Elimination of Cd²⁺ and Mn²⁺ from Wastewaters Using Natural Clinoptilolite and Synthetic Zeolite P

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ABSTRACT*: This study deals with the uptake of Cd^{2+} and Mn^{2+} ions from contaminated water using two Iranian natural clinoptilolite-rich tuffs from Meyaneh (Z-m), and Semnan (Z-s) regions , and a synthetic zeolite-P from Z-m sample (Z-P) under static (batch operation) and dynamic (column operation) conditions. To investigate the selectivity of the zeolites toward Cd^{2+} and Mn^{2+} cations, the ion exchange isotherms were constructed at 298K. According to the data obtained for both cations, the following general trend in distribution coefficient (K_d) and consequently in selectivity was achieved for the investigated exchangers: Z-P>>Z-m> Z-s.*

KEY WORDS: *Clinoptilolite, Zeolite-P, Wastewater, Cadmium ion, Manganese.*

INTRODUCTION

Heavy metal release in wastewaters is a serious environmental problem because of: (i) their known toxic effects on animals and plants as well as on man via the food chain, (ii) their widespread use in various industrial processes [1].

Cadmium and manganese are naturally occurring metallic elements, which are present in the earth crust and everywhere in the environment [2-4]. Some wastewater streams, especially from mineral processing operations, commonly contain dissolved Cd^{2+} and Mn^{2+}, which must be removed prior to discharge to the environment. The current treatment methods for heavy metal containing liquid wastes include pH adjustment with hydroxides, other precipitation methods, reverse osmoses, coagu-lation- sedimentation, and using organic ion-exchangers. However, these procedures have some drawbacks as following: (i) possible failure to attain the concentration limit of pollutants allowed by the law, (ii) long settling and filtration time, (iii) problem of disposal of the resulting sludge, (iv) increasing the alkalinity of the treated wastewater [5]. The use of natural and synthetic zeolites in the clean-up processes of various wastewater streams, as a valid alternative method is under progress due to their unique sorption properties, availability and relatively low costs. Cations can interact with zeolites via ion exchange reaction on negatively charged internal and external surfaces [6-7]. In the present work, the removal of Cd^{2+} and Mn^{2+} from industrial wastewaters were investigated under static (batch operation) and dynamic (column operation) conditions using two Iranian natural clinoptilolites [Meyaneh (Z-m), and Semnan (Z-s)] and a synthetic zeolite-P from Z-m sample (Z-P)[8].

Fig.1: Effect of the cation concentration on distribution coefficient for Mn^{2+}.
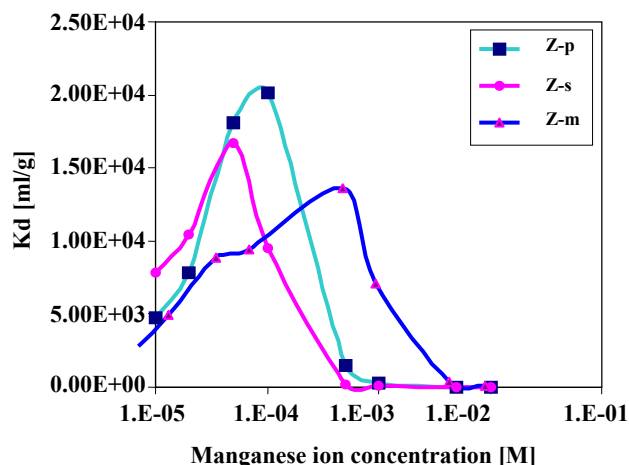

Fig.2: Effect of the cation concentration on distribution coefficients for Cd^{2+}.

EXPERIMENTAL

The natural clinoptilolites used for the experiments were obtained from Meyaneh (Z-m) and Semnan (Z-s) deposits located in the north west and the north east regions of Iran, respectively. The synthetic zeolite-P (Z-P) was prepared from Meyaneh clinoptilolite. The natural samples were ground and wet sieved to a particle size of 224-500μ for further experiments.

The uptake of Cd^{2+} and Mn^{2+} from solutions with a metal concentration of 10^{-5}-10^{-2} mol.dm^{-3} was investigated using a batch type technique. In this regard, 150 mg of each zeolite powder in contact with 25ml of the Cd^{2+} and Mn^{2+} solutions was shaken for 24 hours at 303K. After centrifuging at 400 rpm for 20 minutes, the concentration measurements were carried out on each sample by Inductively Coupled Plasma Atomic Emission Spec-troscopy (ICP-AE) technique**.** The ion exchange isotherm curves of Cd^{2+} and Mn^{2+} were also plotted at 298K for the different zeolites according to the following procedure: 0.15g of each zeolite powder was placed in a number of 50ml polyethylene capped- containers and the same volume of solutions with different amounts of under investigation cations and sodium nitrate solution as a competitor ion with similar molarity were added. After shaking for 74 hours at 240 rpm, centrifuging, and separating the solid phase from the liquid phase, the uptake amounts were calculated using ICP-AE technique results.

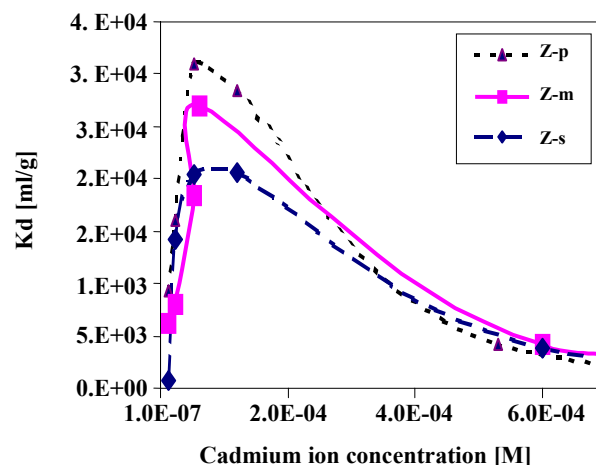For column studies, 1.00 g of each zeolite powder was loaded in a glass column of 1cm in internal diameter and a solution of 0.01 M Cd^{2+} (prepared using $CdNO_3.4H_2O$) or Mn^{2+} (prepared using $MnSO_4.H_2O$) was passed through it at the flow rate of 0.4 ml/min. Small fractions of effluent (5ml) were collected for measuring the solution concentration.

RESULTS AND DISCUSSION

The distribution coefficient (K_d) was calculated using the following equation:

$K_d = [(C_i-C_f) /C_f](V/m)$

Where C_i and C_f are initial and final concentrations of the used cations (in molarity) respectively, m is the weight of sample (exchanger) in grams and V is the volume of solution in milliliters.

Ion exchange isotherms were then obtained by plotting Gama versus $C_{eq.}$, where they were defined as follows:

Gama = The amount of absorbed cation on zeolite phases at equilibrium condition (mg/g of zeolite).

C_{eq} = The amount of cation remained in the solution at equilibrium condition (mg/ml of solution).

Breakthrough curves were obtained by plotting C/C_0 ratio versus V, in which C and C_0 are the final and the initial cations concentration in the solution, respectively and V is the volume of solution in ml.

Distribution coefficients (K_d, ml.g^{-1}) of Cd^{2+} and Mn^{2+} at different concentrations of starting solution are shown in Figs.1 and 2.

Given the results, it can be concluded that the uptake behavior of investigated natural, (Z-s and Z-M), and
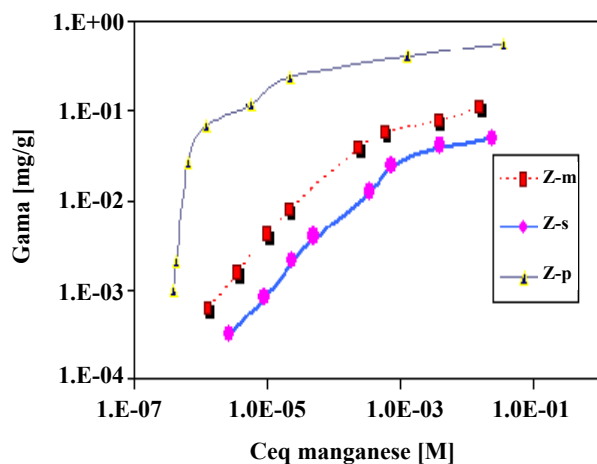
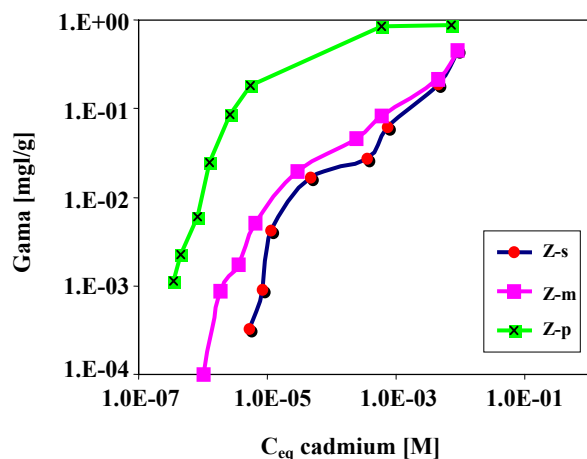*Fig. 3: Ion-exchange isotherms of Mn^{2+} at 298 K.*

Fig. 5: Mn^{2+} breakthrough curves (0.4 ml /min).

Fig. 4: Ion-exchange Isotherms of Cd^{2+} at 298 K.

Fig. 6: Cd^{2+} breakthrough curves (0.4 ml/min).

synthetic (Z-p) ion exchangers is closely related to the structural characteristics (windows and channels dimension) of zeolites used, as well as the effective radii of the cations (Cd^{2+} and Mn^{2+}). As a general conclusion, according to the experimental data, it is found that Z-P zeolite has shown the highest selectivity toward both cations.

The ion-exchange isotherms of Cd^{2+} and Mn^{2+} for three samples, which are plots of Gamma Vs Ceq, are shown in Figs.3 and 4.

The breakthrough curves are shown in Figs.5 and 6. It was indicated that among the studied zeolites, zeolite-P was shown to be more selective toward both Cd^{2+} and Mn^{2+} cations. From mathematical expressions of uptake it was found that the Langmuir model perfectly fitted the results of this work. This model is expressed as:
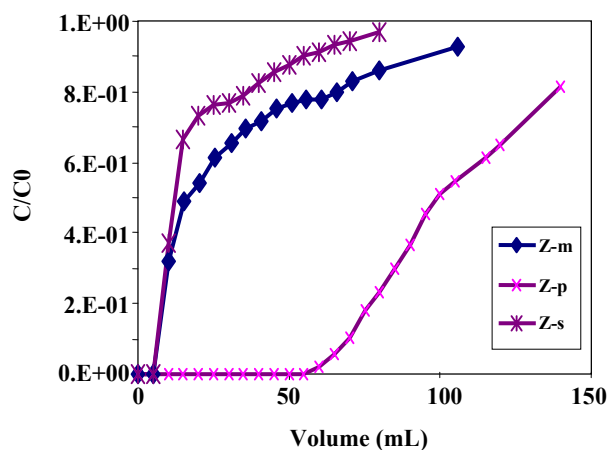
$$C/S = 1/ K_l S_m - K_l S$$

Where S is solute concentration in the zeolite phase (mg.g^{-1}), K_l is isotherm parameter for Langmuir isotherm (ml.mg^{-1}), S_m is maximum capacity toward solute (mg.g^{-1}), and C represents equilibrium solute concentration in the solution (mg.ml^{-1}).

To calculate the separation factor, in order to evaluate the zeolites capability for separation of the cations, some desorption (elution) experiments is under progress. The results of the elution tests and optimized condition for the best separation efficiency will be presented elsewhere.

CONCLUSIONS

In accordance with the calculated distribution coefficient (K_d), the break through curves, and the isotherms for the natural clinoptilolites as well as the relevant synthetic zeolite-P, the following general trend

in the selectivity was observed for both mentioned cations on the exchangers:

Z-P>> Z-m> Z-s

Among the investigated zeolites, the synthetic zeolite-P (Z-P) shows a remarkable capability to remove Cd^{2+} and Mn^{2+} cations from wastewater streams. Furthermore it is the most effective ion-exchanger which can be recommended for separation of those cations in the ion-exchange process.

Acknowledgements

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