

Removal of Heavy Metals from Aqueous Solution by Zeolite in Competitive Sorption System

Sabry M. Shaheen, Aly S. Derbalah, and Farahat S. Moghanm

Abstract—In this study, the sorption behaviour of natural (clinoptilolite) zeolites with respect to cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) has been studied in order to consider its application to purity metal finishing wastewaters. The batch method has been employed, using competitive sorption system with metal concentrations in solution ranging from 50 to 300 mg/l. The percentage sorption and distribution coefficients (K_d) were determined for the sorption system as a function of metal concentration. In addition lability of the sorbed metals was estimated by DTPA extraction following their sorption. The results showed that Freundlich model described satisfactorily sorption of all metals. Zeolite sorbed around 32, 75, 28, 99, and 59 % of the added Cd, Cu, Ni, Pb and Zn metal concentrations respectively. According to the percentage sorption and distribution coefficients values, the selectivity sequence of studied metals by zeolite can be given as $Pb > Cu > Zn > Cd > Ni$. About 57, 47, 78, 22, and 29 % from the total sorbed Cd, Cu, Ni, Pb and Zn recovered by DTPA indicating that lability of the adsorbed Ni was higher than, Cd, Cu, Zn, and Pb respectively. These results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

Index Terms—Sorption, lability, heavy metals, zeolite.

I. INTRODUCTION

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

Various treatment processes are available, among which sorption is considered to be cost-effective if low-cost sorbents such as zeolites are used [4]. 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 [5].

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 [6]. 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. Clinoptilolite is the most abundant natural zeolite and has the chemical formula: $Na_{0.1}K_{8.57}Ba_{0.04}(Al_{9.31}Si_{26.83}O_{72}) \cdot 19.56H_2O$ [7]. Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8- to 10-membered rings [8]. Considerable research has been conducted to characterize the chemical, surface, and sorption properties of clinoptilolite [9]. The sorption capacity of natural zeolite (clinoptilolite) for inorganic cations has been investigated by many authors [10]. The selectivity series of clinoptilolite in the sodium form was determined by Zamzow et al., as follows: $Pb > Cd > Cs > Cu > Co > Cr > Zn > Ni > Hg$ [11]. Mier et al. [12] Studied the sorption of Pb^{2+} , Cu^{2+} , Fe^{3+} , and Cr^{3+} on natural clinoptilolite and showed that equilibrium is favorable for Pb, unfavourable for Cu, and of sigmoid shape for Cr^{3+} and Fe^{3+} . 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 behaviour in sorption processes. In this study, the sorption properties of the natural zeolite (Clinoptilolite, Western Anatolian) with respect to some heavy metal cations in solution were investigated.

Sorption of heavy metals can be described by a linear, Langmuir, or Freundlich sorption model [13]. The Freundlich equation is often useful for modeling sorption of metals onto solids with heterogeneous surfaces and has frequently proved superior to the Langmuir equation for cations or anions sorption [14]. Although, there is disagreement regarding the effectiveness of Langmuir and Freundlich models to interpret sorption of metal cations [15], some parameters of these models, such as maximum sorption quantity and the distribution coefficient are widely acceptable in characterizing metals sorption capacity of soils and other materials [16], [17]

Distribution coefficient is a useful parameter for comparing the sorptive capacity of different soils or materials for any particular ion, when they are measured under the same experimental conditions [18]. The mobility

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under the same experimental conditions [18]. The mobility of metals in the environment are directly related to their partitioning between solid and liquid phases [15] and, therefore, are directly related to their distribution coefficients, which indicate the capability of a sorbent to retain a solute and the extent of its movement to the liquid phase [19]

II. MATERIALS AND METHODS

A. Zeolite Selection and Characterization

Clinoptilolite zeolite selected from 'Beli Plast' mine (Bulgaria). Selected properties of zeolite are analyzed and presented in Table I.

TABLE I: SELECTED PROPERTIES OF STUDIED ZEOLITE

Properties	Concentrations
Chemical composition, %	
SiO ₂	70.1
Al ₂ O ₃	11.4
K ₂ O	3.30
CaO	2.95
Fe ₂ O ₃	0.78
Na ₂ O	0.70
MgO	0.37
TiO ₂	0.13
Exchangeable Cations, (cmol(+) kg ⁻¹)	
Ca ⁺⁺	92.6
Mg ⁺⁺	3.21
Na ⁺	23.1
K ⁺	87.5
DTPA-extractable heavy metals, mgkg ⁻¹	
Cd	0.018
Cr	0.110
Cu	1.192
Ni	0.168
Pb	8.920
Zn	4.896

B. Sorption Experiment

A batch equilibrium experiment was conducted using Cd, Cu, Ni, Pb and Zn in a competitive sorption system with metal concentrations in solution ranging from 50 to 300 mg/l from all metals studied as follows: 1000 mg/l stock solution contain all studied metals have been prepared. Two g of zeolite samples were equilibrated with 20 mL of 0.01 M CaCl₂ solutions containing 50, 100, 150, 200, 250, and 300 mg/l as a chloride salts in 50-mL centrifuge tubes (pre-weighed) for 24 h on a reciprocating shaker at room temperature. Some drops of toluene were added to suppress microbial activity. After equilibration the samples were centrifuged and the supernatant was filtered through a Whitman No. 42 filter paper. Two replicates were used for collecting each data point. Metals concentrations in the supernatant were measured by atomic absorption spectrometry (Varian, SpectrAA-400 Plus, Australia). The amount of metals sorbed was calculated as the difference between the initial and final concentration.

Metals sorption data were fitted to Freundlich equation using the formula:

$$q = k_f c^n$$

where: q is the sorbed metal amount in mg kg⁻¹; c is the equilibrium solution concentration in mg/l. From this equation, the following sorption parameters were determined: k_f , which represents the metal sorbed at $c = 1$ mg/l, n which is an empirical parameter expressing the metal sorption intensity. To fit the data, the model was linearized by using the logarithmic transformation resulting in the predictive equation $\log(q) = \log(K_f) + n \log(c)$. The linearized model fitted to each soil using analysis of covariance to estimate $\log(K_f)$ and n and test if the $\log(K_f)$ and n coefficients differed across the tested treatments. Estimates of K_f were obtained using $\exp(\log(K_f))$. The distribution coefficient (K_d) values were calculated according to Anderson and Christensen, and Gomes et al. [20], [21] by using the formula:

$$\text{Distribution coefficient } (K_d) = q/c = k_f c^n / c = k_f c^{n-1}$$

where K_d was estimated using the estimates of k_f and n obtained as described above. Linear contrasts in the analysis of covariance model were used to test if K_d values differed across each metal. The fit of the models were assessed using root mean square error and R^2 to evaluate the proportion of total variability explained by the model. The Proc GLM procedure in the SAS software package was for computation (SAS Institute, 2003).

C. Lability of Sorbed metals

Lability of sorbed metals was evaluated at the end of sorption experiment by DTPA extraction [22]. A 10-mL DTPA solution was added to each centrifuge tube containing metals-sorbed samples from the sorption experiment. Then the tubes were shaken for 120 min on a reciprocating shaker to extract the sorped metals, centrifuged, and the supernatant solutions were filtered and analyzed for Cd, Cu, Ni, Pb and Zn content by atomic absorption spectrometry (Varian, SpectrAA-400 Plus, Australia). The amounts of Cd, Cu, Ni, Pb and Zn extracted by DTPA at the end of sorption experiment were designated as the portion of sorbed metals retained in the labile pool, whereas the metals un-extractable by DTPA was attributed to zeolite Cd, Cu, Ni, Pb and Zn in the non-labile pool.

III. RESULTS AND DISCUSSIONS

A. Properties of Studied 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 zeolite contained high percentage of SiO₂, followed by Al₂O₃, K₂O, CaO, and negligible percentage of Fe₂O₃, TiO₂, MgO, and Na₂O. A description of the methods used to estimate zeolite composition along with some additional data on the chemical properties of the zeolite from the same mine can be found elsewhere [23]. Also, the zeolite contained high amounts of DTPA-extractable Pb and Zn respectively, while the concentrations of other metals were very low. Calcium and potassium were the dominant exchangeable cations while magnesium was the lowest one, (Table I).

B. Sorption of Cd, Cu, Ni, Pb and Zn Metals on Natural Zeolite

The sorption of Cd, Cu, Ni, Pb and Zn onto natural zeolite as a function of their concentrations was studied at lab temperature by varying the metal concentration from 50 to 300 mg/l using competitive sorption system while keeping all other parameters constant. The results are shown in Table II & III and Fig. 1 & 2.

TABLE II: FREUNDLICH CONSTANTS (K_F AND N), MEAN VALUES OF DISTRIBUTION COEFFICIENTS (K_d) AND MEAN VALUES OF METAL SORPTION PERCENT FOR THE METALS STUDIED BY ZEOLITE.

Metals	n	$K_f l kg^{-1}$	$K_d l kg^{-1}$	Metal Sorption, %	R ²
Cd	0.29	117.0	5.34	31.5	0.99
Cu	0.29	406.7	68.31	74.9	0.93
Ni	0.34	77.34	4.05	27.5	0.99
Pb	0.75	2194.3	2535.7	99.6	0.84
Zn	0.44	143.2	17.05	59.2	0.93

TABLE III: THE DISTRIBUTION COEFFICIENT, K_d (L KG⁻¹) CALCULATED FOR EACH ADDED METAL CONCENTRATION AND $K_{d, MEDIUM}$ FOR THE STUDIED METALS SORBED BY ZEOLITE.

Initial Conc., mg/l	Cd	Cu	Ni	Pb	Zn
50	13.09	266.6	8.83	3135.0	38.7
100	6.22	53.3	4.85	2940.7	19.5
150	4.32	36.6	3.49	2709.7	14.4
200	3.33	23.8	2.77	2434.5	11.9
250	2.76	18.0	2.32	2162.6	10.1
300	2.35	11.6	2.02	1831.6	7.8
$K_{d, medium}$	5.34	68.31	4.05	2535.70	17.05

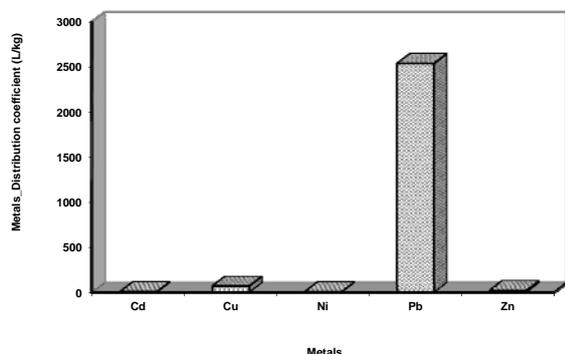


Fig. 1. Mean values of distribution coefficients (K_d) of metal sorption by zeolite

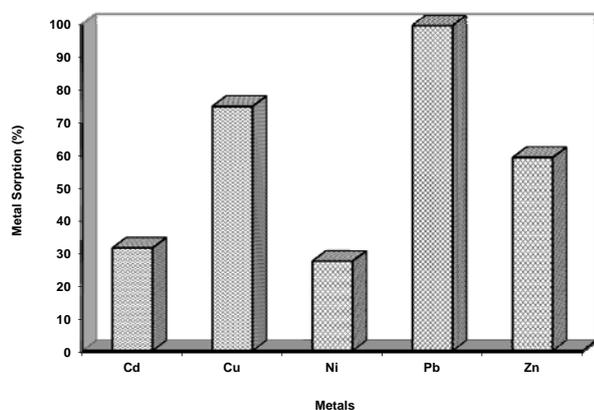


Fig. 2. Mean values of metals sorption percent by zeolite

Freundlich model described very well all metals sorption since R² values were found to be higher than 0.84. The

effectiveness of Freundlich equation in describing metal sorption was reported also by others [24]-[26].

The distribution coefficient (K_d) is a useful index for comparing the sorptive capacities of different soils or materials for a particular ion under the same experimental conditions. It is defined as the ratio of the metal concentration in the solid phase to that in the equilibrium solution after a specified reaction time [18], [20]. Such coefficient represents the net result of all the various processes by which metal ions can be transferred between soil and solution, and are satisfactory for comparing the behaviour of different soils with respect to a given cation under fixed conditions. It is especially useful when the irregularity of empirical sorption and/or desorption isotherms hampers or prevents the fitting of simple empirical curves or theoretical models such as the Freundlich and Langmuir isotherms, as is often the case when the presence of more than one metal results in competition for sorption sites. A high K_d value indicates high metal retention by the solid phase through chemical reactions, leading to low metal bioavailability. Similarly, a low K_d value indicates that a high metal amount remains in the solution [20], [21], [24]-[27]. Therefore, a further analysis of the obtained data based on the distribution coefficients was done. The distribution coefficient (K_d) was calculated over the whole range of the added concentrations of studied metals. Also, the sorption selectivity sequence of the studied metals by the zeolite has been established at K_d medium values to obtain one comparable value for each metal and each soil [16], [24], [25], [28] as shown in Table 3.

Table III illustrates K_d as a function of metal ions concentrations. The data of Table 3 show that the percent of total sorbed Cd, Cu, Ni, Pb and Zn decreased with increasing the initial metals concentration, as suggested by the decrease of K_d values with the increase metals addition. 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. This indicates that changes occur in the nature of the sites involved in the sorption process, depending upon the metal concentration as it was suggested by Shaheen [16]. The higher K_d value obtained in the experiment with lower metal concentrations is associated with the sorption sites of high selectivity, which have relatively strong bonding energies. Otherwise, heavy metal sorption becomes unspecific at higher metal concentrations, when the specific bonding sites become increasingly occupied, resulting in lower K_d values [16], [28], [29].

Increasing rates of Cd, Cu, Ni, Pb and Zn addition to the zeolite may result in saturation of metals sorption sites, thereby decreasing the sorption capacity. In this respect, Saha et al [29] explained that at low metal concentrations metals are mainly sorbed onto specific sorption sites, while at higher metal concentrations soils lose some of their ability to bind heavy metals as sorption overlap, becoming thus less specific for a particular metal. This in turn induces a reduction in metal sorption. Also, these results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution. The heavy metal sorption 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.

C. Distribution Coefficient Values and Selectivity Sequences of Cd, Cu, Ni, Pb and Zn by the Studied Zeolite

According to the percentage sorption and distribution coefficients values, the selectivity sequence of studied metals by zeolite can be given as $Pb > Cu > Zn > Cd > Ni$. Lead presented the highest K_d values followed by Cu, Zn, Cd and Ni, showing that it was retained stronger than the other tested metals especially Cd and Ni (Table 2 & 3). These data demonstrated the preference of zeolite for Pb compared to Cd (Fig 1 & 2). This is usually attributed to differences in metal characteristics and resultant affinity for sorption sites [30]. For example, the hydrated radius of Pb^{2+} is smaller than that of Cd^{2+} ($Pb^{2+} = 0.401$ nm; $Cd^{2+} = 0.426$ nm; [31], favouring coulombic interactions of Pb with exchange sites. Furthermore, Pb has a greater affinity for most functional groups in organic matter including carboxylic and phenolic groups, which are hard Lewis bases. This is mainly attributed to the differences in chemical properties between the two metals. Lead as a harder Lewis acid (Pb^{2+} is a borderline Lewis acid while Cd^{2+} is a soft Lewis acid), has a higher electronegativity (2.33 and 1.69 for Pb and Cd, respectively) and lower pK_H (negative log of hydrolysis constant; 7.71 and 10.1 for Pb and Cd, respectively) than Cd. These factors favour Pb for inner-sphere surface sorption/complexation reactions compared to Cd. Lead (Pb^{2+}) also has 2 valence electrons in its 6s atomic orbital (and empty p orbitals of only slightly higher energy), which can form, depending on the Pb-O symmetry, molecular orbitals with O 2p atomic orbitals originating from an oxide surface. This orbital overlap stabilizes the Pb-O complex. On the other hand, Cd^{2+} has a filled 4d valence atomic orbital, which participates minimally in electron sharing with O 2p atomic orbitals from oxide surfaces.

The previously mentioned support that the sorption preference exhibited by these soils for Pb over the Cd may be attributed to: (i) the greater hydrolysis constant (ii) the higher atomic weight, (iii) the higher ionic radius, and subsequently smaller hydrated radius, and (iv) its larger Misono softness value, making it a better candidate than other metals for electrostatic and inner-sphere surface complexation reactions.

The K_d values indicate that Cu adsorption was higher than Zn sorption (Table 2 & 3). The preferential retention of Cu by the soil is, however, inconsistent with cation exchange theory that predicts selective adsorption on the basis of crystalline radii in a given ionic charge [13]- [14]. The ionic radius of Zn is 0.74\AA , whereas that of Cu is 0.72\AA . Thus, according to cation exchange theory, a preferential retention of Zn against Cu should be expected. The preferential retention of Cu against Zn recorded in this study may be attributed to three factors that which favor Cu sorption: electronegativity, softness parameter, and first hydrolysis

constant. According to [32], selective metal retention can be explained by the differences in electronegativity, which, in this case, is higher for Cu (2.0) than Zn (1.6). However, other investigators pointed out that the first hydrolysis constant is most predictive for metal adsorption selectivity by specimen Fe oxides and soil colloids [33]. The first hydrolysis constant (pK_1) for Cu varies between 7.3 and 8.0, whereas the pK_1 for Zn ranges from 9.0 to 9.4 [33]. Furthermore, Misono et al derived a softness parameter to predict metal affinity sequences or preferential retention of metals by soil colloids. The Misono softness parameter is an index of the tendency of a metal to form covalent bonds with colloids [14], calculated from its ionic charge and the ionization potential (which is greater for Cu than Zn). Thus, the preferential retention of Cu to Zn is in apparent agreement with differences in electronegativity, first hydrolysis constants, and the softness parameter.

Also, data showed that, K_d values of Zn were higher than Cd indicating that this was retained by the zeolite stronger than Cd (Figure 3). These data demonstrated the preference of zeolite for Zn compared to Cd under the competitive sorption system. This order indicates the higher tendency of Cd to remain in solution compared to zinc. This is usually attributed to differences in metal characteristics and resultant affinity for sorption sites which could be summarized as follow: Ionic radii $Cd (0.97 \text{\AA}) > Zn (0.74 \text{\AA})$ [34]; Atomic weight $Cd (112.41) > Zn (65.38)$ [34]; Electronegativity $Cd (1.7) > Zn (1.6)$ [22] Hydrolysis constant $Zn (9.0) > Cd (10.1)$ [35] and softness $Cd (3.04) > Zn (2.34)$ [36].

The sorption isotherms indicated that Cd sorption for the zeolite was larger than Ni. This result may be related to their ionic radii and chemical properties. The electronegativity (X) values are 1.46 and 1.75 and their radii are 0.098 and 0.069 nm for Cd and Ni, respectively. The average electric dipole polarizabilities of Cd and Ni atoms are 7.2 and 6.8×10^{-24} cm^3 , respectively [37].

D. Lability of the Adsorbed Cd and Pb

The sorbed Cd, Cu, Ni, Pb and Zn were partitioned into labile and non-labile pools distinguished by extracting with DTPA at the end of sorption experiment. The amount of labile Cd, Cu, Ni, Pb and Zn as a mean values differed among the tested metals. Generally, on average, about 57, 47, 78, 22, and 29 % from the total sorbed Cd, Cu, Ni, Pb and Zn recovered by DTPA indicating that lability of the adsorbed Ni was higher than, Cd, Cu, Zn, and Pb respectively (Fig. 3).

These data indicate that the lability of Ni, and Cd was the highest while lability of Pb was the lowest one between the studied metals. Therefore, Ni and Cd may pose more threats to the water contamination than Pb and Zn. In this respect, Appel and Ma reported that, Pb demonstrated a higher affinity for materials sorption sites relative to Ni and Cd. The former metal also confirmed its ability to take part in inner-sphere surface reactions, rendering it much less bio-available and mobile in the environment, compared with Ni and Cd [30].

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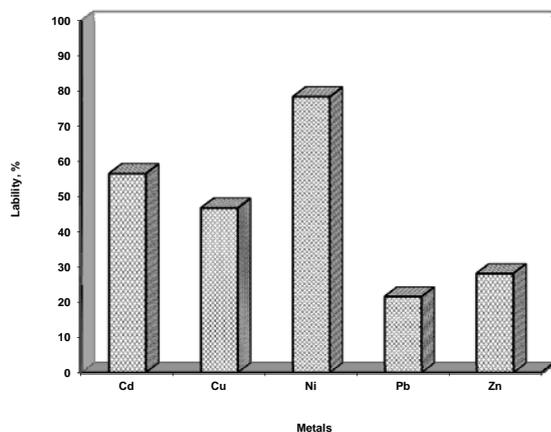


Fig. 3. Average percentage of labile forms of total sorbed metals by zeolite

IV. CONCLUSION

In this study, competitive sorption characteristics and lability of the sorbed Cd, Cu, Ni, Pb and Zn by zeolite were assessed at varying metal concentrations. Freundlich model described well all the studied metals sorption. Apparently due to Pb's chemical characteristics (relatively high electronegativity, lower pK_H , small hydrated radius and electronic structure), this metal was sorbed stronger than other studied metals showing thus lower lability posing thus less threat to ground water systems compared to the other tested metals.

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 other materials as adsorbent due to its availability and its low cost.

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