Evaluation of Heavy Metal Removal from Wastewater Using Iranain Modified Natural Clinoptilolite

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In this study, the absorption properties of the natural zeolite (from east of Iran) with respect to some heavy metal cations in water solution were investigated. Clinoptilolite, a natural zeolite, was used for the removal of Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions from water samples. The batch method has been employed. Satisfactory result was obtained by using pretreatment condition and regeneration. The percentage adsorption and distribution coefficient were determined for the absorption cations as a function of sorbate concentration. In the ion exchange evaluation, two sorption isotherms, Langmuir and Freundlich have been studied. Cation exchange selectivity can be given as $Cd^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. These results show that these natural zeolites can be used efficiently for removal of heavy metal species from wastewater.

Key Words: Wastewater, Heavy metal, Natural zeolites, Clinoptilolite.

INTRODUCTION

Many toxic heavy metals have been dicharched into the environment as wastewater. Heavy metals can be absorbed by living organisms. They enter the food chain and the heavy metals may accumulate in the human body. They can cause serious health disorders[1,2]. Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. The removal of heavy metal can be achieved by conventional treatment processes such as chemical precipitation, ion exchange and electrochemical removal[3-6]. These processes have many drawbacks such as incomplete removal, high-energy requirements and production of toxic sludge[7]. The use of alternative low cost material utilizing local resources would be advantages for treatment of processes, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent[8,9]. The adsorbents may be of mineral, organic or biological origin, industrial by-products, agricultural wastes, biomass and polymeric materials[10-13].

Natural zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimensions[14]. Owing to zeolites structural characteristics and their adsorbent properties, they have been applied as chemical sieves, water softeners and adsorbents. Zeolites can be easily regenerated by washing them with chemical solutions (*e.g.*, NaCl, CaCl₂, KCl, NaOH, HCl) and this is one more advantage of them because they can be re-used many times without losing their adsorption capability[15,16].

For sorption applications, zeolites are often reported to exhibit high sorption capacity and selectivity for divalent elements, which makes the zeolites attractive for environmental applications, such as water softening or removing toxic metals from water[17].

The advantage of zeolites over resins, apart from their much lower cost is their ion selectivity. Among the most frequently studied natural zeolites, clinoptilolite was shown to have high selectivity for certain heavy metal ions. It was demonstrated that the cation-exchange capability of clinoptilolite depends on the pre-treatment method. Modification/pretreatment aims to replace exchangeable cations (Na, K, Ca and Mg) on clinoptilolite with a cations that is more willing to undergo ion exchange, thus improves its ion exchange ability and removal efficiency[18,19]. Sodium chloride seems to be the most widely used for chemical pretreatment[20]. Several aspect of heavy metal removal *via* clinoptilolite such as determination of removal capacity or pretreatment has been investigated by a number of researchers[21-25].

The aim of this work is to show the capability of Iranes modified chemical clinoptilolite (MCC) in removing Co, Cu, Cd and Ni from a highly contaminated industrial water.

EXPERIMENTAL

The natural clinoptilolite used in this study is from a zeolite comes from a layer situated in South Khorasan, (Ferdows City) Iran. The clinoptilolite zeolite (CZ) was ground

and passed through 300-600 μm sieves and was dried in an oven at 100 ºC for 24 h.

Inorganic chemical were supplied by Merck as analytical-grade regents. An initial solution of each cations were prepared from a commercial standard solution (1000 mg L^{-1}) of cations using their nitrate salts. Deionized water (18.2 MΩ cm^{-1}MilliQ Plus type) was used for dilutions.

Elemental analysis for major elements in the clinoptilolite was made by using a Rigaku X-ray fluorescence analyzer (XRF) (ZSX, 100-e). Sample for major elemental analysis was prepared by mixing natural clinoptilolite zeolite powder (325 mesh, 900 ºC) with lithium tetraborate and lithium metaborate and by placing the mixture in a muffle furnace at 1100 ºC for 0.5 h. The dried samples were then placed in the XRF apparatus.

Hitachi type SpectrAA-Z2000 Zeeman. The flame type was air-acetylene and hallow cathode lamps (Hitachi) was used with emitting wavelengths of Co (240.7 nm), Cu (324.7 nm), Cd (228.8 nm), Ni (232 nm). The cations removal by zeolitic rocks was evaluated using a batch method.

Adsorption equilibrium measurements: All chemicals and salts used were of reagent grade. The standards solutions of cobalt, nickel, copper and cadmium cations ranging from 30 to 500 mg/L were prepared from 1000 mg/L stock standard solution of the cations with deionized water in polyethylene plastic bottles. The pH of the prepared solution was adjusted by adding 0.10 M NaOH or 0.1 M HCl solution and measured with the accurate pH meter. One gram of the zeolite was added to 50 mL of each solution. The bottles were closed tightly and placed on the shaker at 100 rpm and after 48 h, the samples were removed from the shaker, filtered (0.45 μm nylon) and analyzed by AAS for cations concentration. The per cent adsorption (%) and distribution ratio (K_d) was calculated using the equation

$$\text{Adsorption (\%)} = \frac{(C_i - C_f)}{C_f} \times 100 \qquad (1)$$

where C_i and C_f are the concentration of metal ion in initial and final solution, respectively.

K_d = Amount of metal in adsorbent/amount of metal in solution × V/m (2)

where V is the volume of solution (mL) and m is the weight of the adsorbent (g).

RESULTS AND DISCUSSION

Physical and chemical properties of natural zeolite: Major and trace element compositions of the clinoptilolite zeolite sample showed that aside from the main Si and Al components, Na is the next highest component at 3.18 wt. % followed by K at 2.44 wt. % (Table-1). Silica to alumina ratio (Si/Al) of 5.92 was obtained for the natural clinoptilolite zeolites. The Si/Al ratio provides the negatively charged structure of the zeolite due to the difference between the $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ tetrahedral[26]. Positive sites may be available from the alkaline and alkaline-earth cations contained in the zeolite that are available for ion exchange.The XRF elemental analysis data shown in Table-1. It was found that the natural zeolite contains approximately 80 % clinoptolite and main impurity identified as quartz by XRD analysis.

TABLE-1
ELEMENTAL ANALYSIS OF A NATURAL CLINOPTILOLITE ZEOLITE FROM IRAN (FERDOWS CITY)

Major elements	Concentration (wt. %)	Major elements	Concentration (wt. %)
SiO$_2$	63.37	MnO	0.02
Al$_2$O$_3$	10.71	CaO	1.69
Na$_2$O	4.09	P$_2$O$_5$	0.05
MgO	1.20	Fe$_2$O$_3$	2.15
K$_2$O	2.00	SO$_3$	0.53
TiO$_2$	0.34	LOI	12.87

Modification of natural zeolit: Different modifier materials (NaCl, MgCl$_2$, KCl, HCl) were tested for pretreatment and regeneration. For this purpes 1 g of zeolite with 50 mL of 1 M of modifier were placed on shaker at 25 ºC and 100 rpm for 24 h. After that washed with water until no Cl$^-$ was detected in washing water. The pretreated samples were dried at 100 ºC for 24 h and stored in desiccators for further use. The regeneration of zeolite after removal cations from sample were used was performed under the same experimental procedure as the pretreatment step.

Fig. 1 shows the result of using modifiers for cations removal capacity sorbent. These result indicated that NaCl increased the metal removal. NaCl-modified clinoptilolite resulted higher cation uptake. This is in agreement with previous studies[18,20].
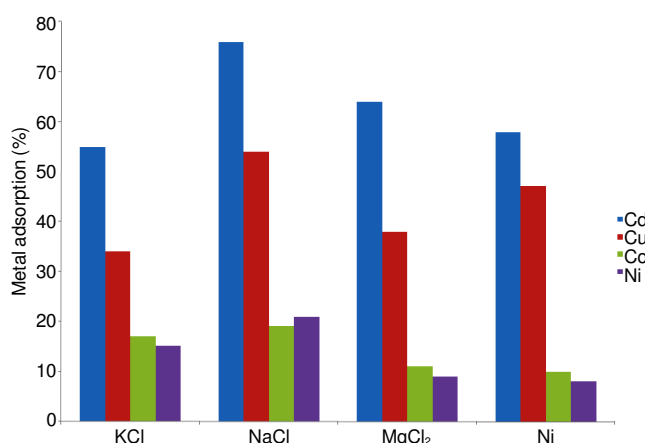

Fig. 1. Result of using modifiers for cations on removal capacity sorbent

Effect of pH on cation adsorption: The effect of pH on cations adsorption by clinoptilolite zeolite was investigated at acidic, neutral and basic conditions. The pH of eight 50 mL solutions of each cation 100 mg/L was adjusted to values ranging from 3 to 8 (each pH level in duplicate) by adding 0.1 M HCl or 0.1 M NaOH. Initial pH-values were recorded. The solutions were then mixed with 1 g of clinoptilolite zeolite in 500 mL, high-density, polyethylene plastic bottles and placed in an automatic shaker at 100 rpm for 48 h to ensure that adsorption equilibrium was obtained. After 48 h, samples were removed from the shaker, filtered (0.45 μm nylon) and analyzed with an atomic absorption spectrometer (AAS). The pH of the initial test solution significantly affected cation uptake over the pH range (3-8) investigated (Fig. 2). The pH of the aqueous solution is an important controlling parameter in the sorption process. Since most specifically sorbet metal ions can form
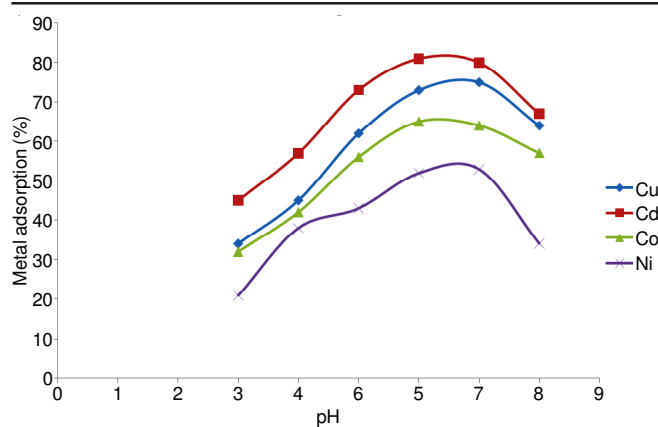
Fig. 2. Effect of pH on cations adsorption

oxides and hydrous oxides, the potential for heterogeneous precipitation will always be present in aqueous systems because of the presence of the constituent OH, ion as coordinated water molecules, hydroxyl species of cations may participate onto the zeolite structure especially at pH above 8. However, such a process could happen for samples with high cation initial concentrations. The extremely weak sorption found at pH 3 was also excluded as it likely resulted probably due to competition of H^+ at low pH, more H^+ occupied the surface of the adsorbent, reducing the access of cation ions to surface sites resulting in a decrease in cation uptake onto clinoptilolite. The optimum pH 6-7 was chosen for uptake of Cd, Cu, Ni and Co cations.

Adsorption of cations on modified clinoptilolite: The adsorption of cations onto the natural zeolite was studied by varying the metal concentration from 10 to 500 mg/L while keeping all parameter constant. Percentage absorption and K_d values for cations decrease with increasing metal ion concentration. The results are shown in Figs. 3 and 4. These results indicate that less favorite sites involved with increasing cation concentrations. The amounts of metal ions removed by the clinoptilolite based on the 48 h batch equilibrium. The retention of ions are ranked as based on percentage mass removal. The results show that there is 81.48 % of Cd^{2+}, 75 % of Cu^{2+}, 67 % of Co^{2+} and 50 % of Ni^{2+} removal from modified chemical clinoptilolite. The retention of ions are ranked as $Cd^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$ based on percentage mass removal. It is known that ion exchange selectivity is determined by the strength of electrostatic forces. Since electrostatic forces are involved in the retention of counter ions, it can be predicted from Coulomb's law that the ion having the smallest "effective" radius will be preferred. As cations present in solution are hydrated, ions with the smaller hydrated size or larger crystalline size are preferred. It has been demonstrated[26] that there is a definite relationship between ion size and ion selectivity.

Batch isotherm studies: The selection of appropriate correlation models for the experimental equilibrium data is important in order to optimize the design of an adsorption system for the removal of cations. Freundlich and Langmuir isotherm models have been demonstrated to fit the equilibrium behaviour of heavy metals[27-28]. These two models were used to correlate the observed behaviour in the present study. The adsorption equilibrium data obtained at pH 6-7 for solutions with initial cations concentrations varying from 30 to 500 mg/L.
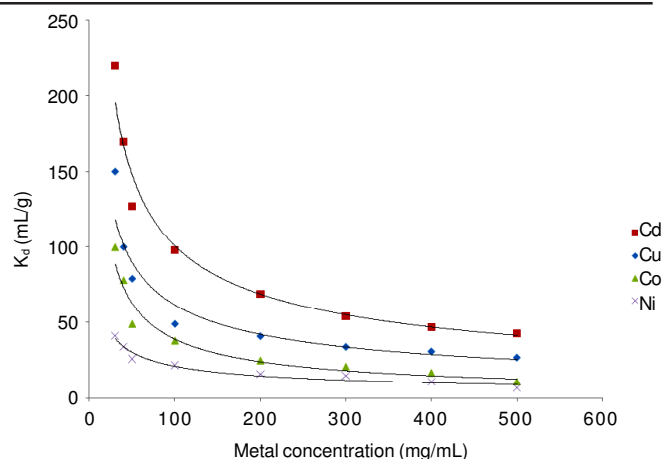
Fig. 3. Distribution ratio (K_d) metal ions on clinoptilolite as a function of initial concentration: m = 1 g, V = 50 mL, pH 6-7, time 48 h
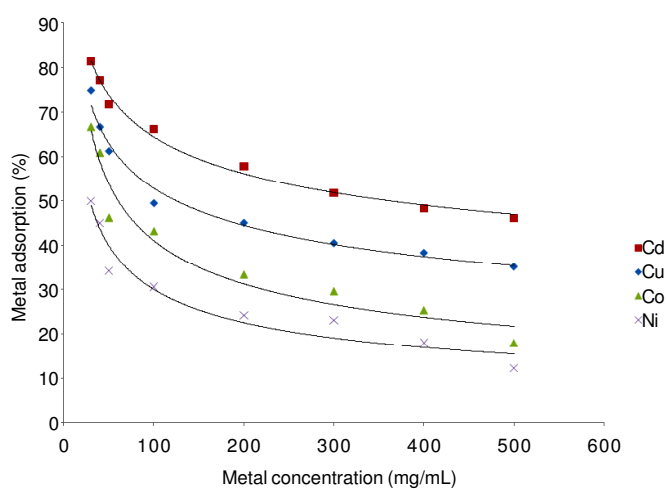
Fig. 4. Per cent adsorption as a function initial concentration: m = 1 g, V = 50 mL, pH 6-7, time 48 h

The Freundlich model indicates the heterogeneity of the adsorbent material and is given by the equation

$$\log q = \log K + \frac{1}{n} \log C_e \qquad (2)$$

where q (mg/g) is the amount of cation adsorbed at equilibrium, C_e (mg/L) is the equilibrium concentration of cation in solution and K and n are the Freundlich constants related to the zeolite adsorption capacity and adsorption intensity, respectively.

This isotherm does not predicate any saturation of the sorbent and indicate multilayer adsorption on the surface.

The Langmuir isotherm model assumes the formation of a monolayer onto the adsorbent surface with a finite number of identical sites and is given by the equation

$$\frac{C_e}{q} = \frac{1}{K_L} + \left(\frac{a}{K_L} \right) C_e \qquad (3)$$

where, K_L and a are the Langmuir constants.

A linear plot is obtained when C_e/q are plotted against over the entire concentration range of metal ions investigated. Results of the isotherm studies were fitted into both the Freundlich and the Langmuir isotherms.

The parameters for the Freundlich and Langmuir models are presented in Table-2. The high values of K suggested that adsorption capacity of the adsorbent is high. Low 1/n values (< 1) from the Freundlich isotherm suggested that any large change in the equilibrium concentration of cations would not result in a marked change in the amount of cation sorbet. The correlation coefficient (R) for all the isotherms ranged between 0.95 and 0.99, representing an excellent fit of the observed data. The *t*-test values showed that the coefficients were not significant at the 95 % confidence level for all the model equations.

TABLE-2
ADSORPTION ISOTHERM MODEL PARAMETERS

Element	Freundlich isotherm			Langmuir isotherm		
	K	1/n	R^2	a	K_L	R^2
Cd	1.41	0.30	0.9920	0.13	0.0180	0.9987
Cu	3.79	0.34	0.9875	0.08	0.0090	0.9835
Co	1.34	0.36	0.9532	0.03	0.0035	0.9563
Ni	5.18	0.45	0.9808	0.01	0.0002	0.9989

Conclusion

Since clinoptilolite has a molecular sieve structure, the adsorption of ions depends on the size of the hydrated ion and whether it can fit into the clinoptilolite channel, as well as the charge and concentration of ions. These results of ion adsorption can be explained by the classification of metal ions in the Periodic Table. The ion retention can also be explained by the binding strength, derived from the Langmuir equation from the ion adsorption isotherms. The constants related to binding strength, the selectivity of the metals for binding sites is ordered $Cd^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$ on the surface of the clinoptilolite.

The adsorption chractristic of the zeolite is dependent upon the chemical and structural properties of sorbent. These properties can be changed by several chemical treatments to improve separation efficiency of natural zeolite. The use of NaCl would allow zeolite exchangeable cations (Na, K, Mg, Ca) to its homoionic Na-form. Sodium as compare to other cations(K, Mg, Ca) has high mobility and weakly bonded and make replacement of with conceded cations easier[20].

These results show that natural zeolite can be used effectively for the removal of metal cations from wastewater. This natural material provided suitable substitute as sorbent with availability low cost materials.

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