeing their products and finishing processes and thus uses a huge amount of water which results in the production of dye containing wastewater. Although textile effluent is not highly toxic, the coloured nature of textile wastewater causes major environmental problems especially towards the aquatic ecosystem (1-2). The discharge of dye effluents from textile, paper, leather and plastic industries into the environment possess severe problems to many forms of life (3-5). Nowadays more than 9000 different types of dyes have been incorporated in the colour index (6).

Many dyes are toxic and may cause destruction or inhibiting of their catalytic capabilities (7). To reduce the risk of environmental pollution from such waste it's necessary to treat them before discharging to the receiving environment (8).

Methylene blue (MB) is the most commonly used substance for dying cotton, wood and silk (9). Methylene blue has wider application, which includes colouring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock etc. Though methylene blue is not strongly hazardous but on inhalation, it can show various harmful effects. It can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea and gastric problem (10-11). Different methods were used for dyes removal, one of them is adsorption method. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity of toxic pollutants (12-13).

The wide spread 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



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concentration, adversely affect the purity of water, lowering its quality, increasing algea 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 (14). Use of ion exchange resins for removal of ammonium ions on large scale is practically difficult due to high input cost.

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 (0.3mg/L) in many parts of the country. It can cause serious environmental contamination if it present at high level (15). The main source of Fe^{+3} present in the soil as well as corrosive water which will pick up iron ions from pipes (16). 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 (17). Iron as an element may not be causing any significant health hazards. But when water containing colourless dissolved Fe^{+3} is allowed to stand in a cooking container or comes in contact with a sink or bath tub, the 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 (18). 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. Therefor purification is one of the widest spread technological processes (19). For the uptake iron metals, different methods are employed, such as physico-chemical (20) and biological methods (21). 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 (22-25), rice husk, bone powder, activated charcoal, saw dust, waste tea leaves, coconut fiber pith, fly ash, feldspar, (26) etc.

Natural zeolite and fly ash zeolite1 now used for removal purpose because of its porosity and the three-dimensional structures, it has high adsorption capacity because of zeolites are microporous crystalline solids with well defined structures. Generally they contain silicon, aluminium and oxygen in their pores. Natural zeolites are low cost adsorbent. Also, many other low-cost adsorbents have been tried for dye removal. In this study natural zeolite and fly ash zeolite1 and methylene blue, ammonium ions, Fe(III) ions was examined in batch adsorption technique. The parameter effect of concentration of MB, NH_4^+ and Fe(III) ions, pH of MB, NH_4^+ and Fe(III) ion solutions, natural zeolite and fly ash zeolite1 dosage and temperature were investigated.

II. MATERIALS AND METHODS

Adsorbents :Natural zeolite of India was collected from Dhule and Jalgaon district (M.S.) India. This zeolite was then crushed, dried and stored in a clean glass bottle. Natural zeolite was used as an adsorbent material without any pre-treatment.

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

Chemicals :All chemicals used were of analytical grade. Ammonium chloride, Ferrous nitrate, methylene blue dye were purchased from Chemox chemicals, Nashik, Maharashtra.

Concentrated Nitric acid (1% HNO₃) and pH buffer solutions were used to adjust pH values of adsorptive solution samples. Double distilled water was used in all experimental work.

Stock solutions : A stock solution of 100 ppm was prepared by dissolving 100 mgm of Methylene blue in 1000 ml double distilled water. The stock solution was further diluted with distilled water to desired concentration for obtaining the test solutions. The MB was chosen in this study because of its known strong adsorption onto solids. MB has molecular weight 319.85 and the maximum wavelength is 668nm. MB is heterocyclic aromatic compound (CI=52015, M.Formula= $C_{18}H_{18}N_3SCl_3H_2O$, Nature = Cationic). Dye concentration was determined by using absorbance measured before and after the treatment with UV-visibleSpectrophotometer.

The experiments were conducted with aqueous solution of NH4Cl prepared by dissolving 3.12 gms 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.

A stock solution of 1000 ppm was prepared by dissolving 1.80 gm of ferric nitrate $[Fe(NO_3).9H_2O]$ in 250 ml double distilled water. The stock solution was further diluted with distilled water to desired concentration for obtaining the test solutions.



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Preparation of Fly Ash Zeolite1 :The material used in this study was 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).

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.

Ion Exchange Property : Because cations are free to migrate in and out of zeolite structures, zeolite are often used to exchange their cations for those of surrounding fluids. Natural zeolites are uniquely effective in adsorbing ammonia and also adsorb hydrogen sulphide. These properties make natural zeolites ideal for use in pet litter to prevent emanation of irritating odours. 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 form 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 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^+ ion, Fe(III) ions and methylene blue dye from aqueous solutions utilizing natural zeolite and fly ash zeolite1.

Experimental:

Determination of Residual Metal Concentration : pH and conductivity was measured using digital pH meter and digital conductivity 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 atomic absorption spectrophotometer systemics model 118.

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

III. RESULT AND DISCUSSION

Adsorption method and the removal of NH_4Cl from aqueous solution : In general the structure of natural zeolite contain specific size and shape. The porous material is therefore useful for adsorbing transition metals inside the porous material. The most of NH_4Cl are adsorbed very fast from a model solution with in 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 NH_4Cl ions over zeolite through adsorption depends mainly on the thermodynamics parameters like temperature, concentration of adsorption of adsorptive and the environmental conditions of the adsorbent surface.

Adsorption and the removal of Iron(III) ions : A set of laboratory scale experiments was performed in which the INZ (Indian Natural Zeolite) was contaminated with acidic media 1% HNO₃ model solution of Fe(NO₃)₃.9H₂O in constant doses (50ml/1g). 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 cm³ Borosil beaker by mixing 50 cm³ of Fe (NO₃)₃.9H₂O solution with 1 gm of zeolite at constant pH of 1% HNO₃. Variant temperatures are carried out. For adsorption studies, some competitive methods will be carried out though using, e.g. stirring, temperature, contact time, as well as reported one, the concentration of sorbent to sorbet (13). The dipping of zeolite through water model solution involves over aperiod of 5 minutes to 150 minutes.

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 hours. After this time generally no increase has been occurred, while the adsorption results are interested during first 60 minutes. 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.



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Effect of pH

The pH is one of the most important factors for controlling the removal of dye. pH of the dye solution was studied with the change in pH the percentage of removal was also changed (27). The pH of the solution was measured on pH meter ME-MAX DIGITAL pH meter with magnetic stirrer (model no. ME-963-P). The pH of Methylene blue solution was adjusted in the range of 3 to 7 pH by adding 1% HCl or 1% HNO₃. About 1.0 gm of natural zeolite was added in the solution in different concentration from 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm and 30 ppm solution of MB (28). Solution was continuously stirred by using magnetic stirrer and the pH change was determined as shown in fig.1 (29-30).



Fig. 1) Effect of adsorption contact time (min) on the pH of the methylene blue solutionat various concentrations by Natural Zeolite:

Effect of Contact Time

Effect of contact time and dye concentration on the removal of Methylene Blue from aqueous solution in presented in Fig. 2 by Natural Zeolite. The experiments were carried out at stirring 200 rpm, 1.0 gm adsorbent natural zeolite per 100 ml of various concentrations of methylene blue solution at room temperature (31). The dye concentrations of Methylene Blue (5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm) for different time intervals up to 120 min. The percentage dye removal increases with increasing time with increasing dye concentration.

Effect on pH of various concentrations of NH_4Cl solution and contact time on the adsorption of NH_4Cl 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 an 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



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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. 2) Effect of adsorption contact time (min) on the removal of the methylene blue solution at various concentrations by Natural Zeolite:



Fig.3) Effect of adsorption contact time (min) on the pH of the NH₄Cl solution at different concentration by using Natural Zeolite



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As shown in **Fig.3**, 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 mgm of treated fly ash as 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 90 minutes.

Asshown in the following **fig.4** 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.4) Effect of adsorption contact time (min) on the pH of the residual NH₄Cl solution at different adsorption time by using Fly Ash Zeolite1.

pH and conductivity for the residual Fe⁺³ solution:

The first test conducted is the pH test, which test the acidity of the remaining solution. As seen from the results, the pH values of the samples increased from the value 1.5 (1% HNO₃ initial solution) towards the pH 3.0 after 2.5 hours 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.

As shown in Fig.5) 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 minute to 2.5 hours in various temperatures from 20° to 50° C. This is due to the adsorption and/or ion exchange equilibrium.



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Fig. 5) Effect of adsorption contact time (min) on the pH of the residual Fe⁺³ solution at different adsorption temperature

The next test conducted is a conductivity, which indicated how a sample could conduct electricity. As shown in **fig. 6**) 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. 6**) 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 Fe^{+3} of the model solution.

Contact Time Effect:

Fig.5 and 6 shows the removal of Fe^{+3} VS the contact time at temperature 30^{°C} and 300 rpm, the maximum removal of Fe⁺³ is found to be around 50% at the first 50 minutes of contact time. As the adsorption contact time increases the concentration of Fe⁺³ in the model solution decreases. It can be seen that 70% of Fe⁺³ is adsorbed first 5 minutes while 15% in the contact time interval of 5 minute to 2.5 hours.

CHARACTERIZATION OF INDIAN NATURAL ZEOLITE :

a) IR Analysis :

The IR spectra of the Indian Natural Zeolite before treatment and after treatment with ferric nitrate solution are shown in the fig.5-6. IR spectroscopy can be used to determine structural changes due to cation exchange and adsorption 4000 cm⁻¹ to 400 cm⁻¹ with KBr using spectrometer model SIMADZU-8400S PC with 400 cm⁻¹ resolution.

The IR spectra of the Indian Natural Zeolite before treatment and after treatment are shown in **fig.7** and **8**. Also the IR spectra of the Indian Natural Zeolite before treatment and after treatment for Fe(III) metal ion solutions are shown in **fig.7** and **9**.

The X-ray diffraction pattern of the natural zeolite before and after treatment (**fig.5** and **6**) shows that it is crystalline (15). This is good agreement with XRD pattern reported (16). In order to study crystal structure of natural zeolite and natural zeolite doped with methylene blue dye, X-ray.



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Fig.6) Effect of adsorption contact time (min) on the conductivity of the residual Fe⁺³ solution at different adsorption temperature



Fig. 7) The IR spectrum of Natural Zeolite (Before Treatment) :



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Fig. 8) The IR spectrum of Natural Zeolite dopped with Mathylene Blue dye (After Treatment) :

Fig.9) The IR spectrum of Natural Zeolite dopped with Fe(III) ion solution (After Treatment)

b) XRD Analysis :

The X-ray diffraction pattern of the natural zeolite before and after treatment for methylene blue dye solution (**fig.10** and **11**) shows that it is crystalline (15). This is good agreement with XRD pattern reported (16). In order to study crystal structure of natural zeolite and natural zeolite doped with methylene blue dye, 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.



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The % crystallanity for natural zeolite was 88.1%, while % amorphosity was 11.9%, while the % crystallanity for natural zeolite doped with methylene blue was 95.8% and the % amorphosity was 4.2%.

The crystalline size D of the samples have been evaluated by using Scherrers's formula $D = K\lambda/\beta \cos\theta$ 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 redians and θ is the Bragg's angle. It is observed that the crystalline size observed and calculated is tabulated in the table-1.

| Sr. | Sample | Observed D value in nm | Calculated D value in nm |
|-----|--|------------------------|--------------------------|
| No. | | | |
| 1) | Natural Zeolite | 25.2 nm | 24.26 nm |
| 2) | Natural Zeolite doped with | 57.34 nm | 58.31 nm |
| | Methylene Blue dye | | |
| 3) | Natural Zeolite doped with Fe (III) | 17.3 nm | 16.84 nm |
| | metal ion | | |
| 4) | Natural Zeolite doped with NH ₄ Cl | 410.8 nm | 356.77 nm |
| | solution | | |
| 5) | Fly Ash Zeolite1 doped with NH ₄ Cl | 388.8 nm | 374.16 nm |
| | solution | | |

Table -1) Crystalline size 'D' of the samples

From the result tabulated in table no. 1), it is observed that the crystalline size of natural zeolite and fly ash zeolite1 changes when doped with methylene blue dye, Fe(III) metal ion and NH_4Cl solution.

| $fable = \Delta f$ the observed and calculated average u values for the samples |
|---|
|---|

| Sr. | Sample | d (observed) average | d (calculated) average |
|-----|--|----------------------|------------------------|
| No. | | value | value |
| 1) | Natural zeolite | 3.6572 | 2.6500 |
| 2) | Natural zeolite doped with Methylene | 1.6056 | |
| | Blue dye | | |
| 3) | Natural zeolite doped with NH ₄ Cl | 4.1136 | 2.4606 |
| | solution | | |
| 4) | Fly ash zeolite1 doped with NH ₄ Cl | 3.4573 | 2.3516 |
| | solution | | |



Fig.10) The XRD spectrum of Natural Zeolite (Before Treatment)



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Fig.13) The X-Ray diffraction pattern of NaturalZeolite doped with NH₄Cl solution

Fig.14) The X-Ray diffraction pattern of Fly Ash Zeolite1 doped with NH₄Cl solution



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Table 3) Result of XRD analysis of Natural Zeolite and Fly Ash Zeolite1

| Sample | 2 Theta | Standard d value | Calculated d value |
|-------------------------|---------|------------------|--------------------|
| 1) Natural | 16.32 | 5.3719 | 5.4285 |
| Zeolite | 17.73 | 4.9690 | 5.1115 |
| | 20.41 | 4.3553 | 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 |
| 2) Natural | 18.63 | 4.7588 | 4.7593 |
| Zeolite doped | 21.53 | 4.1246 | 4.1248 |
| With Methylene | 24.00 | 3.7047 | 3.7043 |
| Blue dve | 41.97 | 2.1507 | 2.1025 |
| | 51.44 | 1 7750 | 1 7751 |
| | 58.81 | 1 5689 | 1 5688 |
| | 71.67 | 1 3118 | 1 3157 |
| 3) Natural | 18 963 | 4 6771 | 4 6756 |
| Zeolite doped | 20.071 | 4.0771 | 4.0750 |
| With Eq.(III) | 20.971 | 3 8716 | 2 9916 |
| Matalian | 22.935 | 3.6710 | 3.6820 |
| Metal Ioli | 24.141 | 3.0637 | 2 5117 |
| | 23.340 | 3.3120 | 3.3117 |
| | 27.115 | 3.2802 | 3.2803 |
| | 28.519 | 3.1273 | 3.1275 |
| | 31.328 | 2.8530 | 2.8530 |
| | 34.085 | 2.6282 | 2.6281 |
| | 37.338 | 2.4064 | 2.4064 |
| | 40.831 | 2.2638 | 2.2081 |
| | 43.717 | 2.0689 | 2.0690 |
| | 49.418 | 1.8428 | 1.8428 |
| | 50.355 | 1.8107 | 1.8108 |
| | 58.564 | 1.5749 | 1.5749 |
| 4) Natural | 18.64 | 4.7566 | 4.7567 |
| Zeolite doped | 21.59 | 4.1133 | 4.1133 |
| With NH ₄ Cl | 29.05 | 3.0712 | 3.0711 |
| solution | 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 |
| 5) Fly Ash | 19.95 | 4.4469 | 4.4469 |
| Zeolite1 doped | 25.74 | 3.4583 | 3.4576 |
| With NH ₄ Cl | 30.07 | 2.9692 | 2.9691 |
| Solution | 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 |
| L | | | |



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c) 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 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. 15** and **16**.



Fig.15) SEM Analysis of Natural Zeolite (Before Treatment)



Fig.16) SEM Analysis of Natural Zeolite doped with Methylene Blue (After Treatment)



1

Fig.17) SEM Analysis of Natural Zeolite doped With Fe(III) metal ion solution Fig.18) SEM Analysis of Natural Zeolite doped with NH4Cl solution (After Treatment)



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Fig.19) SEM Analysis of Fly Ash Zeolite1 doped With NH₄Cl solution (After Treatment)

Fig. 20) EDX spectrum of Natural Zeolite doped with NH₄Cl solution (After treatment)

d) EDX or EDS Analysis (Energy Dispersive X-Ray Spectroscopy) :

Energy dispersive X-ray spectroscopy is a chemical microanalysis technique used in conjugation with SEM (32-33). 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. 20 and 21. EDX data obtain from characterization shows some other elements are detected in analysis such as Si, Ca, K, C, O etc. (34-36). As shown in fig. 20 EDX spectrum of natural zeolite doped with NH₄Cl solution while the fig. 21 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. 21) EDX spectrum of Fly Ash Zeolite1 doped with NH₄Cl solution (After Treatment)

The typical pattern of the natural zeolite before treatment and its parent derivative after treatment with Fe(III) metal ions are shown in figs. 22 and 23. The EDX of fig. 22 shows the major elements of zeolite are Si and Ca before



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treatment while fig. 23 shows the major elements Si, Ca, and Fe after treatment. This result shows that Fr^{3+} ions are adsorbed on the zeolite surface.





8

6

keV

e) TGA Analysis :

5

4.0

3.5

3.0

2.5

1.0

0.5

0.0

The TGA curve of natural zeolite shows that the total weight loss of 16.414 % in two steps (fig. 24). In the first step total weight loss is 11.665 % of which initial rate of weight loss is higher up totemperature 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 again loss in weight of sample observed up to 600°C temperature which is about 4.749 % 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.

10



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Thermal analysis of natural zeolite treated with methylene blue 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 (37). The TGA curve of natural zeolite treated with methylene blue dye solution shows the total weight loss of 18.493 % in two steps (fig. 25). In the first step total weight loss is 12.676 % of which initial rate of weight loss is higher up to the temperature of 300°C due to loss of adsorbed water followed by rate of weight loss decreased up to temperature 763°C due to dehydration. At last from 400°C temperature again loss in weight of sample observed up to 460°C temperature which is about 5.817 % 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 (38).

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 cation (37). 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.26). In the first step total weight loss is 15.471 % of which initial rate of weight loss is higher up to 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 again 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 (38).

Thermal analysis of natural zeolite treated with NH_4Cl 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 (37). The TGA curve of natural zeolite treated with NH_4Cl solution shows the total weight loss of 15.584 % in two steps (fig.27). In the first step total weight loss is 10.584 % 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 763°C due to dehydration. At last from 380°C temperature again loss in weight of sample observed up to 500°C 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 (37). The TGA curve of Fly Ash zeolite1 treated with NH₄Cl solution shows the total weight loss of 10.843 % in two steps (fig.28). In the first step total weight loss is 10.843 % of which initial rate of weight loss is higher up to the temperature of 400°C due to loss of adsorbed water followed by rate of weight loss decreased up to temperature 763°C due to dehydration. At last from 400°C temperature up to 763°C there is no loss in weight. 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 (38).

IV. CONCLUSION

In this present work natural zeolite and fly ash zeolite1 have been successfully used for the removal of ammonium ions from aqueous solution. It has been found out that the best adsorption environment at room temperature. The result shows that the natural zeolite and fly ash zeolite1 both are good ion exchanger for NH⁴⁺ ions.

In this present work natural zeolite have been successfully used for the removal of Fe^{3+} from the aqueous solution. It has been found out that the best adsorption environment 30-40°C.

Also in this present work natural zeolite have been successfully used for the removal of methylene blue solution. It is also found out that the best adsorption environment at room temperature.

Application :

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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Fig. 24) TG curve for Natural Zeolite (Before Treatment)



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Fig. 25) TG curve of Natural zeolite doped with Methylene Blue dye solution (After treatment)





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Fig. 27) TG curve of Natural zeolite doped with NH4Cl solution (After Treatment)





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REFERENCES

1) Al-Degs, Y., Khraisheh, M.A.M., Allen, S.J., Ahmad, M.N., *Water Research*, **34**(3), 927-935(**2000**).

2) Lachheb, H., Puzenat, E., Houas, A., Ksibi, M., Photocatalytic degradation of various types of dyes in water by UV-irradiated titania Applied Catalysis *B: Environmental*, **39**, 75-90 (**2002**).

3) Gregorio, C., Non-conventional low-cost adsorbents to dye removal. A review *Bioresource Technology*, **97**, 1061-1085(**2006**).

4) Sreedhar, S., and Kotaiah, B., Comparative evaluation of commercial and sewage sludge based activated carbons for the removal of textile dye from aqueous solutions. *Iran. J. Environ. Health Sci. Eng.*, **3**, 239-246 (**2006**).

5) Bidhendi, G.N., Torabian, A., Ehsani, H., Razmkhah, N., Evaluation of industrial dyeing wastewater treatment with coagulantsand polyelectrolyte as a coagulant aid. *Iran J. Environ. Health Sci.Eng.*, **4**,29-36(**2007**).

6) Hameed, B.H., Ahmad, A.L., Latiff, K.N.A., Dyes and Pigments, 75(1), 143-149(2007).

7) Espulgas, S.J., Gimenez, S., Contreras, E.P., Rodriguez, M., Comparison of Different Advanced Oxidation Processes for Phenol Degradation., *Water Res.* **36**, 1034-1042(**2002**).

8) Gorgion, D., Melidis, P., Aivasidas, A.A, Use of microbial sensor, inhibition effect of Azo reactive dyes on active sludge, *Bioprocess, BiosystEngg.*, **25**, 79-83(**2002**).

9) Jalajaa. D., Manjuladevi. M., Saravaran, S.V., Removal of Acid dye from Textile wastewater by using activated carbon prepared from PunicaGranatum (Pomegranate) Rind, *Pollution Research*. **28**(2), 287-290 (**2008**).

10) Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M.H., Hashim, R., *Journal of Hazardous materials*, **170**(1), 357-365(**2009**).

11) Rafatullah, M., Sulaiman, Othman, Hashim, R., Ahmad, A., Journal of Hazardous Materials, 177(1-3), 70-80(2010).

12) Fernandes, A.N., Almeida, C.A.P., Debacher, N.A., Sierra, Maria M.de S., *Journal of Molecular structure*, **982**(1-3), 62-65(**2010**).

13) Fernandes, A.N., Almeida, C.A.P., Menezes, C.T.B., Debacher, N.A., Sierra, M.M.D., *Journal of Hazardous Materials*, **144**(1-2), 412-419 (**2007**).

14) Metealf and Eddy, Wastewater Engineering Treatment, Disposal, Reuses, 3rdEdn., Tata McGraw Hill, p-737 (**1995**).

15) Brenzonik, P.L., in ed.: A.j. Rubin, *Aqueous Environmental chemistry of the metals*, Ann Arbor Science Publishers, Ann Arbor, pp. 167-191(**1974**).

16) Zuane, J.D., Handbook of Drinking Water Quality, Van Nostrand Reinhold, New York (1990)

17) Zamzow, M.J. and Murphy, J.E., Sep. Sci. Technol., 14, 1969 (1992).

18) Kim, J.S., Zhang, L. and Keane, M.A., Sep. Sci. Technol., 36, 1509 (2001).

19) Kim, J.S. and Keane, M.A., J. Chem. Tech. Biotech., 77, 633(2002).

20) Volesky, B., Weber, J. and Vieira, R., in eds.: R. Amils and A. Ballester, Biosorption of Cd and Cu by different

type of sagassum biomass, Biohydrometallurgy and the environment towards the mining of 21st century (PartB),

International Biohydrometallurgy Symposium Proceeding, Amsterdam, Elsvier, pp. 473-482 (1999).

21) Kapoor, A. and Viraraghavan, T.F., Biosours Technol., 53, 195 (1995).

22) Navarro, B.V.Y. and Lglesias, P.A., Ingen. Quim. (Madrid), 375, 177 (2001).

23) Gowrek, B., Brogowski, Z. and Borowiak, M., Pol. AchiwumOchronySrodowiska, 1, 193 (1992).

24) Ogiwara, K., Akita Kogyo Koto SenmonGukkoKenkyaKito, 30, 113 (1994).

25) Zorpas, A.A. and Loizidou, M., Hazard Indust. Wast, 94, 835 (2006).

26) Arda, D., Hizal, J. and Apak, R., Radiochim. Acta, 94, 835 (2006).

27) Yamin Yasin, Mohd, Zobin Hussein and FaujanHj Ahmad, Adsorption of Methylene blue on treated activated carbon, *The Malaysian Jour. of Analytical Science*,**11**(11),400-406 (**2007**).

28) Mohamed Bouraada, Mama Lafijah, Mohamd said Quali, Louis Charles, de Menorval, Basic dye removal from aqueoussolution by dedecylsulfate and dodecyl benzenesulphonate intercalated hydrotalcite, *Journal of Hazardous Materials*, **1529**, 601-609(**2008**).

29) Gulnaz O., Kaya, A., Matyar, F., Arikan, B., Sorption of basic dye from aqueous solution by activated sludge, *Journal of Haz. Materials*, **108**, 183-188(**2004**).

30) Forgacs E., Csarhati T., Oros G., Removal of synthetic dyes from waste waters: a review, *Environ*, *Int.*, **30**, 953-971(**2004**).

31) Hammeed, B.H., Khaiary, M.I., Removal of basic dye from aqueous medium using a novel agricultural waste material: Pumpkin seed hull, *Journal of Hazardous Materials*, **155**, 601-609(**2008**).



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[DOI:10.15680/LJIRSET.2021.1007068]

32) Fuoco, Domenico. "A New Method for Characterization of Natural Zeolites and Organic Nanostructure UsingAtomic Force Microscopy." *Nanomaterials***2**,1,79-91(**2012**).

33) AyhanSengil I, MahmutOzacar, Harun Turkmenler., Equilibrium and kinetics studies of copper solution on Chitosanadsorbent, *J. of Hazardous Mater*, **162**, 1046 (**2009**).

34) Israel, U., Eduok, U.M. Archives, Adsorption of Zn(II) from aqueous solution by using Chitin extraction, *AppliedSci research*, **4**(**2**), 809(**2009**).

35) Saeed, A., Akhter, M.W., Iqbal, M., Saeed, A., Akhter, M.W., Iqbal M., Removal of Lead(II) and Copper(II) from aqueoussolution using pomegranate peel as a new adsorbent, *Separ. Purif. Technol.* **45**, 25 (**2005**).

36) Monika Jain, Garg, V.K., Kadirvelu, K., Removal of Ni(II) from aqueous system by chemically modified Sunflower biomass, *Bioremediation J.***17**(1), 30(**2013**).

37) T. Vengris, R. Binkien, A. Sveikauskait, Applied Clay Scienc, 18, 183-190 (2001).

38) G. Vazque, A.J. Gonzalez, A.L. Garcia, M.S. Freire, G. Antorrena, Adsorption of phenol on formaldehyde pretreatedpinuspinaster bark equilibrium and kinetics ,BioresourTechnol, **98** (8) 2535 (2007).





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