

REMOVAL OF METAL CONTAMINANTS AND RADIONUCLIDES WITH NATURAL ZEOLITES – COMPETITIVE SORPTION AND EFFECTS OF ZEOLITE MODIFICATIONS

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ABSTRACT

Metal contaminants including radionuclides found in wastewaters must be reduced to acceptable levels before discharging the wastewater into receiving waters. These cations can accumulate in aquatic organisms causing toxicity and death, hence strict regulatory limits for their allowable discharge levels have been established over the years. This has also prompted the development of cost effective technologies that will permit the efficient removal of contaminants, while concentrating the contaminants in a form suitable for immobilization, storage and disposal. Removal requirements can be met by some inorganic zeolites, which can be natural or synthetic. The zeolites have a strong affinity for transition metal cations, and their cage-like structures offer large internal and external surface areas for ion exchange and adsorption.

In view of these considerations, investigations with two low-cost natural zeolites (clinoptilolite and chabazite) were started, with the objective of developing a cost effective technology for column operations. Sorption tests of Cs^+ , Sr^{2+} and Cu^{2+} ions on chabazite and clinoptilolite were carried out using batch experiments in 125 mL vessels under various test conditions. Competitive sorption was studied in mixed cation solutions containing the commonly occurring non-toxic cations Ca^{2+} and Na^+ . The presence of these non-toxic cations inhibits removal of the targeted cations. Additional pretreatments and modifications of the “as received” sorbent particles were also investigated, which are important in multiple cation systems, to enhance removal selectivity for the target contaminant cations.

Sorption tests with chabazite and clinoptilolite showed that these two natural zeolites can be effectively used to remove cesium, strontium and copper ions from aqueous solutions. The performance can be controlled by maintaining the zeolite to waste volume ratio. The contaminant removal performance of chabazite was approximately 20% superior to that of the clinoptilolite. The presence of calcium ions has an adverse effect on the removal of copper and strontium ions, and this effect is more pronounced with clinoptilolite. The role of the hydrated radius and energy of hydration in the sorption process offered an explanation of the differing removal efficiencies for the various cations by the zeolites. Conditioning of chabazite in a concentrated sodium chloride solution improved its performance by about 10%, while there was little improvement attained by conditioning with calcium or ammonium ions.

This paper also describes a research plan for optimizing field-scale applications in column operations. Considerations such as fluidization and hydraulic behavior, mass transfer and mixing in the zeolite beds, and safety considerations will be investigated. These investigations should lead to the selection of appropriate particle sizes, operating modes and the design of sorption-column internals.

1. INTRODUCTION

A summary of natural zeolites application for adsorption of heavy metals and radionuclides from effluent waters has been presented by Ouki et al. [1.]. The general chemical formula of zeolites is $M_{x/n} [Al_xSi_yO_2(x+y)] \cdot pH_2O$ where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; $y/x = 1-6$, $p/x = 1-4$. A significant characteristic of zeolite is its ability to exchange of ions with the external medium in an isomorphous fashion.

The two types of natural zeolite commonly used for removal of low concentrations of heavy metal ions and radionuclides are clinoptilolite and chabazite. Their performance has been examined by several researchers for heavy metal removal [2.][3.][4.] and adsorption of radionuclides [5.][6.]. Another study [7.] compared their performance for treating effluents contaminated with Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} . It was reported that clinoptilolite and chabazite exhibited different selectivity for all metals studied except Pb^{2+} for which both performed exceptionally well. These authors point out that most research with natural zeolites has primarily focused on identifying metal selectivities and sorption capacities. There has been little work on the issues of implementing natural zeolite technology on a practical basis. It should be noted that the sorption process includes contributions from ion exchange and adsorption processes. A detailed characterization of chabazite and clinoptilolite [8.] showed the following chemical composition for the two natural zeolites: Chabazite ($[Na_2O]_{2.19}[K_2O]_{0.13}[Fe_2O_3]_{0.59}[MgO]_{0.34}[Al_2O_3]_{3.02}[SiO_2]_{8.35}$) and Clinoptilolite ($[Na_2O]_{0.92}[K_2O]_{0.78}[Fe_2O_3]_{0.27}[MgO]_{0.21}[Al_2O_3]_{1.93}[SiO_2]_{9.70}$). Clinoptilolite is the most abundant of the natural zeolites and a member of the heulandite group. Its framework consists of channels formed by 8- and 10-oxygen rings which allow for selective adsorption of metal cations with large dimensions [9.][10.]. These studies have also pointed out the good mechanical strength and ion exchange capacity of clinoptilolite. The higher exchange capability of chabazite compared to clinoptilolite has been attributed to its negatively charged framework resulting from a higher substitution of Si by Al as compared to clinoptilolite. The adsorption characteristics of any zeolite are dependent upon the ratios of Si/Al and other key metals in the minerals, cation type channel structure, etc. [11.].

The primary objective of this study is to examine the exchange capacity and selectivity of the selected as-received natural zeolites and their modified forms for cost-effective removal of low concentrations of metal contaminants (Cu^{2+}) including surrogates for radionuclides (Cs^+ , Sr^{2+}) commonly found in aqueous effluents generated by nuclear plants.

2. EXPERIMENTAL

2.1 Materials and Reagents

The clinoptilolite and chabazite samples were obtained from ZEOX Corporation. Initial characterization of the samples was conducted to determine particle size distribution, pore

volume and density. The physical characteristics of the samples are summarized in Table 1. The sample size distribution was determined using Malvern Mastersizer 2000, helium pycnometry determined the skeletal density, and the particle density was calculated using the pore volume obtained from BET analysis. Samples were homogenized and sieved through an ASTM No. 270, 53 μm sieve. Particles below 53 μm were about 0.31 wt% for chabazite and 0.41 wt% for clinoptilolite. For practical purposes, the zeolite samples contained particle sizes $>53 \mu\text{m}$ in the experiments. Synthetic standard stock solutions of 1000 ppm were prepared for cesium from cesium chloride supplied by EMD Chemicals Inc.; strontium from strontium nitrate, copper from copper II nitrate (penta hydrate), sodium from sodium nitrate and calcium from calcium nitrate tetrahydrate supplied by J.T. Baker. Similarly, 2 mol/L concentrated solutions were prepared for sodium from sodium chloride and ammonia from ammonium chloride supplied by VWR and calcium from calcium chloride dihydrate supplied by EMD Chemicals Inc. Several intermediate mixes of standard solutions of 5, 10, 20, 30, 35, 50, 60 and 100 ppm, with various combinations of all the stock standards, were made by taking a known aliquot from the 1000 ppm standards. Their exact concentrations were determined by analyzing against NIST standard solutions on an Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES). Sample analysis details can be found in ref [12.].

Table 1: Physical Properties of the Tested Natural Zeolites

Type	Mean Particle Diameter (μm)	Skeletal Density (kg/m^3)	Particle Density (kg/m^3)	BET Pore Volume (mL/g)	BET Surface Area (m^2/g)	Static Bed Voidage
Chabazite	930	2106	1630	0.359	495.2	0.35
Clinoptilolite	753	2151	1800	0.205	476.9	0.4

2.2 Sorption Studies

The sorption tests for Cs^+ , Sr^{2+} and Cu^{2+} ions on Chabazite and Clinoptilolite were carried out using batch experiments in 125 mL Teflon vessels at different test conditions with no Ca^{2+} and Na^+ separately, without either cation, and in combinations of these two ions at different concentrations. The experiments were conducted by weighing as-received zeolite samples of 0.1 g, 0.2 g, 0.5 g, 1.0 g and 2.5 g each separately into the containers and mixing with 100 mL of solution. Similarly, a blank experiment was also performed by weighing the same amounts of zeolites samples, mixing with 100 mL with deionized water and subjecting it to the same conditions as for the cation solutions. The containers were then placed on Max-Q 4000 orbital shaker at $25 \pm 1^\circ\text{C}$ for 10 minutes without any pH adjustment and then centrifuged at 180 rpm. The pH of the supernatant liquid was measured. The vessels were then replaced with the caps and kept in the shaker for 24 h for equilibration at 180 rpm. After 24 h, the final pH measurements of the solution were recorded. The samples were then filtered through Whatman no. 1 filter paper into the ICP vials. The equilibrium concentrations of cesium, strontium and copper were determined by analyzing the solution samples in the laboratory using the Varian Vista Pro CCD Simultaneous ICP-OES against a calibration curve of known NIST standards. Deionized water with a conductivity of 1.2 $\mu\text{S}/\text{cm}$ was used in all the experiments.

Experiments were conducted with as-received zeolites and with their washed and modified forms. Washing was carried out three times with deionized water to remove any adhering impurities. For washing, approximately 10.0 g of a well mixed zeolite was weighed into a PTFE bottle, 100 mL of deionized water was added to it and the bottle was shaken at 180 rpm at $25 \pm 1^\circ\text{C}$ for 15 minutes. The solution was allowed to settle for 5 minutes and then the supernatant liquid was drained out. Similar washings were conducted 2 more times and the solution was drained. The zeolite was transferred into a watch glass and dried at $100 \pm 2^\circ\text{C}$ in an oven for 24 h. The washed zeolite was taken out of the oven and cooled in a desiccator and transferred into a clean bottle for further experiments. To prepare Ca-rich, Na-rich and NH_3 -rich zeolite test samples, the zeolite sample was washed and placed in flasks into which 2 mol/L CaCl_2 , 2 mol/L NaCl or 2 mol/L NH_4Cl was added and shaken at 180 rpm at $25 \pm 1^\circ\text{C}$ for 24 h. After the equilibration period, the solution was drained and given 3 washings with 100 mL deionized water. The liquid was drained, and the zeolite was transferred onto a watch glass and dried at $100 \pm 2^\circ\text{C}$ in an oven for 24 h. The dried zeolite was taken out of the oven, cooled in a desiccator and transferred into a clean bottle for further experiments. Another set of experiments was conducted by mixing equal quantities of chabazite and clinoptilolite. The batch experiments were conducted on the mixed zeolite using the same procedure as above by spiking with Ca^{2+} at 50 ppm and 100 ppm, respectively, while Na^+ was kept constant at 50 ppm. For the different sets of batch experiments, the zeolite weights and the volume of spiked standard solution were kept constant while altering the concentration of the spiked solutions to study selectivity, exchange capacity and removal efficiency of Cs^+ , Sr^{2+} and Cu^{2+} individually and also in the presence of Ca^{2+} and Na^+ , and the combination of these two metals in various concentrations. The amount of cation removed was calculated from:

$$q = \frac{(C_o - C_e)V}{M} \quad (1)$$

where q is the amount of total sorbed metal ion (mg/g), C_o and C_e are the initial and equilibrium concentrations of metal in solution (mg/L), respectively, V is the solution volume (L) and M is the sorbent weight (g).

3. RESULTS AND DISCUSSION

3.1 Sorption at Different Cation Concentrations

The percent removal of different cations from solution is shown in Figures 1 and 2 as a function of increasing dosage. Figure 1 shows that at low concentrations almost 100% removal of Cs^+ and Sr^{2+} is achieved at low sorbent dosage, suggesting higher sorption capacity for these cations. For Cu^{2+} , approximately 90% removal is achieved at the lowest sorbent dosage and significantly higher dosages are required for nearly 100% removal. Figure 1 also reveals that there is only a small difference between the two zeolites at low initial concentrations of cations in the solution. The difference between the two zeolites increases with an increase in the initial cation concentration (see Figure 2). As expected, there is a drop in percent removal with increase in cation concentration but the decrease is higher with clinoptilolite by about 15-20% compared to chabazite.

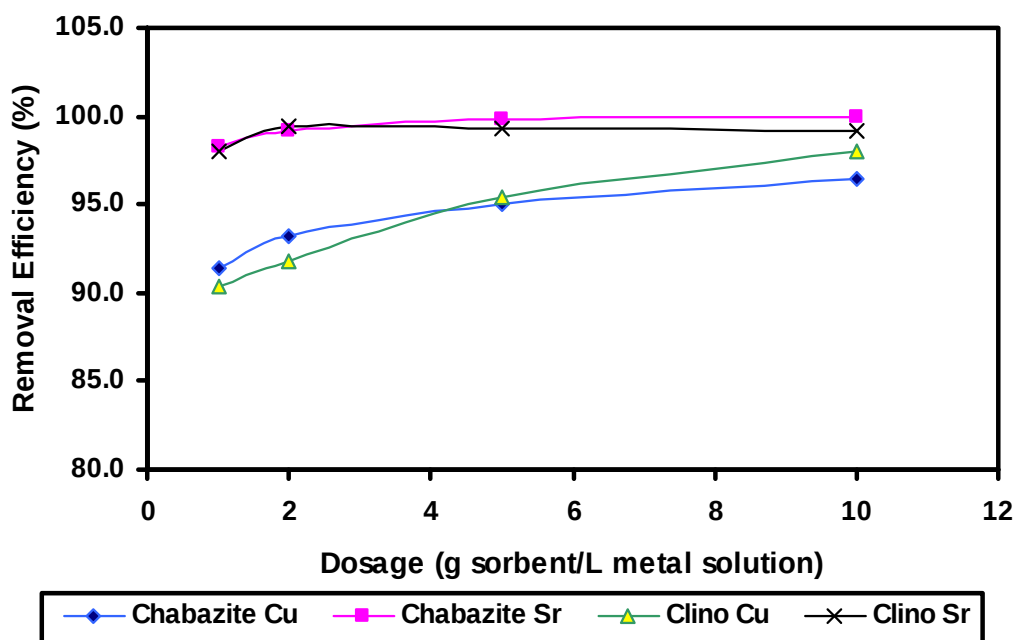


Figure 1: Removal efficiency for Cu and Sr with sorbent (chabazite and clinoptilolite or clino) dosage at initial cation concentrations of Sr 5 ppm and Cu 10 ppm in solution

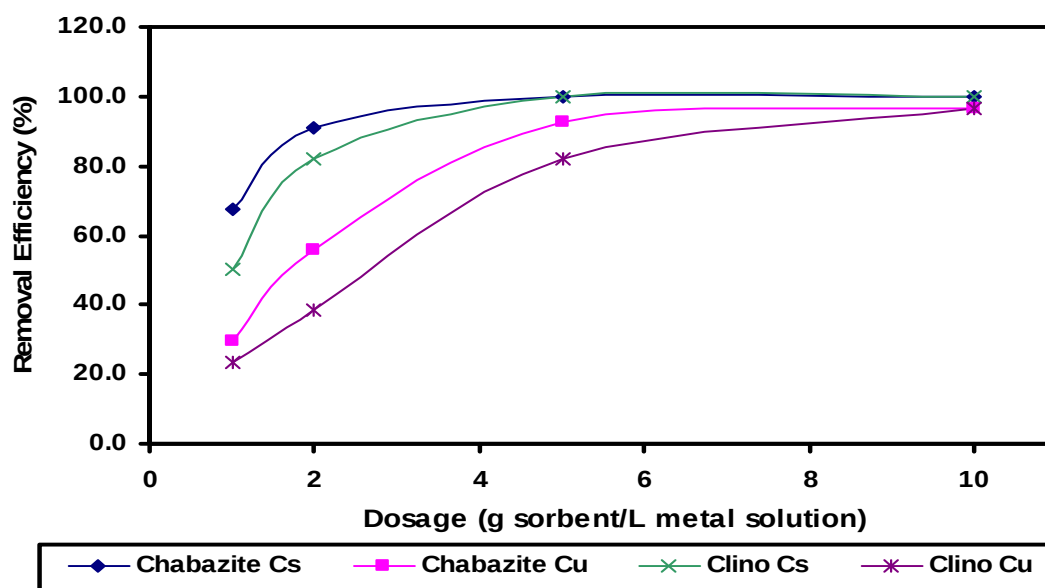


Figure 2: Comparison of cation removal efficiency with chabazite and clinoptilolite (clino) at higher initial concentrations of Cs 35 ppm and Cu 60 ppm in solution

The decontamination factor ($DF = \text{cation concentration in the initial solution} / \text{cation concentration in the treated solution after sorption}$) is another measure for assessing the removal efficiency of the sorbents. The DF values obtained with data in Figures 1 and 2 are plotted in

Figures 3 and 4. The DF values for Sr^{2+} are significantly higher with chabazite and increase faster with increasing dosage compared to clinoptilolite. For other cations, the DF values are comparable for the two zeolites.

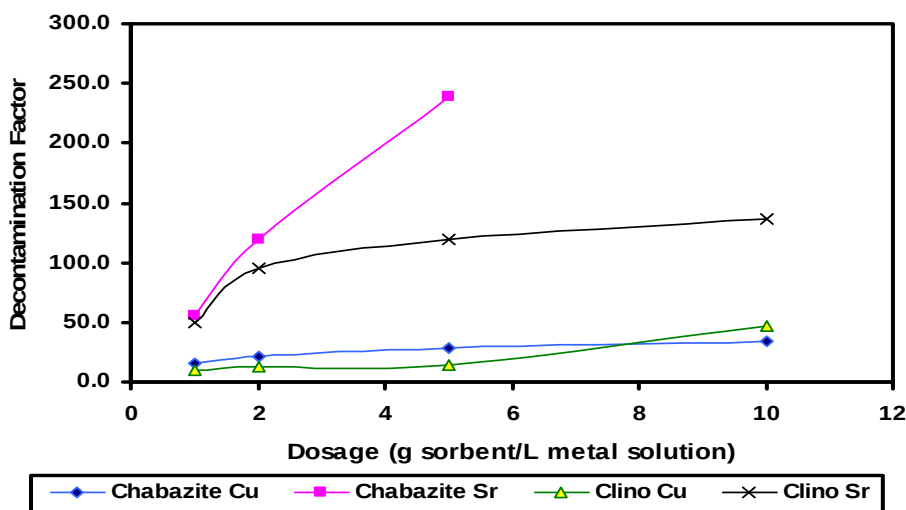


Figure 3: Decontamination Factor for Cu and Sr with sorbent (chabazite and clinoptilolite) dosage at initial concentrations of Sr 5 ppm and Cu 10 ppm in solution

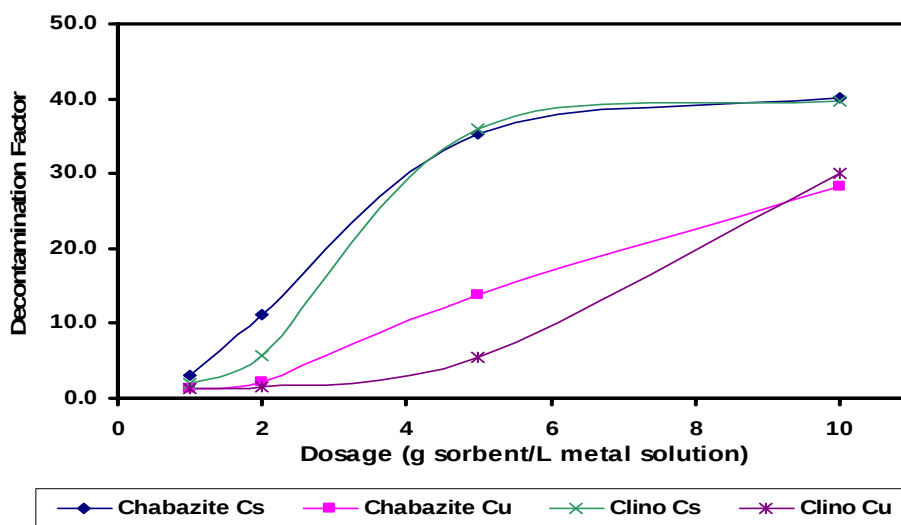


Figure 4: Comparison of Decontamination Factor for Cs and Cu with sorbent (chabazite and clinoptilolite) dosage at initial concentrations of Cs 35 ppm and Cu 60 ppm in solution

The removal of non-radioactive metal ions and radionuclides (as metal ions) from the test solution by natural zeolites is a complex process, involving ion exchange and adsorption, which is likely to be accompanied by the formation of metal hydroxide complexes on active sites of the particle surface [13.] offering resistance to ion-exchange. There are several factors that could lead to the difference in removal efficiencies referred to in the preceding discussion.. One factor

is the framework structure of the zeolite and the dimensions of the channel formed by the tetrahedral units which make up the zeolite. These channels must be large enough to allow passage of hydrated metal ions. It has been reported that the window size that controls access to the pore system is larger in chabazite than clinoptilolite [7.]. Furthermore, higher Al substitution of Si provides a negatively charged framework that is favorable to higher ion-exchange capability. The dosage above which there is small change in removal for chabazite is about half (5 g sorbent/L metal solution) of that for clinoptilolite, indicating a higher sorption capacity for chabazite.

The metal uptake and the removal efficiency of metal ions from the liquid follows the sequence $\text{Cs}^+ > \text{Sr}^{2+} > \text{Cu}^{2+}$. It is also observed that cesium removal was the highest with both zeolites. This can be attributed to low hydrated radius and heat of hydration for cesium ions compared to other cations present [14.][15.]. Cation exchange in zeolites can be characterized by the behavior of the hydration spheres as they move into and out of the channels. Additionally, the hydration sphere radius may change with temperature due to weak electrostatic attraction between the cation and water molecules. Lower adsorption of copper compared to other cations can be attributed to its higher hydrated radius and highest hydration energy (see Table 2). Monovalent cations holding water molecules weakly can shed those molecules easily in order to fit into a site. Higher-charged, smaller-sized cations, however, are bonded more strongly to the water molecules and hence will shed them less readily. In general, there is an inverse relationship between cation radius and hydrated cation radius. Divalent cations are smaller than monovalent cations but usually have a larger hydrated radius than monovalent cations [16.].

Table 2: Properties of test cations related to sorption process [16.]

Cation	Charge	Ionic radius (pm)	Hydrated radius (nm)	Hydration energy (kJ/mol)
Cs^+	+1	167	0.329	-276
Sr^{2+}	+2	118	0.412	-1443
Cu^{2+}	+2	73	0.419	-2100
Ca^{2+}	+2	100	0.412	-1577
Na^+	+1	102	0.358	-406

A further comparison of the sorption capacity of the two zeolites is presented in Figures 5 and 6, which show the amount (in mg) of copper and strontium ions removed, respectively, per gram of zeolite sample. The solution had other cations but their concentrations were kept constant while increasing Sr^{2+} or Cu^{2+} concentration. It can be seen that there is a significant difference between the two sorbents at low dosage (1 g/L) especially at higher initial concentrations of cations, and that the difference essentially disappears at higher dosage. The superior sorption capacity of chabazite becomes visible at low dosage when the availability of active sites is limited. Increasing the initial cation concentration increases the sorption per unit weight of sorbent for constant dosage.

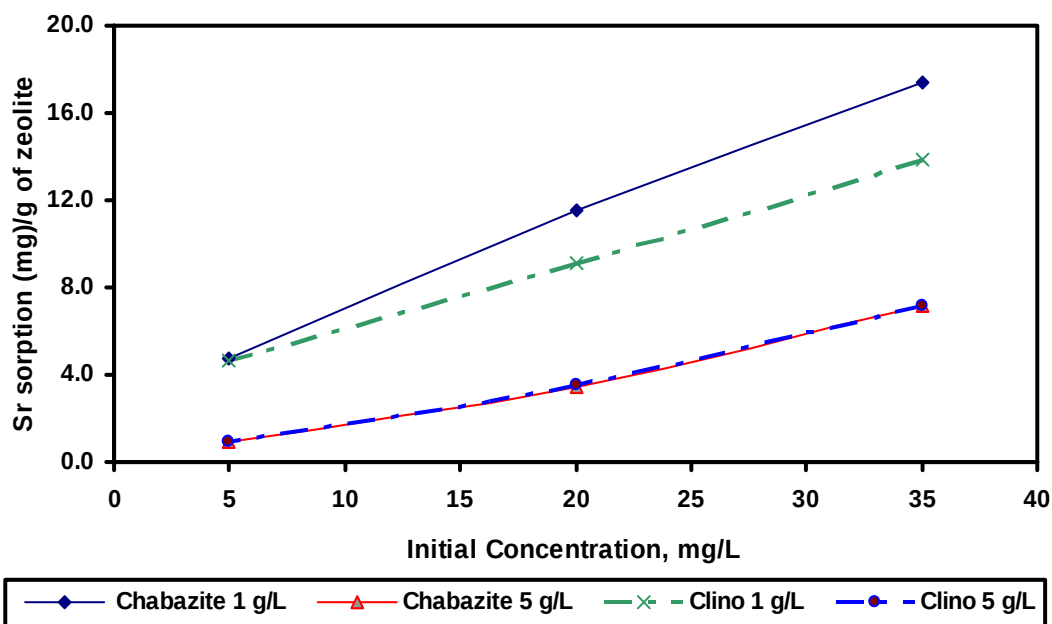


Figure 5: Strontium sorption per gram of zeolite for different initial concentrations at low and high dosages of chabazite and clinoptilolite without calcium

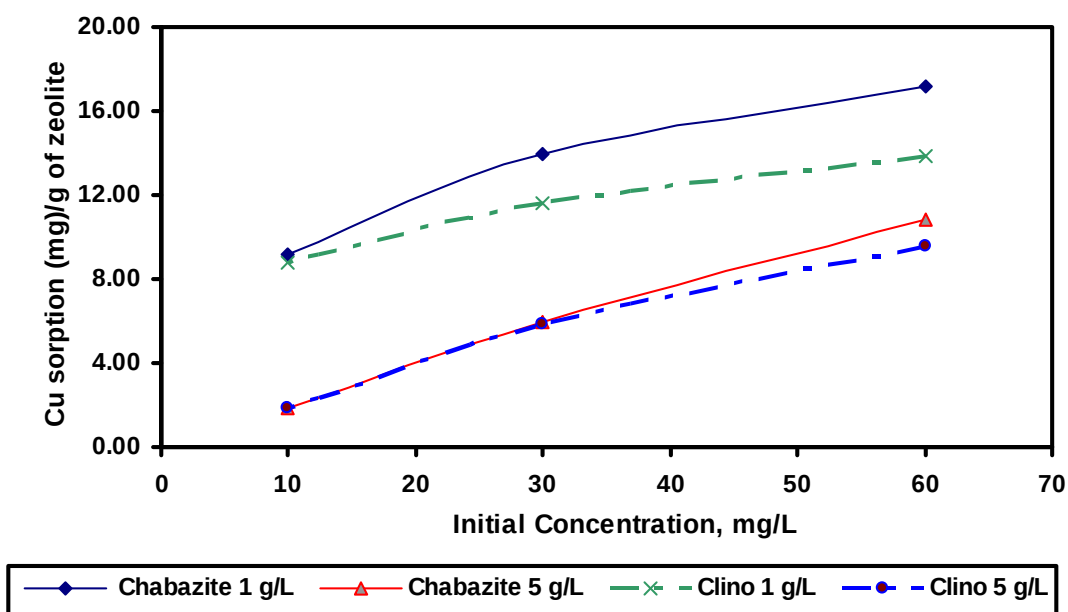


Figure 6: Copper sorption per gram of zeolite for different initial concentrations at low and high dosages of chabazite and clinoptilolite without calcium

3.2 Sorption Studies with Competing Non-toxic Cations

Non-toxic cations such as Ca^{2+} and Na^{+} commonly found in industrial wastewaters can compete with adsorption of targeted cations and inhibit their removal [7.][11.]. Figure 7 shows how the presence of calcium affected sorption-removal of strontium ions on chabazite. Here, the sorption

of strontium ions decreased between 20 to 30 %, depending on the initial concentration of Ca^{2+} . Similar experiments with clinoptilolite show that the sorption reduction for strontium is higher in the presence of calcium ions (Figure 8). As illustrated in Table 2, the hydrated radii of Ca^{2+} and Sr^{2+} are similar but their hydration energy and ionic radii are different. This difference in the hydration energy makes Sr^{2+} slightly more reactive compared to the Ca^{2+} ions. However, the slightly lower energy of activation for calcium ions compared to strontium (see Table 3) would increase the Ca^{2+} sorption rate thus indicating that the two ions will be competing closely for available active sites.

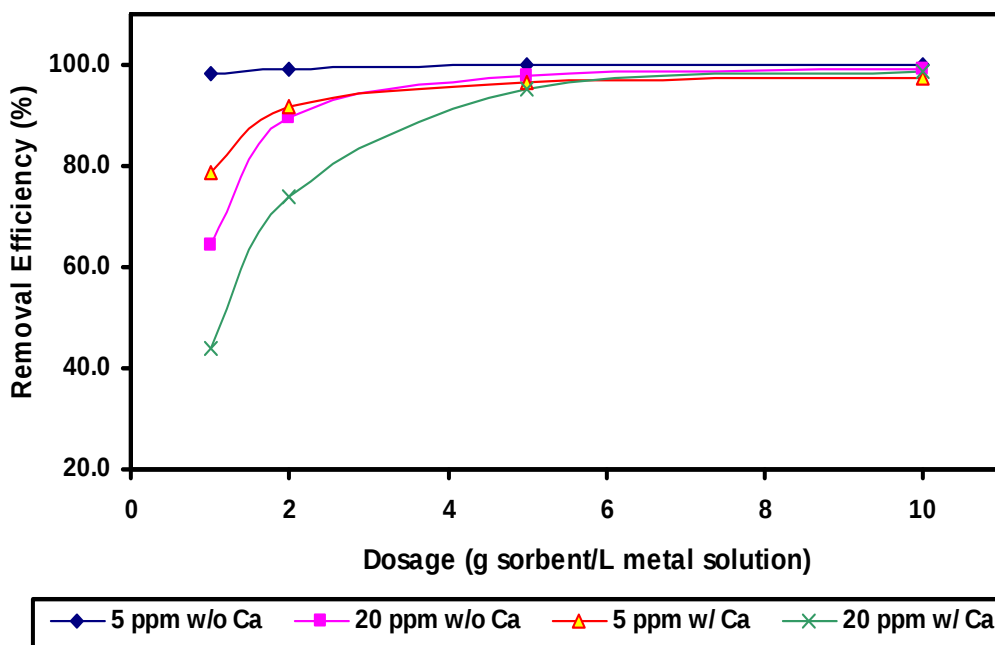


Figure 7: Sorption of strontium on chabazite (with and without Ca) with sorbent dosage

Table 3: Energy and entropy of activation for migrating ions [17.]

Migrating ion	Energy of activation (kJ/mole)	Entropy of activation (J/mol/K)
Ca^{2+}	57.7	-75.3
Sr^{2+}	60.7	-71.1

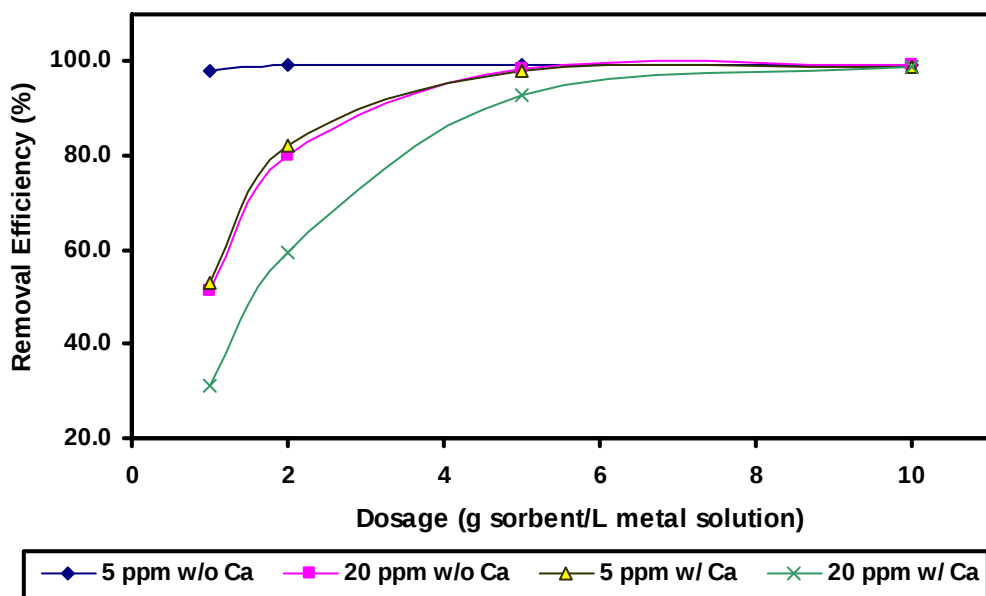


Figure 8: Sorption of strontium on clinoptilolite (with and without Ca) with zeolite dosage

Figures 9 and 10 compare the effects of replacing sodium by calcium on the sorption of cations in the solution. It can be seen that sorption of all cations is lower in the solution containing calcium ions (Figure 10), although the greatest decrease is observed for copper ion.

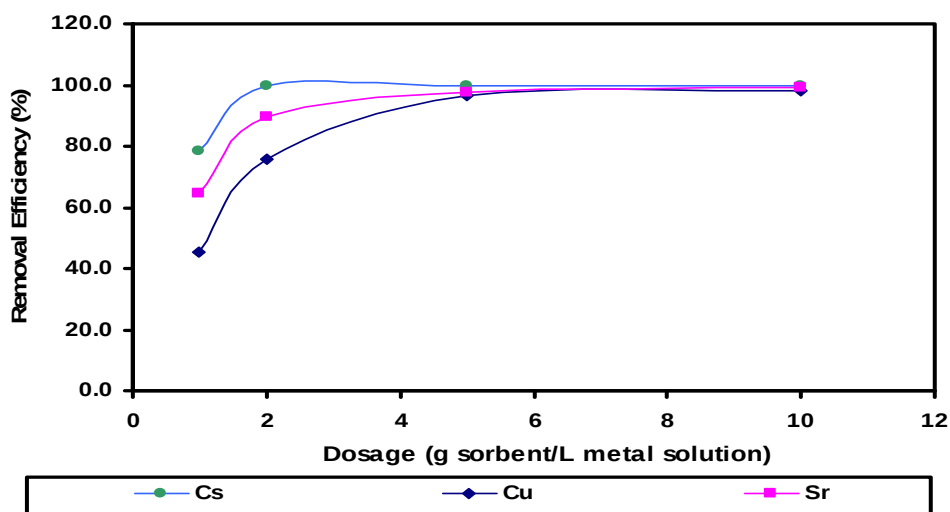


Figure 9: Percent cation removal with chabazite at initial concentrations of Cs 20 ppm, Sr 20 ppm, Cu 30 ppm and Na 50 ppm in solution

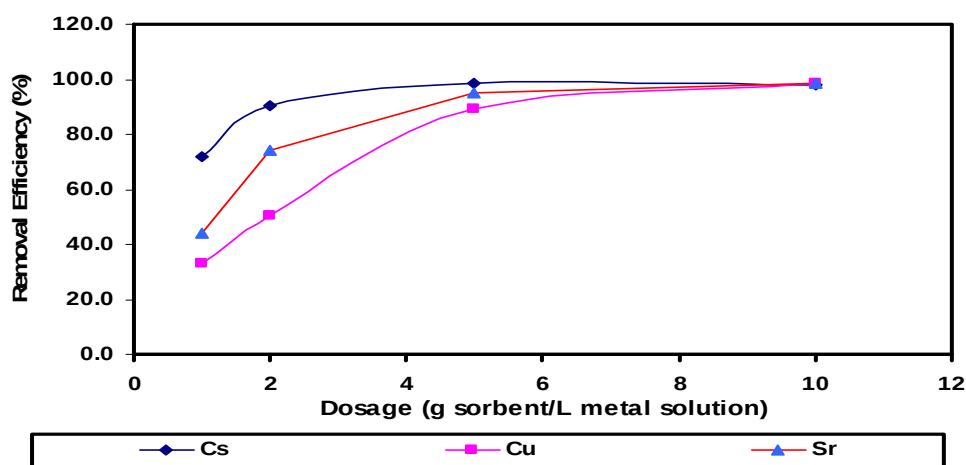


Figure 10: Percent cation removal with chabazite at initial concentrations of Cs 20 ppm, Sr 20 ppm, Cu 30 ppm and Ca 50 ppm in solution

Sorption tests for Cs^+ , Cu^{2+} and Sr^{2+} were also conducted in solutions containing both Na^+ and Ca^{2+} ions. Figures 11 and 12 show that the removal efficiency of both strontium and copper decreases when sodium ion is replaced by calcium ion in solution and decrease further with increasing concentration of calcium ions. It can also be noted from these figures that a higher dosage of sorbent is required to reach near complete removal of the targeted ions in the solution. During the ion-exchange process, the metal ions diffuse faster through the pores but their diffusion is retarded through the channels of the crystal lattice of the zeolite when it is required that they have to replace the exchangeable cations such as sodium and calcium. Na^+ is monovalent and the hydrated radius is less than that of the divalent Ca^{2+} (Table 2). Thus Ca^{2+} moves more slowly in the channels compared to Na^+ thereby slowing the sorption of other cations.

3.3 Effects of Pre-conditioning on Sorbent Performance

Tests were also conducted to investigate the effects of preconditioning on the zeolite performance. These included washing the zeolite thoroughly to remove any adhering impurities and enriching the zeolite with calcium ion, sodium ion and ammonium ion by conditioning in a high strength solution of respective salt solutions. It was observed that for 1 g of chabazite, three washings of 100 mL each were required to bring down the conductivity to that of the wash water. In contrast, for 1 g of clinoptilolite just two washings were sufficient. The results of these tests are presented in Figures 13 and 14. It can be seen from these figures that, with sodium-enriched zeolite, there is an enhancement of about 10% compared to as-received zeolite. However, there is either negative or no improvement with calcium- or ammonium-enriched zeolite. The adverse effects observed with calcium-enriched zeolite for copper removal (Figure 14) need further investigation.

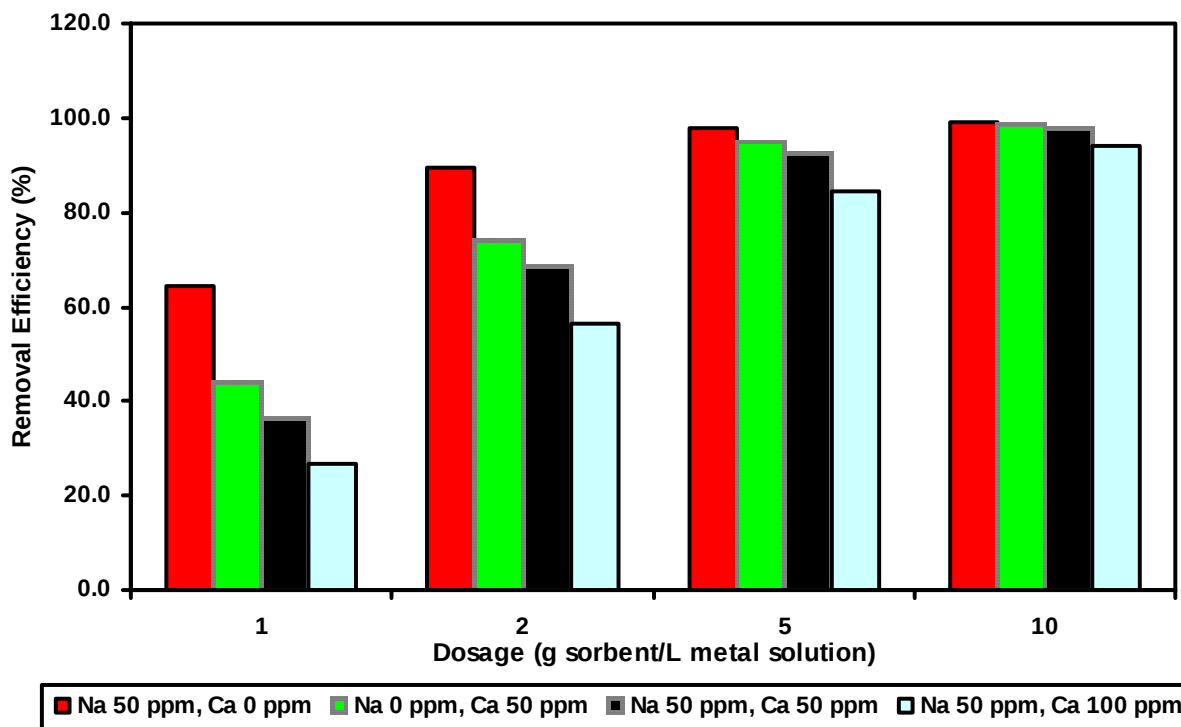


Figure 11: Percent removal efficiency of strontium at different calcium and sodium ion concentrations in solution for chabazite at Cs 20 ppm, Sr 20 ppm and Cu 30 ppm

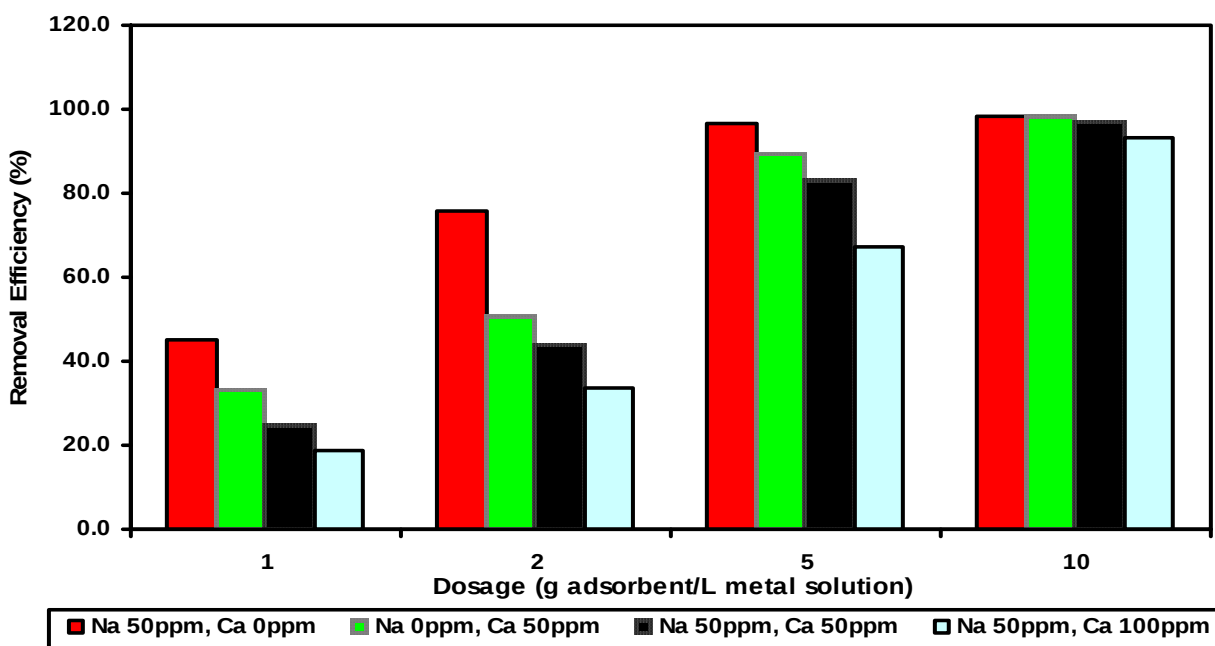


Figure 12: Percent removal efficiency of copper at different calcium and sodium ion concentrations in solution for chabazite at Cs 20 ppm, Sr 20 ppm and Cu 30 ppm

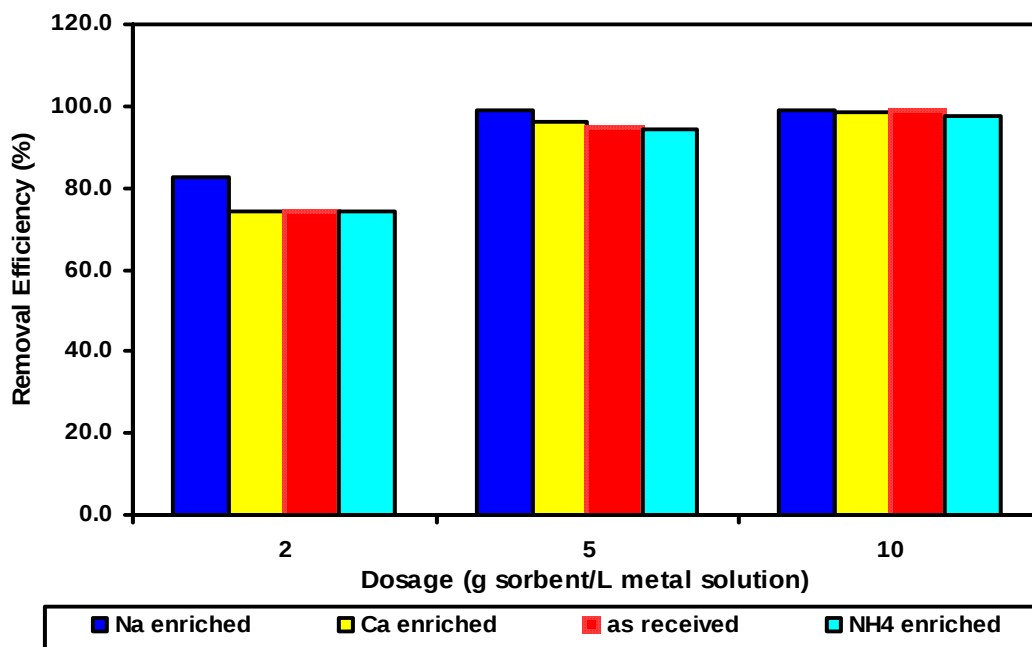


Figure 13: Effects of zeolite conditioning on strontium removal by chabazite at Cs 20 ppm, Sr 20 ppm, Cu 30 ppm and Ca 50 ppm

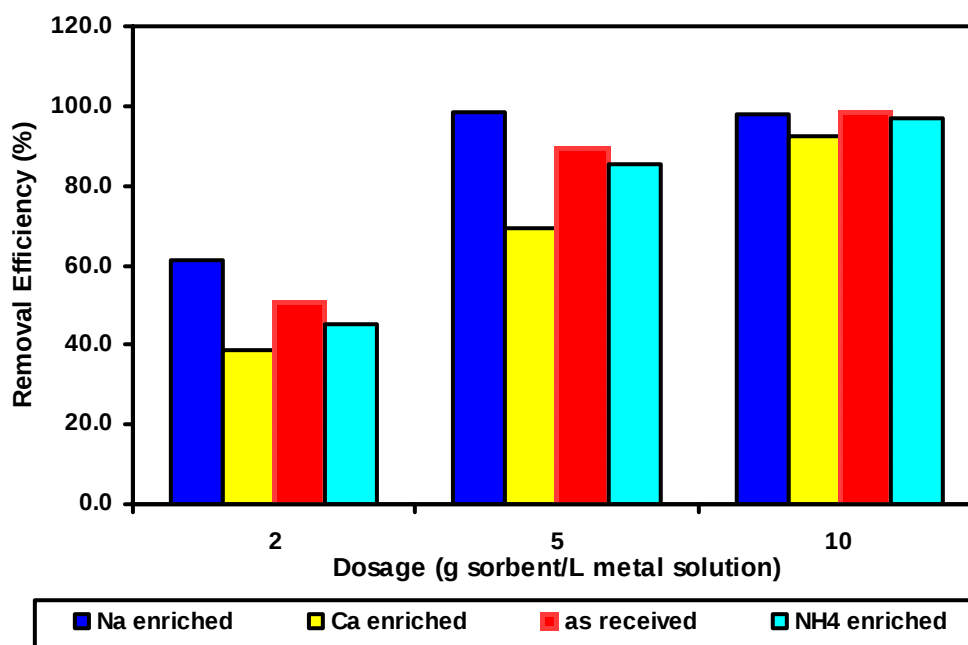


Figure 14: Effects of zeolite conditioning on copper removal by chabazite at Cs 20 ppm, Sr 20 ppm, Cu 30 ppm and Ca 50 ppm

3.4 Mixed Zeolites System

For some applications, the two zeolites used in this study could be applied in sequence or mixed in a bed for more cost-effective treatment. Beds of mixed zeolites with 50 wt% of each zeolite were used and the results are compared in Figures 15 and 16. As expected, the mixed-bed zeolite performance is in between the two individual zeolites. Since clinoptilolite is usually less expensive compared to chabazite, a proper sequence for separation can be devised by performing additional testing.

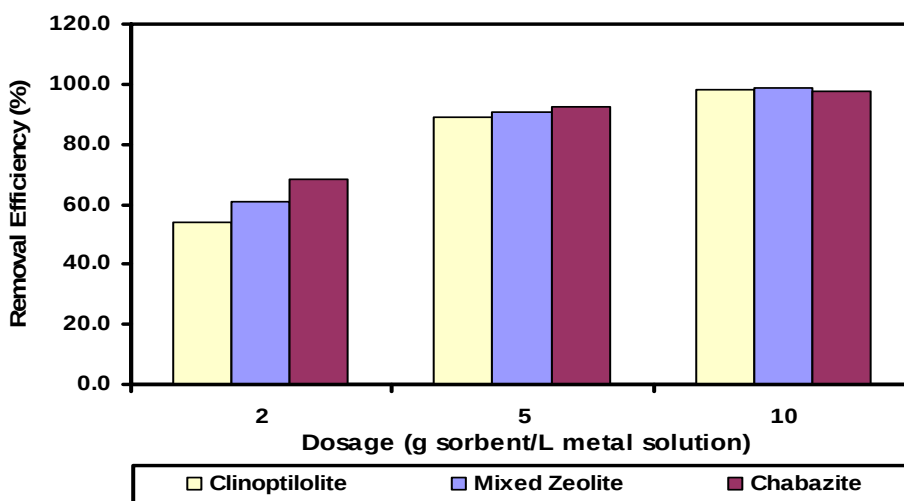


Figure 15: Comparison of chabazite, clinoptilolite and mixed zeolites for strontium removal at initial concentrations of Cs 20 ppm, Sr 20 ppm, Cu 30 ppm, Ca 50 ppm and Na 50 ppm

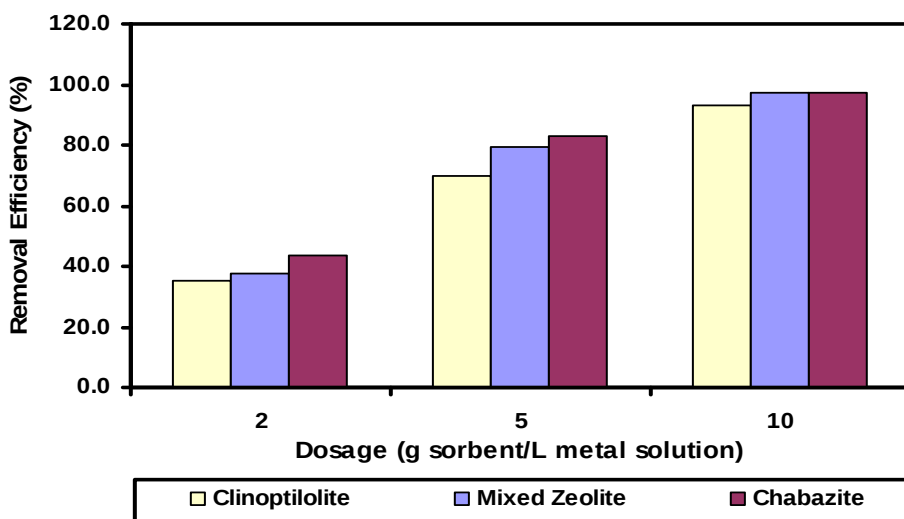


Figure 16: Comparison of chabazite, clinoptilolite and mixed zeolites for copper removal at initial concentrations of Cs 20 ppm, Sr 20 ppm, Cu 30 ppm, Ca 50 ppm and Na 50 ppm

For optimal field-scale applications in column operations, the plan for additional studies is to investigate fluidization and hydraulic behavior, mass transfer and mixing in the bed of the zeolites particles. These investigations should lead to specification of an appropriate particle size mix, operating mode, design of internals, etc. The investigations will include the role of

different size fractions and their mixtures in achieving desirable performance by avoiding back mixing and bypassing in the bed. Preliminary procedures for particle addition and removal from the bed have been investigated. These will be studied in further detail to incorporate remote operation and improved safety. Studies will involve detailed pilot-scale testing after bench-scale experimentation and development efforts to demonstrate a cost-effective and safer process for the removal of toxic cations from aqueous effluents and contaminated ground waters. For proper design and modeling of column operations, there is a need to conduct systematic studies at different conditions of practical importance to determine thermodynamic and kinetic effects, and estimate model parameters. Further work is needed to study the effects of zeolite conditioning to improve contaminant-removal performance. This should include development of a more detailed procedure and characterization before and after conditioning. For column operations, there is a need to study mass transfer and mixing effects for performance estimations and optimum design. The separation sequence needs to be examined systematically to determine cost-effective utilization of sorbents in the removal processes. For example, most of the cesium in water effluents could be removed in a bed of low cost clinoptilolite followed by a polishing bed of the relatively more expensive chabazite.

4. CONCLUSIONS

- Natural zeolites, chabazite and clinoptilolite, were effective sorbents for the removal of cesium, strontium and copper ions from aqueous solutions and their performance can be controlled by maintaining proper sorbent dosage.
- The performance of chabazite was approximately 20% superior to that of clinoptilolite.
- The presence of calcium ions has an adverse effect on removal of copper and strontium from solution and the effect is more pronounced with clinoptilolite.
- The role of the hydrated radius and energy of hydration in the sorption process can explain the observations regarding the removal performance of different cations.
- Conditioning of chabazite in high strength sodium chloride solution improved its performance by about 10%.
- Future work would include pilot and field scale testing in column operations with appropriate particle size mix, operating mode, internals, etc. To advance design and modeling of column operations, systematic studies at different conditions of practical importance will be conducted to determine thermodynamic and kinetic effects, and estimate model parameters.

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