

Partially Cd²⁺ Ion-Exchanged Type-A Zeolites and Their Thermal Analysis

¹SHER AKBAR*, ²RUKHSANA SHAHNAZ,
³TAJAMUL HUSSAIN SHAH AND ¹MUHAMMAD SAMI
¹Department of Chemistry, University of Balochistan, Quetta, Pakistan.
²Government Girls College, Quetta Cantt, Pakistan.
³Government College, Pishin, Pakistan.

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Summary: A series of partially exchanged Cd²⁺ A-zeolites (Cd_{0.86} A, Cd_{1.7} A, Cd_{2.46} A, Cd_{2.86} A, Cd_{3.25} A) were prepared by aqueous cation exchange technique from synthetic NaA-zeolite. The percentage of Cd²⁺ ions exchanged increased with decreasing the concentration of Cd²⁺ ions and increasing temperature of the exchanging solution. This behaviour of Cd²⁺ ion exchange with concentration is attributed due to 'volume effect,' 'salt imbibent' and electroselectivity effect. The uptake of Cd²⁺ ions increased with rise in temperature indicated the process to be endothermic. Ion-exchange isotherms plotted at different temperatures showed the type 'a' isotherm *i.e.*, the entering ion (Cd²⁺) indicated selectivity to the outgoing ions (Na⁺). The ion-exchange equilibrium data also followed the Freundlich and Langmuir adsorption isotherms. Thermogravimetric analysis (TGA) showed that the zeolitic water depends on the number of Na⁺ and Cd²⁺ ions per unit cell (p.u.c.) Thermal analysis curves showed that the minimum endothermic peak of dehydration slightly shifted towards higher temperature for CdA-zeolites indicated that water molecules are more strongly bonded to Cd²⁺ than Na⁺. Three exotherms were clearly observed within the temperature range 780-1000 °C, which are indicative of more than one reaction or crystallization of more phases. The differential thermal analysis (DTA) curves showed that dehydrated NaA zeolite retained its stability from 340 to 780 °C and CdNaA-zeolites from 330-380 °C to 800-820 °C, NaA amorphized at 920 °C and CdNaA-zeolite, from 920 to above 1000 °C.

Introduction

Zeolites found early applications in the removal of undesirable ions from water, *i.e.*, for water softening. Now they are used as catalysts [1, 2], ion-exchangers [3, 4] and adsorbents [5, 6]. Zeolite NaA is a synthetic zeolite whose use as a detergent builder is wide-spread all over the world [7, 8] and its cost is usually lower than other synthetic zeolites. The aluminosilicate framework of the zeolite is generated by placing truncated octahedrons (β -cages) at eight corners of a cube and each edge of the cube is formed by two β -cages by a D4R (double four ring) linkage [9]. Each β -cage encloses a cavity with a free diameter of 6.6 Å and each unit cell encloses a large cavity known as the α -cage enclosing a free-diameter of 11.4 Å. There are two interconnected three dimensional channels in zeolite type-A:

- (i) connected α -cages, separated by 4.2 Å from free apertures,
- (ii) β -cages, alternating with the α -cages separated by 2.2 Å from apertures [10].

Thus, molecules smaller than 4.2 Å in diameter can diffuse easily through the micropores of

the zeolite. Also, the position of Na⁺ ions in NaA-zeolite in the unit cell is important since these ions act as the sites for water sorption. For a typical NaA-zeolite, a unit cell having the composition, Na₁₂Al₁₂Si₁₂O₄₈·27H₂O, eight (out of 12) Na⁺ ions are located with water molecules in the 8-rings. Water molecules form a pentagonal dodecahedron in the α -cage [11]. The extra-framework cations are distributed within the same intracrystalline pore system as the zeolitic water. As a result of the open structure the cations, like the zeolite water can be mobile. However, unlike the water, the cations are not free to leave the crystals unless they are replaced by their electrochemical equivalent of other cations because neutralization of anionic charge of the aluminosilicate framework must be maintained.

Cadmium is found in surface waters as a free ion; its solubility is affected by the hardness, the pH, the soluble complexes, and the colloidal sulfides of the aqueous stream [12]. Cadmium is a dangerous heavy metal that causes severe problems due to its high toxicity. The Na⁺ ions in zeolite NaA are exchangeable with those from the solution such as

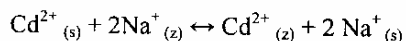
*To whom all correspondence should be addressed.

Pb²⁺, Cd²⁺, Zn²⁺ and Mn²⁺ *etc.* Due to their unique cage-like structure with channel openings of a few angstroms, zeolites have found wide use as molecular sieves, because small organic or inorganic molecules may be trapped within these channels. Molecules and ions too large to fit into the zeolite's channels are excluded from the internal surfaces and interact only with the external surfaces of zeolite crystals. The internal or zeolitic exchange sites potentially remain available for smaller inorganic cations.

The objectives of our investigations are two fold, firstly, to evaluate the retention of Cd²⁺ ions from an aqueous solution having definite concentrations of Cd²⁺ ions by using NaA-zeolite. The Freundlich and Langmuir adsorptions isotherms were also employed on adsorption/ion-exchange of cadmium at different temperatures. Secondly, thermal analysis of NaA and CdNaA-zeolites was performed to know the zeolitic water and thermal stability of the crystalline lattices from ambient temperature to 1000 °C.

Results and Discussion

Table-1 shows the number of exchange of 0.86, 1.70, 2.46, 2.86 and 3.25 Cd²⁺ ions per unit cell (p.u.c) of the zeolite A. They are designated Cd_xA where x is the number of Cd²⁺ ions exchange p.u.c. of zeolite NaA. The Na⁺-Cd²⁺ ion-exchanged reaction in zeolite may be written [13]:



The notation (s) and (z) refer to the ions in solution and zeolite-A phases. The structure factors described in introduction are important for understanding cation exchange, are that the exchanging cations must diffuse through a series of rings of 8 tetrahedra (8-rings) with a free diameter of 4.2 Å [10] in order for ion exchange to occur in the α -cages. They must diffuse from these large cages through a 6-ring with a diameter of 2.2 Å in order for

the ingoing ions to replace the Na⁺ ions located in the network of small cages. The table indicates that the percentage of exchange decreases as the concentration of Cd²⁺ ions in aqueous solution increases. The factors responsible for this decrease are 'volume effect' [14], 'salt imbibition' [15], and 'electroselectivity effect' [13]. These factors are described below.

1. There are 12 Na⁺ ions p.u.c., in hydrated zeolite all are located in the one large cage (α -cage) p.u.c. [13], therefore at higher loadings most likely when too many of Cd²⁺ ions move into the α -cage they crowd out some of the Na⁺ ions into the β -cage. One could look at this as a 'volume effect'. Thus, it is the size of hydrated Cd²⁺ ions that inhibits its movement into the small β -cage through α -ring, therefore, Na⁺ ions replacement may become impossible.
2. 'Salt imbibition' is the uptake of neutral salt molecules into the internal zeolite structure which readily occurs especially when there is a high salt concentration in the solution phase [15]. Salt concentration must be kept below the condition at which neutral salt imbibition can occur via Donnan Mechanism [16].
3. The third reason is the 'electroselectivity effect'. The selectivity of Cd²⁺ ions over Na⁺ ions decreases with increasing total molarity. The statement of the electroselectivity effect is that when the ingoing ions is more highly charged than the outgoing ions, the preference for the ingoing ion decreases with increasing initial solution molarity [13].

Fig. 1 illustrates the Cd²⁺ ion-exchange isotherms at 25, 40, 55 and 70 °C by plotting amount of Cd²⁺ ions exchanged (mol/g) in zeolite A versus equilibrium Cd²⁺ ions concentration (mol/L) in solution. All the isotherms are of type 'a' [10] *i.e.*, selectivity for the entering cation (Cd²⁺) over the entire range of zeolite composition. Hertzberg and Sherry [17] also reported that Cd²⁺ exchange into

Table-1: Preparation and analysis of Cd²⁺ exchanged A-zeolite.

Zeolite Samples	CdCl ₂ mol dm ⁻³	Exchanged Cd ²⁺ cations %	No. of Na ⁺ cations released p.u.c. [†]	Formulae p.u.c. of anhydrous Cd Na A-zeolites*
Cd _{0.862} A	0.010	97.43	1.724	Cd _{0.86} Na _{10.28} -A
Cd _{1.704} A	0.020	97.25	3.408	Cd _{1.70} Na _{8.60} -A
Cd _{2.462} A	0.030	93.67	4.924	Cd _{2.46} Na _{7.08} -A
Cd _{2.861} A	0.040	81.22	5.722	Cd _{2.86} Na _{6.28} -A
Cd _{3.250} A	0.050	74.80	6.500	Cd _{3.25} Na _{5.5} -A

[†] p.u.c. (per unit cell) is used for convenience and strictly refers to the pseudo cell which is one eighth of the true unit cell.

*A=[(AlO₂)₂(SiO₂)₁₂]¹²⁻

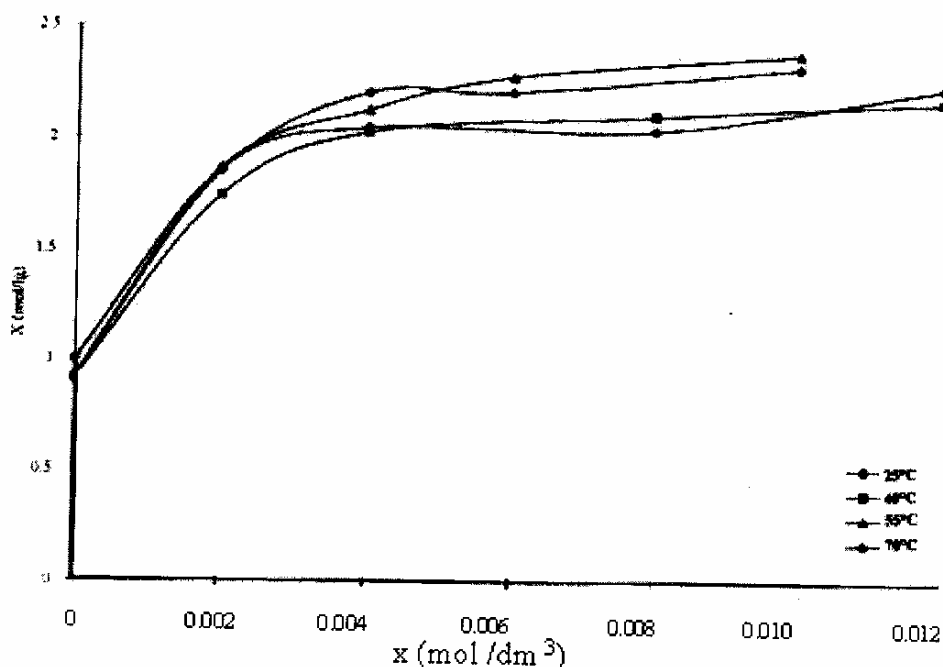


Fig. 1: Effect of temperature on the Cd^{2+} , NaA exchange isotherm.

zeolite NaA is extremely selective for the heavy metal cation. The cause of high selectivity lies in the polarizability of this divalent cation by the strong electric fields within the zeolite crystals. The Fig. 1 shows that the values of “plateau” $-x$ slightly increases with increase of both the molarity, M , and temperature of the exchange process. The increase in equilibrium Cd^{2+} content with increasing exchange temperature is a consequence of the effects appearing at higher temperatures *i.e.*, on increase of the diffusion coefficient due to the reduction of the effective size of Cd^{2+} ions caused by a decrease of the ion hydration shell and a reduction of the limitations for diffusion in the inner part of the pore system arising from a decrease in the effective ionic radius. The selectivity decreases with decreasing size of cation and increasing dehydration energy of the hydrated ion. The least hydrated ion is more preferred. It is suggested that three factors may contribute to the replacement of Na^+ ions by Cd^{2+} ions in the network of small cages (β -cages) at higher temperatures [13]:

1. The increase in temperature supplied energy of dehydration. The least hydrated ion is more preferred.

2. The increase in temperature provides additional kinetic energy for diffusion of the bare ions (ionic radius = 0.97 \AA of Cd^{2+}) [18] into the sodalite cages.
3. The increase in temperature causes greater vibration of the aluminosilicate framework.

Hence, at 298 K the ion-exchange isotherm indicates that the hydrated Cd^{2+} ion is too large to migrate through the 6-ring into the β -cage. At elevated temperature, stripping of water of hydration should enable the ion to penetrate the 6-ring in order to replace Na^+ ions located there.

To quantify adsorption/ion-exchange capacity of zeolite type-A for the removal of Cd^{2+} from water, the equilibrium sorption data were also fitted into the well known Freundlich and Langmuir adsorption equations as given in the linear forms below:

Freundlich adsorption equation, $\log x = \log A + 1/n \log C_e$

Langmuir adsorption equation, $C_e/x = 1/B V_m + C_e/V_m$

where x is the amount of Cd^{2+} adsorbed/exchanged in mol/g, C_e is the equilibrium concentration in

mol/dm³, A and n are Freundlich constants for specific system; V_m is the monolayer capacity of adsorbate/exchanged ion and B is the binding constant. The linear plots were obtained as illustrated in Figs. 2 and 3. The lines at temperatures 55 and 70 °C have overlapped therefore, Fig. 3 shows only three lines instead of 4 lines. Thus, the adsorption exchange pattern followed the Freundlich and Langmuir adsorption isotherms. The results indicated above that zeolite type-A can be used as an efficient ion exchange material for the removal of Cd²⁺ ions from industrial and radioactive waste waters.

Representative examples of TGA and DTA curves (reproduced) of Cd,Na-A (sample 4) are displayed in Figs. 4 (a and b), respectively. The thermal analysis data of the Na₁₂A and Cd,NaA-zeolites are summarized in Table-2. The TGA curves for all zeolites were nearly continuous and smooth and showed that most water is lost between 340-380 °C and dehydration completed at 840-970 °C, depending on the number of Na⁺ and Cd²⁺ ions p.u.c. in the zeolite. The TGA curves indicated that the dehydration of the samples began around 20 -25 °C. The greater difficulty in the dehydration of the samples indicated that the zeolitic water is located

inside the pores/voids of the zeolite. The DTA plots and data of Table-2 show that the endotherms of dehydration are progressively shifted to higher temperatures (340-380 °C) from the Na₁₂A to Cd,Na-zeolites indicating that the water molecules are strongly coordinated with the Cd²⁺ ions. The Table-2 indicates that the loss in weight percentage is from 21.01 to 23.14 depending on the Na⁺ and Cd²⁺ ions p.u.c. in the zeolite framework. A slight weight loss in NaA at 840 °C and in Cd,Na-zeolites at higher temperatures (900-970 °C) may be due to dehydroxylation [19, 20]. McCusker and Seff [21] reported that Cd,Na-zeolite to have unusual dehydration properties retaining water even after evacuating for 2 days at above 500 °C. For strongly polarizing cations, water molecule yields a hydroxyl bonded to the cation plus a proton, which attaches itself to the framework oxygen. Ultimately as the temperature rises, the hydroxyls are destroyed with the expulsion of water [22].

Thermal analysis technique can also be used for interpretation of the nature of water in zeolites. Three sites for Cd²⁺ ions have been shown by X-ray structure of the fully hydrated CdA-zeolite (21). In two of these sites, Cd²⁺ ions are octahedrally coordinated to three framework oxygens and three

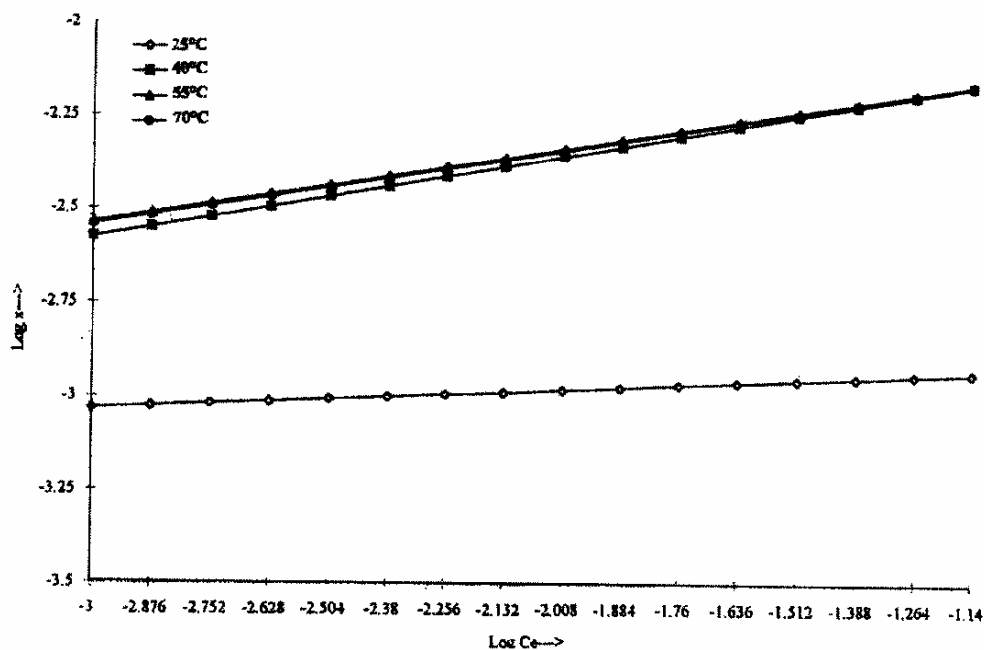


Fig. 2: Freundlich adsorption plots for adsorption of Cd²⁺ ions from aqueous solution onto zeolite type-A.

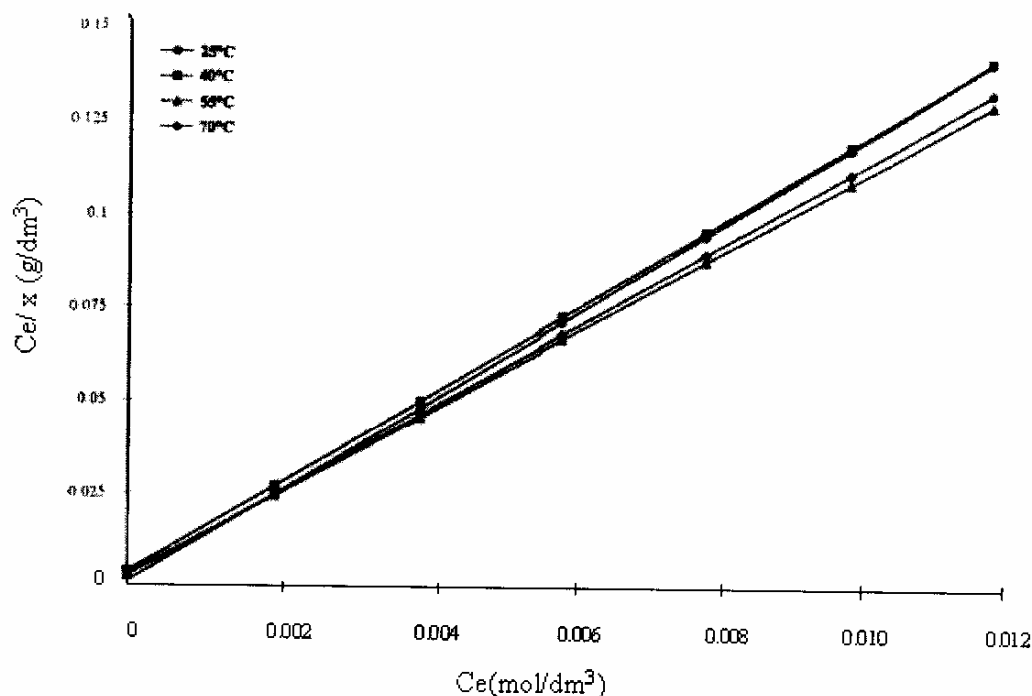


Fig. 3: Langmuir adsorption plots for the adsorption of Cd^{2+} ions from aqueous solution.

Table-2: Summary of thermal analyses data of NaA and partially Cd^{2+} exchanged NaA-zeolites.

Zeolites	Loss in wt %	Temperature °C of				
		Mini. of endothermic peak of dehydration	Mini. of endothermic sharp peaks of recrystallization.	Dehydroxylation	Maxi. of exothermic peaks of crystal collapse	Zeolitic water molecules p.u.c.
$\text{Na}_{12}\text{-A}$	21.01	340	830,880	840	780,860,920	26.50
$\text{Cd}_{0.86}\text{Na}_{10.28}\text{-A}$	19.9	340	830,920	970	800,890,1000	26.05
$\text{Cd}_{1.70}\text{Na}_{8.60}\text{-A}$	20.07	350	837,980	900	800,900,1020	26.50
$\text{Cd}_{2.46}\text{Na}_{7.08}\text{-A}$	22.61	355	840,920	900	800,890,1020	29.01
$\text{Cd}_{2.86}\text{Na}_{6.28}\text{-A}$	22.87	365	845,928	960	800,890,1020	30.40
$\text{Cd}_{3.25}\text{Na}_{5.5}\text{-A}$	23.14	380	845,928	965	820,895,1020	30.74

water oxygens. In the third site Cd^{2+} ions are bound to three framework oxygens and two water oxygens, forming a trigonal bipyramidal structure. The lumpy nature of TGA Fig 4(a) curve results from the formation of a series of intermediate structures during dehydration [22]. In zeolites that undergo dehydration reversibly and continuously, there is no substantial change in the topology of the framework structure. Exchangeable cations that are located in the channels coordinated with water molecules may migrate to different sites located on the channel walls or other position of coordination (Fig.1). Choi *et al* [23] reported that all Cd^{2+} ions in dehydrated NaA-zeolite lie on threefold axes near six-ring centers, four in the large cavity and two in the sodalite cavity. Pavlovskaya *et al* [24] also reported that dehydration

of Cd, Na-A zeolite forces the Cd^{2+} ions to coordinate more strongly with the framework oxygens. This effect is clearly seen in X-ray results where evacuation of CdA-zeolite at room temperature, Cd^{2+} cations become approximately three-coordinate [25]. The DTA curve plays an important role in the detection of mobile and immobile water. The DTA curve of water adsorbed in Cd, Na-A (sample 4) has three dehydration steps two endotherms of low intensities at 140, 180 °C and third a broad endotherm at 365 °C Fig. 4. Dehydration in three steps is attributed to the difference in bonding strength of the water molecules in the zeolite. Two dehydration steps were also noted in the DTA curve of unexchanged NaA-zeolite but appeared at low temperatures first one of low intensity endotherm at

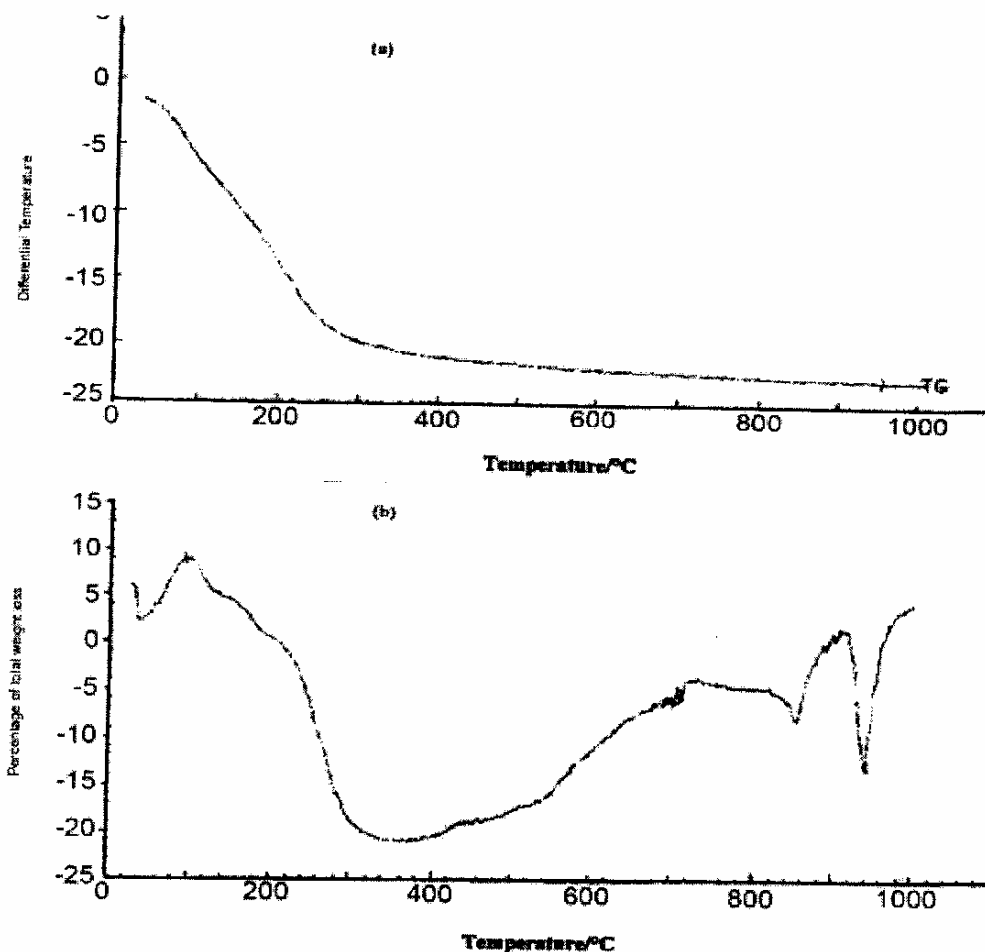


Fig. 4: (a) TGA and (b) DTA curves of the $\text{Cd}_{2.86}\text{A}$ -Zeolite.

180 °C and second broad endotherm at 340 °C. Mobile water on surfaces and in pores are removed at lower temperature and immobile water coordinated with cations and in narrow zeolitic pores is removed at 340 °C and 365 °C, respectively for NaA and Cd, Na-A zeolites [26].

The Table-2 indicates that zeolitic water depends on the number of Na^+ and Cd^{2+} ions p.u.c. of the zeolites. One of the reasons for the higher hydrophilicity of zeolite NaA and Cd, Na-A zeolites is the strong electrostatic interaction between ionic sites and the water molecules (due to its high polar nature). In a structure as rigid as A-zeolite, the increase of water is only possible by a closer packing of water molecules around the Cd^{2+} ions in Cd, Na-A

zeolites. In zeolite type-A with small cavities (β -cavity), the cations are in contact with few water molecules. As the cavities increase in size, the cations may be surrounded by water molecules and in zeolite type-A with large cavities (α -cavity), the water may behave essentially as an isolated liquid phase. It has been reported [11] that each sodalite unit appeared to contain four H_2O molecules in a distorted tetrahedron with bonding to O(3) at 2.8 Å and Na(1) at 2.9 Å [27]. (The bracketed number is merely an arbitrary label to distinguish crystallographically distinct positions). Each large cage contained two sets of water molecules which could correspond to twenty water molecules lying at the corners of a pentagonal dodecahedron. Each 8-ring may contain one Na^+ and one H_2O molecule [28].

The Table-2 indicates that the DTA curves of all zeolite samples showed three exothermic peaks at higher temperatures (780-1000 °C). First of low exothermic peaks indicate partial transformation of zeolite crystals and sharp higher exothermic peaks are attributed to the decomposition of the zeolite structure, two sharp peaks of endotherms (830-928 °C) can be attributed to recrystallization of new phases [10]. These reactions have taken place at lower temperatures in zeolite NaA. The exothermic nature of the crystal collapse is attributed to the large amount of surface energy associate with the zeolitic lattice of higher surface area [29]. The Fig. 4 and Table-2 show that the dehydrated NaA-zeolite lattice is stable up to 780 °C and Cd, Na-A zeolites up to ~820 °C and NaA at 920 °C and Cd, Na-A zeolites above 1000 °C amorphized.

Breck reported [10] that the density of zeolite A increases with atomic weight of the extra-framework cation. The unit cell constant of NaA is 12.32 Å and cation exchange has little effect on the unit cell constant. When dehydrated, the unit cell constant of NaA decreases by only about 0.02 Å, thus confirming the very rigid nature of the aluminosilicate framework.

These observations agree well with previously reported [30-32] zeolitic phase transformation under controlled thermal treatment, may be summarized as below:

Hydrated Cd_xNa_{12-x} A-zeolite (crystalline) $\xrightarrow{\sim 380\text{ }^\circ\text{C}}$ Dehydrated zeolite (crystalline)

$780\text{-}820\text{ }^\circ\text{C}$ partially collapse of micropore system of zeolite (Sodium Cadmium aluminosilicate)

$830\text{-}845\text{ }^\circ\text{C}$ recrystallization in an other form of zeolite
 $860\text{-}945\text{ }^\circ\text{C}$ collapse of structure

$880\text{-}928\text{ }^\circ\text{C}$ recrystallization to mullite and amorphous SiO_2
 $920\text{-}1000\text{ }^\circ\text{C}$ amorphized to aluminosilicate

Experimental

Adsorbent/ion-exchanger synthetic type A-zeolite in the sodium form (NaA) was obtained from BDH, (U.K.) lot # K20959014429. For cadmium ion exchange $CdCl_2 \cdot H_2O$ (E.Merck) lot # 366554, for complexometric titration EDTA (BDH) analar lot # 9744320F and erichrome black-T (E.Merck) lot # 6376852 was used as an indicator. All solutions were

prepared using doubly de-ionized water. The NaA-zeolite was exchanged with Cd^{2+} ions by conventional method [13]. The following procedure to prepare $Cd_{2.86}$ A-zeolite sample is typical of the exchange methods used. Nearly 10 g of the NaA zeolite (powder) was stored in a desiccator over saturated $Ca(NO_3)_2 \cdot 4H_2O$ solution for complete hydration at room temperature for several days. Then completely hydrated NaA-zeolite (5 g) was slurried in 75 cm^3 deionized water and the PH reduced from ~ 11 to 7 by dropwise addition of very dilute hydrochloric acid with constant stirring. A solution (200 cm^3) 0.0402 M of $CdCl_2$ was added slowly with constant stirring and the mixture was stirred for 2 h at 60°C. The slurry was filtered and the exchanged sample was washed several times with hot deionized water. The wet samples were dried over night at 80 °C and then the partially dehydrated dried samples were stored over saturated calcium nitrate solution to rehydrate to their equilibrium water content by exposing them to water vapour from saturated calcium nitrate solution and then characterized by thermal analysis. The Cd^{2+} concentration was analyzed before and after exchange by titration against 0.01 M EDTA with eriochrome black-T as indicator till colour change occurred from wine red to blue. The amount of EDTA used was noted. The concentration of Cd^{2+} ions exchanged was determined as the difference between the concentration of Cd^{2+} ions in the original and the filtrate solutions. The NaA-zeolite exchanged to different degrees by Cd^{2+} ions are listed in Table-1.

In order to study the temperature and concentration effects on the Cd^{2+} ion exchange into zeolite type-A, the optimum amount of zeolite was found 0.1g for 50 cm^3 of 0.01 M $CdCl_2$ solution and optimum time was 22 minutes. Optimization of zeolite quantity and equilibrium time would lead to a more complete exchange. Six stoppered pyrex glass flasks with 100 cm^3 capacity were used for sorption/ion-exchange experiments. In general, a series of solutions of $CdCl_2$ of varying concentrations and definite volume were taken in these flasks. A definite weight of zeolite was added to each of these flasks. These flasks were shaken at different temperatures (25, 40, 55 and 70 °C) for 22 minutes in thermostated shaker until equilibrium was established. The concentration of Cd^{2+} ions in the original solutions and the filtrate were determined as described above.

Thermal analysis technique was used for interpretation of the nature of water in zeolite, zeolitic water and thermal stability of zeolite framework structure. Thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out using a simultaneous thermal analyzer STA-40 NETZSCH (Germany) 25-30 mg of each hydrated sample was taken using high purity nitrogen gas, a flow rate of 200 cm³/min was maintained over the sample heating rate of 10 °C/min was employed and the chart speed was 2.5 mm/min. The water contents of the zeolite were found by the percentage weight losses of the samples upto 1000 °C and the thermal stabilities of the crystal lattices of the frameworks were investigated by DTA curves from room temperature to 1000 °C.

Conclusions

The results of Cd²⁺ ions adsorption by cation exchange showed that synthetic NaA-zeolite is an efficient sorbent media for the removal of cadmium ions from aqueous solutions and waste water. Freundlich and Langmuir isotherm equations are the best choice to describe the observed equilibrium data.

Upon dehydration from ambient temperature to 1000 °C, TGA/DTA curves detected changes in the NaA and Cd,NaA-zeolitic phases. The thermal analysis curves indicated that Cd²⁺ ion exchange enhances the thermal stability of synthetic zeolite A lattice.

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References

1. J. A. Rabo, *Zeolite Chemistry and Catalysis*, American Chemical Society, Washington (1976).
2. J. Weitkamp and L. Puppe (Eds.) *Catalysis and Zeolites, Fundamentals and Applications*, Berlin Springer-Verlag (1999).
3. M. Gracia, M. Salache-Rios, P. Bosch and S. Bulbulion, *Langmuir*, **12**, 4474 (1996).
4. D. Bae and K. Seff, *Zeolites*, **17**, 444 (1996).
5. R.V. Jasra, N. V. Choudhary and S. G. T. Bhat, *Separation Science and Technology*, **26**, 885 (1991).
6. A. Dyer, *An Introduction to Zeolite Molecular Sieves*, John Willey & Sons, 87 (1988).
7. H. E. Allen, S. H. Cho and T. A. Neubecker, *Water Research*, **17**, 1871 (1983).
8. F. D. Renzo and F. Fajula, in J. Cejka and H. Van Bekkum (Eds.), *Zeolites and Ordered Mesoporous Materials: Progress and Prospects*, *Studies Surface Science and Catalysis*, **157**, Elsevier B.V., 1 (2005).
9. A. Dyer, *An Introduction to Zeolite Molecular Sieves*, John Wiley & Sons, N.Y. (1988).
10. D. W. Breck, *Zeolite Molecular Sieves*, New York: Wiley (1974).
11. V. Gramlich and W. M. Meier, *Z. Kristallogr*, **133**, 134 (1971).
12. R.C. Martinez, V. M. Miranda, M. S. Rios and I. G. Sosa, *Separation Science and Technology*, **39**, 2711 (2004).
13. H. S. Sherry in S. M. Auerbach, K. A. Carrado and P. K. Dutta (Eds.), *Handbook of Zeolite Science and Technology*, Marcel Dekker, Inc. N.Y., 1007 (2003).
14. R. M. Barrer, L. V. C. Rees and J. Shamsuzzoha, *Journal of Inorganic and Nuclear Chemistry*, **28**, 629 (1966).
15. R. M. Barrer and A. J. Walkcr, *Transaction Faraday Society*, **60**, 171 (1964).
16. P. Fletcher and R. P. Townsend, *Journal of Chemical Society, Farady Transaction I*, **81**, 1731 (1985).
17. E. P. Hertzberg and H. S. Sherry, in WH Flank, (Ed.), *ACS Symposium Series 135*, Washington DC American Chemical Society, 187(1980).
18. I. J. Gal and P. Randovanov, *Journal of Chemical Society, Farady Transaction I*, **71**, 1671 (1975).
19. V. P. Shiralkar and S. B. Kulkarni, *Journal of Thermal Analysis*, **25**, 399 (1982.)
20. M. A. Heilbron and J. C. Vickermann, *Journal of Catalysis*, **33**, 434 (1974).
21. L. B. McCusker and K. Seff, *Journal of Physical Chemistry*, **86**, 166 (1981)

22. J. V. Smith in J. A. Rabo (Ed.), *Zeolite Chemistry and Catalysis*, ACS Monograph 171, American Chemical Society, Washington, D.C; 1 (1976).
23. E. Y. Choi, Y. Kim and K. Seff, *Microporous and Mesoporous Materials*, **41**, 61 (2000).
24. G. E. Pavlovskaya, C. D. Ren, M. V. Buskirk, C. Dybowski, D. R. Corbin, J. A. Reimer and A. T. Bell, *Catalysis Letters*, **80**, 19 (2002).
25. Y. Lee, B. A. Resiner, J. C. Hanson, G. A. Jones, J. B. Paris, B. H. Toby, A. Freitag and J. Z. Larese, *Journal of Physical Chemistry*, **B 105**, 7188 (2001).
26. F. Uzun, *Zeitschrift für Naturforschung, Sect. A, A-Journal of Physical Science*, **57a**, 281 (2002).
27. J. E. Readman, N. Kim, M. Ziliox and C. P. Grey, *Chemical Communication*, 2808 (2002).
28. F. M. Higgins, N. H. de Leeuw and S. C. Parker, *Journal of Materials Chemistry*, **12**, 124 (2002).
29. C.V. McDaniel and P. K. Maher, in J. A. Rabo (Ed.), *Zeolite Chemistry and Catalysis*, ACS Monograph 171, American Chemical Society, Washington D.C. 285 (1976).
30. C. Kosanovic and B. Subotic, *Microporous Materials*, **12**, 261 (1997).
31. C. Kosanovic and B. Subotic, *Microporous and Mesoporous Materials*, **66**, 311 (2003).
32. A. Simon, J. Kohler, P. Keller, J. W. Kamp, A. Buchholz and M. Hunger, *Microporous and Mesoporous Materials*, **68**, 143 (2004).