The efficiency of clinoptilolite for heavy metals adsorption from industrial wastewater

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ABSTRACT

The use of low-cost sorbents has been investigated as a replacement for current costly methods of removing heavy metals from solution. This paper describes the interactions of Co (II), Pd (II), and Zn (II) competing for ion-exchange sites in naturally occurring clinoptilolite. The percentage adsorption and distribution coefficients (K_d) were determined for the adsorption system as a function of sorbate concentration. Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR) models were used to describe the adsorption isotherms at different metals concentrations. Ion-exchange capacity of heavy metal cations indicates the following selectivity sequence: $Co^{2+} > Zn^{2+} > Pd^{2+}$. Altogether, these results show that clinoptilolite hold great potential to remove cationic heavy metal species from industrial wastewater.
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## 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 activated 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 tetrahedral. The aluminium ion is small enough t 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 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 $Na_{0.1} K_{8.57} Ba_{0.04} (Al_{9.31} Si_{26.83} O_{72})$. 19.56 H_2O[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:
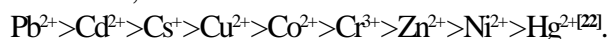
$Pb^{2+} > Cd^{2+} > Cs^+ > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$[22]. Barrer observed that clinoptilolite shows a very high preference for ammonium ions over sodium and calcium but not over potassium[23]. Kesraoui described the interactions of Pb^{2+}, Cd^{2+}, and Cr^{3+} competing 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) 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 supplied by the Institute of Geology and Mineral Exploration .The crushed original

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 (g/cm3), 1.32
Fe_2O_3	1.31	Weight of per unit volume (g/cm3),1.32
CaO	2.07	Water adsorption (original) (%), 31.3
MgO	1.13	Water adsorption (grinding) (%), 103.7
Na_2O	0.52	Oil adsorption (g oil/ 100g sample), 51
K_2O	2.83	Whiteness(%), 68
SO_3	0.10	Original bleaching (g sample/g tonsil), 1.95
H_2O	6.88	Active bleaching (g sample/g tonsil), 1.92
Si/Al	4.66	pH 7.5

zeolite was ground and passed through 300×600-μm sieves and was dried in an oven at 100±5°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.

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), Pd(II) and Zn(II).We prepared a synthetic stock solution of cadmium and cobalt using their nitrate salts, Pd $(NO3)_2 \cdot 6H2O$ and $Co(NO3)_2 \cdot 6H2O$, respectively, in deionized water. The stock solution of Zn (II) was prepared using $ZnCl_2$ salts.

2.3. Adsorption studies

The ion exchange of heavy metals on natural zeolite was carried out using the batch method. Batch adsorption experiments were conducted using 5g of adsorbent with 250 ml of solutions containing heavy metal ions of desired concentrations at constant temperatures (25°C) in 250-ml plastic bottles. The particle size of the sample (clinoptilolite) used was in the range of 63-106μm. The bottles were shaken in a

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sieve for 4.5 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 (atomic absorption spectrophotometer). The flame type was air–acetylene and absorption wavelengths are Pd^{2+}(213.9 nm), Zn^{2+} (240.7 nm), and Co^{2+}(279.5 nm).

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

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

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

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

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

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

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

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 S_i/Al ratio is 4.66 (mol/mol) and the corresponding ratio of (Na + K)/Ca is 1.85. The chemical composition, the theoretical exchange capacity, and the S_i/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 Pd^{2+}, Co^{2+} and Zn^{2+} onto natural zeolite as a function of their concentrations was studied at 30 C° by varying the metal concentration from 50 to 400 mg/l while keeping all other parameters constant.
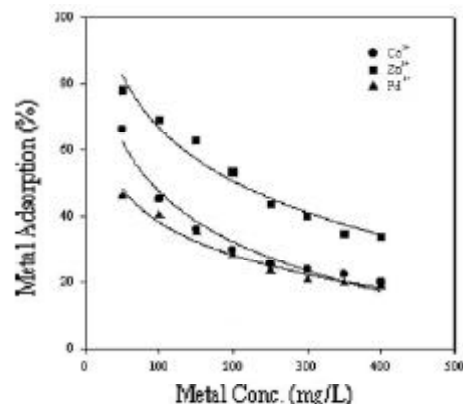

Figure 1: Adsorption of metal ions by natural zeolite sample as a function of initial concentration: m = 5g, V = 250ml, pH 6-7, time 4.5h
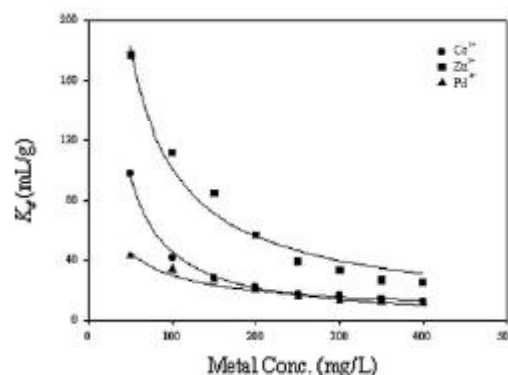

Figure 2 : Variation of metal ions on natural zeolite as a function of initial concentration: m = 5g, V = 250 ml, pH 6-7, time 4.5h

The results are shown in figures 1 and 2. Percentage adsorption for Pd^{2+}, Co^{2+} and Zn^{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 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. Figure 2 illustrates K_d as a function of metal ions concentrations.

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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: Zn^{2+} 66.10%, Co^{2+} 77.96% and Pd^{2+} 45.96%,

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 50 to 400 mg/l at 30°C have been correlated with the Langmuir isotherm[31]:

$$Ce/C_{ads} = 1/Q_b + Ce/Q \qquad (4)$$

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 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 $Co^{2+}>Zn^{2+}>Pd^{2+}$.

Zeolites, in general, are weakly acidic in nature and sodium-form exchangers are selective for hydrogen (R–Na+ $H_2O \Leftrightarrow$ RH + Na$^+$ + 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: $Co^{2+}>Zn^{2+}>Pd^{2+}$. 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

TABLE 2 : Characteristic parameters and determination co-efficient of the experimental data according to the Langmuir equation

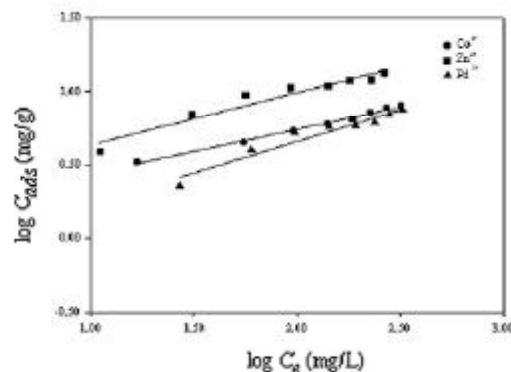| Metal	Q (mmol/kg)	B (l/g)	R^2
Zn^{2+}	141.12	1.16	0.9775
Co^{2+}	244.13	1.75	0.9919
Pd^{2+}	133.85	0.85	0.9803

Figure 3: Freundlich plots for metal ions adsorption onto natural zeolite

charges of the metal cation are the same (+2); therefore Pd^{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 $Co^{2+}>Zn^{2+}>Pd^{2+}$. 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+}, Zn^{2+}, and Pd^{2+} on zeolite (Figure 3),

$$LogC_{ads} = logK + 1/nlogC_e \qquad (5)$$

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

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TABLE 3: Freundlich adsorption equations and constants (logk and n) for metal cations on natural zeolite

Metal	Log k (mg/g)	l/n	R^2
Zn^{2+}	0.13	0.30	0.9914
Co^{2+}	0.28	0.36	0.9390
Pd^{2+}	0.19	0.43	0.9417

TABLE 4: Parameter obtained in the DKR equation

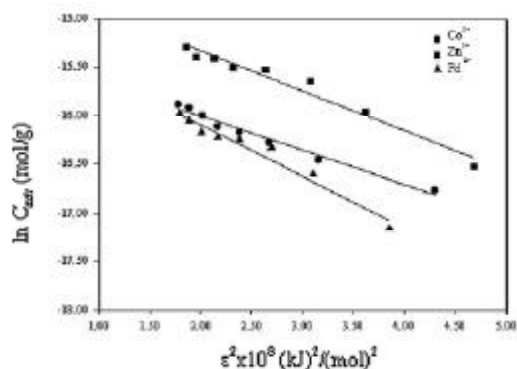| DKR	Zn^{2+}	Co^{2+}	Pd^{2+}
Xm (mmol/kg)	0.22	0.50	0.29
β (mol^2/J^2)	-3.50×10^{-9}	-4.11×10^{-9}	-5.24×10^{-9}
Sorption energy (E,kJ/mol)	11.03	11.03	9.77
Correlation coefficient, R^2	0.9774	0.9644	0.9601

Figure 4: DRK plots of metal ions on natural zeolite at constant temperature

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

$$\ln C_{ads} = \ln X_m - \beta\varepsilon^2 \tag{6}$$

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

$$\varepsilon = RT \ln (1 + 1/C_e) \tag{7}$$

where R is the gas constant (kJmol^{-1} 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 $\ln C_{ads}$ 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:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

The plot of $\ln C_{ads}$ against ε^2 for metal ion sorption on natural zeolite is shown in figure 4. The DKR parameters are calculated from the slope of the line in figure 4 and listed in TABLE 4. As shown in TABLE 4, the E values are 11.03 for Zn^{2+}, 11.95 for Co^{2+} and 9.77 kJ/mol for Pd^{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 Zn^{2+}, 0.50 for Co^{2+} and 0.29 mmol/kg for Pd^{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 $r_{Pd}>r_{Zn}>r_{Co}$ 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 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 Co^{2+}, 11.03 for Zn^{2+}, and 9.77 kJ/mol for Pd^{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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