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TREATMENT OF METALS-CONTAMINATED WASTEWATERS BY USE OF NATURAL ZEOLITES

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ABSTRACT

This paper assesses the potential of natural zeolite utilization as a low-cost ion exchange material for heavy metals removal. Two natural zeolites, clinoptilolite and chabazite, have been evaluated with respect to their selectivity and removal performance for the treatment of effluents contaminated with mixed heavy metals (Pb, Cd, Cu, Zn, Cr, Ni and Co). The effects of relevant parameters such as chemical treatment, metals concentration, pH, and presence of competing ions were examined. The results showed that the received zeolites contained exchangeable K, Ca and Na ions, but exposing them to concentrated NaCl solutions converted them to a homoionic state in the Na form which improved their exchange capacity. Clinoptilolite and chabazite exhibited different selectivity profiles for all metals studied except for Pb for which both zeolites performed exceptionally well.

The results also showed that chabazite exchange capacity is superior to that of clinoptilolite mainly due to the higher Al substitution of Si which provides chabazite with a negative framework favourable to higher exchange capability. The pH was found to have an effect on metal removal as it can influence both the character of the exchanging ions and the zeolite itself. Overall, the removal mechanism was controlled by ion exchange and precipitation was proven negligible. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Natural zeolites; heavy metals; removal efficiency; ion exchange; effluent treatment.

INTRODUCTION

Zeolites have been intensively studied in the last half century although attention has concentrated mainly on synthetic zeolites and it is only in recent years that natural zeolites have started gaining interest (Ouki *et al.*, 1994). Natural zeolites are capable of removing quantities of cations from aqueous solutions by utilising the phenomenon of ion exchange (Ouki *et al.*, 1995). Clinoptilolite for example has received extensive attention due to its attractive selectivities for certain heavy metal ions such as Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Fe^{2+} and Mn^{2+} (Aiello *et al.*, 1980; Blanchard *et al.*, 1984; Semmens and Seyfarth, 1978; Zamzow and Eichbaum, 1990). However, application of natural zeolites on an industrial scale has been limited to the removal of ammonia from municipal wastewaters (Ciambeli *et al.*, 1985; Gaspard *et al.*, 1983; Bray and Fullman, 1971), and to a smaller extent, for the removal of Cs and Sr from radioactive wastes (Koon *et al.*, 1974; Grant and Skriba, 1987). Many industries such as metal finishing, mining and mineral processing, coal mining and oil refining, have problems associated with heavy metals contamination of process and runoff waters. New approaches and technologies must therefore be developed to assist in both the removal and recovery of valuable metals from process and wastewaters. Ion exchange is feasible when an exchanger has a high selectivity for the

metal to be removed and the concentration of competing ions is low. In certain cases special resins may be manufactured which have a very high selectivity for a particular heavy metal. The metal may then be recovered by incinerating the metal saturated resin and naturally the cost of such a process limits application to only the more expensive metals. In many cases however, the heavy metals are not valuable enough to warrant the use of special selective exchangers and they are not easily separated from other metal ions by their chemical character. In such cases a selective cation exchange such as natural zeolites may provide an economical means of removing mixed heavy metals from effluents.

EXPERIMENTAL INVESTIGATION

Naturally occurring zeolites, clinoptilolite and chabazite were provided for study by the American Colloid Company. The as-received zeolites were lightly ground and sieved. Fine particles with a diameter $<150\ \mu\text{m}$ and coarse particles with a diameter between $630\ \mu\text{m}$ and $1000\ \mu\text{m}$ were used in subsequent experiments. The zeolites were washed with distilled water to remove very fine particles prior to conditioning, pretreatment and capacity measurements. All chemicals, salts, acids, and pH buffers used in these studies were 'AnalaR' grade and were supplied by BDH Laboratory Chemicals. All solutions, standards and dilutions were made using distilled water. All metals were analysed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Effect of metal concentration on zeolite exchange performance

The rate of uptake of metals by zeolites from aqueous solution was investigated to determine the optimum time required for the metal-zeolite system to reach equilibrium. A 100 ml of a mixed solution of the seven metals originating from their nitrate salts, were equilibrated with 0.5-g chabazite and clinoptilolite. The concentration range studied for each metal in the solution was 1, 5, 10 15 and 30 mg/l at pH 5. The equilibrium studies were performed for time intervals ranging from 1 to 240 min and 24 hours later. At the designated time the two phases were separated by filtration using Whatman #1 paper and the initial and final metals concentrations remaining in solution were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Kesaroui-Ouki *et al.* (1993).

Effect of on zeolite exchange performance

A 100 ml of a mixed solution of the above-mentioned metals originating from their nitrate salts was prepared containing 10 mg/l of each metal. The solutions were adjusted with reagent grade nitric acid or sodium hydroxide to pH values ranging from 3 to 6 and were equilibrated with 0.5 g of chabazite and clinoptilolite. The experiments were performed for the time intervals of 1 min to 240 min and 24 hours. At the designated time the two phases were separated by filtration using Whatman # 1 paper and the initial and final concentration of the metals were analysed for by ICP-AES.

RESULTS

Effect of metal concentration on removal performance

The results of the analysis of the effects of metal concentration on the kinetics of removal are shown in Figure 1 (A-D) for chabazite and Figure 2 (A-D) for clinoptilolite. The data clearly show that chabazite is more efficient than clinoptilolite for metals removal as illustrated by the corresponding fast kinetics and low residual metal concentrations achieved. This is mainly attributed to the window size that controls access to the pore system, which is larger in chabazite than in clinoptilolite. In addition chabazite has a higher Al substitution of Si, which in turn will provide a negative framework favourable to higher ion exchange capability. The time required to reach equilibrium was assumed to be 24 hours, however, the results demonstrated that more than 90% of the removal was achieved in the first 15 minutes when using clinoptilolite and in the first 5 minutes when using chabazite. The data also show that for both zeolites, 10 mg/l is the optimum concentration for best metal removal efficiency. Table 1 illustrates the maximum adsorption capacity achieved for each metal using clinoptilolite and chabazite.

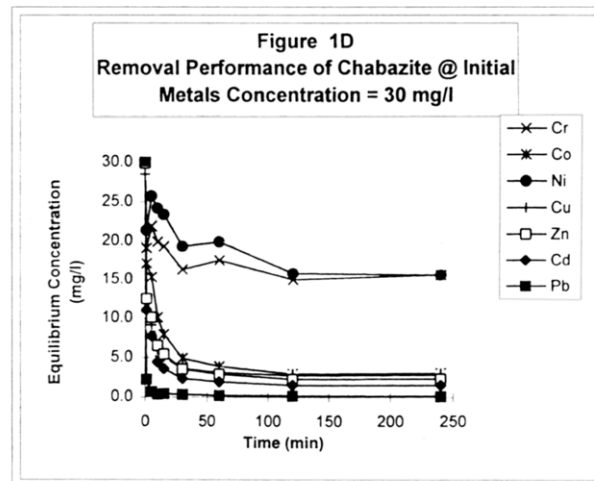
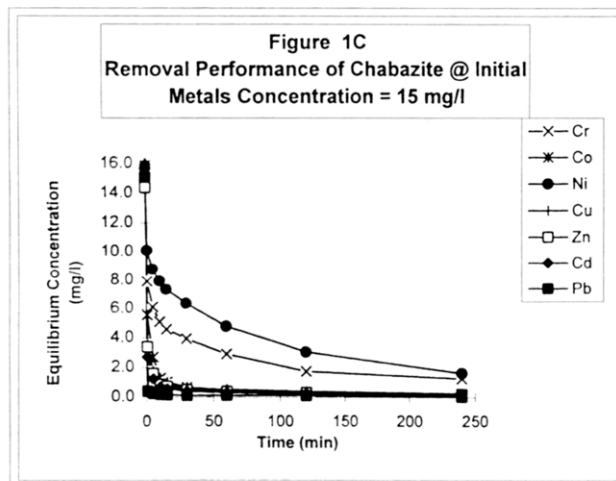
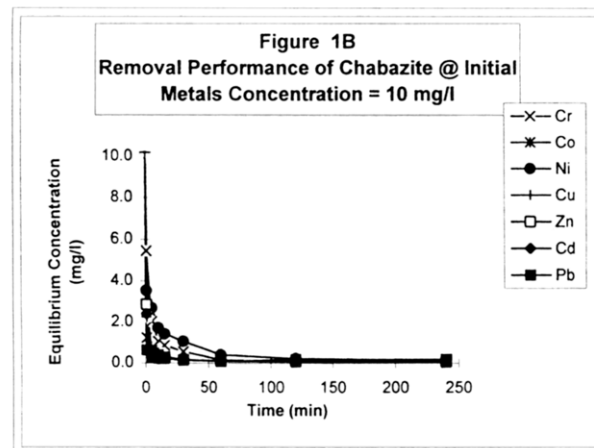
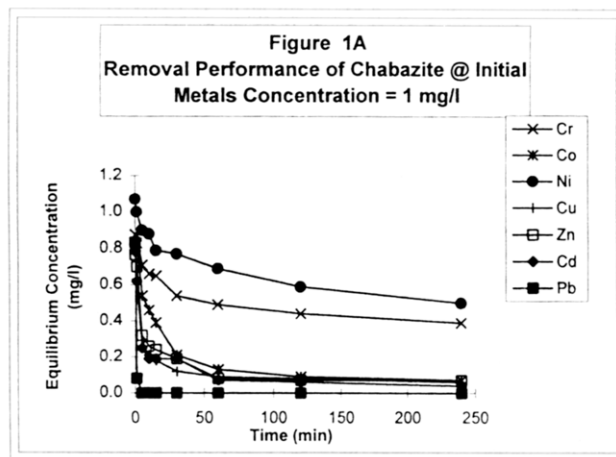


Figure 2A
Removal Performance of Clinoptilolite @ Initial
Metals Concentration = 1 mg/l

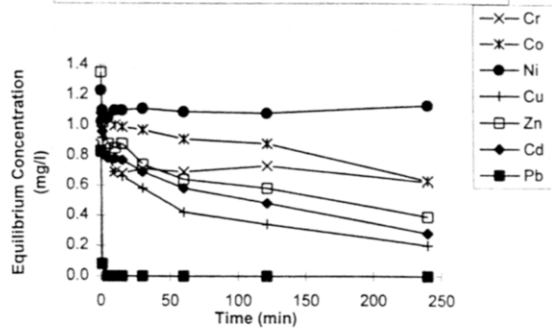


Figure 2B
Removal Performance of Clinoptilolite @ Initial
Metals Concentration = 10 mg/l

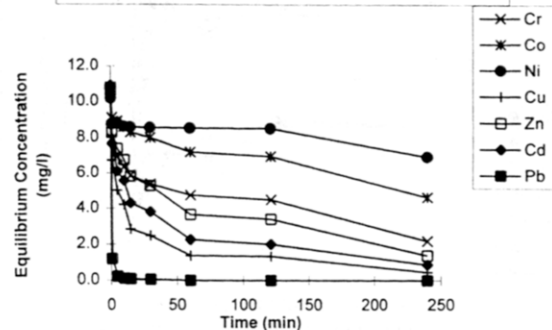


Figure 2C
Removal Performance of Clinoptilolite @ Initial
Metals Concentration = 15 mg/l

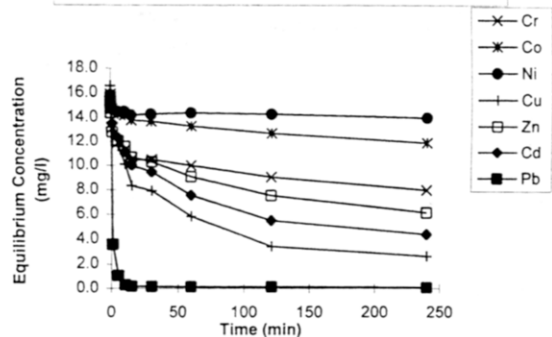


Figure 2D
Removal Performance of Clinoptilolite @ Initial
Metals Concentration = 30 mg/l

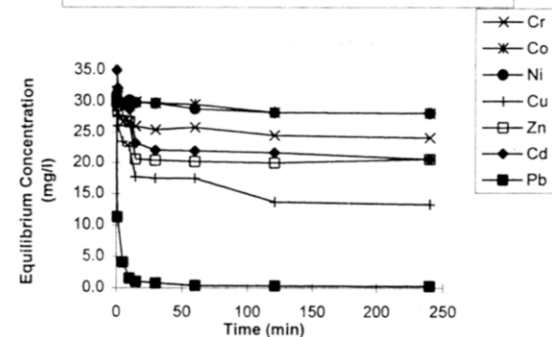


Table 1. Maximum adsorption capacity of chabazite and clinoptilolite for metals removal

Metal	Clinoptilolite (mg/g)	Chabazite (mg/g)
Cr	2.4	3.6
Co	1.5	5.8
Ni	0.9	4.5
Cu	3.8	5.1
Zn	2.7	5.5
Cd	3.7	6.7
Pb	6.0	6.0

Figure 3 exhibits clinoptilolite removal efficiency versus metal concentration. The results clearly show that high selectivities were obtained for lead, copper, cadmium, zinc and chromium and slightly lower values for nickel and cobalt. The clinoptilolite selectivity sequence is as follows: $Pb > Cu > Cd > Zn > Cr > Co > Ni$. Chabazite, on the other hand, is much more efficient than clinoptilolite and can remove in excess of 95% of most mixed metals. The corresponding selectivity sequence was found to be as follows: $Pb > Cd > Zn > Co > Cu > Ni > Cr$.

The selectivity series could be the result of various factors which influence ion exchange behaviour in zeolites. One factor is the framework structure of the zeolite itself. The dimensions of the channel formed by the tetrahedral units which make up the zeolite must be large enough to allow passage of a hydrated metal ion. There is some question as to the space available in the main channels of clinoptilolite because the structure has not been determined but is thought to be related to heulandite (Breck, 1974). If clinoptilolite has channels with dimensions similar to heulandite then few of the hydrated metals would be able to move within the structure. Some of the waters of hydration would have to be removed in order to accommodate the metal ion (Semmens, 1981; Eisenman 1962).

Effect of pH on metal removal

Figures 5 and 6 show the change of concentration versus time at pH values 3, 4, 5, and 6 for both clinoptilolite and chabazite respectively. pH has a significant impact on metals removal by zeolites since it can influence both the character of the exchanging ions and the character of the zeolite itself. Chemically, the solution pH influences metal speciation. Heavy metals may form complexes with inorganic ligands such as OH^- for example. The extent of complex formation varies with pH, the ionic composition, and the particular metal of concern. The exact speciation of a metal has a significant impact on the removal efficiency of the zeolites and the selectivity of the metal for the zeolite will also be influenced by the character of the metal complex that predominates at a particular solution pH. Furthermore, the kinetics of removal may be adversely affected if a large complex is formed and this may in turn reduce the effective exchange capacity of the zeolite for a given contact time (Semmens 1981). The impact of the pH on the zeolite itself is poorly understood at the present time. The zeolite surface (approximately 15-20 m²/g for clinoptilolite) will be influenced by the ambient pH which is not equal to the external solution value. Surface functional groups may dissociate at higher pH values leaving anionic surface sites that may make a significant contribution to the metal removal. Many investigators (Schindler, 1976, Huang and Ostovic, 1978) have observed a strong pH dependence on metal removal by inorganic adsorbents such as silica.

Zeolites such as clinoptilolite and chabazite are not only influenced by pH but in turn are capable of affecting solution pH especially in batch systems. Calcium and sodium are the major cations released to solution and bicarbonates/carbonates are the major anions. This points to the major problem in researching natural zeolites; they are not pure products but rather contain a variety of impurities such as calcium carbonate, unaltered glass, clays, etc. which are occluded during the formation of the zeolite. Unlike synthetic ion exchange resins, which tend to have an internal pH slightly lower than that measured in solution because of the influence of the Donnan potential, natural zeolites tend to have a higher internal pH. The influence of the zeolite on pH must be recognised when metal removal behaviour is interpreted and in certain cases it makes data analysis difficult.

Figure 3
Effect of Initial Metals Concentration on
Clinoptilolite Removal Efficiency

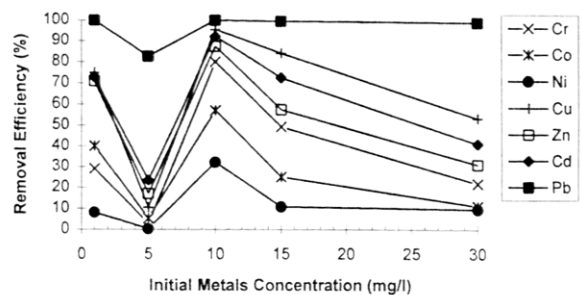


Figure 5
Effect of pH on Removal Efficiency of
Clinoptilolite

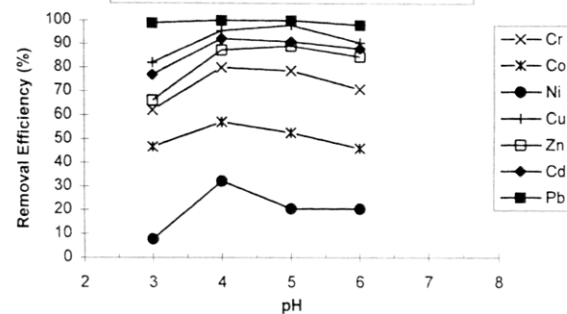


Figure 4
Effect of Initial Metals Concentration on
Chabazite Removal Efficiency

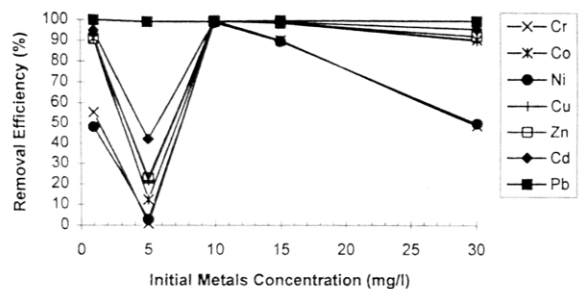
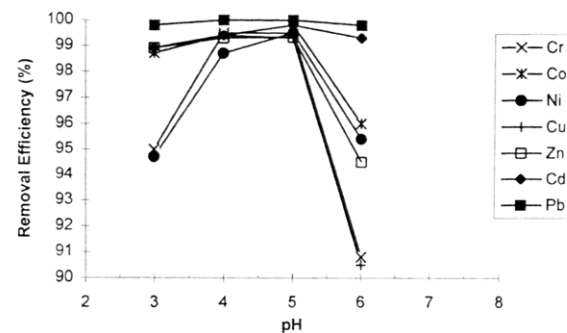


Figure 6
Effect of pH on Removal Efficiency of Chabazite



It should be noted that precipitation occurred at pH 11.7 according to a titration test conducted for a solution containing 10 ppm of each metal. Therefore, one can conclude that the predominant mechanism for metal removal for both zeolites is ion exchange with precipitation being negligible. These results could be explained by two theories: (1) the zeolites were highly selective for H_3O^+ ions and when their concentration was increased, the metal exchange was reduced accordingly, and (2) the zeolites were weakly acidic in character and at low pH values the capacity of the zeolites for exchange was consequently reduced.

CONCLUSIONS

The study revealed that metals removal efficiencies exceeding 99% could be achieved by both clinoptilolite and chabazite and the selectivity series for the various metal cations was found to be independent of their initial concentration. The results also indicated that chabazite has higher exchange capacity than clinoptilolite which is mainly due to its higher Al substitution of Si which provides a negative framework favourable to superior ion exchange capability. Metals removal efficiencies were examined for several concentrations ranging from 1 ppm to 30 ppm for each metal for which both zeolites showed that optimum removal was achieved at an initial metals concentration of 10 ppm.

Clinoptilolite is highly selective for lead, copper and cadmium and its selectivity sequence is as follows: $Pb > Cu > Cd > Zn > Cr > Co > Ni$. Chabazite is highly selective for lead, cadmium, zinc, and cobalt, copper and less selective for nickel and chromium. The selectivity sequence for chabazite is as follows: $Pb > Cd > Zn > Co > Cu > Ni > Cr$. Equilibrium studies conducted at various pH values showed that optimum removal is achieved when operating at pH between 4 and 5. Titration tests showed that precipitation occurred at pH 11.7 and therefore metal precipitation during the ion-exchange mechanism is negligible as the experimental pH was between 3 and 8. Consequently we can conclude that metal removal mechanism in this case is predominantly controlled by ion exchange.

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