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Synthesis of Zeolite using Fly ash and its application in Removal of Cu^{2+}, Ni^{2+}, Mn^{2+} from Paper Industry Effluent

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Abstract

An improved synthesis for fly ash based zeolite has been attempted and studies have been carried out for the removal of Cu^{2+}, Ni^{2+} and Mn^{2+} from paper industry wastewater. The parameters affecting adsorption process, such as initial pH, weight of zeolite, contact time were investigated. The transition metal ions present in the waste Cu^{2+}, Ni^{2+} and Mn^{2+} shows better adsorption capacities on synthesized zeolite. The order of removal of heavy metal ions is $Ni^{2+} > Mn^{2+} > Cu^{2+}$.

Keywords: Fly ash, zeolite, paper industry waste, transition metal ions, adsorption, atomic absorption spectrophotometer.

Introduction

Wastewater from various industries such as electroplating, paper and pulp, metal plating, mining operations, battery manufacturing processes, glass production processes are known to contain heavy metals such as Cu, Ni, Pb, Cr, Zn, Cd and Fe. These heavy metals are non-biodegradable which leads to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in stomach of the rodent[1]. These contaminants must be removed from wastewaters before discharge as they are considered persistent, bio accumulative and toxic substances[2]. Among the advanced methods of heavy metal removal, adsorption is the most effective and economical because of their relative low cost[3].

In India nearly 90 mt of fly ash is generated per annum and is responsible for environmental pollution[4]. The bulk of fly ash is stored in ash dams and landfills. The ash dams are costly to manage, lead to loss of usable land, impact negatively on the environment, cause air and water pollution. Fly ash is primarily composed of aluminosilicate glass, mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2). Low Si / Al ratio zeolite provides an excellent sorbents for the adsorption of transition metals due to high cation exchange capacities (CEC) and large pore volumes[5, 6]. The water pollution in Kanhan river caused due to the disposal of waste from Khaperkheda thermal power station was studied[7]. Fly ash based zeolite shows higher adsorption capacity for the removal of Cu^{2+}, Pb^{2+} and Cd^{2+} from waste water than that of fly ash[8]. It is reported that Na-P1, hydroxysodalite and X-type zeolites synthesized from fly ash are effective in removing Fe, Cu, Zn and Pb from the contaminated effluent streams[9-11]. Among natural zeolites, chitosan, a biopolymer has been studied as a low cost adsorbent for the removal of lead from waste water[12].

Zeolite – A obtained from fly ash (FAZ – A) has been patented nationally and internationally. FAZ –A shows maximum efficiency for lead removal followed by cadmium and copper[13].

The objective of this is to develop an improved synthesis of zeolite from fly ash and find its application in the removal of heavy metal ions from paper industrial effluents. Since the existing methodologies have mostly used NaOH and Na_2CO_3 for hydrothermal synthesis of zeolite from fly ash, we thought of studying the effect of addition of KOH to NaOH and Na_2CO_3. Experiments were carried out to demonstrate the heavy metal removal efficiency of this newly synthesized zeolite from paper industry waste water.

Material and Methods

Material Handling and storage: Pulverized coal fly ash obtained from Khaperkheda Thermal Power Station was used as a raw material. Fresh fly ash samples were collected from precipitators and stored in sealed plastic container having an airtight lid. The plastic containers were stored in a dark cool room away from the sources of moisture, direct sunlight and from fluctuating temperatures[14].

Paper industry waste water was collected from the industry in Maharashtra Industrial Development Corporation (MIDC), Nagpur. Sampling was carried out by following the standard procedures and techniques[15].

After the collection of sample, parameters such as temperature, pH and colour are measured by using thermometer, pH meter and by visual observation. Then the sample was transferred to Amber Coloured glass bottle in order to prevent oxidation of metal ions. Fly ash characterization was done by X-ray fluorescence at Indian Bureau of Mines (IBM), MIDC, Nagpur.

Analysis of paper industrial waste was carried out by atomic absorption spectrophotometer (AAS) (GBC 906 AA) and inductively coupled plasma spectrometer (ICP) (GY 166 Ultrace)[16] from IBM, MIDC, Nagpur. Analysis revealed presence of Cu^{2+}, Ni^{2+}, Mn^{2+}, Cr^{6+} and Fe^{3+}. In this work, we have studied the removal of Cu^{2+}, Ni^{2+} and Mn^{2+} by using newly synthesized zeolite as adsorbent.

Zeolite Synthesis: The fly ash was initially screened to eliminate larger particles by using Mechanical Sieve Shaker (Filterwel test sieves) of mesh size 72 μ. Fly ash was subjected to pretreatment with 8N HCl for 2 hours. Fusion of fly ash with NaOH and Na_2CO_3 was done at the ratio of 1: 1.5: 0.5. KOH (0.1g) was added to it and the mixture was heated in muffle furnace at 700°C for 1 hour. Fused mass was cooled, milled and mixed thoroughly in distilled water with simultaneous addition of sodium aluminate solution. The slurry so obtained was then subjected to stirring and ageing for 8 – 10 hours. It was then subjected to hydrothermal crystallisation in a closed container in an oven at 100°C for 2 – 3 hours. After crystallisation the solid crystalline product was recovered by filtration using vacuum pump. It was washed with double distilled water and dried in oven. The steps after fusion were followed as mentioned in literature[17].

The efficiency of this newly synthesized zeolite as adsorbent for the removal of heavy metal ions from the industrial waste was studied as follows.

Adsorption Experiments: Batch mode experiments were performed in 100 ml conical flasks by addition of desired amount of zeolite to 50 ml of waste water. In all experiments, the flasks were shaken at 100 rpm on the mechanical shaker for predetermined time intervals at temperatures 25^0C. After agitation the zeolite was separated by filtration and some aliquots of filtrate in the supernatant were analysed using atomic adsorption spectrophotometer (AAS) and inductively coupled plasma spectrophotometer (ICP). The amount of metal ion adsorbed on the zeolite was computed by the following equation:

$$\% \text{ removal} = (Ci - Ce)/Ci * 100$$

Where Ci = Concentration before adsorption, Ce = Concentration after adsorption.

The pH of the solution was found to be 5. The effect of weight of zeolite on removal of transition metal ions was studied by adding 50 ml of waste water to the 0.1g, 0.2g, 0.3g, 0.4g and 0.5g of zeolite in conical flasks. The mixtures were shaken in a mechanical shaker at about 100 rpm for 5 hours. The filtrate was analysed by using atomic adsorption spectrophotometer (AAS) and inductively coupled plasma spectrophotometer (ICP). To the 50 ml of industrial waste water 0.1g of zeolite was mixed in order to investigate the effect of contact time on adsorption of transition metal ions. The flasks were shaken for 1, 2, 3, 4 and 5 hrs. The concentration of metal ions was obtained by using AAS and ICP. Similarly the effect of pH on adsorption of transition metal ions was studied by adjusting the pH of the industrial waste water to 1, 2, 3, 4 and 5 by adding HCl. The solutions were treated as previously and analysed using AAS and ICP.

Results and Discussion

Characterisation of zeolite synthesized from fly ash: The results of the elemental composition of zeolitic material was analysed by Energy Dispersive X-ray Fluorescence (EDXR) (Model no.EDX700, Shimadzu) and presented in table 1.

Adsorption Experiments: Effect of weight of zeolite, contact time and pH on sorption of ions Cu^{2+}, Ni^{2+}, Mn^{2+}: The effect of adsorbent doses on the removal of transition metal ions Cu^{2+}, Ni^{2+}, Mn^{2+} is shown in figure 1. The amount of sorbent was varied from 0.1 to 0.5 g/L and equilibrated for 5 hrs. The results indicated that the percent removal of Cu^{2+}, Ni^{2+} and Mn^{2+} decreases with the increase in adsorbent dose and was maximum 54.51% at 0.1 g/L of zeolite.

The equilibrium time required for the sorption of transition metal ions Cu^{2+}, Ni^{2+} and Mn^{2+} on the zeolite with 0.1 g/L at different time intervals was studied. Figure 2 showed that adsorption capacity sharply increased with increase in time and attains equilibrium in 5 hrs. Therefore, the adsorption time was set to 5 hrs. in each experiment. The order of adsorption of transition metal ions on zeolite was $Ni^{2+} > Mn^{2+} > Cu^{2+}$.

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. Hence metal sorption is critically linked with pH[18]. In order to establish the effect of pH on the adsorption of Cu^{2+}, Ni^{2+} and Mn^{2+} onto the synthesized zeolite, batch sorption studies at different values of pH were conducted in the range of 1 to 5 (figure 3). It was observed that the maximum adsorption of transition metal ions was observed at pH 5.

Table-1
EDXR of synthesized Zeolite

	Al_2O_3	SiO_2	Na_2O	MgO	K_2O	CaO	Fe_2O_3	TiO_2	Mn_2O_3	NiO	CuO	SrO	ZrO_2	BaO
Mass %	41.22	46.22	0.75	0.205	0.902	3.621	2.254	0.826	3.036	0.171	0.353	0.125	0.216	0.101

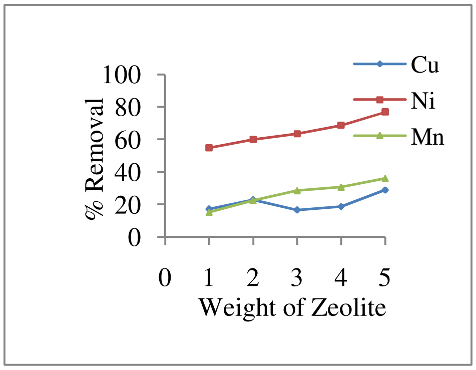

Figure-1
Effect of weight of zeolite on sorption

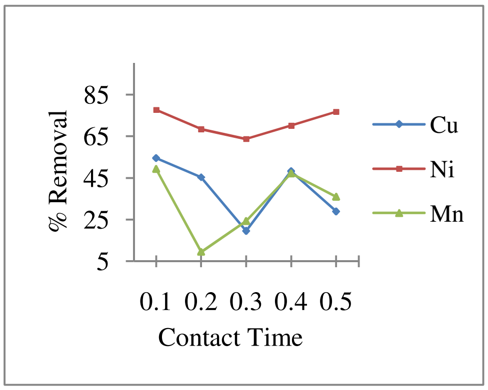

Figure-2
Effect of contact time on sorption

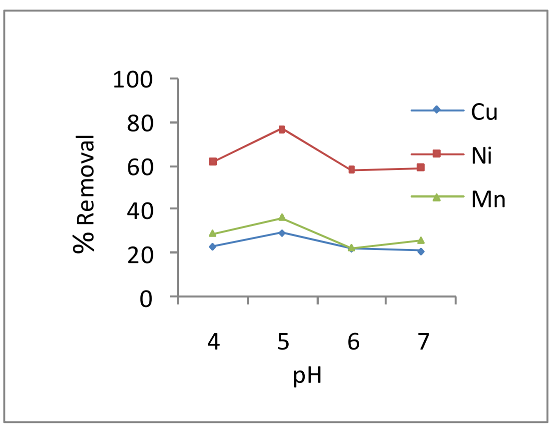

Figure-3
Effect of pH on sorption on metal ions

Adsorption Isotherms: The Langmuir isotherm model is the most common model used to quantify the amount of adsorbate adsorbed on an adsorbent. The Langmuir isotherm can be expressed in terms of a dimensionless constant R_L, is defined as

$$R_L = 1/ (1 + K_A C_o)$$

Where C_o is the initial concentration (mg/l), R_L is the Indicates the isotherm, K_A is the rate of adsorption. The values of R_L were found to be in between 0 to 1, which indicates favourable adsorption of metals under study onto the adsorbent[19].

The liberalized Freundlich model isotherm was applied for the adsorption of heavy metal ions and is expressed as

$$Log(X/m) = Log K_F + 1/n (Log C_e)$$

Where, (x/m) is the amount of heavy metal ions adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of heavy metal ions (mg/l). K_F and n are the constants values calculated from the intercept and slope of the plot.

The regression coefficient R^2 for Langmuir and Freundlich values for Cu^{2+}, Ni^{2+}, Mn^{2+} adsorption were found to be between 0 to 1 indicating favourable adsorption of the metal ions onto the synthesized zeolite. The function of the strength of adsorption in the adsorption process, 1/n for Ni adsorption was found to be above 1, which indicates co-operative adsorption[20].

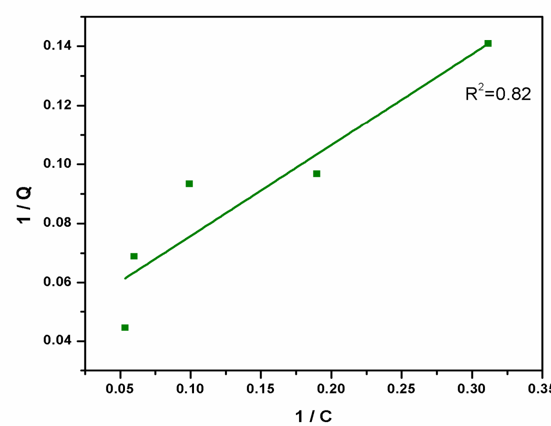

Figure-4
Langmuir isotherm for Cu^{2+}

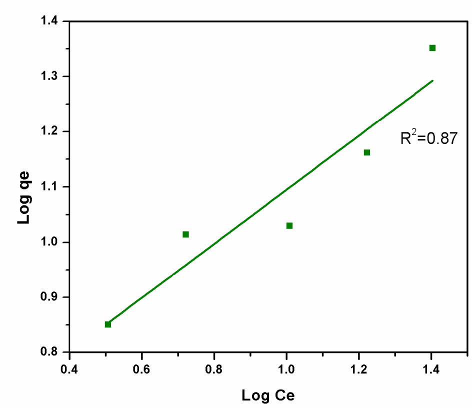

Figure-5
Freundlich isotherm for Cu^{2+}

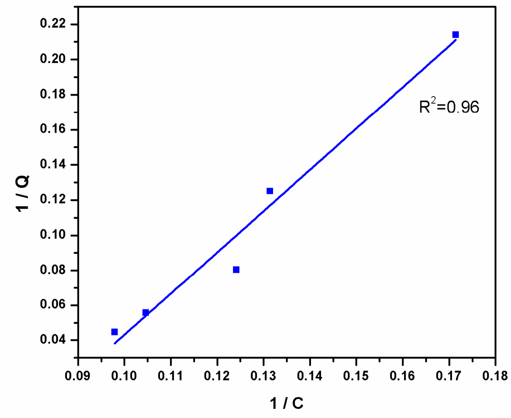

Figure-6
Langmuir isotherm for Ni^{2+}

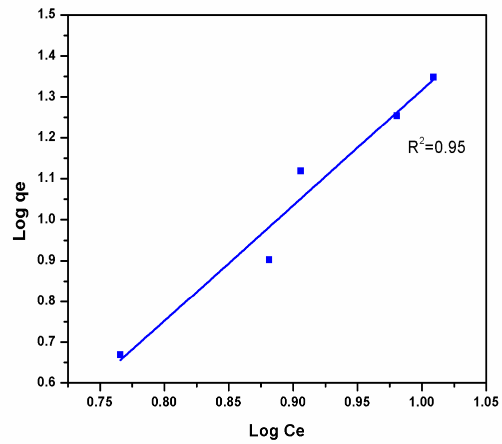

Figure-7
Freundlich isotherm for Ni^{2+}

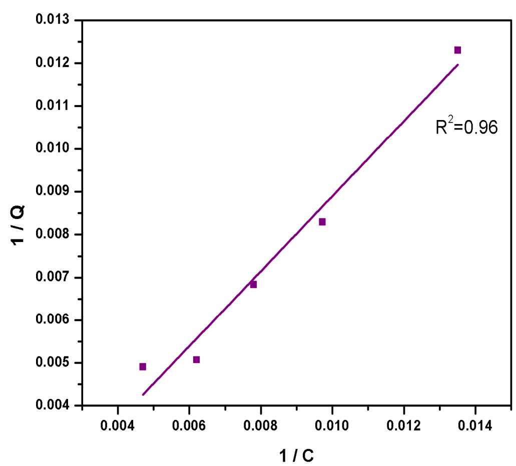

Figure-8
Langmuir isotherm For Mn^{2+}

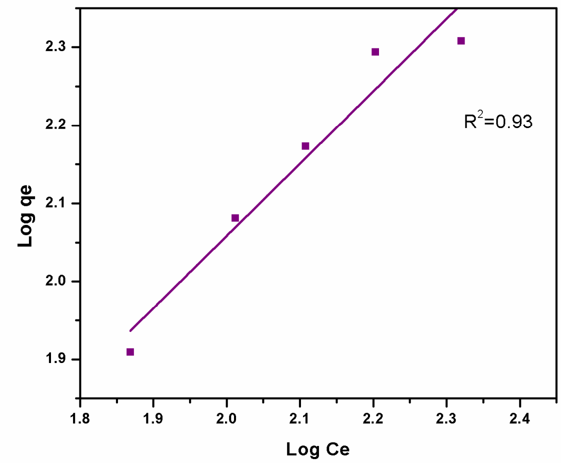

Figure-9
Freundlich isotherm For Mn^{2+}

Conclusion

Zeolite – P have been prepared from coal combustion fly ash by a hydrothermal treatment of the ash with NaOH, Na_2CO_3 and KOH. By varying the fusion ratio zeolite – P was achieved. The resultant zeolite – P was more effective in the removal of transition metal ions present in the paper industry effluent. The order of removal of heavy metal ions was Ni^{2+} >Mn^{2+} > Cu^{2+}.

It is envisaged that this modification procedure can convert fly ash into a beneficial product which would prove effective in removing transition metal ions from paper industrial waste water.

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References

1. Bernard E., Jimoh A. and Odigure J.O., Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell, *Research Journal of Chemical Sciences,* **3(8),** 3-9 **(2013)**
2. Manuel A., Jime´nez V., Rodrı´guez-Castello´n E., Jime´nez-Lo´pez A., Jime´nez-Jime´nez J., Heavy metals removal from electroplating wastewater by aminopropyl-Si MCM-41, *Chemosphere,* **59**, 779–786 **(2005)**
3. Yadla S., Sridevi V. and Chandana L., A Review on Adsorption of Heavy Metals from Aqueous Solution, *Journal of Chemical, Biological and Physical Sciences*, **2(3)**, 1585-1593 **(2012)**
4. Senapati M.R., Fly ash from thermal power plants – waste management and overview, *Current Science*, **100(12)**, 25 **(2011)**

5. Holler H. and Wirsching U., Zeolite formation from fly ash, *Fortschr. Miner*, **(63),** 21-43 **(1985)**.

6. Querol X., Plana F., Alastuey A. and Lopez-Soler A., Andres J.M., Juan R., Ferrer P. and Ruiz C.R.A., Fast method of recycling fly ash: Microwave assisted zeolite synthesis, *Environ. Sci. Technol.*, **(31)** 2527-2532 **(1997b)**

7. Thorat P. and Charde V**.,** Physicochemical Study of Kanhan River Water Receiving Fly Ash Disposal Waste Water of Khaperkheda Thermal Power Station, India, *International Research Journal of Environment Sciences*, **2(9)**, 10-15 **(2013)**

8. Yanxin W., Yonglong G., Zhihua Y., Hesheng C. and Querol X., Synthesis of zeolites using fly ash and their application in removing heavy metals from waters**,** *Science In China (Series D)*, **46(9)**, 967-976 **(2003)**

9. Woolard C.D., Petrus K. and Horst M van der, The use of a modified fly ash as an adsorbent for lead, *Water S.A.,* **26(4)**, 531-536 **(2000)**

10. Vadapalli V., Gitari W., Ellendt A., Petrik L., Balfour G., Synthesis of zeolite-P from coal fly ash derivative and its utilisation in mine-water remediation, *South African Journal of Science*, **106** (5/6), 7, **(2010)**

11. Solanki P., Gupta V. and Kulshreshtra R., Synthesis of Zeolite from Fly Ash and Removal of Heavy Metal Ions from Newly Synthesized Zeolite, *E-Journal of Chemistry*, **7(4),** 1200-1205 **(2010)**

12. Singh D., Mishra M., Mishra A.K. and Singh Anjali, Removal of Lead from Waste Water Using Low Cost Adsorbent**,** *International Research Journal of Environment Sciences,* **2(9),** 23-26 **(2013)**

13. Kumar P., Rayalu S. and Dhopte S., Fly ash based zeolite-A: A suitable sorbent for lead removal, *Indian journal of Chemical Technology*, **11**, 227-233 **(2004)**

14. Musyoka N.M. Petrik L., Balfour G., Natasha M. Gitari W. and Mabovu B., *International Mine Conference Proceeding*, South Africa, 680-687, 19th – 23rd October **2009**.

15. National Environmental Engineering Research Institute, Nagpur, *Manual on water and waste water analysis*, **(1988)**

16. IS: 3025 Part II **(2004)**

17. Udhoji J.S., Bansiwal A.K., Meshram S.U. and Rayalu S.S., Improvement in optical brightness of fly ash based zeolite-A for use as detergent builder, *Journal of Scientific & Industrial Research*, **64**, 367-371, **(2005)**

18. Tiwari S.P., Singh D.K. and Saksena D.N., Hg (II) adsorption from aqueous solutions using rice husk, *J. Environ. Eng*., **121**, 479-481 **(1995)**

19. Pandey P., Sharma S., Sambi S., Kinetics and equilibrium study of chromium adsorption on zeolite NaX, *International Journal of Environmental Science Technology,* **7(2)**, 395-404, **(2010)**

20. Mohan S. and Karthikeyan, Removal of lignin and tannin color from aqueous solution by adsorption on to activated carbon solution by adsorption on to activated charcoal, *Environ. Pollut.,* **97**, 183-187, **(1997)**