

Studies on sorption properties of zeolite derived from Indian fly ash

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Abstract

Indian fly ash has been completely converted to crystalline porous 13X zeolite by NaOH fusion at 600 °C followed by hydrothermal treatment at 105 °C for 20 h. Obtained materials were characterized by XRD, SEM and surface area measurement. Prepared material was used for the sorption study of different metal ions (Cu²⁺, Co²⁺ and Ni²⁺) at different pH, temperature. Thermodynamic data (ΔS , ΔH and ΔG) corresponding to different metal ion uptake were evaluated from Langmuir equation. In all the experiment sorption capacity of prepared zeolite was found to be quite high than that of fly ash at acidic pH. However, the uptake selectivity order for both the materials is Cu²⁺ > Co²⁺ > Ni²⁺.

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1. Introduction

Large number of coal fired thermal power plants all over the world generate huge quantities of fly ash causing serious environmental problem mainly due to its fine structure and toxic elements. In the recent years a number of technologies have been developed for the fruitful utilization of fly ash [1]. In this contest several reports are available on the synthesis of zeolites from fly ash having high silica and alumina content [2–7] by alkali fusion process. Due to the presence of uniform pore size and large surface area, zeolites are widely used as adsorbent and catalyst. However, the composition of fly ash varies from place to place depending on the source of coal, hence the requirement of process modification for the complete conversion of fly ash to zeolites.

The presence of different metals in the environment in different forms is a major concern due to their toxicity to many form of life. The actual toxicity of the waste containing metal ions depends on the type of metal ion, water hardness, pH and synergistic effect of different metal ions. In the last few years, adsorption has been found to be an alternative method for the removal of toxic metals from waste water [8,9]. Therefore, it is of importance to find out a low cost effective adsorbent for larger use in the waste water treatment. In this contest different fly ash

[10–12] as such and zeolites prepared [4,13,14] from fly ash were studied by a number of researchers. It has been observed that the zeolite prepared from the fly ash is much better adsorbent even at low pH [15]. However, there is a need to have a detail investigation of the comparative adsorption of heavy metals by zeolite and the fly ash to have a better understanding on the nature of adsorption and the energy involved in the process.

Therefore, the present work deals with the nature of metal ion (Cu²⁺, Co²⁺ and Ni²⁺) uptake and the energy involved in the process of sorption by fly ash and the prepared zeolite.

2. Experimental

2.1. Zeolite synthesis

Fly ash collected from thermal power plant of Gujarat region, India was used for this study. Zeolite was prepared by alkali fusion method [3] with certain modification. A mixture of 24 g NaOH and 20 g of fly ash was milled and fused in a tray at 500–600 °C for 1 h. The resultant fused mixture was cooled and milled again. The powder thus obtained was mixed with 200 ml of distilled water in a Teflon beaker and kept in stirring condition for 8 h at 27 °C. Then the whole mass was transferred into a pressure bomb and kept for 12 h at 105 °C at autogenous pressure. Finally precipitates were filtered, washed repeatedly with distilled water, dried at 110 °C and kept in powder form for further use.

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2.2. Characterization

Chemical compositions of fly ash and the prepared material were analyzed by wet chemical method after Na_2CO_3 fusion. Trace metal analysis was done by AAS (Chemito-AA203, India).

Micrographs of the fly ash and the prepared zeolite were recorded on a 50 kV SEM Leo 440i (UK) instrument.

Powder XRD analysis of prepared sample and collected fly ash were recorded on Philips-PW1130 X-ray diffractometer using $\text{Co K}\alpha$ radiation in the range of $10\text{--}70^\circ$ with 2°min^{-1} speed.

BET surface area of all the samples was measured by N_2 adsorption–desorption method using Quantasorb (Quantachrome, USA). Prior to the adsorption–desorption measurements all the samples were degassed at 120°C and 10^{-3} Torr for 5 h.

2.3. Sorption experiment

Sorption of heavy metal ions (Cu^{2+} , Co^{2+} and Ni^{2+}) was carried out from 50 ml of the solution with 0.1 g of adsorbent in a 100-ml stoppered flask at a maintained acidic initial pH comparable with the acidic waste water of the metal industries. All the sorption experiments were carried out for 6 h at 292, 300 and 310 K in a shaking water bath. After sorption experiment, the suspension was filtered and the residual metal ion concentration was measured with an Atomic absorption spectrometer (Chemito-AA203, India). The sorption experiment at initial pH 3.5 was carried out at four different concentrations 1.5×10^{-3} , 2.0×10^{-3} , 2.5×10^{-3} and $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ of Cu^{2+} and Co^{2+} and Ni^{2+} . All the metal ion solutions were prepared from corresponding metal nitrate salt (AR grade). Results were reproducible within 5% deviation. In order to study the selectivity of the material towards the different metal ions, a set of mixed solutions containing all the three cations in equal fraction was used.

3. Result and discussion

3.1. Characterization

Synthesized materials were used for characterization without further separation or purification. XRD patterns (Fig. 1) show that the alkali fusion and subsequent hydrothermal treatment of fly ash (FA) resulted in crystalline product having completely different structure. From comparison with the XRD pattern of standard zeolite materials, it is observed that the prepared material completely matches with that of 13X zeolite structure. It is also clear that the fusion at 600°C gives better crystallinity in comparison to the material prepared from fusion at 500°C which may be due to the complete fusion of fly ash at 600°C . Therefore, the zeolite sample (ZFA) prepared at 600°C fusion was selected for the adsorption studies. Chemical compositions of the fly ash and the prepared material are tabulated in Table 1. It is observed that the composition of the prepared material is

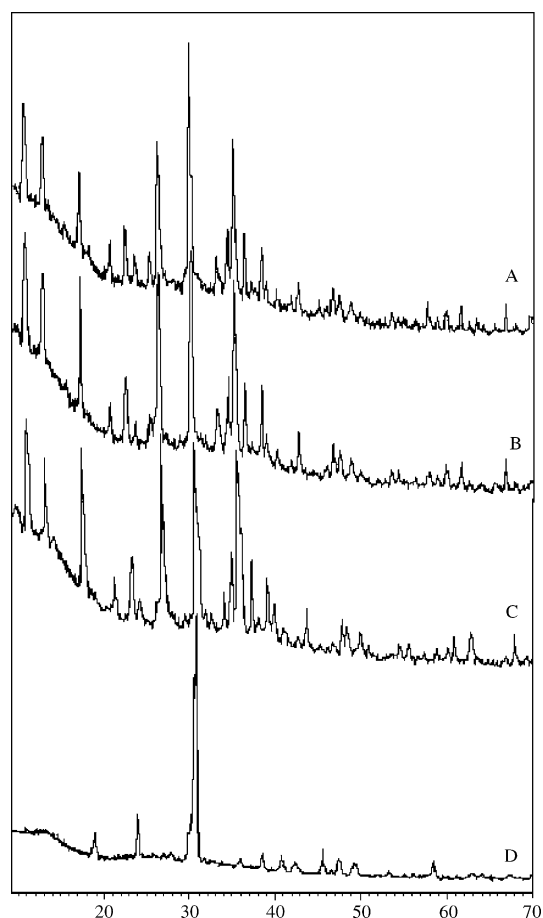


Fig. 1. XRD plots of the synthesized zeolites after fusion at (A) 500°C and (B) 600°C , (C) commercial 13X zeolite and (D) used fly ash.

quite close to that of commercial 13X zeolite available in the market.

SEM micrographs (Fig. 2) clearly show the nonporous and sintered nature of the fly ash having the particle size in the range of $1\text{--}2 \mu\text{m}$ whereas the prepared zeolite represents slightly distorted octahedral like structure having the particle size close to $1 \mu\text{m}$. This again justifies the transformation of fly ash to a crystalline material.

BET surface area of the prepared material was found to be $430 \text{ m}^2/\text{g}$ whereas the surface area of fly ash was only $6 \text{ m}^2/\text{g}$. The increase in surface area may be attributed to the formation of zeolite structure. It appears that the prepared material is highly porous in nature similar to that of commercial zeolite.

Table 1
Comparative chemical composition of fly ash and zeolite materials

Constituents (wt%)	FA	ZFA	Commercial zeolite 13X
SiO_2	52.1	43.6	48.26
Al_2O_3	32.1	29.5	31.85
Fe_2O_3	5.5	3.6	3.2
TiO_2	2.1	1.9	0.08
CaO	0.75	0.7	0.38
Na_2O	1.9	20.5	15.7
K_2O	1.3	0.91	0.07

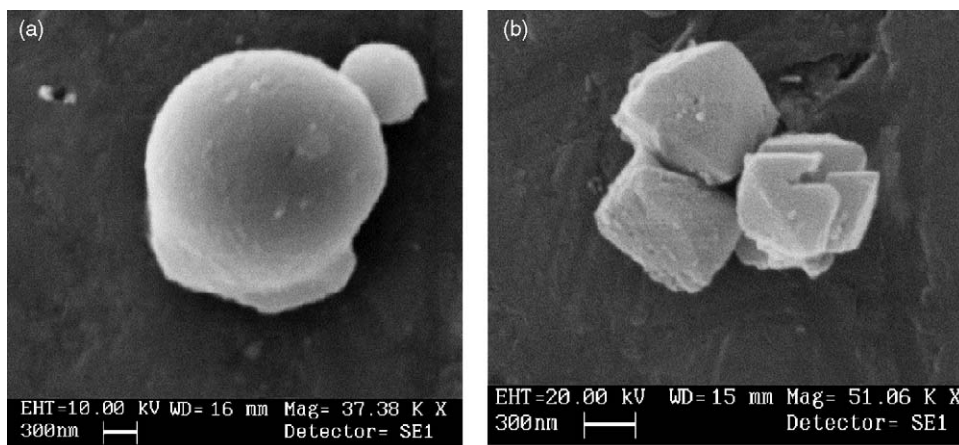


Fig. 2. SEM micrographs of (a) flay ash and (b) prepared zeolite (ZFA).

3.2. Heavy metal sorption

Preliminary experiments [15] revealed that the system attains equilibrium in 6 h duration for Cu^{2+} , Co^{2+} and Ni^{2+} sorption at all pH. It was also observed that with increase in pH sorption of metal ions increased many folds (Fig. 3). Within pH 3.5–5, high metal uptake by the prepared zeolite was observed. With decrease in pH, metal uptake decreased which may be due to the partial destruction of zeolite crystal at low pH [16].

Here, we have studied the sorption properties at acidic pH ranges of 3.5–4.5. It was observed that the final pH increases upto 4.5 due to the basic nature of the adsorbent. In the present study, it was well observed that the metal uptake increased with the increasing concentration, pH and temperature. The order of selectivity of both the samples at all pH and temperature towards the metal ions is $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$. To ascertain the above selectivity order we have also studied the sorption properties in a mixed solution having equal concentration of all the three metal ions. Interestingly the same order of metal uptake was observed (Fig. 4). In addition the plot clearly indicates that the prepared zeolite prefers Cu ion in comparison to that of Co and Ni ions. Similar type of order has also been reported for α -zirconium phosphate [17], AlPO_4 [18] and zeolite [14]. It was earlier stated that this order could neither be related to the stability of hexa-aquo ions nor to the stereochemistry adopted by

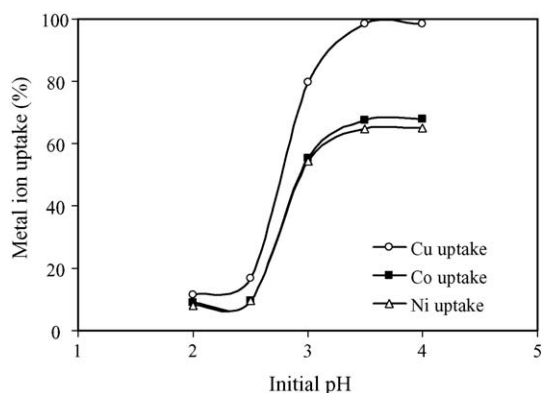


Fig. 3. Variation of different metal uptake at 27 °C with respect to initial pH. Concentration of each metal ion was $1 \times 10^{-3} \text{ mol dm}^{-3}$.

M^{2+} ions on the solid [18]. Of course, the stereochemistry of M^{2+} on the surface of zeolite or fly ash can not be compared with that of metal phosphates due to their structural differences. However, comparing the extent of sorption of metal ions with the ionic potential and hydrolysis constant (K_h) of the metal cations in solution, it is found that the used material prefers the cation with low ionic potential and a low pK_h value. As Cu^{2+} has the lower pK_h (8.00), the Cu^{2+} adsorption is larger in comparison to Co^{2+} ($pK_h = 8.9$) and Ni^{2+} ($pK_h = 9.9$) [19].

All the sorption data were fitted to linearly transformed Langmuir adsorption isotherms:

$$\frac{C_{\text{eq}}}{X} = \frac{1}{b} X_m + \frac{C_{\text{eq}}}{X_m} \quad (1)$$

where C_{eq} is the equilibrium concentration of adsorbate in solution (mol/l), X the amount of adsorbate per unit mass of adsorbent (mol/g), X_m the amount adsorbed to form a monolayer (mol/g) and b is the binding constant.

Plot of C_{eq}/X against C_{eq} gives straight line (Figs. 5–7) for both the adsorbents and adsorbates with correlation coefficient > 0.99 in the case of all the three adsorbates. This favors the applicability of Langmuir equation in the pH range of 3.5–4.5. The values of X_m and b thus determined from the Langmuir plots are tabulated in Tables 2, 3a and 3b. The X_m value for both Cu^{2+} and Co^{2+} sorption (Table 2) are quite higher in case

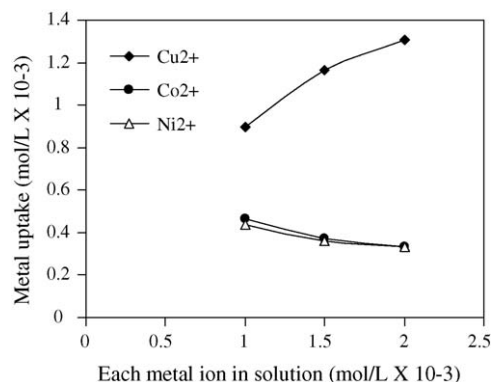


Fig. 4. Comparative metal uptake by the synthesized zeolite from mixed metal solutions.

Table 2
Langmuir parameters (X_m and b) and apparent equilibrium constant (K_a) for the metal ion sorption at initial pH 2 and temperature of 300 K

Samples	X_m ($\times 10^{-5}$ mol/g)		b		K_a	
	Cu ²⁺	Co ²⁺	Cu ²⁺	Co ²⁺	Cu ²⁺	Co ²⁺
FA	0.887	0.866	3686	3643	0.03269	0.03155
ZFA	6.9641	6.901	3872	3770	0.26965	0.26018

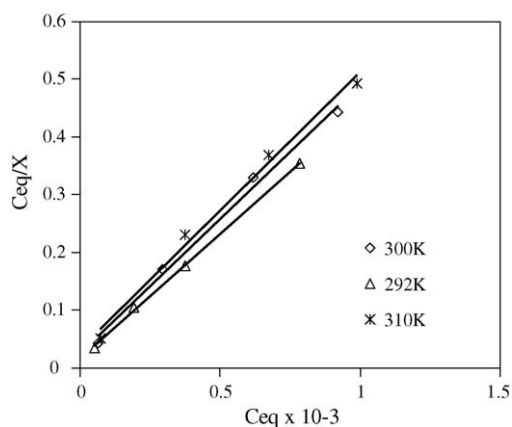


Fig. 5. Langmuir plot for the Cu²⁺ uptake at different temperature.

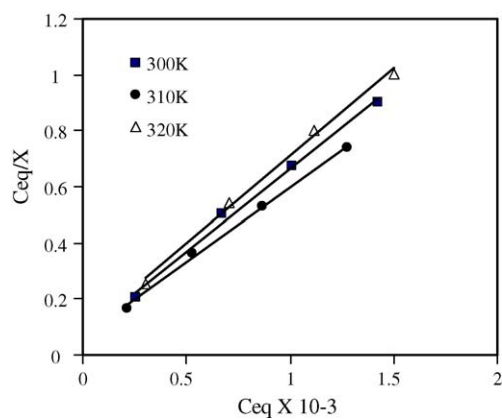


Fig. 6. Langmuir plot for the Co²⁺ uptake at different temperature.

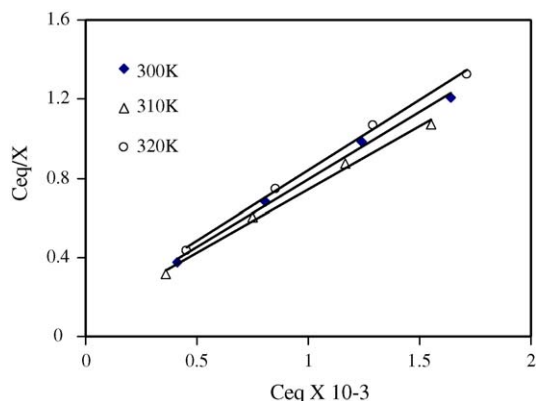


Fig. 7. Langmuir plot for the Ni²⁺ uptake at different temperature.

Table 3a
Langmuir parameters (X_m and b) for the metal ion sorption at initial pH 3.5

Temperature (K)	X_m ($\times 10^{-3}$ mol/g)			b		
	Cu ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Co ²⁺	Ni ²⁺
292	2.087	1.597	1.402	14516	7454	5710
300	2.147	1.692	1.471	17912	7848	5899
310	2.325	1.871	1.568	25006	8379	6047

Table 3b
Apparent equilibrium constant (K_a) calculated from Langmuir equation

Temperature (K)	Cu ²⁺	Co ²⁺	Ni ²⁺
292	30295	11904	8005
300	38457	13279	8677
310	58139	15677	9529

of prepared zeolite sample (ZFA) in comparison to that of FA. This clearly indicates that the prepared zeolite can be utilized as better adsorbent to that of fly ash even for highly acidic waste water treatment. It was also observed that both X_m and b increased with the increase in temperature (Table 3a), indicating the endothermic nature of the adsorption. The apparent equilibrium constant (K_a) corresponding to the sorption process was calculated (Tables 2 and 3b) as the product of b and X_m , and can be used as relative indicators of the affinity of the adsorbent towards the metal ions. These data indicate that the affinity of prepared zeolite is quite high in comparison to that of simple fly ash.

From the plot of $\ln b$ versus T^{-1} (Fig. 8), the standard enthalpy and entropy changes were calculated by using Eq. (2):

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

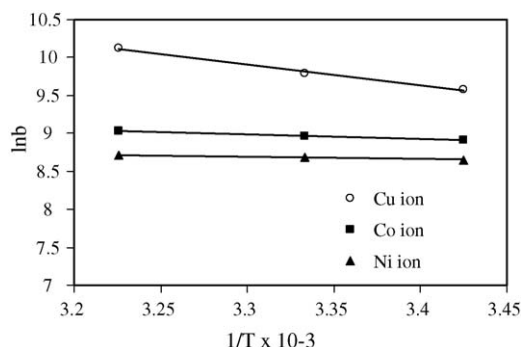


Fig. 8. Plot of $\ln b$ vs. $1/T$ for different metal ion uptake.

Table 4

Entropy (ΔS) and enthalpy (ΔH) changes of metal ions sorption on ZFA at initial pH 3.5

Metal ions	ΔS (J K ⁻¹ mol ⁻¹)	ΔH (kJ mol ⁻¹)
Cu	157.583	22.781
Co	90.864	4.888
Ni	78.477	2.419

Table 5

Gibbs free energy change of metal ions sorption on ZFA as a function of temperature

Temperature (K)	ΔG (kJ mol ⁻¹)		
	Cu ²⁺	Co ²⁺	Ni ²⁺
292	-23.231	-21.645	-21.003
300	-24.492	-22.372	-21.645
310	-26.069	-23.281	-22.447

By using the ΔS and ΔH values in Eq. (3), the Gibbs free energy change (ΔG) can be calculated.

$$\Delta G = \Delta H - T \Delta S \quad (3)$$

All the values of ΔS , ΔH and ΔG are tabulated in Tables 4 and 5. This shows that ΔH and ΔS are positive and ΔG is negative for all the experiments. The positive values again indicate the endothermic nature and increased disorderliness in the system, respectively. So probably the requirement of a large amount of heat to remove the bivalent metal ions from the solution makes the sorption process endothermic. The positive value of the ΔS indicates the partial dehydration of the metal ions before adsorption, thus increasing the spontaneity. Again, both ΔH and ΔS values follows the same order (Cu²⁺ > Co²⁺ > Ni²⁺) as that of selectivity. Similar order was also observed in case of FePO₄ [20]. From these results it can be concluded that changes in the hydration of a metal cations plays the dominant role in determining the selectivity of the exchanger. The highest disorder of the system was observed in case of Cu²⁺, which indicates that Cu²⁺ ion lose most of their water of hydration. This is also supported by the highest value of ΔH in Cu²⁺ sorption. It was also observed that with increase in temperature ΔG became more negative, which justify that adsorption is favored by an increase in temperature.

4. Conclusions

Complete conversion of Indian fly ash to crystalline, porous 13X zeolite is possible by NaOH fusion at 600 °C followed by hydrothermal treatment at 105 °C. Prepared material exhibits high surface area of 430 m²/g. Sorption of metal ions increases with the increase in temperature and pH. All the sorption data were fitted to the Langmuir equation and the thermodynamic parameters (ΔS , ΔH and ΔG) were evaluated. Sorption capacity of the zeolite is quite higher than that of fly ash at acidic pH having the selectivity order of Cu²⁺ > Co²⁺ > Ni²⁺. In all the cases the change in hydration of metal ions plays the dominant

role in determining the selectivity. Present study indicates that the prepared zeolite material can be utilized as better adsorbent for the heavy metal sorption from acidic waste water of metallic industry in comparison to the available fly ash.

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