

# THE ZEOLITE USED AS ADSORBENTS FOR THE TREATMENT OF WASTE WATER MADE FROM SOLID WASTE RESIDUE

Kapure G.P

Department of Physics, S.G.B. College, Purna (Jn) - 431 511.  
Email: gpk\_2010@rediffmail.com

## Abstract :

Zeolite synthesized from fly ash are crystalline micro porous alumino-silicates solids containing cavities and channels of a molecular size. By introducing extra framework species into these alumino-silicates matrix depending on the type of species introduced, the physicochemical properties and the reactivity of the resulting material can vary drastically. The extra-framework species of fly ash aluminosilicates were modified by ion exchange treatments to prepare materials in which transition metal species are well-dispersed, well-mixed and highly accessible to reactants.

The adsorption behavior of the zeolite materials synthesized from coal fly ash for waste water treatment. The zeolites used were zeolite HY and zeolite HZSM-5. Waste water samples were collected, from the bore wells of sugar factory affected areas of Nanded District and effluent waste water along the sugar industry effluent stream. Then water samples were treated with zeolite material by conventional ion exchange method and again analyzed for the comparison.

In order to achieve the greatest efficiency of the process and to optimize the degree of removal during the application of the sorbent material for effluent treatment, the effect of type of adsorbent, the effects on adsorption of the solid to liquid ratio during the ion exchange, and effect of contact time were tested. Water samples were collected before and after treatment were analyzed for the various parameters like pH, EC, COD, TDS, hardness etc.

**Key Words :** Zeolite, Adsorbent, waste residues, Water treatment, pH, EC, COD, TDS, hardness etc.

**Co-ordinator  
IQAC**

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)



**PRINCIPAL**

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn.) Dist. Parbhani



## INTRODUCTION:

Today most of the countries are facing drinking water problems and conditions are very severe especially in developing countries like India, and 70% to 80% of the diseases are due to bacterial contamination of drinking water. India, as one of the major sugar producers of the world, is subjected to a large volume of sugar industrial wastes as well. Biogases, press mud, molasses and distillery water are some of the major objectionable wastes generated from the sugar industry and there have been extensive studies by several workers on remediation thereof<sup>1</sup>. Disposal of Industrial waste water on land or in natural streams and lakes causes physical, chemical and biological hazards. This ultimately creates health problems. the use of such polluted water for irrigation and drinking for longer time effects human bodies tend to bioaccumulation, which may result in damaged or reduced mental and central nervous function, and permanent damage to blood composition, lungs, kidneys and liver. Different treatment techniques such as chemical precipitation, coagulation- precipitation, adsorption and ion exchange have been developed to remove heavy metals from contaminated water, generated in the process of sugar industry waste disposal<sup>2-4</sup>. Coagulation-flocculation and chemical precipitation are perhaps the most widely used, however they both have the drawbacks of difficult sludge disposal and more importantly the diminished effectiveness when treating water with low heavy metal levels<sup>5</sup>. Membrane filtration and reverse osmosis were also reported<sup>6</sup>.

However, these methods usually involve expensive materials and high operation costs. Other methods such as electro dialysis, membrane electrolysis and electrochemical precipitation have also been investigated however their applications have been limited due to the high energy consumption<sup>7</sup>. On the other hand, as a cost effective method ion exchange process normally involve low-cost materials and convenient operations, and they have been proved to be very effective for removing contaminants from water and increase the water quality<sup>8-10</sup>. Moreover, ion exchange is particular effective for treating water with low concentration of heavy metals which is very common in practice<sup>4</sup>. Natural zeolites as well as synthesized zeolites were used in a wide range of environmental applications<sup>11,12</sup>, including water purification, with the emphasis on the ammonia and heavy metal removal, removal of radioactive Cs and Sr from low-level waste streams of nuclear installations, and recently also for the removal of organic pollutants<sup>13-15</sup>, like hydro chlorofluorocarbons (HCFCs) and petroleum products from water. They can be used as barriers to contaminant migration or as binders in waste solidification systems<sup>16</sup>. Adsorption in

  
Co-ordinator  
IQAC

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)



  
PRINCIPAL

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani



zeolites was initially reported by Grandjean in 1910 and later studied by Mc Bain in 1926, the notion of zeolites as "molecular sieves" was introduced by Mc Bain in 1932 to describe the size selectivity of zeolites during molecular adsorption<sup>17</sup>

The use of fly ash prepared zeolite materials for the environmental protection is stimulated by good physico-chemical properties, e.g. selective sorption, by non-toxic nature, availability and low cost. A great deal of research on natural zeolites has been focused on the most commonly occurring types, especially clinoptilolite, mordenite and chabazite.

## EXPERIMENTAL:

### Waste water treatment using HY and HZSM-5 zeolites:

Treatment of waste water by using the Batch ion exchange method (as described in the Chapter 1) with synthesized zeolites HY ( $\text{Si/Al}=5.1$ ) and HZSM-5 ( $\text{Si/Al}=33$ ) is used in this section<sup>33,34</sup>. In order to achieve the greatest efficiency of the process and to optimize the degree of removal of contamination during the application of the sorbent material for waste water treatment,

The samples of sugar industry waste water, polluted Pandu lake water near to by NDSF and four side bore well water of different locations along the effluent stream of NDSF of the Bodhan town were collected. Water samples were collected from these areas and were analyzed for the various parameters like pH, EC, COD, TDS, hardness and bacterial count. Then water samples were treated with zeolite material by conventional ion exchange method and again analyzed for the comparison. pH of each sample was determined by using ELICO LI 612-pH Analyzer while electric conductivity was measured by using water quality checker model ELICO CM 183 EC – TDS Analyzer. All the reagents used in this investigation were of analytical grade. Laboratory incubator/incubation chamber was used for maintaining different incubation temperature. Double distilled water was used for reagent preparation and dilution etc. All the glassware's were of Borosil Grade-A.

### Effect of type of zeolite adsorbate during the ion exchange:

In the first set of adsorption tests, different types of zeolite adsorbate such as HY ( $\text{Si/Al}=5.1$ ) and HZSM-5 ( $\text{Si/Al}=33$ ) synthesized from fly ash were used to test the degree of removal of contamination.

A fixed amount of solid to liquid ratio of adsorbent and simulated effluent were used to determine the type of zeolite required for optimum removal of metals from the solution. To the 100 ml of contaminated water (5 g/100 mL) amount of zeolite HY or HZSM-5 were

  
Co-ordinator  
IQAC

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)



  
PRINCIPAL

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn.) Dist. Parbhani



added and kept for the reflux at the temperature  $60^{\circ}\text{C}$  with continuous magnetic stirring for 6 hrs. After the reflux the sample was cooled down to the room temperature and filtered before investigation of the various parameters.

#### **The effects on adsorption of the solid to liquid ratio during the ion exchange**

In the second set of adsorption tests, different solid to liquid ratio (1, 2, 3 and 5 g/100 mL) of adsorbent (zeolite HY or zeolite HZSM-5) and simulated waste water were tested to determine the mass of zeolite required for optimum removal of metals from the solution. Same ion exchange technique was adopted to treat contaminated water sample before investigation.


#### **The effects of duration of ion exchange:**

The third set of adsorption tests was carried out at different times (i.e. 60 minutes, 90 minutes, 120 minutes, and 180 minutes) intervals in order to evaluate the time dependence of adsorption using the simulated effluent. During the ion exchange a fixed amount of solid to liquid ratio of adsorbent (i.e. 5 g/100 mL) and simulated waste water was taken. Same ion exchange technique was adopted to treat contaminated water sample before investigation.

### **RESULTS AND DISCUSSIONS:**

Water purifications are based on the unique cation-exchange behavior of zeolites through which dissolved cations are removed from water by exchanging with cations on a zeolites exchange sites. Zeolites with high exchange capacities (high charge densities) can easily strip the hydration shell of a water-cation complex. Inside the zeolite pore apertures water molecules and charge balancing mono- and divalent cations, such as  $\text{Na}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  can be found. The negative charge of the framework, caused by the replacement of  $\text{Si}^{4+}$  with  $\text{Al}^{3+}$ , is compensated by these small cations. Larger cations are partially or completely excluded by the zeolite pore size, whereas smaller species can be exchanged or sorbed.

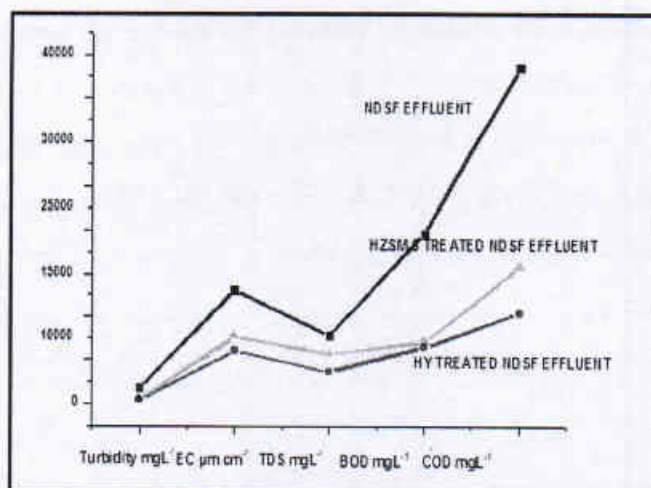
The ready exchangeability, and relatively innocuous nature of the charge-balancing cations, renders them particularly suitable for the removal of undesirable species (particularly metal ions) from wastewaters. An equally important parameter of zeolites is the Si/Al ratio. It is responsible for their thermal and hydrothermal stability, as well as their acidity and relative hydrophobicity. The specification of this ratio also gives the zeolite species its significance in environmental protection. A low Si/Al ratio is indicative of an increased number of terminal

  
Co-ordinator  
IQAC  
Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)



  
PRINCIPAL  
Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani





**Figure 3.1 : Variation of the parameters such as Turbidity, EC, TDS, BOD, and COD, of Effluent samples of the NDSF with HY and HZSM-5 Zeolite adsorbent treatment.**

HY zeolite used for ion exchange in this work shown good results when compare to the HZSM-5. This may be due to the high adsorptive behavior of the HY zeolite over HZSM-5 which basically depends on the surface area of the zeolite. These results are promising for the use of fly ash prepared HY zeolite over commercially available synthetic zeolites to treat contaminated ground water and industrial waste effluents, since these materials possess the high capacity for cation exchange, anion sorption and acid hydrolysis of organic contaminants. The higher aluminum content of HY, higher kinetics of ion exchange were important factor governing the improved performance of this zeolite relative to the HZSM-5 zeolite with higher Si/Al ratio.

#### **The effects on adsorption of the solid to liquid ratio:**

Different solid to liquid ratio (1, 2, 3 and 5 g/100 mL) of adsorbent (zeolite HY or HZSM-5) and simulated waste water were tested to determine the mass of zeolite required for optimum removal of contamination from the waste water sample. Same ion exchange technique was adopted to treat contaminated water sample before investigation of the various parameters. Table 3.3 (a and b) shows the effect of increasing adsorbent dose in quality improvement of waste water with the HZSM-5 and HY adsorbate respectively.

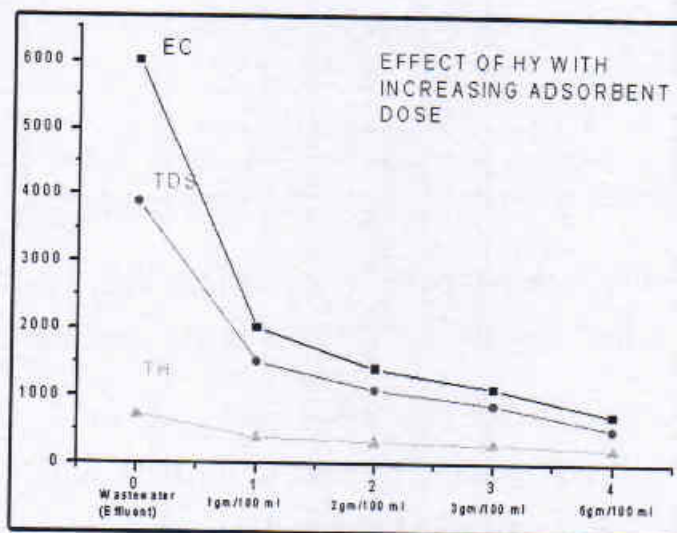
Form the observations the pH value of waste collected from sugar industry was found to be more acidic (i.e. pH = 3.00) and was very low when compare to the permissible limits of pH for

  
**Co-ordinator**  
**IQAC**  
 Shri Guru Buddhiswami Mahavidyalaya  
 Purna (Jn) Dist. Parbhani - 431511 (M.S.)



  
**PRINCIPAL**  
 Shri Guru Buddhiswami Mahavidyalaya  
 Purna (Jn.) Dist. Parbhani

Irrigation, after treatment even with 1 g / 100 m L of zeolite adsorbent the pH enhanced to 5.55 in case of HY zeolite adsorbent and 4.5 in case of HZSM-5 zeolite adsorbent but as the amount of zeolite adsorbate in exchange solution increases the pH value enhanced to 6.88 in case of HY with 5 g / 100 m L and in case of HZSM-5 with 5 g / 100 m L it will be 6.02 which is with in the permissible limits. The same trend is shown in the other parameters also.



exchange in quality improvement of waste water. The pH value of NDSEffluent As the adsorbent dose in exchange solution increases the EC will be reduced from 6017 to 722  $\mu\text{m cm}^{-1}$  in case of HY and 6017 to 754  $\mu\text{m cm}^{-1}$  in case of HZSM- 5, TDS will be reduced from 3887 to 511  $\text{mgL}^{-1}$  for HY treatment and 3887 to 517  $\text{mgL}^{-1}$  in case of HZSM-5 treatment, TH will be reduced from 716 to 223  $\text{mgL}^{-1}$  with the HY and 716 to 246  $\text{mgL}^{-1}$  with the HZSM-5 treatment. As the adsorbent dose increases in exchange solution tremendous decrease in the hazardous metals such as Arsenic, Lead, and Cadmium was examined.

From the observations a dosage of 2g/100 mL of adsorbate will enhance water quality to 90-95%. As the dosage of adsorbate in exchange solution increases water quality enhances to above 95-99%. A dosage of 5g/100 mL has given maximum enhancement. At 5g/100 mL all the parameters reached to the permissible limits of the water quality.

Co-ordinator  
IQAC

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)



PRINCIPAL

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn.) Dist. Parbhani



### Effect of duration of ion exchange process:

The ion exchange was carried out at different time intervals contact of the waste water and zeolite adsorbent (i.e. 60 minutes, 90 minutes, 120 minutes, and 180 minutes) in order to evaluate the time dependence of adsorption using the simulated waste water. A fixed amount of solid to liquid ratio of HY or HZSM-5 zeolite adsorbent (i.e. 5 g/100 mL) and simulated waste water was taken for ion exchange for different contact time intervals.

### Conclusion :

Effect on the adsorptive behavior of modified zeolites prepared from coal fly ash in treatment of effluent water is studied. Treatment of sugar industrial waste water by using the ion exchange method with fly ash synthesized zeolite HY (Si/Al =5.1) and zeolite HZSM-5 (Si/Al = 33) was performed. In order to achieve the greatest efficiency of the process and to optimize the degree of removal of contamination during the application of the sorbent material for waste water treatment, Effect of type of zeolite adsorbate, the effects of adsorption of the solid to liquid ratio, and effect Contact time were investigated.

Form the observations the sugar industrial waste water was found to be strongly acidic with elevated levels of toxic metals. The pH value of the NDSF effluent sample is 3.74 and was very low when compare to the permissible limits of pH for potable and Irrigation. The pH value of NDSF effluent samples was enhanced to 4.34 when treated the waste water with HZSM-5 zeolite adsorbent and 5.54 when treated with HY zeolite adsorbent, these values were very close to the permissible limits and the water can be used for irrigation purpose. After treatment with HY zeolite the samples were reanalyzed, and it is observed that the values of hardness decrease to the permissible limit. The variations in EC reduces from 13050 to 6027  $\mu\text{m cm}^{-1}$ , TDS varies from 7830 to 3616  $\text{mgL}^{-1}$  after treatment with HY zeolite adsorbent. The same trend is observed with HZSM-5 treatment also. HY zeolite used for ion exchange in this work shown good results when compare to the HZSM-5.

### REFERENCES:

- 1 Querol, X., Umana, J.C., Plana, F., Alasuey, A., Lopez-Soler, A., Valreo, M.A., Domingo, M.J. and Garcea-Rojas, E.: Synthesis of zeolites from fly ash at Pilot plant scale: Examples of

  
Co-ordinator  
IQAC

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)



  
PRINCIPAL

Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn.) Dist. Parbhani



potential applications. *Fuel*, 80, (2001), p. 857-865.

2 P.B.Venuto, E.T. Habib Jr., in: Fluid Catalytic Cracking with Zeolite Catalysts, *Marcel Dekker, New York, Basel*, (1979), p.156.

3 R.Von Ballmoos, D.H. Harris, J.S. Magee, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 4, Wiley-VCH, Weinheim, (1997), p. 1955.

4 Holler, H. and Wirsching, U.: Zeolite formation from fly ash. *Fortschritte Mineralogie*, 63, (1985), p 21-43

5 Querol, X., Moreno, N., Umana, J.C., Alastuey, A., Hernandez, E., Lopez- Soler, A. and Plana, A.: Synthesis of zeolites from coal fly ash: an overview. *International Journal of Coal Geology*, 50, (2002), p. 413-423.

6 Moreno, N., Querol, X. and Ayora, C.: Utilisation of zeolites synthesised from coal fly ash for the purification of acid mine waters. *Environmental Science and Technology*, 35 (2001), p. 3526-3534,

7 W. Lowenstein, *Am. Mineralogist* 39 (1954).

8 U.D. Joshi, P.N. Joshi, S.S. Tamhankar, V.V. Joshi, C.V. Rode, V.P. Shiralkar, "Effect of non framework cations and crystallinity on the basicity of NaX Zeolite", *Applied Catalysis A: Elsevier Science. UK*, 239/1-2, p. 209 – 220.

9 Ch. Baerlocher, W.M. Meier, D.H. Olson, *Atlas of Zeolite Framework Type*, 5<sup>th</sup> ed., Elsevier, *Amsterdam* (2001).

10 W.M. Meier and D.H.Olson, *Atlas of Zeolite Structure Types*, 3<sup>rd</sup> ed. *Butterworth –Heinemann, London* (1992).

11 Barthomeuf, D. *Catal. Rev.* 38, (1996), p.521.

12 Joshi U.D., P.N. Joshi, S.S. Tamhankar, V.P. Joshi, B.B. Idage, V.V. Joshi and V.P. Shiralkar, "Influence of the size of extraframework monovalent cation exchange in X-type zeolite on their thermal behavior," *Thermochimica Acta*, 387, 121-130, 2002 (Elsevier Science,

  
Co-ordinator  
IQAC  
Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)



  
PRINCIPAL  
Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn.) Dist. Parbhani



UK)

13. Corma, A. *J. Catal.* 216, (2003), p. 298.

14 Lim, W.T.; Choi, S.Y.; Choi, J.H.; Kim, Y.H.; Heo, N.H.; Seff, K.

*Microporous and Mesoporous Mater.* 93, (2006), p.234.

15 A.F. Cronstedt, *Kongl Ventenskps Acad. Handl. Stockholm*, 18 (1756), p. 120-130.

16 Flanigen E M, in "Introduction to Zeolite Science and Practice" (Van Bekkum H, Flanigen E M, Jansen J C, eds), *Stud. Surf. Sci. Catal.* 58, (1991), p. 13.

17 Breck D W, "Zeolite Molecular Sieves", Krieger, *Malabar (Florida)* (1984).

18 Perego G, Millini R, Bellussi G, in *Molecular Sieves* (Karge H G, Weitkamp J, eds.), 1, (1998), p. 188.

**Co-ordinator  
IQAC**

**Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn) Dist. Parbhani - 431511 (M.S.)**



**PRINCIPAL**

**Shri Guru Buddhiswami Mahavidyalaya  
Purna (Jn.) Dist. Parbhani**