

Separation and estimation of heavy metals on zeolitic material synthesized from fly ash by chemical modification

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ABSTRACT

Here the elution, retention and separation of some heavy metals on the column of synthesized zeolitic material have been investigated. The zeolitic material was synthesized from fly ash by hydrothermal treatment with NaOH for 24 hours. The ion exchange capacity, elution behavior and distribution studies were carried out to determine the preliminary ion exchange properties of the material. The elution behavior of Mn^{2+} , Fe^{3+} , Cd^{2+} , Cr^{3+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , As^{3+} , Mo^{6+} and Hg^{2+} were attempted on zeolitic material. On the basis of distribution coefficients studies some binary separations of heavy metal ions such as $Bi^{3+}-Ni^{2+}$, $Bi^{3+}-Cr^{3+}$, $Mo^{2+}-Cr^{3+}$, $Sb^{2+}-Cd^{2+}$, and $Pb^{2+}-Cd^{2+}$ were achieved on the column of zeolitic ion exchange material. The separation and estimation of Fe^{3+} , Cr^{3+} , Pb^{2+} , Sb^{3+} and Ni^{2+} from the different water samples were also attempted on zeolitic material.

Keywords: zeolitic material; heavy metals; wastewater; separation

INTRODUCTION

Many toxic heavy metals are discharged into environment by industrial and municipal wastewater. These metal ions when present in higher quantity can be harmful to aquatic life and human health. Fe^{3+} , Cu^{2+} , Cr^{3+} and Pb^{2+} are the most common heavy metals that tend to accumulate in organism, causing numerous diseases and disorder¹. Their concentration in water has been analyzed worldwide²⁻⁵. The numerous processes exist for removing the dissolved heavy metals from water and waste water system⁶⁻⁹. The use of alternative low cost materials as potential adsorbents for the removal of heavy metals has been emphasized recently. The low cost ion exchangers such as zeolites have been considered cost effective¹⁰. The zeolitic products have variety of application due to framework structure that contains channels and cavities¹¹. Cation and water molecules that are located in the cavities give rise to ion

exchange capacity that leads to application in separation sciences¹². Most of studies reported have used the zeolites for the retention of selected water pollutants from water system. It has been observed that there was a considerable competition between cations in a solution in order to occupy exchangeable place in zeolite and consequently, the matrix composition play an important role in the pollution uptake efficiency of zeolite¹³.

The mechanism of adsorption by zeolite has been observed due to the ion exchange. In the three dimensional structure of zeolite there are large channel containing negatively charged sites resulting from Al^{3+} replacing of Si^{4+} in O_4 tetrahedral linked by sharing oxygen atoms in rings and cage cavities occupied by cations which are weakly held in the structure to compensate the charge imbalance^{10,14}. Zeolites contain various types of cationic sites¹⁵. The overall negative charge of the anions is balanced

by cations that occupy the channels within the structure and can be replaced with heavy metal ions¹⁶. The variation in cation exchange capacity of zeolites was due to different nature of cage structures of zeolites, natural structural defects, adsorbed ions and their associated gangue minerals¹⁴.

Only few studies have been ventured on the ability of zeolitic material to separate and remove the heavy metals from mixed solution¹⁷⁻¹⁹. The available literature revealed that no systematic study has been conducted on the retention and separation of heavy metals from various waste water sample on the column of zeolitic material.

Therefore, this study was conducted to use the zeolitic material synthesized from chemically modification of fly ash for adsorption, elution, separation and recovery of heavy metals from synthetic and original water samples.

EXPERIMENTAL

Materials

In the present study, all the chemical and reagent were procured from E. Merck (India). Fly ash was procured from Thermal Power Plant, Ropar, Punjab, India. The water samples were collected from different sources in Punjab, India. Water samples (250 ml) were digested with concentrated HCl and HNO₃ on hot plate. When the volume was reduced to 10 mL then the samples were transferred to a 50 mL volumetric flask and diluted to volume with distilled water

Synthesis of Zeolitic Material

One gram of fly ash (mesh size between 50-150 μ) was mixed with 100 ml of 2.5M KOH and 0.1M KCl solutions in demineralized water. The mixture was then refluxed for 36 h at 100 °C in a round bottom glass flask. The product was filtered and washed with demineralized water several times and dried at 40 °C for overnight in an oven. The material was converted to H⁺ form by treating it with 0.1N HNO₃ for 24 hour at 25 \pm 2 °C. The washing was done with double distilled water to remove excess acid and finally the material was dried at 40 °C in an oven. The material was sieved to obtain the particles of 100-150 mesh size.

Ion Exchange Capacity

The ion exchange capacity was determined using column method by placing one gram of the material in H⁺ form in a glass tube fitted with glass wool at its bottom. 0.1 M HNO₃ solution was used as eluant. The flow rate was

maintained at 20 drops per min. The effluent was titrated against a standard alkali solution to determine the total H⁺ ions released.

Chemical Stability

The 0.5 gram of the material in H⁺ form was kept in 30 ml solvent of analytical interest for 12 h at room temperature with intermitted shaking. The supernatant liquid was analyzed for metal ion concentration using atomic absorption spectrophotometer.

Distribution Studies (K_d)

Distribution coefficient for different metal ions was determined in aqueous solution by batch process²⁰. In this method, 0.2 g of zeolitic materials in H⁺ form were taken in Erlenmeyer flask with 50 ml of different metal ion concentrations and kept for 24 h with continuously shaking at room temperature (30 \pm 2 °C) to attain equilibrium. The amount of metal ions before and after adsorption was determined using standard method.

Elution of Metal Ions

One gram of synthesized zeolitic material was supported on glass wool in a glass column (30 cm x 2.7 cm diameter). The solution of metal ions was circulated many times through the column at the rate of 20 drops per minutes to ensure maximum exchange of metal ion on the ion exchange material. The column was washed with double distilled water to remove the unadsorbed metal ions. Different concentration of nitric acids as eluant were prepared and passed through the column. The effluent was collected as 10 ml fraction and tested for metal ions by atomic absorption spectrophotometer (AAS).

Binary Separation of Metal Ions

One gram of zeolitic material in H⁺ form was supported on glass wool in a glass column (30 cm x 2.7 cm diameter). The column was washed with distilled water and mixture of the two metal ions to be separated were passed through the column several times at flow rate of 2 cm³/min, until exchange of H⁺ on the ion exchange material by metal ions was maximum. The column was again washed with distilled water to remove unexchanged metal ion. Different concentration of HNO₃ was used for the elution of metal ions from the material. The collected metal ions thus were determined by AAS.

Separation and Estimation of Heavy Metal Ions in Original Water Samples

One gram of zeolitic material was supported on glass wool in a glass column. Water samples containing mixture of metal ions were passed through the column slowly (20 drops per minutes) and recycled many times to the adsorption of metal ions. The column was then washed with distilled water to remove unadsorbed metal ions. The metal ions adsorbed on the material were then eluted with different concentration of HNO_3 .

RESULTS AND DISCUSSION

The important feature of the synthesized material is that it has good ion capacity for Na^+ ions. The ion exchanger capacity of zeolitic material was found to be 0.81 meq/g at 40 °C. The chemical stability study indicates that the zeolitic material was fairly stable in different acids ($\text{HNO}_3 > \text{HCl} > \text{H}_2\text{SO}_4$), organic and mixed solvents (benzene > acetone > acetone + $\text{HNO}_3 >$ acetone + KOH), while it was less stable in bases (KOH > NaOH). Figures 1 and 2 showed the elution pattern for Mn^{2+} , Fe^{3+} , Cd^{2+} , Cr^{3+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , As^{3+} , Mo^{6+} , and Hg^{2+} on zeolitic material. It has been observed that the elution pattern is quite fast and all the metal ions are eluted out in the first 70 ml of effluent from the column of the material. Thus this material was used for estimation and recovery of heavy metals from aqueous media. In order to explore the potential of the zeolitic material in the separation of metal ions, the distribution studies for 14 metal ions were performed in water system (Table I). The distribution studies showed that the material was found to possess exceptionally high K_d values for many metal ions hence the material was found highly selective for them. These metal ions have been considered to be a major water pollution material. The total adsorption for Mg^{2+} , Cr^{3+} , Cd^{2+} , Ni^{2+} and Sn^{4+} might have been utilized in selective adsorption or separation of these metals from the mixture of metal having low affinity (such as Ca^{2+} , Bi^{3+} and Pb^{2+}) for zeolitic material. The majority of heavy metals, thus studied showed very high adsorption onto zeolitic material. On the basis of the difference in the values of distribution studies some important binary separation such as Bi^{3+} (0.5N) – Ni^{2+} (1.5N), Bi^{3+} (0.5N) – Cr^{3+} (1.5N), Mo^{2+} (0.1N) – Cr^{3+} (1.5N), Sb^{2+} (0.5N) – Cd^{2+} (1N), and Pb^{2+} (0.1N) - Cd^{2+} (1N) were attempted on the column of zeolitic material using HNO_3 , as eluant. The results of the binary separations are shown in Figures 3 and 4. The results inferred

that in the binary separations the different metal ions were eluted at different concentration of eluant.

Table I Distribution coefficient value of different metal ions for zeolitic material in DMW

Sr. No.	Metal ions	K_d values ($\text{cm}^3 \text{g}^{-1}$)
1	Mg^{2+}	TA
2	Ca^{2+}	202
3	Cr^{3+}	TA
4	Mn^{2+}	1011
5	Fe^{3+}	1233
6	Co^{2+}	TA
7	Ni^{2+}	TA
8	Zn^{2+}	TA
9	Mo^{2+}	1808
10	Cd^{2+}	TA
11	Sn^{2+}	TA
12	Sb^{2+}	2437
13	Pb^{2+}	900
14	Bi^{3+}	12

TA = Total adsorption/ ion exchanger

Table II showed the utility of zeolitic material as column material for selective retention and separation of metal ions from different water samples. This was possible due to high distribution coefficient of some metal ions as shown by its elution at higher concentrations of HNO_3 , as reported earlier²¹. The result reported in Table II is the average of five replicate analyses.

Table II Separation and estimation of few heavy metals from the water samples collected from few industrial sites on zeolitic material

Sample	Metal ions separated	Conc. of metal in water sample loaded (ppm)	conc. of metal ion eluted (ppm)
S ₁	^a Fe^{3+}	1.22	1.00
	^b Cr^{6+}	2.00	1.10
S ₂	^a Pb^{2+}	1.24	0.96
	^b Sb^{3+}	1.40	0.65
S ₃	^a Fe^{3+}	4.44	3.21
	^b Ni^{2+}	1.00	0.36
S ₄	^a Fe^{3+}	2.87	1.26
	^b Ni^{2+}	1.20	0.45
S ₅	^a Fe^{3+}	3.03	2.32
	^b Ni^{2+}	1.20	0.40

Volume of eluent: 100 mL, S₁-S₅ are the real water samples ^a indicates 0.1 N, ^b indicates 0.5 N HNO_3

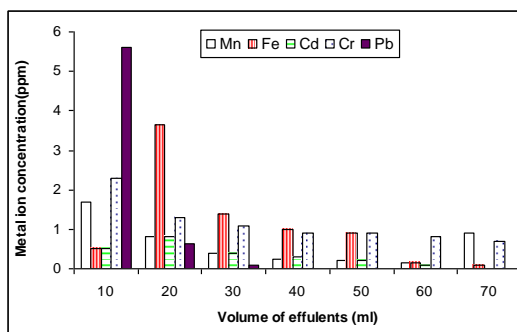


Figure 1

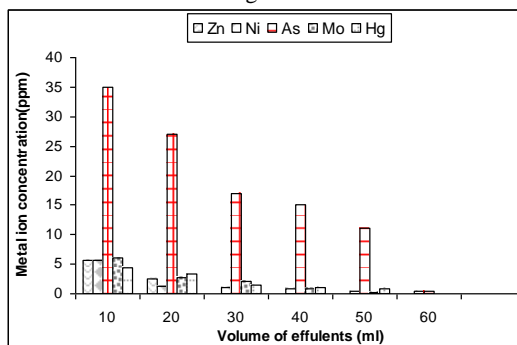


Figure 2

Fig.1-2: Elution pattern of metal ions on zeolitic material

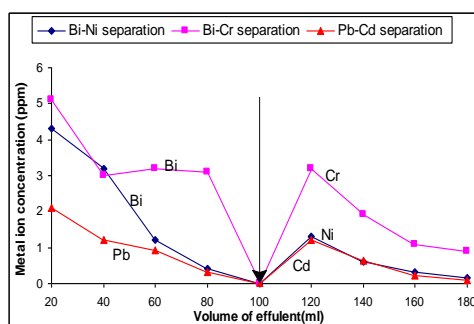


Figure 3

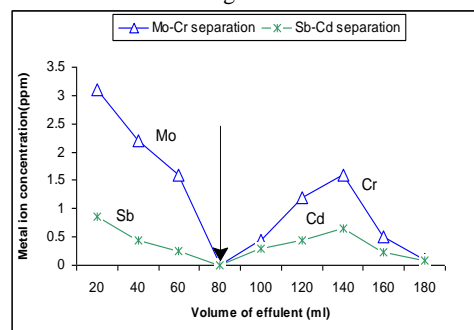


Figure 4

Figure 3-4: Binary separation curves of metal ions on zeolitic material

CONCLUSION

The result showed that the zeolitic material seems to be promising ion exchangers with significant ion exchange capacity. The more stability of the material in mineral acid, organic and mixed solvent confirms its better chemical stability. The distribution coefficient values of indicate high affinity of zeolitic material for certain heavy metal ions. On the basic of distribution coefficient values this material has been successfully used for the removal, separation and estimation of heavy metals from the various water samples. This shows the potential applicability of this method in the water treatment.

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