

The removal of heavy metal cations by natural zeolites

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Received 24 March 2004; accepted 6 August 2004

Available online 25 September 2004

Abstract

In this study, the adsorption behavior of natural (clinoptilolite) zeolites with respect to Co^{2+} , Cu^{2+} , Zn^{2+} , and Mn^{2+} has been studied in order to consider its application to purify metal finishing wastewaters. The batch method has been employed, using metal concentrations in solution ranging from 100 to 400 mg/l. The percentage adsorption and distribution coefficients (K_d) were determined for the adsorption system as a function of sorbate concentration. In the ion exchange evaluation part of the study, it is determined that in every concentration range, adsorption ratios of clinoptilolite metal cations match to Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR) adsorption isotherm data, adding to that every cation exchange capacity metals has been calculated. It was found that the adsorption phenomena depend on charge density and hydrated ion diameter. According to the equilibrium studies, the selectivity sequence can be given as $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. These results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

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Keywords: Adsorption; Wastewaters; Heavy metals; Natural zeolites; Clinoptilolite

1. Introduction

Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution [1]. Pb^{+2} , Cu^{+2} , Fe^{+3} , and Cr^{+3} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders [2]. They are also common groundwater contaminants at industrial and military installations. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis [3–6]. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently.

Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities [7]; however, the use of ac-

tivated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon [8]. Various treatment processes are available, among which ion exchange is considered to be cost-effective if low-cost ion exchangers such as zeolites are used [9].

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as “tectosilicates.” Most common natural zeolites are formed by alteration of glass-rich volcanic rocks (tuff) with fresh water in playa lakes or by seawater [10]. The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc, and manganese [11,12]. The fact that zeolite exchangeable

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ions are relatively innocuous (sodium, calcium, and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. One of the earliest applications of a natural zeolite was in removal and purification of cesium and strontium radioisotopes [13].

Clinoptilolite is the most abundant natural zeolite and has the chemical formula $\text{Na}_{0.1}\text{K}_{8.57}\text{Ba}_{0.04}(\text{Al}_{9.31}\text{Si}_{26.83}\text{O}_{72})\cdot 19.56\text{H}_2\text{O}$ [14]. Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8- to 10-membered rings [15]. Considerable research has been conducted to characterize the chemical, surface, and ion-exchange properties of clinoptilolite [15–19]. The ion-exchange capacity of natural zeolite (clinoptilolite) for inorganic cations has been investigated by many authors [20,21].

The selectivity series of clinoptilolite in the sodium form was determined by Zamzow et al., as follows: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cs}^+ > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$ [22]. Jama and Yücel observed that clinoptilolite shows a very high preference for ammonium ions over sodium and calcium but not over potassium [23]. Mier et al. described the interactions of Pb^{2+} , Cd^{2+} , and Cr^{3+} competing for ion-exchange sites in natural clinoptilolite [24]. Inglezakis et al. studied the ion exchange of Pb^{2+} , Cu^{2+} , Fe^{3+} , and Cr^{3+} on natural clinoptilolite and showed that equilibrium is favorable for Pb^{2+} , unfavorable for Cu^{2+} , and of sigmoid shape for Cr^{3+} and Fe^{3+} [25].

As seen from the literature review, zeolites can be used for the removal of some heavy metals from wastewater. The clinoptilolite samples from different regions show different behavior in ion-exchange processes. In this study, the adsorption properties of the natural zeolite (Clinoptilolite, Western Anatolian) with respect to some heavy metal cations in solution were investigated.

2. Materials and methods

2.1. Zeolite source and conditioning

Samples of zeolite were taken from the Enli Mining Company open pit mine in Manisa-Gördes in Western Anatolia. The crushed original zeolite was ground and passed through $300 \times 600\text{-}\mu\text{m}$ sieves and was dried in an oven at $100 \pm 5^\circ\text{C}$ for 24 h. It was characterized by X-ray diffraction (XRD) and chemical analysis. Chemical composition of zeolite samples was determined by the usual analytical methods for silicate materials. Standard wet chemical analysis, along with instrumental methods, was adopted [26]. Al_2O_3 , Fe_2O_3 , CaO , and MgO were analyzed with titrimetric methods and SiO_2 was analyzed with gravimetric methods. Na_2O and K_2O were found out by flame photometry. The results of the chemical analyses are presented in Table 1.

Table 1
Chemical composition and physical properties of natural zeolite sample (wt%)

Chemical composition	(%)	Physical properties
SiO_2	69.31	Appearance porosity (%), 41.5
Al_2O_3	13.11	Appearance density (g/cm^3), 2.27
Fe_2O_3	1.31	Weight of per unit volume (g/cm^3), 1.32
CaO	2.07	Water absorption (original) (%), 31.3
MgO	1.13	Water absorption (grinding) (%), 103.7
Na_2O	0.52	Oil absorption ($\text{g oil}/100 \text{ g sample}$), 51
K_2O	2.83	Whiteness (%), 68
SO_3	0.10	Original bleaching ($\text{g sample}/\text{g tonsil}$), 1.95
H_2O	6.88	Active bleaching ($\text{g sample}/\text{g tonsil}$), 1.92
Si/Al	4.66	pH 7.5

2.2. Reagents

Inorganic chemicals were supplied by Merck as analytical-grade reagents and deionized water was used. The metal ions studied were Co(II), Cu(II), Zn(II), and Mn(II). We prepared a synthetic stock solution of copper, manganese, and cobalt using their nitrate salts, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively, in deionized water. The stock solution of Zn(II) was prepared using ZnCl_2 salts.

2.3. Batch adsorption studies

The ion exchange of heavy metals on natural zeolite was carried out using the batch method. Batch adsorption experiments were conducted using 10 g of adsorbent with 500 ml of solutions containing heavy metal ions of desired concentrations at constant temperatures (25°C) in 500-ml plastic bottles. The particle size of the sample (clinoptilolite) used was in the range of 63–106 μm . The bottles were shaken in a sieve for 5.5 h and solutions containing heavy metals were filtered through Whatman filter paper (No. 42). The exact concentration of metal ions and filterable metal concentrations were determined by AAS (ATI UNICAM 929 atomic absorption spectrophotometer). The flame type was air-acetylene and absorption wavelengths are Cu^{2+} (324.7 nm), Zn^{2+} (213.9 nm), Co^{2+} (240.7 nm), and Mn^{2+} (279.5 nm).

The percent adsorption (%) and distribution ratio (K_d) were calculated using the equations

$$\% \text{ adsorption} = \frac{C_i - C_f}{C_f} \times 100, \quad (1)$$

where C_i and C_f are the concentrations of the metal ion in initial and final solutions, and respectively, and

$$K_d = \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \times \frac{V}{m} \text{ ml/g}, \quad (2)$$

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

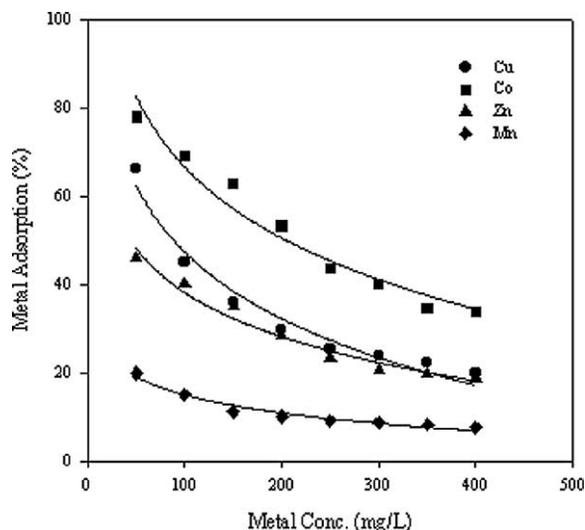


Fig. 1. Adsorption of metal ions by natural zeolite sample as a function of initial concentration: $m = 10$ g, $V = 500$ ml, pH 6–7, time 5.5 h.

The percent adsorption and K_d (ml/g) can be correlated by the following equation [27]:

$$\% \text{ adsorption} = \frac{100K_d}{K_d + V/m}. \quad (3)$$

3. Results and discussion

3.1. Properties of natural zeolites

A chemical analysis of the treated zeolite is presented in Table 1. This study showed that natural zeolite contained a complement of exchangeable sodium, potassium, and calcium ions.

The Si/Al ratio is 4.66 (mol/mol) and the corresponding ratio of $(\text{Na} + \text{K})/\text{Ca}$ is 1.85. The chemical composition, the theoretical exchange capacity, and the Si/Al ratio, generally ranging from 4 to 5.5, are typical for clinoptilolite [28–30]. Low-silica members are enriched with calcium, whereas high-silica clinoptilolites are enriched with potassium, sodium, and magnesium. It was found that the natural zeolite contains approximately 70% clinoptilolite and plagioclase, mica, quartz, smectite, and K-feldsparchlorite minerals by XRD analysis.

3.2. Adsorption of metals on natural zeolite

The adsorption of Cu^{2+} , Co^{2+} , Zn^{2+} , and Mn^{2+} onto natural zeolite as a function of their concentrations was studied at 30°C by varying the metal concentration from 100 to 400 mg/l while keeping all other parameters constant. The results are shown in Figs. 1 and 2. Percentage adsorption for Cu^{2+} , Co^{2+} , Zn^{2+} , and Mn^{2+} decreases with increasing metal concentration in aqueous solutions. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous

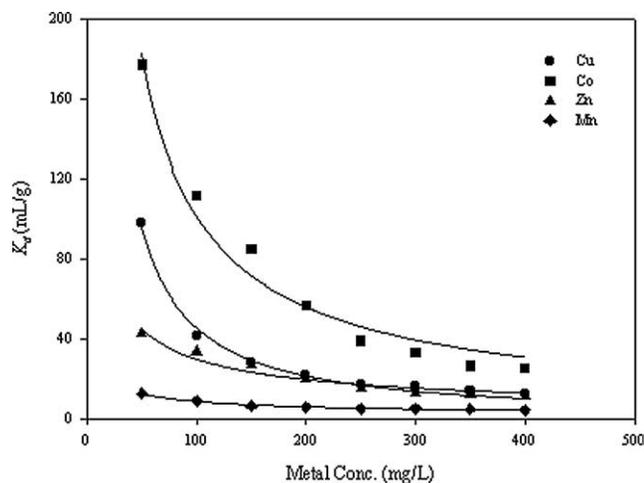


Fig. 2. Variation of metal ions on natural zeolite as a function of initial concentration: $m = 10$ g, $V = 500$ ml, pH 6–7, time 5.5 h.

solution. The heavy metal uptake is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, metal ions had to move through the pores of the zeolite mass, but also through channels of the lattice, and they had to replace exchangeable cations (mainly sodium and calcium). Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channels. In this case the metal ion uptake could mainly be attributed to ion-exchange reactions in the microporous minerals of the zeolite samples. Fig. 2 illustrates K_d as a function of metal ions concentrations. The K_d values increase with the decreasing concentration of metal ions. In other words, the K_d values increase as dilution of metal ions in solution proceeds.

These results indicate that energetically less favorable sites become involved with increasing metal concentration in the aqueous solution. The maximal exchange levels attained were as follows: Cu^{2+} 66.10%, Co^{2+} 77.96%, Zn^{2+} 45.96%, and Mn^{2+} 19.84%.

3.3. Isotherm models

The sorption data have been subjected to different sorption isotherms, namely, Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR). The equilibrium data for metal cations over the concentration range from 100 to 400 mg/l at 30°C have been correlated with the Langmuir isotherm [31]:

$$C_e/C_{\text{ads}} = 1/Qb + C_e/Q, \quad (4)$$

where C_e is the equilibrium concentration of metal in solution (M), C_{ads} is the number of metal ions sorbed onto zeolite, and Q and b are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q) represents monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and should vary with temperature. A linear plot is obtained when

Table 2

Characteristic parameters and determination coefficient of the experimental data according to the Langmuir equation

Metal	Q (mmol/kg)	b (l/g)	R^2
Cu^{2+}	141.12	1.16	0.9775
Co^{2+}	244.13	1.75	0.9919
Zn^{2+}	133.85	0.85	0.9803
Mn^{2+}	76.78	0.33	0.9503

C_e/C_{ads} is plotted against C_e over the entire concentration range of metal ions investigated. The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Table 2. The Langmuir model effectively described the sorption data with all R^2 values >0.95 . According to the Q (mmol/kg) parameter, sorption on zeolite is produced following the sequence $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$.

Zeolites, in general, are weakly acidic in nature and sodium-form exchangers are selective for hydrogen ($\text{R-Na} + \text{H}_2\text{O} \rightleftharpoons \text{RH} + \text{Na}^+ + \text{OH}^-$), which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions [32], making metal hydroxide precipitation feasible. In natural zeolites these metals seem to reach saturation, which means that the metal had filled possible available sites and further adsorption could take place only at new surfaces.

Ion-exchange capacity of heavy metal cations listed in Table 2 indicates the following selectivity sequence: $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. The heavy metal cations are present as hexaaqua complex ions with six surrounding water molecules in the solution and they passed the channel of zeolite in this form [23]. Since the adsorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important. The charges of the metal cation are the same (+2); therefore Mn^{2+} ions (the biggest diameter) have minimum adsorption, and Co^{2+} ions (the least diameter) have maximum adsorption.

The Langmuir model effectively described the sorption data with all R^2 values >0.95 , according to the b (mmol/g) parameter. Sorption on natural zeolite is produced following the sequence $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. The high Si/Al ratio of clinoptilolite results in a typical low anionic field that gives rise to good selectivity.

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich adsorption isotherms were also applied to the removal of Co^{2+} , Cu^{2+} , Zn^{2+} , and Mn^{2+} on zeolite (Fig. 3),

$$\log C_{\text{ads}} = \log K + 1/n \log C_e, \quad (5)$$

where C_e is the equilibrium concentration in mg/l and C_{ads} shows that the adsorption seems to follow the Freundlich

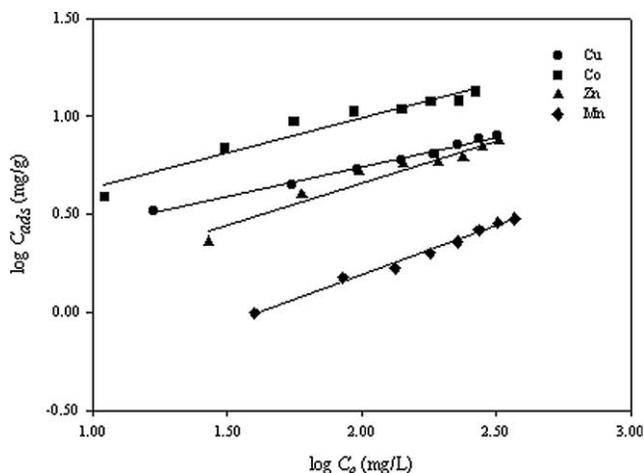


Fig. 3. Freundlich plots for metal ions adsorption onto natural zeolite.

Table 3

Freundlich adsorption equations and constants ($\log k$ and n) for metal cations on natural zeolite

Metal	$\log k$ (mg/g)	$1/n$	R^2
Cu^{2+}	0.13	0.30	0.9914
Co^{2+}	0.28	0.36	0.9390
Zn^{2+}	0.19	0.43	0.9417
Mn^{2+}	0.81	0.50	0.9897

isotherm model as well as the Langmuir isotherm. The constants K and n were calculated for each cation (Table 3). K is a parameter related to the temperature and n is a characteristic constant for the adsorption system under study. Values of n between 2 and 10 shows good adsorption.

The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface [33].

The Dubinin–Kaganer–Radushkevich (DKR) has been used to describe the sorption of metal ions on clays. The DKR equation has the form

$$\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2, \quad (6)$$

where C_{ads} is the number of metal ions adsorbed per unit weight of adsorbent (mg/g), X_m is the maximum sorption capacity, β is the activity coefficient related to mean sorption energy, and ε is the Polanyi potential, which is equal to

$$\varepsilon = RT \ln(1 + 1/C_e), \quad (7)$$

where R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The saturation limit X_m may represent the total specific micropore volume of the sorbent. The sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate [27]. The slope of the plot of $\ln C_{\text{ads}}$ versus ε gives β (mol^2/J^2) and the intercept yields the sorption capacity, X_m (mg/g). The sorption space

in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same sorption potential. This sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate. The sorption energy can also be worked out using the following relationship:

$$E = 1/\sqrt{-2\beta}. \quad (8)$$

The plot of $\ln C_{\text{ads}}$ against ε^2 for metal ion sorption on natural zeolite is shown in Fig. 4. The DKR parameters are calculated from the slope of the line in Fig. 4 and listed in Table 4. As shown in Table 4, the E values are 11.95 for Cu^{2+} , 11.03 for Co^{2+} , 9.77 for Zn^{2+} , and 8.81 kJ/mol for Mn^{2+} on the natural zeolite. They are the orders of an ion-exchange mechanism, in which the sorption energy lies within 8–16 kJ/mol [34,35]. The sorption capacity X_m in the DKR equation is found to be 0.22 for Cu^{2+} , 0.50 for Co^{2+} , 0.29 for Zn^{2+} , and 0.15 mmol/kg for Mn^{2+} .

4. Summary

It was considered that the metal cations are formed as high-spin aqua complexes and the hydrate ion diameter is the same as the diameter of aqua-complex ions. The diameters of hydrated ions are given as $r_{\text{Mn}} > r_{\text{Zn}} > r_{\text{Cu}} > r_{\text{Co}}$ in the literature [36].

If the ionic radii are compared with the free dimensions of the clinoptilolite channels, it is apparent that all of the unhydrated ions can pass readily through the channels, but

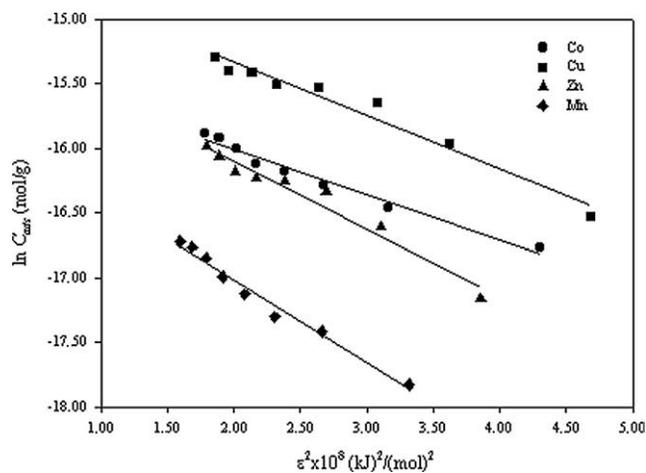


Fig. 4. DRK plots of metal ions on natural zeolite at constant temperature.

Table 4
Parameter obtained in the DKR equation

DKR	Cu^{2+}	Co^{2+}	Zn^{2+}	Mn^{2+}
X_m (mmol/kg)	0.22	0.50	0.29	0.15
β (mol^2/J^2)	-3.50×10^{-9}	-4.11×10^{-9}	-5.24×10^{-9}	-6.44×10^{-9}
Sorption energy (E , kJ/mol)	11.95	11.03	9.77	8.81
Correlation coefficient, R^2	0.9774	0.9644	0.9601	0.9817

since the hydrated ions are approximately the same size as the channel dimensions, they may exchange only with difficulty. It follows that for exchange to take place, at least some of the waters of hydration must be stripped from the solvated ions [37].

The DKR and Langmuir equations were used to describe the sorption isotherms of single-solute systems. The sorption energy E determined in the DKR equation (11.95 for Cu^{2+} , 11.03 for Co^{2+} , 9.77 for Zn^{2+} , and 8.81 kJ/mol for Mn^{2+}) revealed the nature of the ion-exchange mechanism in both systems. The sorption isotherms of binary solute systems could be fitted by the competitive Langmuir model, where the Langmuir parameters were directly adopted from those obtained in single-solute systems.

These results show that natural zeolite can be used effectively for the removal of metal cations from wastewater. This naturally occurring material provides a substitute for the use of activated carbon as adsorbent due to its availability and its low cost.

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